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

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

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

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

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

$$S_2(\lambda) := e^{\frac{\lambda}{2} \boldsymbol{B}} e^{\lambda \boldsymbol{A}} e^{\frac{\lambda}{2} \boldsymbol{B}}$$

$$S_2(\lambda) = e^{\lambda(\boldsymbol{A}+\boldsymbol{B})} + O(\lambda^3). \tag{5}$$

The fourth order integrator [1]

$$S_4(\lambda) := S_2(x_3\lambda)S_2(x_2\lambda)S_2(x_1\lambda)$$

$$x_1 = x_3 := \frac{1}{2 - 2^{\frac{1}{3}}}$$

$$x_2 := -\frac{2^{\frac{1}{3}}}{2 - 2^{\frac{1}{3}}}$$

$$S_4(\lambda) = e^{\lambda(\boldsymbol{A}+\boldsymbol{B})} + O(\lambda^5).$$

(6)

1.3. Canonical ensembles

1.3.1. Nosè-Hoover chain

Nosè-Hoover chain equations:

$$\dot{\boldsymbol{r}}_i = \frac{\boldsymbol{p}_i}{m_i}$$

$$\dot{\boldsymbol{p}}_i = \boldsymbol{F}_i - \frac{p_{\eta_1}}{Q_1}\boldsymbol{p}_i$$

$$\dot{\eta}_j = \frac{p_{\eta_j}}{Q_j} \quad (j = 1, ..., M)$$

$$\dot{p}_{\eta_1} = \sum_{i=1}^{N} \frac{\boldsymbol{p}_i^2}{m_i} - dNkT - \frac{p_{\eta_2}}{Q_2}p_{\eta_1}$$

$$\dot{p}_{\eta_j} = \frac{p_{\eta_{j-1}}^2}{Q_{j-1}} - kT - \frac{p_{\eta_{j+1}}}{Q_{j+1}}p_{\eta_j} \quad (j = 2, ..., M-1)$$

$$\dot{p}_{\eta_M} = \frac{p_{\eta_{M-1}}^2}{Q_{M-1}} - kT$$

(7)

Ref. [2] suggests

$$Q_1 = dNkT\tau^2$$

$$Q_j = kT\tau^2 \quad (j = 2, ..., M).$$

(8)

Nosè-Hoover chain equations conserves

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

(9)

1.3.2. Integrating the Nosè-Hoover chain equations

The Liouville operator

$$iL := iL_{\mathrm{NHC}} + iL_1 + iL_2$$

$$iL_1 := \sum_{i=1}^{N} \frac{\boldsymbol{p}_i}{m_i} \cdot \frac{\partial}{\partial \boldsymbol{r}_i}$$

$$iL_2 := \sum_{i=1}^{N} \boldsymbol{F}_i \cdot \frac{\partial}{\partial \boldsymbol{p}_i}$$

$$iL_{\mathrm{NHC}} := -\sum_{i=1}^{N} \frac{p_{\eta_1}}{Q_1} \boldsymbol{p}_i \cdot \frac{\partial}{\partial \boldsymbol{p}_i} + \sum_{j=1}^{M} \frac{p_{\eta_j}}{Q_j} \frac{\partial}{\partial \eta_j} + \sum_{j=1}^{M-1} \left(G_j - p_{\eta_j} \frac{p_{\eta_{j+1}}}{Q_{j+1}} \right) \frac{\partial}{\partial p_{\eta_j}} + G_M \frac{\partial}{\partial p_{\eta_M}} \tag{10}$$

$$G_1 := \sum_{i=1}^{N} \frac{\boldsymbol{p}_i^2}{m_i} - dNkT$$

$$G_j := \frac{p_{\eta_{j-1}}^2}{Q_{j-1}} - kT \quad (j = 2, ..., M)$$

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

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

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

$$e^{iL_{\text{NHC}}\frac{\Delta t}{2}} = \left(e^{iL_{\text{NHC}}\frac{\Delta t}{2n}}\right)^n$$

$$e^{iL_{\text{NHC}}\frac{\Delta t}{2n}} = S_4^{\text{NHC}}\left(\frac{\Delta t}{2n}\right) + O\left(\left(\frac{\Delta t}{n}\right)^5\right)$$

