# Contents



# 1. The canonical and isobaric ensembles via molecular dynamics

## 1.1. Classical non-Hamiltonian statistical mechanics

Consider a dynamical system $\dot{\boldsymbol{x}} = \boldsymbol{\xi}(\boldsymbol{x})$. We define the compressibility as

$$\kappa(\boldsymbol{x}_t) \coloneqq \boldsymbol{\nabla}_{\boldsymbol{x}_t} \cdot \dot{\boldsymbol{x}}_t \eqqcolon \frac{\mathrm{d}}{\mathrm{d}t} w(\boldsymbol{x}_t). \tag{1}$$

Generalized Liouville's Theorem states that

$$e^{-w(\boldsymbol{x}_t)} d\boldsymbol{x}_t = e^{-w(\boldsymbol{x}_0)} d\boldsymbol{x}_0. \tag{2}$$

The Liouville operator is defined as

$$i\mathcal{L} \coloneqq \boldsymbol{\xi}(\boldsymbol{x}) \cdot \boldsymbol{\nabla}_{\boldsymbol{x}}. \tag{3}$$

Since $\dot{\boldsymbol{x}}_t = iL\boldsymbol{x}_t$, we formally write

$$\boldsymbol{x}_t = e^{it\mathcal{L}} \boldsymbol{x}_0. \tag{4}$$

## 1.2. Matrix exponential

For square matrices $\boldsymbol{A}$ and $\boldsymbol{B}$, we define the 2nd order integrator as

$$\begin{aligned} S_2(\lambda) &\coloneqq e^{\frac{\lambda}{2}\boldsymbol{B}} e^{\lambda \boldsymbol{A}} e^{\frac{\lambda}{2}\boldsymbol{B}} \\ S_2(\lambda) &= e^{\lambda(\boldsymbol{A}+\boldsymbol{B})} + O(\lambda^3). \end{aligned} \tag{5}$$

The fourth order integrator [1]

$$
\begin{aligned}
S_4(\lambda) &\coloneqq S_2(x_3\lambda)S_2(x_2\lambda)S_2(x_1\lambda) \\
x_1 = x_3 &\coloneqq \frac{1}{2 - 2^{\frac{1}{3}}} \\
x_2 &\coloneqq -\frac{2^{\frac{1}{3}}}{2 - 2^{\frac{1}{3}}} \\
S_4(\lambda) &= e^{\lambda(\boldsymbol{A}+\boldsymbol{B})} + O(\lambda^5).
\end{aligned}
\tag{6}
$$

## 1.3. Canonical ensembles

### 1.3.1. Nosè-Hoover chain

Nosè-Hoover chain equations:

$$
\begin{aligned}
\dot{\boldsymbol{r}}_i &= \frac{\boldsymbol{p}_i}{m_i} \\
\dot{\boldsymbol{p}}_i &= \boldsymbol{F}_i - \frac{p_{\eta_1}}{Q_1}\boldsymbol{p}_i \\
\dot{\eta}_j &= \frac{p_{\eta_j}}{Q_j} \quad (j = 1, ..., M) \\
\dot{p}_{\eta_1} &= \sum_{i=1}^{N} \frac{\boldsymbol{p}_i^2}{m_i} - dNkT - \frac{p_{\eta_2}}{Q_2}p_{\eta_1} \\
\dot{p}_{\eta_j} &= \frac{p_{\eta_{j-1}}^2}{Q_{j-1}} - kT - \frac{p_{\eta_{j+1}}}{Q_{j+1}}p_{\eta_j} \quad (j = 2, ..., M-1) \\
\dot{p}_{\eta_M} &= \frac{p_{\eta_{M-1}}^2}{Q_{M-1}} - kT
\end{aligned}
\tag{7}
$$

Ref. [2] suggests

$$
\begin{aligned}
Q_1 &= dNkT\tau^2 \\
Q_j &= kT\tau^2 \quad (j = 2, ..., M).
\end{aligned}
\tag{8}
$$

Nosè-Hoover chain equations converse

$$
\mathcal{H}' = \mathcal{H}(r^N, p^N) + \sum_{j=1}^{M} \frac{p_{\eta_j}^2}{2Q_j} + dNkT\eta_1 + kT\sum_{j=2}^{M}\eta_j. \tag{9}
$$

