Computational Nanoscience

NSE C242 & Phys C203

Spring, 2008

Lecture 2:

Introduction to Molecular Dynamics

January 24, 2008

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Molecular Dynamics: The Beginning

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 31, NUMBER 2 AUGUST, 1959

Studies in Molecular Dynamics. I. General Method*

B. J. Alder and T. E. Wainwright

Lawrence Radiation Laboratory, University of California, Livermore, California

(Received February 19, 1959)

A method is outlined by which it is possible to calculate exactly the behavior of several hundred interacting classical particles. The study of this many-body problem is carried out by an electronic computer which solves numerically the simultaneous equations of motion. The limitations of this numerical scheme are enumerated and the important steps in making the program efficient on the computers are indicated. The applicability of this method to the solution of many problems in both equilibrium and nonequilibrium statistical mechanics is discussed.

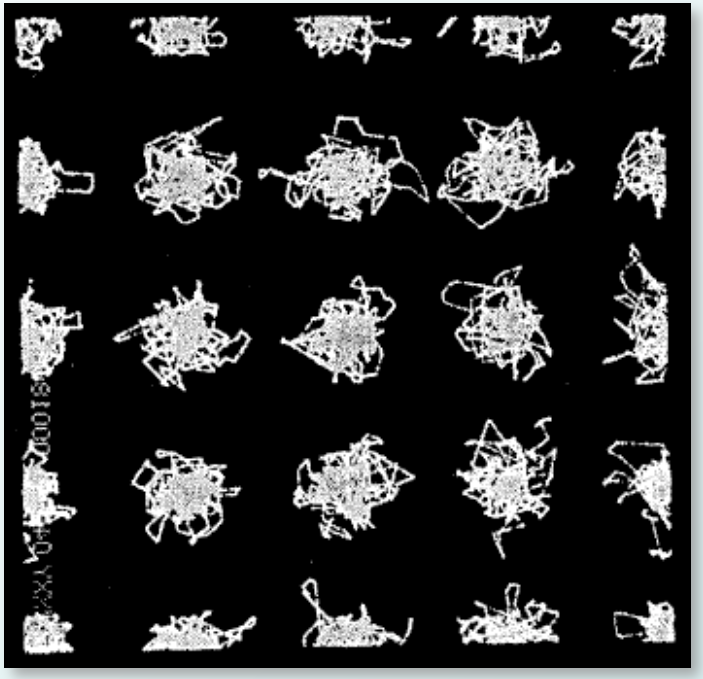
Study of microscopic nature of liquids and solids (32 atoms).

Hard-sphere potentials were used.

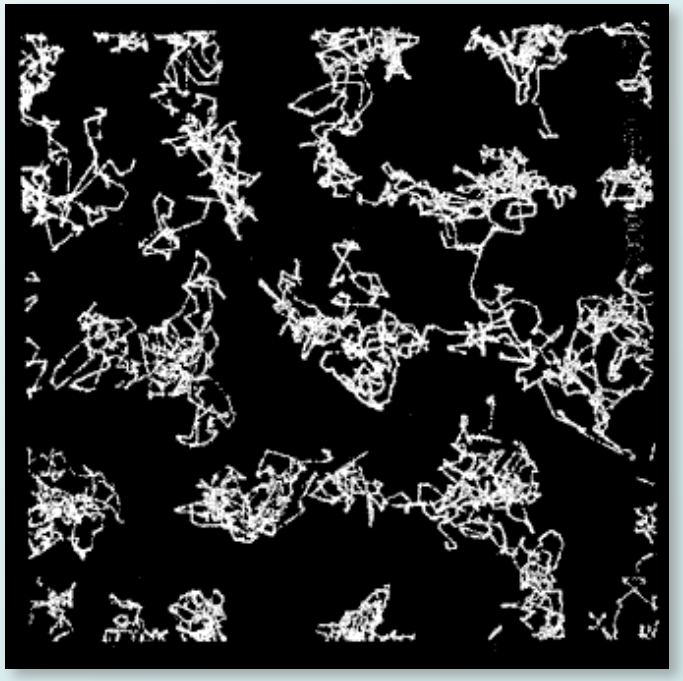
Molecular Dynamics: The Beginning

Simulation approach:

1. Identify next pair of spheres to collide and calculate when the collision will occur.
2. Calculate the positions of all the spheres at the collision time.
3. Determine the new velocities of the two colliding spheres after the collision.
4. Repeat from (1) until finished.



