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SPRING COLLEGES IN COMPUTATIONAL PHYSICS

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MOLECULAR DYNAMICS IV - V

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TIME REVERSIBLE ALGORYTHMS

The operator (Liouville) formulation of classical dynamics in phase space can be used to derive, on a theoretical ground, time reversible algorythms to integrate MD equations of motion

Ex: Velocity Verlet

$$H = \sum_i \frac{p_i^2}{2m_i} + V(r_i) \qquad i\mathcal{L} = \{\cdots, H\}_P =$$

$$= \sum_i \frac{\partial}{\partial r_i}\frac{\partial H}{\partial p_i} - \frac{\partial H}{\partial r_i}\frac{\partial}{\partial p_i}$$

$$\dot{\Gamma} = i\mathcal{L}\,\Gamma = \{\Gamma, H\}_P$$

$$i\mathcal{L} = \sum_i \frac{p_i}{m_i}\frac{\partial}{\partial r_i} + F_i \frac{\partial}{\partial p_i}$$

$\mathcal{L} = \mathcal{L}^{\dagger}$ hermitean operator

Propagator $\mathcal{U}(t) = \exp\left[i\mathcal{L}\,t\right]$

$$\Gamma(t) = \mathcal{U}(t)\,\Gamma(0)$$

$\mathcal{U}^{\dagger}(t) = \mathcal{U}(-t) = \mathcal{U}^{-1}(t)$ Unitary operator

Time reversible property

- Decompose $i\mathcal{L} = i\mathcal{L}_1 + i\mathcal{L}_2$
- Consider partition of time in P intervals $\delta t = \frac{t}{P}$
- Apply Trotter–Suzuki formulas

$$\exp\{i(\mathcal{L}_1 + \mathcal{L}_2)t\} = \left[\exp\{i(\mathcal{L}_1 + \mathcal{L}_2)\delta t\}\right]^P$$

$$\simeq \left[\exp\{i\mathcal{L}_1 \tfrac{\delta t}{2}\} \exp\{i\mathcal{L}_2 \delta t\} \exp\{i\mathcal{L}_1 \tfrac{\delta t}{2}\}\right]^P + \mathcal{O}(P\,\delta t^3)$$

Discrete propagator for small δt

$$G(\delta t) = \mathcal{U}_1\left(\tfrac{\delta t}{2}\right)\mathcal{U}_2(\delta t)\mathcal{U}_1\left(\tfrac{\delta t}{2}\right)$$

Unitary operator

$$= e^{i\mathcal{L}_1 \frac{\delta t}{2}}\, e^{i\mathcal{L}_2 \delta t}\, e^{i\mathcal{L}_1 \frac{\delta t}{2}}$$

Generator of discrete temporal translations

$$G(\delta t)\begin{pmatrix} r(t) \\ p(t) \end{pmatrix} = \begin{pmatrix} r(t+\delta t) \\ p(t+\delta t) \end{pmatrix}$$

Velocity Verlet factorization

$$i\mathcal{L}_1 = \sum_i F_i \frac{\partial}{\partial p_i} \qquad i\mathcal{L}_2 = \sum_i \frac{p_i}{m_i} \frac{\partial}{\partial r_i}$$

$$G(t) = \prod_i \exp\left\{\frac{\delta t}{2} F_i \frac{\partial}{\partial p_i}\right\} \exp\left\{\frac{\delta t}{m_i} p_i \frac{\partial}{\partial r_i}\right\} \exp\left\{\frac{\delta t}{2} F_i \frac{\partial}{\partial p_i}\right\}$$

- Apply $G(\delta t)$ to coordinates r_i, p_i at time t using the relation

$$\exp\left\{c \frac{\partial}{\partial q}\right\} f(q) = f(q + c)$$

where c does not depend on q

1st STEP

$$\exp\left\{\frac{\delta t}{2} F_i \frac{\partial}{\partial p_i}\right\} \begin{pmatrix} r_i \\ p_i \end{pmatrix}$$

$$= \begin{pmatrix} r_i \\ p_i + F_i(r) \frac{\delta t}{2} \end{pmatrix}$$

2nd STEP

$$\exp\left\{\delta t \frac{p_i}{m_i} \frac{\partial}{\partial r_i}\right\} \begin{pmatrix} r_i \\ p_i + \frac{\delta t}{2} F_i(r) \end{pmatrix}$$

$$= \begin{pmatrix} r_i + \frac{p_i}{m_i} \delta t \\ p_i + F_i\left(r_i + \frac{p_i}{m_i} \delta t\right) \frac{\delta t}{2} \end{pmatrix}$$

3rd STEP

$$\exp\left\{\frac{\delta t}{2} F_i \frac{\partial}{\partial p_i}\right\} \begin{pmatrix} r_i + \frac{p_i}{m_i}\,\delta t \\ p_i + F_i\left(r_i + \delta t\,\frac{p_i}{m_i}\right)\frac{\delta t}{2} \end{pmatrix}$$

$$= \begin{pmatrix} r_i + \dfrac{p_i + \frac{\delta t}{2} F_i(r)}{m_i}\,\delta t \\ p_i + F_i(r)\frac{\delta t}{2} + F_i\left(r_i + \frac{\delta t}{m_i}\left(p + F_i(r)\frac{\delta t}{2}\right)\right)\frac{\delta t}{2} \end{pmatrix}$$

AT THE END YOU HAVE OBTAINED THE VELOCITY VERLET - ALGORYTHM.

$$G(\delta t)\begin{pmatrix} r_i(t) \\ p_i(t) \end{pmatrix} = \begin{pmatrix} r_i(t+\delta t) \\ p_i(t+\delta t) \end{pmatrix}$$

$$= \begin{pmatrix} r_i(t) + \frac{p_i}{m_i}(t)\,\delta t + \frac{F_i}{m_i}\frac{\delta t^2}{2} \\ p_i(t) + \frac{\delta t}{2}\left[F_i(t) + F_i(t+\delta t)\right] \end{pmatrix}$$