### 1.3.2. Integrating the Nosè-Hoover chain equations

The Liouville operator

$$
\begin{aligned}
iL &:= iL_{\mathrm{NHC}} + iL_1 + iL_2 \\
iL_1 &:= \sum_{i=1}^{N} \frac{\boldsymbol{p}_i}{m_i} \cdot \frac{\partial}{\partial \boldsymbol{r}_i} \\
iL_2 &:= \sum_{i=1}^{N} \boldsymbol{F}_i \cdot \frac{\partial}{\partial \boldsymbol{p}_i} \\
iL_{\mathrm{NHC}} &:= -\sum_{i=1}^{N} \frac{p_{\eta_1}}{Q_1} \boldsymbol{p}_i \cdot \frac{\partial}{\partial \boldsymbol{p}_i} + \sum_{j=1}^{M} \frac{p_{\eta_j}}{Q_j} \frac{\partial}{\partial \eta_j} + \sum_{j=1}^{M-1} \left( G_j - p_{\eta_j} \frac{p_{\eta_{j+1}}}{Q_{j+1}} \right) \frac{\partial}{\partial p_{\eta_j}} + G_M \frac{\partial}{\partial p_{\eta_M}} \\
G_1 &:= \sum_{i=1}^{N} \frac{\boldsymbol{p}_i^2}{m_i} - dNkT \\
G_j &:= \frac{p_{\eta_{j-1}}^2}{Q_{j-1}} - kT \quad (j = 2, ..., M)
\end{aligned}
\tag{10}
$$

$$
e^{iL\Delta t} = e^{iL_{\mathrm{NHC}} \frac{\Delta t}{2}} e^{iL_2 \frac{\Delta t}{2}} e^{iL_1 \Delta t} e^{iL_2 \frac{\Delta t}{2}} e^{iL_{\mathrm{NHC}} \frac{\Delta t}{2}} + O(\Delta t^3). \tag{11}
$$

$$
e^{iL_1 \Delta t} \begin{pmatrix} \boldsymbol{r}_i \\ \boldsymbol{p}_i \\ \eta_j \\ \boldsymbol{p}_{\eta_j} \end{pmatrix} = \begin{pmatrix} \boldsymbol{r}_i + \frac{\boldsymbol{p}_i}{m_i} \Delta t \\ \boldsymbol{p}_i \\ \eta_j \\ \boldsymbol{p}_{\eta_j} \end{pmatrix} \tag{12}
$$

$$
e^{iL_2 \frac{\Delta t}{2}} \begin{pmatrix} \boldsymbol{r}_i \\ \boldsymbol{p}_i \\ \eta_j \\ \boldsymbol{p}_{\eta_j} \end{pmatrix} = \begin{pmatrix} \boldsymbol{r}_i \\ \boldsymbol{p}_i + \boldsymbol{F}_i \frac{\Delta t}{2} \\ \eta_j \\ \boldsymbol{p}_{\eta_j} \end{pmatrix} \tag{13}
$$

$$
\begin{aligned}
e^{iL_{\mathrm{NHC}}\frac{\Delta t}{2}} &= \left(e^{iL_{\mathrm{NHC}}\frac{\Delta t}{2n}}\right)^{n} \\
e^{iL_{\mathrm{NHC}}\frac{\Delta t}{2n}} &= S_4^{\mathrm{NHC}}\left(\frac{\Delta t}{2n}\right) + O\left(\left(\frac{\Delta t}{n}\right)^{5}\right) \\
S_4^{\mathrm{NHC}}\left(\frac{\Delta t}{2n}\right) &\coloneqq \prod_{\alpha=1}^{3} S_2^{\mathrm{NHC}}\left(x_\alpha \frac{\Delta t}{2n}\right) \quad \left(\delta_\alpha \coloneqq x_\alpha \frac{\Delta t}{2n}\right) \\
S_2^{\mathrm{NHC}}(\delta_\alpha) &\coloneqq \exp\left(\frac{\delta_\alpha}{2} G_M \frac{\partial}{\partial p_{\eta_M}}\right) \\
&\times \prod_{j=M-1}^{1} \left(\exp\left(-\frac{\delta_\alpha}{4}\frac{p_{\eta_{j+1}}}{Q_{j+1}} p_{\eta_j}\frac{\partial}{\partial p_{\eta_j}}\right)\exp\left(\frac{\delta_\alpha}{2} G_j \frac{\partial}{\partial p_{\eta_j}}\right)\exp\left(-\frac{\delta_\alpha}{4}\frac{p_{\eta_{j+1}}}{Q_{j+1}} p_{\eta_j}\frac{\partial}{\partial p_{\eta_j}}\right)\right) \\
&\times \prod_{i=1}^{N} \exp\left(-\delta_\alpha \frac{p_{\eta_1}}{Q_1}\boldsymbol{p}_i \cdot \frac{\partial}{\partial \boldsymbol{p}_i}\right) \\
&\times \prod_{j=1}^{M} \exp\left(\delta_\alpha \frac{p_{\eta_j}}{Q_j}\frac{\partial}{\partial \eta_j}\right) \\
&\times \prod_{j=1}^{M-1} \left(\exp\left(-\frac{\delta_\alpha}{4}\frac{p_{\eta_{j+1}}}{Q_{j+1}} p_{\eta_j}\frac{\partial}{\partial p_{\eta_j}}\right)\exp\left(\frac{\delta_\alpha}{2} G_j \frac{\partial}{\partial p_{\eta_j}}\right)\exp\left(-\frac{\delta_\alpha}{4}\frac{p_{\eta_{j+1}}}{Q_{j+1}} p_{\eta_j}\frac{\partial}{\partial p_{\eta_j}}\right)\right) \\
&\times \exp\left(\frac{\delta_\alpha}{2} G_M \frac{\partial}{\partial p_{\eta_M}}\right)
\end{aligned}
\tag{14}
$$

