Flexible cell NPT integration with an upper triangular cell parameter matrix

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Abstract

We discuss the equations of motion for performing molecular dynamics (MD) in the isothermal-isobaric (NPT) ensemble using a fully flexible simulatin cell, derive an explicitly time-reversible and measure preserving integrator and analyze the stability of its implementation in HOOMD-blue.

1 Introduction

1.1 Trotter expansion

Modern MD integrators are based on the Trotter expansion of the Liouville propagator [1], which yields integration schemes that are explicitly time-reversal symmetric.

If $iL = iL_1 + iL_2$ is a decomposition of the Liouville operator L into two parts and $U(t) = e^{iLt}$ is the classical propagtor, the Trotter theorem yields

$$U(t) = e^{i(L_1+L_2)t} \tag{1}$$

$$= \left[e^{i(L_1+L_2)t/P}\right]^P \tag{2}$$

$$= \left[e^{iL_2\Delta t/2}e^{iL_1\Delta t}e^{iL_2\Delta t/2}\right]^P + \mathcal{O}(\Delta t^3 P), \tag{3}$$

where $\Delta t \equiv t/P$. This implies, that, for a single time step ($P = 1$), the factorization is exact up to and including terms of $\mathcal{O}(\Delta t^2)$.

1.2 Trotter expansion for the constant-energy ensemble

Let us apply the Trotter expansion to the Liouvillian $iL = \sum_i [\dot{\mathbf{p}}_i \nabla_{\mathbf{p}_i} + \dot{\mathbf{r}}_i \nabla_{\mathbf{r}_i}]$ that corresponds to the classical Hamiltonian $H = H[\{\mathbf{r}_i, \mathbf{p}_i\}]$ of a mechanical system. In other words, we are considering the constant-energy (NVE) ensemble. We split the Liouville operator iL into

$$iL_{\mathrm{NVE}} = iL_{1,\mathrm{NVE}} + iL_{2,\mathrm{NVE}} \tag{4}$$

$$iL_{1,\mathrm{NVE}} = \sum_i \dot{\mathbf{r}}_i \nabla_{\mathbf{r}_i} = \sum_i \frac{\mathbf{p}_i}{m} \nabla_{\mathbf{r}_i} \tag{5}$$

$$iL_{2,\mathrm{NVE}} = \sum_i \dot{\mathbf{p}}_i \nabla_{\mathbf{p}_i} = -\sum_i \mathbf{F}_i \nabla_{\mathbf{p}_i}. \tag{6}$$

Then the Trotter expansion for the single-timestep propagator becomes

$$U(\Delta t) \approx G(t) \equiv e^{-(\Delta t/2)\sum_i \mathbf{F}_i \nabla_{\mathbf{p}_i}} e^{\Delta t \sum_i \frac{\mathbf{p}_i}{m} \nabla_{\mathbf{r}_i}} e^{-(\Delta t/2)\sum_i \mathbf{F}_i \nabla_{\mathbf{p}_i}}. \tag{7}$$

This propagator determines the time evolution of all dynamical variables X via

$$X(t + \Delta t) \approx G(\Delta t) X(t). \tag{8}$$

To understand how this translates into update equations for the dynamical variables, consider an operator $A = e^{c\frac{\partial}{\partial X}}$, where c does not depend on X. Its action on any function of the variable X is given by

$$Af(X) = f(X + c). \tag{9}$$

This implies for the factors constituting the Trotter expansion of the Liouville propagator, Eq. (7),

$$e^{i(\Delta t)L_{1,\mathrm{NVE}}} \mathbf{r}_i = \mathbf{r}_i + \Delta t \mathbf{p}_i/m \tag{10}$$

$$e^{i(\Delta t/2)L_{2,\mathrm{NVE}}} \mathbf{p}_i = \mathbf{p}_i + (\Delta t/2)\mathbf{F}_i. \tag{11}$$

$$\tag{12}$$

From Eqs. (7) and (12) we thus easily obtain the time-reversible single-timestep update equations in the NVE ensemble,

$$\mathbf{p}_i(t) \to \mathbf{p}_i(t + \Delta t/2) = \mathbf{p}_i(t) + (\Delta t/2m)\, \mathbf{F}_i(t) \tag{13}$$

$$\mathbf{r}_i(t) \to \mathbf{r}_i(t + \Delta t) = \mathbf{r}_i(t) + \Delta t\, \mathbf{p}_i(t + \Delta t/2)/m \tag{14}$$

$$\mathbf{p}_i(t + \Delta t/2) \to \mathbf{p}_i(t + \Delta t) = \mathbf{p}_i(t) + (\Delta t/2m)\, \mathbf{F}(t + \Delta t). \tag{15}$$

This set of quations is known as the *Velocity-Verlet* integration scheme. We note that since the underlying equations of motion are derived from a Hamiltonian, the integration scheme is also symplectic (measure-preserving).

