Foundations of Multiscale Modelling: Kinetics. Homework 1. Molecular dynamics and the Langevin description of systems. Due 23:59 10 Feb.

February 2, 2021

1. Molecular dynamics (5 points)

Write a simple Molecular Dynamics simulation program which uses the Verlet algorithm as described below. Simulate a gas of 64 spheres in a box $16 \times 16 \times 16$ with the periodic boundary conditions (PBC). The interaction between the spheres is described by the Lennard-Jones (LJ) potential. The LJ potential has a repulsive and an attractive components and reads

$$U_{LJ}(r) = 4\varepsilon \left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right), \tag{1}$$

where r is a distance between the centers of the particles, ε characterizes the strength of the interaction (the depth of the potential well) and σ is the finite distance at which the inter-particle potential is zero. For simplicity, put $\varepsilon = 1$ and $\sigma = 1$.

Velocity Verlet algorithm

The molecular dynamics method is based on a direct solution of equations of motion, i.e.

$$\frac{dr_i^\alpha}{dt} = v_i^\alpha, \tag{2}$$

$$\frac{dv_i^\alpha}{dt} = a_i^\alpha = m^{-1} \sum_j F^\alpha(\mathbf{r}_i, \mathbf{r}_j), \tag{3}$$

where r_i^α are the corresponding cartesian coordinates $\alpha = x, y, z$ of i-th particle, v_i^α are the velocities, a_i^α are the accelerations, m is a mass of the particle and $F^\alpha(\mathbf{r}_i, \mathbf{r}_j)$ is the force acting on a particle i from a particle j.

The equations can be solved by the finite-difference approach. One of the most popular approaches is the Verlet algorithm which for the x coordinate can be formulated as following. If the coordinates, velocities and accelerations $x_i(t_n), v_i(t_n), a_i(t_n)$ are known at t_n then

$$x_i(t_{n+1}) = x_i(t_n) + v_i(t_n)\Delta t + \frac{1}{2} a_i(t_n)(\Delta t)^2. \tag{4}$$

The next step is to update the forces (i.e. accelerations) by using new particles' positions $x_i(t_{n+1})$. The accelerations $a_i(t_{n+1})$ are used then to update the velocities,

$$v_i(t_{n+1}) = v_i(t_n) + \frac{1}{2}\Delta t(a_i(t_{n+1}) + a_i(t_n)). \tag{5}$$

The whole procedure is repeated, etc.

Hint 1. Compute and check the total energy of the system after each step. If this value changes too much that would be a sign of programming errors.

Hint 2. Don't forget to set an initial distribution of velocities and coordinates of the particles. The recommended way for the initial distribution of the particles is to put them in the vertices of a simple cubic lattice. That minimizes the potential energy. Hence the original kinetic energy sets the temperature.

Hint 3. The recommended way to set the initial velocities of the particles is uniform distribution for x, y and z. Then it is easier to see the convergence to Maxwell distribution. Note, that both velocity distribution and VACF should be calculated in the center of mass, which can move, because random velocity initialization can lead to non-zero average velocity.

Hint 4. The forces which define the acceleration can be obtained as corresponding derivatives from the Lennard-Jones potential.

Hint 5. The balls could interact "across" the boundaries in the case of the periodic boundary conditions. Compute the forces from the shortest distance between the two particles ("across" the PBC if necessary).

(a) Equilibrate the system and check that the Maxwell distribution of velocities is obeyed by plotting the final velocity distribution. Plots of either $f(v_x)$ or $f(|v|)$ are accepted.

(b) Calculate and plot the total energy of the system. It should be constant with time.

(c) Calculate and plot the normalized velocity auto-correlation function (VACF) $K_v(t)$ as a function of time for the low density of particles (the simulation of a gas). This function is defined as

$$K_v(t) = \frac{\langle v(0)v(t)\rangle}{\langle v^2(0)\rangle}. \tag{6}$$

Hint. You should get that $K_v(t) \sim \exp(-t/\tau)$ for small density.

C/C++/Fortran realization* **(additional 2 points)** You can choose to implement the MD program using an alternative and more efficient programming language instead of Python. In this case, simulate the system of 1000 particles instead of 64.