Solid phase (3000 collisions).



Fluid phase (3000 collisions).

Alder and Wainwright, JCP 31, 459 (1959)

Molecular Dynamics

A way to generate many-particle trajectories directly from classical equations of motion

Each particle in the system moves in a potential, $V=V(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$, caused by the presence of all the other particles.

This potential should be additive and (at least at this point) contain only one or two-body terms. For example:

$$V(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N) = \sum_{i=1}^{N} U(\mathbf{r}_i) + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} v(\mathbf{r}_i,\mathbf{r}_j)$$

external potential

interaction between two particles

Molecular Dynamics

GOAL: We would like to obtain the trajectories $\mathbf{r}_i(t)$ of all of the *N* particles as a function of the time *t*, in a specified time interval.

- These trajectories are solutions to the classical equations of motion:

$$\frac{d^2\mathbf{r}_i(t)}{dt^2} = \frac{\mathbf{f}_i(t)}{m_i}$$ for i=1,2,3,…,N with some initial conditions

- Analytic solutions are not possible, in general, so we turn to a numerical solution.

- In MD, beginning with the initial conditions, one recursively generates the positions and velocities at successive times:

$$\{\mathbf{r}_i(t), \mathbf{v}_i(t)\} \rightarrow \{\mathbf{r}_i(t+\delta t), \mathbf{v}_i(t+\delta t)\}$$

Integrate Equations of Motion

How do we derive an algorithm to compute **r**(t+dt)?

⟶ Start with a Taylor expansion:

$$\mathbf{r}(t+\delta t) = \mathbf{r}(t) + \mathbf{v}(t)\delta t + \vartheta(\delta t^2)$$

$$\mathbf{v}(t+\delta t) = \mathbf{v}(t) + \frac{\mathbf{f}(t)}{m}\delta t + \vartheta(\delta t^2)$$

This would be a first order integration algorithm.

A couple of things to note:

- the functions **r**(t) and **v**(t) are assumed to be analytically well behaved
- there is a time-step error which grows with dt
- most expensive part of the simulation is in the calculation of the force

A Simple Example: Harmonic Oscillator

Let's assume a 1-dimensional oscillator with mass m:

- x(t) will describe it's position
- The harmonic potential is given by $V(x) = kx^2/2$
- Instantaneous force (Hooke's Law): f = -kx

An exact solution is obtainable in this case.

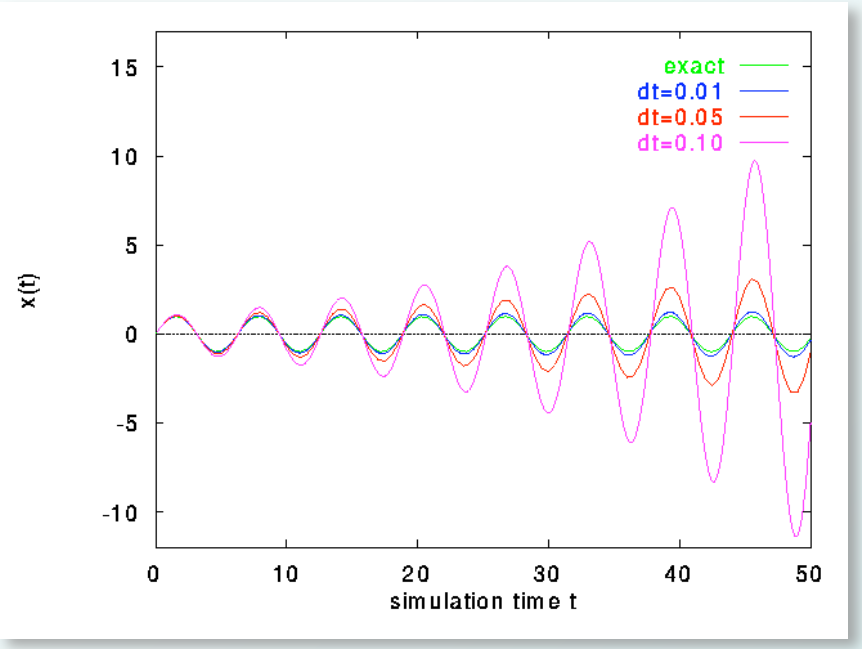
For initial conditions x(0)=0 and $v(0)=v_o$: $x(t) = \frac{v_\circ}{\omega}\sin(\omega t)$ $\omega = \sqrt{\frac{k}{m}}$

