1 Molecular dynamics algorithms

\[
x(t + h) = x(t) + v(t)h + \frac{1}{2}a(t)h^2 + \frac{1}{6} \frac{d^3x}{dt^3}h^3 + O(h^4)
\]

\[
x(t - h) = x(t) - v(t)h + \frac{1}{2}a(t)h^2 - \frac{1}{6} \frac{d^3x}{dt^3}h^3 + O(h^4)
\]

\[
x(t + h) - x(t) = 2x(t) - x(t - h) + a(t)h^2 + O(h^4)
\]

\[
v(t + \frac{1}{2}h) = v(t) + \frac{1}{2}a(t)h + O(h^3)
\]

\[
x(t + h) = x(t) + v(t + \frac{1}{2}h)h + O(h^4)
\]

Eq. (1) is the original Verlet propagation algorithm; Eqs. 2 and 3 are the “leap-frog” version of that. Remember that \(a = \frac{d^2x}{dt^2} = \frac{F}{m} = \left(\frac{\partial V}{\partial x}\right)/m\).

1.1 Regulating temperature

“Temperature” is a measure of the mean kinetic energy. The instantaneous KE is

\[
T(t) = \frac{1}{k_B N_{dof}} \sum_i m_i v_i^2
\]

(cf. classical rule of thumb: “\(k_B T/2\) of energy for every squared degree of freedom in the Hamiltonian”)

Suppose the temperature is not what you want. At each step, you could scale the velocities by:

\[
\lambda = \left[1 + \frac{h}{2\pi} \left(\frac{T_0}{T(t)} - 1\right)\right]^{1/2}
\]

This is the “Berendsen” or “weak-coupling” formula, that has a minimal disruption on Newton’s equations of motion. But it does not guarantee a canonical distribution of positions and velocities. See Morishita, J. Chem. Phys. 113:2976, 2000; and Mudi and Chakravarty, Mol. Phys. 102:681, 2004.
1.2 Langevin dynamics

Consider the stochastic, Langevin equation:

\[ \frac{dv}{dt} = -\zeta v + A(t) \]

By Stokes’ law, the friction coefficient is related to the viscosity of the environment: \( \zeta = 6\pi a \eta / m \).

At long times, we want this system to go to equilibrium at a temperature \( T \), which is a Maxwell-Boltzmann distribution:

\[ W(v; v_0) \sim \exp \left[ -m v^2 / 2 k_B T \right] \]

for every value of \( v_0 \). This places restraints on the properties of the stochastic force \( A(t) \). It can be shown that

\[ \zeta = (\beta / m) < A^2 > \]

where we have assumed that \( < A > = 0 \) and \( < A(0) \cdot A(t) > = < A^2 > \delta(t) \).

2 Periodic boundary conditions
3 Basics of the Ewald approach

\[ \rho_1(r) \]
\[ \rho_2(r) \]

4 Minimization and simulated annealing

5 The Simplex algorithm
6 Molecular models and force fields

6.1 1901 (and earlier?) ball and stick models

6.2 “Quantum” model of a molecule

- atoms and molecules are made up of nuclei and electrons
  - electrons, being very light, are typically in their ground quantum state
  - very general: applies to virtually arbitrary types of chemistry and conformations
  - computationally rather expensive: limited to a few hundred atoms, and a few thousands of conformations

6.3 “Molecular mechanics” model of a molecule

- molecules are constructed from collections of “bonds” and “atoms”
  - electronic motion is effectively averaged out
    - hence the electronic distribution (e.g. atomic partial charges) are insensitive to their environment
  - the list of bonds is fixed, so there can be no making or breaking of chemical bonds (hence no “chemistry”)
  - very cheap: one can (currently) handle a few million atoms, and sample up to few hundred million configurations
6.4 What does a force field look like?

\[
U = \sum_{\text{bonds}} K_b(b - b_{eq})^2 + \sum_{\text{angles}} K_\theta(\theta - \theta_{eq})^2 + \sum_{\text{impropers}} K_ww^2
+ \sum_{\text{tensions}} K_\phi \cos(n\phi) + \sum_{\text{nonbonded pairs}} \left\{ 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right] + \frac{q_iq_j}{r} \right\}
\]