$$S_4^{\text{NHC}}\left(\frac{\Delta t}{2n}\right) := \prod_{\alpha=1}^{3} S_2^{\text{NHC}}\left(x_\alpha \frac{\Delta t}{2n}\right) \quad \left(\delta_\alpha := x_\alpha \frac{\Delta t}{2n}\right)$$

$$
\begin{aligned}
S_2^{\text{NHC}}(\delta_\alpha) &:= \exp\left(\frac{\delta_\alpha}{2} G_M \frac{\partial}{\partial p_{\eta_M}}\right) \\
&\times \prod_{j=M-1}^{1}\left(\exp\left(-\frac{\delta_\alpha}{4}\frac{p_{\eta_{j+1}}}{Q_{j+1}} p_{\eta_j}\frac{\partial}{\partial p_{\eta_j}}\right) \exp\left(\frac{\delta_\alpha}{2} G_j \frac{\partial}{\partial p_{\eta_j}}\right) \exp\left(-\frac{\delta_\alpha}{4}\frac{p_{\eta_{j+1}}}{Q_{j+1}} p_{\eta_j}\frac{\partial}{\partial p_{\eta_j}}\right)\right) \\
&\times \prod_{i=1}^{N}\exp\left(-\delta_\alpha \frac{p_{\eta_1}}{Q_1} \boldsymbol{p}_i \cdot \frac{\partial}{\partial \boldsymbol{p}_i}\right) \\
&\times \prod_{j=1}^{M}\exp\left(\delta_\alpha \frac{p_{\eta_j}}{Q_j}\frac{\partial}{\partial \eta_j}\right) \\
&\times \prod_{j=1}^{M-1}\left(\exp\left(-\frac{\delta_\alpha}{4}\frac{p_{\eta_{j+1}}}{Q_{j+1}} p_{\eta_j}\frac{\partial}{\partial p_{\eta_j}}\right) \exp\left(\frac{\delta_\alpha}{2} G_j \frac{\partial}{\partial p_{\eta_j}}\right) \exp\left(-\frac{\delta_\alpha}{4}\frac{p_{\eta_{j+1}}}{Q_{j+1}} p_{\eta_j}\frac{\partial}{\partial p_{\eta_j}}\right)\right) \\
&\times \exp\left(\frac{\delta_\alpha}{2} G_M \frac{\partial}{\partial p_{\eta_M}}\right)
\end{aligned}
\tag{14}
$$

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

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

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

1.4.2. Isotropic volume fluctuations

MTK equations:

$$\dot{\boldsymbol{r}}_i = \frac{\boldsymbol{p}_i}{m_i} + \frac{p_\varepsilon}{W}\boldsymbol{r}_i$$

$$\dot{\boldsymbol{p}}_i = \tilde{\boldsymbol{F}}_i - \left(1 + \frac{d}{N_f}\right)\frac{p_\varepsilon}{W}\boldsymbol{p}_i - \frac{p_{\eta_1}}{Q_1}\boldsymbol{p}_i$$

$$\dot{V} = \frac{dV}{W}p_\varepsilon$$

$$\dot{p}_\varepsilon = dV(\mathcal{P}^{\mathrm{int}} - P) + \frac{d}{N_f}\sum_{i=1}^{N}\frac{\boldsymbol{p}_i^2}{m_i} - \frac{p_{\xi_1}}{Q_1'}p_\varepsilon$$

$$\dot{\eta}_j = \frac{p_{\eta_j}}{Q_j}$$

$$\dot{\xi}_j = \frac{p_{\xi_j}}{Q_j'}$$

$$\dot{p}_{\eta_j} = G_j - \frac{p_{\eta_{j+1}}}{Q_{j+1}}p_{\eta_j} \quad (j=1,...,M-1)$$

$$\dot{p}_{\eta_M} = G_M$$

$$\dot{p}_{\xi_j} = G_j' - \frac{p_{\xi_{j+1}}}{Q_{j+1}'}p_\xi \quad (j=1,...,M-1)$$

$$\dot{p}_{\xi_M} = G_M'$$

$$(17)$$

where

$$G_1' := \frac{p_\varepsilon^2}{W} - kT$$

$$G_j' := \frac{p_{\xi_{j-1}}^2}{Q_{j-1}'} - kT \quad (j=2,...,M).$$

$$(18)$$

Ref. [3] suggests to set

$$W = (N_f + d)kT\tau^2$$

$$Q_1' = d^2 kT\tau^2$$

$$Q_j' = kT\tau^2 \quad (j=2,...,M),$$

$$(19)$$

where τ is a characteristic time scale for barostat.