$$
\exp\left(cx\frac{\partial}{\partial x}\right) f(x) = f(xe^{c}) \tag{15}
$$

## 1.4. The isobaric ensembles

Refs. [3]

### 1.4.1. Instantaneous stress tensor

Let $\boldsymbol{h}$ be right-handed row-major basis vectors.

Instantaneous stress tensor

$$
\mathcal{P}^{\mathrm{int}}_{\alpha\beta} = \frac{1}{\det \boldsymbol{h}} \sum_{i=1}^{N} \left[\frac{p_{i\alpha}p_{i\beta}}{m_i} + F_{i\alpha} r_{i\beta}\right] - \frac{1}{\det \boldsymbol{h}} \sum_{\gamma=1}^{3} \frac{\partial U}{\partial h_{\alpha\gamma}} h_{\gamma\beta}. \tag{16}
$$

### 1.4.2. Isotropic volume fluctuations

MTK equations:

$$
\begin{aligned}
\dot{\boldsymbol{r}}_i &= \frac{\boldsymbol{p}_i}{m_i} + \frac{p_\varepsilon}{W}\boldsymbol{r}_i \\
\dot{\boldsymbol{p}}_i &= \tilde{\boldsymbol{F}}_i - \left(1 + \frac{d}{N_f}\right)\frac{p_\varepsilon}{W}\boldsymbol{p}_i - \frac{p_{\eta_1}}{Q_1}\boldsymbol{p}_i \\
\dot{V} &= \frac{dV}{W}p_\varepsilon \\
\dot{p}_\varepsilon &= dV\left(\mathcal{P}^{\text{int}} - P\right) + \frac{d}{N_f}\sum_{i=1}^{N}\frac{\boldsymbol{p}_i^2}{m_i} - \frac{p_{\xi_1}}{Q_1'}p_\varepsilon \\
\dot{\eta}_j &= \frac{p_{\eta_j}}{Q_j} \\
\dot{\xi}_j &= \frac{p_{\xi_j}}{Q_j'} \\
\dot{p}_{\eta_j} &= G_j - \frac{p_{\eta_{j+1}}}{Q_{j+1}}p_{\eta_j} \quad (j = 1, \ldots, M-1) \\
\dot{p}_{\eta_M} &= G_M \\
\dot{p}_{\xi_j} &= G_j' - \frac{p_{\xi_{j+1}}}{Q_{j+1}'}p_\xi \quad (j = 1, \ldots, M-1) \\
\dot{p}_{\xi_M} &= G_M'
\end{aligned}
\tag{17}
$$

where

$$
\begin{aligned}
G_1' &:= \frac{p_\varepsilon^2}{W} - kT \\
G_j' &:= \frac{p_{\xi_{j-1}}^2}{Q_{j-1}'} - kT \quad (j = 2, \ldots, M)
\end{aligned}
\tag{18}
$$

The conserved energy

$$
\mathcal{H}' := \mathcal{H}(r, p) + \frac{p_\varepsilon^2}{2W} + PV + \sum_{j=1}^{M}\left(\frac{p_{\eta_j}^2}{2Q_j} + \frac{p_{\xi_j}^2}{2Q_j'} + kT\xi_j\right) + N_f kT\eta_1 + kT\sum_{j=2}^{M}\eta_j \tag{19}
$$

