

Molecular Dynamics vs. Monte Carlo

In many ways, molecular dynamics (MD) methods share many characteristics with Monte Carlo (MC):

{ small systems, periodic boundary conditions, }
 { minimum image convention }

The main differences are:

- * MD samples the microcanonical (NVE) ensemble (but thermostats / barostats can be applied)
- * Instead of phase space sampling MD follows true dynamical evolution of a system \rightarrow direct calculation of transport coefficients (diffusion, viscosity, thermal conductivity)
 - + realistic dynamics
 - less flexible, slower for equilibrium properties

Main elements of MD simulation

① Initialization: Particle positions are initialized at random or on a lattice, just as for MC simulations. However, velocities now need to be initialized as well.

At equilibrium, the mean-square-velocity along any

direction (x, y or z) is

$$\langle v_\alpha^2 \rangle = \frac{k_B T}{m} \quad \alpha \text{ is } x, y \text{ or } z$$

and the distribution of velocity magnitudes is the Maxwell-Boltzmann distribution:

$$P(v) = \frac{\exp\left(-\frac{\beta m v^2}{2}\right)}{(2\pi m k_B T)^{3/2}}$$

However, just as in MC, initial conditions do not matter all that much, except in terms of rate of equilibration. The correct distribution of velocities will establish itself no matter what the initial state.

Since Newton's equations of motion conserve total momentum, it is important to start the system with zero total momentum, otherwise the particles will systematically drift in one direction.

(2) Moving the particles

In MD, particles move according to Newton's Law:

$$\text{acceleration} = \frac{\text{force}}{\text{mass}}$$

$$\frac{d^2 \vec{r}_i}{dt^2} = \frac{\vec{F}_i}{m_i} \quad i = 1, 2, \dots, N$$

In MC, we only needed to worry about the energy

$$u = \sum_i \sum_{j < i} u_{ij}(r_{ij})$$

Now we need the force:

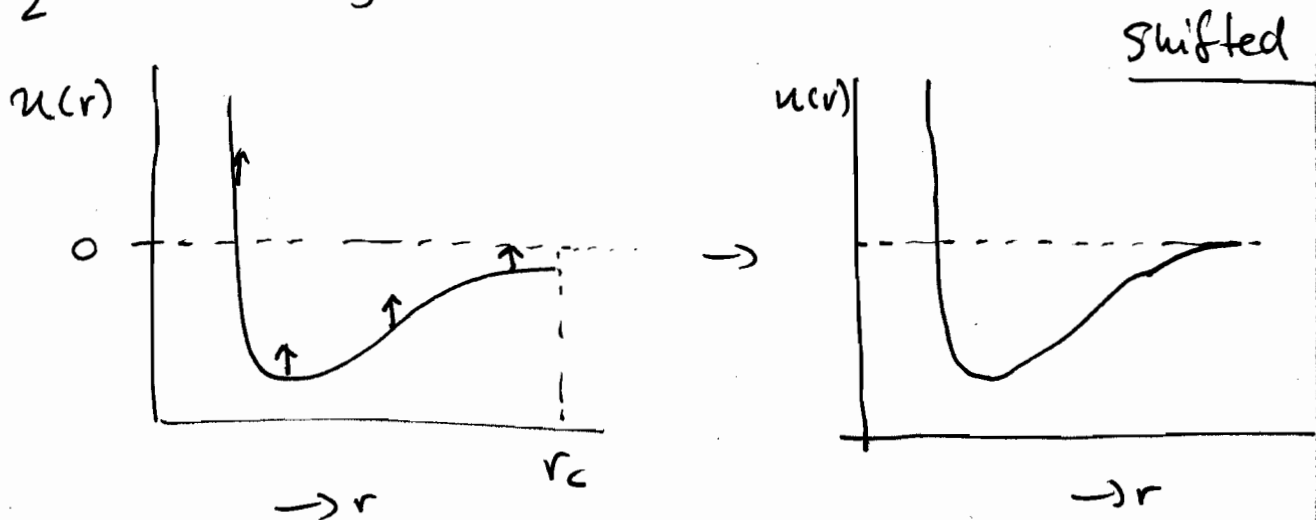
$$f_x(r) = - \frac{\partial u(r)}{\partial x} = - \left(\frac{x}{r} \right) \frac{du(r)}{dr}$$

E.g. for Lennard-Jones potential $u_{ij} = 4\epsilon_{ij} \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$

using $\epsilon = \sigma = 1$, $f_x(r) = \frac{48x}{r^2} \left[\frac{1}{r^{12}} - \frac{1}{2r^6} \right]$

Potentials with discontinuities (e.g. hard spheres, square wells) result in "impulse" (infinite) forces and are handled by special methods that will not be covered here.

