Classical dynamics

When we are dealing with heavy atoms and high enough energy or temperature, it is often sufficiently accurate to neglect quantum effects and calculate the time evolution of a system (such as an atom or a collection of atoms) using the classical equation of motion, Newton's second law, $\vec{F} = \frac{d\vec{P}}{dt}$. Here $\vec{F}$ is the force acting on the classical particle and $\vec{P}$ is the momentum given by $\vec{P} = m\vec{v}$. Since the velocity is the first derivative of position with respect to time, the equation of motion is a second order differential equation for the position of the particle as a function of time (the second derivative being the acceleration)

$$\frac{d^2 x(t)}{dt^2} = F/m \ .$$

In most cases of interest in chemistry, the force is *conservative*, i.e. it can be written as the differential of a scalar function, the potential energy, $V(x)$. In one dimensional systems $F = -dV/dx$. The force is then only a function of the coordinate of the particle, $F(x)$, and not, for example, dependent on the velocity.

The problem of calculating the time evolution of such a system, therefore, reduces to the problem of finding a good representation of the potential energy as a function of the coordinates of the atoms and then solving the second order differential equation for the classical trajectories of the atoms. We will first focus on the second aspect of this problem. We will use a finite difference approximation to calculate numerically the trajectory for a given initial condition and a given potential energy function. The finite difference algorithm is called the Verlet algorithm. Then, we will examine a few potential functions which are commonly used to represent approximately the interaction between atoms.

Simple derivation of the Verlet algorithm

Here, time will be discretized, i.e. time evolves in discrete steps $\Delta t = h$, but the spacial coordinates will not be discretized. To begin with, we will focus on a one-dimensional problem for simplicity, and then generalize the algorithm to three-dimensional space.

Let x_k be the position after k timesteps, i.e. $x_k = x(t = kh)$. The central finite difference approximation for the second derivative is

$$\ddot{x}_k = \frac{x_{k+1} + x_{k-1} - 2x_k}{h^2} \ .$$

16

Inserting this into the left hand side of the equation of motion above gives the most commonly used algorithm in classical molecular dynamics simulations, the Verlet algorithm

$$x_{k+1} = 2x_k - x_{k-1} + h^2 F(x_k)/m .$$

Since the differential equation is second order, we need to know two points to get the recursion started.

Derivation using Taylor's expansions

The Verlet algorithm can also be derived using Taylor expansions. Then it becomes clearer what the accuracy of the algorithm is, in particular how the error scales with the size of the timestep. Taylor expanding $x(t + h)$ about $x(t)$ gives

$$x(t + h) = x(t) + h\dot{x}(t) + \frac{h^2}{2} \ddot{x}(t) + \frac{h^3}{3} x^{(3)} + O(h^4) .$$

Expanding $x(t - h)$ gives a similar expression, except the odd terms have a minus sign

$$x(t - h) = x(t) - h\dot{x}(t) + \frac{h^2}{2} \ddot{x}(t) - \frac{h^3}{3} x^{(3)} + O(h^4) .$$

When the two expressions are added, the odd terms cancel

$$x(t + h) + x(t - h) = 2x(t) + h^2 \ddot{x}(t) + O(h^4) .$$

This expression is general, valid for any function $x(t)$ that is differentiable enough times. The equation of motion for classical dynamics can now be used to eliminate the second derivative

$$x(t + h) + x(t - h) = 2x(t) + h^2 F(x(t))/m + O(h^4) .$$

The Verlet algorithm is obtained by neglecting the fourth and higher order terms. It turns out that this algorithm is 'stable', i.e. the error made at any given step tends to decay rather than magnify later on. There is no guarantee for such behaviour in finite difference algorithms. Some are stable and some are not. The easiest way to find out whether an algorithm is stable is to try it and see if it works.

