Theoretical studies of molecular machines

by

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A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE

Doctor of Philosophy

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Houston, Texas
November 2011
Abstract

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Molecular machines are essential components of living organisms. They are highly efficient and robust, much more than their macroscopic analogs. This stimulated growing interest in construction of artificial molecular machines with a set of functions which may be controlled in a specific way. Such man-made molecular complexes are designed as the building blocks for future nanotechnological devices.

During the last decades many new molecular machines have been synthesized and characterized by various experimental techniques. This significantly increased our knowledge about systems of such kind and their functioning. However, there are only a few real applications of molecular machines. This is because the fundamental principles of operation of such single-molecule systems are not well understood. Existing theoretical studies, although very helpful, are still very sparse. This is because the molecular machines are very complex systems, comprising up to thousands atoms. Thus the progress in our understanding of nanoscale materials is tightly related to development of efficient computational and theoretical methodologies.

In this work we studied two large classes of molecular machines: surface-moving nanocars and molecular rotors/motors, working on the surfaces and in crystalline state. In particular we studied the role of the internal interactions of these machines as well as their interactions with the environment. This included the flexibility of the molecules, including the rotation of the nanocars' wheels, effects of surface and rotors symmetry, charge transfer effects as well as many other factors. We have found out relations which determine the properties of studied classes of molecular machines.

The development of computational and theoretical methods was another essential part of this work. In particular we have developed a family of the surface-molecule interaction potentials, aimed to performing long time scale and molecular simulations of complex systems. We also developed a physics-based model of the charge transfer happening between metals and the nanocars. This opened new ways to control such molecular machines. We also developed a theoretical framework to predict response of molecular rotors on various types of driving. Finally, we developed new and improved existing rigid-body molecular dynamics methods and extensively used them in our studies of molecular machines.
Acknowledgments

First and foremost, I want to cordially thank my adviser, Prof. Anatoly Kolomeisky, for his support and continuous help in any subject during these wonderful years of very interesting and productive research. His confidence and trust in me and my work gave me a freedom to study and master new horizons of the computational and theoretical chemistry and helped me to be more productive and develop many useful skills. His enthusiasm and interest were the continuous stimulation and gave me strength to work very efficiently on all subjects we have studied. It is hard to imagine a better adviser and mentor.

I want also thank Dr. Nikolai Sinitsyn who worked with me on various projects during my summer internships at Los Alamos National Lab. The projects I worked with him allowed me to look broader on the entire field of molecular simulations. I also appreciate his help in organizing and supporting my research in Los Alamos. It was real pleasure to work with him.

This thesis could not be possible without prior training and support from my former scientific adviser, Prof. Alexander Nemukhin and the lab members Dr. Anastasia Bochenkova, Dr. Alexander Moskovsky and Dr. Alexander Granovskii who have helped me a lot to get involved into realm of computational chemistry. I separately want to thanks Dr. Sergei Konyukhov, whose constructive criticism and impartial and detailed analysis and involvement were always serious factors to improve the work and results. I also appreciate distant discussion and debates with him during the work on this thesis, which helped me faster find errors and better solutions.

I also want to express my gratitude to all my teachers both at Rice University and in all my previous schools, who helped me to stay interested in science and in chemistry in particular, to develop my scientific and ideological skills. Especially I want to thank Prof. Erzsebet Merenyi (Rice University), who has inspired and supported my interests in artificial neural networks and their application to chemical problems, Prof. Tsarkov I. G., Dr. Petrov S. V., Prof. Novakovskaja Y. V., Prof. Sidorov L. N., Prof. Romanovskii B. V., (Moscow State University), for excellent courses in mathematical analysis, classical and quantum mechanics, quantum chemistry, thermodynamics and chemical kinetics correspondingly. I also grateful to Prof. Khrustov V. F. who spent a lot of his time in long discussions and colloquia related to different subjects of classical and quantum mechanics. His methods were tough but stimulated me to understand these subjects much deeper. I want to thank all my lyceum teachers, who were constantly inspiring and supporting my very early scientific abilities and skills and showed the logic in many other disciplines, such as history, literature, religion and developed my independent and critical thinking skills. I am glad to think that all training I’ve obtained from all my studies and schools has not gone without impact and the efforts of all my teachers and advisers were not useless.

I am also happy to express my thanks to all my friends and colleagues, especially to Harry Gustavo Saavedra Espinoza, Carlos Jimenez-Hoyos, Takashi Tsuchimochi, Hoang Tran, Alexei Finashin, Alexander Bibin, who have always been with me and helped me as the help was needed. It has always been a pleasure to spend some time with them discussing various topics and doing fun stuff.

At last, but not least, I am happy to thank at this point my mother, Akimova Valentina Petrovna, who made enormous efforts supporting me all this long way, from my middle-school to my Ph.D. thesis. It all would not be possible if not her help and care. And of course I thank my wife and the best friend, Inna Kurganskaya, who was the best example of all best human merits. She constantly was challenging me to grow in many scientific and humanistic aspects and look differently on many things.
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Preface

This thesis, in part, is based on the following articles, which have been published or/and presented as a poster on scientific conferences.

Publications

1. Akimov A. V., Williams C. Kolomeisky A. B. "The Effect of Charge Transfer in Dynamics of Nanocars on Surfaces" (in preparation, 2011)

Poster presentations

1. "Understanding surface-mounted molecular rotors: Molecular dynamics studies", Aug. 27-Sep. 1, Denver, CO (Fall 2011, ACS national meeting)
2. "Using distributed computing to study crystalline molecular rotors", July 18-21, Salt Lake City, Utah (TeraGrid 2011 conference)
3. "Molecular dynamics study of the surface-mounted molecular rotors: Why the activation energy for rotation of the surface-mounted thioethers does not depend on their size" Thermodynamics and Kinetics of Molecular Motors, May 19-22, 2010, Santa Fe, NM
4. "How chain flexibility and surface interaction affect the properties of surface-mounted molecular rotors: Molecular dynamics of thioethers" Southwest Theoretical Chemistry Conference, October 16-17, 2009, Houston, TX
Chapter 1

Thesis overview

Molecular machines is a wide class of molecules, with special properties, re-evaluated from the point of view of their possible applications in emerging and rapidly developing field of nanotechnology. With the new experimental and technological methods it is now possible to fabricate and study such systems on the single molecule level, create nano-scale devices out of them and make such devices working. However, for these objectives to be possible it is crucial to study the nanoscale molecular devices on the theoretical level, which is capable to provide some insights which are not or difficultly accessible by experimental techniques.

This thesis provides some theoretical studies of several classes of molecular machines, in particular the nanocars and the molecular rotors and motors. It should be realized that although some theoretical studies exist, they are still very sparse in comparison to numerous experimental studies. For example, to the best of our knowledge, there are no theoretical studies of the nanocars. This is mainly because the field is relatively new and not well understood. Moreover, the systems are in general very complex, what challenges the theorists to develop various approaches to treat such systems.

In this chapter we will describe the main structure of this thesis, which is written as a collection of the chapters, logically ordered and related to each other in hierarchical way. This means the methodological approaches and studies for more general type of systems will normally be given in earlier chapters. More specific subjects are then discussed in light of more general framework. Yet, each chapter is
relatively independent of the other chapters. Structurally chapters are grouped into a few groups/sections, depending on the general topic they describe.

The first group (Chapters 1-2) gives the overview of this thesis structure (Chapter 1) and introduces the objectives (and subjects) of the studies described in this work (Chapter 2). They mostly serve the introductory and organizing purposes.

The next group (Chapter 3-4) describes the methodological part of the studies. Namely, it gives an overview of existing methods to describe the interactions in the atomic systems and to perform molecular dynamics (MD) simulations in various ensembles and with both all-atomic and rigid-body approaches (Chapter 3). It also gives some practical recipes how to avoid some hidden problems of various methods and gives the critical evaluation of existing approaches.

During the course of this work we focused not only on application of some existing methods to the nanomachines, but we also worked a lot on developing our own methodology and tools. As the result we have found out the efficient and accurate algorithms of performing rigid-body molecular dynamics simulations (RB MD). Such algorithms are described in the Chapter 4. This completes the simulation methodology section.

The next important part of this thesis and essentially one of the most important methodological problems we were working on during this work was the development of the interaction potentials. It is hard to overestimate the importance of the interactions, because the potentials used in molecular simulations essentially define all other observed quantities. Thus it is very important that the interactions to be as accurate as possible. However, because of the size of the systems we deal with, the interaction potentials should also be efficient in computational sense. Therefore, we worked a lot on developing various approaches to construct the effective surface-
molecule interaction potentials, which would provide simplicity of the calculations and the physically meaningful accuracy.

Our first simplistic approaches are described in Chapter 5. More sophisticated surface potential models will be presented in Chapter 6. Chapter 7 describes an alternative point of view on construction of such potentials via using the artificial neural networks (ANN). Even more sophisticated approach, partly based on the semi-empirical calculations, provides some insight on the details of the nanocar-surface interactions, which were not included in our previous models (Chapter 8). Such details allow one to make some interesting predictions regarding the motion and operation of the nanocars on metal surfaces.

The methodology of interactions chapters (5-8) are closely related to the studies of the nanocars – one type of the molecular machines, which are studied in this work. Therefore, the chapters 5-8 may also be considered as another section, which provides some results on how the motion of such molecules depends on the surface-molecule interactions. The other factor, which has a significant impact on the properties of the nanocars, is their internal structure. The study of the effects of internal structure of the molecular machines is described in Chapter 9.

Finally, since our studies used many approximations for the surface-molecule interactions and/or some effective parameters it is always a problem to obtain a direct relation to the experimental data. Thus, the section, dedicated to the nanocars is concluded with the Chapter 10, which describes a statistical-mechanical methodology to relate the qualitative results which might be obtained with some approximate interaction parameters to the parameters which should be used to reproduce the experiments quantitatively.
The next group of chapter (Chapter 11-15) is focused on our theoretical studies of the molecular rotors and motors – another important class of the molecular machines. First, the surface-mounted molecular rotors are studied. We describe in details how the flexibility of the chains of molecular rotors and the interaction of these chains with the surface affects the properties of the rotors (Chapter 11). The effects of the symmetry, – both of the rotor and of the surface binding site – are then described (Chapter 12). The surface-mounted molecular rotors part is then concluded with the application of the MD method to directly study the sensitivity of such rotors to external driving, e.g. in response to rotating electric field (Chapter 13).

We then describe our studies of some other types of molecular rotors, namely the crystalline molecular rotors, which are also known as molecular gyroscopes and compasses (Chapter 14), and the catenane rotors (Chapter 15). The former type of rotors is studied by RB MD method, while for the latter one an alternative technique, based on the graph-theoretical considerations is used.
Chapter 2

Overview of molecular machines

2.1. General overview of molecular machines

One of the first literature records about the design of the molecular machines for possible human application is usually addressed to Richard Feynman[1], who challenged scientists to think about the construction and the possible applications of molecular machines. This stimulated numerous studies, both experimental and theoretical toward the design, synthesis and better understanding of the wide variety of molecular machines, working on a microscopic scale. One of the definitions of the molecular rotor and machine is given by Stoddart[2]. According to that definition they are "any system, usually of rigid bodies formed and connected to alter, transmit, and direct applied forces in a predetermined manner to accomplish a specific objective such as the performance of useful work" and "a device that converts any form of energy into mechanical energy" correspondingly. In further discussion we assume, however, that the molecular machines constitute a wider class of molecular structures, which includes the molecular rotors in particular. Therefore, the term “molecular machine” will mostly be used to refer for such a wider class of compounds. In this work we will mostly focus on two most notable members of this class: nanocars and molecular rotors.

It is also important to realize that molecular machines and rotors are important functional components in all living organisms, playing critical roles in processes such as muscle contraction, cell division, motility, support of cellular metabolism, vesicle...
and neuronal transport as well as signaling and energy processing in cellular membranes\cite{3-5}, \cite{5-8}. High efficiency, flexibility and robustness of biological nanomachines is another factor which significantly increased interest in field of molecular machines and stimulated significant experimental efforts to develop artificial molecular devices with potentially wide applications in nanotechnology, material science and medicine\cite{2}, \cite{7}, \cite{9-18}.

The growing interest resulted in a synthesis of a wide diversity of the artificial molecular systems invented to work as nanomachines. Among those are the catenane and rotaxane-based molecular motors\cite{13}, \cite{19}, \cite{20} and shuttles\cite{12}, \cite{15}, molecular elevators\cite{17}, pedals\cite{21}, gears\cite{22}, turnstiles, gyroscopes and compasses\cite{23-25}. There are several extensive reviews of molecular motors and machines, including biological, which provide some more examples of such systems and discuss their functioning\cite{2}, \cite{6-8}, \cite{26-28}.

Molecular machines are working in different environments such as in solution\cite{20}, \cite{29-33}, in the solid state\cite{24}, \cite{25}, \cite{34-45} and on the interfaces\cite{18}, \cite{28}, \cite{46-61} such as metal or crystal surfaces, cell membranes and filaments. Some examples of such systems are shown on Fig. 2.1, highlighting the wide diversity of the environments where molecular machines have been studied and the wide range of their sizes, starting from relatively simple and small organic molecules build of tens of atoms and finishing by complex membrane proteins, which comprise thousands of atoms.
Figure 2.1. Various environments where molecular machines may work: a) Kelly ratchet, working in solution [adapted from ref.[29]]; b) crystalline molecular rotors, working in solid state [adapted from ref.[25]] and c) massive natural molecular rotor, working on the cell membrane. This figure also shows the wide variety of the size of molecular machines.

Many different approaches have been developed to make molecular machines produce some useful work such as translational or rotational motion. Among them are the driving of molecular motors by light[62], [63], redox[31] or pH-dependent processes, by metal coordination[12], [20], or by the energy of chemical reactions[29], [30]. In the light-driven processes the operation of molecular motors is based on combination of cis-trans isomerization and thermal fluctuations. In redox and pH-driven processes there are usually several states of the system, one of which is energetically more favorable than the other at certain conditions (potential or pH level). Similar situation happens in the systems where one of the states is stabilized by coordination of some parts of the molecule with the metal ions. In both cases the system will eventually evolve to the most stable state. By modulation of the environmental conditions it is possible to alter the target state (the energetically favorable one) and drive the system toward that state.
If the system is symmetric, the number of forward transitions, however, will on average be equal to the number of backward transitions. Therefore the system will not be performing any directional motion. This is however, not a problem in 2-state molecular switches, where it is not important how the switching is performed, but one is rather interested in what state the system occupies at given time. However, if the directed motion is desirable it is necessary to break a spatio-temporal symmetry. This can be achieved for example by creating a chiral centers or planes in the molecule or by performing chemical reactions (driving the system out of equilibrium) which will drive the system toward a desired state. Some examples of possible ways to drive the system in desired way are shown on Fig. 2.2.

A few alternative ways to induce a directed motion in molecular machines have been reported. They include the polymerization reactions[64], [65], which create a drag force acting on the nanomachines and driving them in one direction. The other alternative method was based on the catalytic activity of the part of the molecular machines. Such centers catalyze the reaction, leading to formation of the gaseous products[66], such as oxygen, which creates a reaction force, resulting in unidirectional motion of the catalyst molecule. Finally, there are some works, where the directed motion of some environmental particles, such as water molecules or protons is directly transforms into a rotary motion of the molecular motors[55], [67] due to atomic and molecular collisions. All alternative methods are therefore similar in their mechanistic nature, where the motion of one particle in one direction is possible because of the motion of other particles in opposite direction.
Figure 2.2. Possible ways to drive the molecular machines: a) by metal coordination [adapted from ref.[8]]; b) by pH variations or c) by redox processes [adapted from ref.[31]].

Although the molecular motors and rotors are not yet widely used in practical applications, there are already several of them. Possibly the most famous use of molecular rotors nowadays is based on their fluorescent activity, which depend on their rotation. The rotary properties, in their turn, strongly depend on the environment where the rotor is imposed. This leads to applications where the rotors are used to measure the cell viscosity in biological objects[11], [68]. The viscosity-dependent fluorescence of molecular rotors has also been used as an analytic tool to calibrate the concentrations of the macromolecules in medications[69].

The molecular rotors have also been used for fabrication of the high-density memory application[70]. Although the work was only a demonstration of the molecular rotors capabilities, it is very likely than in near future creation of such devices will be a part of conventional technologies. Another example of the “real-world” applications of the molecular rotors, although not yet practical one, was recent experimental observation of the rotation of the macroscopic object in the liquid crystal film, by much smaller molecular rotors[9].

Among the wide variety of molecular machines there are three classes which have been developed recently and which are the main objects of studies in this thesis. They are the nanocars, the surface-mounted and the crystalline molecular rotors.
Therefore we will now describe each class in more details, reviewing both experimental and theoretical studies, concerning the systems of each type.

2.2. Overview of Nanocars

2.2.1. Introduction

A new type of molecular machines, designed to work on surfaces and mimic macroscopic automobiles has been invented recently in James Tour lab[14], [71–73]. This new class of complex molecular systems is now known as nanocars (see Fig 2.3 for some examples). The structure of the newly constructed molecular machine includes massive fullerene wheels flexibly coupled to the chassis and the axles.
Figure 2.3. Various nanocars [adapted from refs.[14], [59], [74]] a) original nanocar, also called z-car in this work; b) nanotruck; c) nanotrimer; d) 4-wheeled pinwheel; e) nanodragster and f) 4-wheeled carborane nanocar functionalized with Feringa light-driven motor. The chemical structure is chosen for clarity.

After their invention of the fullerene-based nanocar, Tour’s group also synthesized the carborane-based nanocars[14] and the nanocars with the ruthenium-based organometallic wheels[75]. The mixed wheel nanodragster has also been designed and synthesized[59]. Presence of the strongly-binding fullerene wheels is necessary for better binding of the molecule to the metal surfaces, while the weakly-binding carborane groups were added for better mobility and directionality of the nanodragster.

The carborane-wheeled cars have also been functionalized with the Feringa-type light-driven motor[14]. This opens the opportunity to induce a directed motion of such molecules in a controlled manner, by simply exciting the molecule with the light beam. Similar to original nanocars (z-cars), the nanotrucks, nano-wagons and nanoworms have been created[14], [58], [73]. Such molecules differ by their chassis part, which may include the chromophore groups, necessary for adsorption of the light energy. J. Tour group has also created the surface-pivoting systems, which do not
exhibit any translational motion, but perform fast rotation motion around their center[72], [74].

2.2.2. Experimental studies

Immediately after creation of the first nanocar molecules they have been studied with the STM technique[72]. It has been found that the 4-wheeled nanocars remained relatively immobile on the gold surface for temperatures up to 170 °C. For higher temperatures the molecule starts to move in two dimensions by combination of translations and pivoting around its center. However, some directionality in such motion has been observed, suggesting the translation in one direction is easier than in the other. This hypothesis has been verified by direct manipulation of the molecule with the STM tip. The molecule may be moved relatively easy in one direction, while it is much harder to move it in perpendicular direction.

Authors suggested the mechanism according to which the motion of the nanocar is tightly related to the rotation of the fullerene wheels. To verify this hypothesis the 3-wheeled analog of the nanocar has been prepared. According to STM observations it was immobile even for high temperatures. However, the molecule showed significant pivoting motion. This may only be possible if the fullerene wheels were rotating.

In other studies, performed by S. Link group, the motion of the carborane-based nanocars on various non-metallic surfaces has been considered. Using single molecule tracking techniques, based on the use of fluorescent markers, attached to the molecular machines, they have been able to study the diffusion of the molecules on mica surfaces[76], [77]. In addition they have found that the surface structure and properties may significantly impact the mobility of the nanocars[78]. The diffusion
The coefficient has been found to vary in range from $5.8 \times 10^{-17}$ to $2.4 \times 10^{-16} \text{ m}^2/\text{s}$. Using the temperature-dependent measurements, the activation energy for motion of the 4-wheeled carborane nanocar was estimated to be $42 \pm 5 \text{ kJ/mol}$.

![Figure 2.4. Carborane nanocars (or carborane-based nanocars) with the fluorescent dyes [adapted from ref.[78]]: (a) the fluorescent marker is added externally; (b) fluorescent marker is an internal part of the nanocar](image)

The technique has the advantage over the direct STM measurements, which has been used originally to observe the nanocars motility[72], because of its relatively small invasiveness in the system dynamics. Moreover, STM tracking of the nanocars is possible only on conductive substrates, such as metals. The disadvantage of the fluorescent technique is the requirements for the nanocar to have some proper dye moiety (Fig. 2.4, a). Thus such experiments study not the “naked” nanocars, but rather some their modification, containing additional fluorescent label, which may affect the observed properties of the nanocars. Also, it is possible that the excitation of the dye tag may affect the dynamics of the entire molecule, because of the changed electronic state, although such non-adiabatic corrections must be very small for such systems. The problem has been recently solved, by designing the nanocars, with the internal...
parts, which may adsorb and emit light in required range of wavelengths (Fig. 2.4, b), thus allowing to track the molecules without any additional fluorescent tags.

2.2.3. Theoretical studies

Although many theoretical and computational works exist which deal with the various molecular machines, there are practically no such studies of the surface-moving nanocars. However, there are some studies which provide some insight into details of the interactions between possible nanocar parts and the substrates. Such parts include the fullerene or carborane wheels and the conjugated aromatic system as the chassis. The substrates are usually metal or ceramic surfaces. Thus it may also be important to describe some existing studies of the fullerene/carborane/substrate interactions.

In one of the combined experimental/ab-initio studies the STM-induced motion of the fullerene on the silicon surface was described[79]. One of the main results was the proposed bond-breaking and bond-formation mechanism, according to which during C$_{60}$ molecule surface motion the carbon atoms form 2 covalent bonds with the surface. Such bonds then become the pivoting points, resulting in fullerene rolling. There are also many ab-initio studies of the adsorption of the fullerene on various surfaces and the charge transfer effects which are often accompany fullerene chemisorption. These effects, however, will be discussed in more details in one of the later chapters.

The interaction of the carborane with the hydrated silica surface has been studies recently with the DFT method[80]. The model calculations found three local minima for binding the p-carborane on the silica surface, with the binding energies of 6.1, 7.8 and 8.1 kJ/mol. The interactions are dominated by formation of the hydrogen
bonds. If one assumes that all carborane wheels in the corresponding nanocar find the lowest local minimum, the activation energy for initiating motion of such nanocar will be 32 kJ/mol, which is comparable to the experimentally determined value of 42 +/- 5 kJ/mol[77].

2.3. Surface-mounted molecular rotors

2.3.1. Introduction

One of the most promising classes of artificial devices for application in nanotechnology is a class of surface-mounted molecular rotors[18], [46], [53], [55], [61], [81–84]. There are many advantages in using molecules attached to the surfaces, such as the ability to control and manipulate easily these rotors, the possibility of coupling to other nanoscale devices and many other potential nanotechnology applications. In addition, biological motors typically function most efficiently in close association with some surfaces[84].

There are two main types of surface-mounted molecular rotors, depending on the direction of rotation of the lobes – altitudinal and azimuthal[55]. The axle of the rotors of the first type is parallel to the surface, while for the rotors of the second type it is perpendicular to the surface (Fig. 2.5.).

![Figure 2.5. Classification of the surface-mounted molecular rotors: azimuthal rotors rotate in the plane, parallel to the surface, around the axis which is a normal to the surface; altitudinal rotors rotate around the axis, which lies in the plane, parallel to the surface [adapted from ref.[55]].](image-url)
All surface-mounted mounted molecular rotors should contain a group, capable to strongly bind to the corresponding substrate. Such strong bonds suppress the translational motion of the molecule and act as the pivoting centers. Such moieties are thus called anchors. The rotating part of the rotors is called rotator. The rotators may be very diverse, while the anchors comprise relatively limited class of functional groups. Thus the classification of the altitudinal rotors may be based on the type of anchor used. The most widely studied classes are the porphyrines, phthalocyanines, thioethers and thiols, although the other types of the anchors have been created (Fig. 2.6).

**Figure 2.6.** Various types of surface-mounted molecular rotors: a) porphyrin-based molecular rotors [adapted from ref.[85]]; b) phthalocyanine-based molecular rotors [adapted from ref.[53]]; c) thioether molecular rotors [adapted from ref.[46]] and d) decacyclene rotors [adapted from ref.[83]].
2.3.2. Experimental studies

Among the first surface-mounted molecular rotors studied were some very simple molecules, such as $\text{O}_2$ deposited on the Pt(111) surface[56]. Such systems were used to develop the methodology of inducing the single molecule rotations attached to the surface by applying an STM pulse. The response of the system is then monitored resulting in different values of the tunneling currents which correspond to distinct orientations of the molecular rotor. Another technique to experimentally observe the rotations is the electron stimulated desorption ion angular distribution (ESDIAD) method, which was used to study the rotation of PF$_3$ molecules on Ni(111) surface[86].

Thermally-activated rotation of zinc octaethylporphyrin (OPE) on Cu(111) surface[60] has been recently observed. It was found that, depending on the substituents in the porphyrin ring, it is possible to weaken relatively strong $\pi$-interactions between the organics and the metal. Such weakening, however, is not enough for inducing rotations in such systems. Nonetheless, it opens an opportunity to reversibly induce the rotations in such systems by adding and removing the Zn-binding ligands[85], [87]. When the ligand binds between the porphyrin ring and the metal surface it weakens the interactions enough for inducing thermal rotations. Removing such ligand, by e.g. heating will stop the rotations. Similar porphyrin derivatives were found to form self-assembled honeycomb structures, when deposited on metal surfaces, in particular Cu(111). The rotation of individual molecules can then be induced by STM tip manipulations[88].

Structurally similar to the porphyrin derivatives the copper phthalocyanine (Cu-Pc) rotors were studied on the $\text{C}_{60}$ surface. They show not simple axial rotation,
but its combination with the hopping between several binding sites around given fullerene molecule, leading to eccentric rotations[57].

Another structural analog of both porphyrines and phthalocyanines, the decacyclene (DC) compound derivative were also reported as the molecular rotors, the rotations of which may be selectively turned on and off by manipulating the intermolecular separation distance by, e.g. STM tip[83], [89].

The detailed studies of molecular rotations have been performed for the system of thioethers bound to Au surfaces[46]. Thioethers, also known as dialkylsulfides, are linear molecules with the sulfur atom in the middle connected to two symmetric alkyl chains. The sulfur atom is strongly bound to the gold surface, and alkyl branches can rotate around it. Using STM techniques it was found that activation rotational barriers do not depend much on the size of alkyl chains in thioethers, in contrast to naïve expectations.

A different rotational dynamics have been observed for diferrocene derivatives[61]. These molecules can be viewed as single alkyl chains that contain a monocyclopentadienyl iron complex (FeCp) at one end, and the ferrocene (Fc) group at the other end. FeCp group is strongly bound to the metallic surface, while interactions of Fc group with the surface are much weaker. This leads to rotation of the whole molecule around the FeCp complex. Again using STM methods it was shown that the increase in the length of the alkyl chain connectors increases rotational barriers and threshold temperatures for rotation. This dynamic behavior was very different from the rotational dynamics of thioethers.
2.3.3. Theoretical studies

Thioethers and thiolates are very well-studied due to their ability to form self-assembled monolayers (SAMs). There is a number of theoretical[90] and experimental[91], [92] works on alkylthiolate SAMs. Other authors performed theoretical investigations of sulfur-containing organic compounds such as benzenethiol[93–95], butanethiolate[96] or SH and SCH$_3$ species[97] on the metal surfaces. Mostly, they are dealing with the energetics and the geometry of the surface-molecule binding sites. In one work[96] however, they studied a surface diffusion of the butanethiolate molecule and revealed some interesting features affecting the motion of the alkylsulfides.

The adsorption and rotation properties of the CH$_3$SH thioether molecular rotor on Au(111) surface have been studied[98] with the DFT method. The calculations suggested that the molecule adsorbs preferably on atop sites of the gold surface. The rotation activation barrier has been calculated to be very small (~0.1 kcal/mol), what is in good agreement with the available experimental data of similar systems. The DFT method has also been used to study the adsorption of the iron phthalocyanine rotors on Au(111) surface[51].

A general quantum-mechanical solution of the hindered rigid rotor in arbitrary rotational potential is given in terms of the continued fractions[86]. Similar approach, based on solution of the Schrodinger equation for rotational degrees of freedom in the presence of the circularly polarized electromagnetic field, suggest the possibility of inducing the rotations in non-polar rotators[99].

A significant contribution in molecular dynamics studies of the surface-mounted molecular rotors have been made by J. Michl group and collaborators. These studies ranged from simple molecular mechanics optimization of the various
structures[49] to molecular dynamics studies of the response of the surface-mounted molecular rotors to the external electric field[81], [100–103]. Such studies revealed, for example, that there are several regimes of driving the altitudinal or azimuthal molecular rotors by time-dependent electric field. Depending on the particular driving protocol one may achieve either synchronous or asynchronous rotations or even some fractionally quantized rotation, for example ½, meaning that one complete rotation of the electric field will rotate the molecule only half-way.

Molecular dynamics and molecular mechanics studies have been used to study the methyl-size rotors on the graphene or nanotube surfaces[104], the rotation of bacterial flagellum[105] and for interpretation of the STM experiments on rotation of the copper phthalocyanine on the fullerene surface[53]. Combined QM/MM methodology has been successfully applied to study the complex systems such as bacteria sensory rhodopsin, which has been shown to work as a light-driven biological molecular rotor[106].

Numerous statistical-mechanical approaches has been developed for description of functioning of the molecular machines[107–116]. They are based on kinetic and thermodynamics models for description possible ways to perform rotations (reactions). Such models may then be parameterized in a way convenient for analysis. Finally, it may also be possible to modulate the parameters included in kinetic models, thus mimicking the driving processes. In this way one may study how it is necessary to drive the molecular rotors to achieve the best performance.

Similar Markov process model has been developed to describe the kinetics of the light-driven molecular motors on average basis and on the elementary-step-process basis[117]. The authors also defined a set of quantities which provide the quantitative description of the molecular machine performance, including the average
and per-step rotation velocities, the excess rotation, which measures the directionality of the rotors. Such set of parameters may be very useful for unifying the descriptive approaches, which may vary from one researcher to another. This would help to standardize and optimize the performance of molecular motors and rotors.

2.4. Crystalline molecular rotors

2.4.1. Introduction

A new class of molecular rotors functioning in solid-state environment has been developed recently[24–26], [36], [39], [40], [118]. These materials, known as amphidynamic crystals (also called molecular gyroscopes), have been created synthetically by designing systems where strong translational interactions are uncoupled from internal rotational motions[119]. The molecules consist of the massive thiphenylmetyl or tripticene groups and relatively small phenylene groups, connected via linear acetylene bonds. The thiphenylmetyl parts form a crystal frame due to their strong van der Waals interactions with such groups of other molecules. They do not exhibit significant motion, and therefore called stators. The smaller phenylene groups in between of the stators are relatively mobile because the caging effect of the stators provides enough space for any rotated configuration. These phenylene groups exhibit significant rotational motion, and therefore called rotators. Such molecular systems form a crystal structure and therefore called crystalline molecular rotors. Sometimes the crystal structure may also include the solvent molecules.

The crystalline molecular rotors may also be classified on the basis of the amplitude of motions possible for such systems. According to this classification they are called amphidynamic crystals[38], because their parts evolve to both types of
motion – one with small amplitude (stators), which is typical for crystals and the other – with the large amplitude (rotators), which is typical for liquids.

The rotator part may also be protected by some additional chains, connecting the stators[36], [37]. This diminishes the steric repulsion between the rotator and the environment, allowing for faster rotations.

The rotator may be made dipolar, by adding electronodonor and/or electronoacceptor groups, such as fluorine or nitrogen atoms, nitro or nitroso groups, etc[25], [41]. This increases the dipole moment of rotator, allowing one to drive it unidirectionally by external electric field. Because of the analogy of such systems with compasses they are sometimes called molecular compasses.

![Crystalline molecular rotors](adapted from ref.[40])

2.4.2. Experimental studies

The motion of the rotators is a thermally-activated process. It has been studied by temperature-dependent NMR dynamic analysis[118], [120]. Such technique allowed one to extract the activation energies and rotation constants for such rotations for the variety of rotator/statot/solvent combinations[42–44]. One of the observations was that when the rotator part is better protected from the interactions with the environment by inserting bulky substituents on the stator moiety, the rotation constants may increase by several orders of magnitude (Fig. 2.8).
Similar observations have been made for rotors in a confined space (such as porous organic silica). The controlled reversible switching of the rotation frequencies of the molecular rotors in such system has been achieved by adding and removing the guest ligands[35]. The guest ligand worked as a brake, reducing the rotation rates by up to 7 orders of magnitude.

![Figure 2.8. Variation of rotation frequencies of the rotators with the composition of the stator moieties](adapted from ref.[38])

In another study, it was argued that higher symmetry order of the rotator segment must lead to lower rotational barriers[118]. However, the analysis of experimental observations indicates that symmetry alone can only partially explain some dynamic features of molecular rotations.

![Figure 2.9. Crystal structure/packing of the amphidynamic molecular rotors for rotators with different symmetries](adapted from ref.[119])
2.4.3. Theoretical studies

Although the crystalline rotors have been extensively studied experimentally, there are not so many theoretical works. Some works, however, deal with the similar systems, so their results may be used to better understand the amphidynamic rotors. For example, in recent DFT studies the host-guest interactions between a small molecule inserted into a phosphonate cavitand structure and the cavitand itself have been calculated. They revealed low activation barriers to rotation[121], what supports the idea behind the molecular gyroscopes with the chains protecting the rotator part.

On the basis of solving Schrodinger equation for rotational degree of freedom for a rigid body rotation it has been shown that the rotations may be induced and driven by the circularly-polarized electromagnetic field, even for non-polar rotators[99]. This may be especially useful for the amphidynamic rotors with phenylene rotators, which have zero dipole moments and can not be rotated by electric field.

In contrast to surface-mounted molecular rotors the systems of this type are much less studied by means of computational chemistry methods. However, the general statistical-mechanical approaches described in the surface-mounted rotors section are still applicable to the amphidynamic crystals.

2.5. Conclusions and Summary

In this chapter we presented an overview of most recent progress in the field of molecular machinery. We discussed a variety of sizes, properties and working environments of molecular machines as well as their classification based on various criteria. We introduced the most notable classes of molecular machines, which are actively studied by various research groups, including nanocars, surface-mounted and
crystalline molecular rotors. These particular classes of molecular machines have been discussed from the point of view of available experimental and theoretical studies.

Molecular machines constitute a promising class of building blocks for future functional materials. Numerous experimental and synthetical studies open new frontiers in this field, rapidly introducing new types of systems and their properties. However, the practical applications are yet very limited. One of the reasons for that is a limited theoretical knowledge on the subject.

Although there exist some theoretical studies of various types of molecular machines they are still very limited. Most studied systems are the molecular rotors, especially those working on the surfaces. The theoretical studies of the particular classes of thioether-based surface-mounted rotors and crystalline rotors are even less developed, while there are no such studies on nanocars at all. The experimental observations for these systems are sometimes counterintuitive and difficult to interpret.

Moreover it is very hard if not impossible to estimate the optimal conditions for working of the nanomachines by experimental techniques. The physics of the processes behind the functioning of nanomachines and details of such processes must be understood completely for optimizing the performance of nanomachines.

Thus there is a high significance of the development and application of theoretical methods to studies of the molecular machines. It is directly related to ability of the field to transfer from state-of-the-art to a practical nanotechnology branch. In this thesis we will describe our theoretical studies of the molecular machines.
Chapter 3

Overview of computation methods and techniques

3.1. Hierarchy of computational methods

Divide and Conquer

Julius Caesar (creator and ruler of Roman Empire, 100-44 BC)

One of the most fundamental levels of understanding the matter is the ab initio description, based on exact solution of the Schrodinger equation. On one hand, the truly exact solution is possible only for a few special cases. On the other hand, even if the true solution is known it is not always possible to use it in full extent to predict the properties of the matter. This is because the inherent coupling between the parts of the system. This leads to a very general consequence, persistent on all levels of organization of matter, that the whole is not simply a sum of its part.

