1 Molecular Dynamics in curved spaces

Molecular Dynamics is a simulation method for computing trajectories of interacting particles. It consists in solving differential equations coming in most cases from Hamiltonian dynamics. The space in which particles evolve is an Euclidean space in two or three dimensions. Let us denote the position $\vec{x}_i$ and the momentum $\vec{p}_i$ of particle i. The Hamiltonian of the system is given by

$$H = \sum_i^N \frac{\vec{p}_i^2}{2m} + \frac{1}{2}\sum_{i\neq j} v(x_{ij}) \tag{1}$$

where m is the particle mass and $x_{ij} = |\vec{x}_i - \vec{x}_j|$

1. Write the Hamiltonian equations associated with Eq.1.
2. Write the Velocity Verlet algorithm of the equations of motion. The time step will be denoted by Δt. The position and momentum at time t and $t+\Delta t$ will be denoted $\vec{x}_i(t)$, $\vec{p}_i(t)$, $\vec{p}_i(t)$ $\vec{x}_i(t+\Delta t)$, respectively.
3. Show that Velocity Verlet algorithm can be rewritten as

$$\vec{p}_i(t+\Delta t/2) = \vec{p}_i(t) + \frac{\Delta t}{2}\vec{f}_i(t) \tag{2}$$

$$\vec{x}_i(t+\Delta(t) = \vec{x}_i(t) + \frac{\Delta t}{m}\vec{p}_i(t+\Delta t/2) \tag{3}$$

$$\vec{p}_i(t+\Delta t) = \vec{p}_i(t+\Delta t/2) + \frac{\Delta t}{2}\vec{f}_i(t+\Delta t) \tag{4}$$

where $\vec{f}_i$ is a function of $\nabla_{\vec{x}_i} v(x_{ij})$ to be determined.

It is possible to perform simulation in curved spaces by adding the holonomic constraints to the original Hamiltonian system with appropriate Lagrangian multipliers. For the sake of simplicity, we consider here the case of particles moving on a sphere. The Hamiltonian of the system is then given by

$$H = \sum_i^N \frac{\vec{p}_i^2}{2m} + \frac{1}{2}\sum_{i\neq j} v(x_{ij}) + \sum_i^N \lambda_i(t) g(x_i) \tag{5}$$

where m is the particle mass, $g(\vec{x}_i) = \vec{x}_i^2 - R^2$, $\lambda_i(t)$ the Lagrangian multipliers and R the radius of the sphere.

4. Write the Hamiltonian equations associated with the modified Hamiltonian, Eq.5.
5. By using the same method given in Eqs.(2-4), write the Velocity Verlet algorithm of the modified Hamiltonian. Due to the discretization, the Lagrangian mulitpliers cannot be identical for the computation of the position updates and the velocity updates. For the position and velocity updates, they will be denoted as $\mu_i(t)$ and $\kappa_i(t)$, respectively.

The Lagrangian mulitpliers do not have analytical expressions and must be obtained numerically in general. In order to obtain these numbers, one introduces $4D$ vectors

$$\vec{r}_i = \begin{pmatrix} \vec{r}_{i,x} \\ r_{i,g} \end{pmatrix}$$

where

$$\vec{r}_{i,x} = \vec{x}_i(t) - \vec{x}_i(t+\Delta t) + \frac{\Delta t}{m}(\vec{p}_i(t) + \frac{\Delta t}{2}(\vec{f}_i(t) - 2\mu_i(t)\vec{x}_i(t)) \quad (6)$$

$$r_{i,g} = g(x_i(t+\Delta t)) \quad (7)$$

We have to determine $\mu_i(t)$ and the position $\vec{x}_i(t+\Delta t)$ such that the $4D$ vector becomes equal to 0 (or numerically less than an absolute value less than 10^{-6}). Let us define the $4D$ vector

$$\vec{y}_i = \begin{pmatrix} \vec{x}_i(t+\Delta t) \\ \mu_i(t) \end{pmatrix} \quad (8)$$

To obtain $\mu_i(t)$ and $\vec{x}_i(t+\Delta t)$, one uses a Newton-method and the iterative procedure is obtained as follows :

