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

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

With $\sqrt{g(\boldsymbol{x})} := e^{-w(\boldsymbol{x})}$, generalized Liouville's Theorem states that

$$\sqrt{g(\boldsymbol{x}_t)} d\boldsymbol{x}_t = \sqrt{g(\boldsymbol{x}_0)} d\boldsymbol{x}_0. \tag{2}$$

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

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

The fourth order integrator [1]

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

1.3. Canonical ensembles

1.3.1. Nosé-Hoover chain

Nosé-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

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

1.3.2. Conserved quantities of Nosé-Hoover chain equations

Nosé-Hoover chain equations conserves

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

where $\eta_c := \sum_{j=2}^{M} \eta_j$. In the absence of external forces ($\sum_i \boldsymbol{F}_i = 0$), the center-of-mass momentum $\boldsymbol{P} := \sum_i \boldsymbol{p}_i$ also has a conserved quantity

$$
\boldsymbol{K} := \boldsymbol{P} e^{\eta_1}. \tag{10}
$$

1.3.3. Microcanonical distribution given by Nosé-Hoover chain equations

The EOM gives the compressibility

$$
\kappa(\boldsymbol{x}) = -dN\dot{\eta}_1 - \dot{\eta}_c. \tag{11}
$$

Let us consider the distribution function traced over the extended variables,

$$
\begin{aligned}
Z_{V,T}(r^N, p^N) &:= \int dp_\eta^M d\eta^M e^{dN\eta_1 + \eta_c} \delta\left(\mathcal{H}(r^N, p^N) + \sum_{j=1}^{M} \frac{p_{\eta_j}^2}{2Q_j} + dNkT\eta_1 + kT\eta_c - H'\right) \\
&= \left(\prod_{j=1}^{M} \sqrt{2\pi kTQ_j}\right) \exp\left(-\frac{1}{kT}(\mathcal{H}(r^N, p^N) - H')\right) \int d\eta_1 \\
&\propto \exp\left(-\frac{1}{kT}\mathcal{H}(r^N, p^N)\right).
\end{aligned} \tag{12}
$$

This shows that the Nosé-Hoover chain equations generates the canonical ensemble in the physical phase space.

1.3.4. Integrating the Nosé-Hoover chain equations

The Liouville operator

$$
\begin{aligned}
iL &:= iL_{\mathrm{NHC}} + iL_1 + iL_2 \\
iL_1 &:= \sum_{i=1}^{N} \frac{\boldsymbol{p}_i}{m_i} \cdot \frac{\partial}{\partial \boldsymbol{r}_i} \\
iL_2 &:= \sum_{i=1}^{N} \boldsymbol{F}_i \cdot \frac{\partial}{\partial \boldsymbol{p}_i} \\
iL_{\mathrm{NHC}} &:= -\sum_{i=1}^{N} \frac{p_{\eta_1}}{Q_1} \boldsymbol{p}_i \cdot \frac{\partial}{\partial \boldsymbol{p}_i} + \sum_{j=1}^{M} \frac{p_{\eta_j}}{Q_j} \frac{\partial}{\partial \eta_j} + \sum_{j=1}^{M-1} \left(G_j - p_{\eta_j} \frac{p_{\eta_{j+1}}}{Q_{j+1}}\right) \frac{\partial}{\partial p_{\eta_j}} + G_M \frac{\partial}{\partial p_{\eta_M}} \\
G_1 &:= \sum_{i=1}^{N} \frac{\boldsymbol{p}_i^2}{m_i} - dNkT \\
G_j &:= \frac{p_{\eta_{j-1}}^2}{Q_{j-1}} - kT \quad (j = 2, ..., M)
\end{aligned} \tag{13}
$$

$$
e^{iL\Delta t} = e^{iL_{\mathrm{NHC}}\frac{\Delta t}{2}} e^{iL_2\frac{\Delta t}{2}} e^{iL_1\Delta t} e^{iL_2\frac{\Delta t}{2}} e^{iL_{\mathrm{NHC}}\frac{\Delta t}{2}} + O(\Delta t^3). \tag{14}
$$

$$
e^{iL_1 \Delta t} \begin{pmatrix} \boldsymbol{r}_i \\ \boldsymbol{p}_i \\ \eta_j \\ \boldsymbol{p}_{\eta_j} \end{pmatrix} = \begin{pmatrix} \boldsymbol{r}_i + \frac{\boldsymbol{p}_i}{m_i} \Delta t \\ \boldsymbol{p}_i \\ \eta_j \\ \boldsymbol{p}_{\eta_j} \end{pmatrix} \tag{15}
$$

$$
e^{iL_2 \frac{\Delta t}{2}} \begin{pmatrix} \boldsymbol{r}_i \\ \boldsymbol{p}_i \\ \eta_j \\ \boldsymbol{p}_{\eta_j} \end{pmatrix} = \begin{pmatrix} \boldsymbol{r}_i \\ \boldsymbol{p}_i + \boldsymbol{F}_i \frac{\Delta t}{2} \\ \eta_j \\ \boldsymbol{p}_{\eta_j} \end{pmatrix} \tag{16}
$$