Derivation of the Velocity Verlet algorithm

In classical mechanics it is possible to know simultaneously both the position and velocity of particles (particles being atoms, for example). A classical system is often represented as a point in 'phase space', a space of all the coordinates and momenta of particles in the system. Knowing the position and velocity (or momentum) at one point

in time completely specifies the state of the system and, through the equation of motion, the future (and past) motion of the particles, as long as the force acting on the particles are known. The velocity, however, does not appear explicitly in the Verlet algorithm. If it is needed, for example, to calculate the kinetic energy or to implement some kind of temperature control (modifications of the kinetic energy), a central finite difference estimate can be used, $\dot{x}_k = (x_{k+1} - x_{k-1})/2h$. It is a bit awkward that $\dot{x}_k$ cannot be found until x_{k+1} has been calculated. In starting up a calculation, we typically know where the particle is and we have some idea of what velocity it has (for example by knowing the kinetic energy), but this is not enough to start the Verlet algorithm because the positions at two adjacent timesteps are needed. Given the coordinate $x(0)$ and velocity $\dot{x}(0)$, the coordinate at a previous step $x(-h)$ needs to be constructed.

A different algorithm, the Velocity Verlet algorithm, explicitly includes the velocity at each step and is 'self-starting' from the position and velocity at the initial time. It is mathematically identical to the original Verlet algorithm in the sense that it generates the same trajectory in the absence of roundoff errors in the computer.

Any $n-th$ order differential equation can be reduced to a set of n first order differential equations. In particular, the classical equation of motion $\ddot{x}(t) = F(x)/m$ is second order and can be reduced to two first order equations. Let $v(t) = \dot{x}(t) = dx/dt$ and the two equations are

$$\dot{x}(t) \;=\; v(t) \tag{1}$$

and

$$\dot{v}(t) \;=\; F(x(t))/m \tag{2}.$$

A finite difference algorithm can again be derived using Taylor expansions. Starting with $x(t + h)$

$$x(t + h) \;=\; x(t) \;+\; h\dot{x}(t) \;+\; \frac{h^2}{2}\,\ddot{x}(t) \;+\; O(h^3) \;.$$

Using $v(t)$ to eliminate $\dot{x}$ and F/m to eliminate $\ddot{x}$ gives

$$x(t + h) \;=\; x(t) \;+\; hv(t) \;+\; \frac{h^2}{2}\,\frac{F(x(t))}{m} \;+\; O(h^3) \tag{1b}.$$

Then, expanding the second function, $v(t + h)$

$$v(t + h) \;=\; v(t) \;+\; h\dot{v}(t) \;+\; \frac{h^2}{2}\,\ddot{v}(t) \;+\; O(h^3) \;.$$

We can use F/m to eliminate $\dot{v}$, but we need to develop an expression for $\ddot{v}$ in terms of known quantities. This can be done by expanding $\dot{v}(t + h)$

$$\dot{v}(t + h) \;=\; \dot{v}(t) \;+\; h\ddot{v}(t) \;+\; O(h^2) \;.$$

18

It is enough to go up to order h^2 here because we only need an approximation that is good to order h^3 to the quantity $\frac{h^2}{2}\ddot{v}(t)$. Multiplying by $h/2$ and rearranging, gives

$$\frac{h^2}{2}\ddot{v}(t) \;=\; \frac{h}{2}\left(\dot{v}(t+h) \;-\; \dot{v}(t)\right) \;+\; O(h^3)$$

so, the expression for $v(t+h)$ becomes

$$v(t+h) \;=\; v(t) \;+\; h\dot{v}(t) \;+\; \frac{h}{2}\left(\dot{v}(t+h) \;-\; \dot{v}(t)\right) \;+ O(h^3)\;.$$

Using the equation of motion, this can finally be rewritten as

$$v(t+h) \;=\; v(t) \;+\; \frac{h}{2m}\left(F(x(t+h)) \;+\; F(x(t))\right) \;+ O(h^3) \qquad (2b).$$

Schematically, the velocity Verlet algorithm is as follows

Given x_k and v_k and an expression for $F(x)$

Step 1:   calculate $x_{k+1} \;=\; x_k \;+\; h\,v_k \;+\; h^2\,F(x_k)/2m$

Step 2:   evaluate $F(x_{k+1})$

Step 3:   calculate $v_{k+1} \;=\; v_k \;+\; \frac{h}{2m}\left(F(x_k)+F(x_{k+1})\right)$

Now all quantities for the new step, $k+1$, have been found, go back to step 1.