$$
\begin{aligned}
iL &:= iL_1 + iL_2 + iL_{\varepsilon,1} + iL_{\varepsilon,2} + iL_{\text{NHC-baro}} + iL_{\text{NHC-thermo}} \\
iL_1 &:= \sum_{i=1}^{N} \left( \frac{\boldsymbol{p}_i}{m_i} + \frac{p_\varepsilon}{W} \boldsymbol{r}_i \right) \cdot \frac{\partial}{\partial \boldsymbol{r}_i} \\
iL_2 &:= \sum_{i=1}^{N} \left( \tilde{\boldsymbol{F}}_i - \left( 1 + \frac{d}{N_f} \right) \frac{p_\varepsilon}{W} \boldsymbol{p}_i \right) \cdot \frac{\partial}{\partial \boldsymbol{p}_i} \\
iL_{\varepsilon,1} &:= \frac{p_\varepsilon}{W} \frac{\partial}{\partial \varepsilon} \\
iL_{\varepsilon,2} &:= G_\varepsilon \frac{\partial}{\partial p_\varepsilon} \\
iL_{\text{NHC-thermo}} &:= -\sum_{i=1}^{N} \frac{p_{\eta_1}}{Q_1} \boldsymbol{p}_i \cdot \frac{\partial}{\partial \boldsymbol{p}_i} + \sum_{j=1}^{M} \frac{p_{\eta_j}}{Q_j} \frac{\partial}{\partial \eta_j} + \sum_{j=1}^{M-1} \left( G_j - p_{\eta_j} \frac{p_{\eta_{j+1}}}{Q_{j+1}} \right) \frac{\partial}{\partial p_{\eta_j}} + G_M \frac{\partial}{\partial p_{\eta_M}} \\
iL_{\text{NHC-baro}} &:= -\frac{p_{\xi_1}}{Q'_1} p_\varepsilon \frac{\partial}{\partial p_\varepsilon} + \sum_{j=1}^{M} \frac{p_{\xi_j}}{Q'_j} \frac{\partial}{\partial \xi_j} + \sum_{j=1}^{M-1} \left( G'_j - p_{\xi_j} \frac{p_{\xi_{j+1}}}{Q'_{j+1}} \right) \frac{\partial}{\partial p_{\xi_j}} + G'_M \frac{\partial}{\partial p_{\xi_M}}
\end{aligned} \tag{20}
$$

with

$$
\begin{aligned}
\varepsilon &:= \frac{1}{d} \ln \frac{V}{V_0} \\
\mathcal{P}^{\text{int}} &:= \frac{1}{d} \operatorname{Tr}[\boldsymbol{\mathcal{P}}^{\text{int}}] = \frac{1}{dV} \sum_{i=1}^{N} \left( \frac{\boldsymbol{p}_i^2}{m_i} + \boldsymbol{r}_i \cdot \boldsymbol{F}_i \right) \\
G_\varepsilon &:= dV(\mathcal{P}^{\text{int}} - P) + \frac{1}{N} \sum_{i=1}^{N} \frac{\boldsymbol{p}_i^2}{m_i}.
\end{aligned} \tag{21}
$$

$$
\begin{aligned}
e^{iL\Delta t} &= e^{iL_{\text{NHC-baro}} \frac{\Delta t}{2}} e^{iL_{\text{NHC-thermo}} \frac{\Delta t}{2}} \\
&\quad \times e^{iL_{\varepsilon,2} \frac{\Delta t}{2}} e^{iL_2 \frac{\Delta t}{2}} \\
&\quad \times e^{iL_{\varepsilon,1} \Delta t} e^{iL_1 \Delta t} \\
&\quad \times e^{iL_2 \frac{\Delta t}{2}} e^{iL_{\varepsilon,2} \frac{\Delta t}{2}} \\
&\quad \times e^{iL_{\text{NHC-thermo}} \frac{\Delta t}{2}} e^{iL_{\text{NHC-baro}} \frac{\Delta t}{2}} + O(\Delta t^3).
\end{aligned} \tag{22}
$$

$$
\begin{aligned}
e^{iL_1 \Delta t} \boldsymbol{r}_i &= \exp\left( \Delta t \left( \frac{\boldsymbol{p}_i}{m_i} + \frac{p_\varepsilon}{W} \boldsymbol{r}_i \right) \cdot \frac{\partial}{\partial \boldsymbol{r}_i} \right) \boldsymbol{r}_i \\
&= \boldsymbol{r}_i e^{\frac{p_\varepsilon \Delta t}{W}} + \Delta t \frac{\boldsymbol{p}_i}{m_i} \operatorname{exprel}\left( \frac{p_\varepsilon \Delta t}{W} \right)
\end{aligned} \tag{23}
$$

$$
\begin{aligned}
e^{iL_2 \frac{\Delta t}{2}} \boldsymbol{p}_i &= \exp\left(\frac{\Delta t}{2}\left(\tilde{\boldsymbol{F}}_i - \left(1 + \frac{d}{N_f}\right)\frac{p_\varepsilon}{W}\boldsymbol{p}_i\right) \cdot \frac{\partial}{\partial \boldsymbol{p}_i}\right)\boldsymbol{p}_i \\
&= \boldsymbol{p}_i e^{-\frac{\kappa \Delta t}{2W}} + \frac{\Delta t}{2}\tilde{\boldsymbol{F}}_i \ \mathrm{exprel}\left(-\frac{\kappa \Delta t}{2W}\right) \\
\kappa &:= \left(1 + \frac{d}{N_f}\right) p_\varepsilon
\end{aligned}
\tag{24}
$$