2 Simulations in the NPT ensemble

Martyna, Tobias and Klein [2] (MTK) proposed a set of equations that is designed to rigorously sample the NPT ensemble. Here, we recapitulate their equations of motion and derive a measure-preserving integration scheme from them. In the next section we present the most general case of a fully flexible simulation cell, and then specialize to the case of more symmetric simulation boxes, i.e. cubic, orthorhombic and tetragonal shapes.

2.1 Fully flexible simulation cell

Let $\mathbf{h} = (h_{\alpha\beta})$ be the cell parameter matrix, i.e. the matrix whose columns are the vectors representing the edges of the triclinic simulation box.

2.1.1 Equations of motion

The equations of motion proposed by Martyna et al. [2, 3] for a flexible simulation cell take the following form.

$$\dot{r}_{i,\alpha} = v_{i,\alpha} + \nu_{\alpha,\beta} r_{i,\beta} \tag{16}$$

$$\dot{v}_{i,\alpha} = \frac{F_{i,\alpha}}{m_i} - \left[\xi\delta_{\alpha\beta} + \nu_{\alpha\beta} + \delta_{\alpha\beta}\frac{1}{N_f}\mathrm{Tr}\,\nu\right] v_{i,\beta} \tag{17}$$

$$\dot{h}_{\alpha\beta} = \nu_{\alpha\gamma} h_{\gamma\beta} \tag{18}$$

$$\dot{\nu}_{\alpha\beta} = \frac{\det \mathbf{h}}{W}(P_{\alpha\beta} - P\delta_{\alpha\beta}) + \delta_{\alpha\beta}\frac{1}{WN_f}\sum_i m_i \mathbf{v}_i^2 \tag{19}$$

$$\dot{\eta} = \xi \tag{20}$$

$$\dot{\xi} = \frac{1}{\tau_T^2}\left(\frac{\sum_i m_i \mathbf{v}_i^2}{N_f k_B T} - 1\right) \tag{21}$$

Here, ν is the barostat matrix and

$$P_{\alpha\beta} = \frac{1}{\det \mathbf{h}} \sum_i m_i \left[v_{i,\alpha} v_{i,\beta} + F_{i,\alpha} r_{i,\beta}\right]. \tag{22}$$

denotes the internal pressure tensor. These equations conserve the quantity

$$H_{\mathrm{NPT,flex}} = H_0 + \frac{W}{2}\mathrm{Tr}\,\nu^T\nu + P\det\mathbf{h} + N_f k_B T\left(\tau_T^2\frac{\xi^2}{2} + \eta\right), \tag{23}$$

where $H_0 = \sum_i \frac{1}{2} m_i \mathbf{v}_i^2 + V(\{\mathbf{r}_i\})$ is the Hamiltonian from classical mechanics. This is easily confirmed by plugging in the equations of motion (16)-(21).

We note that despite the existence of a conserved quantity the equations of motion Eqs. (16-21) are not Hamiltonian, i.e. they do not conserve phase space volume.

2.1.2 Phase-space measure

According to the principle of non-Hamiltonian statistical mechanics [4] we find a time-dependent measure of phase-space volume as follows. If $\kappa = \nabla_X \cdot \dot{X}$ is the phase space compressibility, where X denotes the phase space vector, and if κ can be written as a total derivative $\kappa = \mathrm{d}w/\mathrm{d}t$, then the phase space measure is given by $\sqrt{g(X)} = e^{-w(X)}$. We now apply these ideas to find the metric of the above integrator.

$$\kappa(\{\mathbf{v}_i, \mathbf{r}_i\}, h_{\alpha\beta}, \nu, \xi, \eta) = \sum_i \left[\nabla_{\mathbf{r}_i}\cdot\dot{\mathbf{r}}_i + \nabla_{\mathbf{v}t_i}\cdot\dot{\mathbf{v}}_i\right] + \sum_{\alpha\beta}\left[\frac{\partial\dot{h}_{\alpha\beta}}{\partial h_{\alpha\beta}} + \frac{\partial\dot{\nu}_{\alpha\beta}}{\partial\nu_{\alpha\beta}}\right] + \frac{\partial\dot{\xi}}{\partial\xi} + \frac{\partial\dot{\eta}}{\partial\eta} \tag{24}$$

