Humboldt University Berlin
Department of Physics
Advanced Lab course in Master Program of Polymer Science

Molecular Mechanic and Molecular Dynamic Methods

Person in charge: See announcement in guidelines

Theme:

In the framework of this lab course it will be shown how to use the molecular mechanics and molecular dynamics methods of simulation of polymers and polymeric systems.

Duration: one day

The protocol should be handed in one week after the experiment.

Literature

1. Discover © 96.0/4.0.0 manuals, MSI Molecular Simulations, Incorporated.

2. D.C. Rapaport, The Art of Molecular Dynamics Simulation, Cambridge University Press.

3. Advances in Polymer Science 116, Atomistic Modelling of Physical Properties, Springer-Verlag

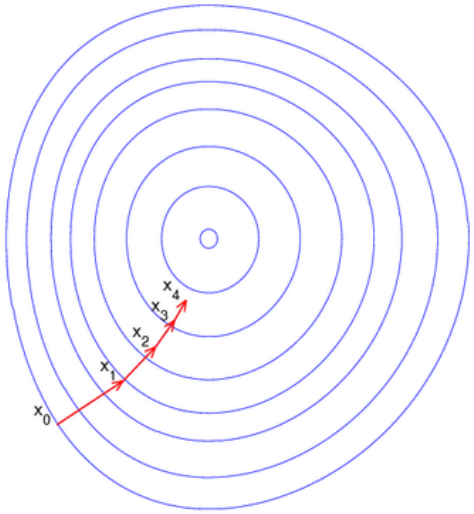
Introduction:

All molecular compounds are built from the elementary atoms. By combining certain atoms to form small units, so called monomers, larger structures, named polymers, are developed by repeated addition of the monomer. In order to study specific aspects of molecules, such as their preferred structure or reaction to changes in the ambient conditions, the atomistic interactions within the molecule have to be examined. These interactions are determined by the masses m_i and the coordinates R_i of the nuclei. The index i represents the different atoms in the molecule. The electronic properties of the atoms along with their coordinates form potential energy surfaces $E(R_i)$. A potential energy surface $E(R)$ or force field is a set of potential energy functions of inter-atomic distances and of molecular internal coordinates, which represents the energy of molecules and of assemblies of molecules normally in the electronic ground state. From the knowledge of the force field one can calculate all molecular properties which are determined by the energy of the system. The calculation of the potential energy, along with its first and second derivatives with respect to the atomic coordinates, yields the information necessary for minimisation, harmonic vibrational analysis and dynamics simulations. If an expression for $E(R_i)$ is known, the behaviour of the molecule is determined by plain mechanics and therefore the fundamental equation to approximate the structure and dynamic of a molecule is Newton's second law of motion.

$$-\frac{dE(R_i)}{dR_i} = m\frac{d^2R_i}{dt^2} \qquad \textbf{Eq. 1}$$

Molecular mechanics ignores the time evolution of the system and instead focuses on finding particular geometries and their associated energies or other static properties. This includes finding equilibrium structures, transition states, relative energies, and harmonic vibrational frequencies.

Molecular mechanics is an important method for exploring the potential energy surface which allows finding configurations that are stable points on the surface. This means finding points in the configuration space where the net force on each atom vanishes (local minima on the surface). By simply minimising the energy, stable conformations can be identified. Perhaps more important, the addition of external forces to the molecule in the form of restraints allows for the development of a wide range of modelling strategies. For example, the question 'How much energy is required for one molecule to adopt the shape of another?' can be answered by forcing specific atoms to overlap of a template structure during an energy minimisation. The "steepest descent" method of a local minimum search is given below as an example. The equipotential lines are indicated in blue. The program moves the atoms of the molecule in small steps in the direction of the negative of the harmonic vibrational frequencies of the potential energy function: i.e. $x_o \rightarrow x_1 \rightarrow x2 \rightarrow x3 \rightarrow x4$ on the picture below.



Source: http://upload.wikimedia.org/wikipedia/commons/f/ff/Gradient_descent.svg (2012-12-10)

The solution of Eq. 1 using an empirical fit to the potential energy surface $E(R_i)$ is called molecular dynamics. In this sense molecular dynamics solves the classical Newton's equations (**Eq. 1)** of motion for a system of N atoms interacting according to a potential energy force field. During dynamics simulations the system undergoes conformational and momentum changes so that different parts of the phase space accessible to the molecule can be explored. The conformational search capability of dynamics is one of its most important uses.

By providing several mechanisms for controlling the temperature and pressure of simulated systems, molecular dynamics also allows you to generate statistical ensembles from which various energetic, thermodynamic, structural and dynamic properties can be calculated.

The advantages of molecular mechanics are clear: it is much faster in comparison with molecular dynamics simulations. On the other hand structure minimisations always end up in the nearest minimum on the potential surface. One cannot give algorithms for finding the global minimum and that is why molecular mechanics is some kind of art. In addition minimisation does not take into account time evolution of the system.

1. Practical instructions:

During the lab course you will first familiarize yourself with the software: learn how to build a molecule, run molecular mechanic and molecular dynamic simulations. You will perform simulations of butane and polyethylene molecules.

The tutor will demonstrate you the software basics. Build a butane molecule; find out, how atoms of different type can be defined, how to change bonds, etc. Find out, how to save the structure, how to measure bond length, bond angle, and dihedral angles.