### 1.4.3. Anisotropic cell fluctuations

MTK equations:

$$
\begin{aligned}
\dot{\boldsymbol{r}}_i &= \frac{\boldsymbol{p}_i}{m_i} + \frac{\mathbf{p}_g}{W_g}\boldsymbol{r}_i \\
\dot{\boldsymbol{p}}_i &= \tilde{\boldsymbol{F}}_i - \left(\mathbf{p}_g + \frac{\mathrm{Tr}\left[\mathbf{p}_g\right]}{N_f}\ \mathbf{I}\right)\frac{\boldsymbol{p}_i}{W_g} - \frac{p_{\eta_1}}{Q_1}\boldsymbol{p}_i \\
\dot{\mathbf{h}} &= \frac{\mathbf{h}\ \mathbf{p}_g}{W_g} \\
\dot{\mathbf{p}}_g &= \det[\mathbf{h}](\boldsymbol{\mathcal{P}}^{\mathrm{int}} - P\ \mathbf{I}) + \frac{1}{N_f}\sum_{i=1}^{N}\frac{\boldsymbol{p}_i^2}{m_i}\ \mathbf{I} - \frac{p_{\xi_1}}{Q_1'}\mathbf{p}_g \\
\dot{\eta}_j &= \frac{p_{\eta_j}}{Q_j} \\
\dot{\xi}_j &= \frac{p_{\xi_j}}{Q_j'} \\
\dot{p}_{\eta_j} &= G_j - \frac{p_{\eta_{j+1}}}{Q_{j+1}}p_{\eta_j} \quad (j = 1, ..., M-1) \\
\dot{p}_{\eta_M} &= G_M \\
\dot{p}_{\xi_j} &= G_j' - \frac{p_{\xi_{j+1}}}{Q_{j+1}'}p_{\xi_j} \quad (j = 1, ..., M-1) \\
\dot{p}_{\xi_j} &= G_M'
\end{aligned}
\tag{25}
$$

where

$$
\begin{aligned}
G_1 &:= \sum_{i=1}^{N} \frac{\boldsymbol{p}_i^2}{m_i} - N_f kT \\
G_j &:= \frac{p_{\eta_{j-1}}^2}{Q_{j-1}} - kT \quad (j = 2, ..., M) \\
G_1' &:= \frac{\mathrm{Tr}\left[\mathbf{p}_g^\top \mathbf{p}_g\right]}{W_g} - d^2 kT \\
G_j' &:= \frac{p_{\xi_{j-1}}^2}{Q_{j-1}'} - kT \quad (j = 2, ..., M)
\end{aligned}
\tag{26}
$$

The conserved energy

$$
\begin{aligned}
\mathcal{H}' := \mathcal{H}(r, p) + \frac{\mathrm{Tr}\left[\mathbf{p}_g^\top \mathbf{p}_g\right]}{2W_g} + P \det[\mathbf{h}] \\
+ \sum_{j=1}^{M} \left( \frac{p_{\eta_j}^2}{2Q_j} + \frac{p_{\xi_j}^2}{2Q_j'} \right) + N_f kT \eta_1 + d^2 kT \xi_1 + kT \sum_{j=2}^{M} \left(\eta_j + \xi_j\right)
\end{aligned}
\tag{27}
$$

Ref. [3] suggests to set

$$
\begin{aligned}
W_g &= \frac{N_f + d}{d} kT\tau^2 \\
Q_1' &= d^2 kT \tau^2 \\
Q_j' &= kT\tau^2 \quad (j = 2, ..., M),
\end{aligned}
\tag{28}
$$

where $\tau$ is a characteristic time scale for barostat.

## 1.5. Integrating the MTK equations

Ref. [4]

