Phys 516 Assignment 3—Molecular Dynamics Simulation
Due: February 22 (Mon), 2016

The purpose of this assignment is to get familiar with basic concepts in ordinary differential equations using a simple molecular dynamics (MD) program, `md.c`, as an example.

1. **(Liouville's theorem)** For a particle in one-dimensional space, prove that the velocity Verlet algorithm exactly preserves the phase space volume for arbitrary time discretization unit, Δ.

   Submit your proof.

   (Hint) Let the coordinate and momentum of the particle at time t be (x, p), and those at time $t + \Delta$ be (x', p'). Show that the Jacobian of the transformation, $(x'(x, p), p'(x, p))$, is 1. Here the momentum is $p = mv$, where m and v are the mass and velocity of the particle. In the dimensionless form in the lecture note, $p = v$.

2. **(Algorithm variants)** Energy conservation depends on the time-integration algorithm you use. To see this, first rewrite function `SingleStep()` in program `md.c`, such that the Euler algorithm is used for time integration, instead of the velocity Verlet algorithm. Plot the total energy as a function of time using (a) velocity Verlet and (b) Euler algorithms for `DeltaT` = 0.001 and `StepLimit` = 500 (keep the other parameters the same as the default values in md.in in the class home page). Which algorithm conserves the total energy better?

   Submit your plot.

(Euler Algorithm)

Given a configuration $\{\vec{r}_i(t), \vec{v}_i(t) \mid i = 1, \ldots, N_{\text{atom}}\}$

1. Compute the acceleration $\vec{a}_i(t)$
2. Update the positions: $\vec{r}_i(t+\Delta) \leftarrow \vec{r}_i(t) + \vec{v}_i(t)\Delta + \frac{1}{2}\vec{a}_i(t)\Delta^2$
3. Update the velocities: $\vec{v}_i(t+\Delta) \leftarrow \vec{v}_i(t) + \vec{a}_i(t)\Delta$

3. **(Velocity autocorrelation)** Here, we calculate the velocity autocorrelation (VAC) function,

$$Z(t) = \frac{\left\langle \vec{v}_i(t+t_0) \bullet \vec{v}_i(t_0) \right\rangle}{\left\langle \vec{v}_i(t_0) \bullet \vec{v}_i(t_0) \right\rangle} = \frac{\sum_{t_0} \sum_{i=0}^{N-1} \vec{v}_i(t+t_0) \bullet \vec{v}_i(t_0)}{\sum_{t_0} \sum_{i=0}^{N-1} \vec{v}_i(t_0) \bullet \vec{v}_i(t_0)},$$

   where $\vec{v}_i(t)$ is the velocity of the i-th atom at time t. The bracket denotes averages over atoms, i, and the time origin, t_0 (please see the lecture note on "Velocity autocorrelation function").

i) Modify `md.c` in order to compute $Z(t)$ as a function of time. Define `double v0[NMAX][3]` to store the starting atomic velocities. At each time step, sum the products between `rv[n][k]` and `v0[n][k]` for all atoms `n` and directions `k`, and accumulate the sum across time steps. Add an outer loop in the program to repeat this procedure `NSAMPLE` times and take statistics.

Submit your program, with your modifications clearly marked.

ii) Using `InitUcell` = {3,3,3}, `DeltaT` = 0.005 and `StepAvg` = 10, run the program for `StepLimit` = 2000 steps to calculate VAC in the time range of [0, t_{max} = `DeltaT`×`StepLimit` = 0.005×2000 = 10.0] for both gas phase (`Density` = 0.1, `InitTemp` = 1.0) and solid phase (`Density` = 1.0, `InitTemp` = 0.1). Accumulate the sum for `NSAMPLE` = 100 samples. Plot $Z(t)$ as a function of time for both gas and solid phases.

Submit your plot.

4. **(Split-operator formalism)** Derive the velocity Verlet algorithm (p. 8 in the lecture note on "molecular dynamics basics"), using the Trotter expansion of the Liouville operator. You can do this by following Eqs. (2.1) to (2.18) in Ref. [1] and filling all the missing algebra and proof steps between the lines.

Submit your derivation.

Reference

1. "Reversible multiple time scale molecular dynamics," M. Tuckerman, B. J. Berne, and G. J. Martyna, *J. Chem. Phys*. **97**, 1990 (1992).