M2 PTSC et MSA
2014-2015

Simulation numérique en physique statistique
TD n° 3

Molecular dynamics at constant temperature

Références

[1] S. Nosé, J. Chem. Phys. **81** (1984), 511

[2] W.G. Hoover, Phys. Rev. A **31** (1985), 1695

1 Velocity scaling in the leapfrog algorithm

This scheme aims at integrating the equations of motion for constant temperature molecular dynamics simulations in the framework of the leapfrog algorithm. The idea is to scale the velocities so as to maintain the kinetic energy constant at each time step. Let us call T_+ the kinetic energy at time $t + \Delta t/2$ in the leapfrog algorithm, so $T_+ = \frac{1}{3Nk}\sum_i m v_i^2(t + \Delta t/2)$, where N is the number of particles, m their mass, and k_B the Boltzmann constant. The algorithm should maintain this quantity constant at the imposed value T_0.

▷ **1-1** Derive the scaling factor $S(t)$ by which the velocities must be multiplied in order to do this. Express this factor in terms of T_0 and T_+. Explicit the different steps of the modified leapfrog algorithm to account for $S(t)$? We recall that

$$\vec{v}_i(t + \frac{\Delta t}{2}) = \vec{v}_i(t - \frac{\Delta t}{2}) + \Delta t \frac{\vec{F}_i}{m}(t),$$

where Δt is the time step of the simulation and $\vec{F}_i$ is the force imposed by other particles on particle i. Hint : $v(t) = (v(t + \Delta t/2) + v(t - \Delta t/2))/2$.

▷ **1-2** Another idea to maintain the kinetic energy constant is to add an appropriate friction force in the dynamics. We call the corresponding friction coefficient $\zeta(t)$. The equations of motion then become

$$\frac{d\vec{r}_i}{dt} = \vec{v}_i \quad (1)$$

$$\frac{d\vec{v}_i}{dt} = \frac{\vec{F}_i}{m} - \zeta(t)\vec{v}_i, \quad (2)$$

where $\vec{r}_i$, $\vec{v}_i$ are respectively the position and the velocity of particle i. By invoking the conservation of kinetic energy constraint, show that

$$\zeta(t) = \frac{\sum_i \vec{v}_i(t).\vec{F}_i(t)}{\sum_i m\vec{v}_i^2}$$

▷ **1-3** Show that both methods (velocity scaling and additional friction force) are equivalent and that to order 1 in Δt

$$S(t) = 1 - \zeta\Delta t + o(\Delta t).$$

▷ **1-4** Same question but construct an algorithm which is accurate to second order in Δt.

2 Algorithm of Nosé-Hoover

In the approach developed by Nosé [1], the system is coupled to a thermal bath which is characterized by a degree of freedom s, a mass Q, and a conjugate momentum p_s. The parameter Q describes the inertia of the contact with the thermal bath. The Hamiltonian of the system is :

$$H = \sum_{i=1}^{N} \frac{p_i^2}{2ms^2} + U(\vec{r}^N) + \frac{p_s^2}{2Q} + LkT_0 \ln s \tag{3}$$

where $\vec{r}$, $\vec{p}$ are virtual particle coordinates and their corresponding momenta.

▷ **2-1** Show that when $L = 3N + 1$ the partition function of this system (N particles and the thermal bath s) is equivalent to that of the canonical partition function of the initial system composed of N particles with real variables $\vec{r'} = \vec{r}$, $\vec{p'} = \vec{p}/s$, $s' = s$, $p_s^{'} = p_s/s$ and t' such that $dt' = dt/s$. Note that the latter equation means in practice unequal time step dt in the simulation.

▷ **2-2** Obtain from the above Hamiltonian (3), the equations of motion for the virtual variables.

▷ **2-3** Hoover improved upon the algorithm proposed by Nosé in Ref. [2], by replacing the virtual time dt by the real time dt' in the equation of motion. Deduce the new equations of motion as function of r, $\dot{r}$ and $\ddot{r}$.

$$\ddot{r}_i = \frac{F_i}{m} - \xi(t)\dot{r}_i \tag{4}$$

$$\dot{\xi}(t) = \frac{1}{Q}(\sum_{i=1}^{N} m\dot{r}_i^2 - LkT_0) \tag{5}$$

where $\xi(t) = \frac{\dot{s}}{s}$ and the derivatives are taken with respect to real time t'.

▷ **2-4** Show that $L = 3N$ is now the appropriate choice after this change of variables.

▷ **2-5** Write a modified version of the leapfrog algorithm in order to describe the equations of motion of (4) and (5).