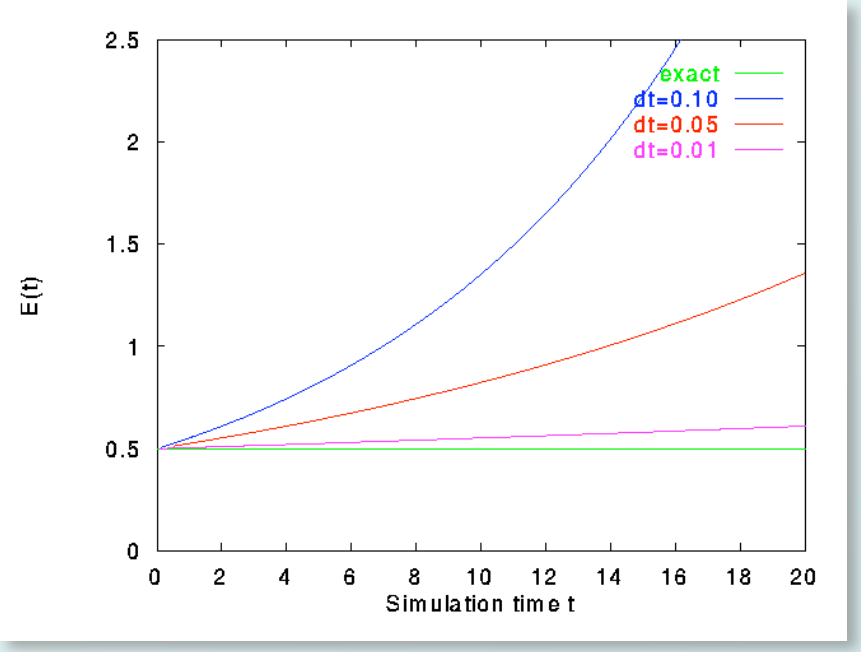
We can compute the total energy of the system as:

$$E(t) = K(t) + V(t) = \frac{1}{2}mv(t)^2 + \frac{1}{2}kx(t)^2 = E(t=0) = \frac{1}{2}mv_o^{\ 2}$$

First Order Integration Results

Here is the position and total energy vs. time for the exact solution compared with our MD integration using several time steps:





Why is the precision so bad? What can we do?

More Accurate Integration

Expand Taylor series to second order:

$$\mathbf{r}(t+\delta t) = \mathbf{r}(t) + \mathbf{v}(t)\delta t + \frac{\mathbf{f}(t)}{2m}\delta t^2 + \vartheta(\delta t^3)$$

$$\mathbf{v}(t+\delta t) = \mathbf{v}(t) + \frac{\mathbf{f}(t)}{m}\delta t + \frac{1}{2m}\frac{d\mathbf{f}(t)}{dt}\delta t^2 + \vartheta(\delta t^3)$$

The d**f**(t)/dt part looks like something we may want to avoid…

One thing we could do is to use the first equation to compute r(t+dt), and then compute v(t+dt) from the new position as v(t+dt)=[(r+dt)-r(t)]/dt

This is called the “Euler” algorithm and it is a complete disaster - catastrophic energy drifts and not reversible, for starters.

