1 Nosé-Poincaré Algorithm and multiple thermostats

The method introduced by Nosé proposes to couple un système 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 shorhand notation for the set of variables q_i). s is a 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 made of n particles (in three dimensions for a simple liquid $N = 3n$) 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.

Solution: Taking the partial derivatives of the Hamiltonian, one obtains

$$\frac{dq_i}{dt} = \frac{\partial H_{\text{Nosé}}}{\partial \tilde{p}_i} = \frac{\tilde{p}_i}{m_i s^2}, \tag{2}$$

$$\frac{d\tilde{p}_i}{dt} = \frac{\partial H_{\text{Nosé}}}{\partial q_i} = -\frac{\partial V(q)}{q_i} \tag{3}$$

$$\frac{ds}{dt} = \frac{\partial H_{\text{Nosé}}}{\partial \tilde{p}_s} = \frac{\tilde{p}_s}{Q}, \tag{4}$$

$$\frac{d\tilde{p}_s}{dt} = \frac{\partial H_{\text{Nosé}}}{\partial s} = -\sum_{i=1}^{N} \frac{\tilde{p}_i^2}{m_i s^3} - \frac{\tilde{g}}{\beta s} \tag{5}$$

2. One performs the change of variables $p_i = \frac{\tilde{p}_i}{s}$ and $p_s = \frac{\tilde{p}_s}{s}$. What do the equations of motion become ?

Solution: By using the change of variables, one obtains

$$s\frac{dq_i}{dt} = \frac{p_i}{m_i}, \tag{6}$$

$$s\frac{dp_i}{dt} = -p_i\frac{ds}{dt} - \frac{\partial V(q)}{q_i} \tag{7}$$

$$\frac{ds}{dt} = \frac{sp_s}{Q}, \tag{8}$$

$$s\frac{dp_s}{dt} = -p_s\frac{ds}{dt} - \sum_{i=1}^{N} \frac{p_i^2}{m_i s} - \frac{\tilde{g}}{\beta s} \tag{9}$$

3. One makes the temporal change of variables $d\tau = \frac{dt}{s}$. For reasons going beyond this exercice, $\tilde{g}$ becomes equal to N. Show that the equations of motion become

$$\frac{dq_i}{d\tau} = \frac{p_i}{m_i}, \qquad \frac{dp_i}{d\tau} = -\frac{\partial V(q)}{\partial q_i} - p_i \frac{sp_s}{Q}$$
$$\frac{ds}{d\tau} = \frac{s^2 p_s}{Q}, \qquad \frac{dp_s}{d\tau} = \frac{1}{s}\left(\sum_i \frac{p_i^2}{m_i} - \frac{N}{\beta}\right) - \frac{sp_s^2}{Q} \tag{10}$$

Solution: By using the last change of variable, one obtains trivially the above equations

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 ?

Solution: The previous equations become (the first one is unchanged)

$$\frac{dp_i}{d\tau} = -\frac{\partial V(q)}{\partial q_i} - \xi p_i \tag{11}$$
$$\frac{d\eta}{d\tau} = \xi \tag{12}$$
$$\frac{d\xi}{d\tau} = \frac{1}{Q}\left(\sum_i \frac{p_i^2}{m_i} - \frac{N}{\beta}\right) \tag{13}$$

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

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

$$E_{ext} = \sum_i \frac{p_i^2}{2m_i} + V(q) + Q\frac{\xi^2}{2} + \frac{N\eta}{\beta} \tag{14}$$

is a conserved quantity.

Solution: By taking the time derivative of E_{ext} and by using the equations obtains in Question 3, one obtains that

$$\frac{dE_{ext}}{dt} = 0$$

and the total energy of the total system is conserved

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

$$\mathcal{H} = (\mathcal{H}_{\text{Nosé}}(\tilde{p}_i, q_i, \tilde{p}_s, s, g) - \mathcal{H}_0)s \tag{15}$$

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.

6. Write the microcanonical partition function of the complete system.

Solution:

$$Z(E) = \int ds d\tilde{p}_s dq_i d\tilde{p}_i \delta(\mathcal{H} - E)$$

where the integral is over all available configurations.

7. By using the change of variables $p_i = \tilde{p}_i/s$, integrate over the variable s when $E = 0$. (Hint : see the glossary for a property of the δ distribution.)