$$
\begin{aligned}
iL &\coloneqq iL_1 + iL_2 + iL_{g,1} + iL_{g,2} + iL_{\text{NHC-baro}} + iL_{\text{NHC-thermo}} \\
iL_1 &\coloneqq \sum_{i=1}^{N} \left( \frac{\boldsymbol{p}_i}{m_i} + \frac{\mathbf{p}_g}{W_g} \boldsymbol{r}_i \right) \cdot \frac{\partial}{\partial \boldsymbol{r}_i} \\
iL_2 &\coloneqq \sum_{i=1}^{N} \left( \tilde{\boldsymbol{F}}_i - \left( \mathbf{p}_g + \frac{\mathrm{Tr}\left[\mathbf{p}_g\right]}{N_f} \mathbf{I} \right) \frac{\boldsymbol{p}_i}{W_g} \right) \cdot \frac{\partial}{\partial \boldsymbol{p}_i} \\
iL_{g,1} &\coloneqq \frac{\mathbf{h}\ \mathbf{p}_g}{W_g} \odot \frac{\partial}{\partial \mathbf{h}} \\
iL_{g,2} &\coloneqq \mathbf{G}_g \odot \frac{\partial}{\partial \mathbf{p}_g} \\
iL_{\text{NHC-thermo}} &\coloneqq -\sum_{i=1}^{N} \frac{p_{\eta_1}}{Q_1} \boldsymbol{p}_i \cdot \frac{\partial}{\partial \boldsymbol{p}_i} + \sum_{j=1}^{M} \frac{p_{\eta_j}}{Q_j} \frac{\partial}{\partial \eta_j} + \sum_{j=1}^{M-1} \left( G_j - p_{\eta_j} \frac{p_{\eta_{j+1}}}{Q_{j+1}} \right) \frac{\partial}{\partial p_{\eta_j}} + G_M \frac{\partial}{\partial p_{\eta_M}} \\
iL_{\text{NHC-baro}} &\coloneqq -\frac{p_{\xi_1}}{Q'_1} \mathbf{p}_g \odot \frac{\partial}{\partial \mathbf{p}_g} + \sum_{j=1}^{M} \frac{p_{\xi_j}}{Q'_j} \frac{\partial}{\partial \xi_j} + \sum_{j=1}^{M-1} \left( G'_j - p_{\xi_j} \frac{p_{\xi_{j+1}}}{Q'_{j+1}} \right) \frac{\partial}{\partial p_{\xi_j}} + G'_M \frac{\partial}{\partial p_{\xi_M}}
\end{aligned}
\tag{29}
$$

with

$$
\mathbf{G}_g \coloneqq \det[\mathbf{h}] (\boldsymbol{\mathscr{P}}^{\text{int}} - P\ \mathbf{I}) + \frac{1}{N_f} \sum_{i=1}^{N} \frac{\boldsymbol{p}_i^2}{m_i} \mathbf{I}. \tag{30}
$$

$$
\begin{aligned}
e^{iL\Delta t} &= e^{iL_{\text{NHC-baro}} \frac{\Delta t}{2}} e^{iL_{\text{NHC-thermo}} \frac{\Delta t}{2}} \\
&\quad \times e^{iL_{g,2} \frac{\Delta t}{2}} e^{iL_2 \frac{\Delta t}{2}} \\
&\quad \times e^{iL_{g,1} \Delta t} e^{iL_1 \Delta t} \\
&\quad \times e^{iL_2 \frac{\Delta t}{2}} e^{iL_{g,2} \frac{\Delta t}{2}} \\
&\quad \times e^{iL_{\text{NHC-thermo}} \frac{\Delta t}{2}} e^{iL_{\text{NHC-baro}} \frac{\Delta t}{2}} + O(\Delta t^3).
\end{aligned}
\tag{31}
$$

The actions of $e^{iL_{\text{NHC-baro}} \frac{\Delta t}{2}}$ and $e^{iL_{\text{NHC-thermo}} \frac{\Delta t}{2}}$ can be evaluated similarly to the Nosè-Hoover chain equations. The action of $e^{iL_{g,2} \frac{\Delta t}{2}}$ just translates $\mathbf{p}_g$.

Since $\mathbf{p}_g$ is a symmetric real matrix, we can diagonalize it as

$$
\begin{aligned}
\mathbf{p}_g &= \sum_{\mu=1}^{3} \lambda_\mu \boldsymbol{u}_\mu \boldsymbol{u}_\mu^\top \\
\boldsymbol{U} &\coloneqq (\boldsymbol{u}_1, \boldsymbol{u}_2, \boldsymbol{u}_3) \\
\boldsymbol{U} \begin{pmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_3 \end{pmatrix} \boldsymbol{U}^\top &= \mathbf{p}_g
\end{aligned}
\tag{32}
$$

with

$$
\begin{aligned}
\lambda_\mu &\in \mathbb{R} \\
\boldsymbol{u}_\mu^\top \boldsymbol{u}_\nu &= \delta_{\mu\nu}.
\end{aligned}
\tag{33}
$$

