Tutorial 5: Thermostats in Molecular Dynamics

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Course Outline

- Extended System Dynamics
- Nosé–Hoover Thermostat
- Nosé–Hoover Chain Thermostat
- Multiple Time Scales in Molecular Dynamics

Extended System Dynamics

Idea coming from Andersen
H. Andersen, JCP **72**, 2384 (1980)

The Essense

- Auxilary variables added to “control”
- Coupling via momentum and/or coordinate dependent terms to physical system
- Fluctuations of auxilary variables made appropriately

Applications

- To create ensembles other than *NVE*; for e.g. *NVT* and *NPT*
- path–integral MD
- Car–Parrinello
- Metadynamics, etc.

Classical non–Hamiltonian Statistical Mechanics

Tuckerman, Mundy, & Martyna, EuroPhys. Lett. **45**, 149 (1999).

Nosé–Hoover Thermostat

- Canonical ensemble achieveable by extended system approach
  - S. Nośe, J. Chem. Phys. **81**, 511 (1984)
  - S. Nośe, Mol. Phys. **52**, 255 (1984)
  - W. G. Hoover, Phys. Rev. A **31**, 1695 (1985)
- Auxilary variables have no physical meaning
- They force the system to be in *NVT* while total system (=system+auxilary) in *NVE*

$$
\begin{aligned}
\mathcal{L}_{\text{nose}} &= \sum_{I}^{N} \frac{M_I}{2} s^2 \dot{\mathbf{R}}_I^2 - U(\mathbf{R}^N) + \frac{Q}{2}\dot{s}^2 - g k_B T \ln s \\
\mathbf{P}_I &= \frac{\partial \mathcal{L}_{\text{nose}}}{\partial \mathbf{R}_I} = M_I s^2 \dot{\mathbf{R}}_I \\
\dot{p}_s &= \frac{\partial \mathcal{L}_{\text{nose}}}{\partial \dot{s}} = Q\dot{s}
\end{aligned}
$$

s: aux. variable
Q: eff. mass of s (units: energy time^2)
g: some constant
$\mathbf{P}'_I = \mathbf{P}_I/s$ where $\mathbf{P}$ is real momentum, and $\mathbf{P}'_I$ virtual/scaled momentum
$p'_s = p_s/s$
$\Delta t' = \Delta t/s \Rightarrow$ not a constant
A constant time step possible with g=3N for NVT

$$
\begin{aligned}
H_{\text{nose}} &= \sum_{I}^{N} \frac{1}{2\,M_I s^2}\mathbf{P}_I^2 + U(\mathbf{R}^N) + \frac{1}{2Q}p_s^2 + g k_B T \ln s \\
\dot{\mathbf{R}}_I &= \nabla_{\mathbf{P}_I} H_{\text{nose}} = \frac{\mathbf{P}_I}{M_I s^2} \\
\dot{\mathbf{P}}_I &= -\nabla_{\mathbf{R}_I} H_{\text{nose}} = -\nabla_{\mathbf{R}_I} U(\mathbf{R}^N) \\
\dot{s} &= \frac{\partial H_{\text{nose}}}{\partial p_s} = \frac{p_s}{Q} \\
\dot{p}_s &= -\frac{\partial H_{\text{nose}}}{\partial s} = \frac{1}{s}\left(\sum_{I} \frac{\mathbf{P}_I^2}{M_I} - g k_B T\right)
\end{aligned}
$$

$$
\begin{aligned}
d\mathbf{R}'_I/dt' &= s\ d\mathbf{R}_I/dt = \frac{\mathbf{P}_I}{M_I s} = \frac{\mathbf{P}'_I}{M_I} \\
d\mathbf{P}'_I/dt' &= s\ d(\mathbf{P}_I/s)/dt = d\mathbf{P}_I/dt - \frac{1}{s}\mathbf{P}_I ds/dt \\
&= -\nabla_{\mathbf{R}_I} U(\mathbf{R}^N) - (sp'_s/Q)\mathbf{P}_I \\
\frac{1}{s} ds/dt' &= s\frac{p'_s}{Q} \\
\frac{d(sp'_s/Q)}{dt'} &= \frac{s}{Q}\frac{dp_s}{dt} = \frac{1}{Q}\left(\sum_I \frac{\mathbf{P}'^2_I}{M_I} - gk_BT\right)
\end{aligned}
$$

