CHM1465: Foundations of Molecular Simulation

PROBLEM SET 3

Notes:

- This set contains 3 problems.
- This third set is due in two weeks, November 5, 2008.

1. Consider a Hamiltonian of the form

$$H = \frac{|\mathbf{P}^N|^2}{2m} + U(\mathbf{R}^N),$$

where $|\mathbf{P}^N|^2 = \sum_{i=1}^{N} \frac{\mathbf{p}_i \cdot \mathbf{p}_i}{2m}$. This Hamiltonian will be split into the kinetic and potential parts

$$K = \frac{|\mathbf{P}^N|^2}{2m} \text{ and } U = U(\mathbf{R}^N).$$

(a) Compute the action of the partial Liouvillians on a phase point $\Gamma = \begin{pmatrix} \mathbf{R}^N \\ \mathbf{P}^N \end{pmatrix}$, i.e. $\mathcal{L}_K\Gamma = \{K, \Gamma\}$ and $\mathcal{L}_U\Gamma = \{U, \Gamma\}$ and prove that

$$\begin{aligned} e^{\mathcal{L}_K \Delta t} \begin{pmatrix} \mathbf{R}^N \\ \mathbf{P}^N \end{pmatrix} &= \begin{pmatrix} \mathbf{R}^N + \frac{\Delta t}{m}\mathbf{P}^N \\ \mathbf{P}^N \end{pmatrix} \\ e^{\mathcal{L}_U \Delta t} \begin{pmatrix} \mathbf{R}^N \\ \mathbf{P}^N \end{pmatrix} &= \begin{pmatrix} \mathbf{R}^N \\ \mathbf{P}^N - \Delta t \frac{\partial U}{\partial \mathbf{R}^N} \end{pmatrix} \end{aligned}$$

(hint: expand the exponentials.)

(b) Use these relations to show that a single step of the Verlet scheme:

$$e^{\mathcal{L}_U \Delta t/2} e^{\mathcal{L}_K \Delta t} e^{\mathcal{L}_U \Delta t/2} \tag{1}$$

conserves phase space volume.

(c) Show that applying the Verlet scheme to a harmonic oscillator

$$H = \frac{1}{2}(p^2 + r^2).$$

leads to a linear map: $\Gamma(t + \Delta t) = \mathsf{M}(\Delta t) \cdot \Gamma(t)$, where M is a 2×2 matrix independent of Γ. Give the explicit form of M.

(d) How can you see that this map conserves phase space volume? What does this imply for the eigenvalues of the map?

(e) Use the eigenvalues of the map to determine the time step at which the Verlet integrator for the harmonic oscillator becomes unstable.

2. The force between two Lennard-Jones particles with a smooth cutoff is given by

$$\varphi(r) = 4\varepsilon\left(\frac{\sigma^{12}}{r^{12}} - \frac{\sigma^6}{r^6}\right) \times \begin{cases} 1 & r < r_c' \\ \frac{(r_c-r)^2(r_c-3r_c'+2r)}{(r_c-r_c')^3} & r_c' \le r \le r_c \\ 0 & r > r_c \end{cases} . \quad (2)$$

where $r = |\mathbf{r}_i - \mathbf{r}_j|$ is the (scalar) distance between two particles at (three-dimensional) positions $\mathbf{r}_i$ and $\mathbf{r}_j$.

(a) Show that the potential is everywhere differentiable.

(b) Derive the force that the two particles feel. What is the sum of these forces?

Consider an N particle system interacting through the smooth Lennard-Jones interaction.

(c) How do the momenta and positions of the particles change in a single Verlet step?

(d) Prove that momentum and angular momentum are conserved in a single Verlet step (neglect boundary conditions).

(e) For large enough time steps, the Verlet scheme applied to the N particle Lennard-Jones system starts to exhibit energy drift. Why does this drift go towards higher energies?

(f) The potential and forces can be computed using cell divisions or a Verlet list. Assuming most of the numerical cost is in computing the potential and forces, which one is more efficient and by how much? Why do these techniques only work for larger systems?

3. Write a small program to simulate a Lennard-Jones system of 343 particles (cf. Eq. (2)) in a cubic periodic simulation box, using the Verlet scheme (1). Set the mass m, interaction range σ and interaction strength ε to 1 (Lennard-Jones units), and set the density at 1. Choose cutoff parameters $r_c' = 2.5$ and $r_c = 3$. (Note: why is there no reason to use cells?) As initial conditions, put the particles on a cubic lattice and draw their initial momenta from a Gaussian with a standard deviation of 0.1. For a range of time steps, determine

- the appropriate length of the burn-in time,
- the average kinetic temperature $T_{\text{kin}} = K/(\frac{3}{2}N)$ in equilibrium,
- the total energy in equilibrium, and
- the fluctuations of the total energy in the simulation.

Demonstrate that the fluctuations of the total energy scale as Δt^2 and determine the time step at which numerical instability sets in.