Therefore, for real (not the special, exactly solvable) systems a number of approximations are commonly used. The approximations may be classified according to the level of organization of matter (coarse-graining level) they are dealing with and the accuracy of such approximations within this level (level of theory) (Fig 3.1, a).

The coarse-graining level ranges from subatomic particles, atoms, molecules and molecular complexes to the biological objects, such as cells, tissues and organs. One should not directly compare the models from different levels of coarse-graining, because the accuracy for each such level may have different meaning from the accuracy of other levels. For example, the molecular mechanical force field may be so
well parameterized, so its accuracy for prediction of some properties, e.g. the binding affinities may be much better than those obtained with a very approximate quantum description method, such as Hartree-Fock. Moreover, one often does not even need to know all the details of interactions to develop theories, such as those in statistical mechanics, which will then predict some quantities with even better agreement with experiment than those obtained from rough classical or quantum mechanical simulations.

Thus for each level of representation (coarse-graining) of the reality there should be appropriate way to describe it in reasonable amount of time, with reasonable accuracy and with required level of detailization. A particular way how this is achieved defines the levels of theory, which thus may be directly compared among them.

For example, for finding out how the cell membrane is functioning we should know the interactions among its components. Such interactions may be described on the level of coarse-grained models of lipids, proteins and other organic and inorganic components of the membrane. Moreover, the precise coarse-grained model is the only
thing which is really needed. One does not have to consider the all-atomic nor quantum mechanical description of the interactions, as long as such description is already included in the coarse-grained model.

In reality, however, different levels of description intermix with each other. Such approach is called multi-scale modeling (Fig 3.1, a), where different levels of coarse-graining are used within the same system to treat its different parts. From one hand this proved to be an efficient way to study complex systems where phenomena of different nature and time scale are important. From the other hand, this shows the weaknesses in construction of the precise coarse-grained models and in definitions of the techniques to construct such models.

All the levels of theory and coarse-graining are based on the accuracy and extent of detalization for description of a static system. If one wishes, this is a qualitative side of the model, which answers the question “How well can you describe the system and the processes?”. However, one is often interested in time-evolution of such system or in monitoring the time-dependent processes. This pushes one to develop methods to treat bigger systems for longer time scales, at given level of accuracy (level of theory and coarse-graining).

Obviously, more detailed and precise models may be used mostly for small systems and describe the processes on relatively short times scales, while for description of large system and for monitoring their dynamics for significant time scales one is bound to use more approximate and coarser models. However, it is also possible to use more clever algorithms to achieve longer time scales and/or to treat larges systems using the same model (level). For example, if the interactions are described with the all-atomic force field, the evolution time scales of the system may be extended by using rigid-body MD (RB-MD) over conventional all-atomic MD.
(AA-MM). Even better speedup may be achieved with use of the kinetic Monte Carlo (KMC) scheme. Using the temperature accelerated dynamics (TAD) or the hyperdynamics methods the speedup may be increased by many orders of magnitude, leading to the experimentally observable time scales (Fig. 3.2, b). The algorithms used thus answer the quantitative question “How big is the system to be simulated?” and “For how long it may be simulated?”.

Thus, the computational models may be formulated in terms of two parts – computations of interactions and computation of evolution. This thesis is focusing on the understanding the properties of the molecular machines working on the surfaces and in the solid state. Interesting processes happen in such systems at the timescale ranging from the femtoseconds to the nano- and microseconds. Thus it is most appropriate to use molecular mechanics description of the interactions and the molecular dynamics, in particular, the rigid-body molecular dynamics (RB-MD) method for studies of the time-evolution of such systems.

We will now describe each side of the methods used in this work, sufficient for understanding the results obtained and, hopefully, for starting doing analogous calculations. In hope that this work will be self-contained in some extent, some methods will be discussed in more details and the corresponding derivations will be given.

3.2. Molecular mechanics method

Molecular mechanics, or a force field, method uses computationally efficient functional form, which express the energy of the entire system as a sum of contributions from different types of system interactions which are usually grouped into bonded and non-bonded terms (3.1, a). The bonded terms (3.1, b) describe the
valence interactions – intuitive chemical concept, which operates with the interatomic bonds. Such terms describe the deformations due to the bond stretching \( (E_{\text{bonds}}) \), angle bending \( (E_{\text{angles}}) \), dihedral \( (E_{\text{dihedrals}}) \) and out-of-plane angles \( (E_{\text{oop}}) \). The non-bonded terms \((3.1, c)\) include dispersion van der Waals \( (E_{\text{vdw}}) \) and electrostatic Coulomb \( (E_{\text{el}}) \) interactions.

\[
E_{\text{tot}} = E_{\text{bonded}} + E_{\text{non-bonded}}
\]

\( (3.1, \text{a}) \)

\[
E_{\text{bonded}} = E_{\text{bonds}} + E_{\text{angles}} + E_{\text{dihedrals}} + E_{\text{oop}}
\]

\( (3.1, \text{b}) \)

\[
E_{\text{non-bonded}} = E_{\text{vdw}} + E_{\text{el}}
\]

\( (3.1, \text{c}) \)

The bonded and non-bonded functionals may be expressed in various ways, but all such expressions should capture essential physics of corresponding interactions (Fig 3.2).

Figure 3.2. The functional forms of the force field terms corresponding to different types of interactions: a) bonded interactions; b) non-bonded interactions

More general way to look on the molecular mechanical expression for the energy is by considering the Taylor series expansion of the true potential energy (which is assumed to be known somehow, e.g. from ab initio calculations):

\[
E(\bar{x}) = E(\bar{0}) + \sum_{i=1}^{N} \frac{\partial E}{\partial x_i} \bar{x}_i + \frac{1}{2} \sum_{i,j=1}^{N} \frac{\partial^2 E}{\partial x_i \partial x_j} \bar{x}_i \bar{x}_j + \ldots
\]

\( (3.2) \)
Since the expansion is made around some local minimum, the first-order derivatives are zero. If one retains only the pure (diagonal) second-order terms one will essentially obtain the functionals in Eq. 3.1 shown on Fig. 3.2. In this case the generalized coordinates \( \bar{x} \) will be internal degrees of freedom, such as bond lengths, angles between bonds, etc. This approximation makes up what is known as class I force fields. If one also considers the mixed second-order terms, the obtained functionals will constitute a class II force fields.

The functional form of the potentials used in Eq. 3.1 determines the limitations where the corresponding force field may be reliably used. For example, the use of the harmonic approximation to describe the bonding between atoms prevents the bond from the dissociation, because the energy of a pair of atoms taken apart on infinitely long distance will be infinitely big, while in reality it should be zero. Using the Morse or the Lennard-Jones types of the functions may potentially solve this problem at least it might provide asymptotically correct description.

Another essential part of the force field is its parameterization. The functionals in the potential energy expression are parameterized to represent some experimentally available data and/or high-level ab initio calculations on various molecular and/or crystal properties, such as structural data, vibrational frequencies, thermochemical data, etc. The parameters are usually supplied for given functional form of potential energy and usually can not be used for different functional form. Thus, more correct definition of the force field is the combination of the functional form for the potential energy and a set of parameters corresponding to such functional form.

The development of force field parameters is based on the atom type concept. From the chemical intuition and experience it is known that the atoms of the same element show different properties, depending in which environment they are inserted.
Also the properties of the atoms in different hybridization states are very different. For example the carbon atom in sp-hybridization will form linear fragments, those in sp² will form trigonal-planar fragments. Thus for each element there may be more than one atom type, to give enough flexibility for parameterization procedure to obtain accurate fit to experimental or ab initio data.

Thus the parameterization procedure may become a very difficult task because there are different parameters for each combination N atoms, where N is the order potential term. Thus for 2-particle terms (such as vdw-interactions or bond stretching) the number of required parameters is of the order M², while for 4-particle terms (dihedrals, oop) this number increased to M⁴, where M is the number of atom types in given force field. In most force field this problem is solved by neglecting many of the required interactions. The parameterization procedure is then focused on special kind of the systems which the force field is targeting on, such as liquids[122–124], crystals[125], macromolecules[126–130] or small molecules[131–136].

In recent generations of the force fields[136–140], the empirical rules are used to calculate the parameters for N-particle term parameters using the information for each of N atoms. This greatly reduces the number of the required parameters and makes the force field more convenient for implementation and more transferrable.

One of the most important limitations of the molecular mechanics methods is their inability to describe the chemical reactions. However, this problem has partially been addressed in recent studies, where the reactive force fields have been developed for bulk non-metals such as carbon[141], silicon[142–144], for bulk metals and alloys[145–147] and for multicomponent systems[148–151]. Such force fields are based on much more complex functional forms of the potential energy. The complex functional form of such force fields is based on the quantum-mechanical
considerations, requirements to have correct asymptotic behavior and chemical concept of hybridization and oriented chemical bonds. The parameterization strategy is also quite elaborate and may require much more parameters to describe atom of single type. However, the overall number of parameters necessary to describe interactions between atoms of different type is much smaller in comparison to standard force field parameter sets.

Such construction makes the force fields of this type suitable for description of the chemical reactions (hence their name) in amount of time much smaller that required by semi-empirical or ab initio methods, but much bigger in comparison to standard force fields. The accuracy of the reactive force fields is usually much higher than that of standard force fields. It may even be comparable to high-level ab initio results.

The analysis of the reactive force field construction reveals its relation to the bond order concept. However, such bond order may be defined in slightly different way than it is given in general chemistry courses. The bond order between two atoms is usually defined as:

\[ bo_{ij} = Ae^{-\alpha r_{ij}} \]

where \( r_{ij} \) - is a distance between atoms, \( A \) and \( \alpha \) - are some parameters. As we can see, the bond order vanishes for infinite separation of the atoms and is finite for all other distances. As we can see, the bond order is a two-particle function. Using it as independent variable and expressing the potential energy of the system in terms of a set of such bond-order functions would significantly enhance the quality of the potential, as it will inherently be many-body potential.

A construction of the force fields in terms of the bond order variable has been discussed and applied in some previous works[152–156]. Especially encouraging
results of such approach have been obtained by Sellers and Shustorovich[97], [157–
163] for description of ad-atom and small ad-molecules chemisorption on the metal
surfaces. The approach was based on the combination of the potential energy
representation in terms of the bond-order variables (Eq. 3.4, a) and the empirical
bond-order conservation principle (Eq. 3.4, b):

\[ E = \sum_{(i,j)} D_{ij} \left[ b_{\alpha_{ij}}^2 - 2 b_{\alpha_{ij}} \right] \quad a) \]

\[ \sum_{(i,j)} b_{\alpha_{ij}} = 1 \quad b) \quad (3.4) \]

The energy expression (Eq. 3.4, a) is optimized with respect to bond-order parameters
\( b_{\alpha_{ij}} \) subject to constraint (Eq. 3.4, b). Resulting optimized bond-orders \( b_{\alpha_{ij}}^0 \) are then
used in (Eq. 3.4, a) to calculate the energy of the system.

The origins of the bond-order conservation principle are discussed in details
elsewhere[162]. Although this principle is not rigorous it provides very accurate
results which are comparable to high-level DFT calculations. Moreover, the approach
is very inexpensive from the computational point of view, what makes it suitable for
performing the molecular dynamics simulation of small molecules adsorbed on the
metal surfaces[157].

As we can see the method used by Sellers and Shustorovich is based on
expression of the potential energy as the second-order polynomial in bond-order
variable, which in fact, is nothing but a simple Morse potential. More generally, the
potential may be written in form:

\[ E = \sum_{(i,j)} a_{ij} b_{\alpha_{ij}} + \sum_{(i,h,j,k)} a_{i,h,j,k} b_{\alpha_{i,h}} b_{\alpha_{j,k}} + \ldots + \sum_{(i_{n}, \ldots, i_{1})} a_{i_{n}, \ldots, i_{1}} b_{\alpha_{i_{n}}} \cdot \ldots \cdot b_{\alpha_{i_{1}}} \quad (3.5) \]

However, in order to be practically used such potential needs to be
parameterized. For polynomials of the second order, retaining only diagonal elements
this problem reduces to the parameterization of the More-type potential and is may be
done easily. As one increases the order of the polynomial (Eq. 3.5) the parameterization procedure becomes more expensive. However once it is done the resulting potential would be of great use for description of the chemical reactions, e. g. in molecular dynamics simulations.

3.3. Classical Hamiltonian dynamics

The basics of the (all-atomic) molecular dynamics method are well described in many sources, and have been successfully applied to a wide range of system types, ranging from proteins[164–167], membranes[168–170] and ion channels[171], [172] to self-assembled monolayers,[90], [97], [173], [174] interfacial systems[48], [81], [101], [175], crystalline objects[176], [177] and biological[178] and artificial[80], [179], [180] nanomachines.

The molecular dynamics method relies on the classical mechanical description of the system’s temporal evolution, that is the particles’ positions and velocities (momenta) change in time according to solution of the Hamilton equations of motion, generated by Hamiltonian function (or just Hamiltonian) $H$:

$$
\begin{align*}
\dot{r}_i &= \frac{\partial H}{\partial \dot{p}_i} \\
\dot{p}_i &= -\frac{\partial H}{\partial r_i}
\end{align*}
$$

(3.6)

Such description is simply a reformulation of the Lagrangian formalism, with the Newton equations being its special case. Such reformulation translates the system of second-order differential equations to different system of coupled first-order differential equations. This makes them easier to solve, especially by numerical methods and also significantly enhances the development of Hamiltonian dynamics methods and analysis.
The equations (3.6) may further be generalized to define any arbitrary Hamiltonian system. To do this we consider the motion of the phase space variable 
\[ \tilde{q} = \begin{pmatrix} \tilde{r} \\ \tilde{p} \end{pmatrix} \in R^d \times R^d \] in an even-dimensional phase space \( R^d \times R^d \), where \( 2d - \) is a dimensionality of the system. For the system of \( N \) particles in 3D physical space \( d = 3N \) and \( \tilde{r} = \begin{pmatrix} \tilde{r}_1 \\ \vdots \\ \tilde{r}_N \end{pmatrix} \in R^{3N} \) is a vector of all coordinates and \( \tilde{p} = \begin{pmatrix} \tilde{p}_1 \\ \vdots \\ \tilde{p}_N \end{pmatrix} \in R^{3N} \) is a vector of all conjugate momenta. It is also necessary to introduce the structure matrix \( J \), which in case \( J = \begin{pmatrix} 0 & I_d \\ -I_d & 0 \end{pmatrix} \) is called canonical structure matrix (\( I_d \) is a \( d \)-dimensional identity matrix). With the help of the canonical structure matrix \( J \), the canonical Hamiltonian equations (3.6) may then be written as:

\[
\frac{d\tilde{q}}{dt} = J \frac{dH(\tilde{q})}{d\tilde{q}} \tag{3.7}
\]

The generalization is then achieved by considering different structure matrices, such that they within (3.7) produce the required equations of motion. This may require the matrix \( J \) to depend on the phase space variable \( \tilde{q} \).

For all-atomic system representation the Hamiltonian takes the form:

\[
H = T + V(\{\tilde{r}\}) = \sum_{i=1}^{N} \frac{\tilde{p}_i^2}{2m_i} + V(\{\tilde{r}\}) \tag{3.8}
\]

where \( T \) is a kinetic energy term and \( V(\{\tilde{r}\}) \) - a potential energy, which is given in some computationally tractable way, for example, by a force field expression (3.1). Since the functional form of the potential energy is known explicitly (at least in force-field approach) it is easy to obtain the explicit expression for its derivatives with respect to the system coordinates (negative forces). The computational cost to
calculate the forces is slightly higher than for calculation of the energy alone. However, for both energy and the forces such computations are orders of magnitude faster than even for semi-empirical methods.

Application of (3.6) to the Hamiltonian (3.8) gives:

\[
\begin{align*}
\dot{r}_i &= \frac{\ddot{p}_i}{m_i} \\
\dot{p}_i &= -\frac{\partial V}{\partial \dot{r}_i} = f_i
\end{align*}
\]

(3.9)

The most common and reasonable algorithm to solve these equations is the Verlet algorithm[181]. Originally (position Verlet) it has been obtained by combination of the second-order Taylor series expansions of the positions for different times:

\[
\begin{align*}
\ddot{r}_i(t + dt) &= \ddot{r}_i(t) + dt \cdot \frac{\dddot{r}_i(t)}{m_i} + \frac{dt^2}{2!} \frac{\dddot{r}_i(t)}{m_i} + O(dt^3) + O(dt^4) \\
\ddot{r}_i(t - dt) &= \ddot{r}_i(t) - dt \cdot \frac{\dddot{r}_i(t)}{m_i} + \frac{dt^2}{2!} \frac{\dddot{r}_i(t)}{m_i} - O(dt^3) + O(dt^4) \\
\Rightarrow \ddot{r}_i(t + dt) &= 2 \cdot \ddot{r}_i(t) - \ddot{r}_i(t - dt) + \frac{dt^2}{m_i} \frac{\dddot{r}_i(t)}{2} + O(dt^4) \\
\ddot{p}_i &= \frac{\ddot{r}_i(t + dt) - \ddot{r}_i(t - dt)}{2 \cdot dt}
\end{align*}
\] (3.10)

Further re-arrangement of variables leads to a velocity Verlet form:

\[
\begin{align*}
\forall i \quad \ddot{p}_i(dt) &= \ddot{p}_i(0) + \frac{dt}{2} \left[ \dddot{f}_i(0) + \dddot{f}_i(dt) \right] \\
\forall i \quad \ddot{r}_i(t) &= \ddot{r}_i(0) + dt \ddot{p}_i(0) + \frac{dt^2}{2} \dddot{f}_i(0)
\end{align*}
\] (3.11)

More general approach to construct the algorithms for solving dynamical equations of motion (the integration algorithms, or integrators) has been developed recently[182–187]. It is based on a Liouville formulation of the classical mechanics. According to such formulation, the motion of the phase space variable may be
characterized by the distribution function $\rho(\dot{q})$. According to Liouville theorem, this
distribution function is constant along any trajectory in phase space. Mathematically
this may be described as the incompressible flow of the density function in the
configuration phase space:

$$\frac{d\rho(\dot{q})}{dt} = \frac{\partial \rho(\dot{q})}{\partial t} + \sum_{i=1}^{N} \left[ \frac{d\rho(\dot{q})}{d\dot{r}_i} \dot{r}_i + \frac{d\rho(\dot{q})}{d\dot{p}_i} \dot{p}_i \right] = 0 \quad (3.12)$$

Using the Hamiltonian equations of motion (3) the Liouville equation (9) may
be rewritten:

$$\frac{d\rho(\dot{q})}{dt} = -\sum_{i=1}^{N} \left[ \frac{d\rho(\dot{q})}{d\dot{r}_i} \frac{\partial H}{\partial \dot{r}_i} - \frac{d\rho(\dot{q})}{d\dot{p}_i} \frac{\partial H}{\partial \dot{p}_i} \right] = -\{\rho(\dot{q}), H\} = -iL\rho(\dot{q}) \quad (3.13),$$

where $iL = \sum_{i=1}^{N} \left[ \frac{\partial H}{\partial \dot{r}_i} \frac{\partial}{\partial \dot{r}_i} - \frac{\partial H}{\partial \dot{p}_i} \frac{\partial}{\partial \dot{p}_i} \right] = \{\cdot, H\}$ is so-called Liouville operator, which has a
structure of a Poisson bracket of the Hamiltonian and the operator of differentiation
with respect to generalized coordinates and their conjugate momenta.

If the Liouville operator does not depend on time explicitly, the formal
solution to equation (3.13) may be then written as:

$$\rho(\dot{q}(t)) = e^{-iLt} \rho(\dot{q}(0)) \quad (3.14)$$

The exponential operator on the right-hand side is called the evolution operator, or
propagator, because it determines how the generalized coordinates and momenta
propagate in time.

In simple cases the Liouville operator may depend on only one coordinate or
one momentum, e.g. $iL_r = x \frac{\partial}{\partial \dot{r}_i}$ or $iL_p = y \frac{\partial}{\partial \dot{p}_i}$, where $x$ and $y$ are some functions or
constants which do not depend on $\dot{r}_i$ and $\dot{p}_i$, correspondingly. In such simple cases the
action of the corresponding propagators is calculated by considering their Taylor
series representation, for example:
\[ \rho(q(t)) = e^{-iut} \rho(q(0)) = \left[ 1 - xt \frac{\partial}{\partial \vec{r}_i} + \frac{(xt)^2}{2!} \frac{\partial^2}{\partial^2 \vec{r}_i} + \ldots \right] \rho(q(0)) = \]
\[ \left[ \rho(q(0)) - xt \frac{\partial \rho(q(0))}{\partial \vec{r}_i} + \frac{(xt)^2}{2!} \frac{\partial^2 \rho(q(0))}{\partial^2 \vec{r}_i} + \ldots \right] = \rho(q'(0), \vec{r}_i(0) - xt) \]

where the prime means all the coordinates except for \( \vec{r}_i \). Thus the action of the simple
operators of type \( iL_x = \alpha \frac{\partial}{\partial x} \) consists of shift of the coordinate \( x \) on amount \( \alpha \):
\[ iL_x = \alpha \frac{\partial}{\partial x} : x \rightarrow x + \alpha \quad (3.16) \]

Similarly to (3.15) the action of the operator \( iL_x = \alpha \frac{\partial}{\partial x} \) may be shown to be simple
scaling of the coordinate \( x \):
\[ iL_x = \alpha \frac{\partial}{\partial x} : x \rightarrow \alpha x \quad (3.17) \]

In most cases, however, the Liouville operator may contain expressions, depending on all positions and momenta or part of them. In this case the calculation of the action of the evolution operator is based on the Trotter formula (factorization)[183], [187–190]. If the entire operator \( iL \) may be decomposed into pieces: \( iL = iL_1 + iL_2 \), then the Trotter factorization will read:
\[ e^{itL} = e^{(itL_1) + (itL_2)} = \left\{ \left( e^{itL_1/2P} e^{itL_2/2P} e^{itL_1/2P} \right)^P \right\} a) \]
\[ \left\{ \left( e^{itL_1/2P} e^{itL_2/2P} e^{itL_1/2P} \right)^P \right\} b) \quad (3.18) \]

As we can see the factorization may be performed in two different ways. Although for both cases the order of approximation is the same, namely \( 2P \), the choice of one decomposition way over the other may lead to slight difference in the accuracy of the corresponding scheme. It may also lead to more convenient expressions and, most importantly, to significant difference in the computational costs.
Note, that if the parts $iL_1$ and $iL_2$ commute, that is their commutator $[iL_1, iL_2] = iL_1 iL_2 - iL_2 iL_1$ is zero, then the factorization (3.18) is exact and also redundant, since in this case it is possible to simply write $e^{iL} = e^{(iL_1+iL_2)} = e^{iL_1} e^{iL_2} = e^{iL_2} e^{iL_1}$.

To demonstrate how the technique is working and how the factorization schemes in (3.18) differ from each other we will now consider the evolution of the systems, governed by equations (3.9). In this case the Liouville operator may be written as: $iL = \sum_{i=1}^{N} \left[ \frac{\tilde{p}_i}{m_i} \frac{\partial}{\partial \tilde{r}_i} + \tilde{f}_i \frac{\partial}{\partial \tilde{p}_i} \right]$. Obviously, the factorization can be done in a following way: $iL_1 = \sum_{i=1}^{N} \left[ \frac{\tilde{p}_i}{m_i} \frac{\partial}{\partial \tilde{r}_i} \right]$ and $iL_2 = \sum_{i=1}^{N} \left[ \tilde{f}_i \frac{\partial}{\partial \tilde{p}_i} \right]$. Since these operators do not commute with each other we should use the Trotter formula (15). We restrict ourselves on the second-order factorization scheme, that is we consider $P=1$. This will lead to:

$$\exp\left( \frac{dt}{2} \sum_{i=1}^{N} \left[ \tilde{f}_i \frac{\partial}{\partial \tilde{p}_i} \right] \right) \exp\left( dt \sum_{i=1}^{N} \left[ \frac{\tilde{p}_i}{m_i} \frac{\partial}{\partial \tilde{r}_i} \right] \right) \exp\left( \frac{dt}{2} \sum_{i=1}^{N} \left[ \tilde{f}_i \frac{\partial}{\partial \tilde{p}_i} \right] \right)$$  \hspace{1cm} (3.19, a)

$$\exp\left( \frac{dt}{2} \sum_{i=1}^{N} \left[ \frac{\tilde{p}_i}{m_i} \frac{\partial}{\partial \tilde{r}_i} \right] \right) \exp\left( dt \sum_{i=1}^{N} \left[ \frac{\tilde{p}_i}{m_i} \frac{\partial}{\partial \tilde{r}_i} \right] \right) \exp\left( \frac{dt}{2} \sum_{i=1}^{N} \left[ \tilde{f}_i \frac{\partial}{\partial \tilde{p}_i} \right] \right)$$  \hspace{1cm} (3.19, b)

The 1-particle operators in the sums $iL_1 = \sum_{i=1}^{N} \left[ \frac{\tilde{p}_i}{m_i} \frac{\partial}{\partial \tilde{r}_i} \right]$ and $iL_2 = \sum_{i=1}^{N} \left[ \tilde{f}_i \frac{\partial}{\partial \tilde{p}_i} \right]$ do commute with each other (with the same type of 1-particle operator, but for different particle index), because the forces do not depend on the momenta (in $iL_2$), and the momenta do not depend on positions (in $iL_1$). Thus the operations may be performed in any order, for all particles.
Using the action of the simple shift operators (3.16) we may write the explicit form of the algorithms, corresponding to factorizations (3.18):

\[ \forall i \quad \vec{p}_i\left(\frac{dt}{2}\right) = \vec{p}_i(0) + \frac{dt}{2} \vec{f}_i(0) \]

\[ \forall i \quad \vec{r}_i(dt) = \vec{r}_i(0) + dt \vec{p}_i\left(\frac{dt}{2}\right) \]  

(3.20, a)

\[ \forall i \quad \vec{f}_i(dt) = \vec{f}_i(\{\vec{r}_i(dt)\}) \]

\[ \forall i \quad \vec{p}_i(dt) = \vec{p}_i\left(\frac{dt}{2}\right) + \frac{dt}{2} \vec{f}_i(dt) \]

(3.20, b)

Here by writing \( \forall i \quad \vec{f}_i(t) = \vec{f}_i(\{\vec{r}_i(t)\}) \) we emphasized that the forces at time \( t \) should be recalculated as they depend on the updated positions of the atoms. As one can see in a factorization scheme (3.20, b) the force at the end of integration interval \( dt \) are not known. For performing MD they are not needed. However, if one needs them for other purposes they should be recalculated again, while in the scheme (3.20, a) they are already known. Since the calculation of the forces is computationally most expensive part of the entire calculations, the efficiency of the scheme (3.20, b) will be two times less than for (3.20, a).

The set of equations (3.20, a) may be rewritten in a compact form, which immediately gives the velocity Verlet update rule (3.11), while the scheme (3.20, b) is equivalent to position Verlet (or just Verlet) scheme (3.10).
The Trotter factorization technique is now a standard approach for construction of the integration algorithms. This is because, in contrast to other methods used, such as predictor-corrector or Runge-Kutta methods, the Trotter-derived methods possess important property, which is not always the case for other methods – the time reversibility. This is a fundamental property of the time-space continuum, which follows from the symmetry considerations. The microscopic reversibility is one of the fundamental principles for building statistical-mechanical theories and thus it should be preserved in all molecular simulations techniques, such as molecular dynamics.

The time reversibility of the Trotter-based algorithms simply follows from the structure of the evolution operator. If one propagates the system for some time \( t \) and then reverses the direction of time-flow and propagates the system for the same amount of time but in opposite direction \(-t\), one will end up with the initial configuration:

\[
\rho(0) \rightarrow e^{ilt} \rho(0) \rightarrow e^{-ilt}(e^{ilt} \rho(0)) = \mathbb{I} \rho(0) = \rho(0)
\]

Another important property which is the case for the Trotter-based algorithms is the symplecticity. This property is related to conservation of the phase volume during its evolution. The symplecticity property may formally be defined in a following way.

The evolution operator, constructed by Trotter factorization of the Liouville operator defines a composite of some smooth mappings of the phase space onto itself. Such mappings are, for example, given by composition of elementary mapping such as (3.16) and (3.17). The transformations are parameterized by some constant \( t \), which usually has the meaning of time, and by the Hamiltonian function:

\[
\psi_{t,t'}(\vec{q}) : \mathbb{R}^{2d} \rightarrow \mathbb{R}^{2d}
\]

(3.22)
The symplecticness of the map (19) with respect to the structure matrix $J$ is then given by:

$$ \Psi^T_q(q) J^{-1} \Psi^T_q(q) = J^{-1}, \forall \bar{q}, $$

(3.23)

where $\Psi^T_q(q)$ is a Jacobian of the map (3.22).

It may be shown that for any Hamiltonian system, as defined in (3.7), the flow map (3.22) is a symplectic map. Thus, the Trotter-derived integrators for Hamiltonian systems are both time-reversible and symplectic. The symplecticity condition may be lost for factorization of the Liouville operator which involves non-commuting parts.

Importance of the symplecticity for the molecular dynamics simulations lies in its physical interpretation. In very simple language it means the conservation of the phase space volume during the trajectory. In other words the distribution density $\rho(\bar{q})$ in (3.12) is incompressible. As a result of volume conservation, the error accumulation does not happen during the trajectory. Moreover, it can be shown that the approximate evolution of the system with Hamiltonian $H(\bar{q})$ according to symplectic maps, is in fact, an exact evolution of some nearby Hamiltonian $\bar{H}(\bar{q}) = H(\bar{q}) + \delta H(\bar{q})$. Thus, the algorithms based on such approach will have no systematic trends in conserved properties, in particular in the total energy.

### 3.4. Rigid-body molecular dynamics

Standard all-atomic molecular dynamics utilizes the all-atomic description of the inter- and intra-molecular potentials. This however implies that many interactions should be computed explicitly at every step of MD algorithm. However, many degrees of freedom of the molecular system might be not important for understanding its dynamics and for calculation of the properties. For example the fast vibrational
motions of the aminoacid fragments may be of no particular importance for the protein folding process, which happens on much longer time scales. Analogously, very fast motions are unlikely to be of significant effect for determining opening/closing the membrane channels. However, in all-atomic approach such fast motions are integrated (solved) as any other type of motions. This usually does not increase the computational costs significantly, because such types of interactions are computationally very efficient (bond stretching, angle bending, etc.) and their number usually scales as the size of the system.

The problem arises from the fact, that for stable integration of equations of motion (e.g. 3.7) the integration time step $dt$ should satisfy the condition:

$$dt < \frac{\tau_{\text{min}}}{2},$$

(3.24)

where $\tau_{\text{min}}$ is a minimal period of the vibrations for given system. For example, the period of C-H vibrations in alkanes is of order of $10^{-14}$ s. Thus the integrations time steps up to 5 fs (1 fs = $10^{-15}$ s) may be used. Practically, the time steps of 0.5 – 1.0 fs are used to increase the accuracy and stability of the calculations. As we can see, the presence of high-frequency modes in the systems leads to bigger number steps, just to describe accurately useless vibrations.

In effort to increase effective integration time step by removing fast vibrational modes from the system, several approaches have been developed. They achieve such goal be imposing the holonomic constrains on some of the system’s internal variables, such as bonds, angles, dihedrals, etc. From the computational point of view the equations of motion are usually obtained starting from the Lagrangian formulation. According to it the initial Lagrangian function (Lagrangian)

$$L = T - V(\{r\})$$

(3.25)
is modified by adding holonomic constrains (which are zeroes):

\[ \tilde{L} = T - V(\{\vec{r}\}) + \sum_i \lambda_i f_i(\{\vec{r}\}), \quad (3.26) \]

where functions \( f(\{\vec{r}\}) \) define constraints, for example for fixing a bond it may look like \( f_i(\{\vec{r}\}) = r_{ij}^2 - (r_{ij}^0)^2 = 0 \) and \( \lambda \) - are the Lagrangian multipliers. Optimizing the modified Lagrangian with respect to \( \lambda \) multipliers and then writing Lagrange equations of the second kind one obtains the equations of motion to be solved. Most notable techniques of this kind are called LINCS[191], SHAKE[192] and RATTLE[193] and their variations[194–199]. Numerically such optimization/solving procedure is usually performed in iterative way, which is not efficient and destroys the time-reversal symmetry. Moreover, if the bond constrains are relatively simple, for constraining some other types of motions, such as angles of dihedrals the resulting expression will be much less attractive. Also as the number of constraints increases, the computation costs might become comparable to calculation of the potential and forces, thus significantly reducing the efficiency.

Alternative approach to avoid unnecessary expensive calculations and to increase acceptable integration time step is related to combination of several atoms in the rigid fragments and description of the motion of such fragments in contrast to the motion of all individual atoms. Such approach is known as the rigid body molecular dynamics (RBMD). Thus the RBMD helps to constrain the high frequency internal degrees of freedom. Another advantage of RBMD is that for the interactions between atoms of the same rigid body need not be computed, what may significantly accelerate the calculations.
In RBMD method the motion of rigid bodies comprising the systems is computed explicitly, including both translational and rotational (orientation) degrees of freedom. The Hamiltonian of the system of rigid bodies may be written as

$$H = H_T + H_{rot} + V(\{r\}) = \frac{1}{2} \sum_{i=1}^{rb} \frac{\vec{p}_i^2}{M_i} + \frac{1}{2} \sum_{i=1}^{rb} \left( \vec{r}_i^{(b)} \right)^T \mathbf{I}_i^{(b)-1} \vec{r}_i^{(b)} + V(\{\vec{R}, \mathbf{A}\}),$$

(3.27)

where the kinetic energy is split into two parts – translational and rotational. In addition to \(rb\) positions of centers of mass \(\vec{R}_i\) of all fragments and their conjugate momenta \(\vec{p}_i\), the orientation variables \(A_i\) are introduced in combination with the angular momenta \(\vec{L}_i\) of the rigid bodies.

Before going further it is useful to describe the coordinate systems conventions and transformation (Fig. 3.3). The motion of the system takes place in some fixed external (laboratory) coordinate system \(OI_1I_2I_3\) (or lab frame). In all-atomic MD the coordinates of the atoms \(\vec{r}_i\) are expressed in this coordinate system.

![Diagram of coordinate systems](image)

**Figure 3.3.** Definition of the coordinate systems used in formulation of the rigid body equations of motion

However, the equations of motion for the rigid body may be expressed and solved much more conveniently in other coordinate system \((OE_1E_2E_3)\), which is
conventionally called body-fixed, or just body coordinate system (or body frame). To construct such system we first separate the translational and rotational motions by considering an intermediate coordinate system $O_{i_1i_2i_3}$, centered on the center of mass of the rigid body $\overline{R}_a$ and moving with the body. Thus the coordinate of the center of mass is zero in such system. Next, the inertia tensor of the body in $O_{i_1i_2i_3}$ system may be computed $I_a^{(i)}$. Since the inertia tensor is symmetric, it is possible to find such transformation matrix $A_{\text{lab}}$, which diagonalizes the inertia tensor:

$$A_{\text{lab}}^{(i)} A_{\text{lab}}^{T} = I_a^{(e)} = \text{diag}(I_1, I_2, I_3) \quad (3.28)$$

The matrix $A_{\text{lab}}$ defines the orientation of the rigid body with respect to the intermediate coordinate system $O_{i_1i_2i_3}$ and therefore with respect to the lab frame as well (where the observer is located). Such matrix is usually called an attitude matrix. The body frame may be imagined as a part of the body itself. Thus in this coordinate system the positions of all atoms, constituting the rigid body are time-independent.