Conserved quantity for the above E.O.M.

$$
H'_{\text{nose}} = \sum_I^N \frac{1}{2\,M_I s^2}\mathbf{P}'^2_I + U(\mathbf{R}^N) + \frac{1}{2Q}s^2 p'^2_s + gk_BT\ln s
$$

E.O.M. not derived from the above, thus not Hamiltonian

Hoover's formalism

Simplified by
$\zeta = s p_s'/Q$, and rewriting without primes

$$\begin{aligned}
\dot{\mathbf{R}}_I &= \frac{\mathbf{P}_I}{M_I} \\
\dot{\mathbf{P}}_I &= -\nabla_{\mathbf{R}_I} U(\mathbf{R}^N) - \zeta \mathbf{P}_I \\
\dot{\zeta} &= \frac{1}{Q}\left(\sum_I \frac{\mathbf{P}_I^2}{M_I} - g k_B T\right) \\
\dot{s}/s &= \frac{d \ln s}{dt} = \zeta
\end{aligned}$$

Conserved quantity:

$$H_{\text{nose}} = \sum_I^N \frac{1}{2\, M_I s^2} \mathbf{P}_I'^2 + U(\mathbf{R}^N) + \frac{1}{2}\zeta^2 Q + g k_B T \ln s$$

Integration of E.O.M. of NH Thermostat

Force is velocity dependent!
Numerical integration is not trivial!

Nosé–Hoover: Issues

Canonical distribution not guaranteed for all cases

- with more than one conserved quantity
- small systems
- high frequency vibrational modes

See Ref. Tuckerman, Liu, Ciccotti & Martyna, JCP **116**, 1678 (2001).

Nosé–Hoover Chains

$$\dot{\mathbf{R}}_I = \frac{\mathbf{P}_I}{M_I} \tag{1}$$

$$\dot{\mathbf{P}}_I = \mathbf{F}_I - \mathbf{P}_I \frac{p_{\zeta_1}}{Q_1} \tag{2}$$

$$\dot{\zeta}_I = \frac{p_{\zeta_i}}{Q_I} \tag{3}$$

$$\dot{p}_{\zeta_1} = \left[\sum_{I=1}^{N} \frac{\mathbf{P}_I^2}{M_I} - N_f k_B T \right] - p_{\zeta_1} \frac{p_{\zeta_2}}{Q_2} \tag{4}$$

$$\dot{p}_{\zeta_j} = \left[\frac{p_{\zeta_{j-1}}^2}{Q_{j-1}} - k_B T \right] - p_{\zeta_j} \frac{p_{\zeta_{j+1}}}{Q_{j+1}} \qquad \text{for } j = 2, \cdots, M-1 \tag{5}$$

$$\dot{p}_{\zeta_M} = \left[\frac{p_{\zeta_{M-1}}^2}{Q_{M-1}} - k_B T \right] \tag{6}$$

The conserved quantity for the NHC is

$$H_{\mathrm{NHC}} = \sum_{I=1}^{N} \frac{\mathbf{P}_I^2}{2M_I} + \sum_{i=1}^{M} \frac{p_{\zeta_i}^2}{2Q_i} + U(\mathbf{R}^N) + N_f k_B T \zeta_1 + k_B T \sum_{i=2}^{M} \zeta_i \quad (7)$$

Masses for the extended system variables are taken as

$$\begin{aligned} Q_1 &= N_f k_B T/\omega^2 \\ Q_j &= k_B T/\omega^2 \quad \text{for } j > 1 \end{aligned} \quad (8)$$

where ω is the frequency at which the thermostat particles fluctuate.

