Molecular Dynamics

Peter Virnau, 04.12.2007

This introduction to Molecular Dynamics follows closely Frenkel & Smit (p63-77).

Molecular Simulation / Recap

Goal: **Determine equilibrium and transport properties of a classical many-body system**, f.i., by numerical integration of Newton's equations of motion.

Usually, quantum mechanical effects need not be considered (see next problem set.)
Exception: Translation and rotation of very small atoms and molecules (H_2, He,…), vibrations with frequency ν for which $h\nu > k_B T$.

This approach is in some ways similar to a real experiment:
Experiment: 1. Set up system and measuring instruments.
2. Determine properties of the system by measuring an observable over some time (f.i. temperature). The longer we measure, the more accurate results will become.

Simulation: 1. Set up a system with n particles.
2. Let the system "evolve", f.i., through successive iterations of Newton's equations of motion and measure observables after predefined time-intervals (MD: "time average" vs. MC: "ensemble average")
Example: Temperature: For each degree of freedom we get:

$$<1/2\ m v_\alpha^2> = 1/2\ k_B T \rightarrow \quad T(t) = \sum_{i=1}^{N} \frac{m_i v_i^2}{k_B N}$$

Advantage of simulations: **full control**
(We know the position of each particle at any particular point in time.)

Disadvantage: Systems need to be **modeled** and usually we are restricted to **small time and length scales** (nm and ns in atomistic simulations.)

Structure of a Molecular Dynamics Program

1. Prepare a staring configuration (→ Initialization)
|: 2. Calculate forces between all particles
3. Integrate Newton's equation of motion
4. Determine averages of observables :|

1. Initialization

Example: Lennard-Jones system
1. Put particles on a lattice

2. Assign velocities from Maxwell-Boltzmann distribution such that the sum over all velocities is 0.

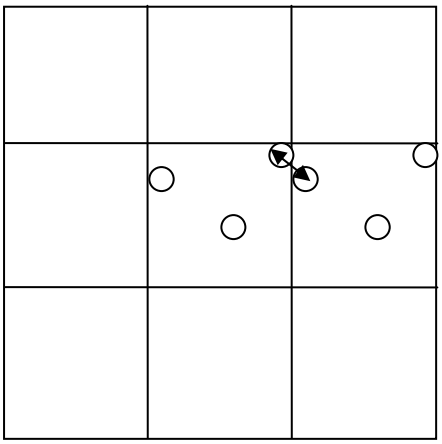
2. Calcuation of forces

$$f_x = -\frac{\partial E(r)}{\partial x} = -\frac{\partial E(r)}{\partial r}\frac{\partial r}{\partial x} = -\frac{x}{r}\frac{\partial E(r)}{\partial r}$$

Example: Lennard-Jones system

$$E = 4\varepsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} + \text{const}\right) \qquad f_x = \frac{48\varepsilon x}{r^2}\left(\left(\frac{\sigma}{r}\right)^{12} - 0.5\left(\frac{\sigma}{r}\right)^{6}\right)$$

Periodic boundary conditions



Minimum Image Convention
Distance=minimum of distances between a particle and any periodic image of its interaction partner

3. Integration of Newton's equation of motion: Verlet algorithm

Problem: We can only evolve the system in finite time steps → errors
Goal: Find an algorithm with which we can calculate equilibrium and transport properties without errors.

Taylor expansion:

$$r(t+\Delta t) = r(t) + \dot{r}\Delta t + \frac{1}{2}\ddot{r}\Delta t^2 + \frac{1}{3!}\dddot{r}\Delta t^3 + \ldots$$

$$r(t+\Delta t) = r(t) + v(t)\Delta t + \frac{1}{2}\frac{f}{m}\Delta t^2 + \frac{1}{3!}\dddot{r}\Delta t^3 + \ldots$$

$$r(t-\Delta t) = r(t) - v(t)\Delta t + \frac{1}{2}\frac{f}{m}\Delta t^2 - \frac{1}{3!}\dddot{r}\Delta t^3 + \ldots$$

$$r(t+\Delta t) + r(t-\Delta t) = 2r(t) + \frac{f}{m}\Delta t^2 + O(\Delta t^4)$$

$$\boxed{r(t+\Delta t) \approx 2r(t) - r(t-\Delta t) + \frac{f}{m}\Delta t^2}$$

We need the positions of all particles at time step t and t-Δt and the forces at time t to evolve the system to t+Δt.

Determination of temperature:

$$r(t+\Delta t) - r(t-\Delta t) \approx 2v(t)\Delta t$$

→ v(t), temperature up to O(Δt^3)

Alternative Integration schemes

Euler algorithm

$$r(t+\Delta t) = r(t) + v(t)\Delta t + \frac{1}{2}\frac{f}{m}\Delta t^2 + \ldots$$

Comments: one of the first MD integrators
substantial energy drift, do not use!!! (→ next problem set)

Velocity-Verlet

$$r(t+\Delta t) = r(t) + v(t)\Delta t + \frac{1}{2}\frac{f}{m}\Delta t^2$$

$$v(t+\Delta t) = v(t) + \frac{f(t+\Delta t) + f(t)}{2m}\Delta t$$

We need to store r(t), v(t), f(t) and f(t+Δt). Velocities are calculated after determination of forces and particle positions.

Justification:

$$r(t+2\Delta t) = r(t+\Delta t) + v(t+\Delta t)\Delta t + \frac{f(t+\Delta t)}{2m}\Delta t^2$$

$$r(t) = r(t+\Delta t) - v(t)\Delta t - \frac{f}{2m}\Delta t^2$$

$$r(t+2\Delta t) + r(t) = 2r(t+\Delta t) + (v(t+\Delta t) - v(t))\Delta t + \frac{f(t+\Delta t) - f(t)}{2m}\Delta t^2$$

Insertion of v(t+Δt) yields same evolution equation as Verlet algorithm.

Other alternatives: Leap-Frog, Beeman, …

What are the characteristics of a good integrator?

We need high precision for equilibrium and transport properties, large time steps.

We don't need exact trajectories (we do not calculate orbits of satellites!)
→ Lyapunov instability: two starting configurations which are almost identical diverge exponentially with time.

Nevertheless it is generally believed (!) that calculated trajectories resemble "real" trajectories and can be used to determine equilibrium and dynamical properties.

- Good integration schemes conserve energy on long time scales
  Verlet: ok, Euler: x
- The integrator should be time reversible (like Newton's equations!), i.e., if time steps are reversed, the trajectory should regress to the starting configuration.
  Verlet: ok, Euler: x (→ next problem set)
- Phase space should be conserved (more difficult to prove)
  Verlet: ok, Euler: x