

## Phys 516 Assignment 4 — Molecular Dynamics Simulation

Due: March 1 (Mon), 2021

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,  $\Delta$ .

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

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

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. 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 = 1000`, run the program for `StepLimit = 2000` steps to calculate VAC in the time range of  $[0, t_{\max} = \text{DeltaT} \times \text{StepLimit} = 0.005 \times 2000 = 10.0]$  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 plots.*

3. **(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).