The conserved energy

$$\mathcal{H}' := \mathcal{H}(r,p) + \frac{p_\varepsilon^2}{2W} + PV + \sum_{j=1}^{M}\left(\frac{p_{\eta_j}^2}{2Q_j} + \frac{p_{\xi_j}^2}{2Q_j'} + kT\xi_j\right) + N_f kT\eta_1 + kT\sum_{j=2}^{M}\eta_j \quad (20)$$

$$iL := iL_1 + iL_2 + iL_{\varepsilon,1} + iL_{\varepsilon,2} + iL_{\text{NHC-baro}} + iL_{\text{NHC-thermo}}$$

$$iL_1 := \sum_{i=1}^{N} \left(\frac{\boldsymbol{p}_i}{m_i} + \frac{p_\varepsilon}{W} \boldsymbol{r}_i \right) \cdot \frac{\partial}{\partial \boldsymbol{r}_i}$$

$$iL_2 := \sum_{i=1}^{N} \left(\tilde{\boldsymbol{F}}_i - \left(1 + \frac{d}{N_f} \right) \frac{p_\varepsilon}{W} \boldsymbol{p}_i \right) \cdot \frac{\partial}{\partial \boldsymbol{p}_i}$$

$$iL_{\varepsilon,1} := \frac{p_\varepsilon}{W} \frac{\partial}{\partial \varepsilon} \tag{21}$$

$$iL_{\varepsilon,2} := G_\varepsilon \frac{\partial}{\partial p_\varepsilon}$$

$$iL_{\text{NHC-thermo}} := -\sum_{i=1}^{N} \frac{p_{\eta_1}}{Q_1} \boldsymbol{p}_i \cdot \frac{\partial}{\partial \boldsymbol{p}_i} + \sum_{j=1}^{M} \frac{p_{\eta_j}}{Q_j} \frac{\partial}{\partial \eta_j} + \sum_{j=1}^{M-1} \left(G_j - p_{\eta_j} \frac{p_{\eta_{j+1}}}{Q_{j+1}} \right) \frac{\partial}{\partial p_{\eta_j}} + G_M \frac{\partial}{\partial p_{\eta_M}}$$

$$iL_{\text{NHC-baro}} := -\frac{p_{\xi_1}}{Q_1'} p_\varepsilon \frac{\partial}{\partial p_\varepsilon} + \sum_{j=1}^{M} \frac{p_{\xi_j}}{Q_j'} \frac{\partial}{\partial \xi_j} + \sum_{j=1}^{M-1} \left(G_j' - p_{\xi_j} \frac{p_{\xi_{j+1}}}{Q_{j+1}'} \right) \frac{\partial}{\partial p_{\xi_j}} + G_M' \frac{\partial}{\partial p_{\xi_M}}$$

with

$$\varepsilon := \frac{1}{d} \ln \frac{V}{V_0}$$

$$\mathcal{P}^{\text{int}} := \frac{1}{d} \operatorname{Tr}[\boldsymbol{\mathcal{P}}^{\text{int}}] = \frac{1}{dV} \sum_{i=1}^{N} \left(\frac{\boldsymbol{p}_i^2}{m_i} + \boldsymbol{r}_i \cdot \boldsymbol{F}_i \right) \tag{22}$$

$$G_\varepsilon := dV \left(\mathcal{P}^{\text{int}} - P \right) + \frac{1}{N} \sum_{i=1}^{N} \frac{\boldsymbol{p}_i^2}{m_i}.$$

$$\begin{aligned}
e^{iL\Delta t} = {}& e^{iL_{\text{NHC-baro}} \frac{\Delta t}{2}} e^{iL_{\text{NHC-thermo}} \frac{\Delta t}{2}} \\
& \times e^{iL_{\varepsilon,2} \frac{\Delta t}{2}} e^{iL_2 \frac{\Delta t}{2}} \\
& \times e^{iL_{\varepsilon,1} \Delta t} e^{iL_1 \Delta t} \\
& \times e^{iL_2 \frac{\Delta t}{2}} e^{iL_{\varepsilon,2} \frac{\Delta t}{2}} \\
& \times e^{iL_{\text{NHC-thermo}} \frac{\Delta t}{2}} e^{iL_{\text{NHC-baro}} \frac{\Delta t}{2}} + O(\Delta t^3).
\end{aligned} \tag{23}$$