DIRECT TRANSLATION TECHNIQUE

$$G(t) = \prod_{i=1}^{N} e^{\frac{\delta t}{2} F_i \frac{\partial}{\partial p_i}} \; e^{\frac{\delta t}{m_i} p_i \frac{\partial}{\partial r_i}} \; e^{\frac{\delta t}{2} F_i \frac{\partial}{\partial p_i}}$$

Instead of considering only one translation of δt (obtained by means of the application of all the factors one after the other) one can consider that each factors realizes a partial translation in phase space. ('Path' in phase space)

$e^{\frac{\delta t}{2} F_i \frac{\partial}{\partial p_i}} \longrightarrow$ $p_i = p_i + \frac{\delta t}{2} F_i$

$e^{\delta t / m_i \, p_i \frac{\partial}{\partial r_i}} \longrightarrow$ $r_i = r_i + \frac{\delta t}{m_i} p_i$

Update F_i

$e^{\frac{\delta t}{2} F_i \frac{\partial}{\partial p_i}} \longrightarrow$ $p_i = p_i + \frac{\delta t}{2} F_i$

'PSEUDO' CODE FORM

Almost one by one mapping between factors in the propagator and lines of the computer program!

MOLECULES — intermolecular motion slow
— Intramolecular fast

Time step δt is determined by the fast motion

$\Rightarrow$ Δt slow motion $\qquad \delta t = \frac{\Delta t}{n}$ fast motion

1^{st} STEP

$$i\mathcal{L} = i\mathcal{L}_1 + i\mathcal{L}_2$$

$$i\mathcal{L}_1 = \sum_i F_i^{(inter)} \frac{\partial}{\partial p_i}$$

$$i\mathcal{L}_2 = \sum_i \left[\dot{r}_i \frac{\partial}{\partial r_i} + F_i^{(intra)} \frac{\partial}{\partial p_i} \right]$$

2^{nd} STEP

$$i\mathcal{L}_2 = i\mathcal{L}_2^{(K)} + i\mathcal{L}_2^{(u)}$$

$$i\mathcal{L}_2^{(K)} = \sum_i \dot{r}_i \frac{\partial}{\partial r_i}$$

$$i\mathcal{L}_2^{(u)} = \sum_i F_i^{(intra)} \frac{\partial}{\partial p_i}$$

1^{st} step

Δt: $$e^{i\mathcal{L}\Delta t} = e^{i\mathcal{L}_1 \Delta t} e^{i\mathcal{L}_2 \Delta t} e^{i\mathcal{L}_1 \Delta t}$$

2^{nd} step $$e^{i\mathcal{L}_2 \Delta t} = \left[e^{i\mathcal{L}_2 \frac{\Delta t}{n}} \right]^n$$

$\delta t = \frac{\Delta t}{n}$ $$= \left[e^{i\mathcal{L}_2^{(u)} \frac{\delta t}{2}} e^{i\mathcal{L}_2^{(K)} \delta t} e^{i\mathcal{L}_2^{(u)} \frac{\delta t}{2}} \right]^n$$

The propagator has been broken in a series of n terms with step δt and 2 (initial and final) equal propagator with a bigger time step Δt

$$G(\Delta t) = e^{i\mathcal{L}_1 \frac{\Delta t}{2}} \left[e^{i\mathcal{L}_2^{(n)} \frac{\delta t}{2}} \, e^{i\mathcal{L}_2^{(k)} \delta t} \, e^{i\mathcal{L}_2^{(n)} \frac{\delta t}{2}} \right]^n \times$$

$$\times \; e^{i\mathcal{L}_1 \frac{\Delta t}{2}}$$

Using the direct traslation tecnique you obtain the algorythm

$$v_i = v_i + \frac{\Delta t}{2m_i} F_i^{(inter)}$$

$$\boxed{\begin{array}{l} v_i = v_i + \frac{\delta t}{2m_i} F_i^{(intra)} \\ r_i = r_i + v_i \, \delta t \\ \text{compute } F^{(intra)} \text{ with new } r_i \\ v_i = v_i + \frac{\delta t}{2m_i} F_i^{(intra)} \end{array}} \quad \text{iterate } n \text{ times}$$

Compute $F_i^{(inter)}$ at new r_i

$$v_i = v_i + \frac{\Delta t}{2m_i} F_i^{(inter)}$$

NOSE' HOOVER THERMOSTAT

$$
\begin{cases}
\dot{r}_i = p_i/m_i \\
\dot{p}_i = F_i - p_i \dfrac{\dot{s}}{s} \\
\dfrac{\dot{s}}{s} = p_s/m_s \\
\dot{p}_s = \sum_i \dfrac{p_i^2}{m_i} - g k_B T
\end{cases}
$$

define $\eta = \ln s$

$$\dot{\eta} = \frac{\dot{s}}{s}$$

$$F_\eta = \sum_i \frac{p_i^2}{m_i} - g k_B T$$

$$\downarrow$$

$$
\begin{cases}
\dot{r}_i = p_i/m_i \\
\dot{p}_i = F_i - p_i \dot{\eta} \\
\dot{\eta} = p_\eta/m_\eta \\
\dot{p}_\eta = F_\eta(p_i)
\end{cases}
$$

Constant of motion

$$\mathcal{H} = \mathcal{H}_T + g k_B T \eta$$

$$\mathcal{H}_T = \sum_i \frac{p_i^2}{2m_i} + V(\{r_i\}) + \frac{p_\eta^2}{2m_\eta}$$

HOOVER demonstration

It does not use the virtual variable approach. Instead from the (guessed) non-canonical equation of motion it finds out the behaviour of the density in phase space.

