МИНИСТЕРСТВО ОБРАЗОВАНИЯ И НАУКИ РЕСПУБЛИКИ
КАЗАХСТАН

Казахский национальный технический университет имени К.И. Сатпаева

Институт промышленной инженерии им. А. Буркитбаева

Кафедра инженерной физики

Имаш Ә.А

Метод молекулярной динамики для системы взаимодействующих частиц
The molecular dynamics method for a system of interacting particles
(на английском языке)

ДИПЛОМНАЯ РАБОТА

специальность 5В072300 - Техническая физика

Алматы 2019

МИНИСТЕРСТВО ОБРАЗОВАНИЯ И НАУКИ РЕСПУБЛИКИ КАЗАХСТАН

Казахский национальный технический университет имени К.И. Сатпаева

Институт промышленной инженерии им. А. Буркитбаева

Кафедра инженерной физики

ДОПУЩЕН К ЗАЩИТЕ
Заведующий кафедрой
«Инженерной физики»
доктор PhD
_________Р.Е. Бейсенов,
«14» _мая_______ 2019 г.

ДИПЛОМНАЯ РАБОТА

На тему: «Метод молекулярной динамики для системы взаимодействующих частиц»
The topic: "The molecular dynamics method for a system of interacting particles"
(на английском языке)

по специальности 5В072300 – Техническая физика

Выполнил Имаш Ә.А

Рецензент
Доцент кафедры Физики твердого тела
и нелинейной физики, доктор PhD ,
________ М.К.Ибраимов

«14» _мая_______ 2019 г.

Научный руководитель
Доктор технических наук,
профессор,
_________А.Т. Мустафин

«14» _мая_______ 2019 г.

Алматы 2019

МИНИСТЕРСТВО ОБРАЗОВАНИЯ И НАУКИ РЕСПУБЛИКИ КАЗАХСТАН

Казахский национальный технический университет имени К.И. Сатпаева

Институт промышленной инженерии им. А. Буркитбаева

Кафедра инженерной физики

5В072300 – Техническая физика

УТВЕРЖДАЮ
Заведующий кафедрой
«Инженерной физики»
доктор PhD
_________Р.Е. Бейсенов,
«14» мая 2019 г.

ЗАДАНИЕ
на выполнение дипломной работы

Обучающемуся *Имаш Әйгерім Абайқызы*

Тема: *Метод молекулярной динамики для системы взаимодействующих частиц. (The molecular dynamics method for a system of interacting particles).*

Утверждена приказом ректора университета № 1252 - б. –П. от. «06» 11. 2018 г.

Срок сдачи законченной работы «15» 05. 2019 г.

Исходные данные к дипломной работе: *Построить компьютерную модель двумерного газа неполярных молекул, парное взаимодействие между которыми задаётся потенциалом Леннард-Джонса. Сформулировать модель в рамках метода молекулярной динамики, предусматривающего прямое численное решение микроскопических уравнений движения взаимодействующих частиц.*

Краткое содержание дипломной работы:
а) статистическая термодинамика;
б) молекулярная динамика;
в) силовые поля. Ковалентные взаимодействия. Растяжение валентных связей. Деформация валентных углов. Нековалентные взаимодействия. Взаимодействия Ван-дер-Ваальса. Потенциал Леннард-Джонса;
г) главные уравнения. Интегрирование уравнений движения. Алгоритм Верле;
д) математическая модель статистической системы.

Перечень графического материала:
1 Figure 3.2 Initial configuration of the statistical system
2 Figure 3.6 Dependence of the number of particles in the left half of the box on time (Nleft = Nleft (t))
3 Figure 3.7 Dependence of the kinetic energy per particle on time (Ek = Ek (t))

ГРАФИК
подготовки дипломной работы

Наименование разделов, перечень разрабатываемых вопросов	Сроки представления научному руководителю и консультантам	Примечание
Постановка задачи	19.11.2018г. 14.01.2019г.	
Обзор литературы, выбор метода исследования	18.01 - 25.02. 2019г.	
Изучение и освоение метода исследования	28.02 - 04.03.2019г.	
Построение моделей статистических систем и получение численного расчета	04.03 - 27.03.2019г.	
Результаты исследования и их обсуждение	15.04 - 30.04.2019г.	

Подписи
консультантов и нормоконтролера на законченную дипломную работу с указанием относящихся к ним разделов работы

Наименование разделов	Консультанты И.О.Ф. (уч.степень, звание)	Дата подписания	Подпись
Обзор литературы, выбор метода исследования	А.Т. Мустафин, д.т.н, профессор	14.05	
Построение моделей статистических систем и получение численного расчета	А.Т. Мустафин, д.т.н, профессор	14.05	
Результаты исследования и их обсуждение	А.Т. Мустафин, д.т.н, профессор	14.05	
Нормоконтролер	Ассистент Б.Д. Сарсембаева	14.05	

Научный руководитель ____________ А.Т. Мустафин

Задание приняла к исполнению обучающийся ____________ Ә.А. Имаш

Дата "14" мая 2019г.

Министерство образования и науки Республики Казахстан
Казахский национальный исследовательский технический университет имени К.И. Сатпаева
Институт промышленной инженерии имени А. Буркитбаева
Кафедра инженерной физики

ОТЗЫВ

научного руководителя Мустафина А.Т. о научно-исследовательской работе студентки Имаш А.А.

Имаш Айгерим Абайкызы (Имаш Әйгерім Абайқызы) обучалась на программе бакалавриата кафедры инженерной физики по специальности 5В072300 – «Техническая физика» и выполняла дипломную работу “The molecular dynamics method for a system of interacting particles” («Метод молекулярной динамики для системы взаимодействующих частиц») на английском языке под моим руководством.

За время подготовки дипломного проекта в период с осени 2018 г. по весну 2019 г. А. Имаш проявила самостоятельность, организованность, творческий подход к выполнению научных исследований. Благодаря целеустремленности в научном поиске, в сочетании с хорошими способностями к анализу и обобщению материала, студентка-дипломница сумела достичь поставленной цели при написании выпускной работы.

Тема дипломной работы А. Имаш относится к области вычислительной статистической физики. Метод классической молекулярной динамики позволяет с использованием современных компьютеров моделировать системы, состоящие из нескольких большого числа атомов на временах порядка нескольких пикосекунд. За последние годы получены впечатляющие результаты по применению метода в физике плазмы, биофизике и биохимии. Таким образом, тема научно-исследовательской работы А. Имаш достаточно актуальна.

По теме дипломного проекта были выполнены следующие работы:

1) Изучена литература по аналитической механике и методам численного интегрирования траекторий классических частиц с заданным потенциалом взаимодействия;
2) Изучены теоретические вопросы построения реалистических потенциалов межатомного взаимодействия;
3) На языке MATLAB составлены программы расчёта движения системы из небольшого числа частиц на торе с потенциалом взаимодействия Леннард-Джонса;
4) Проделаны численные эксперименты по наблюдению за эволюцией потенциальной, кинетической и полной энергии системы в расчёте на одну частицу и температуры.

Календарный график выполнения дипломной работы студенткой соблюдался дисциплинированно. Задание по подготовке дипломного проекта в целом выполнено, за исключением запланированных расчётов давления (из функции вириала Клаузиуса) и среднеквадратичного смещения атомов, что можно считать некоторым недостатком работы. Материал изложен литературно, логически последовательно и оформлен в соответствии с установленными требованиями.

В целом выпускная квалификационная работа А. Имаш выполнена на хорошем теоретическом и практическом уровне, соответствует требованиям, предъявляемым к дипломным работам программы бакалавра по специальности 5В072300 – «Техническая физика», заслуживает по мнению руководителя оценки 90% и рекомендуется к защите.

Научный руководитель,
профессор кафедры инженерной
физики, д.т.н. Мустафин А.Т.

15 апреля 2019 г.

Ф КазНИТУ 704-21. Отзыв научного руководителя

МИНИСТЕРСТВО ОБРАЗОВАНИЯ И НАУКИ РЕСПУБЛИКИ КАЗАХСТАН
СӘТБАЕВ УНИВЕРСИТЕТІ

РЕЦЕНЗИЯ

на дипломную работу

Имаш Әйгерім Абайқызы

5В072300 Техническая физика

На тему: Метод молекулярной динамики для системы взаимодействующих частиц
The topic: The molecular dynamics method for a system of interacting particles
(на английском языке)

Выполнено:
а) графическая часть на 11 листах
б) пояснительная записка на 23 страницах

ЗАМЕЧАНИЯ К РАБОТЕ

Выявлены несущественные недостатки дипломной работы: Слишком обширное использование литературных источников во втором разделе. Однако найденные недостатки не влияют на качество исследования по данной проблеме.

Оценка работы

Дипломная работа состоит из следующих разделов: введение, основная часть работы, состоящая из трех глав, заключение, список литературы и приложения. Работа аккуратно оформлена, написана грамотным языком, хорошо читается и воспринимается. Автор хорошо знает проблему, умеет формулировать научные и практические задачи и находить адекватные средства их решения. В заключении автором приведены конкретные предложения смоделировать трехмерные системы для получения более качественных результатов.

В работе есть логичность изложения анализа, изложенный текст в исследовании полностью соответствует названиям разделов. В целом работа соответствует всем требованиям, предъявляемым к дипломным работам по техническим специальностям.

Оценка качества выполнения графической части проекта «отлично»

Отзыв о проекте в целом и предлагаемая оценка «отлично»

В целом дипломный проект заслуживает оценки: (95% А) - «отлично»

Рецензент
Доцент кафедры Физики твердого тела
и нелинейной физики, доктор PhD,
_________ М.К.Ибраимов

«14» мая 2019г.

ФИЗИКА-ТЕХНИКАЛЫҚ ФАКУЛЬТЕТІ

ABSTRACT

The 21st century is experiencing an incredible growth of science, including nanotechnology. The rapid advancement of this new science and its applications of interest required new, challenging and physically sound ways to design and predict productivity. A predominantly direct and intelligible approach to modeling is the molecular dynamics method (Leach, 1996), in which an acceptable inter atomic potential is chosen to reproduce the interaction between atoms and then integrate the classical equations of motion with suitable boundary conditions.

A computer model of a two-dimensional gas of non-polar molecules has been constructed, the pair interaction between which is given by the Lennard-Jones potential. The model is formulated within the framework of the molecular dynamics method, which provides for the direct numerical solution of microscopic equations of motion of interacting particles. The greatest interest is not the trajectories themselves, but the thermodynamic macro-characteristics of the system under study, which are calculated because of their statistical averaging.

This paper presents a brief summary of key elements indispensable for performing molecular dynamics modeling, with a peculiar focus on macro molecular systems.

We consider the shape of the intermolecular potential for molecules consisting of atoms and non-spherical sub units, giving examples of how to calculate forces and moments. We will also outline some molecular dynamic algorithms currently. Finally, we briefly refer to determinants, some affect the size of the systems and the length of the runs, which are valuable for calculating statistical properties.

We carry our computer simulations in the hope of evaluating the properties of molecular assemblies in terms of their structure and microscopic interactions between them. This serves as an addition to the usual experiments, giving us something new to learn, something that cannot be demonstrated by other methods.

АҢДАТПА

XXI ғасыр ғылым, соның ішінде, нанотехнологияның, қарқынды даму кезеңін бастан кешіруде. Бұл жаңа ғылымның лезде дамуы – оның тиімділігін жобалау мен болжау үшін түрлі, жаңа, күрделі және физикалық жолдарды талап етті. Атомдар арасындағы әсерлесуді сипаттайтын, қолайлы, атомаралық потенциалды таңдап, сәйкес шекаралық шарттар қолдана отырып, классикалық қозғалыс теңдеуін интегралдайтын тура және түсінікті модельдеу тәсілі – молекулалық динамика (Leach, 1996) әдісі болып табылады.

Жұптар арасындағы әсері, Леннард-Джонс потенциалы арқылы берілген екі өлшемді газдың полярлы емес молекулалары үшін компьютерлік модель құрастырылды. Өзара әрекеттесуші бөлшектердің қозғалысы жөніндегі микроскопиялық теңдеудің тура сандық шешімін қарастыратын бұл модель – молекулалық динамика әдісі негізінде құрылды. Осыған қарамастан, зерттелініп отырған жүйе үшін аса жоғары қызығушылықты: траекторияның өзі ғана емес, сонымен қатар, оларды есептеу нәтижесінде алынған статистикалық орташаланған термодинамикалық макро-сипаттамалары тудыруда.

Бұл жұмыста макромолекулалық жүйеге бағытталған, молекулалық динамика әдісін модельдеуді іске асыру үшін қажетті болып табылатын маңызды элементтердің қысқаша сипаттамалары берілген.