$$\begin{aligned}
e^{iL_1 \Delta t} \boldsymbol{r}_i &= \exp\left(\Delta t \left(\frac{\boldsymbol{p}_i}{m_i} + \frac{p_\varepsilon}{W} \boldsymbol{r}_i \right) \cdot \frac{\partial}{\partial \boldsymbol{r}_i} \right) \boldsymbol{r}_i \\
&= \boldsymbol{r}_i e^{\frac{p_\varepsilon \Delta t}{W}} + \Delta t \frac{\boldsymbol{p}_i}{m_i} \operatorname{exprel}\left(\frac{p_\varepsilon \Delta t}{W} \right)
\end{aligned} \tag{24}$$

$$e^{iL_2 \frac{\Delta t}{2}} \boldsymbol{p}_i = \exp\left(\frac{\Delta t}{2}\left(\tilde{\boldsymbol{F}}_i - \left(1 + \frac{d}{N_f}\right) \frac{p_\varepsilon}{W} \boldsymbol{p}_i \right) \cdot \frac{\partial}{\partial \boldsymbol{p}_i} \right) \boldsymbol{p}_i$$

$$= \boldsymbol{p}_i e^{-\frac{\kappa \Delta t}{2W}} + \frac{\Delta t}{2} \tilde{\boldsymbol{F}}_i \, \mathrm{exprel}\left(-\frac{\kappa \Delta t}{2W} \right) \tag{25}$$

$$\kappa := \left(1 + \frac{d}{N_f}\right) p_\varepsilon$$

1.4.3. Anisotropic cell fluctuations

MTK equations:

$$\dot{\boldsymbol{r}}_i = \frac{\boldsymbol{p}_i}{m_i} + \frac{\mathbf{p}_g}{W_g} \boldsymbol{r}_i$$

$$\dot{\boldsymbol{p}}_i = \tilde{\boldsymbol{F}}_i - \left(\mathbf{p}_g + \frac{\mathrm{Tr}[\mathbf{p}_g]}{N_f} \mathbf{I} \right) \frac{\boldsymbol{p}_i}{W_g} - \frac{p_{\eta_1}}{Q_1} \boldsymbol{p}_i$$

$$\dot{\mathbf{h}} = \frac{\mathbf{h} \, \mathbf{p}_g}{W_g}$$

$$\dot{\mathbf{p}}_g = \det[\mathbf{h}](\mathcal{P}^{\mathrm{int}} - P \, \mathbf{I}) + \frac{1}{N_f} \sum_{i=1}^{N} \frac{\boldsymbol{p}_i^2}{m_i} \mathbf{I} - \frac{p_{\xi_1}}{Q_1'} \mathbf{p}_g$$

$$\dot{\eta}_j = \frac{p_{\eta_j}}{Q_j} \tag{26}$$

$$\dot{\xi}_j = \frac{p_{\xi_j}}{Q_j'}$$

$$\dot{p}_{\eta_j} = G_j - \frac{p_{\eta_{j+1}}}{Q_{j+1}} p_{\eta_j} \quad (j = 1, ..., M - 1)$$

$$\dot{p}_{\eta_M} = G_M$$

$$\dot{p}_{\xi_j} = G_j' - \frac{p_{\xi_{j+1}}}{Q_{j+1}'} p_{\xi_j} \quad (j = 1, ..., M - 1)$$

$$\dot{p}_{\xi_j} = G_M'$$

where

$$G_1 := \sum_{i=1}^{N} \frac{p_i^2}{m_i} - N_f kT$$

$$G_j := \frac{p_{\eta_{j-1}}^2}{Q_{j-1}} - kT \quad (j = 2, ..., M)$$

$$G_1' := \frac{\mathrm{Tr}\left[\mathbf{p}_g^\top \mathbf{p}_g\right]}{W_g} - d^2 kT$$

$$G_j' := \frac{p_{\xi_{j-1}}^2}{Q_{j-1}'} - kT \quad (j = 2, ..., M)$$

(27)

The conserved energy

$$\mathcal{H}' := \mathcal{H}(r, p) + \frac{\mathrm{Tr}\left[\mathbf{p}_g^\top \mathbf{p}_g\right]}{2W_g} + P \det[\mathbf{h}]$$

$$+ \sum_{j=1}^{M} \left(\frac{p_{\eta_j}^2}{2Q_j} + \frac{p_{\xi_j}^2}{2Q_j'} \right) + N_f kT \eta_1 + d^2 kT \xi_1 + kT \sum_{j=2}^{M} (\eta_j + \xi_j)$$

(28)

Ref. [3] suggests to set

$$W_g = \frac{N_f + d}{d} kT\tau^2$$

$$Q_1' = d^2 kT\tau^2$$

$$Q_j' = kT\tau^2 \quad (j = 2, ..., M),$$

(29)

where τ is a characteristic time scale for barostat. d^2 in Q_1' should be substituted with the degree of freedoms in basis vectors.