$$\vec{y}_{i,j+1} = \vec{y}_{i,j} - J_i^{-1}\vec{r}_i \quad (9)$$

where J_i is the Jacobian matrix defined as

$$J_i = \frac{\partial \vec{r}_i}{\partial \vec{y}_i} = \begin{pmatrix} \frac{\partial r_{1,i}}{\partial y_{1,i}} & \frac{\partial r_{1,i}}{\partial y_{2,i}} & \frac{\partial r_{1,i}}{\partial y_{3,i}} & \frac{\partial r_{1,i}}{\partial y_{4,i}} \\ \frac{\partial r_{2,i}}{\partial y_{1,i}} & \frac{\partial r_{2,i}}{\partial y_{2,i}} & \frac{\partial r_{2,i}}{\partial y_{3,i}} & \frac{\partial r_{2,i}}{\partial y_{4,i}} \\ \frac{\partial r_{3,i}}{\partial y_{1,i}} & \frac{\partial r_{3,i}}{\partial y_{2,i}} & \frac{\partial r_{3,i}}{\partial y_{3,i}} & \frac{\partial r_{3,i}}{\partial y_{4,i}} \\ \frac{\partial r_{4,i}}{\partial y_{1,i}} & \frac{\partial r_{4,i}}{\partial y_{2,i}} & \frac{\partial r_{4,i}}{\partial y_{3,i}} & \frac{\partial r_{4,i}}{\partial y_{4,i}} \end{pmatrix} \quad (10)$$

6. Compute the Jacobian matrix J_i

For the velocity updates, one introduces $4D$ vectors

$$\vec{s}_i = \begin{pmatrix} \vec{s}_{i,x} \\ s_{i,g} \end{pmatrix}$$

where

$$\vec{s}_{i,x} = \vec{p}_i(t+\Delta t/2) - \vec{p}_i(t+\Delta t) + \frac{\Delta t}{2}(\vec{f}_i(t+\Delta t) - 2\kappa_i(t)\vec{x}_i(t)) \quad (11)$$

$$s_{i,g} = \frac{\partial g(x_i(t+\Delta t))}{\partial t} = 2\vec{x}_i\frac{\vec{p}_i}{m} \quad (12)$$

We have to determine $\kappa_i(t)$ and the momentum $\vec{p}_i(t+\Delta t)$ such that the $4D$ vector $\vec{s}_i$ becomes equal to 0 (or numerically less than an absolute value less than 10^{-6}). Let us define the $4D$ vector

$$\vec{z}_i = \begin{pmatrix} \vec{p}_i(t+\Delta t) \\ \kappa_i(t) \end{pmatrix} \quad (13)$$

To obtain $\kappa_i(t)$ and $\vec{p}_i(t+\Delta t)$, one uses a Newton-method and the iterative procedure is obtained as follows :

$$\vec{z}_{i,j+1} = \vec{z}_{i,j} - K_i^{-1}\vec{s}_i \tag{14}$$

where K_i is the Jacobian matrix defined as

$$K_i = \frac{\partial \vec{s}_i}{\partial \vec{z}_i} \tag{15}$$

7. Compute the Jacobian matrix K_i
8. This algorithm, called RATTLE algorithm, is implemented in LAMMPS. What is LAMMPS ? Is it suitable for parallel computing ?

2 A bound particle coupled to two thermostats

One considers a particle of mass m in one dimension subjected to a harmonic force and coupled to two heat reservoirs. The equations of motion are given by

$$\frac{dx}{dt} = v \tag{16}$$

$$m\frac{dv}{dt} = -(\gamma_1+\gamma_2)v - kx + \xi_1(t) + \xi_2(t) \tag{17}$$

where γ_i are the viscosity coefficients and the two Gaussian white noises are given by

$$\langle \xi_i(t) \rangle = 0 \tag{18}$$

$$\langle \xi_i(t)\xi_j(t') \rangle = 2\gamma_i T_i \delta_{ij}\delta(t-t') \tag{19}$$

with δ_{ij} is the Kronecker symbol. ($\delta_{ij} = 1$ for $i = j$ and $\delta_{ij} = 0$ for $i \neq j$) and $\delta(t)$ is the Dirac distribution. At $t = 0$, one has $v(0) = 0$ and $x(0) = 0$. Let us define the Laplace transform $\tilde{f}(u) = \int_0^\infty dt e^{-ut} f(t)$ (see Glossary for additional properties of Laplace transforms).

1. Show that the Laplace transform of the velocity $\tilde{v}(u)$ can be expressed as

$$\tilde{v}(u) = \tilde{G}(u)[\tilde{\xi}_1(u) + \tilde{\xi}_2(u)] \tag{20}$$

where $\tilde{G}(u)$ is a function to be determined.

Solution: Taking the Laplace transforms of the differential equations one has

$$u\tilde{x} = \tilde{v} \tag{21}$$

$$u\tilde{v} = -(\gamma_1+\gamma_2)\tilde{v} - k\tilde{x} + \tilde{\xi}_1 + \tilde{\xi}_2 \tag{22}$$

Consequently, one has

$$\tilde{G}(u) = \frac{u}{k + (\gamma_1+\gamma_2)u + mu^2} \tag{23}$$

2. Show that $\tilde{G}(u)$ can be written as

$$\tilde{G}(u) = \frac{1}{m(u_1 - u_2)}\left(\frac{u_1}{u - u_1} - \frac{u_2}{u - u_2}\right) \tag{24}$$

where u_1 and u_2 are functions of γ_1 ,γ_2 and k.