Introduce Generalized Liouville Equation

$$\frac{\partial}{\partial t}\rho + \frac{\partial}{\partial \Gamma}(\dot{\Gamma}\rho) = 0$$

continuity equation for the phase space current $J = \dot{\Gamma}\rho$

Generalized divergence term

The variation of ρ along phase space trajectory will be

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \dot{\Gamma}\frac{\partial \rho}{\partial \Gamma}$$

$$\frac{d\rho}{dt} = -\frac{\partial}{\partial \Gamma}(\dot{\Gamma}\rho) + \dot{\Gamma}\frac{\partial \rho}{\partial \Gamma}$$

$$\boxed{\frac{d\rho}{dt} = -\rho\left(\frac{\partial \dot{\Gamma}}{\partial \Gamma}\right)}$$

if $\frac{\partial \dot{\Gamma}}{\partial \Gamma} \neq 0$ the flux in phase space will have a non-hamiltonian behaviour

Non canonical equation of motion.
Choose equation of motion that will give you the desired ensemble dependence for the distribution ρ of phase space.

$$\mathcal{H} = \mathcal{H}_T + g k_B T \eta$$

$$\mathcal{H}_T = \sum_i \frac{p_i^2}{2m_i} + V(\{r_i\}) + \frac{p_\eta^2}{2m_\eta}$$

If $\mathcal{H}$ is really a conserved quantity

then $\frac{d\mathcal{H}}{dt} = 0 \Rightarrow$

$$\Rightarrow \frac{d\mathcal{H}_T}{dt} = -\frac{d}{dt}(g k_B T \eta) = -g k_B T \dot{\eta}$$

Let's verify

$$\frac{d\mathcal{H}_T}{dt} = \sum_i \left(\frac{\partial H_T}{\partial p_i} \dot{p}_i + \frac{\partial H_T}{\partial r_i} \dot{r}_i \right) + \frac{\partial H_T}{\partial p_\eta} \dot{p}_\eta$$

substitute the equation of motion

$$\frac{d\mathcal{H}_T}{dt} = \sum_i \left[\frac{\partial H_T}{\partial p_i} \left(F_i - p_i \dot{\eta} \right) + \frac{\partial H_T}{\partial r_i} \frac{p_i}{m_i} \right] + \frac{\partial \mathcal{H}_T}{\partial p_\eta} F_\eta$$

$$= \sum_i \left[\frac{p_i}{m_i} F_i - \frac{p_i^2}{m_i} \dot{\eta} - F_i \frac{p_i}{m_i} \right] + \frac{p_\eta}{m_\eta} F_\eta =$$

$$= -\sum_i \frac{p_i^2}{m_i} \dot{\eta} + \dot{\eta} \left[\sum_i \frac{p_i^2}{m_i} - g k_B T \right] = -g k_B T \dot{\eta}$$

$$\boxed{\frac{d\mathcal{H}_T}{dt} = -g k_B T \dot{\eta}}$$

It is now possible to write down the equation for the distribution probability of phase space

$$\frac{d\rho}{dt} = -\rho \frac{\partial \dot{\Gamma}}{\partial \Gamma}$$

$$= -\rho \left[\sum_i \left(\frac{\partial \dot{p}_i}{\partial p_i} + \frac{\partial \dot{r}_i}{\partial r_i} \right) + \frac{\partial \dot{p}_\eta}{\partial p_\eta} + \frac{\partial \dot{\eta}}{\partial \eta} \right]$$

$$= -\rho \left[\sum_i (-\dot{\eta}) \right] = \rho \, 3N \dot{\eta}$$

$$\frac{1}{\rho} \frac{d}{dt} \rho = \frac{3N}{g k_B T} \dot{\eta} \, g k_B T = \frac{-3N}{g k_B T} \frac{d \mathcal{H}_T}{dt}$$

Choose $g = 3N$

$$\frac{1}{\rho} \frac{d}{dt} \rho = -\frac{1}{k_B T} \frac{d \mathcal{H}_T}{dt}$$

$$\boxed{\rho \propto e^{-\frac{1}{k_B T} \mathcal{H}_T}}$$

Canonical dependence for the distribution function in phase space.

It is obtained by means of non canonical equation of motion

NOSE'-HOOVER CHAIN

$$\begin{cases} \dot{r}_i = \dfrac{p_i}{m_i} \\ \dot{p}_i = F_i - \dfrac{p_{\eta_1}}{Q_1} p_i \\ \dot{\eta}_1 = \dfrac{p_{\eta_1}}{Q_1} \\ \dot{p}_{\eta_1} = F_\eta(p_i) - \dfrac{p_{\eta_2}}{Q_2} p_{\eta_1} \\ \dot{p}_{\eta_2} = F_{\eta_1}(p_{\eta_1}) \\ \dot{\eta}_2 = \dfrac{p_{\eta_2}}{Q_2} \end{cases}$$

$$F_\eta(p_i) = \sum_i \frac{p_i^2}{m_i} - k_B T$$

$$F_{\eta_1} = \frac{p_{\eta_1}^2}{Q_1} - k_B T$$

For simplicity
Just one degree of
freedom

Constant of motion

$$\mathcal{H} = \frac{p_i^2}{m} + V(r) + \frac{p_{\eta_1}^2}{2Q_1} + \frac{p_{\eta_2}^2}{2Q_2} + k_B T \eta_1 + k_B T \eta_2$$

FACTORIZATION OF LIOUVILLE OPERATOR

$$iL_1 = \frac{p}{m}\frac{\partial}{\partial r}$$

$$iL_2 = F(r)\frac{\partial}{\partial p}$$

$$iL_3 = -\frac{p_{\eta_1}}{Q_1} p \frac{\partial}{\partial p}$$

$$iL_4 = \frac{p_{\eta_1}}{Q_1}\frac{\partial}{\partial \eta_1}$$

$$iL_5 = F_\eta(p)\frac{\partial}{\partial p_{\eta_1}}$$

$$iL_6 = -\frac{p_{\eta_2}}{Q_2} p_{\eta_1}\frac{\partial}{\partial p_{\eta_1}}$$

$$iL_7 = \frac{p_{\eta_2}}{Q_2}\frac{\partial}{\partial \eta_2}$$

$$iL_8 = F_{\eta_1}(p_{\eta_1})\frac{\partial}{\partial p_{\eta_2}}$$

Time reversible finite time step propagator

$$G(\Delta t) = \exp\left[\frac{\delta t}{2} iL_8\right] \exp\left[\frac{\delta t}{2} iL_7\right] \exp\left[\frac{\delta t}{2} iL_6\right]$$
$$\exp\left[\frac{\delta t}{2} iL_5\right] \exp\left[\frac{\delta t}{2} iL_4\right] \exp\left[\frac{\delta t}{2} iL_3\right]$$
$$\exp\left[\frac{\delta t}{2} iL_2\right] \exp\left[\delta t \, iL_1\right] \exp\left[\frac{\delta t}{2} iL_2\right]$$
$$\exp\left[\frac{\delta t}{2} iL_3\right] \exp\left[\frac{\delta t}{2} iL_4\right] \exp\left[\frac{\delta t}{2} iL_5\right]$$
$$\exp\left[\frac{\delta t}{2} iL_6\right] \exp\left[\frac{\delta t}{2} iL_7\right] \exp\left[\frac{\delta t}{2} iL_8\right]$$