1.5. Integrating the MTK equations
Ref. [4]

$$iL := iL_1 + iL_2 + iL_{g,1} + iL_{g,2} + iL_{\text{NHC-baro}} + iL_{\text{NHC-thermo}}$$

$$iL_1 := \sum_{i=1}^{N} \left(\frac{\boldsymbol{p}_i}{m_i} + \frac{\mathbf{p}_g}{W_g} \boldsymbol{r}_i \right) \cdot \frac{\partial}{\partial \boldsymbol{r}_i}$$

$$iL_2 := \sum_{i=1}^{N} \left(\tilde{\boldsymbol{F}}_i - \left(\mathbf{p}_g + \frac{\text{Tr}[\mathbf{p}_g]}{N_f} \mathbf{I} \right) \frac{\boldsymbol{p}_i}{W_g} \right) \cdot \frac{\partial}{\partial \boldsymbol{p}_i}$$

$$iL_{g,1} := \frac{\mathbf{h}\,\mathbf{p}_g}{W_g} \odot \frac{\partial}{\partial \mathbf{h}} \tag{30}$$

$$iL_{g,2} := \mathbf{G}_g \odot \frac{\partial}{\partial \mathbf{p}_g}$$

$$iL_{\text{NHC-thermo}} := -\sum_{i=1}^{N} \frac{p_{\eta_1}}{Q_1} \boldsymbol{p}_i \cdot \frac{\partial}{\partial \boldsymbol{p}_i} + \sum_{j=1}^{M} \frac{p_{\eta_j}}{Q_j} \frac{\partial}{\partial \eta_j} + \sum_{j=1}^{M-1} \left(G_j - p_{\eta_j} \frac{p_{\eta_{j+1}}}{Q_{j+1}} \right) \frac{\partial}{\partial p_{\eta_j}} + G_M \frac{\partial}{\partial p_{\eta_M}}$$

$$iL_{\text{NHC-baro}} := -\frac{p_{\xi_1}}{Q_1'} \mathbf{p}_g \odot \frac{\partial}{\partial \mathbf{p}_g} + \sum_{j=1}^{M} \frac{p_{\xi_j}}{Q_j'} \frac{\partial}{\partial \xi_j} + \sum_{j=1}^{M-1} \left(G_j' - p_{\xi_j} \frac{p_{\xi_{j+1}}}{Q_{j+1}'} \right) \frac{\partial}{\partial p_{\xi_j}} + G_M' \frac{\partial}{\partial p_{\xi_M}}$$

with

$$\mathbf{G}_g := \det[\mathbf{h}](\mathscr{P}^{\text{int}} - P\,\mathbf{I}) + \frac{1}{N_f} \sum_{i=1}^{N} \frac{\boldsymbol{p}_i^2}{m_i} \mathbf{I} . \tag{31}$$

$$e^{iL\Delta t} = e^{iL_{\text{NHC-baro}} \frac{\Delta t}{2}} e^{iL_{\text{NHC-thermo}} \frac{\Delta t}{2}}$$

$$\times\, e^{iL_{g,2} \frac{\Delta t}{2}} e^{iL_2 \frac{\Delta t}{2}}$$

$$\times\, e^{iL_{g,1} \Delta t} e^{iL_1 \Delta t} \tag{32}$$

$$\times\, e^{iL_2 \frac{\Delta t}{2}} e^{iL_{g,2} \frac{\Delta t}{2}}$$

$$\times\, e^{iL_{\text{NHC-thermo}} \frac{\Delta t}{2}} e^{iL_{\text{NHC-baro}} \frac{\Delta t}{2}} + O(\Delta t^3).$$