$$
\begin{aligned}
e^{iL_{\text{NHC-baro}}\frac{\Delta t}{2}} &= \left(e^{iL_{\text{NHC-baro}}\frac{\Delta t}{2n}}\right)^n \\
e^{iL_{\text{NHC-baro}}\frac{\Delta t}{2n}} &= S_4^{\text{NHC-baro}}\left(\frac{\Delta t}{2n}\right) + O\left(\left(\frac{\Delta t}{n}\right)^5\right) \\
S_4^{\text{NHC-baro}}\left(\frac{\Delta t}{2n}\right) &:= \prod_{\alpha=1}^{3} S_2^{\text{NHC-baro}}\left(x_\alpha \frac{\Delta t}{2n}\right) \quad \left(\delta_\alpha := x_\alpha \frac{\Delta t}{2n}\right) \\
S_2^{\text{NHC-baro}}(\delta_\alpha) &:= \exp\left(\frac{\delta_\alpha}{2} G'_M \frac{\partial}{\partial p_{\xi_M}}\right) \\
&\times \prod_{j=M-1}^{1}\left(\exp\left(-\frac{\delta_\alpha}{4}\frac{p_{\xi_{j+1}}}{Q'_{j+1}} p_{\xi_j}\frac{\partial}{\partial p_{\xi_j}}\right)\exp\left(\frac{\delta_\alpha}{2} G'_j \frac{\partial}{\partial p_{\xi_j}}\right)\exp\left(-\frac{\delta_\alpha}{4}\frac{p_{\xi_{j+1}}}{Q'_{j+1}} p_{\xi_j}\frac{\partial}{\partial p_{\xi_j}}\right)\right) \\
&\times \exp\left(-\delta_\alpha \frac{p_{\xi_1}}{Q'_1}\mathbf{p}_g \odot \frac{\partial}{\partial \mathbf{p}_g}\right) \\
&\times \prod_{j=1}^{M}\exp\left(\delta_\alpha \frac{p_{\xi_j}}{Q'_j}\frac{\partial}{\partial \xi_j}\right) \\
&\times \prod_{j=1}^{M-1}\left(\exp\left(-\frac{\delta_\alpha}{4}\frac{p_{\xi_{j+1}}}{Q'_{j+1}} p_{\xi_j}\frac{\partial}{\partial p_{\xi_j}}\right)\exp\left(\frac{\delta_\alpha}{2} G'_j \frac{\partial}{\partial p_{\xi_j}}\right)\exp\left(-\frac{\delta_\alpha}{4}\frac{p_{\xi_{j+1}}}{Q'_{j+1}} p_{\xi_j}\frac{\partial}{\partial p_{\xi_j}}\right)\right) \\
&\times \exp\left(\frac{\delta_\alpha}{2} G'_M \frac{\partial}{\partial p_{\xi_M}}\right)
\end{aligned}
\tag{34}
$$

#### 1.5.1. Actions of $e^{iL_1\Delta t}$ and $e^{iL_2\frac{\Delta t}{2}}$

$$
\begin{aligned}
\boldsymbol{x}_i &:= \boldsymbol{U}^\top \boldsymbol{r}_i \\
e^{iL_1\Delta t}\boldsymbol{r}_i &= \exp\left(\Delta t\left(\frac{\boldsymbol{p}_i}{m_i} + \frac{1}{W_g}\mathbf{p}_g \boldsymbol{r}_i\right)\cdot\frac{\partial}{\partial \boldsymbol{r}_i}\right)\boldsymbol{r}_i \\
&= \boldsymbol{U}\exp\left(\Delta t\left(\frac{\boldsymbol{p}_i}{m_i} + \frac{1}{W_g}\mathbf{p}_g \boldsymbol{r}_i\right)\cdot\frac{\partial}{\partial \boldsymbol{r}_i}\right)\boldsymbol{x}_i \\
&= \boldsymbol{U}\exp\left(\Delta t\left(\frac{\boldsymbol{U}^\top\boldsymbol{p}_i}{m_i} + \frac{1}{W_g}\boldsymbol{U}^\top\mathbf{p}_g \boldsymbol{U}\boldsymbol{x}_i\right)\cdot\frac{\partial}{\partial \boldsymbol{x}_i}\right)\boldsymbol{x}_i \\
&= \boldsymbol{U}\left(\exp\left(\Delta t\left(\frac{\left[\boldsymbol{U}^\top\boldsymbol{p}_i\right]_\alpha}{m_i} + \frac{1}{W_g}\lambda_\alpha x_{i\alpha}\right)\frac{\partial}{\partial x_{i\alpha}}\right)x_{i\alpha}\right)_{\alpha=1,2,3} \\
&= \boldsymbol{U}\left(x_{i\alpha}e^{\frac{\lambda_\alpha\Delta t}{W_g}} + \Delta t\frac{\left[\boldsymbol{U}^\top\boldsymbol{p}_i\right]_\alpha}{m_i}\ \operatorname{exprel}\left(\frac{\lambda_\alpha\Delta t}{W_g}\right)\right)_{\alpha=1,2,3} \\
\operatorname{exprel}(x) &:= \frac{e^x - 1}{x}
\end{aligned}
\tag{35}
$$