The Velocity Verlet Algorithm

We can expand the force derivative as:

$$\frac{d\mathbf{f}(t)}{dt} = \frac{\{\mathbf{f}(t+\delta t) - \mathbf{f}(t)\}}{\delta t} + \vartheta(\delta t)$$

Substituting into the 2nd order Taylor expansion:

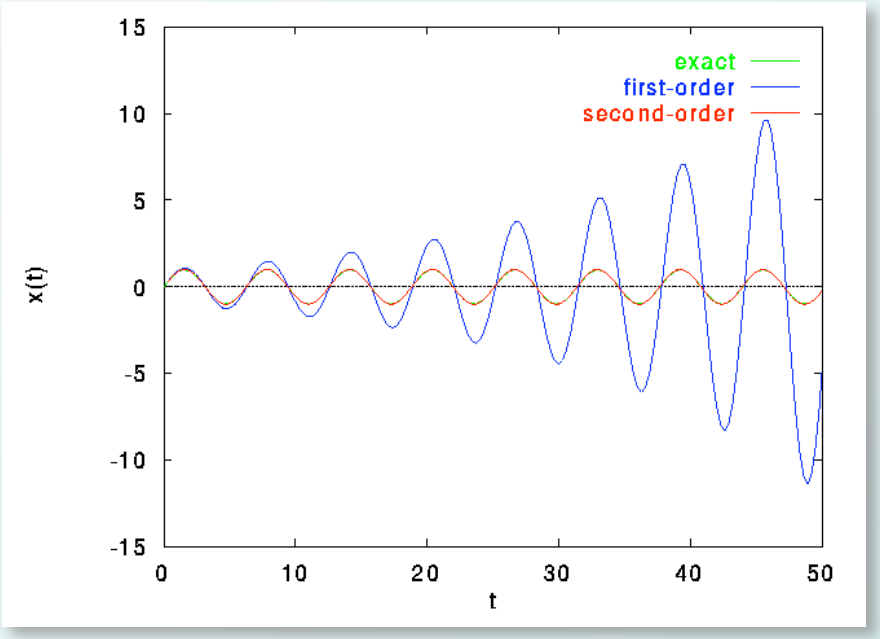
$$\mathbf{v}(t+\delta t) = \mathbf{v}(t) + \frac{\mathbf{f}(t)}{m}\delta t + \frac{1}{2m}\frac{d\mathbf{f}(t)}{dt}\delta t^2 + \vartheta(\delta t^3)$$

$$= \mathbf{v}(t) + \frac{1}{2m}\{\mathbf{f}(t) + \mathbf{f}(t+\delta t)\}\delta t + \vartheta(\delta t^3)$$

Now we can compute new velocities after computing new positions which gives us the new forces.

Verlet Algorithm for MD

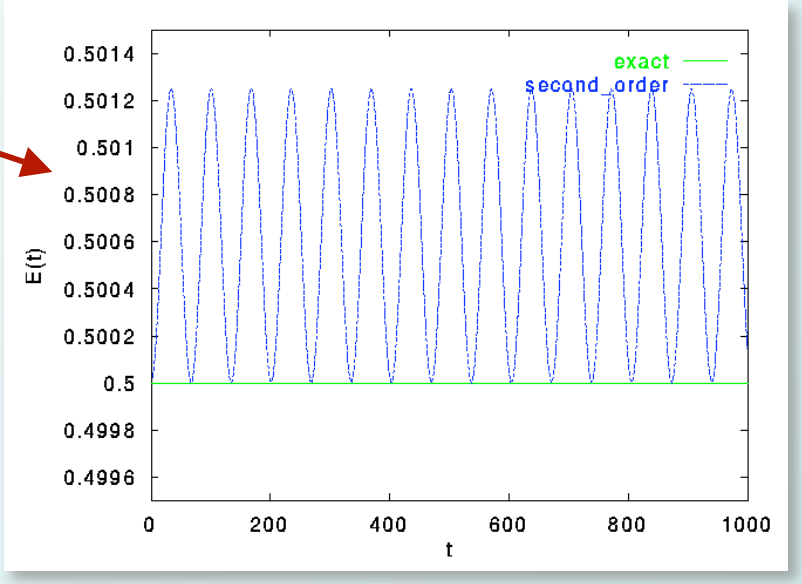
The Verlet algorithm is substantially better than a 1st order approximation.