$$
\begin{aligned}
e^{iL_{\mathrm{NHC}} \frac{\Delta t}{2}} &= \left(e^{iL_{\mathrm{NHC}} \frac{\Delta t}{2n}} \right)^n \\
e^{iL_{\mathrm{NHC}} \frac{\Delta t}{2n}} &= S_4^{\mathrm{NHC}} \left(\frac{\Delta t}{2n} \right) + O\left(\left(\frac{\Delta t}{n} \right)^5 \right) \\
S_4^{\mathrm{NHC}} \left(\frac{\Delta t}{2n} \right) &:= \prod_{\alpha=1}^{3} S_2^{\mathrm{NHC}} \left(x_\alpha \frac{\Delta t}{2n} \right) \quad \left(\delta_\alpha := x_\alpha \frac{\Delta t}{2n} \right) \\
S_2^{\mathrm{NHC}}(\delta_\alpha) &:= \exp\left(\frac{\delta_\alpha}{2} G_M \frac{\partial}{\partial p_{\eta_M}} \right) \\
&\times \prod_{j=M-1}^{1} \left(\exp\left(-\frac{\delta_\alpha}{4} \frac{p_{\eta_{j+1}}}{Q_{j+1}} p_{\eta_j} \frac{\partial}{\partial p_{\eta_j}} \right) \exp\left(\frac{\delta_\alpha}{2} G_j \frac{\partial}{\partial p_{\eta_j}} \right) \exp\left(-\frac{\delta_\alpha}{4} \frac{p_{\eta_{j+1}}}{Q_{j+1}} p_{\eta_j} \frac{\partial}{\partial p_{\eta_j}} \right) \right) \\
&\times \prod_{i=1}^{N} \exp\left(-\delta_\alpha \frac{p_{\eta_1}}{Q_1} \boldsymbol{p}_i \cdot \frac{\partial}{\partial \boldsymbol{p}_i} \right) \\
&\times \prod_{j=1}^{M} \exp\left(\delta_\alpha \frac{p_{\eta_j}}{Q_j} \frac{\partial}{\partial \eta_j} \right) \\
&\times \prod_{j=1}^{M-1} \left(\exp\left(-\frac{\delta_\alpha}{4} \frac{p_{\eta_{j+1}}}{Q_{j+1}} p_{\eta_j} \frac{\partial}{\partial p_{\eta_j}} \right) \exp\left(\frac{\delta_\alpha}{2} G_j \frac{\partial}{\partial p_{\eta_j}} \right) \exp\left(-\frac{\delta_\alpha}{4} \frac{p_{\eta_{j+1}}}{Q_{j+1}} p_{\eta_j} \frac{\partial}{\partial p_{\eta_j}} \right) \right) \\
&\times \exp\left(\frac{\delta_\alpha}{2} G_M \frac{\partial}{\partial p_{\eta_M}} \right)
\end{aligned} \tag{17}
$$

Here, we use the following formula to evaluate the actions,

$$
\exp\left(cx \frac{\partial}{\partial x} \right) f(x) = f(xe^c). \tag{18}
$$

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

$$\mathcal{P}^{\mathrm{int}}_{\alpha\beta} = \frac{1}{\det \boldsymbol{h}} \sum_{i=1}^{N} \left[\frac{p_{i\alpha} p_{i\beta}}{m_i} + F_{i\alpha} r_{i\beta} \right] - \frac{1}{\det \boldsymbol{h}} \sum_{\gamma=1}^{3} \frac{\partial U}{\partial h_{\alpha\gamma}} h_{\gamma\beta}. \tag{19}$$

1.4.2. Isotropic volume fluctuations

1.4.2.1. MTK equations for isotropic volume fluctuations

MTK equations:

$$\begin{aligned}
\dot{\boldsymbol{r}}_i &= \frac{\boldsymbol{p}_i}{m_i} + \frac{p_\varepsilon}{W} \boldsymbol{r}_i \\
\dot{\boldsymbol{p}}_i &= \tilde{\boldsymbol{F}}_i - \left(1 + \frac{d}{N_f}\right) \frac{p_\varepsilon}{W} \boldsymbol{p}_i - \frac{p_{\eta_1}}{Q_1} \boldsymbol{p}_i \\
\dot{V} &= \frac{dV}{W} p_\varepsilon \\
\dot{p}_\varepsilon &= dV\left(\mathcal{P}^{\mathrm{int}} - P\right) + \frac{d}{N_f} \sum_{i=1}^{N} \frac{\boldsymbol{p}_i^2}{m_i} - \frac{p_{\xi_1}}{Q'_1} p_\varepsilon \\
\dot{\eta}_j &= \frac{p_{\eta_j}}{Q_j} \\
\dot{\xi}_j &= \frac{p_{\xi_j}}{Q'_j} \\
\dot{p}_{\eta_j} &= G_j - \frac{p_{\eta_{j+1}}}{Q_{j+1}} p_{\eta_j} \quad (j = 1, ..., M-1) \\
\dot{p}_{\eta_M} &= G_M \\
\dot{p}_{\xi_j} &= G'_j - \frac{p_{\xi_{j+1}}}{Q'_{j+1}} p_{\xi_j} \quad (j = 1, ..., M-1) \\
\dot{p}_{\xi_M} &= G'_M
\end{aligned} \tag{20}$$

where

$$\begin{aligned}
G'_1 &:= \frac{p_\varepsilon^2}{W} - kT \\
G'_j &:= \frac{p_{\xi_{j-1}}^2}{Q'_{j-1}} - kT \quad (j = 2, ..., M).
\end{aligned} \tag{21}$$