Since $\partial\dot{\nu}_{\alpha\beta}/\partial\nu_{\alpha\beta} = 0$ and $\partial\dot{\eta}/\partial\eta = \partial\dot{\xi}/\partial\xi = 0$, we have

$$\kappa = \sum_{i,\alpha}\sum_{\alpha\beta}\nu_{\alpha\beta} + \sum_i\left[-\sum_{\alpha\beta}\nu_{\alpha\beta} - \frac{d}{N_f}\sum_{\alpha\beta}\nu_{\alpha\beta} - d\xi\right] + \sum_{\alpha\beta}\nu_{\alpha\beta} \tag{25}$$

$$= -N_f\xi - (1-d)\mathrm{Tr}\,\nu_{\alpha\beta} = -N_f\dot{\eta} - (1-d)\frac{\mathrm{d}}{\mathrm{d}t}\ln(\det\mathbf{h}) \tag{26}$$

Hence, $w = N_f\eta + (1-d)(\det\mathbf{h})$ and

$$\sqrt{g(t)} = (\det\mathbf{h})^{1-d} e^{N_f\eta(t)} \tag{27}$$

is the phase space measure.

2.1.3 NPT ensemble

It remains to be shown that the equations of motion actually generate the desired ensemble. The partition sum of the NPT ensemble generalized to full cell shape fluctuations can be written as

$$\Omega_{\mathrm{NPT,flex}} = \int d\mathbf{r}^N d\mathbf{p}^N dV d\mathbf{h}_0 \, e^{-[F(N,V,T,\mathbf{h}_0)+PV]/k_BT} \delta(\det \mathbf{h}_0 - 1), \tag{28}$$

where the cell parameter matrix is expressed as $h_{\alpha\beta} = V^{1/d} h_{0,\alpha\beta}$. This form of the partition function guarantees that for a free energy that does not depend on shape (i.e., that only depends on on V) the usual NPT ensemble for isotropic box shape fluctuations is reproduced. The integral in Eq. (28) can be transformed by changing variables $\mathbf{h}_0 \to \mathbf{h}$ ($\mathrm{d}\mathbf{h}_0 = V^{-d}\mathrm{d}\mathbf{h}$), giving

$$\Omega_{\mathrm{NPT,flex}} = \int d\mathbf{r}^N d\mathbf{p}^N dV d\mathbf{h} V^{-d} \, e^{-\left[F(N,V,T,V^{-1/d}\mathbf{h})+PV\right]/k_BT} \delta\left(\frac{\det \mathbf{h}}{V} - 1\right) \tag{29}$$

$$= \int d\mathbf{r}^N d\mathbf{p}^N dV d\mathbf{h} \, V^{1-d} e^{-\left[F(N,V,T,V^{-1/d}\mathbf{h})+PV\right]/k_BT} \delta(\det \mathbf{h} - V) \tag{30}$$

$$= \int d\mathbf{r}^N d\mathbf{p}^N d\mathbf{h} \, (\det \mathbf{h})^{1-d} e^{-[F(N,\mathbf{h},T)+P \det \mathbf{h}]/k_BT}. \tag{31}$$

The factor of $(\det \mathbf{h})^{1-d}$ multiplying the Boltzmann weight is exactly produced by the MTK equations of motion, as shown in the following. Since H is the conserved quantity and $\sqrt{g}$ the phase space metric, they sample the distribution

$$\Omega = \int d\mathbf{r}^N d\mathbf{v}^N d\mathbf{L} \prod_\alpha \nu_\alpha d\eta d\xi \, \sqrt{g} \, \delta(H - H'), \tag{32}$$

where H' is the initial value of the quantity H. We can rewrite this as

$$\Omega = \int d\mathbf{r}^N d\mathbf{v}^N d\mathbf{h} \prod_{\alpha\beta} d\nu_{\alpha\beta} d\eta d\xi \, (\det \mathbf{h})^{1-d} e^{N_f \eta} \tag{33}$$

$$\delta\left[H_0 + W \sum_\alpha \frac{\nu_\alpha^2}{2} + P \det \mathbf{h} + N_f k_B T \left(\tau_T^2 \frac{\xi^2}{2} + \eta\right)\right] \tag{34}$$