Velocity Verlet MD Results

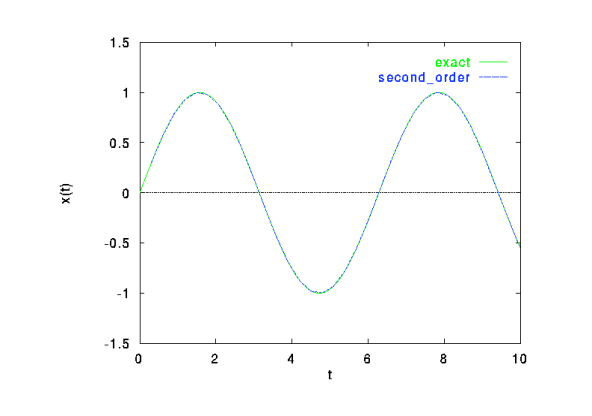
Energy is also very well conserved (better than 0.2%)

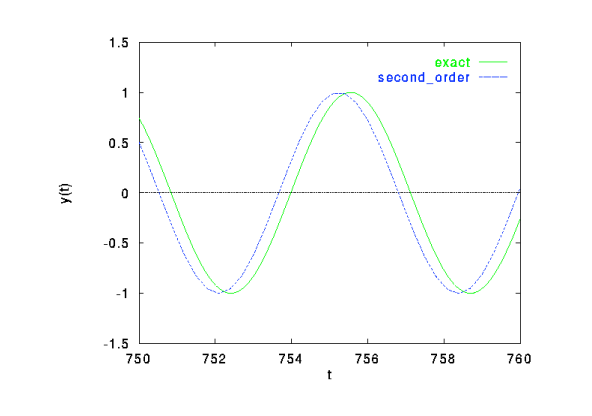
Note scale

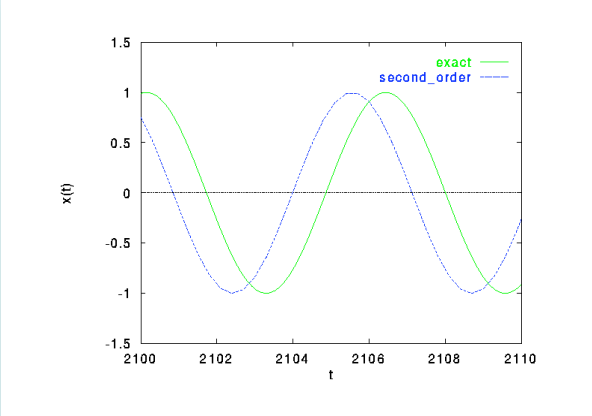


As simulation time increases, even the 2nd order algorithm fails to match the exact trajectory.