Ref. [3] suggests to set

$$\begin{aligned}
W &= \left(N_f + d\right) kT\tau^2 \\
Q'_1 &= d^2 kT\tau^2 \\
Q'_j &= kT\tau^2 \quad (j = 2, ..., M),
\end{aligned} \tag{22}$$

where τ is a characteristic time scale for barostat.

1.4.2.2. Conserved quantities of MTK equations

The conserved energy

$$H' := \mathcal{H}(r,p) + \frac{p_\varepsilon^2}{2W} + PV + \sum_{j=1}^{M}\left(\frac{p_{\eta_j}^2}{2Q_j} + \frac{p_{\xi_j}^2}{2Q_j'} + kT\xi_j\right) + N_f kT\eta_1 + kT\eta_c, \tag{23}$$

where $\eta_c := \sum_{j=2}^{M}\eta_j$.

In the absence of external forces ($\sum_i \boldsymbol{F}_i = 0$), the center-of-mass momentum $\boldsymbol{P} := \sum_i \boldsymbol{p}_i$ also has a conserved quantity

$$\boldsymbol{K} := \boldsymbol{P}\exp\left(\left(1 + \frac{d}{N_f}\right)\varepsilon + \eta_1\right), \tag{24}$$

where $\varepsilon := \frac{1}{d}\log\frac{V}{V_0}$ with some reference volume V_0.

1.4.2.3. Microcanonical distribution given by MTK equations

Let $Q(N,V,T)$ be a partition function for NVT ensemble. The partition function for isotropic-NPT ensemble is defined as

$$\Delta(N,P,T) := \frac{1}{V_0}\int dV e^{-\beta PV} Q(N,V,T). \tag{25}$$

The EOM gives the compressibility

$$\begin{aligned}\kappa(\boldsymbol{x}) &= -\frac{\mathrm{d}}{\mathrm{d}t}(dN\eta_1 + \eta_c + \xi_1 + \xi_c)\\ \therefore \sqrt{g(\boldsymbol{x})} &= e^{dN\eta_1 + \eta_c + \xi_1 + \xi_c},\end{aligned} \tag{26}$$

where $\xi_c := \sum_{j=2}^{M}\xi_j$. Because this metric $\sqrt{g(\boldsymbol{x})}d\boldsymbol{x}$ does not depends on physical variables, the extended variables are traced out in $\Delta(N,P,T)$.

1.4.2.4. Integrating the MTK equations for isotropic volume fluctuations

$$\begin{aligned}iL &:= iL_1 + iL_2 + iL_{\varepsilon,1} + iL_{\varepsilon,2} + iL_{\text{NHC-baro}} + iL_{\text{NHC-thermo}}\\ iL_1 &:= \sum_{i=1}^{N}\left(\frac{\boldsymbol{p}_i}{m_i} + \frac{p_\varepsilon}{W}\boldsymbol{r}_i\right)\cdot\frac{\partial}{\partial \boldsymbol{r}_i}\\ iL_2 &:= \sum_{i=1}^{N}\left(\tilde{\boldsymbol{F}}_i - \left(1 + \frac{d}{N_f}\right)\frac{p_\varepsilon}{W}\boldsymbol{p}_i\right)\cdot\frac{\partial}{\partial \boldsymbol{p}_i}\\ iL_{\varepsilon,1} &:= \frac{p_\varepsilon}{W}\frac{\partial}{\partial\varepsilon}\\ iL_{\varepsilon,2} &:= G_\varepsilon\frac{\partial}{\partial p_\varepsilon}\end{aligned} \tag{27}$$

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

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

with

$$
\begin{aligned}
\varepsilon &:= \frac{1}{d} \ln \frac{V}{V_0} \\
\mathcal{P}^{\text{int}} &:= \frac{1}{d} \operatorname{Tr}[\boldsymbol{\mathcal{P}}^{\text{int}}] = \frac{1}{dV} \sum_{i=1}^{N} \left(\frac{\boldsymbol{p}_i^2}{m_i} + \boldsymbol{r}_i \cdot \boldsymbol{F}_i \right) \\
G_\varepsilon &:= dV\left(\mathcal{P}^{\text{int}} - P\right) + \frac{1}{N} \sum_{i=1}^{N} \frac{\boldsymbol{p}_i^2}{m_i}.
\end{aligned}
\tag{28}
$$