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

$$\mathbf{p}_g = \sum_{\mu=1}^{3} \lambda_\mu \boldsymbol{u}_\mu \boldsymbol{u}_\mu^\top$$

$$\boldsymbol{U} := (\boldsymbol{u}_1, \boldsymbol{u}_2, \boldsymbol{u}_3) \tag{33}$$

$$\boldsymbol{U} \begin{pmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_3 \end{pmatrix} \boldsymbol{U}^\top = \mathbf{p}_g$$

with

$$\lambda_\mu \in \mathbb{R}$$

$$\boldsymbol{u}_\mu^\top \boldsymbol{u}_\nu = \delta_{\mu\nu}. \tag{34}$$

$$e^{iL_{\text{NHC-baro}}\frac{\Delta t}{2}} = \left(e^{iL_{\text{NHC-baro}}\frac{\Delta t}{2n}}\right)^n$$

$$e^{iL_{\text{NHC-baro}}\frac{\Delta t}{2n}} = S_4^{\text{NHC-baro}}\left(\frac{\Delta t}{2n}\right) + O\left(\left(\frac{\Delta t}{n}\right)^5\right)$$

$$S_4^{\text{NHC-baro}}\left(\frac{\Delta t}{2n}\right) := \prod_{\alpha=1}^{3} S_2^{\text{NHC-baro}}\left(x_\alpha \frac{\Delta t}{2n}\right) \quad \left(\delta_\alpha := x_\alpha \frac{\Delta t}{2n}\right)$$

$$S_2^{\text{NHC-baro}}(\delta_\alpha) := \exp\left(\frac{\delta_\alpha}{2} G_M' \frac{\partial}{\partial p_{\xi_M}}\right)$$

$$\times \prod_{j=M-1}^{1}\left(\exp\left(-\frac{\delta_\alpha}{4}\frac{p_{\xi_{j+1}}}{Q_{j+1}'}p_{\xi_j}\frac{\partial}{\partial p_{\xi_j}}\right)\exp\left(\frac{\delta_\alpha}{2}G_j'\frac{\partial}{\partial p_{\xi_j}}\right)\exp\left(-\frac{\delta_\alpha}{4}\frac{p_{\xi_{j+1}}}{Q_{j+1}'}p_{\xi_j}\frac{\partial}{\partial p_{\xi_j}}\right)\right) \tag{35}$$

$$\times \exp\left(-\delta_\alpha \frac{p_{\xi_1}}{Q_1'}\mathbf{p}_g \odot \frac{\partial}{\partial \mathbf{p}_g}\right)$$

$$\times \prod_{j=1}^{M} \exp\left(\delta_\alpha \frac{p_{\xi_j}}{Q_j'}\frac{\partial}{\partial \xi_j}\right)$$

$$\times \prod_{j=1}^{M-1}\left(\exp\left(-\frac{\delta_\alpha}{4}\frac{p_{\xi_{j+1}}}{Q_{j+1}'}p_{\xi_j}\frac{\partial}{\partial p_{\xi_j}}\right)\exp\left(\frac{\delta_\alpha}{2}G_j'\frac{\partial}{\partial p_{\xi_j}}\right)\exp\left(-\frac{\delta_\alpha}{4}\frac{p_{\xi_{j+1}}}{Q_{j+1}'}p_{\xi_j}\frac{\partial}{\partial p_{\xi_j}}\right)\right)$$

$$\times \exp\left(\frac{\delta_\alpha}{2}G_M'\frac{\partial}{\partial p_{\xi_M}}\right)$$

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

$$\boldsymbol{x}_i := \boldsymbol{U}^\top \boldsymbol{r}_i$$

$$e^{iL_1\Delta t}\boldsymbol{r}_i = \exp\left(\Delta t\left(\frac{\boldsymbol{p}_i}{m_i} + \frac{1}{W_g}\mathbf{p}_g \boldsymbol{r}_i\right)\cdot\frac{\partial}{\partial \boldsymbol{r}_i}\right)\boldsymbol{r}_i$$

$$= \boldsymbol{U}\exp\left(\Delta t\left(\frac{\boldsymbol{p}_i}{m_i} + \frac{1}{W_g}\mathbf{p}_g \boldsymbol{r}_i\right)\cdot\frac{\partial}{\partial \boldsymbol{r}_i}\right)\boldsymbol{x}_i$$

$$= \boldsymbol{U}\exp\left(\Delta t\left(\frac{\boldsymbol{U}^\top \boldsymbol{p}_i}{m_i} + \frac{1}{W_g}\boldsymbol{U}^\top \mathbf{p}_g \boldsymbol{U}\boldsymbol{x}_i\right)\cdot\frac{\partial}{\partial \boldsymbol{x}_i}\right)\boldsymbol{x}_i \tag{36}$$