Similarily

$$\boldsymbol{y}_i \coloneqq \boldsymbol{U}^\top \boldsymbol{p}_i$$

$$\begin{aligned}
e^{iL_2\frac{\Delta t}{2}}\boldsymbol{p}_i &= \exp\left(\frac{\Delta t}{2}\left(\tilde{\boldsymbol{F}}_i - \frac{1}{W_g}\left(\mathbf{p}_g + \frac{\mathrm{Tr}[\mathbf{p}_g]}{N_f}\ \mathbf{I}\right)\boldsymbol{p}_i\right)\cdot\frac{\partial}{\partial \boldsymbol{p}_i}\right)\boldsymbol{p}_i \\
&= \boldsymbol{U}\exp\left(\frac{\Delta t}{2}\left(\tilde{\boldsymbol{F}}_i - \frac{1}{W_g}\left(\mathbf{p}_g + \frac{\mathrm{Tr}[\mathbf{p}_g]}{N_f}\ \mathbf{I}\right)\boldsymbol{p}_i\right)\cdot\frac{\partial}{\partial \boldsymbol{p}_i}\right)\boldsymbol{y}_i \\
&= \boldsymbol{U}\exp\left(\frac{\Delta t}{2}\left(\boldsymbol{U}^\top\tilde{\boldsymbol{F}}_i - \frac{1}{W_g}\boldsymbol{U}^\top\left(\mathbf{p}_g + \frac{\mathrm{Tr}[\mathbf{p}_g]}{N_f}\ \mathbf{I}\right)\boldsymbol{U}\boldsymbol{y}_i\right)\cdot\frac{\partial}{\partial \boldsymbol{y}_i}\right)\boldsymbol{y}_i \\
&= \boldsymbol{U}\left(\exp\left(\frac{\Delta t}{2}\left(\left[\boldsymbol{U}^\top\tilde{\boldsymbol{F}}_i\right]_\alpha - \frac{1}{W_g}\left(\lambda_\alpha + \frac{\mathrm{Tr}[\mathbf{p}_g]}{N_f}\right)y_{i\alpha}\right)\frac{\partial}{\partial y_{i\alpha}}\right)y_{i\alpha}\right)_{\alpha=1,2,3} \\
&= \boldsymbol{U}\left(y_{i\alpha}e^{-\frac{\kappa_\alpha\Delta t}{2W_g}} + \frac{\Delta t}{2}\left[\boldsymbol{U}^\top\tilde{\boldsymbol{F}}_i\right]_\alpha\ \mathrm{exprel}\left(-\frac{\kappa_\alpha\Delta t}{2W_g}\right)\right)_{\alpha=1,2,3}
\end{aligned} \tag{36}$$

$$\kappa_\alpha \coloneqq \lambda_\alpha + \frac{\mathrm{Tr}[\mathbf{p}_g]}{N_f}$$

## 1.6. Action of $e^{iL_{g,1}\Delta t}$

$$\begin{aligned}
\mathbf{n} &\coloneqq \mathbf{h}\ \mathbf{U} \\
e^{iL_{g,1}\Delta t}\ \mathbf{h} &= \exp\left(\Delta t\frac{\mathbf{h}\ \mathbf{p}_g}{W_g}\odot\frac{\partial}{\partial \mathbf{h}}\right)\ \mathbf{h} \\
&= \exp\left(\frac{\Delta t}{W_g}\ \mathrm{Tr}\left[(\mathbf{h}\ \mathbf{p}_g)^\top\frac{\partial}{\partial \mathbf{h}}\right]\right)\ \mathbf{h} \\
&= \exp\left(\frac{\Delta t}{W_g}\ \mathrm{Tr}\left[\mathbf{p}_g\ \mathbf{U}\ \mathbf{n}^\top\frac{\partial}{\partial \mathbf{n}}\mathbf{U}^\top\right]\right)\ \mathbf{n}\ \mathbf{U}^\top \\
&= \left(\prod_{\mu\alpha}\exp\left(\frac{\Delta t\lambda_\alpha}{W_g}n_{\mu\alpha}\frac{\partial}{\partial n_{\mu\alpha}}\right)\ \mathbf{n}\right)\mathbf{U}^\top \\
&= \left(e^{\frac{\Delta t\lambda_\alpha}{W_g}}n_{\mu\alpha}\right)_{\mu\alpha}\mathbf{U}^\top
\end{aligned} \tag{37}$$

## 1.7. LAMMPS

- tchain=3
- pchain=3
- tloop=1 ($n$ in $\delta t = \frac{\Delta t}{n}$)
- ploop=1

LAMMPS uses the first-order Suzuki-Yoshida scheme

# 2. Appendix

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