Note: deviation is solely a phase shift - trajectory is physically correct

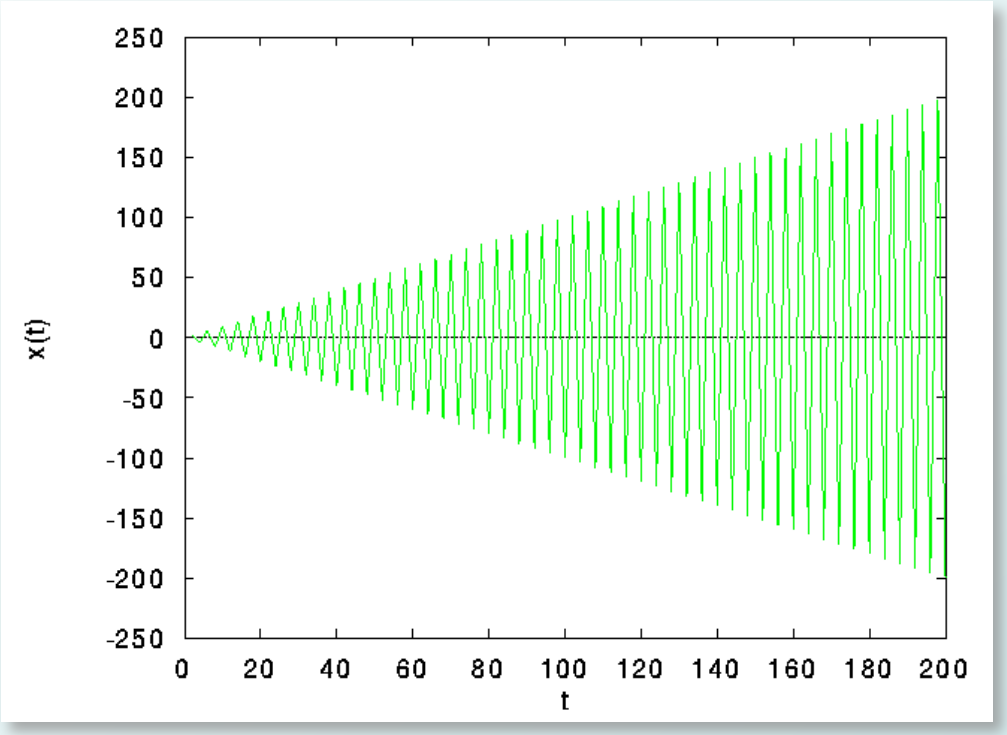






Timestep

We still need to pay careful attention to the time step, as can be seen here if a time step that is too large is chosen.



Velocity Verlet MD

The fact that the second-order algorithm enjoys a range of stability is related to its partially *implicit* character: the determination of the velocity at a successive time requires knowledge of the acceleration at that same time, which has a *feedback* effect on the position.

In the first-order algorithm, which is *fully explicit,* quantities at a successive time can be determined solely on the basis of their value at a previous time, and this causes the runaway of the trajectory at long times.

Other MD Integration Schemes

There are actually a number of MD integrations schemes. It turns out that the Verlet algorithm is often (but not always) the best choice.

Here are some of the main reasons for this:

- It is very fast computationally
- It requires little memory
- Short-term energy conservation is decent
- Long-term energy conservation is excellent
- It is time-reversible

Other, “Verlet-type” schemes are common, such as the “Leap-Frog” algorithm.

Higher order methods, such as the “Predictor-Corrector” scheme are less common. One can use larger time steps, but these algorithms suffer from being slower, requiring more storage, not being reversible, and needing to take differences of large numbers.

Accuracy in MD

Is it possible, in theory, to develop an algorithm that accurately predicts the trajectory of all particles at both short and long times?

No such algorithm exists!

The trajectory of a system is usually very sensitive to the initial conditions.

This means that two trajectories that are initially very close will diverge exponentially as time progresses.

If we consider the integration error as the source of an initial (small) difference, then we always have a simulated trajectory divergent from the “true” one.

Is this a devastating blow to molecular dynamics?

Not really - in MD we’re essentially always interested in making *statistical* predictions, not in knowing *precisely* what will happen given some initial condition.