$$= \int d\mathbf{r}^N d\mathbf{v}^N d\mathbf{h} \prod_\alpha d\nu_\alpha d\eta d\xi \, (\det \mathbf{h})^{1-d} e^{N_f \eta} (N_f k_B T)^{-1} \tag{35}$$

$$\delta\left[\eta + \frac{1}{N_f k_B T}\left(H_0 + W \sum_\alpha \frac{\nu_\alpha^2}{2} + P \det \mathbf{h} + N_f k_B T \tau_T^2 \frac{\xi^2}{2}\right) - H'\right] \tag{36}$$

$$= \int d\mathbf{r}^N d\mathbf{v}^N d\mathbf{L} \prod_\alpha \nu_\alpha d\xi \, (\det \mathbf{h})^{1-d} e^{-\left(H_0 + W \sum_\alpha \frac{\nu_\alpha^2}{2} + P \det \mathbf{h} + N_f k_B T \tau_T^2 \frac{\xi^2}{2} - H'\right)/k_BT} \tag{37}$$

After the second equal sign we have rearranged the argument of the δ function and pulled out a factor of $(N_f k_b T)^{-1}$. The third equation follows from integrating out the δ function using the integral over η. Finally, integrating out the Gaussian degrees of freedom ν_α and ξ, we find that $\Omega \propto \Omega_{\mathrm{NPT,flex}}$, and thus the equations of motion Eqs. (16-21) produce the NPT ensemble Eq. (31).

2.1.4 Elimination of cell rotations

When allowing for generic values of the pressure tensor elements, fluctuations of the overall cell orientation are possible. These result from internal torques are generated by an asymmetric pressure tensor, i.e. by off-diagonal elements for which $P_{\alpha\beta} \neq P_{\beta\alpha}$. They make analysis of trajectories difficult. Recognizing that usually the Hamiltonian $\mathbf{H}_0$ is invariant under rotations, we can eliminate cell rotations by ignoring the antisymmetric part of the pressure tensor. There are two possible ways for achieving this [2], either by symmetrizing the pressure tensor or by simply discarding all pressure tensor elements below the diagonal. In the latter case, because upper triangular matrices form a closed algebra, this amounts to working with the upper triangular part of the equations of motions only. Though the update equations have hithero only been worked out for a symmetrized pressure tensor [2], here we show how an upper triangular version can be implemented.

The reason why we choose this form of the equations of motion is that an upper triangular cell parameter matrix only has six non-zero matrix elements and thus involves the least amount of arithmetic operations to implement to periodic boundary conditions compared to a full cell parameter matrix.

We begin by adding a Lagrange multiplier to the equations of motion to constrain the lower half of the cell parameter matrix $h_{\alpha\beta}$ ($\alpha > \beta$) to zero. A Lagrange multiplier term in the Lagrange functional used Parrinello and Rahman [5] would produce a constraint force in the Euler-Lagrange equation for the cell parameter matrix $\mathbf{h}$. Assuming this still holds for our set of equations, which however are not directly derived from a Lagrangian, we introduce a corresponding force in the equation of motion Eq. (18), giving

$$\dot{\nu}_{\alpha\beta} = (\det \mathbf{h})(P_{\alpha\beta} - \delta_{\alpha\beta}) + \delta_{\alpha\beta}\frac{1}{N_f}\sum \frac{\mathbf{p}_i^2}{m} + \lambda_{\alpha\beta}, \tag{38}$$

where $\lambda_{\alpha\beta}$ is the Lagrange multiplier matrix (a torque), and $\lambda_{\alpha\beta} = 0$ for $\alpha \leq \beta$. We now need to solve for that multiplier using the constraints. Employing Einstein's summation convention,

$$0 = h_{\alpha\beta} \qquad (\alpha > \beta) \tag{39}$$

$$0 = \dot{h}_{\alpha\beta} \equiv \nu_{\alpha\gamma} h_{\gamma\beta} \qquad (\alpha > \beta) \tag{40}$$

$$\begin{aligned} 0 = \ddot{h}_{\alpha\beta} &= \dot{\nu}_{\alpha\gamma} h_{\gamma\beta} + \nu_{\alpha\gamma}\dot{h}_{\gamma\beta} \qquad (\alpha > \beta) \\ &= (\det \mathbf{h}) P_{\alpha\gamma} h_{\gamma\beta} + \lambda_{\alpha\gamma} h_{\gamma\beta} + \nu_{\alpha\gamma}\nu_{\gamma\delta} h_{\delta\beta} \qquad (\alpha > \beta) \end{aligned} \tag{41}$$

