1 Nosé-Poincaré Algorithm and multiple thermostats

The method introduced by Nosé proposes to couple un system defined by an Hamiltonian $\mathcal{H}(\tilde{p}_i, q_i)$ to an additional degree of freedom denoted s as follows

$$H_{\text{Nosé}}(\tilde{p}_i, q_i, \tilde{p}_s, s, \tilde{g}) = \sum_{i=1}^{N} \frac{\tilde{p}_i^2}{2m_i s^2} + V(q) + \frac{\tilde{p}_s^2}{2Q} + \tilde{g}\frac{\ln(s)}{\beta} \tag{1}$$

where q_i, $\tilde{p}_i$ et m_i are the position, the momentum and the mass of the particle i, respectively. (q is a shorthand notation for the set of variables q_j where $j = 1..d$). s is an one-dimensional positive variable , $\tilde{p}_s$ the momentum and Q the masse of the fictive particle. $\tilde{g}$ si equal to the *number of degrees of freedom* N of the system consisting in n particles (in three dimensions for a simple liquid, one has $N = 3n$) and of the fictive particle.

1. Calculate the Hamiltonian equations of the complete system, namely for the variables $\tilde{p}_i$, q_i and also $\tilde{p}_s$ et s.
2. One performs the changes of variables $p_i = \frac{\tilde{p}_i}{s}$ and $p_s = \frac{\tilde{p}_s}{s}$. What are the equations of motion with these new variables ?
3. One makes the following change for the time variable $d\tau = \frac{dt}{s}$. For reasons going beyond this exercice, $\tilde{g}$ becomes equal to N. Show that the equations of motion become

$$\frac{dq_i}{d\tau} = \frac{p_i}{m_i}, \qquad \frac{dp_i}{d\tau} = -\frac{\partial V(q)}{\partial q_i} - p_i\frac{sp_s}{Q}$$
$$\frac{ds}{d\tau} = \frac{s^2 p_s}{Q}, \qquad \frac{dp_s}{d\tau} = \frac{1}{s}\left(\sum_i \frac{p_i^2}{m_i} - \frac{N}{\beta}\right) - \frac{sp_s^2}{Q} \tag{4}$$

4. The last change of variables is $\xi = \frac{sp_s}{Q}$ et $\eta = \ln(s)$. Give the equations of motion for p_i, ξ et η. Why can one sat that ξ can be interpreted as an effective viscous friction coefficient ?

The change of variables in question 3 looses the initial Hamiltonian structure, but the total energy remains a conserved quantity.

1. Show that the total energy of the complete system given by

$$E_{ext} = \sum_i \frac{p_i^2}{2m_i} + V(q) + Q\frac{\xi^2}{2} + \frac{N\eta}{\beta} \tag{6}$$

is constant.

The Nosé-Hoover algorithm does not keep the symplectic structure of the reduced system. In order to correct this drawback, the Nosé-Poincaré Hamiltonain aims to cure this problem. Consider the following Hamiltonian :

$$\tilde{\mathcal{H}} = (\mathcal{H}_{\text{Nosé}}(\tilde{p}_i, q_i, \tilde{p}_s, s, g) - \mathcal{H}_0)s \tag{7}$$

where $\mathcal{H}_0$ is a constant. Note that this time, one uses g and not $\tilde{g}$. On seeks to determine the equilibrium distribution of the particles.

2. Write the microcanonical partition function of the complete system for a total energy $\tilde{\mathcal{H}}_0$.
3. By using the change of variables $p_i = \tilde{p}_i/s$, integrate over the variable s. (Hint : see the glossary for a property of the δ distribution.)
4. Integrate over the variable p_s and give the distribution obtained for the reduced system.

   The correction performed by the Nosé-Poincaré method is not sufficient. Indded, one also observes for small systems an ergocity breaking in a simulation. This phenomenon can be illustrated with a harmonic oscillator. Whereas in a canonical ensemble, the system can explore the full set of spatial configurations, the Nosé-Hoover or Nosé-Poincaré method restricts the exploration in in a confined region of the phase space. In order to cure this situation, it is possible to increase the number of thermostats. Consider the simplest case of two thermostats. The Hamitonian is given by

$$
\begin{aligned}
H_{\mathrm{MT}}(\tilde{p}_i, q_i, \tilde{p}_{s_1}, s_1) = &\sum_{i=1}^{M} \frac{\tilde{p}_i^2}{2m_i s_1^2 s_2^2} + \sum_{j=M+1}^{N} \frac{\tilde{p}_j^2}{2m_j s_1^2} + V(q) \\
&+ \frac{\tilde{p}_s^2}{2Q} + (N+1)\frac{\ln(s_1)}{\beta} + \frac{\tilde{p}_{s_2}^2}{2Q} + g\frac{\ln(s_2)}{\beta} + f(s_2)
\end{aligned} \tag{11}
$$

   where $f(s)$ is a function and g a constant to be determined.
5. By integrating over s_1 and s_2, show that one obtains a canonical distribution for the reduced system with the condition that $g = M$ and $\int ds \exp(-\beta f_2(x))$ remains finite.