Solution: The partition function becomes

$$Z = \int ds d\tilde{p}_s dq_i dp_i s^{N_f} \delta(s(\sum_{i=1}^{N} \frac{p_i^2}{2m_i} + V(q) + \frac{\tilde{p}_s^2}{2Q} + g\frac{\ln(s)}{\beta} - H_0))$$

where N_f is the number of degrees of freedom of the N particles.
Using the glossary, one has

$$\delta(s(\sum_{i=1}^{N} \frac{p_i^2}{2m_i} + V(q) + \frac{\tilde{p}_s^2}{2Q} + g\frac{\ln(s)}{\beta} - H_0)) = \delta(s - \exp(\frac{-\beta}{g}(\sum_{i=1}^{N} \frac{p_i^2}{2m_i} + V(q) + \frac{\tilde{p}_s^2}{2Q} - H_0)))$$

Integrating over s gives (up to an irrelevant multiplicative factor)

$$Z = \int d\tilde{p}_s dq_i dp_i \exp(\frac{-N_f\beta}{g}(\sum_{i=1}^{N} \frac{p_i^2}{2m_i} + V(q) + \frac{\tilde{p}_s^2}{2Q})$$

8. Integrate over the variable p_s and give the distribution obtained for the reduced system.

Solution: By using $g = N_f$, one obtains

$$Z \sim \int dq_i dp_i \exp(-\beta(\sum_{i=1}^{N} \frac{p_i^2}{2m_i} + V(q))$$

which corresponds to the canonical distribution of the system of N particles.

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

$$H_{\mathrm{MT}}(\tilde{p}_i, q_i, \tilde{p}_{s_1}, s_1) = \sum_{i=1}^{M} \frac{\tilde{p}_i^2}{2m_i s_1^2 s_2^2} + \sum_{j=M+1}^{N} \frac{\tilde{p}_j^2}{2m_j s_1^2} + V(q) + \frac{\tilde{p}_s^2}{2Q} + (N+1)\frac{\ln(s_1)}{\beta} + \frac{\tilde{p}_{s_2}^2}{2Q} + g\frac{\ln(s_2)}{\beta} + f(s_2) \tag{16}$$

where $f(s)$ is a function and g a constant to be determined.

9. 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 Self intermediate scattering function

This problem aims to understand the change of behavior of the self Van Hove correlation function $G_s(r,t)$ (or its Fourier transform, known as the self intermediate scattering function $F_s(k,t)$) when a system goes from a "normal" phase to the "glassy" phase, in which dynamics is slowing down. For the fake of simplicity, one writes the self Van Hove function as $G_s(\mathbf{r},t) =< \delta(\mathbf{r} + \mathbf{r}_i(0) - \mathbf{r}_i(t)) >$ where i is a label for a tagged particle.

We are interested in the behavior of this function at long time and long distance.

1. Write the equation associated with the mass conservation of the small volume (of tagged particles) by using the local density $\rho^{(s)}(\mathbf{r},t)$ and the local current $\mathbf{j}^{(s)}(\mathbf{r},t)$.
2. One assumes that the particles undergo a diffusion motion with the Fick law $\mathbf{j}^{(s)}(\mathbf{r},t) = -D\nabla\rho^{(s)}(\mathbf{r},t)$. Write the partial differential equation for the local density $\rho^{(s)}(\mathbf{r},t)$?

Solution: The local conservation of the mass is given by

$$\frac{\partial\rho^{(s)}(\mathbf{r},t)}{\partial t} + \nabla.\mathbf{j}^{(s)}(\mathbf{r},t) = 0$$

3. Defining the Fourier transform of $\rho^{(s)}(\mathbf{r},t)$, as $\hat{\rho}^{(s)}(\mathbf{k},t) = \int d\mathbf{r}^3 \rho^{(s)}(\mathbf{r},t)e^{-i\mathbf{kr}}$, obtain the differential equation for $\hat{\rho}^{(s)}(\mathbf{k},t)$. Solve this equation. Let us denote $\hat{\rho}^{(s)}(\mathbf{k},0)$ the initial condition.