In contrast to all-atomic MD the positions of the atoms are indexed by two indices – the index of the atom among other atoms in given rigid body $(i)$ and the index of the rigid body, to which the atom belongs $(a)$. We also denote the atomic variables by small letters and the rigid-body variables by big letters. Assuming such convention the relation between the atomic coordinates and the rigid-body variables in different coordinate systems is given by the following equations:

$$\tilde{r}_a^{(i)} = \overline{R}_a^{(i)} + A_{\text{lab}}^T r_a^{(e)}$$

$$\overline{R}_a^{(i)} = \frac{1}{M_a} \sum_{i=1}^{N_a} m_i r_{i,a}^{(i)}$$

$$M_a = \sum_{i=1}^{N_a} m_i \quad (3.29)$$

The orientation of the rigid body may be specified in several different ways. Most common choices are the attitude matrix (which is described earlier) or the
quaternions. Other alternative choices such as Euler angles, yaw-pitch-roll, Andoer-Deprit variables[200], [201] are less common for molecular dynamics applications. In general, the angular momenta are not conjugate momenta for the orientational variables chosen. Thus the Hamiltonian equations (3.6) are not applicable to the pairs: attitude matrix – angular momentum or quaternion – angular momentum. Instead, the equations of evolution of the orientation variables (3.30, c) and the angular momenta (3.30, d) are derived from the laws of conservation of the angular momenta. The equations for translational variables (3.30, a and b), however, still may be obtained from the Hamilton equations (3.6):

\[
\begin{align*}
\ddot{\vec{R}}_a &= \frac{\vec{P}_a}{M_a} \quad a) \\
\ddot{\vec{P}}_a &= -\frac{\partial V}{\partial \vec{R}_a} \equiv \vec{F}_a \quad b), \\
\dot{A}_a &= -\text{skew}\left(\vec{I}_a^{(e)}\right)^\top \vec{I}_a^{(e)} A_a \quad c) \\
\dot{\vec{I}}_a &= \vec{r}_a - \text{skew}\left(\vec{I}_a^{(e)}\right)^\top \vec{I}_a^{(e)} F_a \quad d)
\end{align*}
\]

where \(\text{skew}(\vec{x}), \vec{x} \in \mathbb{R}^3\) defines a skew-symmetric matrix:

\[
\text{skew}(\vec{x}) = \begin{pmatrix}
0 & -x_3 & x_2 \\
x_3 & 0 & -x_1 \\
-x_2 & x_1 & 0
\end{pmatrix}
\] (3.31)

In fact, the skew-symmetric matrices are used here to conveniently represent the vector products, by recalling the identity:

\[
\text{skew}(\vec{x})\vec{y} = \vec{x} \times \vec{y}
\] (3.32)

Integration of the equations of motion for translational variables (position of the central of mass and the translational momentum) is usually performed in the same way as for all-atomic MD, using Verlet-like schemes. The most challenging part of the computations of dynamics of the rigid bodies is related to a solution for rotational variables (e.g. angular momentum and the attitude matrix).
Several RBMD methods have been developed recently[202–212]. Most of them were constructed in such a way that they have important geometric properties of corresponding evolution operations (mapping), such as symplecticity, time reversibility or both. The properties mentioned are usually the consequence of the propagator construction, based on Trotter decomposition[188], [189] of the corresponding Liouville operator. As it has already been discussed such schemes always generate the time reversible mapping, but it is not necessary that the mappings will always be symplectic.

Using the Trotter decomposition technique the rigid body dynamics problem is usually decomposed into two parts – the torque-free (or just free) rigid body (FRB) problem and the rest of problem which includes the effect of forces and torques. The solution of the latter part is usually the same for most of the methods. The diversity of RBMD methods is due to various approaches to solve the FRB problem. This may be achieved by 5 rotations[202], 4 rotations and Rodrigues formula[203], [208], rotations in quaternion space[203], [206] as well as the use of the fact that this problem is analytically solvable in terms of Jacobi elliptic functions[204], [205], [211], [212]. It should be noted that there are some other techniques[209] that do not split FRB problem from the part which includes the effect of the forces and torques.

The analytic solution of the FRB problem, utilizing the Jacobi elliptic functions is obviously one which should be chosen due to its exact nature. However, its implementation is quite elaborate because of the necessity of considering many special cases, which may arise from one or another set of initial conditions and properties of the inertia tensors of the rigid bodies. Moreover, although there are various libraries which implement the Jacobi elliptic functions and integrals, they may introduce some code dependencies, which are not always desirable. In addition use of
such functions may require extra calculations to be performed. On the contrary, although approximate, the methods based on 5 or 4 rotations are easier to implement and more robust to the choice of initial conditions of properties of the rigid bodies as well as cheaper to calculate.

In this work (see Chapter 4) the rigid-body algorithms have been tested and compared to each other. In addition we have developed a new method to solve the FRB problem up to machine precision, which provides certain advantages over all other methods discussed. The details of such comparisons will be presented and discussed in Chapter 4.

3.5. Non-Hamiltonian molecular dynamics

The approaches for all-atomic and the rigid-body molecular dynamics described in previous sections generate the trajectories with the constant energy (Hamiltonian). Many realizations of such trajectories, obtained with different starting conditions form the microcanonical, or the constant number of particles – constant volume – constant energy (NVE) ensemble. The distribution function for such ensemble is a delta-function (3.33), what is basically a reformulation (or a consequence) of Liouville’s theorem (3.12):

\[ \rho(q) = \delta(H(q) - E) \]  

(3.33)

The sampling in microcanonical ensemble, however, leads to significant fluctuations of the thermodynamic observables, such as temperature, pressure, etc., which are usually considered constant in real experimental setups. This makes the comparison between experimental and theoretical (simulation) results difficult. Therefore, it is very important to be able to perform MD simulations at constant temperature or/and pressure. For this purpose a number of methods of non-
Hamiltonian molecular dynamics have been developed. In this section we will only describe the basics of such methods.

3.5.1. NVT ensemble

The algorithms for simulations at constant temperature are extremely well-developed since the temperature is, perhaps, the most important parameter which can be varied in experiments and provides most information about thermodynamics of the systems.

The simplest method to constrain the temperature is based on the statistical-mechanical definition of temperature as an average kinetic energy of system (3.34) per degree of freedom:

\[ N_f k_B T = \langle E_{\text{kin}} \rangle, \quad (3.34) \]

where \( N_f \) is number of degrees of freedom for given system, \( k_B \) - is a Boltzmann constant and \( \langle \rangle \) - denotes a statistical averaging. According to this definition the constant temperature may be maintained by re-scaling the velocities of the particles. Such re-scaling procedure may be performed on each MD step or after some predefined number of steps. Alternatively it can be done by weak coupling of the system of interest with the fictitious thermostat. The latter approach is known as Berendsen thermostat[213]. Both methods, however, fails to correctly describe the fluctuations of temperature, thus they do not produce correct NVT ensemble (canonical) distributions (3.35):

\[ \rho(\tilde{q}) \sim \exp\left(-\frac{H(\tilde{q})}{k_B T}\right) \quad (3.35) \]

Another approach to maintain the temperature of the system and correctly describe its fluctuations is by coupling system to a stochastic thermostat. There are
several stochastic thermostat approaches. One of the first such methods was proposed by H. Andersen, and therefore is known as Andersen thermostat[214]. According to Andersen’s prescription a certain number of particles are chosen randomly with given frequency. Their velocities are then chosen randomly from the Gaussian distribution with given temperature:

\[
P(v_i) = \left( \frac{1}{2\pi m_i k_B T} \right)^{3/2} \exp\left( -\frac{m_i v_i^2}{2k_B T} \right)
\]  

Alternative approach is the Langevin thermostat method[215]. In this method, the dynamical equations of motion (3.6) are modified by addition of the friction and stochastic forces, which simulate random collision of the particles of real system between each other and with fictitious particles of the thermostat correspondingly:

\[
\begin{align*}
\dot{r}_i &= \frac{\partial H}{\partial \dot{p}_i} \\
\dot{p}_i &= -\frac{\partial H}{\partial r_i} - \gamma \dot{r}_i + \xi(t)
\end{align*}
\]  

where \( \gamma \) is a molecular friction coefficient and \( \xi(t) \) is a Gaussian white noise:

\[
\langle \xi(t) \xi(t') \rangle = 6k_B T \gamma \delta(t-t') \delta_{ij}
\]  

Both Andersen and Langevin thermostats correctly sample from the canonical distribution and thus correctly reproduce temperature fluctuations and related properties. However, because of the presence of random variables, the momenta (velocities) are not continuous functions of time. This results in failures of such methods to correctly calculate dynamical properties of the systems, such as diffusion coefficients or velocity autocorrelation functions (and hence vibrational spectra).

Finally, the next generation of thermostatting techniques, which both correctly sample from the canonical distribution and provide continuous trajectories, is based on the extended phase space (or extended Hamiltonian, virtual variables) approach.

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The method was firstly developed by H. Andersen for performing MD simulations at constant pressure (NPH and/or NPT ensembles)[214] and then extended by S. Nose for constant temperature (NVT) simulations[216], [217]. Here we will summarize the key steps of the method applied to all-atomic MD.

### 3.5.2. Real and virtual variables

...can I take off my pants over my head?

*(Sheldon Cooper, Big Bang Theory)*

The extended variables method for all-atomic molecular dynamics starts with the standard form of Hamiltonian (3.8). It is then modified by adding terms describing effects of thermostat – corresponding kinetic and potential energies of thermostat:

\[
H_{\text{Nose}} = \sum_{i=1}^{N} \left( \frac{\tilde{p}_i^2}{2m_i} + V(\tilde{r}_i) \right) + p_s^2 + \frac{p_s^2}{2Q} + gk_bT \ln(s), \quad (3.39)
\]

where \( s \) - is the “position” variable of the thermostat, and \( p_s \) - is its conjugate momentum variable and \( Q \) - is an inertia parameter (mass) of thermostat. Here the prime denotes the virtual variables, while the variables without primes are real variable. Relation between these two sets of variables is given by:

\[
\begin{align*}
\tilde{p}_i &= \frac{\tilde{p}_i}{s} \\
p_s &= \frac{p_s}{s} \\
s &= s' \\
\tilde{r}_i &= \tilde{r}_i' \\
t &= \int \frac{d\tau}{s}
\end{align*}
\]

(3.40)

The last equation states that the time variable has its own virtual analog. In other words the integration time step is not constant along the trajectory.
evolution or dynamics of the given system may be described in terms of each separate set of variables – real or virtual. Introduction of virtual variables is in fact a key step for construction of the required algorithm.

The description of the system’s dynamics in virtual variables is an essential ingredient for performing non-Hamiltonian MD simulations. The dynamics is called non-Hamiltonian because the equations of motion can not be obtained from the Hamiltonian function using the Hamiltonian equations (3.6), although the Hamiltonian itself is a conserved quantity. In this case it is often incorrect to call such function a true Hamiltonian. Instead it is usually named a conserved quantity or a total energy function.

The importance of the virtual variables approach lies in the possibility to obtain correct equations of motion from the total energy function, if it is expressed in terms of the virtual variables. Therefore the equations in virtual variables are Hamiltonian in sense that they satisfy (3.6). Further transformation of the obtained equations to real variables using relations (3.40) leads to required equations of motions, which are no longer Hamiltonian. Let us demonstrate these general words in actual example of Nose thermostat for all-atomic MD.

The Nose Hamiltonian in virtual (primed) variables may be written:

\[ H_{\text{Nose}} = \sum_{i=1}^{N} \left( \frac{p_i'^2}{2m_i s^2} \right) + V(r) + \frac{p_i'^2}{2Q} + gk_BT \ln(s) \]  (3.41)

Using the Hamiltonian equations (3.6) it generates the equations of motion (in intrinsic or virtual time \( \tau \)):

\[
\frac{d\dot{r}_i}{d\tau} = \frac{\partial H_{\text{Nose}}}{\partial \dot{p}'_i} = \frac{\dot{p}'_i}{m_is^2} \quad \text{and} \quad \frac{dp'_i}{d\tau} = -\frac{\partial V}{\partial \dot{r}_i} \\
\frac{ds}{d\tau} = \frac{\partial H_{\text{Nose}}}{\partial \dot{s}} = \frac{p'_i}{Q} \\
\frac{d\dot{p}'_i}{d\tau} = \frac{-\partial V}{\partial r_i} \\
\frac{dp'_i}{d\tau} = -\frac{\partial H_{\text{Nose}}}{\partial s} = \sum_{i=1}^{N} \left( \frac{p_i'^2}{m_is^2} \right) - gk_BT \frac{1}{s} \]  (3.42)
Now if one uses the definition of the intrinsic time scale as: \( d\tau = sdt \), where \( dt \) – is a real time scale and other relations between real and virtual variables (3.40) the equations (3.42) may be expressed in real variables (and in real time scale):

\[
\frac{dr_i}{dt} = \frac{dr_i}{d\tau} \frac{d\tau}{dt} = s \frac{p'_i}{m_{s_{i}}} = \frac{p_i}{m_{i}},
\]

\[
\frac{dp_i}{dt} = \frac{1}{s} \frac{dp'_i}{dt} - \frac{1}{s^2} \frac{ds}{dt} p'_i = \frac{1}{s} \frac{dp'_i}{dt} = \frac{1}{s} \frac{d\tau}{dt} \frac{d\tau}{dt} p_i = \frac{dp'_i}{d\tau} \frac{d\tau}{dt} = \frac{dp'_i}{d\tau} \frac{d\tau}{dt} = \frac{dV}{d\tau} \frac{d\tau}{dt} = \frac{sp_i}{Q},
\]

\[
\frac{ds}{dt} = \frac{ds}{d\tau} \frac{d\tau}{dt} = s \frac{p'_i}{Q} = s^2 \frac{p_i}{Q},
\]

\[
\frac{dp_i}{dt} = \frac{1}{s} \frac{dp'_i}{dt} = \frac{1}{s} \frac{dp'_i}{dt} = \frac{1}{s} \frac{d\tau}{dt} \frac{d\tau}{dt} p_i = \frac{dp'_i}{d\tau} \frac{d\tau}{dt} = \frac{dp'_i}{d\tau} \frac{d\tau}{dt} = \frac{1}{s} \left[ \sum_{i=1}^{N} \frac{p_i^2}{m_i} - gk_{s}T \right] - \frac{sp_i^2}{Q}.
\]

(3.43)

These equations can not be obtained by direct application of the Hamiltonian equations (3.6) to the total energy function (3.39) and using real variables as independent. Thus the trick is to use some hidden relations and variables (which are thus called virtual) to obtain the necessary equations for real variables.

Further improvement of the Nose method has been done by Hoover[218–220], who noticed that variables \( s \) and \( p_s \) enter the equations (3.43) as their product. This allowed him to reformulate equations (3.43) in new variables:

\[
\xi = \frac{sp_s}{Q},
\]

(3.44)

\[
\eta = \ln s
\]

Such transformation leads to simpler system of equations, which are called Nose-Hoover equations (hence the thermostat name):

\[
\frac{dr_i}{dt} = \frac{p_i}{m_i},
\]

\[
\frac{dp_i}{dt} = -\frac{\partial V}{\partial \xi} - \frac{\xi}{s} \frac{dp_i}{dt},
\]

(3.45)

\[
\frac{d\eta}{dt} = \frac{1}{s} \frac{ds}{dt} = \frac{s \frac{p_s}{Q}}{s} = \xi,
\]

\[
\frac{d\xi}{dt} = \frac{ds}{dt} \frac{p_s}{Q} + s \frac{dp_s}{dt} = s \left( \frac{p_s}{Q} \right) + \frac{1}{Q} \left[ \sum_{i=1}^{N} \frac{p_i^2}{m_i} - gk_{s}T \right] - s^2 \frac{p_s^2}{Q} = \frac{1}{Q} \left[ \sum_{i=1}^{N} \frac{p_i^2}{m_i} - gk_{s}T \right]
\]

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In contrast to original Nose equations which lead to trajectories in virtual time, the Nose-Hoover equations are expressed in real time. This leads to convenient sampling along the trajectory, where all points are equidistant in time axis. As a consequence it significantly simplifies calculation of some properties, such as velocity autocorrelation functions.

The obvious drawback of the Nose-Hoover method is its inherent non-Hamiltonian structure. The total energy (3.39) is not a true Hamiltonian, only a conserved quantity (one of the integrals of motion). The true Hamiltonian is not known for Nose-Hoover equations (3.45). As a consequence one can not speak about the symplectic structure of corresponding dynamical system and can not develop symplectic integrators. This stimulated further development of Hamiltonian-based dynamics methods which could produce required probability distribution functions and which would generate the trajectory in real time. One of such methods is known as Nose-Poincare thermostat[216], [221], [222].

The method starts with the Nose Hamiltonian written in virtual variables (3.41) followed by its Poincare transformation:

$$H_{NP} = s\left\{ \sum_{i=1}^{N} \left( \frac{p_i^2}{2m_i s^2} \right) + V(r) + \frac{p_i^2}{2Q} + g k_b T \ln(s) - H_0 \right\}, \quad (3.46)$$

where $H_0$ - is initial value of the Nose Hamiltonian at time $t = 0$. Note, that for the Nose dynamics $H_{Nose}$ is a conserved quantity, leading to $H_{NP} = 0$.

The property of such Hamiltonian is that it generates the same equations of motion in real time that the Nose Hamiltonian generates in virtual time (but in virtual variables). In other words, the virtual variables propagate (evolve) in real time:
\[
\begin{align*}
\frac{d\vec{r}_i}{dt} &= \frac{\partial H_{NP}}{\partial \vec{p}'_i} = \frac{p'_i}{m_is} \\
\frac{ds}{dt} &= \frac{\partial H_{NP}}{\partial p'_s} = \frac{sp'_s}{Q} \\
\frac{dp'_i}{dt} &= -\frac{\partial H_{NP}}{\partial \vec{r}_i} = -s \frac{\partial V}{\partial \vec{r}_i} \\
\frac{dp'_s}{dt} &= -\frac{\partial H_{NP}}{\partial s} = \left[ \sum_{i=1}^{N} \left( \frac{p'^2_i}{m_is^2} \right) - gk_bT \right]
\end{align*}
\] (3.47, a)

with

\[
\Delta H = \sum_{i=1}^{N} \left( \frac{p'^2_i}{2m_is^2} \right) + V(r) + gk_bT \ln s + \frac{p'^2_s}{2Q} - H_0
\] (3.47, b)

These equations govern the evolution of the virtual variables in real time. Using them along with transformations (3.40) the original Nose-Hoover equations (3.43) may be obtained.

A comparison of Nose and Nose-Poincare-generated equations of motion is given in Table 3.1. Taking into account the chain rule: \( \frac{d^*}{dt} = \frac{d^*}{d\tau} = s \frac{d^*}{d\tau} \) we see that the equations are equivalent.

| Table 3.1. Comparison of the dynamical equations of motion, generated from Nose Hamiltonian (3.41) in virtual time and those generated from the Nose-Poincare Hamiltonian (3.46) in real time. |
|-----------------|-----------------|
| **Nose**       | **Nose-Poincare, assume \( \Delta H = 0 \)** |
| \( \frac{d\vec{r}_i}{d\tau} \) | \( \frac{p'_i}{m_is^2} \) |
| \( \frac{dp'_i}{d\tau} \) | \( -s \frac{\partial V}{\partial \vec{r}_i} \) |
| \( \frac{ds}{d\tau} \) | \( \frac{p'_s}{Q} \) |
| \( \frac{dp'_s}{d\tau} \) | \( \left[ \sum_{i=1}^{N} \left( \frac{p'^2_i}{m_is^2} \right) - gk_bT \right] \) |

The interpretation of Table 3.1 may be formulated as:
The evolution of the virtual variables in real time guided by Nose-Poincare Hamiltonian is equivalent to evolution of the virtual variables in virtual time guided by Nose Hamiltonian.

Thus, solving the Hamiltonian equations of motion, generated by Nose-Poincare Hamiltonian we calculate the virtual variables (and thus real variables), but in real time. The equations might be re-written for evolution of real variables in real time, but this requires a bit more derivation than the explicit derivation from the Hamiltonian.

Finally, let us compare the equation of motion for NVE and NVT ensembles (Table 3.2). We only compare the common parts, because in NVE case there are no s and P variables.

<table>
<thead>
<tr>
<th>Table 3.2. Comparison of the NVE and NVT methods</th>
</tr>
</thead>
<tbody>
<tr>
<td>NVE</td>
</tr>
<tr>
<td>( \frac{d \vec{r}_i}{dt} = \frac{p_i}{m_i} )</td>
</tr>
<tr>
<td>( \frac{dp_i}{dt} = -\frac{\partial V}{\partial \vec{r}_i} )</td>
</tr>
</tbody>
</table>

In computational sense, the NVT equations are just NVE equations written for virtual variables with the time step dt/s for positions evolution and s*dt for momenta evolution. This idea may be extended to the case of rotational degrees of freedom: the orientation and the attitude matrix will propagate with the dt/s time step during the free rotation step, while the linear and angular momenta would evolve with the s*dt time step during the interaction step. The evolution of the P_i and s variables will be calculated according to additional set of equations.
3.5.3. NPT ensemble

For physically relevant simulations of the solid-state objects one should particularly be concerned with proper sampling techniques. Namely, not only thermal fluctuations should be correctly described, but also fluctuations of the pressure and the average mass density as well as the packing motifs of the compound. Thus the simulations should be performed within the constant pressure – constant temperature ensemble (NPT).

Historically the simulations allowing the system to change its volume (NPH) have been formulated even earlier than the constant-temperature techniques (at least those based on extended system approach). In fact, the extended system method has been developed in the framework of the NPH-simulation algorithm[214]. Yet, the implementation of the NPT ensemble in MD code is, perhaps one of the most difficult among most popular ensembles, especially if the cell shape is allowed to vary as well as the volume. The method becomes even more involved for the systems with rotational degrees of freedom (rigid bodies). The detailed derivation and description of such method is very scarce. Since we have invested a lot of work in this problem it deserves to be described in full details in hope it will be useful for someone else.

Molecular dynamics simulations techniques at constant pressure and temperature are described and discussed in several studies[185], [223–225]. However, most of those techniques were developed for all-atomic descriptions of molecules. Although there are several works where the presence of holonomic constraints is considered[195], [197], [226], [227], there are only a few papers[203], [207], [226] describing the techniques for generating NPT ensemble in the rigid-body molecular dynamics. Two of the most detailed of them and which are based on the Liouville
operator splitting technique are the methods described by Kamberaj-Low-Neal[203] (KLN) and by Ikeguchi[207].

Each of these two methods, however, has some advantages and disadvantages with respect to each other. The KLN method, for example, contains several inaccuracies and potentially dangerous assumptions that will be addressed later, but the method uses separate thermostats coupled to barostat and system particles, what helps to avoid problems of poor sampling. At the same time, the approach of Ikeguchi[207] does not contain such inaccuracies in formulations, although it considers only one common thermostat coupled to both barostat and system particles simultaneously. Thus it seems that combining both approaches might be beneficiary for our goals.

The detailed derivation of the equations of motion for NPT ensemble is presented in Appendix A. We also provided the verification of the conservation of the extended energy as well as verification of the pressure tensor. Here we present the resulting re-formulation of KLN methods with some corrections. It can be shown that equations Eq. 3.48 are capable to reproduce the isobaric-isothermal (NPT) ensemble and they possess a conserved quantity Eq. 3.49.
\[
\ddot{q}_i = \frac{P_i}{m_i} + \xi_{\dot{q}_i} q_i
\]

\[
\ddot{p}_i = f_i - \xi_{\dot{p}_i} p_i - \frac{Tr(\dot{\xi}_i)}{g_f} p_i - \xi_{\dot{\xi}_i} p_i
\]

\[
\ddot{P}_i = 2MT_i - \frac{3}{4} \sum_{k=0}^{3} \frac{1}{4I_k} (P'_i D_k Q) D_k P_i - \frac{Tr(\dot{\xi}_i)}{g_f} P_i - \xi_{\dot{\xi}_i} P_i
\]

\[
\dot{\xi}_i = \frac{1}{2} M(Q_i) \dot{\alpha}_n = \sum_{k=0}^{3} \frac{1}{4I_k} (P'_i D_k Q) D_k Q_i
\]

\[
\dot{H} = \xi_{\dot{H}}
\]

\[
\dot{\xi}_{\dot{q}_i} = \frac{G_{\dot{q}_i}}{W} - \xi_{\dot{q}_i} \xi_{\dot{q}_i}
\]

\[
\dot{\xi}_{\dot{p}_i} = \frac{G_{\dot{p}_i}}{Q_{\dot{p}_i}} - \xi_{\dot{p}_i} \xi_{\dot{p}_i}
\]

\[
\dot{\xi}_{\dot{P}_i} = \frac{G_{\dot{P}_i}}{Q_{\dot{P}_i}} - \xi_{\dot{P}_i} \xi_{\dot{P}_i}
\]

\[
\dot{\eta}_k = \xi_{\dot{\eta}_k}
\]

\[
\dot{\xi}_{\dot{\eta}_k} = \frac{G_{\dot{\eta}_k}}{Q_{\dot{\eta}_k}} - \xi_{\dot{\eta}_k} \xi_{\dot{\eta}_k}
\]

\[
\dot{\xi}_{\dot{\eta}_n} = \frac{G_{\dot{\eta}_n}}{Q_{\dot{\eta}_n}} - \xi_{\dot{\eta}_n} \xi_{\dot{\eta}_n}
\]

(3.48)

\[
H_{NPT} = H_{NVT} + \frac{W \text{Tr}(\xi_{\ddot{\xi}} \dot{\xi})}{2} + P_0 \text{det}[H] + kT \left( d^2 \eta_i + \sum_{k=0}^{N} \eta_k \right) + \sum_{i=1}^{N} \left( \frac{Q_{\dot{\eta}_n} \xi_{\dot{\eta}_n}^2}{2} \right) = H_{NVT} + H_3
\]

\[
H_{NVT} = H_{NVE} + kT \left( g'_i s'_i + g'_j s'_j + \sum_{k=0}^{N} (s'_k + s'_k') \right) + \sum_{i=1}^{N} \left( \frac{Q_{\dot{\eta}_n} \xi_{\dot{\eta}_n}^2}{2} + \frac{Q_{\dot{\eta}_n} \xi_{\dot{\eta}_n}^2}{2} \right) = H_{NVE} + H_2
\]

(3.49)

\[
H_{NVE} = \sum_{i} \frac{p_i^2}{2m_i} + \sum_{k=0}^{N} \frac{(P'_i D_k Q)^2}{8I_k} + V((q_i),(Q_i),(H)) = H_1
\]

Here the barostat \( \tilde{G}_e \) and thermostat \( G_{\eta} - \) coupled to barostat, \( G'_{i'j'} - \) coupled to translational/rotational degrees of freedom of the rigid bodies) forces are given by:

\[
\tilde{G}_e = \text{V} \left( \tilde{P}_{\text{int}} - P_0 \tilde{I} \right) + \frac{1}{g_f} (K' + K') \tilde{I}
\]

(3.50, a)

\[
G_{\dot{q}_i} = W \text{Tr} \left( \xi_{\dot{q}_i} \dot{\xi}_{\dot{q}_i} \right) - d^2 kT
\]

\[
G_{\dot{\eta}_k} = Q_{\dot{\eta}_k} \left( \xi_{\dot{\eta}_k} \dot{\xi}_{\dot{\eta}_k} \right) - kT, k \geq 2
\]

(3.50, b)
\[ G_{1}^{(rr)} = K^{(rr)} - g_{1}^{(rr)} kT \]
\[ G_{k}^{(rr)} = Q_{p_{k+1}}^{(rr)} \left( \xi_{k+1} \right)^{2} - kT \]  

(3.50, c)

Here \( V = \text{det}(\hat{H}) \) - the cell volume and internal stress tensor \( \tilde{P}_{\text{int}} \) defined as:

\[
\tilde{P}_{\text{int}} = \frac{1}{V} \sum_{i} \left( \frac{p_{i} \otimes p_{i}}{m_{i}} + f_{i} \otimes q_{i} \right) - \left( \frac{\partial H_{H}}{\partial H} \right) \tilde{H}^{T} \]  

(3.51)

The last term in equation (3.51) is the contribution to the internal pressure due to the periodic images of the simulated system. This term would be zero for a finite system with no PBC conditions. The computational expression for this correction term in both all-atomic and rigid-body representations is given in Appendix B.

On the basis of our re-derivation of the original KLN method we found that some of the equations proposed in KLN[203] work are not accurate and must be properly modified. The differences we found are following:

1) The pressure tensor (24) and the pressure (21) from the original KLN paper should not contain any terms involving rotational degrees of freedom.

2) Moreover, the calculation of the pressure (21) and its tensor (24) should include the extra term, \(- \left( \frac{\partial H_{t}}{\partial H} \right) \tilde{H}^{T} \), which is omitted in the KLN work, although it was justified by using rigid walls of the simulation cell. As it is stated in the work of Louwerse and Baerends[228] for correct calculation of the pressure (tensors) in case of periodic boundary conditions, the term \(- \left( \frac{\partial H_{t}}{\partial H} \right) \tilde{H}^{T} \) is particularly important as well as the way how virial terms are added. According to this view, the term \( \frac{1}{V} \left( \sum_{i} (f_{i} \otimes q_{i}) - \left( \frac{\partial H_{t}}{\partial H} \right) \tilde{H}^{T} \right) \) should be
calculated as $\frac{1}{2V} \sum_{i=1}^{N} \sum_{j=1}^{NM} \tilde{F}_{ij} \tilde{r}_{ij}$. For more detailed derivation of this expression and for its extension to the case of rigid bodies see Appendix B.

3) The term of conserved quantity $\sum_{k=1}^{M} (kT\eta_k + \frac{Q_{\eta_k} \xi^2_{\eta_k}}{2})$ in the case of NPT ensemble should be written as

$$kT \left( d^2 \eta + \sum_{i=1}^{M} \eta_k \right) + \sum_{i=1}^{M} \left( \frac{Q_{\eta_k} \xi^2_{\eta_k}}{2} \right).$$

4) Finally, the definition of the thermostat forces, acting on the barostat should be corrected from $G_{\eta_k} = Q_{\eta_k} \left( \frac{\xi_{\eta_k}}{\gamma_{\eta_k}} \right)^2 - kT, k \geq 2$ to $G_{\eta_k} = Q_{\eta_k} \left( \frac{\xi_{\eta_k}}{\gamma_{\eta_k}} \right)^2 - kT, k \geq 2$.

3.6 Conclusions and Summary

In this chapter we have discussed the main methodological components of the simulations used in this thesis as well as in many other works. We introduced basic concepts of the molecular simulations and in particular the molecular mechanics and molecular dynamics methods.

In summary, our findings presented in this chapter are as follows:

1) The most general approach to formulation of the classical force fields potentials should be based on the concept of the bond-order variable, what allows one to take into account many-body effects in convenient functional form. Such formulation can then be combined with some conservation principle providing efficient and convenient way to describe chemical reactions with simple classical force fields;

2) Most general way to construct classical propagators should be based on the Liouville formulation of classical mechanics and Trotter factorization.
methods. This approach allows one to obtain time-reversible and symplectic (often) integrators. This also applies to the rigid-body dynamics, provided the correct structure matrix is used.

3) Non-Hamiltonian dynamics (NVT, NPT and other ensembles) may be reformulated in terms of Hamiltonian dynamics. Generation of non-microcanonical ensembles may be performed by using extended systems/virtual variables method.

4) Solution of the equation of motion for system variables in NVT ensemble is equivalent to solution of analogous equations for NVE ensemble but with time flow scaled differently for positions and their conjugate momenta.

5) We have clarified some details of the rigid-body MD method in NPT ensemble. Particular attention should be paid to correct calculation of the internal pressure in case of periodic boundary conditions. We have derived corresponding equations for both all-atomic and rigid-body cases.
Chapter 4

New method for rigid-body molecular dynamics:

Recursive Taylor series expansion method

4.1. Introduction

The basics of the molecular dynamics method, in particular the rigid-body molecular dynamics, have been discussed in previous chapter. In that chapter we mostly focused on the general methods for construction and characterization of integration schemes as well as on the formulations of the mechanics of the rigid bodies.

We now will focus more on rigid-body molecular dynamics methods, including their formulations and implementation issues. Although the most calculations of the molecular machines discussed in later chapters were performed with one of the previously developed RB MD methods (DLML, see later), recently we have developed an alternative approach, which is robust and easy-to-implement and is based on numerically exact solution of the free rigid problem.

In this chapter we will describe this method and overview other existing methods for RBMD. Our method relies only on recursive relations defined by Euler equations and does not employ any special functions. This might be advantageous in many situations. It is important to note that our method might be considered simultaneously both symplectic and time-reversible. The time reversibility immediately follows from the propagator construction. Although the symplecticity
does not follow from the method structure it is a consequence of the exact nature of solution (if properly converged).

We also extended our method as well as some of those reported recently to the case of NVT ensemble by combining them with Nose-Poincare thermostat[216], [221], [229]. Finally, the case study of water cluster is used to evaluate and compare different integrators.

4.2. Methods

4.2.1. NVE ensemble

One of the outstanding methods of developing the rigid body molecular dynamics integrators is a symplectic splitting technique[182–185]. It leads to time-reversible and symplectic (usually, but not always) integrators, which are necessary for performing long-time simulations. More detailed discussion of such approaches has been presented in Chapter 3. Here we will apply this general theory to rigid-body equations of motion.

One of the common splitting ways is to split the full Hamiltonian \( H \) of the system of interest into Hamiltonian of the free rigid body \( h_1 \) and the additional Hamiltonian of interactions \( h_2 \):

\[
H = h_1 + h_2
\]

\[
h_1 = T(\tilde{p}^N, \tilde{\mathcal{I}}^N)
\]

\[
h_2 = \phi(\tilde{r}^N, A^N)
\]

where \( T(\tilde{p}^N, \tilde{\mathcal{I}}^N) \) is a kinetic energy term, that depends on momenta of the rigid body centers of mass \( \tilde{p}^N = \{\tilde{p}_i\}, i \in 1...N \) and the angular moment of the rigid bodies \( \tilde{\mathcal{I}}^N = \{\tilde{I}_i\}, i \in 1...N \) and \( \phi(\tilde{r}^N, A^N) \) is a potential energy term, that depends on the
positions of the rigid body centers of mass $\hat{r}^N = \{\hat{r}_i\}, i \in 1...N$ and the orientations (attitude matrices) of the rigid bodies $A^N = \{A_i\}, i \in 1...N$.

Then the full evolution operator can be factorized:

$$e^{iLdt} = e^{\frac{iL_1}{2}dt} e^{\frac{iL_2}{2}dt} e^{\frac{iL_3}{2}dt} + O(dt^3),$$

where

$$iL : H \rightarrow iL$$

$$iL = iL_1 + iL_2$$

$$iL = \{\cdot, H\}, iL_1 = \{\cdot, h_1\}, iL_2 = \{\cdot, h_2\}$$

are the Liouville operators for corresponding Hamiltonians and $\{\cdot, H\}$ denotes the Poisson bracket generated by Hamiltonian $H$.

In other words, it is possible to split the torqued rigid body problem into the free rigid body problem (FRB) and a perturbation term[202] (Fig. 4.1).

Equations in Fig. 4.1 can be solved separately. As one can see the equations (4.1, a) are the FRB problem, which can be solved in different ways. We will now present the general skeleton of different methods to solve the FRB problem, which have been previously described in the literature. Since the details of each method are well-described in corresponding articles, we will only present a comparative description of each method, to highlight their differences.
The methods for numerical solving the FRB problem may be classified according to the order in which splitting and Liouville operator construction is performed.