$$
\begin{aligned}
e^{iL\Delta t} = {} & e^{iL_{\text{NHC-baro}} \frac{\Delta t}{2}} e^{iL_{\text{NHC-thermo}} \frac{\Delta t}{2}} \\
& \times e^{iL_{\varepsilon,2} \frac{\Delta t}{2}} e^{iL_2 \frac{\Delta t}{2}} \\
& \times e^{iL_{\varepsilon,1} \Delta t} e^{iL_1 \Delta t} \\
& \times e^{iL_2 \frac{\Delta t}{2}} e^{iL_{\varepsilon,2} \frac{\Delta t}{2}} \\
& \times e^{iL_{\text{NHC-thermo}} \frac{\Delta t}{2}} e^{iL_{\text{NHC-baro}} \frac{\Delta t}{2}} + O(\Delta t^3).
\end{aligned}
\tag{29}
$$

$$
\begin{aligned}
e^{iL_1 \Delta t} \boldsymbol{r}_i &= \exp\left(\Delta t \left(\frac{\boldsymbol{p}_i}{m_i} + \frac{p_\varepsilon}{W} \boldsymbol{r}_i \right) \cdot \frac{\partial}{\partial \boldsymbol{r}_i} \right) \boldsymbol{r}_i \\
&= \boldsymbol{r}_i e^{\frac{p_\varepsilon \Delta t}{W}} + \Delta t \frac{\boldsymbol{p}_i}{m_i} \ \operatorname{exprel}\left(\frac{p_\varepsilon \Delta t}{W} \right)
\end{aligned}
\tag{30}
$$

$$
\begin{aligned}
e^{iL_2 \frac{\Delta t}{2}} \boldsymbol{p}_i &= \exp\left(\frac{\Delta t}{2} \left(\tilde{\boldsymbol{F}}_i - \left(1 + \frac{d}{N_f} \right) \frac{p_\varepsilon}{W} \boldsymbol{p}_i \right) \cdot \frac{\partial}{\partial \boldsymbol{p}_i} \right) \boldsymbol{p}_i \\
&= \boldsymbol{p}_i e^{-\frac{\kappa \Delta t}{2W}} + \frac{\Delta t}{2} \tilde{\boldsymbol{F}}_i \ \operatorname{exprel}\left(-\frac{\kappa \Delta t}{2W} \right) \\
\kappa &:= \left(1 + \frac{d}{N_f} \right) p_\varepsilon
\end{aligned}
\tag{31}
$$

1.4.3. Anisotropic cell fluctuations

1.4.3.1. MTK equations for anisotropic cell fluctuations

MTK equations:

$$
\begin{aligned}
\dot{\boldsymbol{r}}_i &= \frac{\boldsymbol{p}_i}{m_i} + \frac{\mathbf{p}_g}{W_g}\boldsymbol{r}_i \\
\dot{\boldsymbol{p}}_i &= \tilde{\boldsymbol{F}}_i - \left(\mathbf{p}_g + \frac{\mathrm{Tr}\left[\mathbf{p}_g\right]}{N_f}\mathbf{I}\right)\frac{\boldsymbol{p}_i}{W_g} - \frac{p_{\eta_1}}{Q_1}\boldsymbol{p}_i \\
\dot{\mathbf{h}} &= \frac{\mathbf{h}\mathbf{p}_g}{W_g} \\
\dot{\mathbf{p}}_g &= \det[\mathbf{h}](\boldsymbol{\mathcal{P}}^{\mathrm{int}} - P\mathbf{I}) + \frac{1}{N_f}\sum_{i=1}^{N}\frac{\boldsymbol{p}_i^2}{m_i}\mathbf{I} - \frac{p_{\xi_1}}{Q_1'}\mathbf{p}_g \\
\dot{\eta}_j &= \frac{p_{\eta_j}}{Q_j} \\
\dot{\xi}_j &= \frac{p_{\xi_j}}{Q_j'} \\
\dot{p}_{\eta_j} &= G_j - \frac{p_{\eta_{j+1}}}{Q_{j+1}}p_{\eta_j} \quad (j = 1, ..., M-1) \\
\dot{p}_{\eta_M} &= G_M \\
\dot{p}_{\xi_j} &= G_j' - \frac{p_{\xi_{j+1}}}{Q_{j+1}'}p_{\xi_j} \quad (j = 1, ..., M-1) \\
\dot{p}_{\xi_M} &= G_M'
\end{aligned}
\tag{32}
$$

where

$$
\begin{aligned}
G_1 &:= \sum_{i=1}^{N}\frac{\boldsymbol{p}_i^2}{m_i} - N_f kT \\
G_j &:= \frac{p_{\eta_{j-1}}^2}{Q_{j-1}} - kT \quad (j = 2, ..., M) \\
G_1' &:= \frac{\mathrm{Tr}\left[\mathbf{p}_g^\top \mathbf{p}_g\right]}{W_g} - d^2 kT \\
G_j' &:= \frac{p_{\xi_{j-1}}^2}{Q_{j-1}'} - kT \quad (j = 2, ..., M)
\end{aligned}
\tag{33}
$$

Ref. [3] suggests to set

$$
\begin{aligned}
W_g &= \frac{N_f + d}{d} kT\tau^2 \\
Q_1' &= d^2 kT\tau^2 \\
Q_j' &= kT\tau^2 \quad (j = 2, ..., M),
\end{aligned}
\tag{34}
$$

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.