Күштер және моменттерді есептеудің мысалдарын келтіре отырып, бейсфералық суббірліктен және атомдардан тұратын молекула үшін молекулааралық потенциалдың пішінін қарастырдық. Сонымен қатар, қазіргі таңдағы кейбір молекулалық динамика алгоритмдері туралы сипаттайтын боламыз. Статистикалық жүйенің қасиеттерін есептеуде жүйенің өлшеміне және айналым санына әсер ететін детерминанттарға қысқаша сілтеме жасаймыз.

Сондай-ақ, молекула жиынтығының қасиеттерін бағалау үшін олардың арасындағы құрылымдық және микроскопиялық әсерлесуді анықтау мақсатында компьютерлік модельдеу құрастырдық. Бұл кәдімгі тәжірбиелік жұмыстар үшін алынған, яғни басқа тәсілдерді қолдану арқылы анықталмаған жаңа ақпараттарды білуге мүмкіндік береді және тәжірибелік жұмыстарға үлкен үлес болып табылады.

АННОТАЦИЯ

XXI век испытывает невероятный рост науки, в том числе, нанотехнологии. Быстрое продвижение этой новоприобретенной науки и ее интересующих применений потребовало новых, непростых и физически обоснованных путей для проектирования и прогнозирования продуктивности. Преимущественно, прямым и вразумительным подходом к моделированию является метод молекулярной динамики (Leach, 1996), в котором выбирают приемлемый межатомный потенциал для воспроизведения взаимодействия между атомами, а затем, интегрируют классические уравнения движения с подходящими граничными условиями.

Построена компьютерная модель двумерного газа неполярных молекул, парное взаимодействие между которыми задаётся потенциалом Леннард-Джонса. Модель сформулирована в рамках метода молекулярной динамики, предусматривающего прямое численное решение микроскопических уравнений движения взаимодействующих частиц. При этом наибольший интерес представляют не сами траектории, а вычисляемые в результате их статистического усреднения термодинамические макро-характеристики изучаемой системы.

В этой работе дается краткое изложение ключевых элементов, незаменимых для выполнения моделирования молекулярной динамики, со своеобразным акцентом на макромолекулярные системы.

Мы рассматриваем форму межмолекулярного потенциала для молекул, состоящих из атомов и несферических субъединиц, приводя примеры того, как рассчитать силы и моменты. Мы также изложим некоторые из алгоритмов молекулярной динамики. Наконец, мы кратко ссылаемся на детерминанты, некоторые влияют на размер систем и длину прогонов, которые ценны для расчета статистических свойств.

Мы осуществляем компьютерное моделирование в надежде оценить свойства сборок молекул с точки зрения их структуры и микроскопических взаимодействий между ними. Это служит прибавлением к обычным экспериментам, предоставляя нам узнать что-то новое, то, что не может быть продемонстрировано другими приемами.

CONTENTS

INTRODUCTION 10
1. Statistical Thermodynamics 12
  1.1 First and second law of thermodynamics 12
  1.2 Criteria for thermodynamic equilibrium. Free energy calculation 14
  1.3 Statistical mechanics. Ensembles in statistical mechanics. Coupling between microscopic and macroscopic properties 18
2. Theoretical basis and numerical method 22
  2.1 Molecular dynamics. Governing equations 22
  2.2 Integration of the equations of motion. The Verlét algorithm 22
  2.3 Force fields. Bonded interactions. Bond stretching. Angle bending. Non-bonded interactions. Van der Waals interactions. The Lennard-Jones potential. Electrostatic interactions 24
  2.4 Periodic boundary conditions 28
  2.5 Temperature control. The Berendsen thermostat. The Nosé-Hoover thermostat. Pressure control 29
3. Visualization Tools and Graphics Programming 32
  3.1 Matlab - as a means of mathematical modeling 32
  3.2 Mathematical model of the statistical system 32
  3.3 Numerical algorithm for solving the system of equations of motion 34
  3.4 Modeling a system consisting of a large number of particles using the molecular dynamics method 38
  3.5 Method of implementation of MD modeling and calculation of thermodynamic parameters 39
CONCLUSION 42
REFERENCES 43

INTRODUCTION

Computer experiments represent the ultimate leading function in science. In a specific physical experiment, the characteristics of the system under study are recorded and the results are formulated in numerical form. In concept, the system model is based simply in the form of a collective of mathematical equations. Next, the susceptibility of the model is controlled to state the behavior of the system on a few conceived variations of the implementation of the model, rather ordinary, in order to allow fixing the solution of the equations. In most cases, this implies a significant amount of changes in order to eliminate all the difficulties connected with the tasks of a specific sphere and to fulfill the task being calculated.

Computer modeling sometimes appears as a theory, and sometimes as an experiment. On the one hand, we are dealing with models, and not with a “real object”, and this gives the right to systematize computer simulation like a theoretical method. On the other hand, the operation of proving the validity of a model in computer simulation strongly resembles an experiment: we turn on the calculations and then analyze the answers in a significant degree in the same way as experimental physicists do. How we are obliged to classify computer simulations, there is no definite answer to this question. However, there is some meaningful reflection. One way to understand the behavior of a classical many particle system is to simulate the trajectory of each particle. This approach, known as molecular dynamics, has been applied to systems of up to 10^9 particles and has given us much insight into a variety of systems in which the particles obey the laws of classical dynamics.

A calculation of the trajectories of many particles would not be very useful unless we know the right questions to ask. Saving these trajectories would quickly fill up any storage medium, and we do not usually care about the trajectory of any particular particle. What are the useful quantities needed to describe these many particle systems? What are the essential characteristics and regularities they exhibit? Questions such as these are addressed by statistical mechanics, and some ideas of statistical mechanics are discussed in this chapter. However, the only background needed for this chapter is a knowledge of Newton’s laws of motion.

In fact, any theoretical study of a difficult event traditionally rests on the reduction path: a complex system is simplified to a collection of much natural subsystems that can be explored using solvable models. When we see computer modeling as a primitive practical tool for “proving and testing” a model in situations that are extremely difficult for analytical discussion, we tacitly imply that the model shows that “theoretical level” on which interest is concentrated.

Nevertheless, the main thing to know that modeling may be of more significant and remarkable significance. We can analyze it not as a benefit of the reduction approach, but up to a certain stage, as an alternative to it. Simulation increases the limit of difficulty, which distinguishes between “solvable” and “intractable” models. We can use this threshold elevation in our horizons and advance to an unusual level of complexity in our representation of physical systems. Due to the potentialities of computer modeling, we can deal with incomparably more complex models, compared with those that were practiced in the past. This gives us an auxiliary degree of freedom for studies and shows the latest features.

As one of the cases of this point of view, the problem of inter atomic potentials can be thrown. In the past, inter atomic interactions were investigated using two-particle potentials with an elementary analytical form, Morse or Lennard-Jones species. Today, the most reliable potentials encompass multiparticle terms, which are determined totally from first glances. These new potentials could not have arisen without modeling; similarly, computer modeling is not only a link between experiment and theory, it is also a significant tool for achieving growth in newly acquired industries.

1 Statistical Thermodynamics

Thermodynamics is a branch of physics that focuses on temperature and energy. Though thermodynamics is based on a set of four axiomatic laws, engineers whose goal was to maximize efficiency of steam engines have originally developed this discipline. Statistical thermodynamics can successfully be applied to common everyday processes. For example, thermodynamics can be applied to the Carnot cycle that makes the refrigerator cool the beverages based on a refrigerant that follows a cycle where it at one point condenses into liquid and then evaporates. Thermodynamics can also be used to understand the meaning of an ice cube, where the phase transition of solid ice to liquid water occur at constant temperature and is due to energy absorbed by the ice cube. Another example of a thermodynamic system is the combustion engine where mechanical work is generated by compression and ignition of fuel.

1.1 First and second law of thermodynamics

The first and second laws of thermodynamic are two very useful statements. They will in this chapter be used to quickly derive an expression for both entropy and Gibbs free energy that can be used to evaluate the thermodynamic equilibrium conditions of a thermodynamic system. Consider a tank of a gas phase and a liquid phase, as shown in figure 1.1. There are N number of components in both phases. The tank (the system) is isolated from the rest of the universe (the surroundings), meaning that no heat or mass can be released/added to the tank. The gas phase and liquid phase are touching each other at the gas/liquid interface. Molecules can exchange between the two phases across the gas/liquid interface, as indicated by the two arrows.

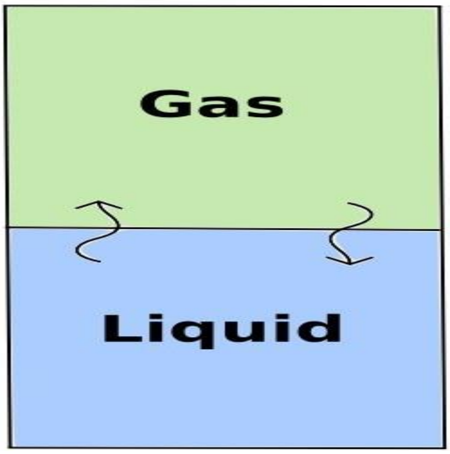


Figure 1.1 – Liquid/gas container

The first law of thermodynamics notifies that the internal energy of a closed system is invariably stored. Energy can step over from one substance to another, but it will never disappear. Energy can spread from substance to another as work or heat. In relation to the tank in figure 1.1, the first law of thermodynamics for the sake of the liquid phase can be expressed as:

$$dU^{liquid} = dQ^{liquid} + dW^{liquid} + \sum \mu_i^{liquid} dN_i^{liquid} \tag{1.1}$$

Moreover, the same for the gas phase:

$$dU^{gas} = dQ^{gas} + dW^{gas} + \sum \mu_i^{gas} dN_i^{gas} \tag{1.2}$$

dU^{liquid} is the conversion of the internal energy of the liquid phase, dQ^{liquid} is the heat conversion for the liquid phase, the term $dW^{liquid} = -P^{liquid} dV^{liquid}$ is the transformation mechanical work for the liquid phase and the term $\sum \mu_i^{liquid} dN_i^{liquid}$ is a transformation of the chemical work for the liquid phase for a multicomponent concept where i is the component. The same designation for gas phase. The reformation of heat dQ in equation (1.1) and (1.2) is associated with the change in entropy dS and absolute temperature T follows:

$$dS = \frac{dQ_{reversible}}{T} > \frac{dQ_{irreversible}}{T} \tag{1.3}$$

The convertible process is a transformation that is invariably present in equilibrium with the environments and does not have the generation of exact entropy, and this means that equation (1.3) maintains equality. Such a process can be achieved if infinitely small changes are made when the system moves from the initial position to the final position. Similarly, for a reversible process, the system reinforces the equilibrium with the embracing environment for any infinitesimal change. On the other hand, the irreversible process is performed in such a way that the change leads to the fact that energy leaves the system and entropy is formed, and this means that equation (1.3) includes inequality. All processes in nature are irrevocable. The reversible process is usually used as an ideal case and reference. As for example, an internal combustion engine can be 100% efficient for a reversible process, but in real life it is never 100% effective, for example, due to friction and heat loss.

The second concept of thermodynamics notifies that for the irreversible process, the total entropy of the system always progresses. It also means that heat cannot naturally transfer from low temperature to high temperature. According to the reservoir in figure 1.1, the second concept of thermodynamics can be expressed as:

$$dS^{tot} \geq dS^{gas} + dS^{liquid} \geq 0 \tag{1.4}$$

The infinitely small entropy change for each phase can be set as:

$$dS^{liquid} = \frac{dQ^{liquid}}{T^{liquid}} \quad and \quad dS^{gas} = \frac{dQ^{gas}}{T^{gas}} \tag{1.5}$$

For the heat-insulated system, $dQ^{liquid} = -dQ^{gas}$, which determines that heat cannot be advanced or added to the reservoir system, equation (1.5) takes on the character:

$$dS^{liquid} = -\frac{dQ^{liquid}}{T^{liquid}} \quad and \quad dS^{gas} = -\frac{dQ^{gas}}{T^{gas}} \tag{1.6}$$

Combining equation (1.4) – (1.6) with equation (1.1) – (1.2), the internal energy for both phases can be expressed as:

$$dU^{liquid} \leq T^{gas} dS^{liquid} - P^{liquid} dV^{liquid} + \sum \mu_i^{liquid} dN_i^{liquid}, \tag{1.7}$$

$$dU^{gas} \leq T^{liquid} dS^{gas} - P^{gas} dV^{gas} + \sum \mu_i^{gas} dN_i^{gas} \tag{1.8}$$

For an isolated system, the volume is conserved, meaning that $dV^{liquid} = -dV^{gas}$. The total internal energy is also conserved, meaning that $dU^{liquid} = -dU^{gas}$. In addition, so is the number of molecules, which gives $dN^{liquid} = -dN^{gas}$. Those three conservation laws combined with the expressions for internal energy for each phase in equation (1.7) – (1.8) and with equation (1.4) gives an interesting expression for the change in total entropy:

$$dS^{tot} \geq \left[\frac{1}{T^{liquid}} - \frac{1}{T^{gas}}\right] dU^{gas} + \left[\frac{P^{gas}}{T^{liquid}} - \frac{P^{liquid}}{T^{gas}}\right] dV^{gas} - \sum \left[\frac{\mu_i^{gas}}{T^{liquid}} - \frac{\mu_i^{liquid}}{T^{gas}}\right] dN_i^{gas} \geq 0 \tag{1.9}$$

By combining equation (1.7) – (1.8) with the relation between Gibbs free energy *G*, enthalpy *H* and entropy *S* and $dG = dH - d(TS)$ (the so called Legendre transformation), it is possible to obtain a very interesting term for the change in Gibbs free energy for the liquid phase:

$$dG^{liquid} \leq -S^{liquid} dT^{gas} + V^{liquid} dP^{liquid} + \sum \mu_i^{liquid} dN_i^{liquid} \leq 0 \tag{1.10}$$

In addition, the same for the gas phase:

$$dG^{gas} \leq -S^{gas} dT^{liquid} + V^{gas} dP^{gas} + \sum \mu_i^{gas} dN_i^{gas} \leq 0 \tag{1.11}$$

Equation (1.10) and (1.11) are very useful. They relate the change in Gibbs free energy to easy accessible properties of the system, and they contain the three thermodynamic driving forces that drive a thermodynamic system towards equilibrium. $-SdT$ describes the thermal driving force, related to change in temperature. VdP describes the mechanical pressure driving force, related to change in pressure.