In the first group of methods (DLML (4.3, a), NO_SQUISH (4.3, b)) the FRB Hamiltonian is first splitted into several parts:

\[
H_{FRB} = \sum_{i=1}^{N} \left( \frac{1}{2} \vec{I}_{i}^{T} \vec{I}_{i} \right) = \sum_{i=1}^{N} (H_{i,1} + H_{i,2} + H_{i,3})
\]

\[
H_{i,k} = \frac{l_{i,k}^{2}}{2I_{i,k}}, k = 1,2,3
\]

\[
H_{FRB} = \sum_{i=1}^{N} \left( \sum_{k=0}^{3} \frac{1}{8I_{i,k}} p_{i}^{T} p_{i} q_{i} \right) = \sum_{i=1}^{N} (H_{i,0} + H_{i,1} + H_{i,2} + H_{i,3})
\]

\[
H_{i,k} = \frac{p_{i}^{T} p_{i} q_{i}}{8I_{i,k}}, k = 0,1,2,3
\]

where \( q = \{ q_{1}, q_{2}, q_{3}, q_{4} \} \) is a unit quaternion for given rigid body, \( p_{0} q = \{ q_{1}, q_{2}, q_{3}, q_{4} \} \), \( p_{1} q = \{ q_{2}, q_{1}, q_{3}, q_{4} \} \), \( p_{2} q = \{ -q_{4}, -q_{3}, q_{1}, q_{2} \} \), \( p_{3} q = \{ -q_{4}, q_{1}, -q_{2}, q_{3} \} \) - are the permutations of the unit quaternion, \( p = \{ p_{1}, p_{2}, p_{3}, p_{4} \} \) is a quaternion analog of the angular momentum, which is also a conjugate momentum for the quaternion variable.

For each part (or sub-Hamiltonian) a corresponding Liouville (and hence evolution) operator is then constructed:

\[
H_{i,k} \rightarrow L_{i,k} = \text{Rot}_{i,k} \left( \frac{l_{i,k}}{I_{i,k}} \right)
\]

\[
\exp \left( dt \cdot L_{i,k} \left( \frac{l_{i,k}}{A_{i}} \right) \right) = \left( \begin{array}{c} R_{i} \left( dt \cdot \varphi_{i,k} \right) l_{i,k} \nonumber \\
R_{k} \left( dt \cdot \varphi_{i,k} \right) A_{i}^{T} \end{array} \right).
\]

\[
\varphi_{i,k} = \frac{l_{i,k}}{I_{i,k}}
\]
where $R_k(\phi)$ is a rotation matrix for rotation on the angle $\phi$ around the axis $k$. Thus the action of the resulting Liouville operators reduces to orthogonal transformation (rotation) of the angular momentum and the attitude matrix or analogous quaternion variables.

The composition of resulting evolution operators is finally constructed using the Trotter factorization, leading to the final integration algorithm. This is equivalent to separately solving the Hamiltonian equations generated by corresponding sub-Hamiltonian. Since each sub-Hamiltonian usually have very simple form it is possible to solve the corresponding problem exactly. Combination of such effectively one-dimensional solutions (perhaps exact) leads to final algorithm. Moreover, since the mappings constructed from the Hamiltonian are symplectic, their composition is also symplectic. As a consequence the group of methods based on Hamiltonian splitting is always symplectic.

Another approach is based on reverse sequence of actions. The Liouville operator for the entire system is first constructed:

$$H_{FRB} = \sum_{i=1}^{N} \left( \frac{1}{2} \dot{I}_i + \mathbf{q}_i \cdot \nabla_{\mathbf{q}_i} \right) \rightarrow L = \sum_{i=1}^{N} \left[ \mathbf{I}_i \cdot \frac{\partial}{\partial \mathbf{I}_i} + \mathbf{q}_i \cdot \frac{\partial}{\partial \mathbf{q}_i} \right] = \sum_{i=1}^{N} \left[ \mathbf{I}_i \times \mathbf{I}_i \cdot \frac{\partial}{\partial \mathbf{I}_i} + \frac{1}{2} \mathbf{A}(\mathbf{I}_i) \cdot \frac{\partial}{\partial \mathbf{q}_i} \right] \quad (4.5)$$

Here note, however, that in order to obtain the Liouville operator (4.5), a non-Hamiltonian formulation is employed. For this particular case this means that the time-derivatives of the angular momentum and the quaternions are taken from the Euler equations of motion (plus the equation for orientational variable which is a
consequence of the angular momentum conservation), not from the Hamiltonian equations of motion. The generalized Hamiltonian formulation is also possible is one uses the rigid-body structure matrix:

\[
J = \begin{pmatrix}
0 & 0 & 0 & \bar{u}_1 \\
0 & 0 & 0 & \bar{u}_2 \\
0 & 0 & 0 & \bar{u}_3 \\
\bar{u}_1 & \bar{u}_2 & \bar{u}_3 & \bar{I}
\end{pmatrix} \in \mathbb{R}^{12} \times \mathbb{R}^{12},
\]

(4.6)

where \( A = [\bar{u}_1, \bar{u}_2, \bar{u}_3] \)

The angular momentum part of Liouville operator in (4.5) may be rearranged into 2 terms:

\[
L_{i,j} = \sum_{i=1}^{\infty} \left[ I_i \times I_i^{-1} i_j \right] \frac{\partial}{\partial I_i} = \sum_{i=1}^{\infty} \left[ \phi_{i,1} \left( I_i \frac{\partial}{\partial I_i} - I_i \frac{\partial}{\partial I_i} \right) + \phi_{i,2} \left( I_i \frac{\partial}{\partial I_i} - I_i \frac{\partial}{\partial I_i} \right) \right]
\]

(4.7)

(1 1 \( i_x \)) (1 1 \( i_y \)) (1 1 \( i_z \))

\[
\phi_{i,1} = \left( \frac{1}{I_{i,3}} - \frac{1}{I_{i,3}} \right) I_{i, x} \quad \phi_{i,2} = \left( \frac{1}{I_{i,3}} - \frac{1}{I_{i,3}} \right) I_{i, z}
\]

The action of the evolution operator \( \exp \left( \phi_k \left( I_i \frac{\partial}{\partial I_j} - I_i \frac{\partial}{\partial I_j} \right) \right) \) is equivalent to rotation in \((l_i, l_j)\) plane on angle \( \phi_k \) around axis \( l_k \).

Using the Trotter factorization the composite evolution operator is constructed. As a result the sub-Liouville operators, which are used for splitting do not correspond to any Hamiltonian. Therefore the resulting mappings (as well as their composition) are not in general symplectic. This methodology is used in Matubayasi-Nakahara (MN) integrator.

The next group of methods does not use any Liouville operator nor Hamiltonian function factorizations at all. It is based on standard finite difference technique, where a given variable (attitude matrix and the angular momentum) on next time step is approximated using the quantities from previous time step and/or
intermediate time-step values. Such approximation may be either explicit or implicit, meaning the predicted variable depends not only on known its values (from previous time step), but also on itself. This leads to a system of equations, which have to be solved before propagation of variables. A representative of such group of method, an Omelyan method, starts directly from Euler equation of motion and the equation on the orientational degrees of freedom:

\[
J_\alpha \dot{\omega}_\alpha = \tau_\alpha + (J_\beta - J_\gamma) \omega_\beta \omega_\gamma, \quad \alpha, \beta, \gamma \in x, y, z
\]

\[
\dot{A} = -\text{skew} (\hat{\omega}) A
\]

or

\[
\dot{q} = \text{skew}_{4x4} (\hat{\omega}) q
\]

where

\[
\text{skew}_{4x4} (\hat{\omega}) = \begin{pmatrix}
0 & \omega_z & -\omega_y & \omega_x \\
-\omega_z & 0 & \omega_x & -\omega_y \\
\omega_y & -\omega_x & 0 & \omega_z \\
-\omega_x & \omega_y & -\omega_z & 0
\end{pmatrix}
\]

The Euler equation (4.8, a) can be solved by leap-frog scheme iteratively:

\[
\omega_\alpha^{(n+1)}(t + \frac{dt}{2}) = \omega_\alpha(t - \frac{dt}{2}) + \frac{1}{J_\alpha} \left[ \tau_\alpha(t) + (J_\beta - J_\gamma) \omega_\beta^{(n)}(t) \omega_\gamma^{(n)}(t) \right]
\]

\[
\omega_\beta^{(n)}(t) \omega_\beta^{(n)}(t) = \frac{1}{2} \left[ \omega_\beta(t - \frac{dt}{2}) \omega_\beta(t - \frac{dt}{2}) + \omega_\beta^{(n)}(t + \frac{dt}{2}) \omega_\beta^{(n)}(t + \frac{dt}{2}) \right]
\]

The orientational variables are solved by following implicit formula:

\[
S_i(t + dt) = S_i(t) + dt H_i S_i \left( t + \frac{dt}{2} \right)
\]

\[
S_i \left( t + \frac{dt}{2} \right) = \frac{1}{2} [S_i(t) + S_i(t + dt)]
\]

where \( H = \text{skew}(\hat{\omega}) \), \( S = A \) if the orientation is described in terms of attitude matrix and \( H = \text{skew}_{4x4}(\hat{\omega}) \), \( S = q \) if the quaternion formulation is chosen. Solution of (4.10) is then given by:

\[
S_i(t + dt) = \left( I - \frac{dt}{2} H_i \right)^{-1} \left( I + \frac{dt}{2} H_i \right) S_i(t)
\]
The method in general is not symplectic. Moreover, since the propagation of the angular velocities is calculated by iterative scheme, the algorithm is not time-reversible.

Finally, the FRB problem can be solved analytically. For some special cases (symmetric, spherical top) such solution may easily be obtained in terms of trigonometric functions. For general cases of asymmetric rigid body, the solution is given in terms of special functions, known as Jacobi elliptic functions and Jacobi elliptic integrals. The solution, however, tracks the evolution of the angular momenta (or velocities). The corresponding evolution of the orientational variables was not known until recently. It has been developed by R. van Zon\[204\] and then applied for rigid body molecular dynamics simulations. A detailed derivation and discussion of its implementation is given in corresponding references\[204\], \[205\], \[230\], \[231\]. Because the derivation is too long and complex we will not discuss it here. We will rather focus on some its properties.

Since the solution is analytical it is automatically time reversible and symplectic. However, for the correct functioning many special cases must be treated carefully, including permutations of the axes to satisfy certain conditions. Moreover, the method relies on the set of special functions, which might be expensive to calculate and it might lead to the additional source of rounding errors. Finally, and most important, especially for molecular dynamics, the method depends on the Jacobi ordering.

Assume the principal components of inertia tensor are $I_{xx}, I_{yy}, I_{zz}$, the kinetic energy of rotation is $E_r = \frac{1}{2}(AI_{xx}^2 + BI_{yy}^2 + CI_{zz}^2)$ and the total angular momentum is $L^2 = L_\alpha^2 + L_\beta^2 + L_\gamma^2$. Then if one of the following conditions is satisfied:
we say that the Jacobi ordering is satisfied.

Such ordering is necessary to avoid dealing with complex numbers as part of corresponding solution. Thus it is very important to perform such ordering before solving corresponding equations of motion. It is usually not a big problem to perform such ordering for non-interacting rigid bodies at the very beginning of integration. This is assumed in work of R. van Zon, where it is suggested that if neither of conditions (4.12) is satisfied it could be done by permutation of the x and z axes and inverting y axis.

However, this is still not a complete solution to this problem. One may easily encounter such situation when even the permutation suggested by R. van Zon may not lead to Jacobi ordering (4.12). This is especially important in molecular dynamics (MD) applications, where due to inter-particle interactions the angular momentum component change at every integration time step. Thus it is important to be able to perform Jacobi ordering for arbitrary combination of angular momentum and inertia tensor components.

To accomplish such task one may recognize that it may be done by one of the 6 possible permutations of coordinate system axes, which all together form a group. The group operations most easily can be represented by 3 by 3 matrices. In all there are 6 such matrices (Table 4.1).
Table 4.1. Group of permutation matrices needed for Jacobi ordering

<p>| | | |</p>
<table>
<thead>
<tr>
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<tbody>
<tr>
<td>$U_1 = \begin{pmatrix} 1 &amp; 0 &amp; 0 \ 0 &amp; 1 &amp; 0 \ 0 &amp; 0 &amp; 1 \end{pmatrix}$</td>
<td>$U_2 = \begin{pmatrix} 0 &amp; 1 &amp; 0 \ 1 &amp; 0 &amp; 0 \ 0 &amp; 0 &amp; -1 \end{pmatrix}$</td>
<td>$U_3 = \begin{pmatrix} -1 &amp; 0 &amp; 0 \ 0 &amp; 0 &amp; 1 \ 0 &amp; 1 &amp; 0 \end{pmatrix}$</td>
</tr>
<tr>
<td>$U_4 = \begin{pmatrix} 0 &amp; 0 &amp; 1 \ 1 &amp; 0 &amp; 0 \ 0 &amp; 1 &amp; 0 \end{pmatrix}$</td>
<td>$U_5 = \begin{pmatrix} 0 &amp; 1 &amp; 0 \ 0 &amp; 0 &amp; 1 \ 1 &amp; 0 &amp; 0 \end{pmatrix}$</td>
<td>$U_6 = \begin{pmatrix} 0 &amp; 0 &amp; 1 \ 0 &amp; -1 &amp; 0 \ 1 &amp; 0 &amp; 0 \end{pmatrix}$</td>
</tr>
</tbody>
</table>

In order to satisfy the Jacobi ordering the angular velocity vector $\omega$ should be multiplied by one of the permutation matrices $U_i$. The inertia tensors will transform accordingly:

$$\tilde{\omega} = U_i \omega$$
$$\tilde{I} = U_i I U_i^{-1}$$

(4.13)

As we can see, the permutation matrix $U_6$ will lead to the transformation suggested by R. van Zon. However, it is only one of 6 possible permutations and may be not suitable for Jacobi ordering.

It can be easily verified by direct substitution, that the Euler equation will stay invariant with regard to the transformation (Table 4.1). However, the equation of motion for the orientation degree of freedom (attitude matrix) may change upon such transformation. Let us show that there are two possibilities how the equation of motion for orientation matrix may change.

The equations of motion for orientation matrix we are interested in read:

$$\frac{dA}{dt} = -W(\tilde{\omega})A,$$

(4.14)
where \( \tilde{\omega} \) is the angular velocity vector in body-fixed coordinate system. The Jacobi propagation method is based on transformation of the attitude matrix \( A \) of form: \( A(t) = PA(0) \).

Assume the Jacobi ordering has been achieved with one of six matrices \( U_i \). We are interested now in how the attitude matrix should be transformed to satisfy original equation of motion (4.14) and how the propagation matrix will be transformed.

Assume the transformations we are looking for is \( \tilde{A} = XA \), then we have:

\[
\frac{d\tilde{A}}{dt} = -W(\tilde{\omega})\tilde{A} \iff \frac{1}{c} \frac{dA}{dt} = -W(U,\omega)XA \iff \frac{dA}{dt} = -cX^{-1}W(U,\omega)XA, \tag{4.15}
\]

where we also assumed possible transformation of time: \( \tilde{t} = ct \).

Using the property of the skew-symmetric matrices:

\[
B^T \text{skew}(Ba)B = \text{det}(B)\text{skew}(a) \iff \text{skew}(Ba) = \text{det}(B)\left(B^T\right)^{-1} \text{skew}(a)B^{-1} \tag{4.16}
\]

we have:

\[
\frac{dA}{dt} = -cX^{-1}W(U,\omega)XA = -c\det(U_i)X^{-1}(U_i^T)^{-1}W(\omega)U_i^{-1}XA
\]

It is important to note, that for all matrices in the permutation group \( P \), the condition: \( U_i^T = U_i^{-1} \) is always satisfied. This leads to

\[
\frac{dA}{dt} = -cX^{-1}W(U,\omega)XA = -c\det(U_i)X^{-1}(U_i^{-1})^{-1}W(\omega)U_i^{-1}XA = -c\det(U_i)X^{-1}U_iW(\omega)U_i^{-1}XA,
\]

which leads to conclusion that:

\[
c = \frac{1}{\det(U_i)} \tag{4.17}
\]

\[
X = U_i
\]

Thus we have:

\[
U_iA(t) = \tilde{A}(t) = P\left(\frac{t}{\det(U_i)}\right)\tilde{A}(0) = P\left(\frac{t}{\det(U_i)}\right)U_iA(0)
\]

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That is:

$$A(t) = U_i^{-1} P \left( \frac{t}{\det(U_i)} \right) U_i A(0)$$  \hspace{1cm} (4.18)

As a conclusion we showed that the equation of motion (4.14) will stay invariant with respect to transformation (Table 4.1) up to the direction of time flow, which is determined by the determinant of the permutation matrix. Thus, if one of such matrices will lead to Jacobi ordering, the equation (4.14) should be integrated in reverse direction.

Such change of direction of the time flow may simply be understood in terms of left and right basis orientation. If the permutation $U_i$ does not change the symmetry of space (left basis remains left and right basis remains right) the time direction will also remain unchanged. Once the permutation changes the symmetry of space the time will also change its direction.

Thus the Jacobi integrator for rigid bodies (as given by R. van Zon) is extremely elaborate and tricky method, although it provides the analytical solution to FRB problem. The rest of the chapter will describe a new method, developed in course of this work and based on alternative approach to solution of differential equations with special structure, such as Euler equation. It is based on the use Taylor expansion of both angular momentum $\{ \tilde{I}_i \}, i \in 1..N$ and direction vectors $\{ \tilde{u}_i \}, i \in 1..N$ (which specify the rigid body orientation) in the evolution time:

$$\tilde{I}_\alpha(t + dt) = \sum_{n=0}^{N} \frac{\tilde{I}_\alpha^{(n)}(t)}{n!} dt^n + O(dt^{N+1}) \alpha \in x, y, z$$

$$\tilde{u}_\alpha(t + dt) = \sum_{n=0}^{N} \frac{\tilde{u}_\alpha^{(n)}(t)}{n!} dt^n + O(dt^{N+1}) \alpha \in x, y, z$$  \hspace{1cm} (4.19)

$$\frac{d^n \tilde{I}_\alpha}{dt^n}, \frac{d^n \tilde{u}_\alpha}{dt^n}, \alpha \in x, y, z$$
Here we use the fact that the attitude matrix is essentially a set of 3 orthogonal direction vectors: \( A_{r \rightarrow e} = (\vec{u}_1 \quad \vec{u}_2 \quad \vec{u}_3) \).

Then the evolution of each of these vectors might be directly obtained using the rigid-body Poisson bracket[232]:

\[
\{ F, G \} = -\vec{I} \cdot ( \nabla_{t} F \times \nabla_{t} G ) - \vec{u} \cdot ( \nabla_{t} F \times \nabla_{a} G - \nabla_{t} G \times \nabla_{a} F )
\]  
(4.20),

which explicitly can be written as

\[
\dot{\vec{u}} = \{ \vec{u}, H_{1} \} = \vec{u} \cdot ( \nabla_{t} H_{1} \times \nabla_{a} \vec{u} ) \Leftrightarrow \dot{\vec{u}} = \begin{pmatrix} 0 & \omega_{z} & -\omega_{y} \\ -\omega_{z} & 0 & \omega_{x} \\ \omega_{y} & -\omega_{x} & 0 \end{pmatrix} \vec{u} \]  
(4.21, a)

\[
\dot{\vec{I}} = \{ \vec{I}, H_{1} \} = -\vec{I} \cdot ( \nabla_{t} \vec{I} \times \nabla_{t} H_{1} ) \Leftrightarrow \dot{\vec{I}} = \begin{pmatrix} l_{x} \\ l_{y} \\ l_{z} \end{pmatrix} = \begin{pmatrix} \alpha d_{x} l_{z} \\ \beta l_{y} \\ \gamma l_{x} \end{pmatrix} \]  
(4.21, b),

where

\[
\begin{pmatrix} \omega_{x} \\ \omega_{y} \\ \omega_{z} \end{pmatrix} = \begin{pmatrix} A\ell_{x} \\ B\ell_{y} \\ C\ell_{z} \end{pmatrix} \quad \text{and} \quad \alpha = C - B, \beta = A - C, \gamma = B - A \]  
(4.22).

The equation (4.21, a) corresponds to the equation of Fig. 4.1, a for attitude matrix, while the equation (4.21, b) is nothing else but the Euler equation for the free rigid body.

In order to use equations (4.19) one must calculate the corresponding derivatives of the angular momenta as well as those for direction vectors up to desired expansion order. This may easily be done employing the special structure of the equations of motion, which for convenience may be written as:
\[ i_x = \alpha \dot{l}_x \]
\[ i_y = \beta \dot{l}_y \]
\[ i_z = \gamma \dot{l}_y \]  
(4.23)
\[ \dot{u}_x = C l_x u_y - B l_x u_z \]
\[ \dot{u}_y = -C l_y u_x + A l_y u_z \]
\[ \dot{u}_z = B l_y u_x - A l_y u_y \]

Using the Leibniz rule we can see that each n-th derivative of each variable \((\dot{I}, \ddot{u}_x, \ddot{u}_y, \ddot{u}_z)\) may then be expressed via derivatives of other variables up to the order of \((n-1)\):

\[ (l_x)^{(n)} = (l_x)^{(n-1)} = \sum_{i=0}^{n-1} C_{n-1}^{i} \left( (l_x)^{(i)} (l_x)^{(n-1-i)} \right) \]
\[ (l_y)^{(n)} = (l_y)^{(n-1)} = \sum_{i=0}^{n-1} C_{n-1}^{i} \left( (l_y)^{(i)} (l_y)^{(n-1-i)} \right) \]
\[ (l_z)^{(n)} = (l_z)^{(n-1)} = \sum_{i=0}^{n-1} C_{n-1}^{i} \left( (l_z)^{(i)} (l_z)^{(n-1-i)} \right) \]
\[ (u_x)^{(n)} = (u_x)^{(n-1)} = \sum_{i=0}^{n-1} C_{n-1}^{i} \left( (u_x)^{(i)} (u_x)^{(n-1-i)} \right) \]
\[ (u_y)^{(n)} = (u_y)^{(n-1)} = \sum_{i=0}^{n-1} C_{n-1}^{i} \left( (u_y)^{(i)} (u_y)^{(n-1-i)} \right) \]
\[ (u_z)^{(n)} = (u_z)^{(n-1)} = \sum_{i=0}^{n-1} C_{n-1}^{i} \left( (u_z)^{(i)} (u_z)^{(n-1-i)} \right) \]  
(4.24),

where \(C_{n}^{i} = \frac{n!}{i!(n-i)!}\) are the binomial coefficients.

The first derivatives of all variables are calculated using the initial values of the variables themselves as it is defined by equations (4.23). Second derivatives may then be calculated using the first derivatives as well as the initial values of variables and so on up to the required order. The calculated derivatives then may be plugged in equations (4.19) to propagate variables. The length of expansion may be chosen such that the last terms will be comparable to machine precision, what will result in
numerically exact solution of the FRB problem. We refer to the algorithm described above as Terec (TEylor RECursive, phonetically).

The evolution of the orientation of the rigid body may also be described in terms of unit quaternions. In that case the second part of equations (4.23) will read:

\[
\begin{align*}
\dot{q}_0 &= \frac{1}{2} \left( -A l_x q_1 - B l_y q_2 - C l_z q_3 \right) \\
\dot{q}_1 &= \frac{1}{2} \left( A l_x q_0 - B l_y q_3 + C l_z q_2 \right) \\
\dot{q}_2 &= \frac{1}{2} \left( A l_x q_3 + B l_y q_0 - C l_z q_1 \right) \\
\dot{q}_3 &= \frac{1}{2} \left( -A l_x q_2 + B l_y q_1 + C l_z q_0 \right)
\end{align*}
\]  

(4.25)

Similarly to direction vectors equations (4.24) the recursive equations for unit quaternion will read:

\[
\begin{align*}
(q_0)^n &= (q_0)^{n-1} = \frac{1}{2} \sum_{i=0}^{n-1} C_{i+1} \left( -A (l)_i (q_1)^{(n-1-i)} - B (l)_i (q_2)^{(n-1-i)} - C (l)_i (q_3)^{(n-1-i)} \right) \\
(q_1)^n &= (q_1)^{n-1} = \frac{1}{2} \sum_{i=0}^{n-1} C_{i+1} \left( A (l)_i (q_0)^{(n-1-i)} - B (l)_i (q_3)^{(n-1-i)} + C (l)_i (q_2)^{(n-1-i)} \right) \\
(q_2)^n &= (q_2)^{n-1} = \frac{1}{2} \sum_{i=0}^{n-1} C_{i+1} \left( A (l)_i (q_3)^{(n-1-i)} + B (l)_i (q_0)^{(n-1-i)} - C (l)_i (q_1)^{(n-1-i)} \right) \\
(q_3)^n &= (q_3)^{n-1} = \frac{1}{2} \sum_{i=0}^{n-1} C_{i+1} \left( -A (l)_i (q_2)^{(n-1-i)} + B (l)_i (q_1)^{(n-1-i)} + C (l)_i (q_0)^{(n-1-i)} \right)
\end{align*}
\]  

(4.26),

while the recursive relation for angular momentum will be the same as in equation (4.24). This version we call qTerec (quaternion Terec).

To facilitate the calculations described in MD simulations the binomial coefficients up to required degree may be precomputed once and for all. Also if the length of expansion is not long enough the length of the direction vectors as well as that of quaternion may change. Thus we use the renormalization of the unit vectors (quaternion) to cure such possible problem. It should be noted that although the renormalization of direction vectors will not solve the possible loss of the orthogonality, in quaternion approach this is not a problem. However, in our
simulations we have found that possible error in the orthogonality of vectors has practically no effect on dynamics and its stability and accuracy.

4.2.2. NVT ensemble

All tested integration schemes (except for Omelyan[209]) can be coupled to Nose-Poincare thermostat in a straightforward way. The algorithm of Omelyan[209] due to its leap-frog structure is less suitable for this purpose.

The Nose-Poincare thermostat is introduced via extended system Hamiltonian called Nose-Poincare Hamiltonian[221]:

\[ H_{NP} = s \left[ \sum_{i=1}^{N} \left( \frac{p_i^2}{2m_i s^2} \right) + \sum_{i=1}^{N} \left( \frac{1}{2s^2} \vec{v}_i^T \vec{v}_i \right) + \phi(\vec{r}^N, A^N) + \frac{p_s^2}{2Q} + g k_b T \ln(s) - H_0 \right], \quad (4.27) \]

where the primed letters denote the virtual variables, and non-primed – are real variables,

\[ H_0 = H(0), H = \sum_{i=1}^{N} \left( \frac{p_i^2}{2m_i s^2} \right) + \sum_{i=1}^{N} \left( \frac{1}{2s^2} \vec{v}_i^T \vec{v}_i \right) + \phi(\vec{r}^N, A^N) + \frac{p_s^2}{2Q} + g k_b T \ln(s), \quad (4.28) \]

\[ g \] – number of degrees of freedom, \( k_b \) - Boltzmann constant.

The Hamiltonian (4.27) may then be decomposed into several sub-Hamiltonians:

\[ H_{NP} = H_0 + H_1 + H_2 + H_3 \]

\[ H_{NP} = s \left[ \sum_{i=1}^{N} \left( \frac{p_i^2}{2m_i s^2} + g k_b T \ln(s) - H_0 \right) \right] \]

\[ H_1 = s \sum_{i=1}^{N} \left( \frac{A_{ij} \vec{v}_i^2}{2s^3} + \frac{B_{ij} \vec{v}_j^2}{2s^3} + \frac{C_{ij} \vec{v}_i^2}{2s^3} \right) \]

\[ H_2 = s \phi(\vec{r}^N, A^N) \]

\[ H_3 = s \frac{p_s^2}{2Q} \]

Every sub-Hamiltonian gives rise to its own evolution operator:
\[ H_1(s, p^*) \rightarrow D_2 = \sum_{i=1}^{s} \left( \frac{\partial H_2}{\partial p_i^*} \frac{\partial}{\partial p_i^*} - \frac{\partial H_2}{\partial p_i} \frac{\partial}{\partial p_i} \right) + \left( \frac{\partial H_3}{\partial p_i^*} \frac{\partial}{\partial p_i^*} - \frac{\partial H_3}{\partial p_i} \frac{\partial}{\partial p_i} \right) \]

\[ = \sum_{i=1}^{s} \left( \frac{\partial H_2}{\partial p_i^*} \frac{\partial}{\partial p_i^*} - \frac{\partial H_2}{\partial p_i} \frac{\partial}{\partial p_i} \right) + \sum_{i=1}^{s} \left( \frac{\partial H_3}{\partial p_i^*} \frac{\partial}{\partial p_i^*} - \frac{\partial H_3}{\partial p_i} \frac{\partial}{\partial p_i} \right) \]

\[ H_2(s, p^*, q^*) \rightarrow D_2 = \sum_{i=1}^{s} \left( \frac{\partial H_2}{\partial p_i^*} \frac{\partial}{\partial p_i^*} - \frac{\partial H_2}{\partial p_i} \frac{\partial}{\partial p_i} \right) + \sum_{i=1}^{s} \left( \frac{\partial H_3}{\partial q_i^*} \frac{\partial}{\partial q_i^*} - \frac{\partial H_3}{\partial q_i} \frac{\partial}{\partial q_i} \right) + \sum_{i=1}^{s} \left( \frac{\partial H_4}{\partial p_i^*} \frac{\partial}{\partial p_i^*} - \frac{\partial H_4}{\partial p_i} \frac{\partial}{\partial p_i} \right) \]

\[ + \sum_{i=1}^{s} \left( \frac{\partial H_5}{\partial q_i^*} \frac{\partial}{\partial q_i^*} - \frac{\partial H_5}{\partial q_i} \frac{\partial}{\partial q_i} \right) + \sum_{i=1}^{s} \left( \frac{\partial H_6}{\partial q_i^*} \frac{\partial}{\partial q_i^*} - \frac{\partial H_6}{\partial q_i} \frac{\partial}{\partial q_i} \right) \]

Finally, the full propagator (evolution operator) may be represented as:

\[ e^{D t} = e^{D_2 \frac{d t}{2}} e^{D_2 \frac{d t}{2}} e^{D_{dt}} e^{D_{dt}} e^{D_{dt}} e^{D_{dt}} + O(d t^3) \]

\[ e^{D t} = e^{D_2 \frac{d t}{2}} e^{D_{dt}} e^{D_{dt}} + O(d t^3) \]

thus leading to the second-order factorization scheme. To build the explicit integrator we only have to define the action of every composing operator.

The action of operators in \( D_0, D_2 \) and \( D_1 \), results in translation of corresponding variables. The non-trivial operators are thus \( D_2 \) and \( \tilde{D} \). The action of the first one was described by Nose[216] and may be represented as:

\[ \exp[D_2 d t] \left( \begin{array}{c} s \\ \frac{p_s}{2} \end{array} \right) = \left( \begin{array}{c} s \left( 1 + \frac{p_s}{2 Q} d t \right)^2 \\ \frac{p_s}{2} \left( 1 + \frac{p_s}{2 Q} d t \right) \end{array} \right) \]

\[ D \]

The operator \( \tilde{D} \) describes the FRB problem in scaled angular momenta.

Hence the equations of motion it generates are similar to (4.21, a) and (4.21, b):

\[ \tilde{u} = \{ \tilde{u}, H_1 \} = \tilde{u} \cdot \left( \nabla_{\tilde{u}} H_1 \times \nabla_{\tilde{u}} \tilde{u} \right) \Rightarrow \tilde{u} = \frac{1}{s} \left( \begin{array}{ccc} 0 & \omega_y & -\omega_z \\
 \omega_y & 0 & \omega_z \\
 -\omega_z & -\omega_x & 0 \end{array} \right) \tilde{u} \]

(4.33, a)
Effectively this means that the operator \( e^{\hat{D} dt} \) is equivalent to solution of the FRB problem for the time \( \frac{dt}{s} \). This follows from the fact that if for some operator \( D = \frac{\partial}{\partial C} \), the evolution operator action is \( e^{D dt} : C(t) \rightarrow C(t + dt) \), then for operator \( D' = \frac{1}{s} \frac{\partial}{\partial C} \) the evolution operator \( e^{D' dt} \) action will be:

\[
e^{D' dt} = e^{\frac{D dt}{s}} : C(t) \rightarrow C\left(t + \frac{dt}{s}\right).
\]

Thus the coupling of the rigid-bodies to Nose-Poincare thermostat is simply the application of the integrators for NVE case for scaled time with corresponding propagation of the thermostat variables.

For convenience, we present now the full explicit integration scheme to perform RBMD simulations in the NVT ensemble.

1) \( e^{D dt} \frac{p_s}{2} : \left( \begin{array}{c} s \\ \frac{p_s}{s} \end{array} \right) \rightarrow \left( \begin{array}{c} s \left( 1 + \frac{p_s dt}{2Q 2} \right) \\ \frac{p_s}{s} \left( 1 + \frac{p_s dt}{2Q 2} \right) \end{array} \right) \) \hspace{0.5cm} (4.34)

2) \( e^{D dt} \frac{\vec{p}_i}{2} : \left( \begin{array}{c} \vec{p}_i' \\ \hat{\vec{r}}_i \end{array} \right) \rightarrow \left( \begin{array}{c} \vec{p}_i' + s \vec{p}_i \frac{dt}{2} \\ \hat{\vec{r}}_i + s \vec{\tau}_i \frac{dt}{2} \\ p_s - \phi(p^N, q^N) \frac{dt}{2} \end{array} \right) \) \hspace{0.5cm} (4.35)

3) \( e^{D dt} \frac{p_s}{2} : p_s + \frac{dt}{2} \sum_{i=1}^{N} \left( \frac{A_i}{2s^2} \vec{I}_{x,i} + \frac{B_i}{2s^2} \vec{I}_{y,i} + \frac{C_i}{2s^2} \vec{I}_{z,i} \right) \) \hspace{0.5cm} (4.36)

4) FRB problem propagation with the time step \( \frac{dt}{s} \), e.g. Terec (see equations 4.24):
5) Exactly step 3

\[
6) \ e^{Q_{0}dt} : \left( \frac{\vec{r}_{i}}{p_{i}} \right) \rightarrow \left( \frac{\vec{r}_{i} + \frac{\vec{P}_{i}}{m_{i}}dt}{p_{i} + \left( \sum_{i=1}^{N} \frac{\vec{P}_{i}^{2}}{2m_{i}s^{2}} - gk_{b}T(\ln(s) + 1) + H_{0} \right)dt} \right)
\]

(4.37)

7) update atomic coordinates, calculate forces and torques

8) Exactly step 2

9) Exactly step 1

4.3. Results and Discussion

In order to test the developed integrators we performed MD simulations of the \((H_{2}O)_{23}\) cluster. The TIP3P\[233\] interaction potential was used to describe intermolecular interactions. Each water molecule was treated as separate rigid fragment. Thus the inclusion of intra-molecular interactions was not necessary. Each simulation runs \(10^{7}\) steps, which for time step of 1 fs is equivalent to 10 ns trajectory. The initial velocity distribution corresponded to temperature of 250 K.

The algorithms were tested in three stages. In the first stage we compared the performance of both Terec and qTerec algorithms for different integration time steps using different expansion sizes. The methods were characterized by two quantities the total energy trend (b quantity in equation 4.38, a) and the total energy standard deviation (sd(E) in equation 4.38, b). The former quantity describes the stability of the method and therefore may be a quantitative measure of symplecticity of the method. We calculated it via linear fit of the total energy versus trajectory time (eq. 4.38, a). It should also be noted that the symplecticity of the method cannot be simply judged on the basis of its stability. For this purpose one should consider the phase space volume preservation. However, in most cases the good stability of the method
might reflect its symplecticness. Therefore we consider the total energy trend as the measure of symplecticity in this sense. The latter quantity describes how much of the total energy fluctuates around its mean value and thus it is a measure of the method precision.

\[ |E(t)| = a + bt \]  
\[ sd(E) = \sqrt{\frac{\sum_{i=1}^{N} (E_i - \bar{E})^2}{N}} \]

For each method we considered the expansion sizes of 5, 7, 10, 12, 15 and 20 terms. It explains terms in Fig. 4.2. For each expansion size the simulations with time steps of 0.5, 1, 2.5, 5 and 7.5 fs have been performed. The trajectory lengths varied from 5 ns to 75 ns accordingly.