1.4.3.2. Conserved quantities of anisotropic MTK equations

The conserved energy

$$\begin{aligned} H' &\coloneqq \mathcal{H}(r,p) + \frac{\mathrm{Tr}\left[\mathbf{p}_g^\top \mathbf{p}_g\right]}{2W_g} + P\det[\mathbf{h}] \\ &+ \sum_{j=1}^{M}\left(\frac{p_{\eta_j}^2}{2Q_j} + \frac{p_{\xi_j}^2}{2Q'_j}\right) + N_f kT\eta_1 + d^2kT\xi_1 + kT\sum_{j=2}^{M}(\eta_j + \xi_j) \end{aligned} \tag{35}$$

In the absence of external forces ($\sum_i \boldsymbol{F}_i = 0$), the center-of-mass momentum $\boldsymbol{P} \coloneqq \sum_i \boldsymbol{p}_i$ also has a conserved quantity

$$\boldsymbol{K} \coloneqq \mathbf{h}\boldsymbol{P}(\det\mathbf{h})^{1/N_f}e^{\eta_1}. \tag{36}$$

1.4.3.3. Microcanonical distribution given by anisotropic MTK equations

Let $Q(N,V,T)$ be a partition function for NPT ensemble. The partition function for anisotropic-NPT ensemble is defined as

$$\begin{aligned} \Delta(N,P,T) &\coloneqq \frac{1}{V_0}\int dVe^{-\beta PV}\int d\mathbf{h}_0 Q(N, V\mathbf{h}_0, T)\delta(\det\mathbf{h}_0 - 1) \\ &= \frac{1}{V_0}\int dV\int d\mathbf{h}V^{1-d}e^{-\beta PV}Q(N,\mathbf{h},T)\delta(\det\mathbf{h} - V) \end{aligned} \tag{37}$$

The EOM gives the compressibility

$$\begin{aligned} \kappa(\boldsymbol{x}) &= -\frac{\mathrm{d}}{\mathrm{d}t}((1-d)\ln\det\mathbf{h} + dN\eta_1 + \eta_c + d^2\xi_1 + \xi_c) \\ \therefore \sqrt{g(\boldsymbol{x})} &= (\det\mathbf{h})^{1-d}e^{dN\eta_1 + \eta_c + d^2\xi_1 + \xi_c}. \end{aligned} \tag{38}$$

Because this metric $\sqrt{g(\boldsymbol{x})}d\boldsymbol{x}$ depends on physical variables as same as the integral in $\Delta(N,P,T)$, the extended variables are traced out in $\Delta(N,P,T)$.

1.4.3.4. Integrating the MTK equations for anisotropic cell fluctuations

Ref. [4]

$$
\begin{aligned}
iL &\coloneqq iL_1 + iL_2 + iL_{g,1} + iL_{g,2} + iL_{\text{NHC-baro}} + iL_{\text{NHC-thermo}} \\
iL_1 &\coloneqq \sum_{i=1}^{N} \left(\frac{\boldsymbol{p}_i}{m_i} + \frac{\mathbf{p}_g}{W_g} \boldsymbol{r}_i \right) \cdot \frac{\partial}{\partial \boldsymbol{r}_i} \\
iL_2 &\coloneqq \sum_{i=1}^{N} \left(\tilde{\boldsymbol{F}}_i - \left(\mathbf{p}_g + \frac{\mathrm{Tr}\left[\mathbf{p}_g\right]}{N_f} \mathbf{I} \right) \frac{\boldsymbol{p}_i}{W_g} \right) \cdot \frac{\partial}{\partial \boldsymbol{p}_i} \\
iL_{g,1} &\coloneqq \frac{\mathbf{h}\mathbf{p}_g}{W_g} \odot \frac{\partial}{\partial \mathbf{h}} \\
iL_{g,2} &\coloneqq \mathbf{G}_g \odot \frac{\partial}{\partial \mathbf{p}_g} \\
iL_{\text{NHC-thermo}} &\coloneqq -\sum_{i=1}^{N} \frac{p_{\eta_1}}{Q_1} \boldsymbol{p}_i \cdot \frac{\partial}{\partial \boldsymbol{p}_i} + \sum_{j=1}^{M} \frac{p_{\eta_j}}{Q_j} \frac{\partial}{\partial \eta_j} + \sum_{j=1}^{M-1} \left(G_j - p_{\eta_j} \frac{p_{\eta_{j+1}}}{Q_{j+1}} \right) \frac{\partial}{\partial p_{\eta_j}} + G_M \frac{\partial}{\partial p_{\eta_M}} \\
iL_{\text{NHC-baro}} &\coloneqq -\frac{p_{\xi_1}}{Q'_1} \mathbf{p}_g \odot \frac{\partial}{\partial \mathbf{p}_g} + \sum_{j=1}^{M} \frac{p_{\xi_j}}{Q'_j} \frac{\partial}{\partial \xi_j} + \sum_{j=1}^{M-1} \left(G'_j - p_{\xi_j} \frac{p_{\xi_{j+1}}}{Q'_{j+1}} \right) \frac{\partial}{\partial p_{\xi_j}} + G'_M \frac{\partial}{\partial p_{\xi_M}}
\end{aligned} \tag{39}
$$