Solution:

$$\tilde{G}(u) = \frac{u}{(u - u_1 0(u - u_2))} \tag{25}$$

The algebraic equation is

$$u^2 + \frac{(\gamma_1 + \gamma_2)}{m}u + \frac{k}{m} = 0 \tag{26}$$

The solutions are

$$u_{1,2} = \frac{1}{2}\left(-\frac{(\gamma_1 + \gamma_2)}{m} \pm \sqrt{\left(\frac{(\gamma_1 + \gamma_2)}{m}\right)^2 - 4\frac{k}{m}}\right) \tag{27}$$

3. Determine the values of k for which the system is overdamped and for which one has a damped oscillatory behavior

Solution: When the roots are real the motion is overdamped, namely $\frac{(\gamma_1+\gamma_2)}{m} \geq 2\sqrt{\frac{k}{m}}$. When the roots are complex, the motion is underdamped, namely $\frac{(\gamma_1+\gamma_2)}{m} < 2\sqrt{\frac{k}{m}}$.

4. By taking the inverse Laplace transform, give the velocity $v(t)$.

Solution:

$$v(t) = \frac{1}{m}\int_0^t dt' \frac{u_1 e^{u_1 t'} - u_2 e^{u_2 t'}}{u_1 - u_2}(\xi_1(t') + (\xi_2(t')) \tag{28}$$

5. Express the rates of heat $\frac{dQ_1}{dt}$ and $\frac{dQ_2}{dt}$ received by the reservoir 1 and 2, respectively.

Solution:

$$\frac{dQ_i}{dt} = -\gamma_i v^2(t) + v(t)\xi_i(t) \tag{29}$$

6. Calculate $\langle v(t)^2 \rangle$.

Solution: For calculating the mean square of the velocity one uses that the cross correlations of the noise are equal to 0.

$$\langle(\xi_1(t)+\xi_2(t))(\xi_1(t')+\xi_2(t'))\rangle = 2\gamma_1\delta(t'-t)+2\gamma_2\delta(t'-t) \tag{30}$$

Expanding the square velocity and using the property of the delta function , one obtains

$$\langle v^2(t)\rangle = \left(\frac{2\gamma_1 T_1}{m^2}+\frac{2\gamma_2 T_2}{m^2}\right)\int_0^t \left(\frac{u_1 e^{u_1 t'}-u_2 e^{u_2 t'}}{u_1-u_2}\right)^2 \tag{31}$$

Once integrated one obtains a lengthy formula with a constant term and trois decaying exponetials.

7. Calculate $\langle\xi_i(t)v(t)\rangle$.

Solution: Once again, one uses that the cross correlations of the noise cancel. Finally one obtains a constant term and two decaying exponentials.

8. Show that the two above quantities converge to stationary values when t is larger than a typical time to be determined.

Solution: When t is large, one obtains

$$\langle v^2\rangle = \frac{\gamma_1 T_1+\gamma_2 T_2}{m(\gamma_1+\gamma_2)} \tag{32}$$

and similarly, one has

$$\langle v\xi_i\rangle = \frac{\gamma_i T_i}{m} \tag{33}$$

The inverse characteristic time $1/u_1$

9. Show that the mean stationary value of $\frac{d\langle Q_i\rangle}{dt}$ is given by

$$\frac{d\langle Q_i\rangle}{dt} = \frac{\gamma_1\gamma_2}{m(\gamma_1+\gamma_2)}(T_i-T_j) \tag{34}$$

where $j=2$ for $i=1$ and $j=1$ for $i=2$.

Solution: By combining the results of the above questions, one obtains

$$\frac{d\langle Q_1\rangle}{dt} = \frac{\gamma_1\gamma_2}{m(\gamma_1+\gamma_2)}(T_1-T_2) \tag{35}$$

and

$$\frac{d\langle Q_2\rangle}{dt} = \frac{\gamma_1\gamma_2}{m(\gamma_1+\gamma_2)}(T_2 - T_2) \tag{36}$$

10. Why is the heat transport independent of the spring constant ?

Solution: One can accumulate energy in the spring !

Glossary

— The inverse Laplace tranform of $\frac{1}{u-u_1}$ is $e^{u_1 t}$

— The inverse Laplace transform of a product of two Laplace transforms $\tilde{f}(u)\tilde{g}(u)$ is given by

$$\int_0^\infty d\tau f(t-\tau)g(\tau) \tag{37}$$

— $\int_0^t dt' f(t')\delta(t'-t) = f(t)/2$

Références

[1] P. Visco, *Work fluctuations for a Brownian particle between two thermostats* J. Stat. Mech., P06006 (2006)