Generalization to many atoms in three dimensions:

The Verlet algorithm can easily be generalized to higher dimensions and many atoms. For N atoms in three dimensional space, the potential function depends on 3N coordinates, $V(x1, y1, z1, x2, y2, z2, x3, \ldots, xN, yN, zN) \;=\; V(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)$. The force on atom number i is

$$\vec{F}_i \;=\; -\nabla_i\, V(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_i, \ldots, \vec{r}_N)$$

where the subscript i on the gradient operator means that the derivatives should be taken with respect to coordinates of atom i. Writing each cartesian component separately

$$Fxi \;=\; -\frac{d}{dxi}\, V(x1, y1, z1, x2, y2, \ldots, xi, \ldots)$$

$$Fyi = -\frac{d}{dyi} V(x1, y1, z1, x2, y2, \ldots, xi, \ldots)$$

$$Fzi = -\frac{d}{dzi} V(x1, y1, z1, x2, y2, \ldots, xi, \ldots) \ .$$

A recursion relation given by the Verlet algorithm or the velocity Verlet algorithm can be used for each [coordinate,velocity] pair, but they all get coupled together through the force, which generally depends on coordinates of all the atoms. Let $x1_k$ be the x coordinate of atom 1 at timestep k and $y1_k$ be the y coordinate of atom 1 at timestep k, etc. Furthermore, let v_x denote the x component of the velocity and v_y denote the y component and v_z the z component. The force components are $Fxi_k \equiv Fxi(x1_k, y1_k, \ldots, yN_k)$. Then a schematic algorithm for N atoms in three dimensions can be written as follows:

Given $x1_k, y1_k, \ldots, yN_k$ *and* $u1_k, v1_k, \ldots, vN_k$ *and an expression for* $Fx1_k, Fy1_k, \ldots, FyN_k$

Step 1: *calculate* $x1_{k+1} = x1_k + h\ v_x1_k + h^2\ Fx1_k/2m$

$\qquad\qquad\qquad y1_{k+1} = y1_k + h\ v_y1_k + h^2\ Fy1_k/2m$

$\qquad\qquad\qquad z1_{k+1} = z1_k + h\ v_z1_k + h^2\ Fz1_k/2m$

$\qquad\qquad\qquad \ldots$

$\qquad\qquad\qquad zN_{k+1} = zN_k + h\ v_zN_k + h^2\ FzN_k/2m$

Step 2: *evaluate* $Fx1_{k+1}, Fy1_{k+1} \ldots, FzN_{k+1}$

Step 3: *calculate* $v_x1_{k+1} = v_x1_k + \frac{h}{2m}(Fx1_k + Fx1_{k+1})$

$\qquad\qquad\qquad v_y1_{k+1} = v_y1_k + \frac{h}{2m}(Fy1_k + Fy1_{k+1})$

$\qquad\qquad\qquad \ldots$

$\qquad\qquad\qquad v_zN_{k+1} = v_zN_k + \frac{h}{2m}(FzN_k + FzN_{k+1})$

Now all quantities for the new step, $k+1$, have been found, go back to step 1.

Potential energy functions

In calculating the dynamics of atoms and molecules, it is very important to choose a potential function that accurately mimics the system of interest. The potential function describes how the potential energy of a system of atoms depends on the coordinates of the

atoms. It is assumed here that the electrons adjust to new atomic positions much faster than the motion of the atomic nuclei (this is called the Born-Oppenheimer approximation) and the potential function that is needed for the nuclear motion is strictly the energy obtained after calculating the electronic wavefunction keeping the atomic coordinates fixed. The calculation of the electronic wavefunction for a system of many atoms is very difficult. Most often, a simple functional form is assumed for the potential function and the parameters adjusted to reproduce some experimental or theoretical data. Those are called empirical or semi-empirical potential functions. Although we use the opportunity here to briefly discuss potential functions in the context of classical simulations, the same considerations and functions apply when the motion of the atoms and molecules is treated quantum mechanically.