$\Sigma \mu_i N_i$ describes the chemical driving force, related to the exchange of particles.

1.2 Criteria for thermodynamic equilibrium

The transformation of the total Gibbs free energy is the sum of the change in Gibbs free energy for each phase.

$$dG^{tot} = dG^{liquid} + dG^{gas} \tag{1.12}$$

The system moves to balance with support dG^{tot} <0 and dS^{tot}> 0. When a system reaches equilibrium conditions due to mitigation of driving forces, then $dG^{tot} = 0,$, which can be stated as:

$$dG^{tot} = dG^{liquid} + dG^{gas} = 0 \tag{1.13}$$

and

$$dG^{liquid} = -dG^{gas} \tag{1.14}$$

This means that under thermodynamic equilibrium conditions, the total free Gibbs energy is minimized. At the same time, the infinitely smallest change in the Gibbs free energy of the liquid phase corresponds with a negative change in the Gibbs free energy of the gas phase. At equilibrium conditions, there is no change in temperature or pressure, so dT=0 and dP=0. Therefore, by combination of equation (1.10)-(1.11) and (1.13), the total Gibbs free energy can written as:

$$dG^{tot} = \sum \mu_i^{liquid} dN_i^{liquid} + \sum \mu_i^{gas} dN_i^{gas} \tag{1.15}$$

The total change in quantity N_i (can be a change in e.g. number of molecules or number of moles) is:

$$dN_i^{tot} = dN_i^{liquid} + dN_i^{gas} \tag{1.16}$$

Consequently, in equilibrium conditions, the transfer of molecules between the liquid phase and the gas phase from one to the other is carried out with exactly the same speed. It looks the same as in the reaction kinetics. When the reaction appears in equilibrium, the direct and reverse reactions are performed at the same rate. Similarly, in equilibrium:

$$dN_i^{tot} = 0 \quad and \quad dN_i^{liquid} = -dN_i^{gas} \tag{1.17}$$

Finally, the change in total Gibbs free energy can be written as:

$$dG^{tot} = \left(\sum \mu_i^{liquid} - \sum \mu_i^{gas}\right) dN_i^{liquid} = 0 \tag{1.18}$$

Equation (1.18) implies that $\mu_i^{liquid} = \mu_i^{gas}$ at equilibrium.

When a system reaches equilibrium conditions, also dS^{tot} =0:

$$dS^{tot} = \left[\frac{1}{T^{liquid}} - \frac{1}{T^{gas}}\right] dU^{gas} + \left[\frac{P^{gas}}{T^{liquid}} - \frac{P^{liquid}}{T^{gas}}\right] dV^{gas} - \cdots$$

$$-\sum \left[\frac{\mu_i^{gas}}{T^{liquid}} - \frac{\mu_i^{liquid}}{T^{gas}}\right] dN_i^{gas} = 0 \tag{1.19}$$

At equilibria the two phases in figure 1.1 can coexist, which is a result from minimization of the total Gibbs free energy and maximization of the total entropy. Therefore, both dG^{tot} =0 and dS^{tot} =0, and the three thermodynamic equilibrium conditions between liquid and gas phase can be expressed as:

Thermal equilibrium $T^{liquid} = T^{gas}$ (1.20)

Mechanical equilibrium $P^{liquid} = P^{gas}$ (1.21)

Chemical equilibrium $\mu_i^{liquid} = \mu_i^{gas}$ (1.22)

No system can achieve thermodynamic equilibrium [1,2]. This is because there will always be some fluctuations in temperature, pressure and the number of molecules between the phases. Often, when applying thermodynamic equilibria in the presentation of a real process, this process is oriented as a quasi-equilibrium process. For a quasi-equilibrium process, the changes in the transition of the system from state 1 to state 2 are so small that it can be foreseen that the system is always in equilibrium for each small change. Therefore, the term “quasi-equilibrium” will be used when it is implied that the modeling carried out in this work has reached equilibrium.

Free energy calculation. Equations (1.10) and (1.11) cover three thermodynamic driving forces: thermal, mechanical, and chemical. Both temperature and pressure can be simply fixed in many thermodynamic systems, including those vital for our daily life. For example, almost all homes have a thermostat that measures the outside temperature. Knowledge of the pressure and temperature of liquids in the working blocks is important for the successful operation of oil refineries and gas processing plants; therefore, numerous pressure and temperature sensors are installed in pipeline systems. On the other hand, chemical potential cannot be measured accurately.

Although the methods for calculating the chemical potential have been prepared. There are two cases - the method of inserting particles Widom and the method of thermodynamic integration. Both of them appear by computational methods, convenient to calculate the chemical potential of a substance. In this research work, the method of thermodynamic integration was chosen, since it could be relatively simply carried out within the framework of purely molecular-dynamic modeling of arbitrary density. The method of introducing particles to Widom will require an auxiliary sample and does not guarantee that it will work for modeling involving dense phases [3,4,5,6]. In short, the Widom particle insertion method is built on a sample of the probability that a test particle will be installed in the

system. A much thoroughly explained method of thermodynamic integration is formed on finding a reversible approach by which the system follows from its initial state to the final state. The system is an isolated one-component system with a constant number of particles at a constant temperature. The discovery of this method can be done by a system modeling approach for a variety of constant temperatures and measuring the potential energy per molecule for each simulation. Then you can create a graph of potential energy per molecule from 1/T. The potential energy per molecule in the simulation system should be measured for temperatures ranging from normal conditions (for example, 298 K) to infinitely high temperatures. Further, the polynomial function can be adapted to a series of information in the potential energy per molecule against the 1/T graph. The obtained polynomial selection function describes the approach by which the system passes from its initial to the final state. The initial state is the potential energy per molecule at the normal temperature of the system, and its final state is the potential energy per molecule at the theoretical infinite temperature. In the final state, the system will behave like an ideal gas. For an ideal gas, free energy and chemical potential are established. The basic integration method can be used to solve a polynomial similarity function.
The integrated function can be demonstrated as [38, 39]:

$$\mu^{residual} = T_{initial} \int_{T_{final}}^{T_{initial}} U^{residual} d(1/T) \tag{1.23}$$

where $\mu^{residual}$ is the residual chemical potential and $U^{residual}$ is the residual potential energy per molecule [38].

The total chemical potential μ^{tot} can be expressed as:

$$\mu_i^{tot} = \mu_i^{residual} + \mu_i^{ideal\ gas} \tag{1.24}$$

The method of thermodynamic integration with equation (1.23) provides for calculating the residual chemical potential of the substance of a real system. The chemical potential of an ideal gas can be calculated analytically. Unobtrusively, this is the total chemical potential that is used to compare the chemical potentials of various substances [7, 8, 9].

The chemical potential can also be defined in terms of thermodynamic state functions. Some examples are (at constant *Nj* where *j≠i*):

$$\mu_i = \left(\frac{\partial G}{\partial dN_i}\right)_{T,P}, \mu_i = \left(\frac{\partial A}{\partial dN_i}\right)_{V,T}, \mu_i = \left(\frac{\partial H}{\partial dN_i}\right)_{S,P}, \mu_i = \left(\frac{\partial U}{\partial dN_i}\right)_{S,V} \tag{1.25}$$

They all tells us how the state variables Gibbs free energy *G*, internal energy *U*, enthalpy *H* and Helmholtz free energy *A* change when one more particle is added to the system by holding the respective state variables temperature *T*, pressure *P*, entropy *S*, volume *V* constant. Therefore, the chemical potential can be defined, as the work required adding one more particle to the system. The chemical has an energy *SI* unit in *kJ/mole*. Heat flows from a system with high temperature to a system with low temperature, a rock falls from high to lower height and molecules diffuse from a region with high chemical potential to a region with lower chemical potential.

1.3 Statistical mechanics. Statistical mechanics. Ensembles in statistical mechanics. Coupling between microscopic and macroscopic properties

The basis of statistical mechanics is probabilistic propagation. The statistical path is used to represent physical phenomena due to the extremely large number of molecules. A significant number of molecules is detected by the Avogadro number, $N_A = 6.023 \cdot 10^{23}$ molecules / mol. An example of the application of probability theory in statistical mechanics is the Maxwell-Boltzmann velocity distribution. Maxwell and Boltzmann studied that for each temperature there is a probability distribution of the velocity of molecules. This means that the molecules do not move at the same speed, but for each temperature, each speed a molecule may have has an established probability. This principle is illustrated in figure 1.2 with the number of molecules (proportional to probability) along the Y axis and velocity along the X axis. The distribution is for ideal gases, which means that the molecules do not interact with each other, with the exception of collisions.

As an example of the molecular velocity, the most probable Maxwell-Boltzmann velocity of the nitrogen molecule (N_2) in air is 422 m/s.

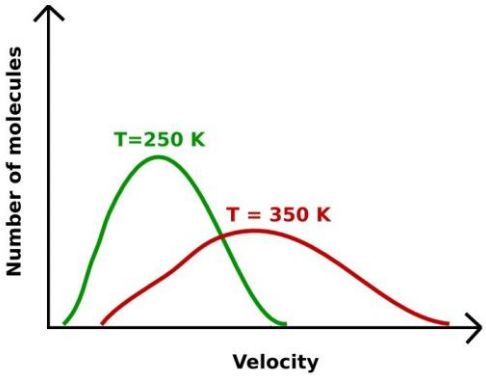
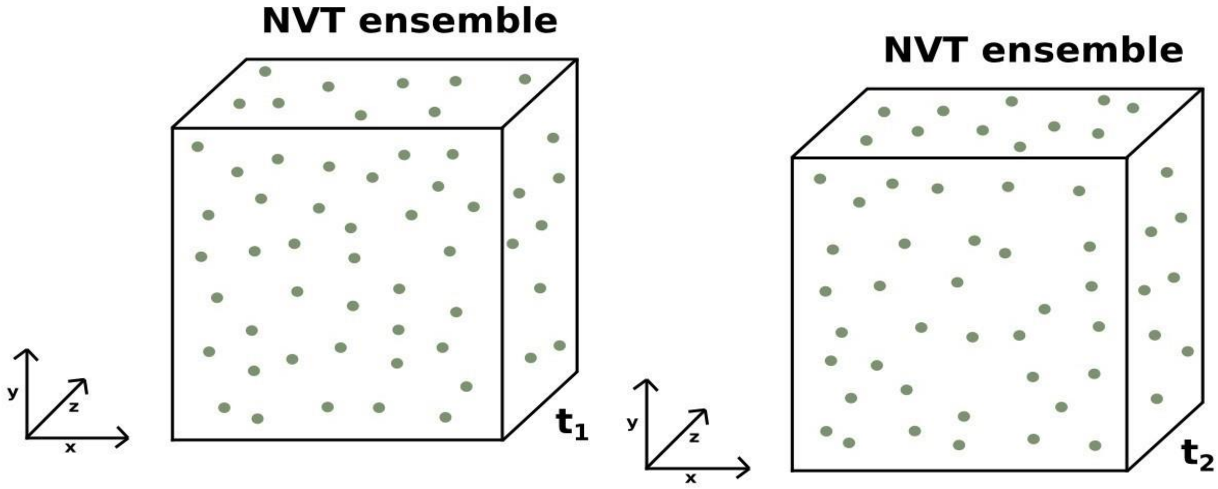


Figure 1.2 – Illustration of Maxwell-Boltzmann velocity distribution

Ensembles in statistical mechanics. The main goal of statistical mechanics is to detect the macroscopic properties of the system, considering it from a molecular point of view. The ensemble consists of a set of microstates, all of which are limited by certain macroscopic properties. In explaining what a statistical ensemble is, let us start with a representation of a large box system with four walls containing gas molecules. In figure 1.3, gas molecules are shown in green dots.