![Figure 4.2. Comparison of the Terec and qTerec methods for different expansion sizes and different time steps. a) energy trend - stability characteristics; b) standard deviation - accuracy characteristics](image)

We found that all methods showed good stability (Fig. 4.2, a) and accuracy properties (Fig. 4.2, b). The only exception was the Terec5 method, where the expansion size was not enough to achieve machine accuracy. It is interesting to note
that the qTerec5 method showed significantly better properties than its Terec5 cousin. This is a consequence of the de-orthogonalization of the direction vectors during simulations in Terec5 method. The use of quaternion in qTerec5 variant precludes any problems with possible de-orthogonalization of the attitude matrix, thus leading to significantly better properties.

As it is shown on Fig. 4.2 for the expansions longer than 5 terms the properties of the corresponding integrators are almost independent on the expansion size. This indicates that the computations converge to machine precision. In some cases the longer expansions are in fact slightly less stable and less precise. This may be due to accumulation of the rounding errors when dealing with very small numbers. Thus for the future use or by default we chose 10 terms series expansions for our methods, that is Terec10 and qTerec10.

All methods are stable and accurate enough for all tested time steps except for 7.5 fs. This is clearly shown on Fig. 4.2 as the abrupt change of linear relations \( \ln(|E|) - \ln(dt) \) and \( \ln(sd(E)) - \ln(dt) \).

In the second stage the developed integrators (namely Terec10 and qTerec10) have been compared to existing integration schemes which we label as DLML[202], NO_SQUISH[206], MN[208], Omelyan[209] and Jacobi\(^{26}\). The first two algorithms are known to be both symplectic and time-reversible, while the next two are not symplectic, but are time-reversible. Finally, the method based on analytical solution to the FRB problem which uses Jacobi integrals of the first kind is by construction exact, so it should in principle be both symplectic and time-reversible as well. The comparison was based on the total energy trend (Fig. 4.3, a) as well as on the standard deviation of the total energy (Fig. 4.3, b).
As the comparison in Fig. 4.3 illustrates, the Terec and qTerec methods show the properties of the known symplectic integrators (DLML and NO_SQUISH). The non-symplectic schemes differ significantly from symplectic ones in both stability and precision. These observations are valid for different time steps up to 5 fs. All integrators become unstable at 7.5 fs. The properties of the Jacobi integrator are very similar to those of symplectic schemes as well as to Terec10 and qTerec10 algorithms. This indicates that all of them achieve the best possible precision and stability for given system. It should also be stressed, that despite the algorithm used for integration of FRB problem the overall order of algorithms is limited by the smallest order in entire decomposition scheme (that is where the forces and torques are applied). However, as it is clear from Fig. 4.3 the algorithm for solving FRB problem may significantly impact the stability of the overall algorithms as well as its precision. Thus it is still important to use appropriate integrator for FRB part.

In addition to quality of conservation of the Hamiltonian (total energy) of the system under consideration we also studied the analogous properties of the total linear and angular momenta of the system (Table 4.2). This is important because the re-
scaling of the direction vectors and quaternions used in Terec and qTerec methods might potentially influence the conservation of these quantities. Thus we were interested how the re-scaling affects these quantities.

Table 4.2. Conservation of squares of linear $P$ and angular $L$ momenta of the system of 23 water molecules characteristics.

<table>
<thead>
<tr>
<th></th>
<th>$\ln\left(\frac{dL^2}{dt}\right)$</th>
<th>$\ln(|sd(L^2)|)$</th>
<th>$\ln\left(\frac{dP^2}{dt}\right)$</th>
<th>$\ln(|sd(P^2)|)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DLML</td>
<td>3.18E-13</td>
<td>1.17E-09</td>
<td>9.09E-28</td>
<td>5.30E-24</td>
</tr>
<tr>
<td>Jacobi</td>
<td>1.71E-14</td>
<td>5.41E-11</td>
<td>5.29E-27</td>
<td>2.03E-23</td>
</tr>
<tr>
<td>MN</td>
<td>1.58E-06</td>
<td>0.005584</td>
<td>2.13E-26</td>
<td>6.44E-23</td>
</tr>
<tr>
<td>NO_SQUISH</td>
<td>2.68E-13</td>
<td>8.35E-10</td>
<td>-4.31E-28</td>
<td>1.19E-23</td>
</tr>
<tr>
<td>Omelyan</td>
<td>-1.15E-06</td>
<td>0.070208</td>
<td>1.30E-26</td>
<td>4.00E-23</td>
</tr>
<tr>
<td>qTerec5</td>
<td>4.80E-14</td>
<td>1.48E-10</td>
<td>7.78E-28</td>
<td>1.62E-23</td>
</tr>
<tr>
<td>qTerec10</td>
<td>1.63E-13</td>
<td>5.97E-10</td>
<td>3.37E-26</td>
<td>1.06E-22</td>
</tr>
<tr>
<td>qTerec15</td>
<td>1.63E-12</td>
<td>7.13E-09</td>
<td>2.52E-27</td>
<td>1.61E-23</td>
</tr>
<tr>
<td>qTerec20</td>
<td>1.63E-12</td>
<td>7.13E-09</td>
<td>2.52E-27</td>
<td>1.61E-23</td>
</tr>
<tr>
<td>Terec5</td>
<td>3.30E-05</td>
<td>0.127033</td>
<td>-7.27E-29</td>
<td>3.50E-24</td>
</tr>
<tr>
<td>Terec10</td>
<td>1.99E-13</td>
<td>6.62E-10</td>
<td>1.68E-27</td>
<td>7.80E-24</td>
</tr>
<tr>
<td>Terec15</td>
<td>2.69E-13</td>
<td>1.17E-09</td>
<td>2.47E-27</td>
<td>1.09E-23</td>
</tr>
<tr>
<td>Terec20</td>
<td>1.98E-14</td>
<td>7.05E-11</td>
<td>1.63E-26</td>
<td>5.02E-23</td>
</tr>
</tbody>
</table>

As we expected, the re-scaling practically does not affect neither of linear nor angular momenta significantly, as long as the Taylor series expansion possess sufficiently large number of terms. This may be understood in the following way. Assume some quantity $x$ (in our case it may be either quaternion of direction vector) has exact value of $x_{exact}$ and the Taylor series approximation of $x_{Taylor} = x_{exact} + dx$ where $dx$ is the error. The rescaled value of $x$ will be $\frac{x_{Taylor}}{x_{exact}} = 1 + \frac{dx}{x_{exact}}$. As the number of terms in Taylor series expansion increases the
error goes to zero very rapidly \((dx \to 0)\). In that case the rescaling operation will practically be the identity operation and thus will not have significant impact on conserved properties. We have found that for relatively small number of terms \((\text{Terec5})\) the rescaling affects conservation of the total linear momentum. However starting from 10 terms \((\text{Terec10})\) it practically has no effect on conserved properties and is needed only for consistency.

It should also be noted, that if one wants to combine the exact solution to the FRB problem with the torques and forces part of integrator it is crucial to consider more than two possible ways to perform Jacobi ordering used in Jacobi algorithm as implemented by R. van Zon\(^{26}\). We have already discussed that there are six distinct permutations of the axes, one of which may lead to required Jacobi ordering. We also derived how the direction of time flow may change depending on the symmetry of necessary permutations.

Finally we tested the performance of above algorithms (except for Omelyan) in the NVT ensemble. As the Fig. 4.4 shows the temperature distributions are very similar for all methods and for all time steps up to 5 fs. At \(dt = 5\) fs the MN integrator is no longer stable and does not generate the correct distribution, while other methods still perform correctly.
Figure 4.4. Temperature distribution in NVT ensemble generated by different methods and with different integration time steps: a) 0.5 fs; b) 1.0 fs; c) 2.5 fs; d) 5.0 fs. The target temperature was set to 250 K.

We also studied the stability and accuracy of the methods by examining the properties similar to those defined in equations (4.38), but using Nose-Poincare Hamiltonian (4.27) instead of the total energy. It should be noted that the quantity (4.27) is not only the conserved quantity but it is a true Hamiltonian. Thus, its trend gives information about the symplecticity of the NVT integrator, as the trend of total energy characterizes the symplecticity of the NVE integrators in the sense discussed earlier. The comparison of such quantities is presented in Fig. 4.5.

Figure 4.5. Comparison of Terec and qTerec methods with other existing integrators for NVT ensemble: a) Nose-Poincare Hamiltonian trend - stability characteristics; b) standard deviation – accuracy characteristics
Similarly to NVE ensemble one may observe 2 groups of methods – one is non-symplectic (MN in this case) and the other group has all symplectic methods (DLML, NO_SQUISH, Terec10 and qTerec10). In contrast to NVE ensemble, the properties of the integrator have more effect on the maximal integration time step for which the dynamics is still stable. As we can see, the instability occurs for MN integrator already at $dt = 5$ fs, while such time step is still acceptable for this method in microcanonical ensemble. The Terec and qTerec methods once again show the properties comparable to those of existing symplectic integrators.

Finally, in the third stage, the performance of all methods has been compared to each other. To do this we considered the same system, namely a cluster of 23 water molecules, but without any interactions. This is necessary since the computation time of all interactions is much larger than the time, required for performing integration of equations of motion. That would obscure the actual speed of the integration algorithms. In other words we considered a system of the 23 free rigid bodies, which motion is determined by initial distribution of angular and linear momenta, constrained to correspond to given temperature. In all cases such temperature was set to 300 K. The trajectory time was set to $5 \times 10^6$ steps with integration time step of 1 fs, what corresponds to 5 ns trajectories. It is important to note, that for the purposes of speed comparison the trajectory length has no effect, so it could be chosen to produce any reasonable execution time.

<table>
<thead>
<tr>
<th>Method</th>
<th>Time, s</th>
</tr>
</thead>
<tbody>
<tr>
<td>DLML</td>
<td>184 +/- 4</td>
</tr>
<tr>
<td>MN</td>
<td>274 +/- 5</td>
</tr>
<tr>
<td>NO_SQUISH</td>
<td>560 +/- 4</td>
</tr>
<tr>
<td>Omelyan</td>
<td>92 +/- 1</td>
</tr>
</tbody>
</table>

Table 4.3. Run time for 5 ns simulation of cluster of 23 water molecules.
The results of such comparison are summarized in the Table 4.3. The Terec method turns out to be even faster than the symplectic decomposition scheme NO_SQUISH. This is probably because the latter method uses many trigonometric functions for each integration time step. Both methods in turn are slower than the other decomposition schemes, including quaternion version of Terec method (qTerec). The latter is only slightly slower than the MN algorithm. However, the precision and stability comparisons made in previous stages make the MN algorithm less favorable than qTerec (and even Terec). The fastest Omelyan algorithm also suffers from stability and accuracy problems.

Finally, the only outlier is the Jacobi method. The execution time for this method becomes on average 5 times slower than for most other algorithms. The Terec and qTerec methods also give numerically exact solution (sometimes the precision and stability are even higher, see Fig. 4.3 and 4.5) but for the fraction of cost associated with Jacobi method may thus be more attractive for some MD applications.

As it is expected, as the expansion size increases so do the execution time for corresponding versions of Terec or qTerec algorithms (Table 4.4). We can also note that for all expansion sized the quaternion version is usually faster than orientation directions counterpart. This is because the first method propagates only 4 quaternion components, while the other propagates 3 components of the 3 direction vectors (that is in total 9 components).
### Table 4.4. Speed comparisons for different Taylor series expansion sizes for both Terec and qTerec methods.

<table>
<thead>
<tr>
<th>Expansion size</th>
<th>Terec, s</th>
<th>qTerec, s</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>221 +/- 1</td>
<td>186 +/- 4</td>
</tr>
<tr>
<td>10</td>
<td>373 +/- 3</td>
<td>289 +/- 3</td>
</tr>
<tr>
<td>15</td>
<td>616 +/- 9</td>
<td>453 +/- 4</td>
</tr>
<tr>
<td>20</td>
<td>937 +/- 7</td>
<td>645 +/- 3</td>
</tr>
</tbody>
</table>

### 4.4. Conclusions and Summary

In this Chapter we described new numerically exact method to solve the FRB problem that allows us to develop new integration scheme for rigid-body MD simulations. We showed how this approach might further be used for the construction of symplectic and time-reversible integrators in both microcanonical (NVE) and canonical (NVT) ensembles. Since our approach solves the FRB up to machine precision it may be considered as an efficient and easy-to-implement alternative for existing exact solution methods, which involve Jacobi elliptic functions. Although for big integration time steps the analytic solutions might be more superior, in usual MD simulations the integration time step is limited by the highest vibration frequency in the system. As a result in most cases it is practically impossible to use time steps larger than 5 fs, and it significantly enhances the applicability of our methods.

We showed that our integrators have characteristics not worse (but even better in some cases) that those of existing symplectic integration schemes for all time steps up to 5 fs. However our method differs from those schemes in that it solves the FRB problem exactly (up to machine precision) and it does not need the evaluation of the Jacobi elliptic functions. Moreover, different special cases are treated in the same way as for general asymmetric rigid bodies, what facilitates the implementation of the method in computer code.
In addition, we performed the comparative study of the existing rigid body integration schemes (integrators) focusing on their stability, precision and performance properties. We found that the time-reversible and symplectic schemes of DLML and NO_SQUISH as well as Jacobi method based on analytic solution of FRB show much better properties than those methods which are not symplectic (Omelyan, MN). For our new integrator the properties depend on the expansion length. For expansion lengths as small as 5 terms the integrator based on direction vectors (Terec) shows the properties comparable to tested non-symplectic schemes, while the quaternion-based algorithms (qTerec) shows much better accuracy and stability, comparable to those of symplectic schemes. For bigger number of expansion terms the properties of both integrators become comparable (and even better in some cases) to those of symplectic schemes. Thus, the reported methods are effectively symplectic (which follows from the fact that the exact solution is by definition a symplectic mapping).

In terms of performance our algorithms are much faster than the Jacobi method, providing the same and even better accuracy and stability. Moreover, our method is very robust and does not need to consider many special cases, as well as to deal with some internal (Jacobi) ordering. This makes them very easy to implement and efficient to run. We showed that the new methods are even faster than existing symplectic decomposition scheme NO_SQUISH.

Although for the conventional molecular dynamics the difference in performance of all algorithms is usually neglected by significantly slower interactions calculation step, it may be more important in such methods as discrete molecular dynamics where the interactions are calculated relatively rarely and efficiently. In such methods it may be necessary to solve FRB problem for relatively long times.
This may not be accomplished by conventional splitting schemes, which are approximate by construction. Using exact method (Jacobi) as described by R. van Zon will solve the problem, but it would take approximately 5 times more time than with our algorithms.

We also showed that the new algorithms (as well as most of existing) may be combined with the Nose-Poincare thermostat in a straightforward fashion. The corresponding mappings are similar to those used for NVE ensemble and differ only in intrinsic scaling of integration time step. We demonstrated that such coupling indeed generates correct distributions for all integrators considered. Moreover, our new integrators (Terec and qTerec) work in both NVT and NVE ensembles and show the properties comparable to those of the existing symplectic schemes.

The advantage of our method becomes clear if one compares each of the integrators one by one. In some cases our method is more stable and precise (vs. Omelyan and MN), in others it is faster (vs. Jacobi and NO_SQUISH), in others it is capable to perform exact integration of the FRB problem for longer time steps (vs. all splitting schemes) and in some cases it is more robust and easy to implement (vs. Jacobi). We thus believe that these new integrators will be useful for long time scale simulations of various types of molecular systems.

In summary, our findings presented in this chapter are as follows:

1) The integrators may be classified according to way they are derived. If they are derived from the sub-Hamiltonians the resulting scheme is usually symplectic, while if the integrator is based on sub-Liouvillians it may be non-symplectic;

2) The Jacobi analytic solution of the FRB proposed by R. van Zon is incomplete in sense of the Jacobi ordering. We extended the original approach to make
sure that the Jacobi ordering is satisfied for arbitrary conditions. This, however, may require to reverse the direction of time flow;

3) We proposed a new integrator for FRB problem based on combination of the Taylor series expansion method and recursive approach to calculate n-order derivatives. We also extended all integrators to NVT ensemble by combining them with the Nose-Poincare thermostat.
Chapter 5

Molecular dynamics of surface-moving thermally driven nanocars

5.1. Introduction

The extended overview of the molecular machines and nanocars in particular has been given in Chapter 2. We have also discussed the available experimental and theoretical data. In this chapter we will present our first theoretical studies of the nanocars aimed to support experimental observation and hypothesis about the fullerene wheels rotation.

Figure 5.1. Definition of the forward and lateral (side) direction of motion of the nanocars.

The thermally initiated migration of the nanocars on the surface of gold crystals was tracked by using the STM technique[72]. Direct observations showed that the movement of the nanocars was related to axial rotation of the fullerene
wheels, what resulted in preferential motion the molecule in the forward direction (as defined on Fig. 5.1) rather then in lateral direction.

From the statistical mechanics point of view, in thermal equilibrium there may not be any preference of one direction of motion over the other. However, the statistical mechanics only works for big collections of the molecules (or many realizations/observations of the same molecule). For a single molecule, in a single experiment (realization), however, one may observe any possible outcome, especially if there is a certain degree of asymmetry in the system. This is the case for nanocar molecules. If one assumes that there is a rotation of the fullerene wheels, then the intuition suggests the forward (rolling) motion should be easier than the lateral (which is only possible via sliding mechanism) motion. This is exactly what is observed in STM experiments, where the molecules were allowed to move by themselves, subject to thermal fluctuations from the environment and were only traced by STM (were not manipulated with STM). This intuitive guess was also directly tested by manipulating the nanocar molecule with the STM tip. It was found that it is much more difficult to move the nanocar in a lateral direction than to move it in a forward direction.

The other observation, which indirectly advocates the wheel rotation mechanism, is the following one. For the 4-wheeled nanocar, substantial two-dimensional translations were typically observed, although slightly biased in one direction. On the contrary, for the 3-wheeled trimer, thermal activation leads to rotation on the surface without noticeable translations. Because the most significant contribution to the surface-molecule interaction energy comes from the C_{60}-Au interactions the 4-wheeled nanomachine is bounded to the surface much stronger than the 3-wheeled one. If the diffusion would proceed via slip mechanism the 4-wheeled car should appear as non-moving in comparison to significantly faster moving 3-wheeled
molecule. The only mechanism, consistent with the experimental findings, is the rolling mechanism, which involves the coupling between the rotations of the fullerene wheels and the translation of the center of mass of the entire molecule.

Despite the many experimental observations which suggested the rolling mechanism of the nanocars' motion it is impossible to directly observe the fullerene wheels' rotations in experiment. Moreover, it is unclear if such rotations are correlated or not, what types of interactions between the nanocar and the surface are most important for the motion. There are many other types of information which hard or impossible to obtain experimentally.

Since the nanocars have been synthesized only recently, there are no theoretical studies of such type of systems. Therefore it was very important to verify experimental suggestions about the nanocars' motion mechanisms with theoretical tools. This chapter describes our very early RBMD simulations of the nanocars, moving on the gold surface. In fact, this work was the very first theoretical work performed for the systems of such kind. As a part of these initial studies several models of the nanocar-surface interactions have been developed and tested. This helped us to accelerate the calculations and to understand in some extent the role of the surface.

5.2. Methods

5.2.1. Nanocar description

In this work we considered two hydrocarbon analogs of fullerene-based nanocars originally designated as a "Trimer" (a three-wheeled vehicle) and a "Nanotruck" (a four-wheeled vehicle)[71]. The panels of Fig. 5.2 illustrate the models, showing chemical structures of the parent nanocars in the insets and the
corresponding analogs considered here and shown in ball and stick representations. Starting with the structures of the experimentally studied species \(^3\) (insets in Fig. 5.2) we introduced simplifying modifications to the molecular structure in order to reduce computational expenses in this first attempt to model nanocar dynamics. Specifically, we kept the alkynyl connectors (–C≡C-) to the fullerene wheels, but we replaced the other alkynyl moieties with direct aryl-aryl linkages. As discussed below, we maintained the rigidity of the parent chassis (insets in Fig. 5.2) by using the rigid body MD simulations. It is expected that the most significant features of the parent nanocars, the rolling motion of the wheels, should be the same in our model vehicles.

![Figure 5.2](image)

**Figure 5.2.** Molecular models of nanocars used in molecular dynamics simulations: (a) Trimer, and (b) Nanotruck. The insets show chemical structures of the parent nanocars. Partitioning the molecules into rigid fragments (4 for trimer and 5 for nanotruck) is clarified by the red lines.

For simulations of the thermally activated surface transport of the nanocar models, we applied an original version of the rigid-body molecular dynamics, an extension of the previous approach[234]. This method allowed us to concentrate on the most essential dynamical features of nanovehicles on the surface: the wheels were allowed to rotate, but the wheels and chassis were represented by rigid fragments. As shown in Fig. 5.2, four rigid fragments (three wheels and a chassis) were assumed for Trimer, and five rigid fragments (four wheels and a chassis) were considered for
Nanotruck. Application of rigid-body MD helped us to drastically reduce an array of internal coordinates, to simplify forms of interaction potentials, to decrease the amount of potential parameters and to afford fairly long MD trajectories.

In preliminary steps we implemented and tested several algorithms of rigid-body MD in the canonical ensemble (NVT) and found that the symplectic quaternion scheme described, in particular, by Miller et al.[206], in conjunction with the Nose-Poincare thermostat approach[221], was an optimal choice for constant temperature molecular dynamics calculations of nanocars. All MD runs were performed with an integration time step of 1 fs. The trajectories were typically of about 5 ns lengths. Interactions between rigid fragments were modeled by the site-site potential composed of the Lennard-Jones and Coulomb functions in Eq. 5.1.

\[
E_{\alpha\beta} = \sum_{i=\alpha}^{\alpha} \sum_{j=\beta}^{\beta} \left[ 4\epsilon_{ij} \left( \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right) + \frac{q_i q_j}{r_{ij}} \right] \tag{5.1}
\]

Here \(i\) and \(j\) are the indices of atoms belonging to fragments \(\alpha\) and \(\beta\), respectively, \(r_{ij}\) – distance between atoms \(i\) and \(j\), \(q_i\) and \(q_j\) – partial charges on respective atoms. Potential parameterization was basically consistent with the CHARMM27 force field[125], [126], but corrected in this work as explained below. The hydrogen atoms were assigned to the type HA(1) with the parameters \(\epsilon = 0.022\) kcal/mol, \(\sigma = 1.32\) Å, the carbon atoms were assigned to the type CA(11), except those connecting fullerene wheels with chassis (see Fig. 5.3). For the latter, the type CC(12) was assumed. The Lennard-Jones parameters of all carbon atoms were taken as \(\epsilon = 0.070\) kcal/mol, \(\sigma = 1.9924\) Å. The partial charges on atoms were determined in \textit{ab initio} quantum chemical calculations in the RHF/6-31G** approximation by using the PC GAMESS program[235] as the Mulliken charges for the compounds benzene, biphenyl, biphenylacetylene and phenylfullereny lacetylene, occurring as fragments of
model nanovehicles (Fig. 5.2). The atom types and computed partial charges are shown in Fig. 5.3. The remaining fullerene carbon atoms were assumed as the CA(11) type atoms with zero partial charge.

Figure 5.3. An assignment of the atoms in the model nanocars (Fig. 5.2) to the CHARMM force field types and their partial charges as computed by ab initio calculations in this work.

The parameters required for the bonded interactions when using the CHARMM force fields were selected as follows. For the CA(11)-CC(12) stretching term: $k_b = 320.0 \text{ kcal/mol}$, $r_0 = 1.400 \text{ Å}$; for the CA(11)-CC(12)-CA(11) bending term: $k_a = 40.0 \text{ kcal/mol}$, $\theta_0 = 170.0^\circ$; for the CA(11)-CC(12)-CC(12) bending term: $k_a = 40.0 \text{ kcal/mol}$, $\theta_0 = 120.0^\circ$. The torsional terms were excluded because of their negligible contribution to the total energy. Some precautions were introduced to the computer code for the bending potential in order to exclude singularities of the potential when the CA(11)-CC(12)-CC(12) angle approached $180^\circ$. We verified that such a constructed total interaction potential was consistent with the small rotational barrier of the fullerene-wheel structures without a surface as estimated previously[71].
5.2.2. Surface-molecule interaction models

Several models have been considered for the nanocar–surface interaction potentials assuming that each atom of a nanocar experiences an external force from the resting metal. All models are based on the pairwise 12-6 Lennard-Jones potential function in Eq. 5.2,

\[ E = 4\varepsilon \left( \frac{\rho}{d} \right)^{12} - \left( \frac{\rho}{d} \right)^{6} \]  

(5.2)

where \( d \) is the distance from a particular atom of a nanocar to a specific point in the metal. We considered parameters of these interaction potentials close to the values reasonable for description of the gold crystals. In particular, the lattice parameter \( a = 4.07 \, \text{Å} \) was taken from the fcc gold lattice[236]. Parameter \( \rho \) was slightly varied starting from the gold van der Waals atomic radius \( 1.66 \, \text{Å} \)[236]. The most uncertain parameter in Eq. 5.2 is the potential well depth \( \varepsilon \). An initial selection was the value 0.47 kcal/mol corresponding to the molecular mechanical parameters of metals (Ca\textsuperscript{2+}, Ba\textsuperscript{3+}) from the AMBER force field set[128]. However, we allowed its large variations within two orders of magnitude, from 4.7 kcal/mol to 0.094 kcal/mol. In recent MD simulations of gold nanoparticles inside carbon nanotubes Schoen and co-workers[237] used the 12-6 Lennard-Jones potential function with parameters \( \varepsilon = 0.3 \) kcal/mol and \( \rho = 3 \, \text{Å} \) for interactions between gold and carbon atoms, conditions that are reasonably consistent with our choice.

Within the simplest Model-W, each atom of a nanocar interacts with a structureless metal surface (or with a rigid wall) calculated by the potential (Eq. 5.2), where \( d \) is the distance from an atom to the surface plane. Correspondingly, the only nonzero components of forces acting on the machine’s atoms are directed along the normal to surface. Summation over all atoms of a vehicle defines a total interaction
potential \( E_w \). As discussed below, this model is capable of explaining the thermal activation of Trimer's pivoting, but fails to describe translations of Nanotruck.

The more advanced \textit{Model-L} assumes certain features of \textit{lattice} atomic structure of metals (Fig. 5.4). Applying this model, the current coordinates of a nanocar's atom are projected on the surface plane, and the nearest to this point surface atom of the \textit{fcc} lattice serves as a reference node to construct the interacting shell. To this end, several (9 or 25) nearest lattice points from the surface layer and from the one underneath the surface, contribute to the interaction potential calculated as a sum of the terms defined by Eq. 5.2. For this model the variable \( d \) has the meaning of the distance between the atom of the nanocar and one of the nearest atoms of the lattice. The procedure is repeated for all atoms of a nanocar and all nearest atoms of the lattice. It should be noted that for each atom of the nanocar there may be different (may partially overlap) sets of nearest lattice atoms. This is the most computationally expensive approach for molecular dynamics calculations used in this work.

![Figure 5.4. Specification of the model-L. Open rings represent the gold atoms of the second layer, while the solid circles represent the atoms of the outer surface plane.](image)

The \textit{Model-P} takes into account the 2D-\textit{periodicity} of the surface potential. The corresponding total potential \( E_p \) acting on a nanocar is related to the wall-like potential \( E_w \) by Eq. 5.3:
\[ E_p(x, y, z) = f(x, y)E_w(z) \]
\[ f(x, y) = f(x + na, y + ma) \]
\[ f(x, y) = 1 + \frac{\left( \sin^2 \left( \frac{\pi x}{a} \right) + \sin^2 \left( \frac{\pi y}{a} \right) \right)}{2} \]  

(5.3)

where coordinates \( z \) are counted along the normal to the metal surface, coordinates \( x \) and \( y \) are in the surface plane, \( n \) and \( m \) are integers, \( a \) is the lattice parameter. Application of this model allows us to qualitatively describe translational motion of nanocars.

We also considered a model accounting for charge polarization of metal. In this approach, for each atom with a non-zero partial charge in the nanocar’s structure we introduced its image inside the metal with a charge of the opposite sign, located on the same distance from the outer surface plane as the nanocar’s atom (on the other side of this plane). Then the Coulombic contributions from the nanocar-metal interactions were added to the total interaction potential \( E_w \). Since no noticeable improvements over other models were found, we do not further discuss the results of this approximation.

### 5.3. Results and Discussion

The most essential results of MD simulations are as follows. In complete accord with experimental observations[71], [72], pivoting around the central point was the primary movement for Trimer. This type of motion was detected even within the simplest \( \text{Model-W} \) of the nanocar-metal interaction potential. At temperatures lower than 300 K (27 °C) the nanocar remained stationary, at \( T = 400 \text{ K} \) (127 °C) the mobility was initiated, and at \( T = 500 \text{ K} \) (227 °C) we could observe an apparent rotational rolling motion. Within the more realistic \( \text{Model-L} \), surface rotations mixed with weak displacements of Trimer were observed. The sensitivity of the results to the
parameter $\varepsilon$ of Eq. 5.2 is demonstrated in Table 5.1. These data show that surface dynamics of model nanocars depends on the parameters of this simple potential (Eq. 5.2) in complicated fashion; we do not observe monotonous behavior of the computed trajectories by varying $\varepsilon$.

| Table 5.1. Dependence of the mode of surface movement of Trimer (Fig.5.2. a) on the parameter $\varepsilon$ of potential Eq. (5.2). Other parameters of potential Eq. (5.2) are as follows: $\rho = 1.66$ Å, $a = 4.07$ Å. |
|---|---|---|---|
| Temperature, K | $\varepsilon = 4.7$ kcal/mol | $\varepsilon = 0.47$ kcal/mol | $\varepsilon = 0.094$ kcal/mol |
| 300 | weak rotation, no displacement | no rotation, no displacement | weak rotation, weak displacement |
| 500 | rotation, no displacement | weak rotation, weak displacement | rotation, displacement |
| 600 | rotation, no displacement | | |

We illustrate the pivoting motion of Trimer on the gold surface in (Fig. 5.5, a). Such pivoting motion has been observed in direct visualization of MD trajectories. These data refer to simulations with the Model-L with the potential parameters $\rho = 1.66$ Å, $a = 4.07$ Å, $\varepsilon = 4.7$ kcal/mol. Application of Model-P permits to observe a combination of strong rotations and non-unidirectional displacements of Trimer along the surface.
If we define rotational velocity $k_{rot}$ of Trimer as the ratio of (non-integer) the number of rotation circles (for example, 5.5 at $T = 600$ K) to the trajectory length (5 ns) and assume the temperature dependence of the rotational velocity in the Arrhenius form,

$$k_{rot} = Ae^{\frac{E_a}{RT}},$$

then plotting the values $k_{rot}$ versus $T^{-1}$ ($300 \leq T \leq 800$ K) allows us to estimate the slope of the graph and, therefore, an activation energy barrier $E_a$ for thermally driven Trimer rotation. With the trajectories of the Model-W, such an estimate results in the $E_a$ values between 3 and 4 kcal/mol.

For the four-wheeled Nanotruck, an application of Model-W was an unsuccessful attempt to detect the 2D movement of the vehicle. However, applications of Model-P or more expensive Model-L allowed us to observe a combination of both translation and pivoting. Within the latter models, the use of potential parameter $\varepsilon = 4.7$ kcal/mol in Eq. 5.2, corresponding to the strongest interaction of Nanotruck with the metal surface, precluded migration of the nanovehicle even at higher temperatures (400 and 500 K). For the smaller values of $\varepsilon$.
a desired type of motion (two dimensional combination of both translation and pivoting) could be observed. We illustrate the movement of Nanotruck on the gold surface in (Fig. 5.5, b). These data refer to simulations with the Model-L with the potential parameters $\rho = 1.66 \text{ Å}$, $a = 4.07 \text{ Å}$, $\epsilon = 0.47 \text{ kcal/mol}$.

In Fig. 5.6 we show a typical 2D trajectory of Nanotruck at $T = 500 \text{ K}$ as computed with the Model-L with the potential parameter $\epsilon = 0.47 \text{ kcal/mol}$. According to these MD simulations the nanovehicle can experience large-scale migrations, especially compared to its size shown in green in Fig. 5.6.

![Figure 5.6](image.png)

**Figure 5.6.** Two-dimensional trajectory of Nanotruck in the surface plane ($X, Y$) as computed with the Model-L at $T = 500 \text{ K}$. The shape of the moving molecule is shown for comparison in green.

### 5.4. Conclusions and Summary

Our results indicate that lattice structure and periodicity of the surface play a critical role in the dynamics of thermally driven nanocars. This suggests the following mechanism of the transport: nanocars are bound to the surface by strong bonds (covalent or electrostatic), and they move along the surface by overcoming the barriers with the help of thermal fluctuations, i.e., the dynamics of nanocars is an activated process. The experimentally determined existence of a temperature
threshold below which no motion is observed, and the strong temperature dependence of the dynamics, supports the computational findings here.

We emphasize that molecular models have been developed for surface-moving analogs of fullerene-based nanocars, which successfully reproduce experimentally observed\cite{71}, \cite{72} thermal activation and dynamical features of the nanovehicles. This study presents a first attempt in the theoretical analysis of these complex systems by providing a computationally minimalist approach that allows one to understand the essential features of nanocar dynamics upon a surface. Our theoretical analysis suggests that the dynamics of nanocars is an activated process that strongly depends on the structure and periodic properties of the surface. In addition, we provide an estimate for the activation energy of thermally driven rotation of the Trimer (3-4 kcal/mol) that can be measured in experiments to test the validity of our approach.

In summary, our findings presented in this chapter are as follows:

1) MD simulations of the surface-moving nanocars have been performed for the first time. Obtained results were consistent with experimental findings;

2) It has been shown that the surface periodicity is important factor for translational motion of nanocars
Chapter 6

Development of the effective surface potentials for simulation of the nanocars

6.1. Introduction

In this section we will discuss one of the main factors, affecting the surface motion of the nanocars – the properties of the surface itself. In initial efforts to reproduce experimental observations we developed a family of the theoretical models to describe the molecule-surface interactions (see Chapter 5). Mainly such models were aimed to accelerate calculations by substitution of all explicit ad-molecule-substrate interaction by some effective potential. All the models may be considered as the external conservative potential, which modifies the original intra-molecular potential energy surface on which nanomachines move. This is because, the dynamics of the surface atoms was not considered, and they remained fixed during all simulations. This assumption allows one to develop such phenomenological model, and reduce the computational cost significantly. It is justified by noting that the interactions between the gold atoms in a metal are much stronger than between the surface atoms and the molecule’s atoms. As a result one can assume the motion of the gold atoms is not affected by their interactions with the nanocar.

It is important to understand that the properties of the real surfaces are far more complicated than any of the theoretical model used and even any of the existing surface models up to date. However, it is still possible to compare between the theoretical models between each other as well as to evaluate the quality of any given
theoretical model for surface-molecule interaction on the basis of how well it describes and/or reproduces the experimental observations.

In this chapter we discuss some more advanced surface-molecule interaction models, which extended our initial efforts (Chapter 5). Some of these models were used for other studies in this thesis (see Chapter 9). Therefore it is convenient to describe the surface models here and to focus on other results in later chapters.

6.2. Explicit models of the surfaces

In our further studies we have also tested the explicit all-atomic surface models. Such model was used to study the effect of the molecular flexibility and the correlation of the nanocar's wheels rotations (see Chapter 9).