2. Langevin Equation and Brownian Dynamics (5 points)

Simulate the following Langevin equation with an additive noise,

$$M\frac{dv}{dt} = -\gamma v + F_{rand}(t), \tag{7}$$

where the γ is a viscous friction coefficient and $F_{rand}(t)$ is a random force. This equation belongs to the class of the so-called stochastic equations. Assume that the random force is δ-correlated thermal noise, i.e. $\langle F(t)\rangle = 0$ and $\langle F(t)F(t')\rangle = \Gamma\delta(t-t')$, where Γ is expressed due to the fluctuation-dissipation theorem as $\Gamma = 2k_BT\gamma$.

(a) Find the VACF from the equation analytically

(b) Write a program which produces the values $\xi(n)$ distributed according to the normal Gaussian distribution from the uniform distribution of random numbers which is available these days for all programming languages

Hint. $\sqrt{-2\ln U_1}\sin(2\pi U_2)$ will produce the Gaussian, if U_1 and U_2 are uniformly distributed in $[0,1]$). Generate 10000 values and plot the histogram of their distribution.

(c) Write a program which produces the values $\xi(n)$ approximately distributed according to the normal Gaussian distribution by adding the numbers extracted from a uniform distribution following the spirit of the central-limit theorem. Show that the distribution approximate Gaussian very well for 12 added numbers already. Generate 10000 values and plot the histogram plot of their distribution.

(d) Use the Gaussian-distributed random values obtained above to update the change in velocity according to the explicit finite difference scheme:

$$v_{n+1} - v_n = -\frac{\gamma}{M}v_n\Delta t + \frac{1}{M}\left(\Gamma\Delta t\right)^{1/2}\xi(n). \tag{8}$$

In order to get the numerical results use the following values, $\gamma = 1, M = 1, k_BT = 1$.

Hint. In Python, you can use the numpy package to produce a Gaussian distribution using a standard function.

(e) Compare the normalized VACFs from (a) and (d) by putting them on the same plot.

3. Generalized Langevin Equation* (2 points)

Very often the history of a system plays an important role in defining the current state of the system. In this case, the Langevin equation reads

$$M\frac{dv}{dt} = -\int_0^t G(t-\tau)v(\tau)d\tau + F_{rand}(t), \tag{9}$$

where the random force is correlated $\langle F_{rand}(t)F_{rand}(t')\rangle = 2k_BTG(t-t')$ due to the fluctuation-dissipation theorem, and the expectation value remains to be equal to zero, $\langle F_{rand}(t)\rangle = 0$.

(a) Program the finite difference scheme for Eq. (9) and calculate the VACF $K_v(t)$. (*Hint.* The integral can be represented as a sum over already obtained history of the system). Consider two cases, (i) $G(t) = \exp(-a|t|)$ and (ii) $G(t) = \exp(-b|t|^2)$. For calculations, choose the following parameters $M = 1, k_BT = 1$ and coefficients a and b from your own choice.

Hint 1. For simplicity, you could simulate the noise as uncorrelated (as in problem 2). However, keep in mind that this will be a violation of the FDT. One extra point will be given for the proper simulation of the noise.

Hint 2. In case you do generate correlated noise, part (ii) should be done by generating correlated (multivariate) Gaussian distribution for all time steps $t_i, i = \overline{1, N}$ in advance. The covariance matrix has entries $C_{ij} = \exp\left(-b\left|t_i - t_j\right|^2\right)$.

(b) For the case $G(t) = \exp(-a|t|)$ find an analytic solution for $K_v(t)$.

Hint. Use the Laplace transform to reduce the equation to the algebraic form and inverse Laplace transform to obtain the results in real time. Multipliying both sides of Eq. 9 by $v(0)$ and averaging over the ensemble, we get the equation for normalized VACF (due to the fact that $\langle F_{rand}(t)v(0)\rangle$ equals zero),

$$M\frac{d}{dt}\frac{\langle v(0)v(t)\rangle}{\langle v^2(0)\rangle} = -\int_0^t G(t-\tau)\frac{\langle v(0)v(\tau)\rangle}{\langle v^2(0)\rangle}d\tau. \tag{10}$$

Solve the latter equation for the set of parameters chosen in (a).

4. Fluctuation-Dissipation Theorem (2 points)

Assume that the quantities A and B are correlated as $\langle A(0)B(t)\rangle = C\exp\left(-|t|/\tau\right)$. Find the imaginary part of the linear response function $\chi_{AB}(\omega)$. How would you describe the physical meaning of this function?

Hint. FDT works for asymmetric case too.