Needless to say: use direct translation techinique to derive the reversible Algorythm

Use the identities

$$\exp\left[c \frac{\partial}{\partial q}\right] f(q) = f(q+c)$$ c non depending on q

$$\exp\left[c\, p \frac{\partial}{\partial p}\right] \phi(p) = \phi(p e^c)$$

SPECIAL CASE OF THE GENERAL IDENTITY

$$\exp\left[c \frac{\partial}{\partial (g(q))}\right] f(q) = e^{c\, \partial/\partial g(q)} f\left[g^{-1}[g(q)]\right]$$

$$= f\left[g^{-1}[g(q)+c]\right]$$

NHC REVERSIBLE ALGORITHM

$$p_{\eta_2} = p_{\eta_2} + \frac{\delta t}{2} F_{\eta_1}(p_{\eta_1})$$

$$\eta_2 = \eta_2 + \frac{\delta t}{2} \frac{p_{\eta_2}}{Q_2}$$

$$p_{\eta_1} = p_{\eta_1} \exp\left(-\frac{\delta t}{2Q_2} p_{\eta_2}\right)$$

$$p_{\eta_1} = p_{\eta_1} + \frac{\delta t}{2} F_2(p)$$

$$\eta_1 = \eta_1 + \frac{\delta t}{2Q_1} p_{\eta_1}$$

$$p = p \exp\left(-\frac{\delta t}{2Q_1} p_{\eta_1}\right)$$

$$p = p + \frac{\delta t}{2} F(r)$$

$$r = r + \frac{\delta t}{m} p$$

update $F(r)$

$$p = p + \frac{\delta t}{2} F(r)$$

$$p = p \exp\left(-\frac{\delta t}{2Q_1} p_{\eta_1}\right)$$

$$\eta_1 = \eta_1 + \frac{\delta t}{2Q_1} p_{\eta_1}$$

update $F_2(p)$

$$p_{\eta_1} = p_{\eta_1} + \frac{\delta t}{2} F_2(p)$$

$$p_{\eta_1} = p_{\eta_1} \exp\left(-\frac{\delta t}{2Q_2} p_{\eta_2}\right)$$

$$\eta_2 = \eta_2 + \frac{\delta t}{2} \frac{p_{\eta_2}}{Q_2}$$

update $F_{\eta_1}(p_{\eta_1})$

$$p_{\eta_2} = p_{\eta_2} + \frac{\delta t}{2} F_{\eta_1}(p_{\eta_1})$$

ERGODIC BEHAVIOUR IN PHASE SPACE

BUT IN THIS NAIVE IMPLEMENTATION THE CONSERVATION IS WORSE THAN THE ONE SUPPLIED BY THE USUAL NOSE THERMOSTAT

USE MULTIPLE TIME STEP OR HIGHER ORDER YOSHIDA INTEGRATOR

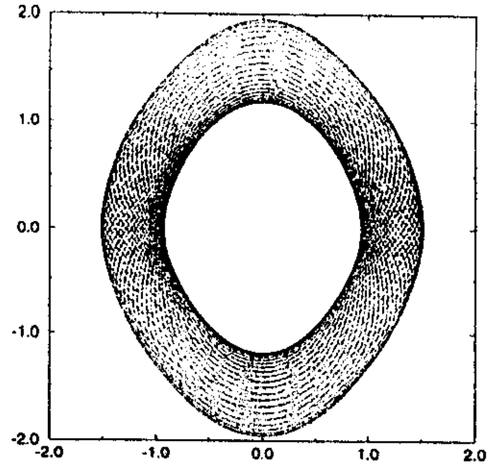

Figure 1: Punti della traiettoria ottenuta integrando le equazioni del moto di Nosè-Hoover per l'oscillatore armonico ($k = m = Q_1 = 1; T = 1$) con la condizione iniziale $\mathbf{r(0) = 1, p(0) = 1, \eta_1} = 0, p_{eta_1} = 1$

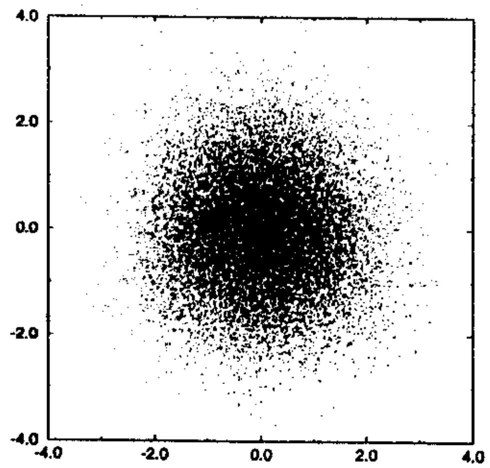

Figure 2: Punti della traiettoria ottenuta integrando le equazioni del moto per una catena di Nosè-Hoover con $M = 2$ per l'oscillatore armonico ($k = m = Q_1 = Q_2 = 1; T = 1$) con la condizione iniziale $r(0) = 1, p(0) = 1, \eta_1 = 0, p_{eta_1} = 1, \eta_2 = 0, p_{eta_2} = 1$

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Another quantum example

PATH INTEGRAL MD

Feynman has taught us how to map a quantum point particle on a string which represents classically all the path in time of the particle. Because of quantum fluctuation you don't have a unique path between two point, but to compute expectation values you have to sum over all the path with the weight $\exp\left[\frac{i}{\hbar} S_{classical}(\text{path})\right]$

If you discretize the path

You will get a 'polymer' with very stiff spring between each beads (time slice of the particle trajectory)

$K \propto \frac{1}{\tau}$ $\tau \equiv$ small imaginary time

So in complex time
Quantum averages $\longrightarrow$ Statistical sum over 'polymers' configurations (sum over path)

You can use MD but because of the stiff spring between each 'polymer' site NHC are useful to gain ergodicity and accuracy in your dynamical sampling.