Even for "smooth" potentials such as the LJ one, problems arise at the cutoff distance ($= \frac{1}{2}$ the box length or less)



Now, how do we actually solve the differential equations:

$$m_i \ddot{\mathbf{r}}_i = \sum_{j \neq i}^N \mathbf{F}_{ji}$$

There are many numerical methods for integration, but only few are suitable for MD simulations:

→ calculation of the force is an ^(expensive) $O(N)$ operation, so this can only be done once per time step.

→ long-term energy conservation is important

→ reversibility and conservation of volume in phase space are required

It turns out that some of the simplest integration schemes are also the best.

The Verlet algorithm:

$$r(t+\Delta t) = r(t) + v(t) \Delta t + \frac{f(t)}{2m} \Delta t^2 + \frac{\Delta t^3}{3} \ddot{r} + O(\Delta t^4) \quad (1)$$

$$r(t-\Delta t) = r(t) - v(t) \Delta t + \frac{f(t)}{2m} \Delta t^2 - \frac{\Delta t^3}{3} \ddot{r} + O(\Delta t^4) \quad (2)$$

Summing (1)+(2)

$$r(t+\Delta t) + r(t-\Delta t) = 2r(t) + \frac{f(t)}{m} \Delta t^2 + \underbrace{O(\Delta t^4)}_{\text{integration error goes as } (\Delta t)^4}$$

To calculate the instantaneous velocities, we can use $\textcircled{1}-\textcircled{2}$ $v(t) = \frac{r(t+\Delta t) - r(t-\Delta t)}{2\Delta t} + \underline{O(\Delta t^2)}$

less accurate than positions!

Implementation:

do $i = 1, \text{ particles}$

$$r_{\text{new}}(i, 1:\text{dim}) = 2 * r(i, 1:\text{dim}) - r_{\text{old}}(i, 1:\text{dim}) + \Delta t * \Delta t * f(i, 1:\text{dim})$$

$$r_{\text{old}}(i, 1:\text{dim}) = r(i, 1:\text{dim})$$

$$r(i, 1:\text{dim}) = r_{\text{new}}(i, 1:\text{dim})$$

enddo

③ Measuring Transport Coefficients

Measuring transport coefficients in "equilibrium" MD simulations is done from "Green-Kubo" relationships - these are a bit convoluted, except for the diffusion coefficient D :

$$\vec{j} = -D * \nabla c$$

flux

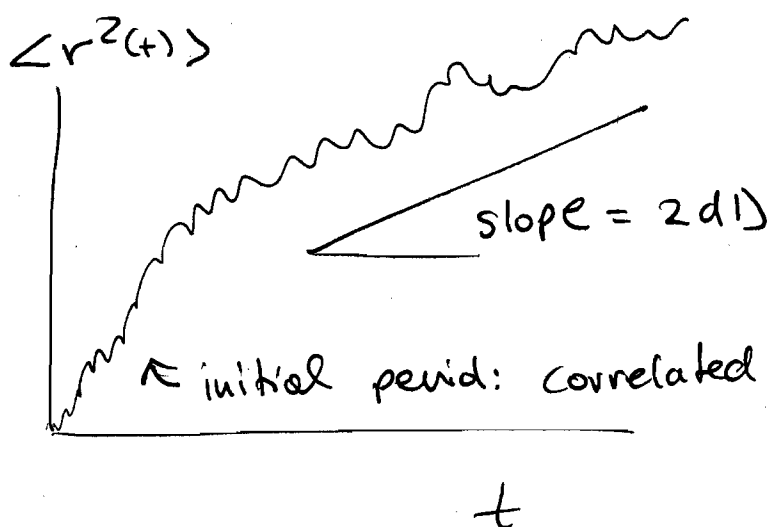
diffusion
coefficient

concentration

For a particle initially at position $(0,0,0)$,
Einstein relationship:

$$\lim_{t \rightarrow \infty} \frac{\partial \langle r^2(t) \rangle}{\partial t} = 2dD$$

↓
dimensionality of space (eg. 3)



To do this calculation properly, we need to keep track of the actual position of a particle in space (not necessarily in the central box):