Interatomic Potentials

Getting back to our "pair-wise" potential: $V(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N) = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} v(\mathbf{r}_i,\mathbf{r}_j)$

Note that if the potential is central, we can write $v(\mathbf{r}_i,\mathbf{r}_j)$ as $v(\mathbf{r}_{ij})$ where $\mathbf{r}_{ij}=|\mathbf{r}_i-\mathbf{r}_j|$

Higher order terms, such as a three-body $v(\mathbf{r}_i,\mathbf{r}_j,\mathbf{r}_l)$ are preferably avoided, as they increase considerably the computational expense (the calculation of three-body forces require a number of operations proportional to N^3, four-body to N^4, etc.).

In those cases where three-body effects are too large to be neglected, such as in molecular hydrogen, often one attempts to incorporate them into an *effective* two-body potential, by modifying the 2-body potential to include some of the effects due to three-body terms.

The Pair Potential

What determines the interaction between two molecules, or two atoms?

Atoms and molecules consist of electrically charged particles, protons and electrons, which, to a very large extent, are responsible for the interaction between them, which is almost exclusively electrostatic.

Also, the distribution of negative charge associated with the electron cloud is not spherically symmetric, resulting in a nonzero *dipole moment* of the atom (molecule).

The electric field generated by a single electrostatic dipole is proportional to $1/r^3$, and this can be shown to lead to a weak interatomic (intermolecular) attraction proportional to $1/r^6$, which is dominant at large distances.

If two atoms or two molecules are brought very close together, the interaction between them becomes more complicated; quantum effects start playing a more important a role, resulting in an effective “hard-core” repulsion of atoms and molecules at sufficiently short distances.

The Pair Potential

It is clearly very difficult, in general, to provide accurate interparticle potentials (we will devote a whole lecture to it soon).

Two routes are typically followed:

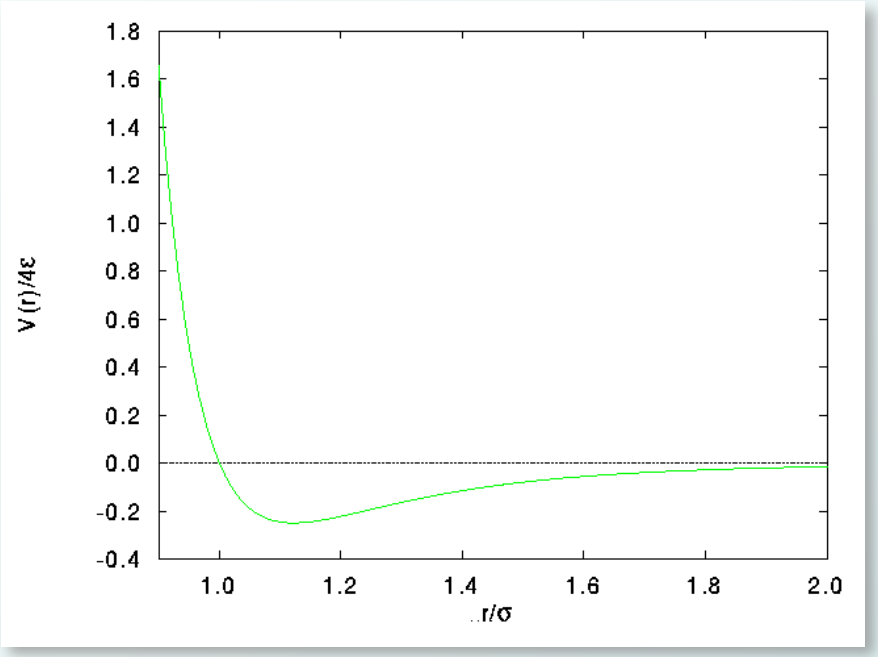
1. *Ab initio* quantum-mechanical calculations: these usually consist of studying a quantum-mechanical system of, say, two atoms, in which the individual electrons and atomic nuclei are considered separately, and the energy of the system at various nuclear separations is computed and tabulated. This is clearly a very difficult task, often undertaken by performing *quantum simulations*.