The all-atomic surface model is just a straightforward application of the molecular mechanics approach to describe the interactions. According to such description there are a quasi-infinite surface slab (by using 2D periodic conditions) and the molecule moving on this slab. The finite piece of substrate metal may be used instead of the quasi-infinite slab as long as the molecule does not reach its boundaries. The functional form of interactions is then assumed. Most often this is simple vdw-type interactions, described by Lennard-Jones (LJ) functional form Eq. 5.1. Other most common type of interaction functionals is the Morse potential:

\[
E = \sum_{i \text{ molecule}} \sum_{j \text{ surface}} \epsilon_{ij} \left( x_{ij}^2 - 2x_{ij} \right) \quad x_{ij} = \exp \left(-A(r_{ij} - r_{ij}^0)\right) \tag{6.1}
\]

The described potentials are usually used with some kind of smoothing (switching) function \( SW(r) \) and interaction cutoff \( R_{\text{off}} \), which make the potential continuous and significantly accelerate the calculations. Exact functional form of \( SW(r) \) is not very important, the only requirement it should satisfy is:
As we can see the previous model-L is basically a computationally minimalist variation of the explicit all-atomic interactions. One of the differences is that in all-atomic models one considers all surface atoms, although not all interactions are taken into account. On the contrary, in the model-L we automatically picked up nearest atoms for each nanocar’s atom and calculated all such interactions. Picking up a shell of closest 9 or 25 atoms of the surface on each time step leads in general to discontinuous potentials (what one would obtain without use of smoothing/switching function Eq. 6.2). However, the effects of discontinuity were relatively small and the conservation of energy was verified to be satisfactory.

Another problem with the all-atomic models is that the parameters of interactions are developed for organic or organometallic molecules, not for metal-adsorbate. Thus the parameters do not proper account for chemisorption and charge transfer effects which happen on metal surfaces.

However, there are a few works where the dedicated potentials for metal-organic interactions have been developed[238–243]. Such approaches are based on Morse or Born-Mayer potentials parameterized to reproduce the strong binding of the organic molecules, such as alkanes, alkenes or fullerene, on the gold and silver surfaces, therefore, they implicitly take into account the chemisorption effects. This is the phenomenological approach to describe the chemisorption processes; however, the details of the physics of the interactions are not considered.
For comparison purposes, we also studied the nanocar motion with the all-atomic (explicit) surface potential model. In particular we employed the organic-silver interaction potential[238] to study the motion of the nanocar on silver surface.

6.3. More advanced model – combination of explicit and implicit models

Despite the ability of the previous simplistic models (Chapter 5) to reproduce experimental observations, they still suffer from various problems. On the other hand, the all-atomic (explicit) surface potential is computationally very demanding.

Therefore the next step in this work was to develop more reliable approach to the effective surface potential. The criteria for a desired interaction potential are the following:

- it should have asymptotically correct behavior;
- it should be computationally efficient;
- it should be periodic in 2 dimensions;
- it should represent a real (explicit) surface potential as good as possible

Since most of the MD studies are based on empirical force fields we decided to construct efficient potential on the basis of the empirical Universal Force Field[138] (UFF). Though this force field may not take into account some of the features of the real surface-molecule interactions it has a very attractive advantage being the force field developed for most of the elements of the entire periodic system. Many other force fields[124], [128], [137], [244] are usually developed for organic molecules only and they include parameters for only a few most popular (“biological”) metal atoms, such as Na⁺, K⁺, Mg²⁺, etc. Since we are interested in the processes which take place on the metal surface we need any force field containing
the corresponding parameters for metal atoms. Therefore the most appropriate choice for the force field is the UFF.

On the basis of the mentioned UFF force field we developed a procedure to create an effective potential which would satisfy the criteria given above. We assume that there is a relatively simple functional form for the surface-adatom interaction potential (Fig. 6.1):

\[ U(x, y, z) = U_{\text{implicit}}(x, y, z) + U_{\text{explicit}}(x, y, z) \]  \hspace{1cm} (6.3)

Figure 6.1. Effective potential region

The explicit part of the potential is given as in model-L, but with only 5 neighbor gold atoms. The functional form of this part is given by the UFF-type Lennard-Jones potential with the geometric mean combination rules for parameters\[138]:

\[ U_{\text{explicit}}(x, y, z) = \sum_{i,j} \left( \epsilon_{ij} \left( \frac{a_{ij}}{\sigma_{ij}} \right)^{12} - \left( \frac{a_{ij}}{\sigma_{ij}} \right)^{6} \right) \]  \hspace{1cm} (6.4)

\[ \epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j} \]

\[ \sigma_{ij} = \sqrt{\sigma_i \sigma_j} \]

On the basis of some preliminary studies of the Potential Energy Surface (PES) profiles we proposed the following functional form for implicit part of the potential
$U_{\text{implicit}}(x, y, z) = A(x, y) \frac{1}{(z + \sigma)^9} + B(x, y) \frac{1}{(z + \sigma)^6} + C(x, y) \frac{1}{(z + \sigma)^3},$

\[ A(x, y) = c_{00} + c_{01} \left[ \cos \left( \frac{2\pi x}{a} \right) \cos \left( \frac{2\pi y}{a} \right) - 1 \right]^2 \]

\[ B(x, y) = c_{10} + c_{11} \left[ \cos \left( \frac{2\pi x}{a} \right) + \cos \left( \frac{2\pi y}{a} \right) \right] \]

\[ C(x, y) = c_{20} + c_{21} \left[ \cos \left( \frac{2\pi x}{a} \right) + \cos \left( \frac{2\pi y}{a} \right) \right] \]

(6.5)

The functional forms of the coefficients $A$, $B$, $C$ were chosen to satisfy the PES profiles in $x$ and $y$ directions for small and big distances between the probe atom and the surface plane. The functional form for $z$-direction has been chosen to obey inverse cubic long-range limit. The power of 9 for the repulsive part (as well as the 3 power for the attractive part) comes from the integration of all interactions over the entire surface[245].

The other approximation is that we set the coefficients $c_{10}$ and $c_{11}$ to zero, what significantly simplifies the procedure of the finding other 4 coefficients. Finally, we require that all 4 remaining coefficients satisfy the conditions $A(x, y) > 0, \forall (x, y)$ and $C(x, y) < 0, \forall (x, y)$.

To determine the parameters $c_{00}, c_{01}, c_{20}, c_{21}$ we follow the authors of ref[246]. Namely, we evaluate the all-atomic potential explicitly at two $(X, Y)$-points for a series of $z$-distance. In other words we construct the PES profiles along two specified directions (Fig. 6.1). Using the potential definition Eq. (6.5) and assuming its validity (or at least that this is a good functional for potential approximation) we obtain:

\[ f_1(z) = U_{\text{implicit}}(0, 0, z) = \frac{c_{00}}{(z + \sigma)^9} + \frac{c_{20} + 2c_{21}}{(z + \sigma)^3}, \]

\[ f_2(z) = U_{\text{implicit}} \left( 0, \frac{a}{2}, z \right) = \frac{c_{00} + 4c_{01}}{(z + \sigma)^9} + \frac{c_{20}}{(z + \sigma)^3} \]

(6.6)
Calculation of sets of z points gives us two curves (profiles), which can be fitted to the following functionals:

\[
\begin{align*}
\tilde{f}_1(z) &= \frac{A_1}{(z + \sigma)^9} + \frac{B_1}{(z + \sigma)^3}, \\
\tilde{f}_2(z) &= \frac{A_2}{(z + \sigma)^9} + \frac{B_2}{(z + \sigma)^3}
\end{align*}
\] (6.7)

As a result the fitting procedure gives us 4 coefficients \(A_1, A_2, B_1, B_2\), from which we can easily calculate the required coefficients \(c_{00}, c_{01}, c_{20}, c_{21}\):

\[
\begin{bmatrix}
c_{00} = A_1 \\
c_{20} = B_2 \\
c_{00} + 4c_{01} = A_2 \\
c_{20} + 2c_{21} = B_1
\end{bmatrix} \iff \begin{bmatrix}
c_{00} = A_1 \\
c_{20} = B_2 \\
c_{01} = \frac{1}{4}(A_2 - A_1) \\
c_{21} = \frac{1}{2}(B_1 - B_2)
\end{bmatrix}
\]

\[\text{Figure 6.2. Two directions of the profile scan.}\]

The fitting procedure mentioned above was performed as a gradient minimization of the sum of squared errors. We run this summation over the set of points with different z coordinates. Exact energy for each point was calculated by
explicit summation of all pairwise interactions, except 5 neighbor lattice atoms. To calculate exact energy this way, the surface was represented as $h=10$ shells and $v=10$ layers, in other words the number of surface atoms taken into account were typically of the order $(4h - 1)^2(v + 1) = 40^2 \times 10 = 16000$ atoms.

This combined model potential is an extension of our early model-P. It would be desirable to retain only implicit part, which is computationally very efficient and is also continuous. However, the implicit part alone can not describe strong interactions (especially repulsion) of the probe atoms (one of the adsorbate atoms) in near vicinity of the surface lattice atoms. This is the reason the explicit part has been included.

The explicit part of this combined potential is not continuous by itself. However, because the implicit part have been parameterized in such a way that it included the effect of other surface atoms we believe that discontinuity effects are rather small, although not exactly vanishing.

### 6.4. Conclusions and Summary

In this chapter we have described some approaches to construction of the effective and computationally efficient surface-molecule interaction potentials. Such methods are the extensions of our early efforts to this problem.

We discussed an explicit method for treating surface-molecule interactions as well as the combined hybrid method. We presented the requirements and the construction procedure for each of them. Some advantages and drawbacks of each method have also been considered. Both potentials were used to study various effects in molecular machines. Corresponding results will be discussed in Chapter 9.

In summary, our findings presented in this chapter are as follows:
1) we have used explicit surface-molecule interaction model which have been parameterized in a way which implicitly takes into account chemisorption and charge transfer effects;

2) we have developed a new effective surface potential, which is an extension of our previous models model-L and model-P. Such potential was designed on a number of physically determined requirements and was parameterized to take into account effect of many surface atoms
Chapter 7

Alternative approach to construction of the effective surface potential – the ANN-based potential

7.1. Introduction

Molecular Dynamics method is an important tool for study of diffusion of different molecules, including nanocars on various substrates, such as metals. However, for accurate description of surface-molecule interaction energies (adsorption energies), the diffusion coefficients and activation energies for diffusion one should consider relatively big slabs of atoms, representing the surface. In order to take into account boundary effects the periodic boundary conditions are often employed. This increases the number of pair-wise interactions one should consider in MD simulations.

In order to speed up calculations of the surface-molecule interactions various approaches has been developed. One of the most common among them is a lattice summation method. The idea behind this approach is to divide the surface into 2 regions – one is small, including a few shells of unit cells and the other is big, including all other atoms of the surface. Summation of the interactions of the ad-atom and the first part of the surface is performed in real-space, while the summation of the other interactions is performed in reciprocal space. The latter summation usually involves special functions, such as modified Bessel functions of the second kind[247]. However it may be difficult to achieve good convergence of such sums. Moreover for complex unit cells of the crystal one may need to use such summation method for
each type of atom in the unit cell what complicates the implementation and decreases
the performance of the method.

In this chapter we derive another approach, namely, we employ the artificial
neural networks (ANN) to describe the potential energy surface (PES) for ad-atom-
substrate interactions. The introduction into ANN as well as in-depth discussion of
this subject may be found in many corresponding textbooks and specialized papers.

We briefly present the basic ANN construction in Appendix C and introduce our
notation. The Appendix C also contains a detailed derivation of several ANN training
algorithms. We emphasize on our extension of the conventional error
backpropagation method to more general case, where the derivatives of the ANN are
also taken into account.

The ANN were successfully used to represent different PES[248–254] or the
molecular mechanics force fields[255], often obtained from quantum-chemical
calculations. There exist several examples of using ANN for MD simulations[255–
257]. However, to the best of our knowledge the ANN were not yet used as a
substitution for the lattice summation methods for acceleration of the MD simulations.

The structure of this chapter is following. First the construction of the surface-
adatom potential is presented. Discussion of discontinuity problem and symmetry of
the surface is given. The procedure of the ANN training is discussed and the quality
of the ANN is presented. Applications of the ANN developed to surface diffusion of
some small molecules is then presented.
7.2. Theory

7.2.1. The potential definition

We consider the simplest cases of the surface symmetry, namely, the Cu(100) surface plane. The total adatom-surface interaction potential in a conventional way may be expresses as a sum of pair-wise contributions:

\[
E(\vec{r}) = \sum_{n_x, n_y, n_z} \sum_s U\left(\vec{r} - \left(\vec{r}_s + n_x \vec{a} + n_y \vec{b} + n_z \vec{c}\right)\right)
\]  

(7.1)

\[
U(r) = \frac{A}{r^{12}} - \frac{B}{r^{6}}
\]  

(7.2)

The most important contribution in the sum written above is due to the central unit cell (we now think in terms of conventional unit cells, thus the central unit cell of Cu(100) contains 9 Cu atoms in contrast to primitive unit cell, containing only 4 atoms) \((n_x = n_y = 0)\) and its first order replicas \((n_x, n_y) \in \{-1, 1\} \cap \{0, 0\}\) all belonging to the first layer \((n_z = 0)\). Thus we can rewrite the potential as:

\[
E(\vec{r}) = E_{\text{main}}(\vec{r}) + E_{\text{rest}}(\vec{r})
\]  

(7.3)

\[
E_{\text{main}}(\vec{r}) = \sum_{n_x, n_y = -1}^{1} \sum_s U\left(\vec{r} - \left(\vec{r}_s + n_x \vec{a} + n_y \vec{b}\right)\right)
\]  

(7.4)

The term \(E_{\text{rest}}(\vec{r})\) can in its turn be split into 2 parts – one due to atoms of the first layer, but not belonging to the central unit cell nor to its first-order replicas and the other - due to all atom layers other than the first layer (in this case including central cell and its first-order replicas):

\[
E_{\text{rest}}(\vec{r}) = E_{\text{lateral}}(\vec{r}) + E_{\text{vertical}}(\vec{r})
\]  

(7.5)

\[
E_{\text{lateral}}(\vec{r}) = \sum_{n_x, n_y \in S(N_{\text{rest}})} \sum_s U\left(\vec{r} - \left(\vec{r}_s + n_x \vec{a} + n_y \vec{b}\right)\right)
\]  

(7.6)

\[
S(N) = \{(n_x, n_y) \in [-N, N]^2 \cap [-1, 1]^2\}
\]
In this work we approximate both $E_{\text{lateral}}(\vec{r})$ and $E_{\text{vertical}}(\vec{r})$ as two distinct ANNs. Moreover, these contributions only include attractive part $-\frac{B}{r^6}$ since the repulsive part is negligibly small in comparison to the attractive one. Also this gives us an opportunity to use the same ANN for different ad-atom types. This is because the single attractive part for one atom type $i$ is linearly related to that of another atom type $j$:

$$
\frac{B_i}{B_j} = \left( \frac{\varepsilon_i \varepsilon_M}{\varepsilon_j \varepsilon_M} \right)^{1/2} \left( \frac{\sigma_i \sigma_M}{\sigma_j \sigma_M} \right)^{3/2} = \left( \frac{\varepsilon_i^{1/2} \sigma_i^3}{\varepsilon_j^{1/2} \sigma_j^3} \right) \Rightarrow -\frac{B_i}{r^6} = \text{const} \left( -\frac{B_j}{r^6} \right)
$$

(7.8)

7.2.2. The discontinuity problem

The surface-atom interaction potential is built of two components. These are: 1) the main contribution due to the original unit cell and its first order replicas (the first shell of replicas) $E_{\text{main}}$ and 2) the contribution due to higher-order replicas which in principle should include the infinite number of such replicas $E_{\text{rest}}$, yet in practice a finite number (normally big enough) is used. Since the number of the replicas in the second contribution increases quadratically and each such replica may contain several basis atoms, it is obvious that if one wants to consider even relatively small number of the shells the amount of computations required increases drastically. From the other hand, the contribution due to these shells may be small, so we obtain only a small correction to the energy and gradients at significant computational cost. That is why it is very important to find a cheap and accurate way to calculate such corrections. Our
initial approaches to solve this problem by treating this correction via implicit potential model or including it directly in one of the early models have been discussed in Chapters 5 and 6. In this chapter we will present an alternative approach which is based on the training an artificial neural network (ANN) so that it might reproduce such correction.

For now let us concentrate on the first contribution to the potential – which is due to the original unit cell and its first replicas. In order to obtain relatively smooth data set for the ANN training we absolutely have to consider the contribution of the first replicas explicitly. This is necessary because if the distance between the adsorbate atom and the surface is set to zero, then even when the atoms of the original unit cell are excluded we might encounter very close atoms from the first replica cells. This will lead to very big values of the potential energy and gradients, which may significantly affect the ability of the ANN to learn and generalize.

![Figure 7.1](image)

Figure 7.1. To discontinuity of the derivatives: a) potentials are calculated as they are; b) potentials are calculated with the switching function correction

Another important problem which arises in conjunction with the first contribution is that since we consider (in this part of the potential) only first shell of
replicas the potential derivatives are discontinuous. For example, consider an atom on a short 1D lattice (Fig. 7.1, a). If the atom rests over the lattice site with \( x = 0 \) the number of atoms pushing it from the right is bigger then the number of such atoms from the left. As a result the total force, acting on this atom has a negative \( x \)-component. If, on the contrary, the atom is placed over the lattice site with \( x = a \) we obtain inverted picture, that is the total force acting on the atom has a positive \( x \)-component. Since all positions of the atom are projected onto the interval \([0, a]\) we should have periodic boundary conditions:

\[
U(0) = U(a) \\
\frac{dU}{dx}(0) = \frac{dU}{dx}(a) \tag{7.9}
\]

However in our example the derivatives are discontinuous even if the potential may be continuous. Discontinuity of the derivatives will lead to MD simulations being impractical since in such a case the invariants will not be conserved.

One of the most straightforward ways to solve this problem is to multiply the potential by some smoothing function which will make the new modified potential continuous as well as its derivatives - \( \bar{U}(\vec{r}) = U(\vec{r}) \cdot f(\vec{r}) \) (Fig. 7.1, b). The switching function may be chosen quite arbitrarily, as long as it satisfies the requirements Eq. 6.2.

Our choice of the switching function for the surface potential (2-D) problem is following: \( f(\vec{r}) = f(x)f(y) \), where

\[
f(x) = \\
\begin{cases} 
1, x \leq x_{on} \\
1 + 3 \frac{x - x_{on}}{x_{off} - x_{on}} + \left(\frac{x - x_{on}}{x_{off} - x_{on}}\right)^2, x_{on} \leq x \leq x_{off} \\
0, x \geq x_{off}
\end{cases} \tag{7.10}
\]

and
\begin{align*}
x &= |x_a - (x_s + n_a)| \\
y &= |y_a - (y_s + n_b)|
\end{align*} \tag{7.11}

and where \( \bar{r}_a = (x_a, y_a) \in [0,1]^2 \) and \( \bar{r}_s = (x_s, y_s) \in [0,1]^2 \) are the coordinates of the probe atom (atom of the adsorbate) and the surface atom correspondingly, expressed in units of the crystal cell dimensions and \( n_a, n_b \) are integers.

If one wants to consider a single conventional unit cell of the fcc(100) surface, the parameters \( R_{on} \) and \( R_{off} \) should be chosen as \( R_{off} = 1 \) and \( R_{on} = R_{off} - s \), where \( s \) is a parameter in this study chosen to be 0.2 and determining the region where the switching function is in \((0,1)\) range. The integers \( n_a \) and \( n_b \) should run from -2 to 2, to insure that all regions where \( f(\bar{r}) \) is nonzero are included.

Another important aspect of the potential calculation is that for each pair-wise term of the surface-molecule interaction there is a corresponding value of the switching function, as opposed to the case where there is a common switching function for all terms on expression for total interaction energy. In other words the multiplication of each pair-wise term by its switching function should precede the summation.

The derivatives of the modified potential will then read as:

\[
\frac{d\tilde{U}}{d\bar{r}} = U(\bar{r}) \frac{df}{d\bar{r}}(\bar{r}) + f(\bar{r}) \frac{dU}{d\bar{r}}(\bar{r})
\] \tag{7.12}

This expression looks simple; however there is a coordinate transformation should be done. This is because the switching function and its derivative are calculated in the unit cell coordinates, while the original potential and its derivatives are calculated in Cartesian coordinates. The coordinate transformations and force derivations are summarized in Appendix D.
7.2.3. Taking into account the surface symmetry

Training of the neural network is often a challenging problem, since for a given data set one needs to find the optimal ANN architecture and then train it such that it delivers smallest fitting and prediction errors. In order to do this it is often necessary to increase the size of the neural network as the training data set increases. One can also do the reverse thing, namely, to reduce the size of the ANN to smallest possible (giving still accurate results) by reducing the size of the training data set.

The data set used in this work was obtained by PES scan. In x and y directions we considered points taken in the range [0, 1] with spacing 0.1. In z directions we considered points in the range [0, 10] also with spacing 0.1. This data set was then divided into two parts – the training and the testing (validation) data sets as will be described further.

Here we made use of the system symmetry in order to shrink the training data set to some smaller subset. In order to do this we need to introduce a symmetry-adapted coordinates, that is such coordinates which do not change upon some set of symmetry operations. The particular choice of such coordinates is quite arbitrary; however, as it will be shown later, this choice may significantly influence the accuracy of trained ANN. Our choice for the symmetry-adapted coordinates is as follow:

\[
\xi = \alpha x^2 (1-x)^2, \quad \eta = \beta y^2 (1-y)^2, \quad \text{where } \alpha, \beta \text{ - are constants} \quad (7.13)
\]

For the simplest case of the fcc(100) surface such coordinates reduce original data set 4 times, thus instead of considering all points in a square lattice cell (Fig 7.2,
a) we can consider only those points which belong to the fourth part of this cell (Fig 7.2, b).

Figure 7.2. Reduction of the configurational space required using symmetry-adapted coordinates. A) The whole range of original coordinates to be considered for ANN training; b) the set of original coordinates to be considered for ANN training with the symmetry-adapted coordinates.

Considering only those points in the shaded area on (Fig. 7.2, b) significantly reduces the number of the points we have to present to the ANN during training thus accelerating the training procedure. Another important consequence of using the symmetry is that the trained ANN is much more accurate then the ANN trained on the full data set.

Each training pattern of our data set consists of 4 components – potential energy and its derivatives with respect to x, y and z coordinates – E and $\frac{dE}{dx}, \frac{dE}{dy}, \frac{dE}{dz}$. However, since we use symmetry-adapted coordinates as inputs we should correspondingly transform the derivatives, and thus for training purposes consider derivatives with respect to input (symmetry-adapted coordinates) - $\frac{dE}{d\xi}, \frac{dE}{d\eta}, \frac{dE}{dz}$. The derivatives are related as given by Eq. 7.14. Since we do not change z coordinate – the derivative with respect to z stay the same.
\[
\frac{dE}{dx} = J \frac{dE}{d\xi} = J^{-1} \frac{dE}{d\xi} = \frac{dE}{dy} = J \frac{dE}{d\eta}
\]

\[
J = \begin{pmatrix}
\frac{d\xi}{dx} & \frac{d\eta}{dx} \\
\frac{d\xi}{dy} & \frac{d\eta}{dy}
\end{pmatrix} = \begin{pmatrix}
2\alpha(1-x)(1-2x) & 0 \\
0 & 2\beta y(1-y)(1-2y)
\end{pmatrix} \implies (7.14)
\]

\[
\implies J^{-1} = \begin{pmatrix}
\frac{1}{2\alpha(1-x)(1-2x)} & 0 \\
0 & \frac{1}{2\beta y(1-y)(1-2y)}
\end{pmatrix}
\]

It turns out that the choice of the constants \(\alpha\) and \(\beta\) is quite important (and thus the particular form of transformation is important). Namely, if both constants are set to unity, then the new coordinates \(\xi\) and \(\eta\) will vary in range \([0, 1/16]\), while the \(z\) coordinate will vary in range \([0,10]\). Although, before ANN training all these coordinates are usually rescaled to the same range \([-1,1]\) as well as the corresponding derivatives, the relative values of these derivatives may differ by several orders of magnitude. That is why it is particularly important to scale the symmetry-adapted coordinates in the original data set (that is before it is presented to ANN training procedure, where it is pre-processed). Thus the constants \(\alpha\) and \(\beta\) should be chosen such that coordinates \(\xi\) and \(\eta\) vary in the same range as \(z\). This gives us the estimates \(\alpha = \beta = 160\).

Since inverse of the Jacobian \(J^{-1}\) has singularities at points \((0,.), (1,.), (.,0), (1/2,1/2)\) they should be excluded from the training set. However, these points are not important for ANN training since whatever ANN recall is at these points the forces are zeroes, since the Jacobian at this points is zero. These properties of the symmetry-adapted coordinates also let us easy and naturally satisfy
the periodic boundary conditions for the potential energy and its first derivatives, what is a necessary requirement for MD applications.

7.2.4. Scaling lattice parameters

The ANN developed takes 3 arguments – x, y and z-coordinated of the probe atom with respect to the surface origin. However, x and y coordinates should be in units of the lattice vectors, but z – coordinate is just a normal Cartesian distance. Taking into account this complication we want to extend the ANN for different lattice parameters.

The ANN approximates the sum of terms like

\[ U(x_a, y_a, z_a) = \frac{-B}{\left( (x_a - x_s)^2 + (y_a - y_s)^2 + (z_a - z_s)^2 \right)^{\frac{3}{2}}} \]

where subscript \( a \) indicates that variables refer to the probe atom and the subscript \( s \) refers to surface atoms. In terms of ANN inputs this may be written as:

\[ U(x_{e,a}, y_{e,a}, z_{a,e}) = \frac{-B}{a^6 \left( (x_{e,a} - x_{e,s})^2 + (y_{e,a} - y_{e,s})^2 + \left( \frac{z_{e,a} - z_{e,s}}{a} \right)^2 \right)^{\frac{3}{2}}} \]

(7.15)

where additional subscript \( e \) indicates that we are using scaled coordinates \( z_{a,e} = \frac{z_{e,a}}{a} \).

Note, z – coordinates are still in Cartesian coordinates. This is approximated by \( \text{ANN}(x_{e,a}, y_{e,a}, z_{a,e}) \).

If we change the lattice parameter \( a \), we then have:
\[ U(x_{e,a}, y_{e,a}, z_2 | a') = \frac{-B}{a^6 \left( (x_{e,a} - x_2)^2 + (y_{e,a} - y_2)^2 + \left( \frac{z_2 - z_1}{a'} \right)^2 \right)^3} \]  

(7.16)

\[ a^6 U(x_{e,a}, y_{e,a}, z_2 | a') = a^6 U(x_{e,a}, y_{e,a}, z_1 | a) \]  

(7.17)

for \( \frac{z_1}{a} = \frac{z_2}{a'} \) or

\[ U \left( x_{e,a}, y_{e,a}, z | a' \right) = \left( \frac{a}{a'} \right)^6 U \left( x_{e,a}, y_{e,a}, \left( \frac{a}{a'} \right) z | a \right) \]  

(7.18)

The same applies to the ANN expression, so:

\[ \text{ANN} \left( x_{e,a}, y_{e,a}, z | a' \right) = \left( \frac{a}{a'} \right)^6 \text{ANN} \left( x_{e,a}, y_{e,a}, \left( \frac{a}{a'} \right) z | a \right) \]  

(7.19)

This lattice scaling approach allows one to use the ANN, trained on some reference structure, e.g. on Cu(100) surface, for description of interaction of the probe atoms with different surfaces, e.g. Au(100). The only requirement is that the reference surface and the surface of interest have homological structures, related by simple scaling of the lattice constants. The different interaction strength can be modeled by application of relation (7.8).
7.3. Results and Discussion

7.3.1. ANN training

Since the surface potential has two contributions – one (lateral) is due to atoms of the first layer and not belonging to the first shell of unit cells and the other (vertical) – due to all atoms not belonging to the first layer, we decided to train a separate ANN for each of these contributions. Experimenting with different ANN architectures we have found that the 3-10-5-1 architecture delivers best compromise between ANN complexity and its accuracy and generalization abilities. For training each of the ANN we used a training set of 1701 data points. Each data point contained values of x, y and z coordinates as inputs and value of the potential energy E as output and its derivatives with respect to inputs $\frac{dE}{dx}$, $\frac{dE}{dy}$, $\frac{dE}{dz}$ for the purposes of better generalization. Here x and y – are actually the symmetry-adapted coordinates $\xi$ and $\eta$, introduced in previous section.

The ANN was trained for $10^6$ epochs using online training with tangent backpropagator algorithm, which approximates not only target outputs but it also tries to approximate the derivatives of the ANN output with respect to the inputs. Since it is impossible to visualize 4-dimensional data set (x,y,z, E(0r dE/dx, dE/dy, dE/dz)) we enumerated each (x,y,z) point, so we could represent the data set in 2 dimensions. The trained ANN output and its derivatives (E and dE/dx,dE/dy,dE/dz) are shown vs. corresponding desired values for both lateral (Fig. 7.3) and vertical (Fig. 7.4) potential contributions.
Figure 7.3. Lateral contribution: a) a part of data set is shown for better resolution; b) full data set is shown (left – training set, right – testing set)

Figure 7.4. Vertical contribution: a) a part of data set is shown for better resolution; b) full data set is shown (left – training set, right – testing set)

Quantitative characteristics of the ANN accuracy are collected in Table 7.1:

<table>
<thead>
<tr>
<th>Table 7.1. Accuracy of the trained ANNs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parameter</td>
</tr>
<tr>
<td>E error, kcal/mol</td>
</tr>
<tr>
<td>dE/dx error, kcal/mol$^*$</td>
</tr>
<tr>
<td>dE/dy error, kcal/mol$^*$</td>
</tr>
<tr>
<td>dE/dz error, kcal/(mol*$^*$Å)</td>
</tr>
<tr>
<td>P(E), %</td>
</tr>
<tr>
<td>P(dE/dx), %</td>
</tr>
</tbody>
</table>
The quantity P(X) is defined as a percent of data points for which the relative error in quantity X is less than 0.5. Errors of the quantity X were calculated as:

\[
error(X) = \sqrt{\frac{\sum_{i=1}^{N} (X_{\text{actual}} - X_{\text{desired}})^2}{N}} \tag{7.20}
\]

where \( N \) is a size of the training data set.

As we can see, the energy itself and its derivative with respect to z coordinate are very well approximated by both neural networks. Derivatives of the energy with respect to symmetry-adapted coordinates x and y are approximated also quite well. The quantity P for these two derivatives is small because all the target values are close to zero, so the relative errors are bigger, and the probability for it to be less than 0.5 is smaller. Also as we can observe from the figures 4 and 5 even if the dE/dx and dE/dy are not exactly the same as target values, the topology of the PES represented by ANN is similar to the original PES (calculated explicitly).

### 7.3.2. Optimization

In order to test accuracy of the ANN-based potential in vertical direction we performed a geometry optimization of set of small molecules (fullerene, coronene and benzene) on the Cu(100) surface with different degrees of accuracy in potential energy calculations. This included considering different number of the central unit cell replicas as well as taking into account different number of layers. We compared this with our ANN-based potential (Tables 7.2-7.4). The ANN architecture was chosen to be 3-10-5-1 for both lateral and in-depth contributions.

<table>
<thead>
<tr>
<th>P(dE/dy), %</th>
<th>17.11</th>
<th>8.64</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(dE/dz), %</td>
<td>93.89</td>
<td>100.0</td>
</tr>
</tbody>
</table>
Table 7.2. Accuracy and speed comparison of the standard potential and ANN-based one for C$_{60}$/Cu(100) system

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Energy</th>
<th>Relative elapsed time, s</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 shell, 1 layer</td>
<td>-1.819</td>
<td>1.0</td>
</tr>
<tr>
<td>5 shells, 1 layer</td>
<td>-3.149</td>
<td>6.26</td>
</tr>
<tr>
<td>5 shells, 5 layers</td>
<td>-3.670</td>
<td>31.09</td>
</tr>
<tr>
<td>10 shells, 5 layers</td>
<td>-3.716</td>
<td>101.45</td>
</tr>
<tr>
<td>1 shell, 1 layer + ANN</td>
<td>-3.970</td>
<td>1.59</td>
</tr>
</tbody>
</table>

Table 7.3. Accuracy and speed comparison of the standard potential and ANN-based one for Coronene/Cu(100) system

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Energy</th>
<th>Relative elapsed time, s</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 shell, 1 layer</td>
<td>-2.899</td>
<td>1.0</td>
</tr>
<tr>
<td>5 shells, 1 layer</td>
<td>-4.401</td>
<td>6.36</td>
</tr>
<tr>
<td>5 shells, 5 layers</td>
<td>-4.921</td>
<td>32.19</td>
</tr>
<tr>
<td>10 shells, 5 layers</td>
<td>-4.944</td>
<td>104.04</td>
</tr>
<tr>
<td>1 shell, 1 layer + ANN</td>
<td>-5.327</td>
<td>1.65</td>
</tr>
</tbody>
</table>

Table 7.4. Accuracy and speed comparison of the standard potential and ANN-based one for Benzene/Cu(100) system

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Energy</th>
<th>Relative elapsed time, s</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 shell, 1 layer</td>
<td>-0.773</td>
<td>1.0</td>
</tr>
<tr>
<td>5 shells, 1 layer</td>
<td>-1.137</td>
<td>6.55</td>
</tr>
<tr>
<td>5 shells, 5 layers</td>
<td>-1.270</td>
<td>30.93</td>
</tr>
<tr>
<td>10 shells, 5 layers</td>
<td>-1.276</td>
<td>100.69</td>
</tr>
<tr>
<td>1 shell, 1 layer + ANN</td>
<td>-1.399</td>
<td>1.62</td>
</tr>
</tbody>
</table>

As we can see the ANN-based potential gives us the energy which one can obtain by considering quite big slab of atoms representing a surface. However, the
time required for such calculations is around 60 times smaller. Also one can see that the ANN contribution (as well as replicas of the order higher than 1 in standard approach) can not be neglected, since it gives almost the same energy as the central unit cell with its first-order replicas.

7.3.3. MD simulations of surface diffusion

In order to test how well the ANN-based potential represents the lateral barriers, that are the energy barriers which are responsible for 2D motion, we performed the molecular dynamics (MD) simulations of several small molecules using both conventional and the ANN-based potentials. MD simulations were performed at several temperatures so we could also calculate the activation energies for diffusion of those test molecules using a simple Arrhenius plot. We calculated 10-15 trajectories 1ns long for each temperature so we could sample a good statistics. At high temperatures some of the molecules fly off the surface. The part of the trajectory corresponding to free motion was excluded from the diffusion coefficients calculations.

The ANN-potential corrections have been obtained as discussed in previous section. It should be noted that only C-Cu(100) ANN-potential has been constructed. This single correction has been used to calculate the interactions between other types of atoms (e.g. H-Cu(100), N-Cu(100), etc.) as given by Eq. 7.8 and for interactions with other lattice parameters (e.g. H-Au(100), C-Au(100), etc.) as given by Eq. 7.19. The results for benzene, coronene, fullerene and glycine molecules diffusing on Cu(100) and Au(100) surfaces are collected in the table 7.5. The corresponding diffusion coefficients are shown on Fig 7.5.
Table 7.5. Activation energies for surface diffusion of small molecules on Cu(100) surface.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Surface</th>
<th>Cu(100)</th>
<th>Au(100)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_a$(Standard), kJ/mol</td>
<td>$E_a$(ANN-based), kJ/mol</td>
<td>$E_a$(Standard), kJ/mol</td>
</tr>
<tr>
<td>Fullerene</td>
<td>2.45 +/- 0.21</td>
<td>2.36 +/- 0.30</td>
<td>4.63 +/- 0.90</td>
</tr>
<tr>
<td>Coronene</td>
<td>1.80 +/- 0.27</td>
<td>1.74 +/- 0.31</td>
<td>2.43 +/- 0.41</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.70 +/- 0.19</td>
<td>0.77 +/- 0.12</td>
<td>1.26 +/- 0.20</td>
</tr>
<tr>
<td>Glycine</td>
<td>0.72 +/- 0.09</td>
<td>0.86 +/- 0.22</td>
<td>1.26 +/- 0.08</td>
</tr>
</tbody>
</table>

Figure 7.5. Comparison of the diffusion coefficients of small molecules on Cu(100) and Au(100) surfaces a) Benzene; b) Coronene; c) Fullerene and d) Glycine

As we can see, in all cases the ANN-based potential gives the same (to the error bar precision) activation energy for diffusion as the standard potential. In most of the cases it also gives almost the same pre-exponents, while for the fullerene the
pre-exponent is slightly bigger than that calculated with standard potential. In general for smaller molecules, especially if they are sufficiently flat the ANN-potentials reproduce the diffusion coefficient obtained by standard explicit potential quite well. The diffusion coefficients are reproduced slightly worse for bigger molecules, although even in that case the activation energies are in good agreement with those obtained from explicit potential calculations.