Figure 1.3 illustrates the idea of statistical ensembles and microstates. The concept is that if we follow the system in time, for example, as a result of molecular dynamics modeling, the system will be in a new microstate for each time interval due to molecular interactions and movement. Each microstate in the ensemble is localized by some fixed macroscopic properties of the system.

Figure 1.3 illustrates only the position of the gas particles in the system. In both classical and statistical mechanics, each particle also has an impulse $p = mv$, where m is the mass of the particle, and v is the velocity of the particle. The basic position xyz and the momentum for each particle are usually described by the phase space. The dimension of the phase space is 6N, where N is the number of particles in the system. That is, 3 measurements for Cartesian xyz-coordinates and 3 measurements for each component of the particle momentum.



a) time t_1 b) time t_2

Figure 1.3 – Illustration of NVT ensemble and microstates

The atomic and molecular properties can be different for each microstate, which is just natural because the molecules change their position and momentum each period. In a), the time is t_1. At this period, the system is in a certain microstate. In b), the time is t_2. From t_1 to t_2, the system changes its microstates because the xyz-position and the momentum of the molecules are updated. The microstate that the system is in at both time t_1 and t_2 are constrained by the governing statistical ensemble. In this case, each microstate have to correspond to the NVT ensemble. For the NVT ensemble, each microstate must have the same number of molecules *N*, the same volume *V* and give the ensemble temperature *T*.

Table 1.1 – Some examples on statistical ensembles and their fixed macroscopic properties

Ensemble	Constant macroscopic variables
Canonical	*N, V, T*

Isothermal-Isobaric	N, P, T
Micro canonical	N, V, E
Grand canonical	N, μ, T

There are many statistical ensembles. Some of them are specified in table 1.1 with matching macroscopic properties constants that identify the ensemble. The macroscopic properties that are fixed for each system in an ensemble can be controlled by accepting an adjustment of the boundaries that the system has with its environment. For example, for a system in a canonical ensemble, the temperature can be kept on average constant, making the system an isolated system surrounded by a thermostat, so that thermal energy can be supplied to the system to adjust the temperature.

Hamiltonian is closely interconnected with the phase space. Hamiltonian is the total energy of the system. This is the sum of the potential energy and kinetic energy and can be expressed as:

$$H(q,p,t) = U + KE = U(q_1, q_2, \dots, q_N) + \sum_{i=1}^{N} \frac{p_i^2}{2m_i} \qquad (1.27)$$

where particle i with mass m_i will have the position q_i and momentum p_i in the phase space.

Coupling between microscopic and macroscopic properties. The decomposition function can be derived for each statistical ensemble. The separation function can provide information about the available microstates for the system in a given ensemble, and it is a function of the thermodynamic unstable state. It can also be detected as the volume that the system captures in the phase space. Similarly, partitioning functions are the link between microscopic and macroscopic properties. The microstate is a point in the phase space, and the macrostate is the distribution of probabilities in the phase space. The disadvantage associated with the use of separation functions in an application is that they are very advanced to solve. For example, the separation function for a microcanonical ensemble can be fixed as:

$$\Omega(N,V,E) = M_N \int \delta(H(q,p,t) - E) d\Gamma \qquad (1.28)$$

where Q is the number of microstates belonging to the microcanonical ensemble;

M_N is the microcanonical ensemble normalization factor;

E is the microcanonical ensemble energy and Γ is the phase space volume [10]. Additionally, the separation function for a canonical ensemble can be obtained from the microcanonical ensemble by connecting the system with an unlimited large external heat reservoir, and it can be expressed as:

$$Q(N,V,T) = C_N \int e^{-H(q,p,t)/Tk_B} d\Gamma \qquad (1.29)$$

where *Ω* is the number of microstates belonging to the canonical ensemble, C_N is the canonical normalization factor and k_β is the Boltzmann constant [11,12].

In the case of the microcanonical ensemble, each microstate with a total energy *H(q,p)* within a certain range of the ensemble energy *E* can be assumed to have the same probability. All the microstates that do not satisfy this ensemble energy can be assumed to have *0* probability. Thus, for the microcanonical ensemble, at equilibrium conditions, the probability $P\nu$ for finding the system in a particular microstate ν is:

$$P_v = \frac{1}{\Omega(N,V,E)} \tag{1.30}$$

And the entropy can be defined as:

$$S = k_B \log \Omega(N, V, E) \tag{1.31}$$

In molecular dynamics simulation studies, usually the Ergodicity theorem is used as a link between the microscopic and the macroscopic properties. In molecular dynamics simulation, we follow the time evolution of the system on a microscopic level. We know the initial start configuration of the molecules in the system and use classical mechanics Newtonian equations of motion to follow the trajectories and evolution of the system.

The Ergodicity theorem states that for both large enough time and large number of molecules, the ensemble average $\langle A\rangle$ is assumed to be the same as the time average

A (*t*). The theorem can be expressed as:

$$\lim_{t\to\infty} \overline{A(t)} = \langle A\rangle \tag{1.32}$$

The ensemble average can be analyzed as the average for all microstates in the phase space. It is preferable that the system provides the entire phase space during the entire simulation time, visiting all possible microstates for given fixed thermodynamic properties of the ensemble, but in reality this is impracticable due to, for example, information losses. The average time can be recognized as the average for all microstates that the system spends during the simulation run.

2 Theoretical basis and numerical method

2.1 Molecular dynamics. Governing equations

A significant advantage, the characteristic molecular dynamics modeling, is the feasibility of having a molecular level of control, visualization and numerical analysis. In many supplements of research and optimization, this is an absolute need, for example, for adsorption processes, where selectivity and diffusion can be really understood at the molecular level. The main goal of molecular dynamics modeling is to gain a deeper understanding of molecular interactions and trajectories that could not be otherwise understood. Conjunction, simulations tend to be as realistic and physical as possible and to simulate a real experiment. Molecular dynamics modeling can be considered as a converter between the microscopic world of molecular statistical mechanics and the macroscopic thermodynamic world [13, 14, 15].

Governing equations. The illustration of the system belonging to the gas molecule box in figure 1.3 can be related to the molecular dynamics simulation. When modeling molecular dynamics, knowing the initial configuration of the launch and some signifying equations of motion, the evolution of particles over time can be approximated. Based on equation 2.1, the total force F acting on each atom in the system can be found by the generally negative gradient of potential energy $U(r)$ between two atoms separated by distance r:

$$F = -\nabla U(r) \tag{2.1}$$

The classical mechanics of the equation of motion of Newton is applied to the numerical gradual calculation of the total force acting on each atom in the system. The initial configuration of the components in the simulation system is determined, and then equation (2.1) is used to calculate the total force acting on each atom in the system and their accelerations.

This gives a time evolution of the system, and the position and momentum of each atom is restored every time step. As mentioned earlier, the position of an atom in phase space is represented by a function (q, p).

2.2 Integration of the equations of motion. The Verlét algorithm

Newton’s second law can be stated as:

$$F_i = m_i a_i = \frac{d^2 q_i}{dt^2} \tag{2.2}$$

where F_i is the total force on particle i;

m_i is the mass;

a_i is the acceleration;

q_i is the position vector;

t is the time.

Combining equations (2.1) and (2.2), it is possible to calculate the acceleration of each particle for each time interval. When modeling molecular dynamics, it is essential to have an integration algorithm to advance the system over time. Modifications of such algorithms exist. Two examples are the Verlét algorithm and the Leap-frog algorithm. The Verlét algorithm will be used for temporal integration of modeling in this work and will be extracted soon below.

Equation (2.2) is a second order differential equation. It would be more feasible to write it as two first order differential equations to more easily access the velocity vector v_i and the position vector q_i:

$$F_i = m_i \frac{dv_i}{dt} \tag{2.3}$$

$$v_i = \frac{dq_i}{dt} \tag{2.4}$$

The Verlét algorithm. One of the best-developed time integration algorithms is the Verlét algorithm. The derivation of the Verlét algorithm starts by considering the Taylor expansion for the position q_i for particle *i* for time *(t +- Δt)*:

$$q_i(t+\Delta t) = q_i(t) + \left(\frac{dq_i}{dt}\right)_t \Delta t + \frac{1}{2}\left(\frac{d^2q_i}{dt^2}\right)_t (\Delta t)^2 + \frac{1}{6}\left(\frac{d^3q_i}{dt^3}\right)_t (\Delta t)^3 + \\ +O(\Delta t)^4 \tag{2.5}$$

$$q_i(t-\Delta t) = q_i(t) - \left(\frac{dq_i}{dt}\right)_t \Delta t + \frac{1}{2}\left(\frac{d^2q_i}{dt^2}\right)_t (\Delta t)^2 - \frac{1}{6}\left(\frac{d^3q_i}{dt^3}\right)_t (\Delta t)^3 + \\ +O(\Delta t)^4 \tag{2.6}$$

where Δ*t* is the time step [43,44]. By adding equation (2.5) and (2.6), the result is:

$$q_i(t+\Delta t) = 2q_i(t) - q(t-\Delta t) + \left(\frac{d^2q_i}{dt^2}\right)_t (\Delta t)^2 + O(\Delta t)^4 \tag{2.7}$$

Equation (2.7) is called the Verlét algorithm. $O(\Delta t)^4$ is the truncation error of the algorithm and is the difference between the approximated Taylor expansion and the true smooth function. By choosing a large time step Δ*t*, the clipping error will be greater than if a minor step was chosen. Notice that in equation (2.7), the velocity term $vi = (dqi\ /\ dt\ )t$ is cancelled out. By applying the numerical finite difference method, the velocity can be obtained:

$$v_i(t) = \left(\frac{q_i(\Delta t) - q_i(t-\Delta t)}{2\Delta t}\right) \tag{2.8}$$

The Verlét algorithm makes it possible to calculate the new position q_i at time *(t+*Δ*t)* for all the particles of the system, and to do this, both the position q_i and velocity v_i at current time *t* as well as the position at previous time *(t-*Δ*t)* are required.

The time step Δt is often chosen to be *1 femtoseconds* (10^{-15} *seconds)* in molecular dynamics simulations.

2.3 Force fields. Bonded interactions. Bond stretching. Angle bending. Non-bonded interactions. Van der Waals interactions. The Lennard-Jones potential. Electrostatic interactions

Force fields are the key and the basis for molecular dynamics modeling. They also provide the input parameters used by the governing equations of motion to calculate the position of atoms in the phase space. Each atom in the system is described by a set of parameters of the force field. There are many different types of force fields, and the choice of the “right” for the modeling system and conditions can be crucial for quality results. The total potential energy U_{tot} is often divided into two groups:

$$U_{tot} = U_{bonded} + U_{nonbonded} \tag{2.9}$$

Bonded interactions. The first constituents of the total potential energy in equation (2.9) is the bonded interactions U_{bonded}. It can be expressed as:

$$U_{bonded} = U_{bond} + U_{angle} + U_{dihedrals} + U_{impropers} \tag{2.10}$$

Inherently, linked interactions are also called intramolecular interactions, because they hold atoms in a molecule together in the system under study. Two molecules that will be used in this work (water and gas); they both have the potential to stretch the bond and bend the angle, but they do not have dihedral or irregular potentials because of their usual triatomic molecular structure.

Bond stretching. The corresponding length of chemical bonds between two atoms in a molecule changes due to vibrations. Changes in bond length are very often described with the potential for stretching a harmonic bond. Hook's law is usually used to describe how the bond stretching potential energy $U_{bond}(r)$ changes as the bond length oscillates around its equilibrium length r_{eq}:

$$U_{bond}(r) = \frac{1}{2} k_{bond} \left(r - r_{eq}\right)^2 \tag{2.11}$$

where r is the distance between the two atoms from atomic center to atomic center;

k_{bond} is the bond stretching constant. A higher bond-stretching constant would result in bonds that are more rigid.

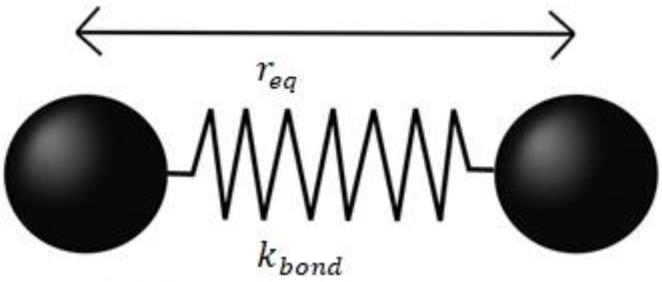


Figure 2.1 – Illustration of intramolecular harmonic bond stretching between two atoms that makes up a molecule. Ball/spring model

Figure 2.1 illustrates this idea, showing two spheres connected to a spring. Each ball is an analog of the atom, and the spring is an analog of the connection between them. Some force field models consider chemical bonds as rigid, which means that bonds cannot stretch and bond lengths are unchangeable in simulation time.