Rearranging Eq. (41),

$$\lambda_{\alpha\gamma} h_{\gamma\beta} = -(\det \mathbf{h}) P_{\alpha\gamma} h_{\gamma\beta} - \nu_{\alpha\gamma}\nu_{\gamma\delta} h_{\delta\beta} \qquad (\alpha > \beta), \tag{42}$$

and assuming $h_{\alpha\beta}$ is invertible, we can right-multiply by $\mathbf{h}^{-1}$ and obtain

$$\lambda_{\alpha\beta} = -\nu_{\alpha\gamma}\nu_{\gamma\beta} - (\det \mathbf{h}) P_{\alpha\beta} \qquad (\alpha > \beta) \tag{43}$$

where the first term on the right hand side is only non-zero for $\gamma \geq \alpha$.

We recalculate the phase-space measure arising from the constrained equations of motion. The term involving $\partial\dot{\nu}_{\alpha\beta}/\partial\nu_{\alpha\beta}$ is now finite and gives and additional contribution

to the phase-space measure. Using Eq. (38),

$$\sum_{\alpha\beta} \frac{\partial \dot{\nu}_{\alpha\beta}}{\partial \nu_{\alpha\beta}} = \sum_{\alpha>\beta} \frac{\partial \lambda_{\alpha\beta}}{\partial \nu_{\alpha\beta}} \tag{44}$$

$$= -\sum_{\alpha>\beta} \sum_{\gamma\geq\alpha} \frac{\partial}{\partial \nu_{\alpha\beta}} \nu_{\alpha\gamma}\nu_{\gamma\beta} \tag{45}$$

$$= -\sum_{\alpha>\beta} \nu_{\alpha\alpha} = -\sum_{\alpha>\beta} \dot{h}_{\alpha\delta} h^{-1}_{\delta\alpha} = -\sum_{\alpha>\beta} \dot{h}_{\alpha\alpha} h^{-1}_{\alpha\alpha} \tag{46}$$

$$= -\sum_{i=1}^{d} (i-1) \frac{\mathrm{d}}{\mathrm{d}t} \ln h_{ii}. \tag{47}$$

To arrive at Eq. (46) from Eq. (45), we have exploited that $\nu_{\alpha\beta}$ is upper triangular. In the subsequent steps, we also used that the diagonal elements of the inverse of an upper triangular matrix are the inverse diagonal elements of the original matrix. Taken together, we find that

$$\exp\left(\sum_{i=1}^{d} (i-1) \ln h_{ii}\right) = \prod_{i=1}^{d} h_{ii}^{i-1} \tag{48}$$

is an extra factor multiplying the phase space measure for the upper triangular equations of motion, Eq. (27). It thus appears also in the NPT ensemble, Eq. (37). It is possible in two dimensions to show that this extra factor is the Jacobian of a transformation to a set of cell parameters to which a rotation matrix has been applied, so as to align the first column of the cell parameter matrix with the x-axis. In three dimensions this calculation would be more tedious, but an analogous result is expected. In other words, the factor arises from separating out cell rotations in the NPT ensemble.

2.2 Reversible and measure-preserving integrator

2.2.1 Operator splitting

Following Refs. [2, 6, 7, 3] we introduce a splitting of the Liouville operator associated with the orthorhombic NPT equations of motion to obtain a Trotter expansion of the propagator.

The overall Liouville operator is

$$iL = iL_1 + iL_2 + iL_{g,1} + iL_{g,2} + iL_T \tag{49}$$

where

$$iL_1 \equiv \sum_i \sum_{\alpha\beta} \left[v_{i,\alpha} + \nu_{\alpha\beta} r_{i,\beta}\right] \frac{\partial}{\partial r_{i,\alpha}} \tag{50}$$

$$iL_2 \equiv \sum_i \sum_{\alpha\beta} \left[\frac{F_{i,\alpha}}{m_i} - \left(\nu_{\alpha\beta} + \delta_{\alpha\beta} \frac{1}{N_f} \mathrm{Tr}\, \nu\right) p_{i,\beta}\right] \frac{\partial}{\partial p_{i,\alpha}} \tag{51}$$

$$iL_{g,1} = \sum_{\alpha\beta\gamma} \nu_{\alpha\gamma} h_{\gamma\beta} \frac{\partial}{\partial h_{\alpha\beta}} \tag{52}$$