Now let us come back to integrating E.O.M.

- Iterative velocity Verlet

$$\dot{\mathbf{P}}_I = \mathbf{F}_I - \mathbf{P}_I \frac{p_{\zeta_1}}{Q_1} \tag{9}$$

and

$$\begin{aligned}
\mathbf{R}_I(t+\Delta t) &= \mathbf{R}_I(t) + \dot{\mathbf{R}}_I(t)\Delta t + \left[\mathbf{F}_I(t)M_I - \zeta(t)\dot{\mathbf{R}}_I(t)\right]\frac{\Delta t^2}{2} \\
\dot{\mathbf{R}}_I(t+\Delta t) &= \dot{\mathbf{R}}_I(t) + \left[\mathbf{F}_I(t+\Delta t)M_I - \zeta(t+\Delta t)\dot{\mathbf{R}}_I(t+\Delta t)\right. \\
&\quad \left. + \mathbf{F}_I(t)M_I - \zeta(t)\dot{\mathbf{R}}_I(t)\right]\frac{\Delta t}{2}
\end{aligned}$$

  - not time reversible
  - numerical problems

- Multiple time step reversible integrator
  Martyna, Tuckerman, Tobias & Klein, Mol. Phys. **87**, 1117 (1996)
- Uses Liouville approach
  (Pronounce Liouville as *Lyoo–veel*)
- One can define an evolution operator as

$$\begin{aligned} \Gamma(t) &= \exp(iLt)\,\Gamma(0) \\ iL &= \dot{\Gamma}\cdot\nabla_\Gamma \end{aligned} \tag{10}$$

  where iL is the Liouville operator and
  $\Gamma = (\mathbf{R}^N, \mathbf{P}^N, \zeta^M, p_\zeta^M)$
- $\Gamma(t)$ make the first order differential equations of the system to evolve from time $t = 0$ to a time t.

- A Discretization of $\Gamma(t)$ in time

$$\Gamma(t) = \prod_{I=1}^{N_t} \left(\prod_{u} \exp(iL_u \Delta t) \right) \Gamma(0) \tag{11}$$

Here $\Delta t = t/N_t$ and u runs over all independent variables.
$\therefore \Gamma(t)$ applied N_t times in succession.

- Liouville operator for NHC thermostat is given by

$$
\begin{aligned}
iL &= \sum_{I=1}^{N} \dot{\mathbf{R}}_I \cdot \nabla_{\mathbf{R}_I} + \sum_{I=1}^{N} \left[\frac{\mathbf{F}_I(\mathbf{R})}{M_I} \right] \cdot \nabla_{\dot{\mathbf{R}}_I} \\
&\quad - \sum_{I=1}^{N} \dot{\zeta}_1 \dot{\mathbf{R}}_I \cdot \nabla_{\dot{\mathbf{R}}_I} + \sum_{i=1}^{M} \dot{\zeta}_i \frac{\partial}{\partial \zeta_i} \\
&\quad + \sum_{i=1}^{M-1} (G_i - \dot{\zeta}_i \dot{\zeta}_{i+1}) \frac{\partial}{\partial \dot{\zeta}_i} + G_M \frac{\partial}{\partial \dot{\zeta}_M}
\end{aligned} \tag{12}
$$

where

$$
\begin{aligned}
G_1 &= \frac{1}{Q_1} \left(\sum_{i=1}^{N} M_I \dot{\mathbf{R}}_I^2 - N_f k_B T \right) \\
G_i &= \frac{1}{Q_i} \left(Q_{i-1} \dot{\zeta}_{i-1}^2 - k_B T \right) \quad \text{for } i > 1.
\end{aligned} \tag{13}
$$

- For noncommuting operators $\hat{A}$ and $\hat{B}$,

$$\exp(\hat{A}+\hat{B}) \neq \exp(\hat{A})\exp(\hat{B})$$

- But using Trotter approximation we have

$$\exp(\hat{A}+\hat{B}) = \lim_{N_t\to\infty}\left[\exp(\hat{A}/2N_t)\exp(\hat{B}/N_t)\exp(\hat{A}/2N_t)\right]^{N_t}$$