Angle bending. Similar to the length of the bond between two atoms, the angle between the three atoms will repeatedly transform over time due to molecular vibrations, as shown in figure 2.1. Potential energy as a function of angle can be demonstrated through the harmonic potential according to the Hook's law:

$$U_{anglebending}(\theta) = \frac{1}{2} k_{angle}\left(\theta - \theta_{eq}\right)^2 \tag{2.12}$$

where θ is the angle between three atoms in the same molecule;

θ_{eq} is the equilibrium angle;

k_a is the angle-bending constant.

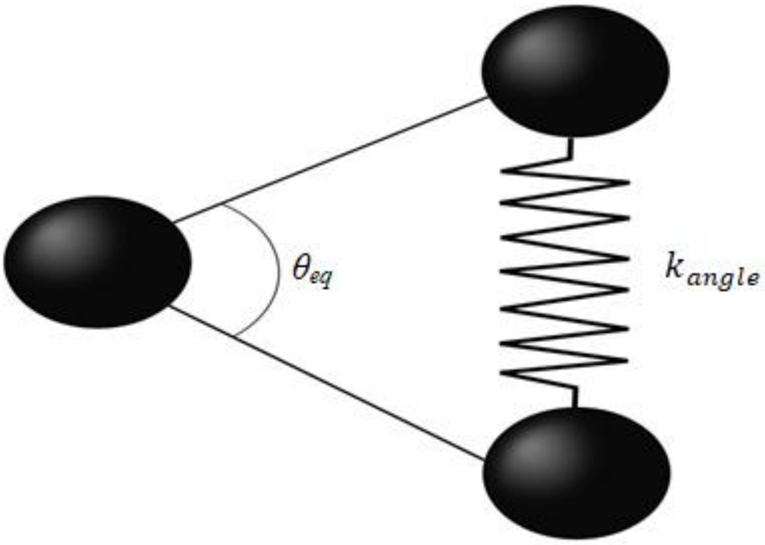


Figure 2.2 – Illustration of intramolecular harmonic angle bending between three atoms that makes up a molecule. Ball/spring model

Non-bonded interactions. Low-bound interactions are represented both intra- and intermolecular, and they can include interactions with all other atoms in the system. They can be sorted into two types: far and near. Long-range interactions are electrostatic forces, usually depicted in models according to Coulomb's law. Short-range interactions are Van der Waal (vdw) interactions and are usually depicted by the Lennard-Jones model or the Buckingham model. The non-bonded interactions $U_{non-bonded}$ can be expressed as:

$$U_{non-bonded} = U_{electrostatic} + U_{vdw} \tag{2.13}$$

Van der Waals interactions. The Lennard-Jones potential. The Van der Waal interactions constitute of three forces, namely Keesom forces, Debye forces and London dispersion forces, as shown in equation (2.14).

$$U_{vdw} = U_{Keesom} + U_{Debye} + U_{London} \tag{2.14}$$

The three parts of the Van der Waal forces are due to different electrostatic interactions:

- Keesome forces: stationary dipole - constant dipole interactions;
- Debye forces: stationary dipole-induced dipole interactions;
- London dispersion forces: induced dipole - induced dipole.

Keesom forces are interactions between two stationary polar molecules. The polarity of molecules can be, for example, dipole-dipole interactions or quadrupole-quadrupole interactions. The polarity of the molecule arises from the difference in electronegativity between the atoms in the molecule.

The Debye forces are interactions between a molecule with a constant dipole and a molecule with an induced dipole. The induced dipole moment of the molecule is due to the time polarization of this molecule, which occurs in the presence of a polar molecule.

London dispersion forces are the interaction of two non-polar molecules. This interaction force is predetermined by the time polarization of non-polar molecules due to the motion and various concentrations of electrons in the electron cloud surrounding the atoms of the molecule. The Van der Waal interactions are short-range and considered as weak forces. They can be written as:

$$U_{vdw} = U_{repulsion} + U_{attraction} \tag{2.15}$$

The Keesom, Debye and London dispersion forces are the attractive contribution of the Van der Waal forces and can be expressed as:

$$U_{attraction} = U_{Keesom} + U_{Debye} + U_{London} \tag{2.16}$$

The most common mathematical model that describes the short-range Van der Waal forces is the Lennard-Jones potential:

$$U_{LJ}(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{2.17}$$

where ε is the well depth of the potential;

σ is the Van der Waal radius;

ε and σ are the parameters that makes the Lennard-Jones potential unique for each component of a simulation system. They can be fitted to experimental data or approximated with advanced quantum mechanics calculations.

There is a certain distance between atoms where the force between them is 0. For a greater distance than that point, an attractive Lennard-Jones force is yielding. For a less distance, a repulsive Lennard-Jones force is yielding.

This is illustrated in figure 1.6. For the Lennard-Jones potential, given by equation (2.17), the attractive forces decrease as a function of $1/r^6$ and the repulsion contribution of the Van der Waal force fall off as $1/r^{12}$. The repulsion happens when two intermolecular atoms are too close and the electron clouds overlap. As the electron clouds overlap, the positively charged nuclei of the atoms results in repulsion according to Paulie's exclusion principle.

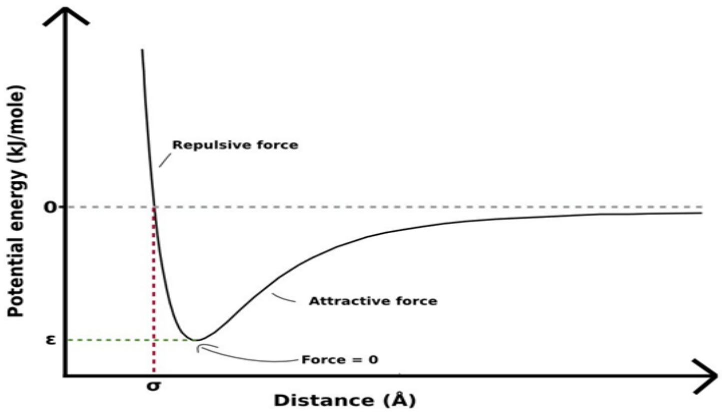


Figure 2.3 – A general form of the Lennard-Jones 12-6 potential interactions between two similar atoms. Potential energy $U(r)$ vs distance between the atoms r

The Lennard-Jones interaction potential is perhaps the most well known, but also unlimited use of Buckingham's potential [17]. Buckingham's potential has a softer repulsion [17], which means that the repulsion curve will not be as steep as the Lennard-Jones repulsive interaction curve in figure 2.3. The Buckingham potential has three parameters, that is, A, B, and C, compared with the two parameters ε, σ in the Lennard-Jones potential. Buckingham potential can be written as [18]:

$$U_{\text{Buckingham}}(r) = A \times exp(-B \times r) - \frac{C}{-r^6} \tag{2.18}$$

Note that the attractive portion of Buckingham’s potential also complies as $1/r^6$. Buckingham's potential has the advantage that the repulsive part expresses itself exponentially because it makes it more physical than the repulsive part for

Lennard-Jones potential [19]. However, on the other hand, the three interaction parameters for Buckingham's potential make it computational more precious.

Electrostatic interactions. Electrostatic fragmentary interactions function over great distances and are considered as powerful forces. For many force fields, the partial charges established for each atom are calculated based on differences in quantum mechanics and electronegativity. This provides to simulate, for example, the dipole moment of water. The partial charge of each atom appears in the center of each atom; therefore, electrostatic interactions can also be called simple point charge interactions. By introducing electrostatic interactions to simple point charge interactions, Coulomb's law can be used to calculate electrostatic forces between two atoms. Coulomb's law can be demonstrated as:

$$U_{\text{Coulomb}} = \frac{1}{4\Pi\varepsilon_0\varepsilon_r} \times \frac{Q_i Q_j}{|r_{ij}|} \tag{2.19}$$

where Q_i and Q_j are the partial simple point charges for atom of type i and j;

$|r|$ is the absolute distance vector between the two atoms;

ε_0 is the permittivity of vacuum and ε_r is the relative permittivity [20, 21].

2.4 Periodic boundary conditions

Consider the system consisting of a box of atoms, as shown in figure 2.4. Imagine that the system is open, so the six surface walls of the box have no mass or interactions. This means that when the simulation opens, and the atoms undertake to interact and move, some of them are likely to leave the box volume. When these atoms go out of the box, they cross the lines of the open system. Thus, the number of atoms in the system is not conserved, and the density of atoms in the box will decrease.

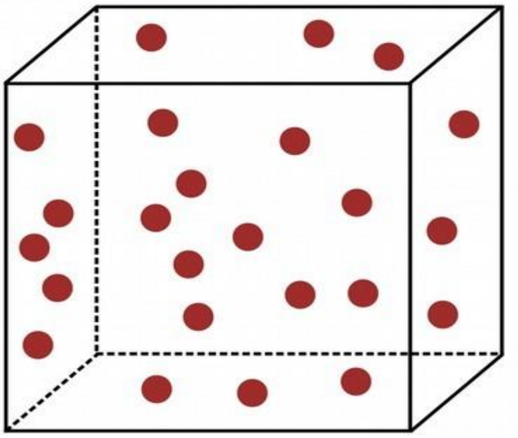


Figure 2.4 – A box of atoms

To address this problem, periodic boundary conditions (PBC) are applied to the modeling system to make it a periodic system. figure 2.4 illustrates the concept of periodic boundary conditions. In figure 2.4, the rectangle in figure 2.3 is for simplicity shown in two dimensions. The original box is a box in the middle with dark red atoms. In such a two-dimensional space as when periodic boundary conditions are correctly applied to the modeling system, there will be a copy of the original box on each side of the original box. The atoms of the copied boxes are colored light red. So, the idea with periodic boundary conditions is that each of the blocks, 9 blocks in this example, will have exactly the same movement as the next block when the atom moves up and into the next block.

When this happens, a copy of this atom will also fall into the box from which it came, from the next box below. This means that an atom that moves from the source box and into the box above, this atom will repatriate back to the source box from below.

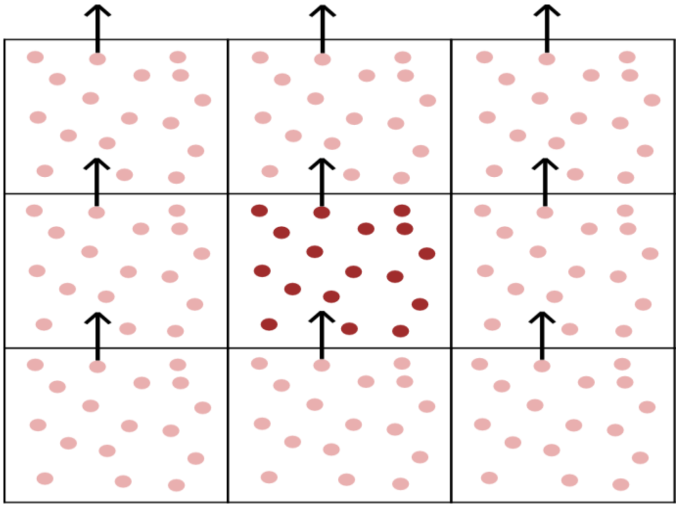


Figure 2.5 – Illustration of a periodic system

Thus, using periodic boundary conditions to the system, it is possible to keep the density of the system constant over time. It also allows you to simulate an infinitely large three-dimensional system in periodic instructions, even with a small number of atoms.

2.5 Temperature control. The Berendsen thermostat. The Nosé-Hoover thermostat. Pressure control

From the illustration of the Maxwell-Boltzmann distribution over the velocity of ideal gases in figure 1.2, it can be seen that a higher temperature gives a higher probability of the existence of molecules with a higher velocity. This leads to a relationship between temperature and average kinetic energy. $\langle KE \rangle$:

$$\langle KE\rangle = \frac{1}{2}\sum_i m_i\langle v_i^2\rangle = \frac{3}{2}k_bT \qquad (2.20)$$

where m_i is the mass of particle i;

v_i is the velocity of particle i;

k_b is the Boltzmann constant and T is the temperature.

A predominantly natural ensemble in the modeling of molecular dynamics would be the use of a microcanonical ensemble due to the conservation of energy and Newton's equations of motion. Nevertheless, in real life, the vast majority of experiments take place under conditions of constant temperature, not constant energy. When the canonical ensemble is used to model molecular dynamics, it is imperative to use a thermostat to maintain a constant temperature. There are many computational algorithms for this purpose. Three examples are the Nose-Hover thermostat, the Berendsen thermostat and the Anderson thermostat.