There is nothing wrong with the Nosé-Hoover thermostat if you have a classical N particle system which does not have very fast oscillating degrees of freedom.

Yet Nosé Hoover Chain are a substantial improvement if you have to control the temperature of a very fast oscillating degree of freedom. As a matter of fact we have seen that the oscillator dynamic with Nosé is not ergodic. Moreover with a NHC you can control all the fluctuations of the thermostat variables (Knotted Chain)

This critical oscillating dynamic is almost always found in the domain of quantum problems.

Ex: Car-Parrinello dynamics

You want to simulate $\mathcal{L}_F = \sum_I \frac{1}{2} M_I \dot{R}_I^2 - E[\psi_i, R_I]$

with the constraint $\delta E / \delta \psi_i^* = 0$

Use again a fictitious dynamics to have the constraint satisfied on average

$$\mathcal{L}_{CP} = \sum_I \frac{1}{2} M_I \dot{R}_I^2 + \sum_i \int dr \, \frac{1}{2} \mu \, \dot{\psi}_i^*(r) \dot{\psi}_i(r) - E[\psi_i, R_i]$$

$$\begin{cases} \mu \ddot{\psi}_i = -\dfrac{\delta E}{\delta \psi_i^*} \\[2ex] M_I \ddot{R}_I = -\dfrac{\partial E}{\partial R_I} \end{cases}$$

The ψ_i follow the ions with very fast oscillations in addition. This fast oscillation increase the error in the constraint. You can use a NHC to thermalize the ψ.

Yoshida Scheme

Define iL_{NHC} as the Liouville operator of the NHC part of the dynamics

Then write your propagator such as

$$G(\delta t) = \exp\left[iL_{NHC}\frac{\delta t}{2}\right]\exp\left[\frac{\delta t}{2}F(r)\frac{\partial}{\partial p}\right]$$
$$\exp\left[\delta t\,\frac{P}{\mu}\frac{\partial}{\partial r}\right]$$
$$\exp\left[\frac{\delta t}{2}F(r)\frac{\partial}{\partial p}\right]\exp\left[iL_{NHC}\frac{\delta t}{2}\right]$$

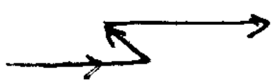
Use Yoshida's recipe to have a higher precision on the NHC part of the dynamics

$$\exp\left[iL_{NHC}\frac{\delta t}{2}\right] \longrightarrow \prod_{j=1}^{n_y}\exp\left[iL_{NHC}\,W(j)\,\frac{\delta t}{2}\right]$$

with $n_y = 3$

$$W(1) = \frac{1}{2-2^{1/3}} \simeq 1.35$$
$$W(2) = 1 - 2W(1) \simeq -1.70$$
$$W(3) = W(1) \simeq 1.35$$

The weight $W(j)$ are computed requiring the error to be of order $\mathcal{O}(\Delta t^5)$



Forward - backward - forward propagation in time

Fractal dynamics in phase space.

WARNING to get, using NHC, a dynamic as stable as the Nose's one You must use a multiple time step procedure or an higher order propagator

Multiple time step propagator

$$G(\delta t) = \left\{ \prod_{j=1}^{n} \exp\left[\frac{\delta t}{2M} F_{\eta_1} \frac{\partial}{\partial p_{\eta_2}}\right] \exp\left[\frac{\delta t}{2M} \frac{p_{\eta_2}}{Q_2} \frac{\partial}{\partial \eta_2}\right] \right.$$

$$\exp\left[-\frac{\delta t}{2M} \frac{p_{\eta_2}}{Q_2} p_{\eta_1} \frac{\partial}{\partial p_{\eta_1}}\right] \exp\left[\frac{\delta t}{2M} F_\eta(p) \frac{\partial}{\partial p_{\eta_1}}\right]$$

$$\left. \exp\left[\frac{\delta t}{2M} \frac{p_{\eta_1}}{Q_1} \frac{\partial}{\partial \eta_1}\right] \exp\left[-\frac{\delta t}{2M} \frac{p_{\eta_1}}{Q_1} p \frac{\partial}{\partial p}\right] \right\}$$

$$\exp\left[\frac{\delta t}{2} F(r) \frac{\partial}{\partial p}\right] \exp\left[\delta t \, p/_{m} \frac{\partial}{\partial r}\right] \exp\left[\frac{\delta t}{2} F(r) \frac{\partial}{\partial p}\right]$$

$$\left\{ \prod_{j=1}^{M} \exp\left[-\frac{\delta t}{2M} \frac{p_{\eta_1}}{Q_1} p \frac{\partial}{\partial p}\right] \exp\left[\frac{\delta t}{2M} \frac{p_{\eta_1}}{Q_1} \frac{\partial}{\partial \eta_1}\right] \right.$$

$$\exp\left[\frac{\delta t}{2M} F_\eta(p) \frac{\partial}{\partial p_{\eta_1}}\right] \exp\left[-\frac{\delta t}{2M} \frac{p_{\eta_2}}{Q_2} p_{\eta_1} \frac{\partial}{\partial p_{\eta_1}}\right]$$

$$\left. \exp\left[\frac{\delta t}{2M} \frac{p_{\eta_2}}{Q_2} \frac{\partial}{\partial \eta_2}\right] \exp\left[\frac{\delta t}{2M} F_{\eta_1} \frac{\partial}{\partial p_{\eta_2}}\right] \right\}$$

M (number for the multiple time step procedure) might be quite large for realistic systems.

Too much expensive from the computational point of view.

A possible solution is the Yoshida higher order scheme.