- Using Trotter identity to the evolution operator (for large N_t), we get

$$\begin{aligned}\exp(iL\Delta t) &= \exp\left(iL_{\mathrm{NHC}}\frac{\Delta t}{2}\right)\exp\left(iL_1\frac{\Delta t}{2}\right)\exp(iL_2\Delta t)\\ &\quad\times\exp\left(iL_1\frac{\Delta t}{2}\right)\exp\left(iL_{\mathrm{NHC}}\frac{\Delta t}{2}\right)+\mathcal{O}(\Delta t^3)\end{aligned}$$

where

$$iL_1 = \sum_{I=1}^{N}\left[\frac{\mathbf{F}_I(\mathbf{R})}{M_I}\right]\cdot\nabla_{\dot{\mathbf{R}}_I}$$

$$iL_2 = \sum_{I=1}^{N}\dot{\mathbf{R}}_I\cdot\nabla_{\mathbf{R}_I}$$

and iL_{NHC} contains all the terms from the thermostat.

$\exp\left(iL_{\text{NHC}}\Delta t/2\right)$, can be further simplified using a multiple time step approach the evolution operator from NHC can be written as,

$$\exp\left(iL_{\text{NHC}}\frac{\Delta t}{2}\right) = \prod_{k=1}^{n_c} \exp\left(iL_{\text{NHC}}\frac{\Delta t}{2n_c}\right) \tag{14}$$

where n_c is the multiple time step.
$n_c > 1$ is necessary if the frequency associated with the NHC is high

$$
\begin{aligned}
&\exp\left(iL_{\mathrm{NHC}}\frac{\Delta t}{2n_c}\right) = \\
&\exp\left(\frac{\Delta t}{4n_c}G_M\frac{\partial}{\partial\dot{\zeta}_M}\right)\exp\left(-\frac{\Delta t}{8n_c}\dot{\zeta}_M\dot{\zeta}_{M-1}\frac{\partial}{\partial\dot{\zeta}_{M-1}}\right) \\
&\times\exp\left(\frac{\Delta t}{4n_c}G_{M-1}\frac{\partial}{\partial\dot{\zeta}_{M-1}}\right)\exp\left(-\frac{\Delta t}{8n_c}\dot{\zeta}_M\dot{\zeta}_{M-1}\frac{\partial}{\partial\dot{\zeta}_{M-1}}\right) \\
&\times\ldots \\
&\times\exp\left(-\frac{\Delta t}{2n_c}\sum_{i=1}^{N}\dot{\zeta}_1\dot{\mathbf{R}}_I\cdot\nabla_{\dot{\mathbf{R}}_I}\right)\exp\left(\frac{\Delta t}{2n_c}\sum_{i=1}^{M}\dot{\zeta}_i\frac{\partial}{\partial\zeta_i}\right) \\
&\times\ldots \\
&\times\exp\left(-\frac{\Delta t}{8n_c}\dot{\zeta}_M\dot{\zeta}_{M-1}\frac{\partial}{\partial\dot{\zeta}_{M-1}}\right)\exp\left(\frac{\Delta t}{4n_c}G_{M-1}\frac{\partial}{\partial\dot{\zeta}_{M-1}}\right) \\
&\times\exp\left(-\frac{\Delta t}{8n_c}\dot{\zeta}_M\dot{\zeta}_{M-1}\frac{\partial}{\partial\dot{\zeta}_{M-1}}\right)\exp\left(\frac{\Delta t}{4n_c}G_M\frac{\partial}{\partial\dot{\zeta}_M}\right)
\end{aligned}
$$