The goal with a thermostat is to maintain a constant average system temperature. For each time step, the system will be in a new microstate with a new instantaneous kinetic energy. If the kinetic energy of each time step were kept constant, it would have affected the system too much. Thus, when modeling molecular dynamics, when a thermostat is used, the temperature will fluctuate around the average temperature of the thermostat. Although it is important to remember that fluctuations are usually smaller for a system with a large number of particles.

The Berendsen thermostat. The Berendsen thermostat uses velocity scaling to control the temperature [22]. The velocities are scaled each time step and the temperature of the system is controlled by the equation:

$$\frac{dT(t)}{dt} = \frac{1}{\tau}\left(T_0 - T(t)\right) \tag{2.21}$$

where $T(t)$ is the temperature of the system at time t [23, 24]. T_0 is the temperature of an external hypothetical heat bath that the Berendsen thermostat uses to maintain the temperature of the system by coupling the two thermostats with the coupling parameter τ. Both T_0 and τ are often used as input parameters in a run script for a molecular dynamics simulation. The value of the communication parameter fixes how active the thermostat is and how much the thermostat acts on the system. On average, the goal is to ensure that the temperature of the system is the same as the required temperature T_0.

The Berendsen thermostat showed good tendencies toward the equilibrium of a non-equilibrium system [25]. Another advantage of the Berendsen thermostat is the simplicity of the code; it follows from this that it is easy to implement. However, it has some drawbacks: it is often said that it cannot generate the canonical splitting function (it cannot create the correct statistical ensemble) [25], it can generate a discontinuity in the trajectories of the phase space, it is non-ergodic and not reversible in time [25]. However, in practice, the magnitude of the deviation from the canonical distribution is inconspicuously small enough [25].

The Nosé-Hoover thermostat. Nosé came up with a set with equations in 1984 [26] before Hoover in 1985 improved and simplified those equations to make the the Nosé-Hoover thermostat [27].

Equalities used in the Noose-Hoover algorithm provide other modifications of Newton's equations of motion. An external thermal bath is added to the system, which gives atoms an auxiliary degree of freedom. Due to this heat bath, the total energy of the modeling system changes. Thus, the additional kinetic energy and potential energy are added to the total energy [28, 29]. Heat energy can spread between the system and the thermostat. In short, the equation of motion for an additional degree of freedom is solved. This equation can be expressed as the expansion of the Hamiltonian with an auxiliary degree of freedom [29]:

$$H_{Nosé-Hoover} = \sum_i^N \frac{p_i^2}{2m_i} + U(q_1, \dots, q_N) + \frac{\zeta^2 Q}{2} + (3N)\frac{\ln(s)}{\beta} \qquad (2.22)$$

In equation (2.19), the two first terms are the kinetic energy and potential energy previously defined for the classical Hamiltonian. Nosé and Hoover add the two next terms, and all together, they make up the Hamiltonian used in the Nosé-Hoover thermostat. ζ is the thermodynamic friction coefficient and s is a time scale variable and is associated with the external heat bath reservoir.

The Nosé-Hover has the advantage of producing the canonical distribution as well as being deterministic and time-reversible for equilibrium systems [28]. Nevertheless, as a drawback, it can result in a non-ergodic system if becoming trapped in a subspace [28].

Pressure control. For an isothermal-isobaric ensemble, it is imperative to use a barostat to control the pressure. Two examples of such barostats are the Nose-Hoover barostat and the Berendsen barostat.

In short, both the Berendsen barostat and the Nose-Hoover barozate inspect the system pressure by adjusting the volume of the box. The pressure of the virial is calculated, and then the volume of the modeling block may fluctuate (probably to obtain a statistical ensemble pressure), so that the required pressure is reached.

3. Visualization Tools and Graphics Programming

3.1 Matlab - as a means of mathematical modeling

MATLAB is one of the oldest, thoroughly developed and time-tested systems for automation of mathematical calculations, built on an extended view and application of matrix operations. This is reflected in the name of the system - Matrix Laboratory - matrix laboratory.

The possibilities of MATLAB are very extensive, and the system often surpasses its competitors in speed of performing tasks. It is applicable for calculations in almost any field of science and technology. For example, it is very widely used in mathematical modeling of mechanical devices and systems, in particular, in dynamics, hydrodynamics, aerodynamics, acoustics, power engineering, etc.

MATLAB is a high-performance technical computing language that combines computing, visualization, and programming in a common to use environment where problems and solutions are demonstrated in a familiar mathematical notation. Typical attachments include:

- Math and computing;
- Development of a numerical algorithm;
- Simulation and simulation;
- Accurate analysis, research and visualization of results;
- Scientific and engineering graphics of the system under study.

The name MATLAB stands for Matrix Lab. MatLab has the highest speed of numerical calculations. However, matrices are widely practiced not only in such mathematical calculations as solving problems of linear algebra and mathematical modeling, calculating static and dynamic systems and objects. They are the basis for the automatic preparation and solution of the equations of state of dynamic objects and systems. Actually, the versatility of the matrix calculator significantly increases the interest in the MatLab system, which encompasses the best achievements in the industry of quickly solving matrix problems. Therefore, MatLab has long gone beyond the boundaries of a specialized matrix system, becoming one of the most powerful universal integrated systems of computer mathematics [30].

3.2 Mathematical model of the statistical system

Setting the goal of understanding the qualitative properties of systems consisting of a large number of particles, we simplify the problem by assuming that the molecules are chemically inert and their movement is classical. In addition, we will assume that the interaction force of two molecules depends only on the distance between them; therefore, the total potential energy U is determined by the sum of the energies of two partial interactions:

$$U=V(r_{12}) + V(r_{13}) +\ldots+ V(r_{23}) +\ldots=\sum_{i<j=1}^{N} V(r_{ij}) \qquad (3.1)$$

where $V(r_{ij})$ depends only on the absolute value of the distance r_{ij} between particles *j and i*. The pair interaction model adequately describes "simple" liquids, for example, liquid argon.

For electrically neutral atoms, it is theoretically possible, using the laws of quantum mechanics, to obtain an analytical expression for the function *V (r)*. However, firstly, such a calculation turns out to be quite cumbersome, and secondly, for most tasks it is sufficient to use a simple phenomenological formula that takes into account that for small r the interaction force between the molecules $\vec{F}(\vec{r}) = -\vec{\nabla}U(\vec{r})$ is the repulsive force, for large r - the force of displacement. Repulsion in accordance with quantum mechanical representations is due to the Pauli prohibition rule [6]. The weak attraction at large r is mainly due to the mutual polarization of each atom. The resulting force of attraction is called the Van der Waals force. Thus, when using the two-particle interaction model, the task of describing the behavior of the statistical system is reduced to choosing the type of potential $\mathrm{V}(\vec{r})$ and solving the Cauchy problem for a system of differential equations:

$$m\frac{d^2\,\vec{r_i}}{d\ t^2} = - \vec{\nabla} \sum_{i<j=1}^{N} V(\overrightarrow{r_{ij}}) \qquad (3.2)$$

One of the most commonly used phenomenological formulas for describing the potential of intermolecular interaction is the Lennard-Johnson potential:

$$V(r) = 4V_0\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \qquad (3.3)$$

where σ defines the "characteristic" length of the potential, and V_0 is the depth of the potential well, which we will later choose as units of measure for distance $\tilde{r}\ =\ r\ /\ \sigma$) and energy ($\tilde{V}^{\sim} = V(r)/V_0$). As can be seen from (3), the potential V (r) reaches its minimum value - V_0 at the point $r_{min} = 2^{\frac{1}{6}}$ σ, V (r) = 0 at the point r_0 = σ.

To select the variable *T* used to dimension the system of equations of motion (3.2), we expand the potential *V (r)* into a Taylor series near the potential minimum $r_{min} = 2^{\frac{1}{6}}$ σ. Keeping the terms of the series proportional to the first and second derivatives and citing similar terms, we finally get:

$$V(\Delta r) \approx -V_0 + \frac{18 \cdot 2^{\frac{2}{3}}}{\sigma^2} V_0 \Delta r^2 \qquad (3.4)$$

where Δr <<r_{min}.

Comparing (3.4) with a known expression for the potential energy of a harmonic oscillator

$$E=\frac{1}{2}kx^2, \qquad (3.5)$$

we conclude that

$$\chi=\frac{2\cdot 18\cdot 2^{\frac{2}{3}}}{\sigma^2} V_0 \qquad (3.6)$$

is an analogue of the spring constant of a harmonic oscillator, i.e., a particle located in the Lennard-Jones potential, at small displacements from the minimum point will perform linear harmonic oscillations with a period T=2π$\sqrt{m/\chi}$. (For example, for liquid argon, for which V_0/k_B=119.8 K ($k_B$is the Boltzmann constant).

$\sigma = 3.405 \cdot 10^{-8}$ cm, mass m=6.69·10^{-23} g, T=1.14·10^{-11} s, next we will use T for dimensioning time ($\tilde{t}=t/T$).

Passing in (3.2) to the dimensionless variables $\tilde{r} = r/\sigma$, $\tilde{V} = V(r)/V_0$ $\tilde{t}=t/T$, taking into account expression (3.6), we obtain the final expression for the dimensionless system of equations of motion

$$\frac{d^2}{d}\frac{\tilde{r}_i}{\tilde{t}^2} = -\frac{2^{\frac{7}{3}}\pi^2}{3}\overrightarrow{\widetilde{\nabla}} \sum_{i<j=1}^{N}\widetilde{V}\left(\overrightarrow{\widetilde{r_{ij}}}\right). \qquad (3.7)$$

The system of differential equations (3.7), supplemented by the initial conditions$\overrightarrow{\widetilde{r_i}}(0)$, $\overrightarrow{\widetilde{v_i}}(0)$), is a mathematical model of the statistical system under consideration.

3.3 Numerical algorithm for solving the system of equations of motion

After compiling a mathematical model of a system consisting of a large number of interacting particles, one should choose a numerical solution algorithm, the accuracy of which depends directly on the correct choice.

Analysis of low-order accuracy algorithms, such as the Euler algorithm and the Euler-Cromer algorithm, shows that these algorithms cannot ensure the conservation of energy in the time intervals considered when modeling molecular dynamics. In these conditions, it is necessary to apply computational algorithms that have a higher order of accuracy, one of which is the Verlet algorithm. We illustrate the essence of this algorithm, following [31], by the example of solving a system of equations of one-dimensional particle motion

$$\frac{dv}{dt} = a, \tag{3.8}$$

$$\frac{dx}{dt} = v \tag{3.9}$$

We write the expansion of the dependences $x_{n+1} \equiv x(t_n + \Delta t)$ and $v_{n+1} \equiv$ $\equiv v(t_n + \Delta t)$ into a Taylor series

$$x_{n+1} = x_n + \dot{x}(t_n)\Delta t + \frac{1}{2}x(t_n)(\Delta t)^2 + O[(\Delta t)^3], \tag{3.10}$$

$$v_{n+1} = v_n + \dot{v}(t_n)\Delta t + O[(\Delta t)^2] \tag{3.11}$$

Noting that $\dot{x}(t_n) = v_n,\ x\ (t_n) = \dot{v}(t_n) = a_n$will rewrite (3.10), (3.11) in the following form

$$x_{n+1} = x_n + v_n\Delta t + \frac{1}{2}a_n(\Delta t)^2 + O[(\Delta t)^3], \tag{3.12}$$

$$v_{n+1} = v_n + a_n\Delta t + O[(\Delta t)^2]. \tag{3.13}$$

By analogy with (3.12), (3.13) we write the decomposition in the Taylor series for $x_{n-1} \equiv x(t_n - \Delta t)$:

$$x_{n-1} = x_n - v_n\Delta t + \frac{1}{2}a_n(\Delta t)^2\ . \tag{3.14}$$

Add (12) and (14), we get

$$x_{n+1} + x_{n-1} = 2x_n + a_n(\Delta t)^2\ , \tag{3.15}$$

from where

$$x_{n+1} = 2x_n - x_{n-1} + a_n(\Delta t)^2. \tag{3.16}$$

Subtracting (3.14) from (3.12), we finally get

$$v_n = \frac{x_{n+1} - x_{n-1}}{2\Delta t} \tag{3.17}$$

The global error of the Verlet algorithm realized by formulas (3.16), (3.17) has the third order for the coordinate and the second order for the velocity. Note that the speed is not involved in the integration of the equations of motion; therefore, in the literature devoted to numerical methods, this algorithm is called an “implicit symmetric difference scheme”. The obvious disadvantage of the implicit difference scheme is that it is not self-starting, so you have to use a different algorithm to get the first few points.

