

Implementation and Application of the MM3 Force Field

Molecular dynamics (MD) is a classical computational method which is used to model atoms directly. In a typical MD simulation, the forces on each atom are calculated and used to solve Newton's equations of motion. These forces are described by a force field which defines what kinds of interactions will be modelled. MM3 is one such force field which was used in one of the papers in my Preliminary exam.^{1,2} In the paper, the researchers modelled an organic molecule to investigate vibrations. For my project, I have simulated a single cyclohexane molecule in the MM3 force field.³

The forces simulated in the MM3 force field are bond stretching, angle bending, torsion, the stretch-bend interaction, the torsion-stretch interaction, the bend-bend interaction, and the van der Waals' Interactions. I implemented all of these based on the original paper. Although the article provided the potentials for these interactions, they failed to include the forces. However, forces can be derived from potentials by taking the derivative with respect to the coordinate of motion.

$$F(x) = - \frac{dU(x)}{dx} \quad 1$$

Once these forces were derived, it was simply a matter of implementing the system. The first step was to define classes for both the atoms and the bonds between the atoms. The key for my implementation was defining atoms as a handle class which enabled me to reference the same set of atoms in various functions and change them in many ways while only having one unique set of atoms. The bonds were defined by two atoms and throughout the code, there is no assumption of which atom is first.

The first force is the bond stretching force. This force is similar to a spring force and acts on each bond. In this case, a Morse potential was used rather than a simple harmonic oscillator model. The Morse potential is considered better because it includes the effects of bond breaking.

Next was the angle bending force. This was modeled with a similar equation to the bond stretching but acted along the angle direction rather than along the length of a bond. The primary challenge for this force was finding all the angles in the molecule. Since an angle is formed when two bonds share a common atom, which is how I defined them. Once the angles were defined, it was simply a matter of determining the direction each force acted in.

After the angle bending force, I implemented the torsion force. This is the first force which can be a little tricky to visualize. Torsion is defined by a torsion angle which is the angle between a bond and the plane defined by two other bonds which form two angles. A torsion group is characterized by two angles which share a common bond. After finding the torsion groups, it is necessary to define the direction of force. In this case it is in the ω direction, toward the plane formed by the other angles. To define this direction, I calculated the vectors

normal to two planes defined by the angles on either side of the torsion group. The force direction was defined by the cross product of these two normal vectors. In this case, a three term Fourier series expansion was used to define the torsion force. In other words, a third order approximation of the torsion function was used.

Next was the stretch-bend force. This is another three-body interaction which comes from the fact that when the angle between atoms reduces, their bond length increases to relieve some of the potential energy. This force acts on each bond in an angle group. It is a function of the bond lengths and the angle between the bonds.

After the torsion-stretch interaction, I implemented the bend-bend interaction. This type of force acts on two angles which share a common vertex. It is a 5-body interaction and the most complex to implement. It required finding all angles in the sample and then finding all pairs of angles which share a center atom. In the case of a cyclohexane molecule, this only occurs for H-C-H and C-C-C angles.

The final force in the MM3 force field is the van der Waals force. This is a generic force between two non-bonded atoms. It can be modelled several ways including Lennard-Jones or Mie potentials. In this case, a Buckingham potential was used. This potential takes the form

$$E = Ae^{-\alpha r} - \frac{C}{r^6} \quad 2$$

Specifically, the equation used was

$$E = \epsilon \left\{ -2.25 \left(\frac{r_v}{r} \right)^6 + 1.84 * 10^5 \exp \left[-12.00 \left(\frac{r}{r_v} \right) \right] \right\} \quad 3$$

The main issue with this type of potential is what happens as r goes to 0. In this case, the potential energy goes toward negative infinity. This means that atoms which are close will become locked together. This behavior can be seen in the implemented code if a random initial velocity is applied. For this reason, an initial velocity of zero was used for my simulations. This prevents the simulation from running into the kind of trouble where it would lead to unrealistic results.

Once the model was complete, I moved on to constructing the molecule. This presented some issues since it is difficult to find the 3D coordinates of a cyclohexane molecule. As a result, I decided to estimate the shapes and sizes between bonds of a chair shaped molecule. The chair shape has the carbon atoms arranged in a hexagon in the x-y projection with each carbon atom offset from its neighbors in the z direction. Two hydrogen atoms are attached to each carbon with one pointing in the positive or negative z-direction depending on the carbon's offset and the other at a roughly 120-degree angle between the other hydrogen and the projection of the two carbon atoms. I decided that I would approximate this shape and allow the molecule to oscillate according to the forces acting on it. Doing this, it was possible to see the equilibrium bond lengths which match perfectly with the reported figures in the original MM3 paper and

also the period of each of these oscillations. All of this indicates that implementation was successful and that I have produced the MM3 force field.

References

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