2. Molecular mechanics:

The force field used in this lab course is the so called *pcff force field* and it is supplied with the provided software. It is designed for the simulation of polymer and organic material systems. The pcff force field and its graphic illustration are presented below (Index 0: equilibrium; *b*: bond distance; θ: bond angle; φ: torsion angle; χ: out of plane distance; *K, H, F, V, A, B*: constants; *q*: charge, *r*: distance between specified atoms; ε: dielectrical constant).

$$E_{pot} = \sum_b K(b-b_0)^2 + \sum_\theta H(\theta-\theta_0)^2$$

(1) (2)

$$+ \sum_\varphi V\left[1+\cos(\varphi-\varphi_0)\right] + \sum_\chi K_\chi \chi^2$$

(3) (4)

$$+ \sum_b \sum_{b'} F_{bb'}(b-b_0)(b'-b_0') + \sum_\theta \sum_{\theta'} F_{\theta\theta'}(\theta-\theta_0)(\theta'-\theta_0')$$

(5) (6)

$$+ \sum_b \sum_\theta F_{b\theta}(b-b_0)(\theta-\theta_0) + \sum_b \sum_\varphi (b-b_0)V\cos\varphi$$

(7) (8)

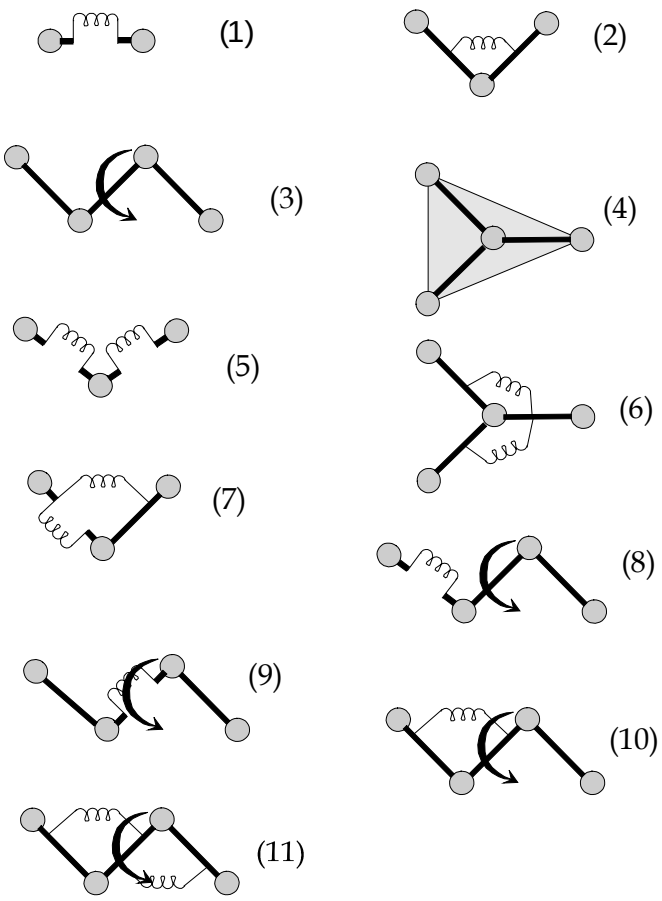
$$+ \sum_{b'} \sum_\varphi (b'-b'_0)V\cos\varphi + \sum_\theta \sum_\varphi (\theta-\theta_0)V\cos\varphi$$

(9) (10)

$$+ \sum_\varphi \sum_\theta \sum_\theta K_{\varphi\theta\theta'}\cos\varphi(\theta-\theta_0)(\theta'-\theta'_0)$$

(11)

$$+ \sum_{i>j} \frac{q_i q_j}{\varepsilon r_{ij}} + \sum_{i>j}\left[\frac{A_{ij}}{r_{ij}^9} - \frac{B_{ij}}{r_{ij}^6}\right]$$



2.1 Perform molecular mechanics – minimisation of the butane structure.
Measure the bond distances and angles again and compare with the initial structure. Pay attention especially to the dihedral angle.

2.2 Repeat the lesson 1.2 for a few random dihedral angles ranging from –180° to 180°. Note dihedral angles and the total Energy $E(\varphi)$ of the minimized structures. Explain the results.

3. Molecular dynamics:

3.1 Perform molecular dynamic simulation of butane at 500K for 1 nanosecond. Save the output structures in the history file each 100 *fs*. Analyse the history of the torsion angle and produce its histogram. Calculate the dependence of the potential energy on the torsion angle from the histogram.

3.2 Perform molecular dynamic simulation of butane at 200K for 1 nanosecond. Save the output structures in the history file each 100 fs. Analyse the history of the torsion angle and produce its histogram. Explain the difference with the simulation at 500K.

3.3 This task is a dynamic simulation of an alkyl polymer chain containing 60 carbons. Simulate the chain for 100ps at 500K first to equilibrate the structure. Run the second simulation over 600ps at 500K, set up saving of the history file every 500fs.

Determine the Kuhn segment length for the polyethylene chain according to the following equation.

$$\left\langle R^2 \right\rangle = Ll$$

R end to end distance
L contour length (the length of a fully stretched chain, i.e. in all trans conformations)
l Kuhn segment.

Calculate $<R^2>$ from the end-to-end distance histogram.

4. Dependence of molecular conformation on its chemical structure

4.1 Polymerise 20 ethane repeat units to an alkyl chain with all trans-conformation and perform a minimisation.

4.2 Replace one carbon atom in the centre of the minimised alkyl chain by a sulphur atom and perform a minimisation.
Discuss the difference between the two structures.