with

$$
\mathbf{G}_g \coloneqq \det[\mathbf{h}] \left(\boldsymbol{\mathcal{P}}^{\text{int}} - P\mathbf{I} \right) + \frac{1}{N_f} \sum_{i=1}^{N} \frac{\boldsymbol{p}_i^2}{m_i} \ \mathbf{I} \ . \tag{40}
$$

$$
\begin{aligned}
e^{iL\Delta t} = {} & e^{iL_{\text{NHC-baro}} \frac{\Delta t}{2}} e^{iL_{\text{NHC-thermo}} \frac{\Delta t}{2}} \\
& \times e^{iL_{g,2} \frac{\Delta t}{2}} e^{iL_2 \frac{\Delta t}{2}} \\
& \times e^{iL_{g,1} \Delta t} e^{iL_1 \Delta t} \\
& \times e^{iL_2 \frac{\Delta t}{2}} e^{iL_{g,2} \frac{\Delta t}{2}} \\
& \times e^{iL_{\text{NHC-thermo}} \frac{\Delta t}{2}} e^{iL_{\text{NHC-baro}} \frac{\Delta t}{2}} + O(\Delta t^3).
\end{aligned} \tag{41}
$$

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 Nosé-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

$$
\begin{aligned}
\mathbf{p}_g &= \sum_{\mu=1}^{3} \lambda_\mu \boldsymbol{u}_\mu \boldsymbol{u}_\mu^\top \\
\boldsymbol{U} &\coloneqq (\boldsymbol{u}_1, \boldsymbol{u}_2, \boldsymbol{u}_3) \\
\boldsymbol{U} \begin{pmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_3 \end{pmatrix} \boldsymbol{U}^\top &= \mathbf{p}_g
\end{aligned} \tag{42}
$$

with

$$
\begin{aligned}
\lambda_\mu &\in \mathbb{R} \\
\boldsymbol{u}_\mu^\top \boldsymbol{u}_\nu &= \delta_{\mu\nu}.
\end{aligned} \tag{43}
$$

$$
\begin{aligned}
e^{iL_{\text{NHC-baro}}\frac{\Delta t}{2}} &= \left(e^{iL_{\text{NHC-baro}}\frac{\Delta t}{2n}}\right)^n \\
e^{iL_{\text{NHC-baro}}\frac{\Delta t}{2n}} &= S_4^{\text{NHC-baro}}\left(\frac{\Delta t}{2n}\right) + O\left(\left(\frac{\Delta t}{n}\right)^5\right) \\
S_4^{\text{NHC-baro}}\left(\frac{\Delta t}{2n}\right) &:= \prod_{\alpha=1}^{3} S_2^{\text{NHC-baro}}\left(x_\alpha \frac{\Delta t}{2n}\right) \quad \left(\delta_\alpha := x_\alpha \frac{\Delta t}{2n}\right) \\
S_2^{\text{NHC-baro}}(\delta_\alpha) &:= \exp\left(\frac{\delta_\alpha}{2} G'_M \frac{\partial}{\partial p_{\xi_M}}\right) \\
&\times \prod_{j=M-1}^{1} \left(\exp\left(-\frac{\delta_\alpha}{4}\frac{p_{\xi_{j+1}}}{Q'_{j+1}} p_{\xi_j}\frac{\partial}{\partial p_{\xi_j}}\right)\exp\left(\frac{\delta_\alpha}{2} G'_j \frac{\partial}{\partial p_{\xi_j}}\right)\exp\left(-\frac{\delta_\alpha}{4}\frac{p_{\xi_{j+1}}}{Q'_{j+1}} p_{\xi_j}\frac{\partial}{\partial p_{\xi_j}}\right)\right) \\
&\times \exp\left(-\delta_\alpha \frac{p_{\xi_1}}{Q'_1}\mathbf{p}_{\boldsymbol{g}} \odot \frac{\partial}{\partial \mathbf{p}_g}\right) \\
&\times \prod_{j=1}^{M} \exp\left(\delta_\alpha \frac{p_{\xi_j}}{Q'_j}\frac{\partial}{\partial \xi_j}\right) \\
&\times \prod_{j=1}^{M-1} \left(\exp\left(-\frac{\delta_\alpha}{4}\frac{p_{\xi_{j+1}}}{Q'_{j+1}} p_{\xi_j}\frac{\partial}{\partial p_{\xi_j}}\right)\exp\left(\frac{\delta_\alpha}{2} G'_j \frac{\partial}{\partial p_{\xi_j}}\right)\exp\left(-\frac{\delta_\alpha}{4}\frac{p_{\xi_{j+1}}}{Q'_{j+1}} p_{\xi_j}\frac{\partial}{\partial p_{\xi_j}}\right)\right) \\
&\times \exp\left(\frac{\delta_\alpha}{2} G'_M \frac{\partial}{\partial p_{\xi_M}}\right)
\end{aligned}
\tag{44}
$$