This deficiency can be eliminated by adding and subtracting from both sides of equality (3.17) the value $x_n/2$:

$$x_{n+1} = x_n + \frac{1}{2}(x_{n+1} - x_{n-1}) - \frac{1}{2}x_{n-1} - \frac{1}{2}x_{n+1} + x_n + a_n(\Delta t)^2 =$$
$$= x_n + v_n\Delta t - \frac{1}{2}(x_{n+1} - 2x_n + x_{n-1}) + a_n(\Delta t)^2 \qquad (3.18)$$

From (3.16) we find

$$a_n = \frac{x_{n+1} - 2x_n + x_{n-1}}{(\Delta t)^2} \qquad (3.19)$$

therefore (3.18) can be written as

$$x_{n+1} = x_n + v_n\Delta t + \frac{1}{2}a_n(\Delta t)^2 . \qquad (3.20)$$

In a similar way, we rewrite (3.17) for v_{n+1} and (3.16) for x_{n+2}:

$$v_{n+1} = \frac{x_{n+2} - x_n}{2\Delta t}, \qquad (3.21)$$

$$x_{n+2} = 2x_{n+1} - x_n + a_{n+1}(\Delta t)^2 \qquad (3.22)$$

respectively.

Substituting (3.22) into (3.21), we obtain

$$v_{n+1} = \frac{x_{n+1} + v_{n+1}\Delta t + \frac{1}{2}a_{n+1}(\Delta t)^2 - x_n}{\Delta t} \qquad (3.23)$$

Then, repeating the described procedure x_{n+1} from (3.16) and substituting x_{n+1} in (3.23), after the obvious calculations, we finally learn

$$v_{n+1} = v_n + \frac{1}{2}(a_{n+1} + a_n)\Delta t. \qquad (3.24)$$

The computational scheme defined by expressions (3.20), (3.24) is mathematically equivalent to the Verlet algorithm described above. This scheme, called the velocity form of the Verlet algorithm, is self-starting, and therefore does not require the use of any additional computational algorithms. A description of other computational schemes used to solve the equations of motion is given in [32].

When using the MD method for modeling the behavior of gases and liquids, as a rule, it is assumed that the system in question is located in a certain cubic cell - the MD-cell. We assume that the MD-cell has a linear size L, its volume is $V = L^3$.

Using a cubic lattice generates six unwanted surfaces. Particles reflected from these surfaces will return inside the cell, so the edges of the cell will make a significant contribution to the macroscopic characteristics of the system, especially for systems with a small number of particles. To reduce the described effect, it is customary to introduce periodic boundary conditions [8] (figure 2.1), the mathematical formulation of which for any observable quantity A has the form:

$$A(\vec{r})=A(\vec{r}+\vec{n}L), \tag{3.25}$$

where $\vec{n} = (n_1, n_{2,} n_3)$, a $n_1 n_2 n_3$-indices of integers.

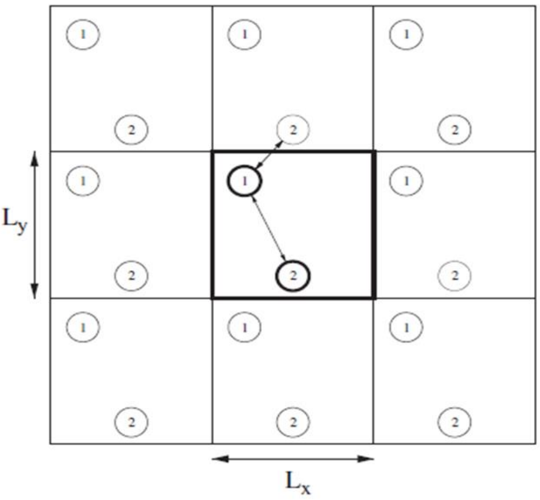


Figure 3.1 – An example of periodic boundary conditions in the two-dimensional case. The rule of the nearest particle means that the length of the vector indicated by the bidirectional arrow determines the distance between particles 1 and 2

This algorithm has the following computational implementation: when a particle crosses the face of the main cell, it returns to the cell through the opposite face at the same speed. By introducing periodic boundary conditions, the influence of faces is eliminated and a quasi-infinite volume is introduced to more accurately describe the macroscopic system, i.e. The MD cell is “embedded” in the area. Each component of the translation radius vector is a number between zero and L. For the i particle located at the point with the radius vector $\vec{r}_i$, there are particle maps at points with radii vectors $\vec{r}+\vec{n}L$, where $\vec{n}$ is an integer vector.

For the selected boundary conditions, the potential energy takes the following form

$$V(\vec{r}_1, \dots, \vec{r}_N) = \sum_{i<j} V(\vec{r}_{ij}) + \sum_n \sum_{i<j} \left(\left| \vec{r}_{-i} - \vec{r}_{-j} + \vec{n}L \right| \right) \tag{3.26}$$

In order to avoid calculating the infinite sum in (3.26), the following rule is adopted [8]: distance $|\vec{r}_{ij}|$ between particles located at points with radius vectors $\vec{r}_i, \vec{r}_j$, respectively, is defined as $|\vec{r}_{ij}| = min(|\vec{r}_{-i} + \vec{r}_{-j} \pm \vec{n}L|)$ over all $\vec{n}$.

This rule means that a particle located in the basic cell interacts with each of the N-1 particles in the basic cell or with its closest mappings (figure 2.1). It is important to understand that the use of this rule leads to the "cutting off" of the potential at distances

$$r_c > \frac{L}{2} \tag{3.27}$$

This leads to a loss of the background contribution of distant particles, therefore, in order to eliminate the effect of the finiteness of the system, the values of L should be chosen large enough so that the forces acting at distances of large L⁄2 are negligible. Note that a more correct catch is to take into account the interaction of each particle with its display. References to original works devoted to this approach and the description of computational algorithms that implement it are given in [32].

We finally formulate the algorithm of the MD method:

- Set the number of particles of the system N;
- Set the initial configuration of the system (set of coordinates $\vec{r}_i(0)$ and speeds $\vec{v}_i(0)$ particles);
- Set h - integration step of the system of differential equations (3.7);
- Set Nh is the number of steps in which the solutions of the system of differential equations (3.7) are calculated;
- Calculate in accordance with (3.20), (3.24) and taking into account the periodic boundary conditions, the values of the coordinates $\vec{r}_i$ and speeds $\vec{v}_i$, i=0,1,…N at successive times $t_n, i = 0,1, \dots Nh$.

3.3 Modeling a system consisting of a large number of particles using the molecular dynamics method

The statistical system under consideration is deterministic, since the Cauchy problem of a system of linear differential equations with constant coefficients is solved to describe its behavior. At the same time, the obtained solutions directly depend on the initial conditions $\vec{r}_i(0), \vec{v}_i(0)$ (initial system configuration). Note that their correct choice is far from a simple task (for example, it is not at all obvious in advance how to choose the initial configuration so that the system under study behaves like a fluid with a given temperature.), Therefore, we first discuss the features of the evolution of a statistical system from arbitrary initial configurations. One of the possible options for specifying the initial conditions is the placement of particles in nodes of a certain rectangular grid (the size of which, obviously, must be less than the size of the MD cell) and the assignment of their velocity vectors randomly, for example, using a random number generator with a uniform distribution law. This approach is used below in the problem of modeling a statistical system using the MD method.

To solve this problem, it is convenient to first create m-files containing descriptions:

- A function that returns the initial system configuration;
- A function that returns the instantaneous acceleration of each particle of the system and the instantaneous value of the potential energy;
- A function that returns the values of the coordinates, the components of the velocity and acceleration along the corresponding coordinate axes;
- A function that returns a composite array containing the values of the coordinates, the projections of the velocities and accelerations on the corresponding coordinate axes in the nodes of the time grid.

3.5 Method of implementation of md modeling and calculation of thermodynamic parameters

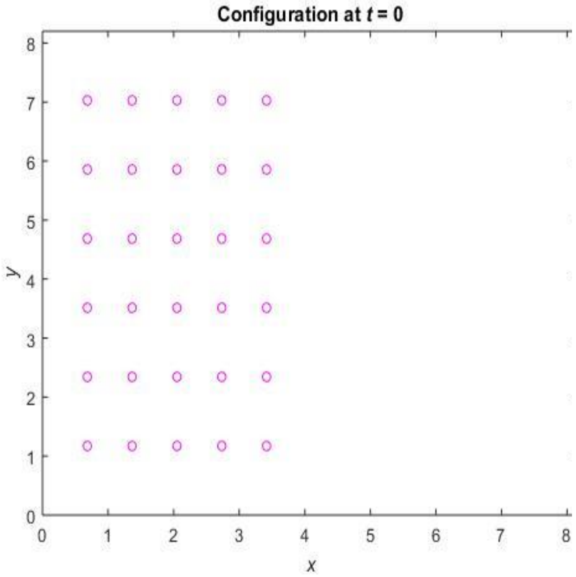


Figure 3.2 – Initial configuration of the statistical system

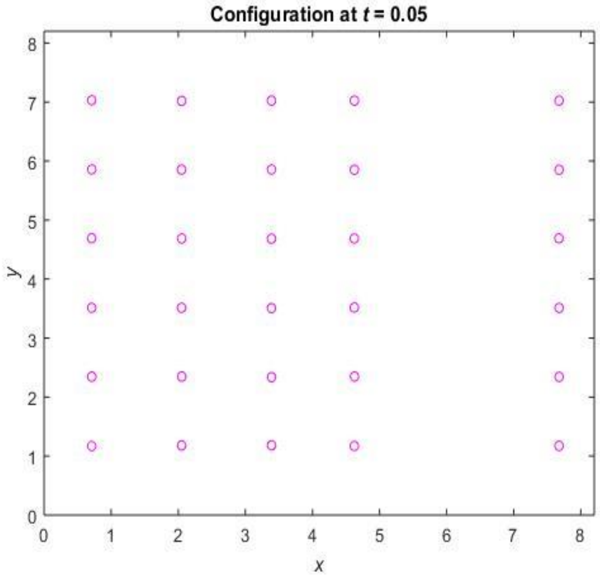


Figure 3.3 – Configuration of the statistical system at time t = 0.05

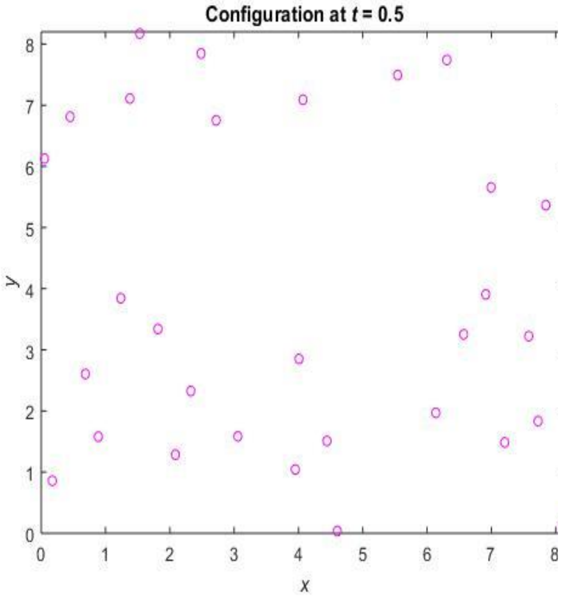


Figure 3.4 – Configuration of the statistical system at time t = 0.5

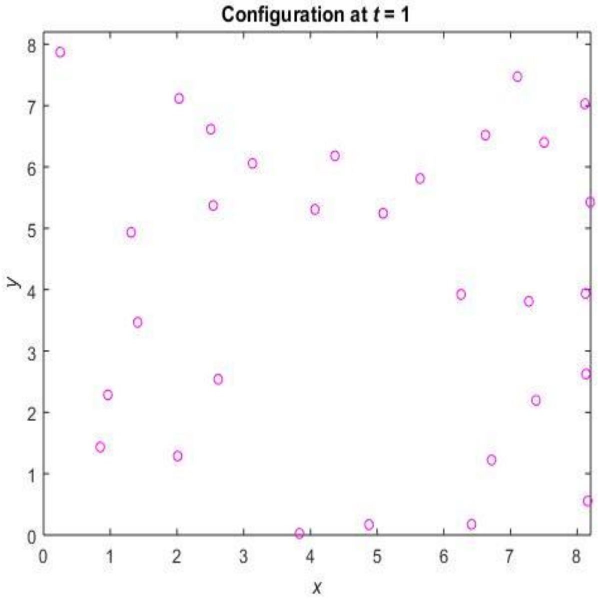


Figure 3.5 – Configuration of the statistical system at time t = 1.0

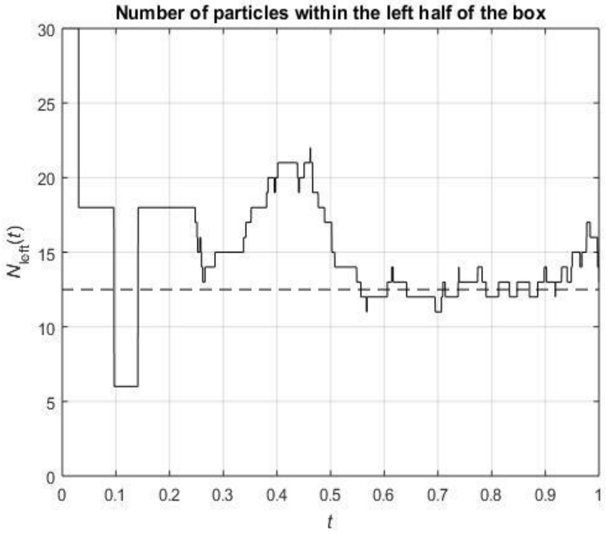


Figure 3.6 – Dependence of the number of particles in the left half of the box on time (Nleft = Nleft (t))