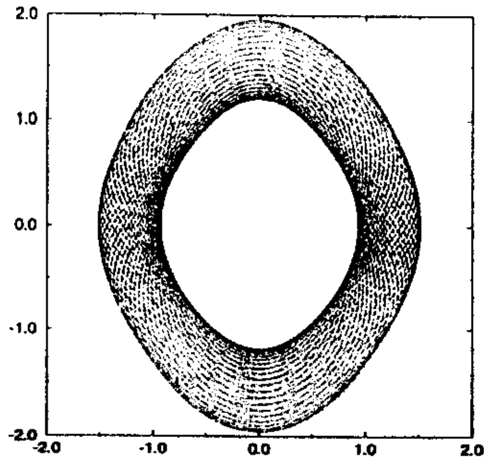


Figure 1: Punti della traiettoria ottenuta integrando le equazioni del moto di Nosè-Hoover per l'oscillatore armonico ($k = m = Q_1 = 1; T = 1$) con la condizione iniziale $r(0) = 1, p(0) = 1, \eta_1 = 0, p_{eta_1} = 1$

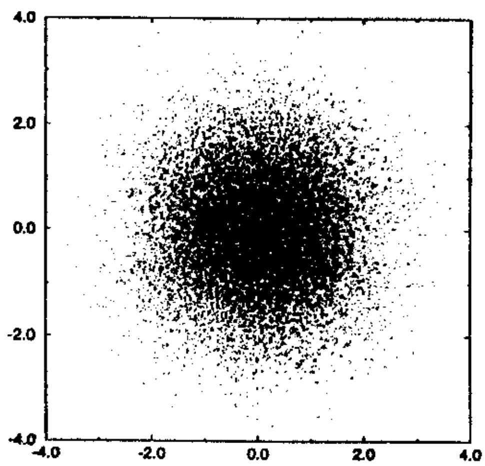


Figure 2: Punti della traiettoria ottenuta integrando le equazioni del moto per una catena di Nosè-Hoover con $M = 2$ per l'oscillatore armonico ($k = m = Q_1 = Q_2 = 1; T = 1$) con la condizione iniziale $r(0) = 1, p(0) = 1, \eta_1 = 0, p_{eta_1} = 1, \eta_2 = 0, p_{eta_2} = 1$

NHC REVERSIBLE ALGORYTHM

$$p_{\eta_2} = p_{\eta_2} + \frac{\delta t}{2} F_{\eta_1}(p_{\eta_1})$$

$$\eta_2 = \eta_2 + \frac{\delta t}{2} \frac{p_{\eta_2}}{Q_2}$$

$$p_{\eta_1} = p_{\eta_1} \exp\left(-\frac{\delta t}{2Q_2} p_{\eta_2}\right)$$

$$p_{\eta_1} = p_{\eta_1} + \frac{\delta t}{2} F_2(p)$$

$$\eta_1 = \eta_1 + \frac{\delta t}{2Q_1} p_{\eta_1}$$

$$p = p \exp\left(-\frac{\delta t}{2Q_1} p_{\eta_1}\right)$$

$$p = p + \frac{\delta t}{2} F(r)$$

$$r = r + \frac{\delta t}{m} p$$

update $F(r)$

$$p = p + \frac{\delta t}{2} F(r)$$

$$p = p \exp\left(-\frac{\delta t}{2Q_1} p_{\eta_1}\right)$$

$$\eta_1 = \eta_1 + \frac{\delta t}{2Q_1} p_{\eta_1}$$

update $F_2(p)$

$$p_{\eta_1} = p_{\eta_1} + \frac{\delta t}{2} F_2(p)$$

$$p_{\eta_1} = p_{\eta_1} \exp\left(-\frac{\delta t}{2Q_2} p_{\eta_2}\right)$$

$$\eta_2 = \eta_2 + \frac{\delta t}{2} \frac{p_{\eta_2}}{Q_2}$$

update $F_{\eta_1}(p_{\eta_1})$

$$p_{\eta_2} = p_{\eta_2} + \frac{\delta t}{2} F_{\eta_1}(p_{\eta_1})$$

ERGODIC BEHAVIOUR IN PHASE SPACE

BUT IN THIS NAIVE IMPLEMENTATION THE CONSERVATION IS WORSE THAN THE ONE SUPPLIED BY THE USUAL NOSE THERMOSTAT

USE MULTIPLE TIME STEP OR HIGHER ORDER YOSHIDA INTEGRATOR

Time reversible finite time step propagator

$$G(\Delta t) = \exp\left[\frac{\delta t}{2} iL_8\right] \exp\left[\frac{\delta t}{2} iL_7\right] \exp\left[\frac{\delta t}{2} iL_6\right]$$
$$\exp\left[\frac{\delta t}{2} iL_5\right] \exp\left[\frac{\delta t}{2} iL_4\right] \exp\left[\frac{\delta t}{2} iL_3\right]$$
$$\exp\left[\frac{\delta t}{2} iL_2\right] \exp\left[\delta t\, iL_1\right] \exp\left[\frac{\delta t}{2} iL_2\right]$$
$$\exp\left[\frac{\delta t}{2} iL_3\right] \exp\left[\frac{\delta t}{2} iL_4\right] \exp\left[\frac{\delta t}{2} iL_5\right]$$
$$\exp\left[\frac{\delta t}{2} iL_6\right] \exp\left[\frac{\delta t}{2} iL_7\right] \exp\left[\frac{\delta t}{2} iL_8\right]$$

Needless to say: use direct translation technique to derive the reversible Algorythm