Solution:

$$\frac{\partial \hat{\rho}^{(s)}(\mathbf{k},t)}{\partial t} = -D\mathbf{k}^2\rho^{(s)}(\mathbf{k},t)$$

Integrating the partial differential equation leads to

$$\rho^{(s)}(\mathbf{k},t) = \rho^{(s)}(\mathbf{k},0)\exp(-Dk^2 t)$$

4. One admits that $F_s(\mathbf{k},t) =< \hat{\rho}^{(s)}(\mathbf{k},t)\hat{\rho}^{(s)}(-\mathbf{k},0) >$ where the bracket denotes an average on the initial conditions. Infer that $F_s(\mathbf{k},t) \sim \exp(-Dk^2 t)$.

Solution: Multiplying the above solution by the density of the initial condition and taking the average leads to the expected behavior.

5. By using the inverse Fourier transform, obtain an expression of $G_s(r,t)$.

Solution:

$$G(r,t) \sim e^{-r^2/4Dt}$$

which corresponds to a diffusive motion of the tagged particle.

One now considers the situation where the dynamics is glassy with the existence of dynamic heterogeneities. Experiments and simulation results reveal that the long distance decay of the Van Hove is not longer a Gaussian. The problem aims to propose a simple model for the particle dynamics. Particle motions due to vibrations are neglected and dynamics is modeled by introducing a lattice on which particles hop from a site to another with a probability distribution which depends on the relative distance $f(r)$. The time distribution for a hop is given by $\phi(t) = \tau^{-1}e^{-t/\tau}$ (One assumes that this time distribution is identical for the first hop. The self Van Hove function is then given by

$$G_s(r,t) = \sum_{n=0}^{\infty} p(n,t)f(n,r) \tag{17}$$

where $p(n,t)$ is the probability of having n hops at time t and $f(n,r)$ the probability of moving on a distance r after n hops.

6. Show that $p(0,t) = 1 - \int_0^t dt'\phi(t')$. Calculate $p(0,t)$.

Solution: The cumulative distribution of ϕ is the complementary probability of the probability of the absence of hops.

$$p(0,t) = e^{-t/\tau}$$

7. Find the relationship between $p(n,t)$ and $p(n-1,t)$.

Solution: The probability of having n hops at time t is the sum of the probability of having $n-1$ hops between 0 and t' and one hop between t' and t.

$$p(n,t) = \int_0^t dt' \phi(t') p(n-1, t-t')$$

8. Same question betwen $f(n,r)$ and $f(n-1,r)$.

Solution: Similarly,

$$f(n,r) = \int_0^r d\mathbf{r}' f(n-1, r') f(|\mathbf{r} - \mathbf{r}')|$$

9. Show that $\hat{f}(n,k) = f(k)^n$ and that $\hat{p}(n,s) = \hat{p}(0,s)\hat{\phi}(s)^n$

Solution: Taking the Laplace transform of $p(n,t)$ and the Fourier transform of $f(n,r)$, one obtains geometric sequences, which gives $\hat{f}(n,k) = f(k)^n$ and that $\hat{p}(n,s) = \hat{p}(0,s)\hat{\phi}(s)^n$

One defines the Fourier-Laplace transform as

$$\tilde{G}(\mathbf{k}, s) = \int d^3\mathbf{r} e^{-i\mathbf{k}\mathbf{r}} \int_0^\infty dt e^{-st} G_s(r,t) \tag{18}$$

10. Show that

$$\tilde{G}(k,s) = \frac{\hat{p}(0,s)}{1 - \hat{\phi}(s)\hat{f}(k)} \tag{19}$$

Solution: By using the definition of $G(r,t)$, the Fourier Laplace transform gives

$$\tilde{G}(k,s) = \sum_{n=0}^{\infty} \hat{p}(n,s)\hat{f}(n,k)$$

By using the expressions of $\hat{p}(n,s)$ and $\hat{f}(n,k)$ the geometric series can be calculated and one obtains

$$\tilde{G}(k,s) = \frac{\hat{p}(0,s)}{1 - \hat{\phi}(s)\hat{f}(k)}$$

11. Let us denote $\tilde{G}_0(k,s) = \hat{p}(0,s)$. Calculate $G_0(r,t)$. What is the physical meaning of this quantity ?

Solution:

$$G(r,t) = \delta(r)e^{-t/\tau}$$

This corresponds to the probability that the particle does not hop between 0 and t.

