16. Langevin Dynamics

In physics, Langevin dynamics is an approach to the mathematical modelling of the dynamics of molecular systems, originally developed by the French physicist Paul Langevin.

The approach is characterized by the use of simplified models while accounting for omitted degrees of freedom by the use of stochastic differential equations.

A molecular system in the real world is unlikely to be present in vacuum. Jostling of solvent air molecules causes friction, and the occasional high velocity collision will perturb the system. Langevin dynamics attempts to extend molecular dynamics to allow for these effects. Also, Langevin dynamics allows controlling the temperature like a thermostat, thus approximating the canonical ensemble.

Langevin dynamics mimics the viscous aspect of a solvent. It does not fully model an implicit solvent; specifically, the model does not account for electrostatic screening or the hydrophobic effect.

For a particle with mass m, with coordinate $x = x(t)$ that constitutes a time-dependent random variable, the resulting Langevin equation is:

$$m\ddot{x} = -\frac{\partial U(x)}{\partial x} - \gamma m\dot{x} + \sqrt{2\gamma k_B T m}\, R(t) \tag{1}$$

where $U(x)$ is the particle interaction potential and its negative derivative is the force calculated from the particle interaction potentials, the dot is a time derivative such that $\dot{x}$ is the velocity and $\ddot{x}$ is the acceleration, T is the temperature, k_B is Boltzmann's constant and $R(t)$ is a delta-correlated stationary Gaussian process with zero-mean, satisfying:

$$\langle R(t) \rangle = 0 \tag{2}$$

$$\langle R(t)R(t') \rangle = \delta(t - t') \tag{3}$$

where δ is the Dirac delta.

Use the velocity Verlet algorithm:

$$x_{n+1} = x_n + v_n \Delta t + \frac{1}{2} a_n (\Delta t)^2 \tag{4}$$

$$v_{n+1} = v_n + \frac{1}{2} \left(a_{n+1} + a_n \right) \Delta t \tag{5}$$

to study the one-dimensional motion of a particle in the Lennard-Jones potential:

$$U(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right] \tag{6}$$

Set the energy unit equal to the characteristic thermal energy $k_B T = 1$, so that $\epsilon = 1$, the length-scale to the particle size $\sigma = 1$ and mass $m = 1$.

(a) Model the particle motion starting from $x(0) = 3$ with timestep $\Delta t = 0.001$ for at least 100,000 steps. Record the positions and velocities at every 10th step.

(b) Calculate the position and velocity distribution histograms and normalise them by requiring that the area under the curve is equal to 1. If the histograms are not smooth, increase the number of steps.

(c) Calculate the average velocity and the temperature from the equipartition theorem and discuss the relation between the observed temperature and the input one.

(d) Calculate the potential of mean force: $U_{\mathrm{PMF}} = -k_B T \ln(1 + h(r))$, where $h(r)$ is the position distribution function, and compare it to the Lennard-Jones potential.