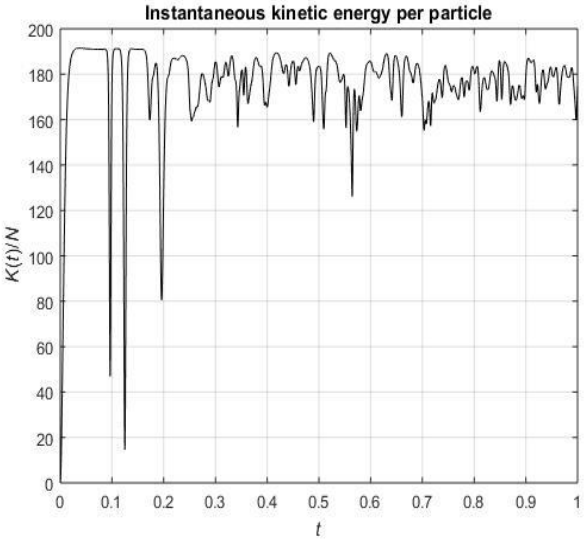
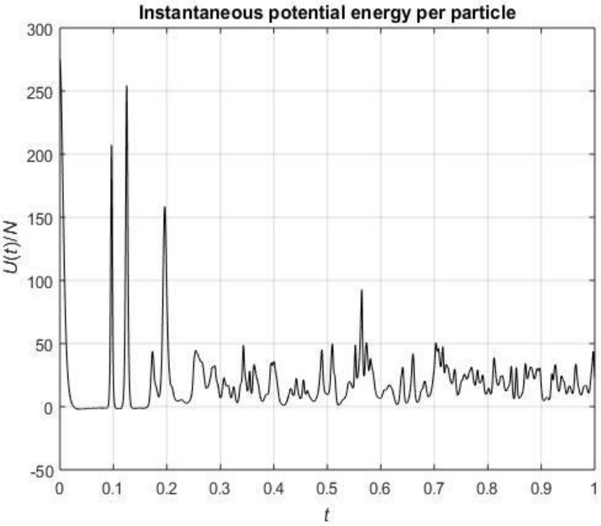


Figure 3.7 – Dependence of the kinetic energy per particle on time (Ek = Ek (t))



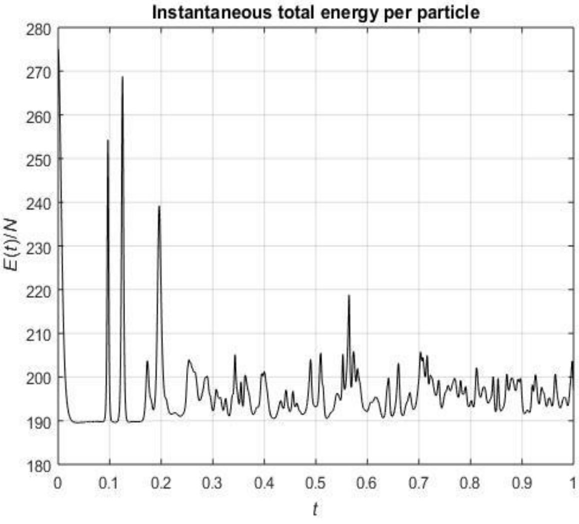


Figure 3.8 – Dependence of potential energy per particle on time (Ep = Ep (t))

Figure 3.9 – Dependence of the total energy per particle on time (E = E (t))

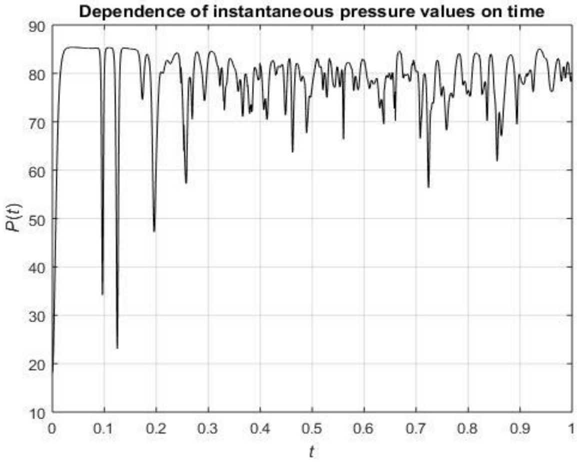


Figure 3.10 – Dependence of instantaneous pressure values on time

Analysis of dependencies presented in figure 3.6-3.10 shows that over time the system tends to an equilibrium state (relaxation process), in which the number of particles in the left and right halves of the MD cell and the total energy of the system remain approximately the same. (Note that since the values of the initial velocity are set using a random number generator, these dependencies obtained during the document recalculation will always differ from the dependencies shown in figure 3.6-3.10, but they should behave in a qualitative manner in a similar way).

CONCLUSION

This paper provides basic information about the molecular dynamics method; it is shown that its use even for a two-dimensional system with a few particles makes it possible to identify at a qualitative level a number of basic properties of statistical systems, to introduce some concepts of kinetic transport theory in liquids and gases.

MD is a fairly convenient and versatile method for conducting numerical experiments with molecular systems of various nature. However, it should be borne in mind that using the results of MD computations to refine the physical picture and determine the dynamic parameters is not a simple matter. Let us briefly list some main problems that arise here:

- The existing force fields are not universal and are intended only types of molecular structures in a certain range of external conditions (temperature and pressure);
- The results of the calculation of the trajectories depend on the numerical procedure used to solve the system of Newton's equations. Especially it concerns the choice of the thermostat type (as well as the barostat, if the calculations are performed under the condition of constant pressure);
- The requirement of ergodicity (or quasi-ergodicity for large systems) requires a special selection of suitable conditions for MD modeling.

The choice of these conditions largely depends on the surface topology of the potential energy levels of the system under consideration. In connection with the above, we note that the formal use of MD procedures most likely will not provide valuable information about the physical properties of the system. Here it is very important to compare the results of MD experiments carried out at different values of parameters and to single out those parameters on which the dynamic properties most significantly depend.

At the same time, physical intuition and understanding of the general physical picture for the phenomena under consideration are of great importance. To obtain quantitative results, it is required to simulate three-dimensional systems, which inevitably leads to an increase in the counting time. The greatest time costs fall on the formation of an equilibrium state and the calculation of forces and energy. To reduce the time spent using different approaches.

REFERENCES

1 Gould H., Tobochnik J., Christian W. An Introduction to Computer Simulation Methods Applications to Physical System. – MA, USA Inc. Boston, 2016. – Page. 142-298.

2 Borgnakke C., Sonntag R. Fundamentals of Thermodynamics – SI Version. Eight edition. University of Michigan. WILEY, 2014. – Page. 6-7.

3 Frenkel D., Smit B. Understanding Molecular Simulation – From Algorithm to Applications. Second edition. University of Amsterdam. ACADEMIC PRESS – An Imprint of Elsevier, 2001. – Page 167-200, 291-320.

4 University of California, Santa Barbara: M Shell. Other free energy techniques. 2012.URL:https://engineering.ucsb.edu/~shell/che210d/Other_free_energy_techniques.pdf.

5 Gould H., Tobochnik J. The Chemical Potential and Phase Equilibria. 2009. Clark University. URL: http://stp.clarku.edu/notes/chap7.pdf.

6 University of Oslo (UiO). Gibbs' phase rule. URL: http://kj-gibbs.uio.no/phase_rule.html.

7 Mark E. Tuckerman. Statistical Mechanics: Theory and Molecular Simulation. 2010. Oxford Graduate Texts. Page 136-138. URL: http://www.nanophysics.pl/3books/Books/Statistical_Mechanics.pdf.

8 Michael Allen. Introduction to Molecular Dynamics Simulation. 2004. URL: https://udel.edu/~arthij/MD.pdf.

9 Bjornar Jensen. Investigation into impact of solid surfaces in aqueous systems. PhD at the University of Bergen. 2016. Page 18-19, 23, 28-30.

10 Tatyana Kuznetsova. Molecular modeling for thermodynamic properties of bulk and interfacial systems. University of Bergen, Norway. 2001.

11 J. W. Eastwood and R. W. Hockney. P3M3DP–The three-dimensional periodic particle-particle/ particle-mesh program. 1980. URL: https://www.sciencedirect.com/science/article/pii/0010465580900521.

12 Block Luty and Wilfred Gunsteren. Calculating Electrostatic Interactions Using the Particle-Particle Particle-Mesh Method with Nonperiodic Long-Range Interactions. 1995. URL: https://pubs.acs.org/doi/pdfplus/10.1021/jp9518623?src=recsys.

13 H Berendsen. Molecular dynamics with coupling to an external bath. 1984. URL: https://aip.scitation.org/doi/pdf/10.1063/1.448118.

14 Philippe Hünenberger. Thermostat Algorithms for Molecular Dynamics Simulations. 2005. URL: https://pdfs.semanticscholar.org/0e83/4dcac5bfdf91a0b0b7fa5488e9324a1d51d5.pdf.

15 Birgit Strodel (Computational Biochemistry Group). Simulation of Biomolecules. URL: http://www.strodel.info/lecture3.pdf.

16 Suichi Nosé. A unified formulation of the constant temperature molecular dynamics methods. 1984. URL: https://aip.scitation.org/doi/pdf/10.1063/1.447334.

17 William Hoover. Canonical dynamics: Equilibrium phase-space

distributions. 1984.URL: https://journals.aps.org/pra/pdf/10.1103/PhysRevA.31.1695.

18 Рейф Ф. Статистическая физика. М.: Наука, 1972.

19 Матвеев А.Н. Молекулярная физика. М.: Высшая школа, 1981.

20 Farid F. Abraham, Computational statistical mechanics methodology, applications and supercomputing, Adv. Phys. 35,1(1986).

21 Anderson J, B. A random walk simulation of Schrodinger equationl/J. Chem, Phys, 63, 1499, 1975.

22 Румер Ю.Б, Рывкин М.В. Термодинамика, статистическая физика и кинетика. М.: Наука, 1977.

23 Metropolis N" Rosenbluth A, W" Rosenbluth M, N" Teller A, H" Keller E, Equation of state calculations for fast computing machines, j, Chem, Phys, 6, 1087, 1953.

24 Alder, B. J.; Wainwright, T. E. (1959). "Studies in Molecular Dynamics. I. General Method". J. Chem. Phys. 31 (2): 459.

25 Rahman, A. (19 October 1964). "Correlations in the Motion of Atoms in Liquid Argon". Physical Review. 136 (2A): A405–A411.

26 D. C. Rapaport (1996) The Art of Molecular Dynamics Simulation.

27 M. Griebel; S. Knapek; G. Zumbusch (2007). Numerical Simulation in Molecular Dynamics. Berlin, Heidelberg: Springer.

28 D. J. Evans and G. P. Morriss (2008) Statistical Mechanics of Nonequilibrium Liquids, Second Edition, Cambridge University Press.

29 Неверов В. С., Комолкин А. В., Волкова Т. Г. Исследование влияния структурной изомерии на молекулярную подвижность жидких кристаллов методом молекулярной динамики // Вестник СПбГУ. Сер. 4. Вып. 1. - 2011. - Т. 1. - С. 34-53.

30 Неверов В. С., Комолкин А. В. Компьютерное моделирование жидких кристаллов, содержащих бензол с заместителями в пара-положении // Вестник СПбГУ. Сер. 4 Вып. 1. - 2012. - Т. 1. - С. 26-41.

31 Neverov V. S., Komolkin A. V. Coarse-grain model of the benzene ring with para-substituents in the molecule // J. Chem. Phys. — 2012. — Vol. 136. — P. 094102.

32 Praprotnik M., Site L. D., Kremer K. Adaptive resolution molecular-dynamics simulation: Changing the degrees of freedom on the fly // «7. Chem. Phys. 2005. - Vol. 123. - P. 224106.

33 Frenkel D., Smit B. Understanding Molecular Simulation: From Algorithms to Applications. San Diego, 2002. - P. 638.

34 Lojkowski W., Blizzard J. R. Molecular dynamics simulation study of the liquid crystal phase in a small mesogene cluster (5cb)22 // Solid State Phenomena. 2008. - Vol. 140. - Pp. 89-96.