12. Show that

$$G(r,t) - G_0(r,t) = \frac{e^{-t/\tau}}{(2\pi)^3}\int d^3\mathbf{k}\left[e^{t\hat{f}(k)/\tau} - 1\right]e^{i\mathbf{kr}} \tag{20}$$

Solution:

$$\tilde{G}(k,s) - G_0(k,s) = \frac{\hat{p}(0,s)\hat{\phi}(s)\hat{f}(k)}{1-\hat{\phi}(s)\hat{f}(k)}$$

Knowing that $\hat{\phi}(s) = \frac{1}{1+\tau s} = \tau\hat{p}(0,s)$, one obtains

$$\tilde{G}(k,s) - G_0(k,s) = \frac{\tau}{1+\tau s - f(k)} - \frac{\tau}{1+\tau s}$$

taking the inverse Laplace transform, one obtains the expected formula.

13. If $f(r) = (2\pi d^2)^{-3/2}e^{-r^2/(2d^2)}$, calculate $\tilde{f}(k)$. One now considers $t = \tau$. Expanding the exponential of Eq. (20) and using the inverse Fourier transform (use the glossary), show that

$$G(r,\tau) - G_0(r,\tau) \sim e^{-\frac{r}{d}} \tag{21}$$

Give a physical meaning of this result.

Solution: The inverse Fourier transform of $\tilde{f}(k)$ is given by

$$\tilde{f}(k) = e^{-(kd)^2/(2)}$$

Using that $\left[e^{t\hat{f}(k)/\tau} - 1\right] = \sum_{n=1}^{\infty}\frac{(t\hat{f}(k)/\tau)^n}{n!}$, and taking the inverse Fourier transform at $t = \tau$ one obtains

$$G(r,\tau) - G_0(r,\tau) \sim \sum_{n=1}\infty\frac{1}{n!n^{3/2}}e^{-r^2/(2d^2n)}$$

Finally, using the glossary, one obtains the expected formula.

This behavior observed in glassformers is associated to particles moving by successive jumps instead of diffusive motion for a liquid at high temperature.

Glossary

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

$$\delta(h(s)) = \frac{\delta(s - s_0)}{|h'(s_0)|} \tag{22}$$

where δ is the Dirac distribution.

The Stirling formula gives

$$\ln(n!) \simeq n \ln(n) - n. \tag{23}$$

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

$$\text{arctanh}(x) = \frac{1}{2} \ln\left(\frac{1+x}{1-x}\right) \tag{24}$$

The three dimensional Fourier trasnsform of a function f is defined as

$$\hat{f}(\mathbf{k}) = \int d^3\mathbf{r} f(\mathbf{r}) e^{-i\mathbf{kr}} \tag{25}$$

and the inverse transform is given by

$$f(\mathbf{r}) = \frac{1}{(2\pi)^3} \int d^3\mathbf{k} \hat{f}(\mathbf{k}) e^{i\mathbf{kr}} \tag{26}$$

For a Gaussian function

$$f(\mathbf{r}) = e^{-a\mathbf{r}^2/2} \tag{27}$$

the Fourier transform is

$$\hat{f}(\mathbf{k}) = \left(\frac{2\pi}{a}\right)^{3/2} e^{-\mathbf{k}^2/(2a)} \tag{28}$$

Conversely, if

$$\hat{f}(\mathbf{k}) = e^{-b\mathbf{k}^2/2} \tag{29}$$

the inverse Fourier transform is

$$f(\mathbf{r}) = \left(\frac{1}{2\pi b}\right)^{3/2} e^{-\mathbf{r}^2/(2b)} \tag{30}$$

Some identities for $\delta(\mathbf{r})$

$$\delta(\mathbf{r}) = \frac{1}{(2\pi)^3} \int d^3\mathbf{k} e^{i\mathbf{kr}}, 1 = \int d^3\mathbf{r} e^{i\mathbf{kr}} \delta(\mathbf{r}) \tag{31}$$

The Laplace transform of f is defined as

$$\hat{f}(s) = \int_0^\infty dt f(t) e^{-st} \tag{32}$$

The inverse Laplace transform is given by

$$f(t) = \frac{1}{2\pi i}\int_{\gamma-i\infty}^{\gamma+i\infty} dz e^{st}\hat{f}(s) \tag{33}$$

where γ is beyond any singularity of $f(s)$.

if

$$f(t) = e^{-at} \tag{34}$$

then

$$\hat{f}(s) = \frac{1}{s+a} \tag{35}$$

One admits that

$$\sum_{n=1}^{\infty}\frac{1}{n!n^{3/2}}e^{-r^2/(2d^2n)} \sim e^{-\frac{r}{d}} \tag{36}$$