$$= \boldsymbol{U}\left(\exp\left(\Delta t\left(\frac{[\boldsymbol{U}^\top \boldsymbol{p}_i]_\alpha}{m_i} + \frac{1}{W_g}\lambda_\alpha x_{i\alpha}\right)\frac{\partial}{\partial x_{i\alpha}}\right)x_{i\alpha}\right)_{\alpha=1,2,3}$$

$$= \boldsymbol{U}\left(x_{i\alpha}e^{\frac{\lambda_\alpha \Delta t}{W_g}} + \Delta t\frac{[\boldsymbol{U}^\top \boldsymbol{p}_i]_\alpha}{m_i}\,\text{exprel}\left(\frac{\lambda_\alpha \Delta t}{W_g}\right)\right)_{\alpha=1,2,3}$$

$$\text{exprel}(x) := \frac{e^x - 1}{x}$$

Similarily

$$y_i := U^\top p_i$$

$$e^{iL_2 \frac{\Delta t}{2}} p_i = \exp\left(\frac{\Delta t}{2} \left(\tilde{F}_i - \frac{1}{W_g} \left(\mathbf{p}_g + \frac{\mathrm{Tr}[\mathbf{p}_g]}{N_f} \mathbf{I} \right) p_i \right) \cdot \frac{\partial}{\partial p_i} \right) p_i$$

$$= U \exp\left(\frac{\Delta t}{2} \left(\tilde{F}_i - \frac{1}{W_g} \left(\mathbf{p}_g + \frac{\mathrm{Tr}[\mathbf{p}_g]}{N_f} \mathbf{I} \right) p_i \right) \cdot \frac{\partial}{\partial p_i} \right) y_i$$

$$= U \exp\left(\frac{\Delta t}{2} \left(U^\top \tilde{F}_i - \frac{1}{W_g} U^\top \left(\mathbf{p}_g + \frac{\mathrm{Tr}[\mathbf{p}_g]}{N_f} \mathbf{I} \right) U y_i \right) \cdot \frac{\partial}{\partial y_i} \right) y_i \quad (37)$$

$$= U \left(\exp\left(\frac{\Delta t}{2} \left([U^\top \tilde{F}_i]_\alpha - \frac{1}{W_g} \left(\lambda_\alpha + \frac{\mathrm{Tr}[\mathbf{p}_g]}{N_f} \right) y_{i\alpha} \right) \frac{\partial}{\partial y_{i\alpha}} \right) y_{i\alpha} \right)_{\alpha=1,2,3}$$

$$= U \left(y_{i\alpha} e^{-\frac{\kappa_\alpha \Delta t}{2 W_g}} + \frac{\Delta t}{2} [U^\top \tilde{F}_i]_\alpha \, \mathrm{exprel}\left(-\frac{\kappa_\alpha \Delta t}{2 W_g} \right) \right)_{\alpha=1,2,3}$$

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

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

$$\mathbf{n} := \mathbf{h} \, U$$

$$e^{iL_{g,1} \Delta t} \mathbf{h} = \exp\left(\Delta t \frac{\mathbf{h} \, \mathbf{p}_g}{W_g} \odot \frac{\partial}{\partial \mathbf{h}} \right) \mathbf{h}$$

$$= \exp\left(\frac{\Delta t}{W_g} \mathrm{Tr}\left[(\mathbf{h} \, \mathbf{p}_g)^\top \frac{\partial}{\partial \mathbf{h}} \right] \right) \mathbf{h}$$

$$= \exp\left(\frac{\Delta t}{W_g} \mathrm{Tr}\left[\mathbf{p}_g \, U \, \mathbf{n}^\top \frac{\partial}{\partial \mathbf{n}} U^\top \right] \right) \mathbf{n} \, U^\top \quad (38)$$

$$= \left(\prod_{\mu\alpha} \exp\left(\frac{\Delta t \lambda_\alpha}{W_g} n_{\mu\alpha} \frac{\partial}{\partial n_{\mu\alpha}} \right) \mathbf{n} \right) U^\top$$

$$= \left(e^{\frac{\Delta t \lambda_\alpha}{W_g}} n_{\mu\alpha} \right)_{\mu\alpha} U^\top$$

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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