7.4. Conclusions and Summary

In this chapter the ANN-based potential was developed and tested on several small molecules moving on the Cu(100) surface. The adsorption energies and the diffusion activation energies obtained with such potential are in good agreement with those calculated using standard approach (explicit consideration of many atoms of the surface). The ANN-based potential is very efficient providing the computational acceleration up to 20-65 times, depending on the complexity of the standard calculations. The lateral and vertical ANNs obtained in this work may easily be generalized to the case of other ad-atom types (just by linear scaling) and to the case of other lattice parameters. The same technique may be extended to different types of the surfaces. Using the symmetry-adapted coordinated one may reduce the size of the data set, needed to train the ANN and significantly improve its generalization ability.

In summary, our findings presented in this chapter are as follows:

1) the ANN-based surface-molecule interaction potential is efficient and convenient way to accelerate calculations of the interfacial phenomena. It provides acceleration up to 60 times, while accurately reproduce adsorption energies and diffusion coefficients and activation energies for diffusion obtained with all-atomic explicit potentials;
2) symmetry-adapted coordinates allow to improve quality of the ANN-based potential;

3) Once the ANN-based potential is obtained for one type of the probe atom and for given lattice constant, the ANN for other atom types and lattice constants can be easily obtained using simple transformations
Chapter 8

Charge transfer model for description of the fullerene adsorption on metal surfaces

8.1. Introduction

In our previous work many models for the surface-adsorbate interactions have been considered. However, most of them treated the phenomenon of the charge transfer, which is known to be very important in C$_{60}$/metal systems, only empirically via some form of parameterization of known form for the dispersion potential. Such approaches, however, do not take into account the electrostatic nature of such interactions and substitute them with only dispersion-type interactions. This, in its turn, may have a significant impact on correct way to describe the interaction of such systems with external electric field.

STM experiments and possible future applications all involve the interaction of the nanocar with external electric field. And this is important for driving such molecules directionally. It is believed that in order to be driven by external electric field the nanocar should possess nonzero dipole moment via introduction of some electronodonor and/or electronoacceptor groups to the nanocar’s chassis. However, the closer look at physics of fullerene adsorption on metal surfaces and taking into account such phenomenon as a charge transfer may open an opportunity to drive the molecular machines without attaching additional functional groups to them.

The fullerene molecule is one of the molecules the special properties of which attract more and more researchers to carry out different studies of complexes
involving C\textsubscript{60} particles as main components. One of particular spheres of interest is its interaction with different surfaces. So far quantum mechanical studies have been performed for diamond\textsuperscript{[258]}, graphite\textsuperscript{[259]}, silicon\textsuperscript{[260]}, silica and polyester\textsuperscript{[261]} surfaces as well as many studies on various metals in particular gold\textsuperscript{[180]}, \textsuperscript{[262–267]}, silver\textsuperscript{[262]}, \textsuperscript{[268]}, copper\textsuperscript{[269]} and others\textsuperscript{[270–272]}. 

Most of the studies of the adsorption of C\textsubscript{60} molecule on gold surfaces report a significant amount of the charge transfer (CT) from the metal to the fullerene, which may also depend on the crystal plane. Experimental studies show quite different results with big measurement or calculation uncertainty. For example, CT is estimated to be 0.8 electrons on Au(111) surface\textsuperscript{[265]}, 1.0 +/- 1.0 on Au(110) surface\textsuperscript{[262]}, \textsuperscript{[264]} (vibrational spectroscopy) and 1.0 +/- 0.2 on polycrystalline Au\textsuperscript{[273]} (XPS with K-doping), while the theoretical model predicts the CT from 0.2 to 0.4 electrons on Au surfaces\textsuperscript{[267]}. The charge transfer is argued to be smaller for more open surfaces such as Au(111) or Au(100) in contrast to more corrugated such as Au(110)\textsuperscript{[264]}.

The adsorption energies of C\textsubscript{60} on Au(111) were studied by both experimental and theoretical methods. Using the temperature desorption technique it was estimated to be ~43 kcal/mol\textsuperscript{[265]} whereas the DFT calculations\textsuperscript{[268]} show somewhat lower energy of only ~31 kcal/mol. The theoretical model in Ref.\textsuperscript{[267]} gives the estimate for the adsorption energy on Au(110) surface from 46 to 71 kcal/mol, depending on proposed substrate structure (not taking in account the relaxation). It is argued that the adsorption energy on reconstructed Au(110) surface is bigger than on Au(111) surface, which almost does not reconstruct on the C\textsubscript{60} binding\textsuperscript{[265]}.

In this chapter we describe a phenomenological model, based on semi-empirical PM6 calculations\textsuperscript{[274]}, that is aimed to reproduce known experimental and/or high quality computational results about C\textsubscript{60} adsorption on both Au(111) and
Au(100) surfaces while giving some insight of the details of charge transfer process and preserving the computational efficiency necessary for long MD simulations of fullerene-based systems. Finally, the model is applied to study the surface diffusion of both fullerene and fullerene-based nanotruck systems and to re-evaluate the previous computational models.

8.2. Theory
8.2.1. Model definition

Our theoretical approach is based on the use of semi-empirical PM6[274], [275] calculations of the fullerene-gold systems for calculation of the charges on carbon atoms of the fullerene, which depend on their distance to the metal surface. Consequently, the obtained data are used to fit the computationally more tractable model, which allows fast calculation of the charge distribution on the fullerene as well as its interaction energy with the metal surface. Since the charge distribution is a function not only of the carbon – surface distance, but also a function of the orientation of carbon atoms with respect to each other and to the surface atoms, the calculations should be performed for many configurations. Thus only the semi-empirical calculations would be practical. Although, the DFT studies of similar system have been reported[268], [271], [276], they are usually performed for only a few points.

We performed the PM6 semi-empirical calculations using Gaussian09[277] program package. Our preliminary results of the C_{60}/Au(100) system show that the charge transfer takes place only for small fullerene-gold distances. Most significant charge transfer is usually happens with the carbon atom which is the closest to any of the gold atoms. This carbon atom is usually becomes positively charged (0.3 – 0.4 a.
The three adjacent carbon atoms which are directly connected to it become negatively charged (-0.6 - -0.7 a. u.). The charge transfer involving other carbon atoms is less significant (Fig. 8.1). Such observations reveal the very local nature of the charge transfer in fullerene-gold system.

**Figure 8.1.** Typical charge transfer pattern in the $C_{60}/Au(100)$ system.

The electron density (charge) distribution pattern similar to one shown on Fig. 8.1 is very pronounced for closest C-Au distances in interval of 1-1.5 Angstrom. At distances around 2.6 Angstrom and more the most of the bottom carbon atoms are negatively charges. Those which are positively charged carry very small positive charge. Moreover, the energy of all configurations is decreasing at least up to 2.6 Angstrom of closest C-Au distance. This means the optimal C-Au bond length should be bigger than 2.6 Angstrom.

The most difficult question now is how to model the charge transfer of such kind with relatively simple approach, allowing us to perform fast charge transfer calculations during MD simulations. Moreover, since our target are the MD simulations the desired approach should also be continuous, meaning that we should be able to calculate the derivatives of the charges on all atoms (of $C_{60}$) with respect to the positions of all atoms (themselves and others).
The most straightforward approach to model the charge transfer in system of our interest would be to find the carbon atom, which form the shortest "bond" with one of the gold atoms available in its vicinity and assign some relatively big positive charge to that atom. Then three neighbor atoms, directly connected to positively charged carbon would be assigned with some big negative charges, which are bigger in magnitude than the positively charged central atom, thus mimicking the charge distribution obtained from PM6 calculations (Fig. 8.1).

In the very first approximation this would be the simplest still reasonable approach. It would finely suite the purpose of predicting the charges on the most important carbon atoms involved in the charge transfer phenomenon. However, this method is not continuous, since it is quantized, meaning that in one moment the atom with index $i$ will be positively charged, while some other atom $j$ may be electroneutral or negatively charged. In the following MD simulation step the situation may be suddenly reversed leading to discontinuity of the charges. This is most likely to happen for the most important 4 carbon atoms at the very bottom of fullerene, where even smallest change in orientation of the fullerene will lead to switch of the roles of the carbon atoms from being carrier of the significant positive charge to being a carrier of big negative charge and vise versa. Thus, another approach should be developed.

Since the shortest C-Au distance defines the most important positively charged carbon atoms there should be some weight function which very rapidly changes for small distance differences, though continuous. Using analogy with the continuous representation of delta-function as well as trying to mimic the exponential decay of the electron density with increasing distance to the closest atom we can write down the total "electron density" on given carbon atom $i$ due to neighbor metal atoms as:
\[ \rho_i = \sum_{k \in \text{Au}} e^{-\alpha r_i} S_i(r_{ik}), \]  

(8.1)

where \( \alpha \) is a model parameter and \( S_i(r) \) is a switching function, for better efficiency of calculations (so not to consider all atoms of the surface). The switching function may in principle be chosen to any sufficiently smooth function (up to at least first derivatives). In this work we use a switching function of the following kind:

\[
S(r | R_{on}, R_{off}) = \begin{cases} 
\left( \frac{R_{off} - r}{R_{off} - R_{on}} \right)^3 & 1, r < R_{on} \\
1 + 3 \left( \frac{r - R_{on}}{R_{off} - R_{on}} \right) + 6 \left( \frac{r - R_{on}}{R_{off} - R_{on}} \right)^2 & R_{on} \leq r \leq R_{off} \\
0, r > R_{off} 
\end{cases}
\]  

(8.2)

where \( R_{on} \) and \( R_{off} \) are model parameters.

Now, to describe the positive charge on the carbon atom with the shortest distance to one of the Au atoms it is reasonable to assume some linear relation:

\[ q_i = \beta \rho_i \]

\[ \beta > 0 \]  

(8.3)

However, this would result in all carbon atoms being positively charged. So we need some extra term describing negatively charged carbon atoms. Here the observation is following. The biggest negative charges are observed on the atoms closest to the most important positively charged carbon. So the expression (8.3) should be modified as:

\[ q_i = \beta \rho_i - \gamma \sum_{j=\text{Au}}^{\text{C}} \rho_j S_2(r_{ij}) \]

\[ \beta > 0 \]  

\[ \gamma > 0 \]  

(8.4)

where \( S_2(r) \) is another switching function, of the same functional form, but with different parameters \( R_{on} \) and \( R_{off} \). This switching function is necessary to model the charge back-donation only from the closest carbon atoms.
The equations (8.1) and (8.4) constitute our charge transfer model. It is important to point out the important asymptotic property of the model. Namely, that the charge transfer amount is zero for big enough C\textsubscript{60}-surface separation distances, that is the pure fullerene is neutrally charged, what is not the case for the charge equilibration scheme[278]. The computational efficiency of the model is achieved due to use of the switching function $S_i$ which allows one to consider quite a few metal atoms per each of the bottom carbon atoms of fullerene molecule. The atoms on the top may even not be involved in charge transfer process at all.

The charges on carbon atoms of fullerene calculated via (8.4) are then used in potential of the form:

$$E = E_{vdw} + E_{elec}$$
$$E_{elec} = \sum_{i \in \text{real}} \left( \chi_i q_i + \frac{1}{2} J_i q_i^2 + q_i \sum_{j \in \text{real}} \frac{q_j}{r_{ij}} + q_i \sum_{j \in \text{image}} \frac{\tilde{q}_j}{r_{ij}} \right)$$

(8.5)

$$E_{vdw} = D \left[ \left( \frac{\sigma_{C-Au}}{r} \right)^{12} - 2 \left( \frac{\sigma_{C-Au}}{r} \right)^6 \right]$$

where the quantities $\tilde{q}_i$ and $r_{ij}$ are the image charge of the particle $i$ and the distance between the particle $i$ and the position of the image of the particle $j$ correspondingly.

Most of the parameters of the chemisorption model (8.5) are taken from different literature sources: $\chi_C = 5.343$ eV, $J_C = 10.126$ eV[278], $D_{C-Au} = 0.064$ kcal/mol[138]. However, we optimized the parameter $\sigma_{C-Au}$ to reproduce the amount of charge transfer on both Au(111) and Au(100) surfaces as well as the adsorption energies on corresponding surfaces[264], [265]. We found that reported[279] value of $\sigma_{C-Au} = 2.74$ Angstrom gave good approximation for average surface-molecule interactions energies as well as average charge transfer amounts. It is also close to value of this parameter of 2.9943 used in other similar studies[280–282].

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In order to perform MD simulation with any given potential the corresponding forces should be defined. Conventionally used potentials for description of the charge interactions assume that the charges are fixed and do not depend on the positions of corresponding atoms. However the potential (8.5) is based on position-dependent charges given by equations (8.4) and (8.1). The potential (8.5) is essentially a many-body potential. This makes the calculation of forces not straightforward. We provide the derivation of the forces due to potential (8.5) in Appendix E.

8.2.2. Data generation

As it has been found in our preliminary calculations the significant charge transfer happens in very local regions of fullerene/gold interface. For the practical purposes this means that the size of the gold slab may be decreased without significant decrease of the accuracy of calculated charges. We tried several sizes of the gold slab with the same relative orientation and position (both set arbitrarily) of the fullerene molecule and the gold surface. Calculated charges for most important four carbon atoms are summarized in the table 8.1.

| Table 8.1. Charges on 4 most important atoms calculated with different slab sizes |
|--------------------------------------|-----------------|---------------|
| Atoms                               | 7x7x4 | 7x7x2 | 4x4x2     |
| C(positive)                         | 0.400668 | 0.327544 | 0.314259 |
| C(negative)                         | -0.637847 | -0.670341 | -0.546218 |
|                                    | -0.726158 | -0.619585 | -0.777108 |
|                                    | -0.775201 | -0.781237 | -0.719942 |
| CPU time                            | 3 hours | 1 hour | 1 minute |
Although the system size 4x4x2 seems to be computationally the most efficient among those 3, we decided to slightly increase the lateral dimensions to 5x6 size, so for each translation in [0, 2.035] range both closest atoms and their immediate neighbors have similar environment of gold atoms.

We performed a series of PM6 single point energy calculations for different configurations of the C_{60}/Au(100) and C_{60}/Au(111) systems. Such configurations were obtained by translating fullerene molecule in x, y and z directions (assuming z direction is normal to the surface). For C_{60}/Au(100) system the orientations of the fullerene with respect to the gold were chosen in following way – one where the edge joining 5 and 6 member rings is parallel to the surface plane and the other with the edge joining two 6-memor rings being parallel to the surface. For C_{60}/Au(111) system we considered two other types of C_{60} orientations – one with the 5-member ring and another – with the 6-membered ring parallel to the gold surface. For each orientation we calculated approximately 175 points, different by amount of translation in x, y and z directions. The systems used for calculations as well as the range of their x and y translations are presented on figure 8.2. The number of metal atoms in gold clusters (representing the surfaces) was 30 for Au(100) surface and 88 for Au(111) surface correspondingly.
Figure 8.2. The systems used for calculations (only bottom atoms of $C_{60}$ are shown for clarity) and the range of translations of the atom shown in purple. The systems differ by the orientation of the fullerene bottom with respect to the surface: a) $C_{60}$ oriented by the edge joining 5 and 6 member rings toward Au(100) surface, b) $C_{60}$ oriented by the edge joining two 6 member rings toward Au(100) surface, c) $C_{60}$ oriented by pentagon parallel to Au(111) surface, d) $C_{60}$ oriented by hexagon parallel to Au(111) surface. The purple dummy atoms define the scan directions (coordinate system).

8.2.3. Fitting model parameters

As it was stated earlier in order to use our model the set of parameters $\alpha, \beta, \gamma, R_{on,1}, R_{off,1}, R_{on,2}, R_{off,2}$ should be found, which allows simultaneous calculation of the most important charges for all configurations. We used a steepest descent optimization algorithm to fit the model to calculated charges. However, we fitted only $\alpha, \beta, \gamma$ parameters. The rest of parameters were predefined following the physical nature of the phenomenon.

The quantity $R_{off,1}$ determines the range of C-Au separation distances where the charge transfer is still significant. Moreover, at C-Au distances bigger equilibrium vdw distance the charge transfer effect should be negligible and we should be able to describe interactions with only vdw terms. Since the vdw equilibrium distance was chosen to be 2.74 we set $R_{off,1} = 3.0$. The quantity $R_{on,1}$ was empirically set to 0.0 Angstrom, since this quantity helped to decrease the fitting error.
Another observation and assumption of the model is that the effect of first neighbors in C-C charge flow is dominating. Thus it is unnecessary to choose parameter $R_{\text{off}, z}$ to be significantly bigger than C-C covalent distance. As such, it was set to value of 2.0 Angstrom. Accordingly, the parameter $R_{\text{on}, z}$ was empirically set to 1.5 Angstrom.

The accuracy of fitting was monitored by average squared error quantity:

$$MSE = \frac{1}{N} \sum_{c=1}^{N} \sum_{i=1}^{60} (q_{c,i}^{\text{Model}} - q_{c,i}^{\text{PM6}})^2$$

(8.6)

where, $N$ – is the number of configurations (~700), $q_{c,i}^{\text{Model}}$ and $q_{c,i}^{\text{PM6}}$ - charges on i-th carbon atom of the c-th configurations calculated by model or taken from PM6 calculations correspondingly.

We achieved the value of $MSE = 0.391$ in our fitting procedure, which gives quite reasonable description of the charges. It should be noted that this value of MSE is a worst possible measure for the accuracy, since it also takes into account those charges which does not participate in training procedure, because of the cut-offs used in the model predicting the charges to be zero, while the actual PM6 charges are not. Using only those charges which are actually involved in training process would only decrease the MSE quantity.

The final values of the optimized parameters are: $\alpha = 1.91948847656 \, \text{Å}^{-1}$, $\beta = 10.1435003541$, $\gamma = 7.89007128485$. The approximation of charges on all 60 carbon atoms for some randomly chosen configurations is shown on Fig. 8.3.
As figures 8.3 suggest, the model gives quite reasonable prediction of the charges on the most important 4 carbon atoms. Moreover, in some cases, the minor charges are also predicted. Obviously, the model is too simple to well predict all the charges. In order to do this, one may choose to use several exponents in the formula (8.1), perhaps with some linear scaling coefficients. The formula (8.1) may be interpreted as a single-term representation of the electron density at given spatial point. Using more than one term would mimic MO LCAO method, however without solving the corresponding secular equations.
8.3. Results and Discussion

8.3.1. MD simulation of C\textsubscript{60} on Au(111) and Au(100) surfaces

We performed rigid body MD simulations of a single C\textsubscript{60} molecule on a quasi-infinite gold surface at series of temperatures in range of 100-1000 K. To maintain the temperature constant the Nose-Hoover chain thermostat was used in combination with rigid-body quaternion integration scheme of Kamberaj-Low-Neal[203]. For each temperature 5 trajectories 2.5 ns long were sampled using integration time step 1 fs. Diffusion coefficients were calculated for each temperature using the formula:

\[ \langle dx^2 + dy^2 \rangle = 2Dt \]  \hspace{1cm} (8.7)

The activation energy for diffusion on each surface was then estimated using Arrhenius equation

\[ D(T) = D_0 e^{-E_a/k_BT} \]  \hspace{1cm} (8.8)

The activation energy for diffusion on Au(111) and Au(100) surfaces were found to be 0.30 kcal/mol and 1.49 kcal/mol. This may be interpreted as Au(111) being flatter decreases the activation energies for diffusion. This leads to diffusion coefficients on Au(111) surface be higher than the diffusion coefficients on Au(100) surface (Fig. 8.4).

![Figure 8.4](image)

**Figure 8.4.** a) Diffusion coefficients of C\textsubscript{60} on both Au(111) and Au(100) surfaces; b) comparison with only vdw interactions.
We also calculated the average charge transfer amounts and the surface-molecule interactions energy, which in our case is identical to adsorption energy. The charge transfer amount is bigger in absolute value for Au(111) surface plane (Fig. 8.5, a), while the adsorption energies are similar for both surfaces. This may be explained by higher number density of gold atoms per unit of area.

![Figure 8.5](image)

**Figure 8.5.** Average charge transfer amount (a) and the adsorption energy (b) for $C_{60}$ molecule on Au(111) and Au(100) surfaces.

The average amount of charge transferred per $C_{60}$ molecule varies in range of -0.9 to -0.7 electrons, what is in good agreement with experimental findings[265]. The average surface-molecule interaction energy is little bit higher that experimentally obtained value of ~43 kcal/mol. This is intentionally forced by choosing such vdw sigma parameter. This is necessary because the value of 43 kcal/mol was obtained for desorption energy from the monolayer. It is known that the co-adsorption[158], [161], [162] usually results in weaker interactions between adsorbate and the surface. To account for this effect we choose vdw sigma parameter such that the adsorption energy of a single molecule was bigger than that reported for monolayer.

In order to evaluate the importance of the charge transfer model we performed similar simulations taking into account only vdw interactions between the molecule and the surface. As it was expected the difference in diffusion coefficients was of several orders of magnitude (Fig. 8.4, b). The average surface-molecule interaction
energy was found to be comparable to the thermal energy $k_B T$ for temperatures as low as 100-200 K indicating that only vdw interactions are not enough to describe strong binding of the fullerene molecules on metal surfaces. This also prohibited use of the Arrhenius relation (8.8) for estimation of the activation energies for diffusion, which are apparently very small.

8.3.2. MD simulation of Nanotruck molecule on Au(111) and Au(100) surfaces

We also performed a series of MD simulations of the nanotruck molecule[73] which contains four fullerene groups attached to one common chassis group and functioning as wheels. In order to improve sampling quality we extended temperature range over which simulations were performed to 100-2000 K.

Due to geometric constraints the fullerene groups in nanotruck molecule more closely resemble the monolayer of $C_{60}$ molecules. Therefore we should expect some co-adsorption effects taking place for this system. The average $C_{60}$ – surface interaction energy as well as the charge transfer amount per $C_{60}$ molecule are presented in Fig. 8.6. Average adsorption energies are indeed smaller than for individual fullerene molecules and are comparable to experimental value for monolayer of 43 kcal/mol. The charge transfer amount is also smaller than for single $C_{60}$ molecule, but is still in good comparison with experimental values.

![Figure 8.6](image)

**Figure 8.6.** Average charge transfer amount (a) and the surface-molecule interaction energy (b) for nanotruck molecule per fullerene group calculated for flexible and rigid nanocars on both Au(111) and Au(100) surfaces.
The mobility of the nanotrucks is 1-2 orders of magnitude smaller than that of single fullerene molecules (Fig. 8.7, a). Similarly to C$_{60}$/Au system the diffusion coefficients calculated without charge transfer effects taken into account were several orders of magnitude higher (Fig. 8.7, b).

![Figure 8.7](image.png)

**Figure 8.7.** Diffusion coefficients of the nanotruck (with rotating “wheels”) on both Au(111) and Au(100) surfaces

The estimated activation energies for diffusion of the flexible nanocar molecule on Au(111) and Au(100) surfaces are 4.0 +/- 0.6 and 6.7 +/- 1.0 kcal/mol correspondingly. Without charge transfer effects taken into account the activation energies were 2.1 +/- 0.3 and 2.7 +/- 0.7 kcal/mol correspondingly.

### 8.3.3. Importance of the wheels’ rotations

In order to assess the importance of the wheels’ rotation on the mobility of the nanotruck we performed RB-MD simulation with all C$_{60}$ fragments and the chassis moiety combined into a single rigid body. In other words we impose the artificial constraints, leading to inability of fullerene wheels to rotate. We performed the calculations of this type for both Au(111) and Au(100) surfaces. The comparison with 5-fragment model is presented on Figure 8.8. In both cases the diffusion on Au(111) surface is much faster than that on Au(100).
The diffusion coefficients for the rigid nanocars, where the rotation of the wheels is prohibited and the only way to diffuse is via sliding or jumping is by 1-2 orders of magnitude smaller than that for 5-fragment nanocars with rotating fullerene wheels. Additional examination of the charge transfer amounts in both cases as well as corresponding surface-molecule interaction energies (Fig. 8.6) shows that both these quantities are smaller for the rigid molecule.

The smaller charge transfer amount for the rigid molecules as well as smaller surface-molecule interaction energy suggests faster diffusion of the rigid molecules in contrast to nanocars with flexible wheels, capable to rotate. However this is in contrast to the calculated diffusion coefficients as shown on Fig. 8.8. This indicates that the rotation of the fullerene “wheels” significantly influences the mechanism of diffusion.

The explanation of this finding is following. The surface-molecule interaction energy determines the processes of adsorption-desorption of the ad-molecules as well as the processes involving motion of the molecules in direction normal to the surface, such as jumps. Thus the surface-molecule interaction energy itself does not determine the activation barriers for diffusion and consequently the diffusion coefficients.
According to simple, yet very helpful transition state theory the latter is determined by the minimum energy path connecting the reactant and the product states. The particular sequence of the configurations in coordinate space comprising the minimum energy path is known as reaction mechanism.

It turns out that when one prohibits the internal rotation of the fullerene wheels in the nanocar molecule, the mechanism for diffusion changes drastically (Fig. 8.9). It is important to note here than the charge transfer process is important aspect of the nanocar motion which is tightly related to the mechanism of diffusion.

![Diagram](image)

**Figure 8.9.** To explanation of the effect of the charge transfer on the diffusion mechanism of the nanomachines. Four possible mechanisms are compared: a) rotation with charge redistribution; b) rotation with fixed charges; c) jump with charge redistribution and d) jump with fixed charges. The color scale of the carbons is proportional to their charge. In cases (a) and (b) $z_1 < z_3 < z_2$; in cases (c) and (d) $z_1 < z_3$ and $z_2 < z_4$. 

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Figure 8.9 shows four possible types of behavior of the fullerene “wheel” during the motion of nanocar. For simplicity we focused on only two carbon atoms of the C\textsubscript{60} fragment on its bottom. For each mechanism one may calculate the energy cost associated with the transition between the reactant (left) and the transition (right) states. The initial and final positions and the charges of each carbon atom determine whether the system gains or looses some energy. For the conceptual simplicity we consider only the energy change due to the charge-image interactions and neglect self and intramolecular interactions in formula (8.5). Also the energy change due to vdw interaction will be omitted, since it (almost) does not depend on the charge transfer process. In such assumptions the energy change due to motion of atom \(i\) can be written as:

\[
\Delta E = E_{rs} - E_{react} = \left( -\frac{q^2(z_{rs})}{2z_{rs}} \right) - \left( -\frac{q^2(z_{react})}{2z_{react}} \right) \tag{8.9}
\]

Thus, one needs to spend some energy to bring the charged atom away from the surface. Moreover, such energy gain or loss is bigger if the charge transfer effect is involved in contrast to fixed charge.

It is obvious that the jumping mechanism would result in higher activation energies, because both atoms will be brought away from the surface (Fig. 8.9 c, d) while for rotation mechanism one of the atoms will be moving toward the surface (Fig. 8.9 a, b). This will lower the energy change between the states, which is proportional to the activation energy. The analysis may be extended further and it can be shown that for rotation mechanism the energy barrier will be smaller for position-dependent charges (Fig. 8.9, a) than for fixed charges (Fig. 8.9, b). On the contrary, for the case where the rotation of the fullerene groups is restricted (jumping
mechanism) the energy barriers will be smaller in the case of position-dependent charges as opposed to fixed charges model.

As it follows from comparison of two main mechanisms (rotation and jumps) for motion of the nanocars, the average surface-molecule interaction energy as well as the average amount of charge transfer should be smaller for jump diffusion mechanism. This is directly observed in our MD calculations for the full-rigid molecules, where the rotation of C$_{60}$ "wheels" is forbidden (Fig. 8.6).

Another important consideration is that for correct calculation of the activation energies the states corresponding to crossing of the saddle point with the highest energy connecting reactant and product states should be sampled with high statistical weight. Such transition path determines the true activation barrier for the diffusion. However, if the simulation temperature is low, the highest statistical weight will correspond to saddle points with smallest energies. In chemical language this means that we are focusing on the easiest ("elementary") processes taking place during diffusion, escaping from our sight the true bottleneck of reaction, which determines its activation energy. Thus for correct calculation of the activation energies for diffusion of the nanocar molecule we used only high temperature data. The similar technique was used in our previous studies of the crystalline rotors. The calculated activation energies for completely rigid molecules are much higher as it is expected: 13.1 +/- 2.6 and 20.0 +/- 5.4 kcal/mol for Au(111) and Au(100) surfaces correspondingly. This agrees with the analysis of the diffusion mechanisms shown on Fig. 8.9.

**8.3.4. Electric-field-induced motion of nanocars**

The original experimental approach to nanocar studies involved their manipulation by STM tips. As one way to check the preferred direction of nanocar's
motion the experimentalists pushed the molecule in each of orthogonal directions (by STM tip). However, the STM setup works at some voltage, which creates a significant local electric field around the manipulated objects. Thus the question of how the external electric field interacts with the nanocars is important. Moreover, understanding such type of interactions might be used in future nanocars applications.

In our earlier work (see, for example Chapter 5) we described the surface-molecule interaction with phenomenological models, not considering physical origins of the strong fullerene-metal interactions. It is obvious now that such interaction is partially realized by significant charge transfer from the metal to fullerene. Moreover, since the charge distribution depends on the orientation of the fullerene group with respect to metal surface there is a possibility to control motion of the nanomachines by external electric field. From the previous phenomenological points of view it would be necessary to introduce some polar group in order to create non-vanishing dipole moment of entire molecule. The answer to the question of possibility to drive original (non-polar) version of molecular machine with external electric field would be negative. This is what one would intuitively think if not aware of the charge transfer phenomenon. As a consequence some efforts were applied to synthesize the molecular machines with non-zero dipole moment.

Our current model, however, suggests a possibility to drive the non-polar (original version) nanomachines with external electric field. Such opportunity is possible because of the charge transfer which induces the orientation-dependent dipole moments on fullerene wheels, allowing them to react on external electric field. Moreover, such dipole-field interaction would lead to a unidirectional motion of the nanomachine along the intuitively-obvious direction of motion.
In order to quantitatively characterize the possibility of the fullerenes to react on external electrical field we performed a series of quasi-equilibrium MD simulations of both fullerenes and nanomachines in presence of external filed.

For each temperature in range of 100-1000K we considered several values of the external electric field strengths: 1, 5, 10 and 20 units (where each unit is $4.146 \times 10^8$ V/m). Since the system is non-conservative the total energy ("conserved" quantity H) of the system is no longer an integral of motion, but rather it is linearly increasing with time. The deviation of the H quantity from its initial value is a work performed by external field and may be used for estimation of the driving efficiency. Moreover, since the system is no longer at equilibrium the thermostatting should be understood as a quasi-equilibrium analog of true equilibrium thermostatting. It is possible to reformulate the equations of motion in terms of new set of equations for extended system, which treats the physical time as dependent variable. In such approach the meaning of equilibrium and thermostats becomes conventional and there exists a Hamiltonian which is now conserved quantity (for such approach see Chapter 13).

However, it is still possible to treat the system in the presence of external field in conventional way, although achieved temperature distributions will be different from corresponding equilibrium counterparts. As a re-pay for not being able to achieve correct temperature distributions we have the measure of how much work the external field produced, which is convenient for the purposes of characterization of nanomachines efficiency.

The results of our non-equilibrium MD simulations are presented on Fig. 8.10. The diffusion coefficient of the fullerene molecule increases significantly even for
smallest fields applied (Fig. 8.10, a). So one can expect a monotonous increase of the C$_{60}$ mobility with the increase of the strength of external field applied.

On the contrary, for the nanocar molecule there exists a threshold value of the field strength (Fig. 8.10, b). For fields weaker than that threshold the mobility of the nanocar stays relatively independent on the field strength and is small. Once the field is stronger than the threshold, the nanocar's mobility becomes sensitive to the field applied, similarly to the case of single fullerene molecule and increases by several orders of magnitude.

Figure 8.10. Diffusion coefficients (logarithmic scale) of fullerene (a), flexible nanocar with the field orthogonal to rolling direction (b) and the field parallel to rolling direction (d) and rigid nanocar with the field orthogonal to rolling direction (c) and the field parallel to rolling direction (e) on both Au(111) and Au(100) surfaces.
The existence of the threshold is a consequence of the screening effects of the fullerene wheels which are in close proximity to each other – the effective field acting on each of the fullerenes is smaller than external field, due to additional electrostatic field created by other charged fullerenes. As a consequence, for the nanomachines with more fullerene wheels the threshold values would be much higher that those for nanocars with smaller number of wheels. So the required fields would be much higher, which would probably prohibit the use of such nanocars, although their directionality might be better. If one would continue even further – to a fullerene monolayer – one would realize that it is almost impossible to induce a notable motion of such monolayer by external electric field, what is consistent with experimental data – no such successful experiment were reported so far.

Another interesting effect which was found during our MD simulations is that the diffusion coefficients strongly depend on the direction of the field applied, indicating different mobility mechanisms (Fig. 8.10, b-e). If the external field is applied in direction parallel to the expected direction of motion of the nanocar with its wheels rolling (rolling direction) the diffusion coefficients are several orders of magnitude larger than if the driving field applied in orthogonal directions (Fig. 8.10, b, d). This indicates that the rotation of the fullerene wheels indeed facilitates the directional diffusion of the nanocars. The differences become smaller, however, for very strong fields and very high temperatures. This may be caused by nanocar’s reorientation, such that it aligns its rolling direction with the direction of the external field.

Direct visualization of obtained MD trajectories shows that when the field is parallel to the rolling direction the nanocar moves indeed because of fullerene wheels rotations. On the other hand, when the applied field is perpendicular to the rolling
direction one might observe some kind of crawling with $C_{60}$ being “legs” rather than wheels. The displacements in latter case are considerably smaller than those observed for rolling.

In order to relate the observed effect with the motion of the fullerene groups we also conducted similar calculations but with all four wheels and the chassis considered as a single rigid fragment, thus intentionally prohibiting the motion of $C_{60}$ wheels. Our calculations show that there is no any preferred direction of motion of the nanocar in this case (Fig. 8.10, c, e). This confirms the specific role of the fullerene wheels rolling in fast and directional motion of the nanocars.

The results of our simulations are in good agreement with available experimental findings. Namely, the similar experiment has been performed in which the nanocar was pushed by STM tip along two orthogonal directions. If was found that if it is pushed along the rolling direction with relatively small impulse the directional motions was induced. On the contrary, the molecule remained immobile if it was pushed in orthogonal direction. During the experiment the voltage at STM tip was 0.1 V. If the tip is 1 nm apart from the atom the local electric field at that atom will be $1*10^8$ V/m what is comparable in order of magnitude to those field strengths used in our simulations. Thus one may argue that during the experimental manipulations the charge transfer and electrostatic interactions played significant role, which ultimately resulted in anisotropy of molecular mobility. Moreover, it might be possible to create such conditions at which the non-polar nanocar might be driven by external electric field.
8.4. Conclusions and Summary

In this chapter we described a phenomenological model for simultaneous description of the charge transfer and the chemisorption processes taking place in fullerene-gold systems. The model possess correct asymptotic properties, what is important for correct description of the fullerene desorption from the surface, and what is not the case for the charge-equilibration scheme due to its internal problems. The model was developed using semi-empirical calculations as well as available experimental and theoretical data. The model is expected to be computationally more efficient than straightforward PM6 method, yet give quite reasonable results. This makes it especially suitable for use in MD simulations of the fullerene-containing compounds on the gold surfaces.