In principle, the interaction potential of N atoms can be expanded in a many-body expansion

$$V(r_1, r_2, \ldots, r_N) = \sum_i v_i(\vec{r}_i) + \sum_i \sum_{j>i} v_2(\vec{r}_i, \vec{r}_j) + \sum_i \sum_{j>i} \sum_{k>j>i} v_3(\vec{r}_i, \vec{r}_j, \vec{r}_k) + \ldots$$

where the first sum is over one-body terms, the second sum over pairwise interactions, the third one over three-body contributions, etc. The one-body terms arise if an external field is applied (for example, the interaction with an external electrical field, or the potential describing the wall of a container). The pairwise interactions are usually most important and are at short range repulsive due to repulsion of the two electron clouds and at long range attractive due to the induced-dipole/induced-dipole interactions. The three-body terms arise because the interaction of a pair of atoms is modified by the presence of a third atom. For rare gases, the pairwise potentials alone describe quite well the potential energy function, but even there the three-body corrections are significant (amounting to ca. 10% in the binding energy of the crystals of heavier rare gases). For systems with strong, bonding interactions, the many-body expansion is a very poor approach, because the expansion converges very slowly.

The most commonly used pair potential is the Lennard-Jones potential

$$v(r) = 4\epsilon \left(\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right)$$

where the first term describes the repulsion at short range as the electron clouds overlap more than is optimal and the second term represents the long range attraction. The form of the second term r^{-6} has the correct behaviour for the induced-dipole/induced-dipole interaction. The form of the repulsive term is, however, not supported by theoretical calculations and is simply chosen for convenience.

A more accurate pair potential form, for example, for describing the interaction of rare gas atoms is

$$v(r) = Ae^{-\alpha r} - f_\alpha(r) \frac{C}{r^6} \, .$$

The overlap of the closed shell electron clouds is usually well described with an exponential form. The function $f_\alpha(r)$ is a switching function, which is 1 at long range but goes to zero at short range and prevents the attractive energy term from diverging.

Bonded interactions, where the attractive interaction comes from the formation of a chemical bond, is better described with a Morse potential.

$$v(r) \; = \; D\left(e^{-2\alpha(r-r_0)} \; - \; 2e^{-\alpha(r-r_0)}\right) \; .$$

The attraction decays exponentially as the overlap of the electron clouds decreases. In addition to this exponential attraction, a longer range van der Waals attraction should be added, but in comparison to chemical bond energies, this can often be neglected.

When bonding constraints need to be taken into account, for example, when the number of bonded neighbors is small and the angle between bonds has a prefered value, the many-body terms are very important and the potential function becomes quite complicated. One good example is carbon, which only bonds to at most 4 other atoms if sp^3 hybridized (as opposed to rare gas atoms that can surround themselves with up to 12 near neighbors), but in different hybridization states will prefer 2 or 3 neighbors. A great deal of effort in theoretical chemistry goes into the development of accurate and yet convenient functional forms that take into account many-body effects.

One functional form that has been used extensively in modeling chemical reactions involving formation and breaking of chemical bonds is the LEPS form. As an example, the 'extended LEPS' potential for a three atom system A, B and C, capable of describing a substitution reaction

$$A \; + \; BC \; \rightarrow \; AB \; + \; C$$
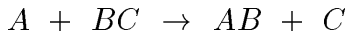
is of the form

$$E(r_{ab}, r_{bc}, r_{ac}) \; = \; \frac{Q_{ab}}{1+a} \; + \; \frac{Q_{bc}}{1+b} \; + \; \frac{Q_{ac}}{1+c} \; -$$

$$\left[\frac{J_{ab}^2}{(1+a)^2} \; + \; \frac{J_{bc}^2}{(1+b)^2} \; + \; \frac{J_{ac}^2}{(1+c)^2} \; - \; \frac{J_{ab}J_{bc}}{(1+a)(1+b)} \; - \; \frac{J_{bc}J_{ac}}{(1+b)(1+c)} \; - \; \frac{J_{ab}J_{ac}}{(1+a)(1+c)}\right]^{\frac{1}{2}}$$

The parameters can be chosen in such a way that the energy is large when all three atoms are close to each other, i.e. when only one bond is allowed at a time. The parameters a, b and c can be adjusted to change the height and location of the potential barrier for the reaction. The functional form is inspired by approximate calculations of the interaction of three H atoms. The Qs stand for Coulomb interactions between the electron clouds and the nuclei and the Js stand for exchange interactions (terms that arise because of the indistinguishability of the quantum mechanical electrons). A typical form for the distance dependence of the Q and J terms is similar to the Morse potential

$$Q(r) \; = \; \frac{D}{2} \; \left(\frac{3}{2}e^{-2\alpha(r-r_0)} \; - \; e^{-\alpha(r-r_0)}\right)$$

and

$$J(r) \; = \; \frac{D}{4} \left(e^{-2\alpha(r-r_0)} \; - \; 6e^{-\alpha(r-r_0)} \right) \; .$$

The bonded interaction of two atoms is $Q+J$ (in the singlet state, where unpaired electrons on each atom have opposite spin and can pair up as the atoms approach each other) and the non-bonded interaction is $Q - J$ (purely repulsive as would be the case if the unpaired electrons have the same spin, a triplet).

