

# MOLECULAR DYNAMICS

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# Introduction

Science requires both **observation** and **comprehension**. Without observation there are no facts to be comprehended; without comprehension science is mere documentation. The basis for comprehension is theory, and the language of theoretical science is mathematics. Theory is constructed on a foundation of hypothesis; the fewer the hypotheses needed to explain existing observations and predict new phenomena, the more ‘elegant’ the theory – Occam’s razor.

The question arises as to how **simulation** is related to physical theory.

What distinguishes computer simulation in general from other forms of computation, if such a distinction can be made, is the manner in which the computer is used: instead of merely performing a calculation, the *computer becomes the virtual laboratory* in which a system is studied – *a numerical experiment*.



The equations of motion can only be solved numerically. Because of the nature of the interatomic interaction, exemplified by the Lennard-Jones potential with a strongly repulsive core, atomic trajectories are *unstable* in the sense that an infinitesimal perturbation will grow at an exponential rate, and it is fruitless to seek more than moderate accuracy in the trajectories, even over limited periods of time. Thus a comparatively low-order numerical integration method often suffices; whether or not this is adequate emerges from the results, but the reproducibility of MD measurements speaks for itself.

Where softer interactions are involved, such as harmonic springs or torsional interactions, either or both of which are often used for modeling molecules with internal degrees of freedom, a higher-order integrator, as well as a smaller timestep than before, may be more appropriate to accommodate the fast internal motion. The numerical treatment of constraints introduces an additional consideration.



MD deals with a world that, while intuitively appealing to late nineteenth-century science, not to mention antiquity, has little concern for anything that is ‘nonclassical’.

This fact has in no way diminished the power and effectiveness of the method.



# BASIC MOLECULAR DYNAMICS



# Model Selection

The interactions, again at the simplest level, occur between pairs of atoms and are responsible for providing the *two principal features of an interatomic force*.

The first is a *resistance to compression*, hence the interaction repels at close range. The second is to bind the atoms together in the solid and liquid states, and for this the *atoms must attract each other over a range of separations*.

Potential functions exhibiting these characteristics can adopt a variety of forms and, when chosen carefully, actually provide useful models for real substances.



# LJ Potential

The best known of these potentials, originally proposed for liquid argon, is the Lennard-Jones (LJ) potential.

$$u(r_{ij}) = \begin{cases} 4\epsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6 \right] & r_{ij} < r_C \\ 0 & r_{ij} \geq r_C \end{cases}$$



The force corresponding to  $u(r)$  is

$$f = - \nabla u(r)$$

so the force that atom  $j$  exerts on atom  $i$  is

$$\mathbf{f}_{ij} = \begin{cases} \left( \frac{48\varepsilon}{\sigma^2} \right) \left[ \left( \frac{\sigma}{r_{ij}} \right)^4 - \frac{1}{2} \left( \frac{\sigma}{r_{ij}} \right)^8 \right] \mathbf{r}_{ij} & r_{ij} < r_C \\ 0 & r_{ij} \geq r_C \end{cases}$$



The equations of motion follow from Newton's second law,

$$m\ddot{\mathbf{r}}_i = \mathbf{f}_i = \sum_{\substack{j=1 \\ j \neq i}}^{N_m} \mathbf{f}_{ij}$$

these equations which must be numerically integrated.

Newton's third law implies that,

$$\mathbf{f}_{ji} = -\mathbf{f}_{ij}$$

so each atom pair need only be examined once.



The amount of work<sup>†</sup> is proportional to *squared number of atoms*, so that for models in which  $r_c$  is small compared with the size of the container it would obviously be a good idea to determine those atom pairs for which  $r_{ij} \leq r_c$  and use this information to reduce the computational effort.



# Boundary conditions

The introduction of **periodic boundaries** is equivalent to considering an infinite, space-filling array of identical copies of the simulation region. There are two consequences of this periodicity.

The *first* is that an atom that leaves the simulation region through a particular bounding face immediately reenters the region through the opposite face. The *second* is that atoms lying within a distance  $r_c$  of a boundary interact with atoms in an adjacent copy of the system, or, equivalently, with atoms near the opposite boundary – a wraparound effect.

Another way of regarding periodic boundaries is to think of mapping the region (topologically, not spatially) onto the equivalent of a torus in four dimensions (a two-dimensional system is mapped onto a torus); then it is obvious that there are no physical boundaries.



# Integration

Integration of the equations of motion uses the simplest of numerical techniques, the leapfrog method. The method has excellent energy conservation properties and is widely used.

If  $h = \Delta t$  denotes the size of the timestep used for the numerical integration, then the integration formulae applied to each component of an atom's coordinates and velocities are

$$v_{ix}(t + h/2) = v_{ix}(t) + (h/2)a_{ix}(t)$$

$$r_{ix}(t + h) = r_{ix}(t) + hv_{ix}(t + h/2)$$

$$v_{ix}(t + h) = v_{ix}(t + h/2) + (h/2)a_{ix}(t + h)$$



# PROGRAMMING