Use the identities

$$\exp\left[c \frac{\partial}{\partial q}\right] f(q) = f(q+c)$$ c non depending on q

$$\exp\left[c\, p \frac{\partial}{\partial p}\right] \phi(p) = \phi(p e^{c})$$

SPECIAL CASE OF THE GENERAL IDENTITY

$$\exp\left[c \frac{\partial}{\partial(g(q))}\right] f(q) = e^{c\, \partial/\partial g(q)} f\left[g^{-1}[g(q)]\right]$$

$$= f\left[g^{-1}[g(q)+c]\right]$$

NOSÉ–HOOVER CHAIN

$$\begin{cases} \dot{r}_i = \dfrac{p_i}{m_i} \\ \dot{p}_i = F_i - \dfrac{p_{\eta_1}}{Q_1} p_i \\ \dot{\eta}_1 = \dfrac{p_{\eta_1}}{Q_1} \\ \dot{p}_{\eta_1} = F_\eta(p_i) - \dfrac{p_{\eta_2}}{Q_2} p_{\eta_1} \\ \dot{p}_{\eta_2} = F_{\eta_1}(p_{\eta_1}) \\ \dot{\eta}_2 = \dfrac{p_{\eta_2}}{Q_2} \end{cases}$$

$$F_\eta(p_i) = \sum_i \frac{p_i^2}{m_i} - k_B T$$

$$F_{\eta_1} = \frac{p_{\eta_1}^2}{Q_1} - k_B T$$

For simplicity Just one degree of freedom

Constant of motion

$$\mathcal{H} = \frac{p_i^2}{m} + V(r) + \frac{p_{\eta_1}^2}{2Q_1} + \frac{p_{\eta_2}^2}{2Q_2} + k_B T \eta_1 + k_B T \eta_2$$

FACTORIZATION OF LIOUVILLE OPERATOR

$$iL_1 = \frac{p}{m}\frac{\partial}{\partial r}$$

$$iL_2 = F(r)\frac{\partial}{\partial p}$$

$$iL_3 = -\frac{p_{\eta_1}}{Q_1} p \frac{\partial}{\partial p}$$

$$iL_4 = \frac{p_{\eta_1}}{Q_1}\frac{\partial}{\partial \eta_1}$$

$$iL_5 = F_\eta(p)\frac{\partial}{\partial p_{\eta_1}}$$

$$iL_6 = -\frac{p_{\eta_2}}{Q_2} p_{\eta_1}\frac{\partial}{\partial p_{\eta_1}}$$

$$iL_7 = \frac{p_{\eta_2}}{Q_2}\frac{\partial}{\partial \eta_2}$$

$$iL_8 = F_{\eta_1}(p_{\eta_1})\frac{\partial}{\partial p_{\eta_2}}$$

SOME WARNING (THING TO TAKE CARE OF)

USING NPH DYNAMICS

- $$\dot{r}_i = \frac{p_i}{m_i} + r_i \frac{\dot{V}}{3V}$$

$$p_i \neq m_i \dot{r}_i$$

So in the calculation of the 'stress' force $F_v = \sum_i \frac{p_i^2}{m_i} + F_i r_i$

you do have to use $\boxed{p_i = m_i \dot{r}_i - \frac{\dot{V}}{3V} r_i}$

- Take in account minimum image

$$\sum_i F_i \cdot r_i \longrightarrow \sum_{i<j} F_{ij} \, r_{ij}$$

for pair potential $F_{ij} = - F_{ji}$

- In principle there are stability problems with boundary conditions when the volume fluctuate.
The system should be invariant under homogenous scaling transformations
(Conformal Weyl invariance)

- The equations of motion strongly perturbate the dynamics of the physical system.
NPH time correlation functions are not reliable.

PSEUDO CODE FORM

$\mathcal{P}_V = \mathcal{P}_V + \frac{\delta t}{2} F_V$	$\exp\left[\frac{\delta t}{2} F_V \frac{\partial}{\partial \mathcal{P}_V}\right]$
$p_i = p_i \exp\left[-\frac{\delta t}{2} \frac{\dot{V}}{3V}\right]$	$\exp\left[-\frac{\delta t}{2} \frac{\dot{V}}{3V} p_i \frac{\partial}{\partial p_i}\right]$
$p_i = p_i + \frac{\delta t}{2} F_i$	$\exp\left[\frac{\delta t}{2} F_i \frac{\partial}{\partial p_i}\right]$
$V = V + \frac{\delta t}{2M_V} \mathcal{P}_V$	$\exp\left[\frac{\delta t}{2M_V} \mathcal{P}_V \frac{\partial}{\partial V}\right]$
$r_i = r_i \exp\left[\frac{\delta t}{2} \frac{\dot{V}}{3V}\right]$	$\exp\left[\frac{\delta t}{2} \frac{\dot{V}}{3V} r_i \frac{\partial}{\partial r_i}\right]$
$r_i = r_i + \delta t \frac{p_i}{m_i}$	$\exp\left[\delta t \frac{p_i}{m_i} \frac{\partial}{\partial r_i}\right]$
$r_i = r_i \exp\left[\frac{\delta t}{2} \frac{\dot{V}}{3V}\right]$	$\exp\left[\frac{\delta t}{2} \frac{\dot{V}}{3V} r_i \frac{\partial}{\partial r_i}\right]$
$V = V + \frac{\delta t}{2M_V} \mathcal{P}_V$	$\exp\left[\frac{\delta t}{2M_V} \mathcal{P}_V \frac{\partial}{\partial V}\right]$
Update $F(r_i)$	
$p_i = p_i + \frac{\delta t}{2} F_i$	$\exp\left[\frac{\delta t}{2} F_i \frac{\partial}{\partial p_i}\right]$
$p_i = p_i \exp\left[-\frac{\delta t}{2} \frac{\dot{V}}{3V}\right]$	$\exp\left[-\frac{\delta t}{2} \frac{\dot{V}}{3V} p_i \frac{\partial}{\partial p_i}\right]$
update $F_V(r_i, p_i, V)$	
$\mathcal{P}_V = \mathcal{P}_V + \frac{\delta t}{2} F_V$	$\exp\left[\frac{\delta t}{2} F_V \frac{\partial}{\partial \mathcal{P}_V}\right]$
	$\parallel$
	$G(\delta t)$

ANDERSEN NPH TIME REVERSIBLE ALGORYTHM

$\dot{\Gamma} = i\hat{L}\,\Gamma$ so from Andersen equation of motion

$$iL_1 = \frac{p_i}{m_i}\frac{\partial}{\partial r_i} \qquad iL_4 = F_i\frac{\partial}{\partial p_i}$$

$$iL_2 = r_i\frac{\dot{V}}{3V}\frac{\partial}{\partial r_i} \qquad iL_5 = -\frac{\dot{V}}{3V}\,p_i\frac{\partial}{\partial p_i}$$

$$iL_3 = \frac{P_V}{M_V}\frac{\partial}{\partial V} \qquad iL_6 = F_V(r_i, p_i, V)\frac{\partial}{\partial P_V}$$