2 Wang-Landau and statistical temperature algorithms

The Wang-Landau algorithm is a Monte-Carlo method which allows obtaining the density of states $g(E)$ of a systems in a finite interval of energy.

1. Why is it necessary to decrease the modification factor f to each iteration ? Justify your answer.
2. Why is it numerically interesting of working with the logarithm of the density of states ?
3. At the beginning of the simulation, the density of states $g(E)$ is generally chosen equal to 1. If one takes another initial condition, does it obtain the same density of states at the end of the simulation.
4. Wang-Landau dynamics is generally performed by using elementary moves of a single particle, in a similar manner of a Metropolis algorithm. If dynamics involves several particles, why does the efficiency decreases rapidly with the systems size, and not for the Wang-Landau algorithm ?

   For models with a continuous energy spectra, the Wang-Landau algorithm is generally less efficient and sometimes does not converge towards the equilibrium density of states. We are going to determine the origin of this problem ; for calculating the density of states, it is necessary to discretize the spectra of the density of states. Let us denote the bin size ΔE of of the histogram of the density of states.

5. If the mean energy change of a configuration is $\delta E_c << \Delta E$, and if the initial configuration has an energy located within the interval of the mean energy E, what can one say about the acceptance probability of the new configuration ? Why does it imply a certain bias in the convergence of the Wang-Landau method ?

   In order to correct the drawback of the Wang-Landau method, Kim and coworkers proposed to update the effective temperature $T(E) = \dfrac{\partial E}{\partial S}$, where $S(E)$ is the microcanonical entropy, instead of the density of states

6. By discretizing the derivative of the density of states with respect to the energy (with $k_B = 1$) :

$$\left.\frac{\partial S}{\partial E}\right|_{E=E_i} = \frac{1}{T_i} = \beta_i \simeq \frac{(S_{i+1} - S_{i-1})}{2\Delta E} \tag{12}$$

   show that for a elementary move whose new configuration has an energy E_i, two statistical temperatures must be changed according to the formula

$$\beta'_{i\pm1} = \beta_{i\pm1} \mp \delta f \tag{13}$$

   where $\delta f = \dfrac{\ln f}{2\Delta E}$ and f is the modification factor. Show that

$$T'_{i\pm1} = \alpha_{i\pm1} T_{i\pm1}$$

   where $\alpha_{i\pm1}$ is a parameter to be determined. How doe T_{i+1} and T_{i-1} evolve along the simulation ? What can one conclude about the temperature variation with energy ?

7. One then calculates the entropy of each configuration by using a linear interpolation of the temperature between two successive intervals i and $i+1$, show that the entropy is then given by the equation

$$S(E) = S(E_0) + \sum_{j=1}^{i} \int_{E_{j-1}}^{E_j} \frac{dE}{T_{j-1} + \lambda_{j-1}(E - E_{j-1})} + \int_{E_i}^{E} \frac{dE}{T_i + \lambda_i(E - E_i)} \tag{14}$$

   where λ_i is a parameter to be determined as a function of ΔE and of temperature T_i and T_{i+1}.

8. What can one say about the entropy difference between two configurations belonging to the same interval for the statistical temperature and separated by an energy δE_c ? What can one conclude by comparing this algorithm to the original Wang-Landau algorithm ?

Glossary

If $h(s)$ is a function which vanishes once at the value $s = s_0$

$$\delta(h(s)) = \frac{\delta(s - s_0)}{|h'(s_0)|} \tag{15}$$

where δ is the Dirac distribution.

The Stirling formula gives

$$\ln(n!) \simeq n \ln(n) - n. \tag{16}$$

The arctanh function can be expressed as a function of the logaritmh as

$$\text{arctanh}(x) = \frac{1}{2} \ln\left(\frac{1+x}{1-x}\right) \tag{17}$$