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

$$
\begin{aligned}
\boldsymbol{x}_i &:= \boldsymbol{U}^\top \boldsymbol{r}_i \\
e^{iL_1\Delta t}\boldsymbol{r}_i &= \exp\left(\Delta t\left(\frac{\boldsymbol{p}_i}{m_i} + \frac{1}{W_g}\mathbf{p}_g \boldsymbol{r}_i\right)\cdot\frac{\partial}{\partial \boldsymbol{r}_i}\right)\boldsymbol{r}_i \\
&= \boldsymbol{U}\exp\left(\Delta t\left(\frac{\boldsymbol{p}_i}{m_i} + \frac{1}{W_g}\mathbf{p}_g \boldsymbol{r}_i\right)\cdot\frac{\partial}{\partial \boldsymbol{r}_i}\right)\boldsymbol{x}_i \\
&= \boldsymbol{U}\exp\left(\Delta t\left(\frac{\boldsymbol{U}^\top\boldsymbol{p}_i}{m_i} + \frac{1}{W_g}\boldsymbol{U}^\top\mathbf{p}_g \boldsymbol{U}\boldsymbol{x}_i\right)\cdot\frac{\partial}{\partial \boldsymbol{x}_i}\right)\boldsymbol{x}_i \\
&= \boldsymbol{U}\left(\exp\left(\Delta t\left(\frac{\left[\boldsymbol{U}^\top\boldsymbol{p}_i\right]_\alpha}{m_i} + \frac{1}{W_g}\lambda_\alpha x_{i\alpha}\right)\frac{\partial}{\partial x_{i\alpha}}\right)x_{i\alpha}\right)_{\alpha=1,2,3} \\
&= \boldsymbol{U}\left(x_{i\alpha}e^{\frac{\lambda_\alpha\Delta t}{W_g}} + \Delta t\frac{\left[\boldsymbol{U}^\top\boldsymbol{p}_i\right]_\alpha}{m_i}\ \operatorname{exprel}\left(\frac{\lambda_\alpha\Delta t}{W_g}\right)\right)_{\alpha=1,2,3} \\
\operatorname{exprel}(x) &:= \frac{e^x - 1}{x}
\end{aligned}
\tag{45}
$$

Similarly

$$
\begin{aligned}
\boldsymbol{y}_i &:= \boldsymbol{U}^\top \boldsymbol{p}_i \\
e^{iL_2 \frac{\Delta t}{2}} \boldsymbol{p}_i &= \exp\left(\frac{\Delta t}{2}\left(\tilde{\boldsymbol{F}}_i - \frac{1}{W_g}\left(\mathbf{p}_g + \frac{\mathrm{Tr}[\mathbf{p}_g]}{N_f}\mathbf{I}\right)\boldsymbol{p}_i\right) \cdot \frac{\partial}{\partial \boldsymbol{p}_i}\right)\boldsymbol{p}_i \\
&= \boldsymbol{U} \exp\left(\frac{\Delta t}{2}\left(\tilde{\boldsymbol{F}}_i - \frac{1}{W_g}\left(\mathbf{p}_g + \frac{\mathrm{Tr}[\mathbf{p}_g]}{N_f}\mathbf{I}\right)\boldsymbol{p}_i\right) \cdot \frac{\partial}{\partial \boldsymbol{p}_i}\right)\boldsymbol{y}_i \\
&= \boldsymbol{U} \exp\left(\frac{\Delta t}{2}\left(\boldsymbol{U}^\top\tilde{\boldsymbol{F}}_i - \frac{1}{W_g}\boldsymbol{U}^\top\left(\mathbf{p}_g + \frac{\mathrm{Tr}[\mathbf{p}_g]}{N_f}\mathbf{I}\right)\boldsymbol{U}\boldsymbol{y}_i\right) \cdot \frac{\partial}{\partial \boldsymbol{y}_i}\right)\boldsymbol{y}_i \\
&= \boldsymbol{U}\left(\exp\left(\frac{\Delta t}{2}\left(\left[\boldsymbol{U}^\top\tilde{\boldsymbol{F}}_i\right]_\alpha - \frac{1}{W_g}\left(\lambda_\alpha + \frac{\mathrm{Tr}[\mathbf{p}_g]}{N_f}\right)y_{i\alpha}\right)\frac{\partial}{\partial y_{i\alpha}}\right)y_{i\alpha}\right)_{\alpha=1,2,3} \\
&= \boldsymbol{U}\left(y_{i\alpha}e^{-\frac{\kappa_\alpha \Delta t}{2W_g}} + \frac{\Delta t}{2}\left[\boldsymbol{U}^\top\tilde{\boldsymbol{F}}_i\right]_\alpha \operatorname{exprel}\left(-\frac{\kappa_\alpha \Delta t}{2W_g}\right)\right)_{\alpha=1,2,3} \\
\kappa_\alpha &:= \lambda_\alpha + \frac{\mathrm{Tr}[\mathbf{p}_g]}{N_f}
\end{aligned}
\tag{46}
$$