ANDERSEN LIOUVILLE PROPAGATOR

$$G(\delta t) = \exp\left[\frac{\delta t}{2}F_V\frac{\partial}{\partial P_V}\right]\exp\left[-\frac{\delta t}{2}\frac{\dot{V}}{3V}p_i\frac{\partial}{\partial p_i}\right]\cdot$$
$$\cdot\exp\left[\frac{\delta t}{2}F_i\frac{\partial}{\partial p_i}\right]\exp\left[\frac{\delta t}{2}\frac{P_V}{M_V}\frac{\partial}{\partial V}\right]\exp\left[\frac{\delta t}{2}\frac{\dot{V}}{3V}r_i\frac{\partial}{\partial r_i}\right]\cdot$$
$$\cdot\exp\left[\delta t\,\frac{p_i}{m_i}\frac{\partial}{\partial r_i}\right]$$
$$\cdot\exp\left[\frac{\delta t}{2}\frac{\dot{V}}{3V}r_i\frac{\partial}{\partial r_i}\right]\exp\left[\frac{\delta t}{2}\frac{P_V}{M_V}\frac{\partial}{\partial V}\right]\exp\left[\frac{\delta t}{2}F_i\frac{\partial}{\partial p_i}\right]\cdot$$
$$\cdot\exp\left[-\frac{\delta t}{2}\frac{\dot{V}}{3V}p_i\frac{\partial}{\partial p_i}\right]\exp\left[\frac{\delta t}{2}F_V\frac{\partial}{\partial P_V}\right]$$

$$\Gamma \equiv (r_i, p_i, V, P_V)$$

$$\exp\left(c\frac{\partial}{\partial q}\right)f(q) = f(q+c)$$

$$\exp\left(c\,q\frac{\partial}{\partial q}\right)\phi(q) = \phi(q\exp[c])$$

Use this two identities and the DIRECT TRANSLATION TECHNIQUE to derive the algorythm

ANDERSEN THERMODYNAMIC CONSTRAINT FOR PRESSURE

So this time the constraint is

$$P_{int} - P_{ext} = 0$$

$$\frac{1}{3V} \sum_i \frac{p_i^2}{m_i} + F_i r_i - P_{ext} = 0$$

Andersen uses a Fictitious dynamics to satisfy the constraint 'on average'

$$\begin{cases} \dot{r}_i = \frac{p_i}{m_i} + r_i \frac{\dot{V}}{3V} \\ \dot{p}_i = F_i - p_i \frac{\dot{V}}{3V} \\ \dot{V} = \frac{P_V}{M_V} \\ \dot{P}_V = \frac{1}{3V} \left[\sum_i \frac{p_i^2}{m_i} + F_i \cdot r_i \right] - P_{ext} = F_V \end{cases}$$

'ON SHELL'

$\dot{P}_V = 0$

the constraint will be exactly satisfied

THIS TIME WE ARE CONSIDERING THE VOLUME TO BE A DYNAMICAL VARIABLES

Scaling relation $r_i = V^{1/3} \rho_i$ $\quad p_i = \frac{\pi_i}{V^{1/3}}$

It is possible to obtain the non canonical equation of motion in REAL SPACE from a CANONICAL HAMILTONIAN in virtual space (unit cube)

$$\mathcal{H}_{virt} = \sum_i \frac{\pi_i^2}{2m_i V^{2/3}} + \mathcal{V}(\rho_i V^{1/3}) + \frac{P_V^2}{M_V} + P_{ext} V$$

Conserved quantity in real space

$$\mathcal{H}_A = \sum_i \frac{p_i^2}{2m_i} + \mathcal{V}(\{r\}) + \frac{P_V^2}{M_V} + P_{ext} V$$

$\downarrow$

IT IS NOT A HAMILTONIAN

THERMODYNAMICS CONSTRAINTS FOR PRESSURE

$$P_{\substack{\text{piston}\\\text{external}}} = -\frac{\partial E}{\partial V} \quad (= P_{\text{internal}})$$ constraint

$r_i = V^{1/3} \rho_i$ $\qquad$ ρ_i = coordinates scaled inside a unit cube

$$\frac{\partial}{\partial V} r_i = \frac{\partial}{\partial V} V^{1/3} \rho_i = \frac{1}{3V} V^{1/3} \rho_i = \frac{1}{3V} r_i$$

Consider a constant volume V

The lagrangian for a system of particles can be written using scaled coordinates

$$\mathcal{L} = \sum_i \frac{1}{2} m_i V^{2/3} \dot{\rho}_i^2 - \mathcal{V}(\{V^{1/3} \rho_i\})$$

$$\pi_i = \frac{\partial \mathcal{L}}{\partial \dot{\rho}_i} = m_i V^{2/3} \dot{\rho}_i \implies \dot{\rho}_i = \frac{\pi_i}{m_i V^{2/3}}$$

$$\mathcal{H} = \sum_i \dot{\rho}_i \pi_i - \mathcal{L}$$

$$= \sum_i \frac{\pi_i^2}{m_i V^{2/3}} - \frac{1}{2} \frac{\pi_i^2}{m_i V^{2/3}} + \mathcal{V}(\{r\})$$

$$= \sum_i \frac{\pi_i^2}{2 m_i V^{2/3}} + \mathcal{V}(\{r\}) = E$$

$$\frac{\partial \mathcal{H}}{\partial V} = -\frac{2}{3V} \sum_i \left[\frac{\pi_i^2}{2 m_i V^{2/3}}\right] - \frac{1}{3V} \sum_i F_i \cdot r_i$$

$$= -\frac{1}{3V} \left[\sum_i \frac{\pi_i^2}{m_i V^{2/3}} + F_i \cdot r_i\right]$$

$$P_{int} = \frac{1}{3V} \sum_i \left[\frac{\pi_i^2}{m_i V^{2/3}} + F_i \cdot r_i\right] \longrightarrow \frac{1}{3V} \sum_i \frac{p_i^2}{m_i} + F_i \cdot r_i$$

VIRIAL