Although the present work focused on the gold metal as surface on which fullerene adsorption takes place, the method may be applied for other metals or even non-metallic substrates.

In addition, the model was successfully used for molecular dynamics simulations of both fullerene and nanocar diffusion on the gold surface. Taking the charge transfer into account results in significantly stronger binding of the fullerene and the surface than it would be if only dispersion interactions are included. Moreover, the calculated diffusion coefficients are significantly smaller and consequently closer to experimentally determined values, than those obtained with only vdw interaction.

Finally, we showed how the charge transfer process is involved in rotation of the nanocars' wheels. This provides a better understanding of physics behind the motion of the nanomachines. Such knowledge may be helpful for development and
control of the molecular devices and ultimately for further progress in growing field of nanotechnology.

In summary, our findings presented in this chapter are as follows:

1) our relatively simple charge transfer model is capable to reproduce available experimental and theoretical data on charge transfer and adsorption energies for the fullerene-gold systems;

2) the diffusion coefficients for both nanocar and the fullerene are much higher without charge transfer effects taken into account, corresponding activation energies are smaller: $2.1 \pm 0.3$ and $2.7 \pm 0.7$ kcal/mol for Au(111) and Au(100) surfaces respectively. The charge transfer effects increase these energies to $4.0 \pm 0.6$ and $6.7 \pm 1.0$ for analogous surfaces.

3) within presented charge transfer model the wheels rotations is especially important factor for directionality of nanocar's motion. For the model which prohibits such rotations and allows only slip and jump mechanism of diffusion the activation energy increases significantly: $13.1 \pm 2.6$ and $20.0 \pm 5.4$ kcal/mol for Au(111) and Au(100) surfaces correspondingly;

4) charge transfer in C$_{60}$/Au(surface) system opens an opportunity to drive the non-polar nanomachines by external electric field (which can be produced near the STM tip);

5) wheels rotation and charge transfer on fullerene-gold interface support the directional motion of the field-driven nanocars;

6) there exists a threshold value of the electric field below which the nanocar is not responsive to external fields; for the fields stronger than given threshold there is significant increase of nanocar's mobility in the presence of external field. The existence of the threshold field is explained by screening effects of
the nearby fullerene wheels. Thus for bigger number of wheels one should use much stronger fields for moving the nanocars.
Chapter 9

Effects of the internal structure of nanomachines

9.1. Introduction

In this chapter we switch the gears from the effects of the surface to the effects induced by certain features of the internal structure of the nanomachines. In other words we will now focus on how the internal potential of the nanomachines affects their properties in contrast to effect of the external (surface-molecule) potential. The external potential will be the same for most of the calculations (unless otherwise stated). Thus all observed differences can be attributed to internal molecular features. To be more specific, for most studies presented in this chapter we used the combined effective surface potential (see Chapter 6).

9.2. Effects of molecular flexibility

9.2.1. Method

Our studies are mostly addressed to the understanding of some basic features of the surface motion of big molecules. Particularly we are interested in the role of the wheels motion in the nanocars molecules. Stated in a broader sense this means the revealing the role of the internal structure and the flexibility of the nanocars in determining their properties and mobility.

In this work we studied the following molecules, which are shown on Fig. 9.1: the nanotruck, the carborane-based nanocar with 6 wheels (nanotrain), the Z-car (originally called nanocar), the nanotrimer and the molecule we called nanospider.
The latter has some similarity with the famous “lander” molecule[283], which has been studied experimentally and may be considered as a special case of the nanocars.

For each system we performed rigid body molecular dynamics (RBMD) simulations with different number of degrees of freedom (DOF) in each of them. This strategy has been applied to reveal the role of the different parts of those molecules and to understand their interplay. Further we will refer to this strategy as freezing. Indeed this is a freezing of the molecule’s DOFs. The particular way of freezing of the degrees of freedom will be later referred to as a representation. For the nanotruck molecule we considered up to 7 representations (Table 9.1).

For all other molecules the representations are defined in similar way so we do not present them. Thus for the nanotrimer there are 4 different representations, for the carborane-based nanocar – 8, for the nanospider and z-car – up to 5. These numbers correspond to maximal number of the reasonable rigid fragments which one can
define in each molecule. Actual number of representations may be much bigger because of the possible distinct isomers (see e.g. 3_GROUPS variations in Table 9.1).

In case where there are more than one distinct isomer for given nanocar's representation we considered all possible isomers and averaged the calculated activation energies over them.

<table>
<thead>
<tr>
<th>Representation name</th>
<th>Pictorial form</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1_GROUP</td>
<td><img src="1" alt="Image" /></td>
<td>The entire molecule is considered as one rigid fragment (all wheels therefore are frozen).</td>
</tr>
<tr>
<td>2_GROUPS</td>
<td><img src="2" alt="Image" /></td>
<td>3 wheels and a chassis are frozen as one fragment, 1 remaining wheel is free.</td>
</tr>
<tr>
<td>3_GROUPS</td>
<td><img src="3" alt="Image" /></td>
<td>The chassis and 2 wheels are frozen in T-shaped conformation, the remaining 2 wheel are free.</td>
</tr>
<tr>
<td>3_GROUPS_diag</td>
<td><img src="4" alt="Image" /></td>
<td>The same as 3_GROUPS or 3.Groups_side, but 2 free wheels are on the opposite side to each other and they placed diagonally to each other.</td>
</tr>
<tr>
<td>3_GROUPS_side</td>
<td><img src="5" alt="Image" /></td>
<td>2 wheels and a chassis are considered as one fragment and these wheels are at the same side of the chassis (not T-shaped), 2 other wheels are free.</td>
</tr>
<tr>
<td>4_GROUPS</td>
<td><img src="6" alt="Image" /></td>
<td>1 wheel and a chassis are frozen as one fragment, 3 remaining wheels are free.</td>
</tr>
<tr>
<td>5_GROUPS</td>
<td><img src="7" alt="Image" /></td>
<td>All 4 wheels and a chassis are treated as the separate rigid fragments.</td>
</tr>
</tbody>
</table>

All calculations were performed within the rigid body molecular dynamics paradigm as have been described in previous chapters (Chapter 3 and 4). The DLML
integration scheme along with the Nose-Poincare thermostat have been used to perform the calculations.

For each particular representation we calculated 10 trajectories at each of 4 temperatures (so totally 40 trajectories per representation). All these trajectories were then used to extract data about the diffusion rates (translational as well as rotational) and the activation energies of the corresponding processes. The translational diffusion coefficients were calculated as a coefficient of the linear fitting to the MSD:

\[ MSD(t) = A + Bt, \]
\[ MSD(t) = \frac{1}{4} [ (X(t) - X(0))^2 + (Y(t) - Y(0))^2 ], \]

(9.1) where the slope \( B \) determines the diffusion (in 2D) coefficient. The activation energies for diffusion were then calculated from the Arrhenius law \( D = D_0 \exp\left( \frac{-E_a}{k_B T} \right) \) using the diffusion coefficients calculated at different temperatures.

9.2.2. Results and Discussion

The results of calculations are summarized in Fig. 9.2 which presents the activation energies for surface diffusion for all studied systems as a function of the rigid fragments in corresponding representation (flexibility). The 1-fragment representations are in general very stiff systems, thus the results for such representations are hard to evaluate. Apart from that one may distinguish three cases: a) the activation energy is almost independent on the flexibility (Nanotruck, Z-car); b) the activation energy decreases with the increase of flexibility (Nanotrain, Nanospider); and c) the activation energy increases with the increase of flexibility (Nanotrimer).
The molecules of the first kind (Nanotruck, Z-car) have relatively large wheels, what increases the distance between the chassis and the surface. Such large separation is energetically unfavorable. As a consequence un-freezing the fullerene wheels leads to more stable minima of the resulting systems (representations). As one adds more flexibility, the system finds more stable minima. This is especially important when adding a few first additional degrees of freedom. On Fig. 9.2 this is represented as drastic increase of the activation energy when the number of fragment changes from 1 to 2.

Unfreezing more and more degrees of freedom allows the system to find more energetically favorable minima. However this effect decreases very rapidly for flexible systems. Moreover making the system more flexible also lets it find better transition states (with lower energies). Thus the total effect is negligible, so the activation energy becomes relatively independent on the number of rigid bodies in the nanocar’s representation.
After a certain number of DOFs in the system, addition of new DOFs improves the transition states much more than it improves the minima. As a result we observe the activation energies decreasing as the functions of number of fragments. This is the case for the nanocars of the second kind. This type of molecules may be characterized by many possible DOFs (many wheels) of smaller size (Nanotrain, Nanospider).

Since wheels are of small size the chassis is already on almost optimal distance from the surface. Thus the flexibility does not contribute much to such conformational changes which bring the chassis closer to the surface. Presence of many wheels in the molecule means that the optimal transition state corresponds to a particular orientation of such wheels. For frozen conformations such transition states are inaccessible. Adding new DOFs opens the opportunity to find such transition states. As a result the activation energy decreases with the increase of the number of fragments.

Finally, the most controversial result is one obtained for the nanotrimer system. In that case, the activation energy increases as the system’s flexibility increases. One factor contributing to such behavior has been described, namely the possibility to find better minima. The other factor comes from the system’s structure. The rotation of the wheels leads to the pivoting motion of the entire system and will decrease its mobility. This was not the case for all other systems, because of their symmetry. Thus for the nanotrimer the observed increase of the activation energy for translation may also be explained by effective (dynamic) hindrance of the wheels each other.
9.3. Intramolecular steric and electrostatic interactions

9.3.1. Method

Additional calculations for nanotruck system have been performed. In these studies we considered a nanotruck molecule with “artificially” modified potential. Namely, we placed some big charge (-1.0; 0.0; +1.0) on each of four nitrogen atoms in its chassis, which are the part of the original nanotruck structure. Since interactions between the atoms of the same fragment are not considered, the most important interaction target for those charges is a nearest hydrogen atom (the only hydrogen on fullerene wheel). The hydrogen atom is typically positively charged (around + 0.2). Thus, depending on the sign of the nitrogen atoms we may have either attractive (nitrogens are negative) or repulsive (nitrogens are positive) interactions. In addition to variation of the charges on the nitrogen atoms we also varied the potential by turning off all electrostatic and vdw interactions.

Another set of trial molecules was designed to reveal the role of wheel-wheel interactions, which might be important for the nanocar diffusion. The interactions between pairs of front and rear wheels have been varied by increasing the length of the chassis moiety. We have considered the chassis composed from 3 to 10 conjugated benzene rings (Fig. 9.3).
9.3.2. Results and Discussion

The results obtained with the intramolecular potential modified by adding charge on the nitrogen atoms (as described in previous section) are summarized in Table 9.2. The activation energies for diffusion are the same (within the error bar) for positively and negatively charged nitrogen atoms. They are both bigger than the neutral case. This may be explained on the basis of simple electrostatic energy considerations.

<table>
<thead>
<tr>
<th>Charge on nitrogen</th>
<th>Ea, kcal/mol</th>
<th>error, kcal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>negative</td>
<td>2.04</td>
<td>0.15</td>
</tr>
<tr>
<td>neutral</td>
<td>1.70</td>
<td>0.12</td>
</tr>
<tr>
<td>positive</td>
<td>1.91</td>
<td>0.20</td>
</tr>
<tr>
<td>no electrostatic at all</td>
<td>1.11</td>
<td>0.05</td>
</tr>
<tr>
<td>no electrostatic, no vdw</td>
<td>0.74</td>
<td>0.07</td>
</tr>
</tbody>
</table>

In the case of negatively charged nitrogens the energy minimum are greatly effected, which correspond to the closest separation between the wheel’s hydrogen
atoms (positively charged) and the chassis nitrogen atoms (negatively charged). As a result the activation energy increases with respect to the neutral case.

For the positively charged nitrogen the picture is similar, except than the transition states are now modified. The transition state also corresponds to the configuration where all hydrogen atoms are oriented toward the nitrogens. Because the nitrogens carry the positive charge the interactions are repulsive. This increases the energy of the transition state and therefore the activation energy of the entire process.

The further modification of the intramolecular potential may be achieved by turning off all electrostatic interactions or turning off both electrostatic and vdw interactions between fragments. The corresponding results are presented in Table 9.2. In both these cases we decrease the effective friction between the chassis and the wheels of the nanocars. As a result the activation energy decreases.

Our studies of the nanotrucks with different steric interactions between wheels as controlled by the length of the chassis indicate that this factor is also important for diffusion of such molecules. The calculations indicate that the activation energy decreases with and the increase of the chassis length/size (Fig. 9.4).

![Figure 9.4](image)

**Figure 9.4.** Activation energy for diffusion of the nanotruck as a function of its length.
This may simply be explained by vdw (steric interactions) between the front and rear pairs of the wheels. If they are close to each other, this causes higher hindrance to their rotation, similar to what one have for the nanocar representations with small number of DOFs. As the chassis gets bigger the repulsion between the wheels vanishes. This leads to higher flexibility of the molecule and hence to smaller activation energies for diffusion. Note, however, that this dependence has a maximum as well (Fig. 9.4). This is because for intermediate fullerene-fullerene separation distances there is an increased attractive interaction, leading to better minimum. This is similar to nanotruck with negatively charged nitrogens.

We can conclude that the modeled electrostatic and vdw (steric) interactions work as brakes on the nanocar's wheels, increasing the barrier for rotation and decreasing the mobility of the molecule. This also means that the intramolecular potential is also important for nanocar mobility, similar to the external potential due to the surface. Moreover we have showed the particular ways to control the mobility of the nanocars. Although in reality it is impossible to switch on and off any of the interactions, these results provide the ideas how the potential should be modified synthetically (by adding functional groups) in order to achieve desired properties.

9.4. Correlation of rotations of the nanocar wheels

9.4.1. Method

As it has been shown in our previous studies (described in previous sections and chapters), the rotation of wheels is a dominating factor in the mobility and directionality of nanocars. However it was unclear if the rotations of the wheels were correlated. This has important implication on the mechanism of diffusion and determination of the directionality of such motion. Thus to understand the mechanism
of the motion of these molecules it is important to estimate correlations in the wheel rotations.

To study the correlation of wheels’ rotations we compared the motion of the z-car (Fig. 9.5, a) molecule with dynamics of a system consisting of only four fullerene wheels (Fig. 9.5, b).

![Figure 9.5. Model of the z-car with 4 fullerene wheels chemically bound to a chassis.](image)

The original z-car molecule has several tail fragments that increase its solubility in organic solvents and make the molecule more rigid. In our computations we used a smaller molecule without tails in order to have more comprehensive description of the system dynamics. In further discussions, we call this simplified version a z-car molecule.

The molecules move along the gold surface that is viewed as an ideal two-dimensional fcc(100)-lattice plane with the lattice parameters equal to 4.07 Å. Our main assumption here is that the metal lattice is rigid and interactions with z-car do not change the underlying lattice geometry of the surface. Effectively it corresponds to taking into account only the upper surface atoms layer although an effect of bottom levels has been analyzed as well.
The structure of the z-car molecule suggests that it is reasonable to divide it into five rigid segments: four corresponding to the wheels and one to the chassis. Since we are interested in correlations and interactions between different parts of the z-car molecule, for comparison we also analyzed the molecular dynamics of a separate system consisting of only four fullerene wheels moving on the same surfaces. Schematic picture of considered particles and their geometries are presented in Fig. 9.5, b.

The interaction parameters for the present simulations have been taken from the CHARMM27[125], [126] force field augmented with those from the UFF[138] parameter set. In our calculations on the gold surface we explicitly considered non-covalent interactions with 625 closest surface gold atoms. The MD simulations have been performed with the help of Nosé-Poincaré thermostat at T=300K. The length of each trajectory was 20 ns with time step of 1 fs. All obtained dynamic properties have been averaged over 48 trajectories.

9.4.2. Results and Discussion

Our MD simulations indicate that if we position four fullerene wheels like in the z-car molecule, then after some time they come together and stay as one dynamic cluster with a distance between neighboring fullerenes of order of 1 nm. This is due to van der Waals interactions between the particles. For z-car these interactions between wheels are very weak and fullerenes do not affect directly each other. Any possible correlations are the result of the effective interactions with the whole system.

To quantify rotational correlations we introduce several functions that we might call correlation functions. Specific values for these functions, as described below, will provide a relative measure of correlations. First, we define a function $C$, \[ 177 \]
where \((\mathbf{w}_i, \mathbf{w}_j)\) is a scalar product of two angular velocity vectors for the wheels \(i\) and \(j\). The physical meaning of this function is the following. If the absolute values and directions of all angular velocities are the same, i.e., the case of very strong correlations, the value of this function is equal to one. If the motion of wheel is uncorrelated the value of the function \(C\) should be between zero and \(-1/3\). The last value, for example, can be obtained in the case when the absolute values of all angular velocities are the same, and two vectors are in the upper direction while two other vectors are in the opposite direction.

The function \(C\) provides a measure of both correlations in the direction and in the absolute values of rotational speeds of the wheels. We also introduce two other functions, \(C_{dir}\) and \(C_{abs}\), that are more specific indicators of the corresponding correlations,

\[
C_{dir} = \frac{1}{4} \sum_{i=1}^{4} (\mathbf{n}_i \cdot \mathbf{n}_{av}),
\]

(9.3)

with

\[
\mathbf{n}_i = \frac{\mathbf{w}_i}{|\mathbf{w}_i|}, \quad \mathbf{n}_{av} = \frac{\sum_{i=1}^{4} \mathbf{n}_i}{\sum_{i=1}^{4} |\mathbf{n}_i|}.
\]

(9.4)

The possible numerical values for this function range from zero (no correlations) to one (very strong correlations). The correlations in the absolute values of angular velocities can be measured with the help of another function,
\[ C_{abs} = \sqrt{\frac{\sum_{i=1}^{4} (|w_i| - \bar{|w|})^2}{|w|}}, \quad \bar{|w|} = \frac{1}{4} \sum_{i=1}^{4} |w_i|. \] (9.5)

Figure 9.6. Typical temporal dependences of the correlation function \( C \) (equation 9.2) for the 4xC\(_{60}\) system (left) and for the z-car (right).

Figure 9.7. Typical temporal dependences of the correlation function \( C_{dir} \) (Eq. 9.3) for the 4xC\(_{60}\) system (left) and for the z-car (right).

Figure 9.8. Typical temporal dependences of the correlation function \( C_{abs} \) (Eq. 9.5) for the 4xC\(_{60}\) system (left) and for the z-car (right).
Typical temporal dependencies of the correlation functions are presented in Figs. 9.6 – 9.8 and the averaged distributions of values are given in Tables 9.3 and 9.4. All functions start from zero since at \( t=0 \) it is assumed that there are no correlations. It is interesting to note that correlations in the wheels of \( z \)-car molecule are similar to four separate fullerene wheels. Our results indicate that correlations in the motion of wheels of the nanocars are small but not negligible. This is the result of complex interactions between different fragments of the molecule and interactions with the surface.

**Table 9.3.** Distribution \( C \) (Eq. 9.2) for the systems \( 4xC_{60} \) and \( z \)-car

<table>
<thead>
<tr>
<th>System</th>
<th>0 ≤ ( C &lt; 1/4 )</th>
<th>1/4 ≤ ( C &lt; 1/2 )</th>
<th>1/2 ≤ ( C &lt; 3/4 )</th>
<th>3/4 ≤ ( C &lt; 1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 4xC_{60} )</td>
<td>0.121</td>
<td>0.452</td>
<td>0.356</td>
<td>0.071</td>
</tr>
<tr>
<td>( z )-car</td>
<td>0.121</td>
<td>0.468</td>
<td>0.344</td>
<td>0.067</td>
</tr>
</tbody>
</table>

**Table 9.4.** Distributions \( C_{\text{dir}} \) (Eq. 9.3) and \( C_{\text{abs}} \) (Eq. 9.5) for the systems \( 4xC_{60} \) and \( z \)-car

<table>
<thead>
<tr>
<th>System</th>
<th>( C_{\text{dir}} )</th>
<th>( \Delta C_{\text{dir}}/C_{\text{dir}}, % )</th>
<th>( C_{\text{abs}} )</th>
<th>( \Delta C_{\text{dir}}/C_{\text{abs}}, % )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 4xC_{60} )</td>
<td>0.469</td>
<td>0.4</td>
<td>0.679</td>
<td>0.4</td>
</tr>
<tr>
<td>( z )-car</td>
<td>0.465</td>
<td>0.4</td>
<td>0.686</td>
<td>0.4</td>
</tr>
</tbody>
</table>

**9.5. Conclusions and Summary**

In this chapter we described out studies of the internal structure of nanocars and their flexibility. We used one of our surface-molecule interaction models for all simulations and focused on intramolecular interactions. With the help of rigid-body molecular dynamics method one can study effects of various internal degrees of freedom by constraining them via rigid bodies. This proved to be a useful and
convenient tool to obtain detailed information on the role of all interactions taking place for given molecular system.

In summary, our findings presented in this chapter are as follows:

1) there are at least three classes of molecular machines:
   a) For the molecules of the first class increase of the number of DOFs does not affect activation energies for diffusion. Such molecules have relatively big wheels, increasing the distance between the nanocar's chassis and the surface. The wheels are oriented in the intuitive way, consistent with directed motion. This phenomenon is related to the possibility of finding better minima by nanocar-surface system.
   b) For the molecules of the second type the increased flexibility usually lowers the activation barriers. Such molecules usually have relatively small wheels, comparable with the equilibrium distance between chassis and the metal surface. This phenomenon is related to the possibility of finding better transition states.
   c) Finally, for the molecules of the third kind the activation energies increase with increased number of degrees of freedom. This happens for the nanotrimer molecule, where the orientation of wheels is predetermined in a way which prohibits the surface rolling.

2) we have showed how the intramolecular friction between wheels and the chassis may be modified, by turning on and off electrostatic and vdw interactions, leading to different activation energies and diffusion coefficients;
3) the friction between rear and front pairs of wheels is also important. By increasing their separation it is possible to lower the activation energies and increase the mobility of the nanocars (at least up to some extent)

4) we also found that the rotation of the nanocar's wheels is correlated, although not strongly. Still such correlations are not negligible.
Chapter 10

Diffusion of nanocars: approaching experimental time scales

10.1. Introduction

The most results of this work focused mostly on the qualitative characterization of the nanomachines' motion. For this purpose the effective surface potentials, discussed earlier (see Chapters 5-7), provide an efficient and qualitatively correct way to perform such calculations. However, the use of the relatively weak vdw-type interactions between the surface and the nanocar molecule resulted in overestimation of the diffusion coefficients as opposed to the experimental findings. Such discrepancy may be of several orders of magnitude.

The primary reason for such big difference between the theoretical and experimental results is in the parameters of the surface potentials used. We intentionally restricted ourselves to the vdw-type interactions, because this is the only way to see any notable motion of the nanomachines on the time scales used in simulations. In reality, however, the surface-molecule interactions are much stronger, what results in much slower diffusion. However, if the realistic parameters for such interactions are used, one will hardly see any translations, what would make diffusion coefficients calculations practically impossible.

In this chapter we will discuss the approach to estimate the diffusion coefficients which one would obtain with realistic parameters using the coefficients obtained with some model parameters. This approach would be an extrapolation
alternative to existing methods for closing gap between the experimental and theoretical time scales, such as TAD[284–288] and hyperdynamics[288], [289] methods.

10.2. Theory

The simplest case is a diffusion of a single rigid body. In this case the intramolecular interactions are not considered, so they do not affect the results we are going to obtain. Thus in most of the cases the rest of interactions are the surface-molecule pairwise interactions $U(\{\sigma\}, \{e\})$. Here the letters in the curly braces represent the sets of parameters for pairwise interactions in our system. Most common form of such potential is a Lennard-Jones potential $U(\{\sigma\}, \{e\}) = \sum_{i \in \text{pairs}} 4\varepsilon \left( \left( \frac{\sigma_i}{r} \right)^{12} - \left( \frac{\sigma_i}{r} \right)^6 \right)$.

Suppose we know true parameters describing the system, that is we have a true potential $U_{\text{true}}(\{\sigma_{\text{true}}\}, \{e_{\text{true}}\})$. We can perform MD simulations of the surface diffusion of our rigid molecule with such a potential. The diffusion coefficients will be given by $D_{\text{true}}(T) = D_0 \exp \left( - \frac{E_{a,\text{true}}}{k_B T} \right)$, where the quantity $E_{a,\text{true}}$ is a true activation energy for diffusion.

However, if the surface-molecule interactions are too strong, the time required for observation of small admolecule displacements may be too big. In this situation neither diffusion coefficient nor the activation energies for diffusion may be calculated from direct MD simulations. In order to extend the time scale of the MD simulations various methods of boosting have been invented. Among them are the temperature-accelerated dynamics (TAD)[284–286] and the hyperdynamics methods[287], [289].
In the TAD method one performs a MD simulation at temperatures, which are much higher than the temperature of real process under consideration. However, during such simulation not all the possible barrier-crossing events are realized (accepted). Instead, only those transitions which would have occurred at lower temperature at equivalent time are accepted. This method requires knowledge of the activation barriers for all possible transitions during so-called constrained dynamics step.

On the contrary in the hyper-dynamics method the simulations are performed at the temperature of interest, but in modified potential. This means it does not require the knowledge of barriers for all possible transitions from a given basin. However it introduces the correction to the potential, which is aimed to modify such barriers. Often such potential surface correction is hard to guess, especially for complex systems. One should have some ideas about where those barriers are or how to invent such a potential modification correction. Such potential energy surface corrections have been studied in several works [289–293]. However, they are usually suitable for specific systems, where some symmetries and structural features are known.

Here we combine ideas from both TAD and hyperdynamics approaches and apply it to surface diffusion phenomenon. In fact we do not need knowledge of the microscopic details of the potential energy surface. Instead we use the macroscopic considerations to solve our task.

Returning back to our potential we may see that in order to be able to see some displacements of the ad-molecule on a typical MD simulation timescale we might change the potential in a certain way. Namely, if we keep the structural parameters \(\{r\}\) the same, but will scale all \(\{e\}\) by the same constant value \(\alpha\) the positions of the barriers (minima, maxima as well) will not change, thus the topology of the PES will
be the same as for non-modified potential. However, the heights of all barriers will change, allowing for faster system evolution (for $\alpha < 1$).

Using such modified potential $U_{\text{mod}}(\{\sigma_{\text{mod}}\}, \{\epsilon_{\text{mod}}\}) = U_{\text{true}}(\{\sigma_{\text{true}}\}, \{\alpha \epsilon_{\text{true}}\})$
or simply $U_{\text{mod}} = \alpha U_{\text{true}}$ will result in a new diffusion coefficients $D_{\text{mod}}(T) = D_0 \exp\left(-\frac{E_{a,\text{mod}}}{k_BT}\right)$ as well as new activation energies $E_{a,\text{mod}} = \alpha E_{a,\text{true}}$. The pre-exponential factors will not change because the topology of the PES remains unchanged.

In order to relate the diffusion coefficients obtained from the MD simulations using modified potential with the results obtained using true potential we should consider how the ratio of escape rates in different directions changes. Let say our system is in a state A with the energy $\epsilon_A$. It may escape to either state B or state C with energies $\epsilon_B$ and $\epsilon_C$ correspondingly. The energies of corresponding transition states are $\epsilon_B^*$ and $\epsilon_C^*$ respectively. The activation barriers for escapes in each direction are thus $\epsilon_{A\rightarrow B} = \epsilon_B^* - \epsilon_A$ for A to B transition and $\epsilon_{A\rightarrow C} = \epsilon_C^* - \epsilon_A$ for A to C transition. For original (non-scaled) potential the ratio of escape rates in different directions will be:

$$K_{\text{true}}(T) = \frac{k_{A\rightarrow B}}{k_{A\rightarrow C}} = \frac{\exp\left(-\frac{\epsilon_{A\rightarrow B}}{k_BT}\right)}{\exp\left(-\frac{\epsilon_{A\rightarrow C}}{k_BT}\right)} = \exp\left(-\frac{\Delta \epsilon}{k_BT}\right)$$

$$\Delta \epsilon = \epsilon_{A\rightarrow B} - \epsilon_{A\rightarrow C} = \epsilon_B^* - \epsilon_C^*$$  \hspace{1cm} (10.1)

If we scale the potential this equilibrium constant will change:

$$K_{\text{mod}}(T) = \frac{k_{A\rightarrow B}}{k_{A\rightarrow C}} = \frac{\exp\left(-\frac{\alpha \epsilon_{A\rightarrow B}}{k_BT}\right)}{\exp\left(-\frac{\alpha \epsilon_{A\rightarrow C}}{k_BT}\right)} = \exp\left(-\frac{\alpha \Delta \epsilon}{k_BT}\right) = (K_{\text{true}}(T))^\alpha$$  \hspace{1cm} (10.2)
In hyperdynamics (HD) method this ratio does not change because the potential is modified by the same amount for each transition state:

\[
K_{HD} = \frac{k_{A \rightarrow B}}{k_{A \rightarrow C}} = \frac{\exp \left( -\frac{\varepsilon_{A \rightarrow B} + d\varepsilon}{k_B T} \right)}{\exp \left( -\frac{\varepsilon_{A \rightarrow C} + d\varepsilon}{k_B T} \right)} = \exp \left( -\frac{\Delta \varepsilon}{k_B T} \right) = K_{true}
\]

(10.3)

Thus if we scale the potential energy surface we must scale the temperature in order to maintain the same ratio of escape rates in different directions:

\[
K_{modif}(\alpha T) = \frac{k_{A \rightarrow B}}{k_{A \rightarrow C}} = \frac{\exp \left( -\frac{\alpha \varepsilon_{A \rightarrow B}}{k_B \alpha T} \right)}{\exp \left( -\frac{\alpha \varepsilon_{A \rightarrow C}}{k_B \alpha T} \right)} = \exp \left( -\frac{\alpha \Delta \varepsilon}{k_B \alpha T} \right) = K_{true}(T)
\]

(10.4)

This brings a basic conclusion of this method:

**The dynamics with the scaled potential** \( U_{modif} = \alpha U_{true} \) **at temperature** \( \alpha T \) **is equivalent to the dynamics with the original potential** \( U_{true} \) **at correspondingly scaled temperature** \( T \).

This may also be obtained from simple mathematics:

\[
D_{modif}(\alpha T) = D_0 \exp \left( -\frac{E_{a,modif}}{k_B \alpha T} \right) = D_0 \exp \left( -\frac{\alpha E_{a,true}}{k_B \alpha T} \right) = D_0 \exp \left( -\frac{E_{a,true}}{k_B T} \right) = D_{true}(T),
\]

(10.5)

This may be thought in inverse way:

**The dynamics with the scaled potential** \( U_{modif} = \alpha U_{true} \) **at temperature** \( T \) **is equivalent to the dynamics with the original potential** \( U_{true} \) **at correspondingly scaled temperature** \( T / \alpha \).
Once we know the true dynamics at scaled temperature \( T / \alpha \) we may use Arrhenius law to calculate true dynamics at original temperature \( T \):

\[
D_{\text{true}}(T) = D_{\text{true}}(T / \alpha) = D_0 \exp \left( -\frac{E_{a,\text{true}}}{k_B T} \right)
\]

and hence

\[
D_{\text{true}}(T) = \exp \left( \frac{E_{a,\text{modif}}}{k_B T} (1 - \alpha) \right) D_{\text{modif}}(T)
\]

Since the diffusion coefficient is defined as \( \langle R^2 \rangle(t) = dDt \), where \( d \) is a dimensionality of the problem, we may think of the same spatial configuration as being sampled at different times. This is analogous to the one of the ideas behind the standard hyperdynamics method. So, using the modified potential is equivalent to changing the speed of the time flow in MD.

This means that the time \( t_{\text{modif}} \) of the MD trajectory obtained with modified potential \( U_{\text{modif}} \) is equivalent to the time \( t_{\text{real}} \) of the MD trajectory obtained with true potential \( U_{\text{true}} \). The relation is given by:

\[
\frac{t_{\text{real}}}{t_{\text{modif}}} = \frac{D_{\text{modif}}}{D_{\text{true}}} = \exp \left( \frac{E_{a,\text{modif}}}{\alpha k_B T} (1 - \alpha) \right)
\]

### 10.3. Application to nanocars

From the existing literature for C-Au interactions we have: \( \sigma = 2.9943 \text{ Å}, \epsilon = 0.01273 \text{ eV}[281], \sigma = 2.74 \text{ Å}, \epsilon = 0.022 \text{ eV}[279] \). In most of our MD simulations of fullerene, nanocar on gold surfaces we used UFF potential with parameters \( x_{\text{min}} = \).
3.561, \( D = 0.06399 \text{ kcal/mol} \), what corresponds to \( \sigma = 3.1724 \text{ Å} \), \( \varepsilon = 0.0027746064 \text{ eV} \).

Now let us extrapolate the values of the activation energy and the diffusion coefficients obtained with UFF onto those which we would obtain using the true potentials (Table 10.1):

<table>
<thead>
<tr>
<th>Variable</th>
<th>UFF</th>
<th>Luedtke-Landman[281]</th>
<th>Lewis at al.[279]</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \varepsilon )</td>
<td>0.0027746064</td>
<td>0.01273</td>
<td>0.022</td>
</tr>
<tr>
<td>alpha</td>
<td></td>
<td>0.218</td>
<td>0.126</td>
</tr>
<tr>
<td>( E_{\text{model}, \text{kJ/mol}} )</td>
<td>5.593</td>
<td>25.66</td>
<td>44.39</td>
</tr>
<tr>
<td>( T, K )</td>
<td>200</td>
<td>200</td>
<td>200</td>
</tr>
<tr>
<td>(1-(\alpha))( E_{\text{true}, \text{kJ/mol}} )/( k_{\text{B}} T )</td>
<td>12.068</td>
<td>23.33</td>
<td></td>
</tr>
<tr>
<td>( D_{\text{model}(200), \text{m}^2/\text{s}} )</td>
<td>( 2.08 \times 10^{-9} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( D_{\text{true}(200), \text{m}^2/\text{s}} )</td>
<td>( 1.19 \times 10^{-14} )</td>
<td>( 1.53 \times 10^{-19} )</td>
<td></td>
</tr>
<tr>
<td>Experimental (estimate from above)</td>
<td>( \frac{1}{4} \times 5^{1/10} \text{nm}^2/\text{min} \sim 1 \times 10^{-18} \text{m}^2/\text{s} )</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

As we can see, the extrapolation to parameters from Lewis at al.[279] gives much better agreement with experiment than those obtained from extrapolation onto parameters from Luedtke-Landman[281] or those obtained using only UFF potential, which may be considered as a scaled true potential.

One should be careful doing such kind of extrapolation for molecular models consisting of several fragments. In this case the inter-fragmental interactions should also be scaled by the same factor as the surface-molecule interactions. Thus for the purposes of study of the dynamics of surface-moving molecules one may employ quite arbitrary potential, provided it is linearly related to the real potential describing the system.
Another important issue of using this method is the range of its applicability. Since the entire method is valid until the transition state theory remains valid. This means the scaling factor can not approach zero, flattening the PES, and effectively switching the motion regime to ballistic/free.

10.4. Conclusions and Summary

In this chapter we discussed a possible way to interpret the simulation data, which obtained with model potentials. We argue that if one knows the dynamics obtained with the model potential, then the dynamics which one would obtain with true potential may be predicted in a straightforward way. This helped us to find better agreement between observed slow motion of the nanocars on metal surfaces and our predictions based on simple vdw-type force fields. The method may be extended to provide an approach to accelerated molecular dynamics.

In summary, our findings presented in this chapter are as follows:

1) The dynamics with the scaled potential $U_{\text{mod}} = \alpha U_{\text{true}}$ at temperature $\alpha T$ is equivalent to the dynamics with the original potential $U_{\text{true}}$ at correspondingly scaled temperature $T$;

2) using the modified potential is equivalent to changing the speed of the time flow in MD;

3) extrapolated diffusion coefficients for the nanocars on gold surface are in very good agreement with experimental data