2. More often, one chooses a relatively simple, parametric form for the potential, incorporating some physical effects deemed relevant, and adjust the parameters in a phenomenological fashion, by fitting numerical predictions to known experimental results. Typically, scattering experiments are good sources of quantitative information, as well as specific heat, compressibility, sound velocity measurements etc.

Good Reference: M. P.Allen and D. J. Tildesley, Computer Simulation of Liquids, Oxford University Press (1994)

Lennard-Jones (LJ) Potential

One of the most important and popular potentials is the Lennard-Jones potential:



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

two adjustable parameters, σ and ε

The LJ Potential

The long-range part, proportional to $1/r^6$ attempts to describe the dipole-dipole attractive interaction.

The short-range part has much less of a physical motivation, and is only aimed at representing a hard-core repulsion between two atoms.

In fact, the short-range part of LJ is largely unphysical and typically must be softened to obtain a closer description of the short-range properties of the interaction.

The Lennard-Jones potential is rather ubiquitous in the simulation literature, and it is widely considered a paradigmatic potential to simulate most atomic liquids.

It is occasionally “hidden” behind other appearances. For example, the so-called “3-9” potential, aimed at representing the interaction of an atom with a surface is simply the LJ potential where one of the two atoms is replaced with an infinite, two dimensional uniform atomic distribution.

The LJ Potential

Another important advantage of the LJ potential is its relatively simple analytical expression, which permits its evaluation with few computer operations.

This is an important aspect, as the calculation of the forces from the potential is the most expensive part of the simulation.

If a more sophisticated potential is required, involving more terms and/or more involved analytical expressions, making use of transcendental functions such as fractional powers, trigonometric functions and exponentials, the toll to be paid in terms of execution time quickly becomes prohibitive.

This is not to say that more complicated potentials cannot be used, but that appropriate strategies have to be considered, such as the use of *spline-fit potentials* based on *look-up table*; we will examine this later.

Beyond the Pair Potential

A central potential may be an acceptable approximation for atomic systems, but when one is dealing with complex molecules, often it is necessary to consider explicitly their spatial extension as well as their detailed chemical structure.

This typically involves considering potentials that have a well-defined angular part, i. e. they depend on the relative orientation of the molecules.

One possibility of dealing with molecular systems consists of representing molecules as a collection of individual atoms, where chemical bonds are represented by further interatomic potentials.

In other words, molecules would lose their identity as far as the simulation is concerned, as only individual atoms (possibly of different elements) appear.

Beyond the Pair Potential

Two issues to consider:

- It is often the case that the energy scale corresponding to chemical bonds within a molecule is much different than the one corresponding to the self-bonding of the molecular liquid or solid.

- The classical approach might be acceptable to describe a molecular liquid, but a full quantum mechanical description is needed to characterize intramolecular bonds.

A possible remedy to the first point consists of simply eliminating intramolecular potential and replacing them with rigid “dumbbells” or with flexible “springs”, whose characteristic frequencies are chosen to match the experimentally observed vibrational spectra of the molecules.

In this case, the molecule has a center of mass and the constituent atoms move together with it while rotating around it.The second problem can only be addressed by attempting to incorporate quantum-mechanical effects in the motion of the molecules.

Choice of Time Step

There are no hard and fast rules. In general, if dt is too small, not enough of phase space is explored, and if dt is too large, it will lead to instabilities in the integration

Typical timesteps fall in the range of 0.1-10 femtoseconds.

For a liquid, the time step should be small compared to the mean time between collisions.

For a flexible molecule, the time step should be no greater than 1/10 the time of the shortest period of motion.

Some examples* (dt in seconds) :

- Atoms: translation, dt ~ 10^{-14}
- Rigid Molecules: translation and rotation, dt ~ $5x10^{-15}$
- Flexible Molecules: translation, rotation, torsion, dt ~ $2x10^{-15}$
- Flexible Molecules & Flexible Bonds: translation, rotation, torsion, vibration, dt < 10^{-15}

* From “Molecular Modeling,” 2nd edition, A. Leach, Prentice Hall