Yoshida and Suzuki Integration for the NHC part

$$\exp\left(iL_{\text{NHC}}\frac{\Delta t}{2}\right) = \prod_{k=1}^{n_c}\left[\prod_{j=1}^{n_{ys}}\exp\left(iL_{\text{NHC}}\frac{w_j\Delta t}{2n_c}\right)\right] \tag{15}$$

where the values of $\{n_{ys}, w_j\}$ are
$\{n_{ys} = 3, w_1 = w_3 = 1/\left(2 - 2^{1/3}\right), w_2 = 1 - 2w_1\}$ or
$\{n_{ys} = 5, w_1 = w_2 = w_4 = w_5 = 1/\left(4 - 4^{1/3}\right), w_3 = 1 - 4w_1\}$

Algorithm

$$\exp(iL\Delta t) = \exp\left(iL_{\text{NHC}}\frac{\Delta t}{2}\right)\exp\left(iL_1\frac{\Delta t}{2}\right)\exp(iL_2\Delta t)$$
$$\times\exp\left(iL_1\frac{\Delta t}{2}\right)\exp\left(iL_{\text{NHC}}\frac{\Delta t}{2}\right)$$

1. Operator $\exp(iL_{\text{NHC}}\Delta t/2)$ updates $\{\zeta, \dot{\zeta}, \dot{\mathbf{R}}\}$
2. New nuclear velocities updated by iL_1 and iL_2 (velocity Verlet)
3. This again modified by the operation of $\exp(iL_{\text{NHC}}\Delta t/2)$

First operation in $\exp(iL\Delta t)f(\mathbf{R}^N, \mathbf{P}^N, \zeta^M, p_\zeta^M)$ is

$$\begin{aligned}
&\exp\left(\frac{G_M \Delta t}{4}\frac{\partial}{\partial \dot{\zeta}_M}\right) f(\mathbf{R}^N, \mathbf{P}^N, \zeta_1, \cdots, \zeta_M, \dot{\zeta}_1, \cdots, \dot{\zeta}_M) \\
&= \sum_{n=0}^{\infty} \frac{(G_M \Delta t/4)^n}{n!} \frac{\partial^n}{\partial \dot{\zeta}_M^n} f(\mathbf{R}^N, \mathbf{P}^N, \zeta_1, \cdots, \zeta_M, \dot{\zeta}_1, \cdots, \dot{\zeta}_M) \quad (16) \\
&= f(\mathbf{R}^N, \mathbf{P}^N, \zeta_1, \cdots, \zeta_M, \dot{\zeta}_1, \cdots, \dot{\zeta}_M + G_M \Delta t/4) \quad (17)
\end{aligned}$$

$$\exp(iL\Delta t)f(\mathbf{R}^N, \mathbf{P}^N, \zeta^M, p_\zeta^M): \qquad \dot{\zeta}_M \rightarrow \dot{\zeta}_M + G_M \Delta t/4$$

$$\exp(ax\frac{\partial}{\partial x})f(x) = \exp(a\frac{\partial}{\partial \ln(x)})f(\exp[\ln(x)]) = f(\exp[\ln(x)+a]) = f(x\exp[a])$$

$$\exp\left(-\frac{\Delta t}{8}\dot{\zeta}_j\dot{\zeta}_{j-1}\frac{\partial}{\partial\dot{\zeta}_{j-1}}\right)f(\mathbf{R}^N,\mathbf{P}^N,\zeta_1,\cdots,\zeta_M,\dot{\zeta}_1,\cdots,\dot{\zeta}_M)$$
$$= f\left(\mathbf{R}^N,\mathbf{P}^N,\zeta_1,\cdots,\zeta_M,\dot{\zeta}_1,\cdots,\exp(-\frac{\Delta t}{8}\dot{\zeta}_j)\dot{\zeta}_{j-1},\cdots,\dot{\zeta}_M)\right)$$

with

$$\exp(-\frac{\Delta t}{8}\zeta_j)\dot{\zeta}_{j-1}: \qquad \dot{\zeta}_{j-1} \to \exp(-\dot{\zeta}_j\Delta t/8)\dot{\zeta}_{j-1}$$

Rest in the next lecture...

but I expect that you follow the above derivations before the next lecture.