Derivation of the force for L-J potentials:

In calculating the classical dynamics of atoms it is necessary to be able to evaluate the force acting on the atoms. Given a potential energy surface, the task is to calculate the gradient

$$\vec{F}_i \; = \; -\vec{\nabla}_i \, V(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_i, \ldots)$$

with respect to the coordinates of each atom. This equation says that the force acting on atom i is obtained by taking the potential function, which depends on the coordinates of all the atoms in the system, and differentiate it with respect to the coordinates of atom i. This can be a bit involved when the potential function is complicated. Fortunately, Mathematica and similar programs can be of great help.

As a simple example, a derivation of the force acting on atoms interacting via a pairwise additive potential is given below. The total potential energy of the system is a sum over a potential, $v(r)$, for each distinct pair of atoms

$$V(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) \; = \; \sum_i^N \sum_{j<i}^N v(r_{ij})$$

where r_{ij} is the distance between atoms i and j.

The distance can be obtained from the coordinates of the atoms (which refer to some arbitrary origin of the coordinate system)

$$r_{ij} = \sqrt{(\vec{r}_i - \vec{r}_j) \cdot (\vec{r}_i - \vec{r}_j)} = \sqrt{x_{ij}^2 + y_{ij}^2 + z_{ij}^2}$$

where $x_{ij} = x_i - x_j$.

The force on atom k is a vector pointing in the direction of the steepest descent of the potential energy. The expression is

$$\vec{F}_k = -\vec{\nabla}_k \, V(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_k, \ldots)$$

$$= -\sum_{j \neq k} \vec{\nabla}_k \, v(r_{kj})$$

$$= -\sum_{j \neq k} \left(\hat{x} \frac{\partial}{\partial x_k} + \hat{y} \frac{\partial}{\partial y_k} + \hat{z} \frac{\partial}{\partial z_k} \right) v(r_{kj}) \, .$$

Using the chain rule for differentiation, we can see that $\frac{\partial}{\partial x_k} = \frac{\partial}{\partial x_{kj}}$ since $\frac{\partial x_{kj}}{\partial x_k} = 1$. Therefore, the derivative of the pair potential above can be written in terms of v', i.e. the derivative with respect to the argument of the function. For the x component of the force

$$\frac{\partial v(r_{kj})}{\partial x_{kj}} = v'(r_{kj}) \frac{\partial r_{kj}}{\partial x_{kj}} = \frac{x_{kj}}{r_{kj}} v'(r_{kj}) \, .$$

For all three components

$$\vec{\nabla}_{r_k} v(r_{kj}) = \frac{v'(r_{kj})}{r_{kj}} \left(x_{kj} \hat{x} + y_{kj} \hat{y} + z_{kj} \hat{z} \right)$$

$$= \frac{(\vec{r}_k - \vec{r}_j)}{r_{kj}} v'(r_{kj})$$

$$= \hat{r}_{kj} \, v'(r_{kj})$$

where $\hat{r}_{kj}$ is a unit vector in the direction from atom j to k.

In the particularly simple case where the pair poential is a Lennard-Jones potential

$$v(r) = 4\epsilon \left(\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right)$$

we get

$$v'(r) = 4\epsilon \left(-12 \frac{\sigma^{12}}{r^{13}} + 6 \frac{\sigma^6}{r^7} \right) \, .$$

The force on atom k becomes

$$\vec{F}_k = -\sum_{j \neq k} \frac{(\vec{r}_k - \vec{r}_j)}{r_{kj}} \frac{24\epsilon\sigma^6}{r_{kj}^8} \left(1 + 2 \left(\frac{\sigma}{r} \right)^6 \right) \, .$$