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

$$
\begin{aligned}
\mathbf{n} &:= \mathbf{hU} \\
e^{iL_{g,1}\Delta t}\mathbf{h} &= \exp\left(\Delta t \frac{\mathbf{h}\mathbf{p}_g}{W_g} \odot \frac{\partial}{\partial \mathbf{h}}\right)\mathbf{h} \\
&= \exp\left(\frac{\Delta t}{W_g}\ \mathrm{Tr}\left[\left(\mathbf{h}\mathbf{p}_g\right)^\top \frac{\partial}{\partial \mathbf{h}}\right]\right)\mathbf{h} \\
&= \exp\left(\frac{\Delta t}{W_g}\ \mathrm{Tr}\left[\mathbf{p}_g \mathbf{U}\mathbf{n}^\top \frac{\partial}{\partial \mathbf{n}}\mathbf{U}^\top\right]\right)\mathbf{n}\mathbf{U}^\top \\
&= \left(\prod_{\mu\alpha} \exp\left(\frac{\Delta t \lambda_\alpha}{W_g} n_{\mu\alpha}\frac{\partial}{\partial n_{\mu\alpha}}\right)\mathbf{n}\right)\mathbf{U}^\top \\
&= \left(e^{\frac{\Delta t \lambda_\alpha}{W_g}} n_{\mu\alpha}\right)_{\mu\alpha}\mathbf{U}^\top
\end{aligned}
\tag{47}
$$

1.4.4. Cell fluctuations with mask

1.4.4.1. MTK equations

Consider the case when the cell fluctuations are allowed only n_c axes of the cell matrix $\mathbf{h}$. For $c = 1, \ldots, n_c$, let p_c be the momentum conjugate to the cth axis of $\mathbf{h}$.

$$
\mathbf{p}_g = \sum_c p_c \boldsymbol{e}_c \boldsymbol{e}_c^\top \tag{48}
$$

EOM are the same as the anisotropic MTK equations except for

$$
\begin{aligned}
\dot{p}_c &= \det[\mathbf{h}] \cdot \boldsymbol{e}_c^\top (\boldsymbol{\mathcal{P}}^{\text{int}} - P\mathbf{I})\boldsymbol{e}_c + \frac{1}{N_f} \sum_{i=1}^{N} \frac{\boldsymbol{p}_i^2}{m_i} - \frac{p_{\xi_1}}{Q'_1} p_c \quad (c = 1, ..., n_c) \\
G'_1 &:= \sum_c \frac{p_c^2}{W_g} - n_c kT \\
Q'_1 &= n_c kT\tau^2,
\end{aligned}
\tag{49}
$$

where τ is a characteristic time scale for barostat.

1.4.4.2. Conserved quantities

The conserved energy

$$
\begin{aligned}
H' := {} & \mathcal{H}(r, p) + \sum_c \frac{p_c^2}{2W} + P \det[\mathbf{h}] \\
& + \sum_{j=1}^{M} \left(\frac{p_{\eta_j}^2}{2Q_j} + \frac{p_{\xi_j}^2}{2Q'_j} \right) + N_f kT\eta_1 + n_c kT\xi_1 + kT \sum_{j=2}^{M} (\eta_j + \xi_j)
\end{aligned}
\tag{50}
$$

1.4.4.3. Integrating the MTK equations

$$
\begin{aligned}
iL &:= iL_1 + iL_2 + iL_{g,1} + iL_{g,2} + iL_{\text{NHC-baro}} + iL_{\text{NHC-thermo}} \\
iL_{g,2} &:= \sum_c G_c \odot \frac{\partial}{\partial p_c}
\end{aligned}
\tag{51}
$$

with

$$
G_c := \det[\mathbf{h}] \cdot \boldsymbol{e}_c^\top (\boldsymbol{\mathcal{P}}^{\text{int}} - P\mathbf{I})\boldsymbol{e}_c + \frac{1}{N_f} \sum_{i=1}^{N} \frac{\boldsymbol{p}_i^2}{m_i}. \tag{52}
$$

Bibliography

[1] H. Yoshida, “Construction of higher order symplectic integrators,” *Physics Letters A*, vol. 150, no. 5, pp. 262–268, 1990, doi: https://doi.org/10.1016/0375-9601(90)90092-3.

[2] G. J. Martyna, M. L. Klein, and M. Tuckerman, “Nosé-Hoover chains: The canonical ensemble via continuous dynamics,” *The Journal of Chemical Physics*, vol. 97, no. 4, pp. 2635–2643, 1992, doi: 10.1063/1.463940.

[3] G. J. Martyna, D. J. Tobias, and M. L. Klein, “Constant pressure molecular dynamics algorithms,” *The Journal of Chemical Physics*, vol. 101, no. 5, pp. 4177–4189, 1994, doi: 10.1063/1.467468.

[4] M. E. Tuckerman, J. Alejandre, R. López-Rendón, A. L. Jochim, and G. J. Martyna, “A Liouville-operator derived measure-preserving integrator for molecular dynamics simulations in the isothermal-isobaric ensemble,” *Journal of Physics A: Mathematical and General*, vol. 39, no. 19, p. 5629, Apr. 2006, doi: 10.1088/0305-4470/39/19/S18.