$$iL_{g,2} = W^{-1} \left[(\det \mathbf{h}) \left(P_{\alpha\beta} - P\delta_{\alpha\beta}\right) + \delta_{\alpha\beta} \frac{1}{N_f} \sum_i m_i \mathbf{v}_i^2\right] \frac{\partial}{\partial \nu_{\alpha\beta}}, \tag{53}$$

is the splitting into particle ($L_{\{1,2\}}$), barostat ($L_{g,\{1,2\}}$) and thermostat (L_T) operators, and where

$$iL_T = iL_{T,1} + iL_{T,2} + iL_{T,3}, \tag{54}$$

is the splitting of the thermostat operator,

$$iL_{T,1} = -\sum_i \xi \mathbf{v}_i \cdot \nabla_{\mathbf{v}_i} \tag{55}$$

$$iL_{T,2} = \frac{1}{\tau_T^2}\left(\frac{\sum_i m_i \mathbf{v}_i^2}{N_f k_B T} - 1\right)\frac{\partial}{\delta \xi} \tag{56}$$

$$iL_{T,3} = \xi \frac{\partial}{\partial \eta}. \tag{57}$$

We then use the following Trotter expansion of the propagator,

$$e^{iL\Delta t} \approx e^{iL_{g,2}\Delta t/2} e^{iL_T \Delta t/2} e^{iL_2 \Delta t/2} e^{iL_1 \Delta t} e^{iL_{g,1}\Delta t} e^{iL_2 \Delta t/2} e^{iL_T \Delta t/2} e^{iL_{g,2}\Delta t/2}, \tag{58}$$

additionally decomposing the thermostat propagator into

$$e^{iL_T \Delta t/2} \approx e^{iL_{T,2}\Delta t/4} e^{iL_{T,1}\Delta t/2} e^{iL_{T,3}\Delta t/2} e^{iL_{T,2}\Delta t/4}. \tag{59}$$

2.2.2 Action of individual factors

In the following, we examine the action of the individual factors in Eqs. (58) and (59) in detail.

iL_1**:** The factor $U = e^{iL_1 \Delta t}$ acts on $\mathbf{r}_i(t)$ by transporting it to $\mathbf{r}_i(t + \Delta t) \equiv U\mathbf{r}_i$. This quantity obeys the matrix ODE

$$\dot{r}_{i,\alpha} = v_{i,\alpha} + \nu_{\alpha\beta} r_{i,\beta} \tag{60}$$

The approach taken in Ref. [3] was to solve this ODE by transforming coordinates onto the principal axes of the pressure tensor. This required, however, that $P_{\alpha\beta}$ was diagonalizable which is not generally the case for an upper triangular matrix. Only in the case where $P_{\alpha\beta}$ was symmetric, this property was guaranteed and a numerically stable scheme was to solve for the eigenvalues and -vectors using Jacobi rotations. The appropriate generalization to an upper triangular pressure tensor would be to work with its Jordan normal form, which is numerically inpracticable. Hence, we choose a different approach.

We observe that Eq. (60) is *formally* solved in terms of the initial conditions by

$$r_{i,\alpha}(\Delta t) = [\exp(\nu_{\alpha\beta}\Delta t)]_{\alpha\beta} r_{i,\beta}(0) + \int_0^{\Delta t} dt' \, \exp(\nu_{\alpha\beta}\, t') v_{i,\alpha}, \tag{61}$$

and $\exp(\dots)$ is the matrix exponential. In general, the matrix exponential is an infinite power series. However, since $\nu_{\alpha\beta}$ is an upper triangular matrix, it can be written as a sum of a diagonal and a nilpotent matrix, i.e.

$$\nu = \begin{pmatrix} \nu_{xx} & \nu_{xy} & \nu_{xz} \\ 0 & \nu_{yy} & \nu_{yz} \\ 0 & 0 & \nu_{zz} \end{pmatrix} = \mathrm{diag}(\nu_{xx}, \nu_{yy}, \nu_{zz}) + \begin{pmatrix} 0 & \nu_{xy} & \nu_{xz} \\ 0 & 0 & \nu_{yz} \\ 0 & 0 & 0 \end{pmatrix} \equiv \mathbf{D} + \mathbf{N}. \tag{62}$$

All powers higher than square of the matrix $\mathbf{N}$ are zero. Obviously, this can be exploited for the calculation of the matrix exponential of the individual terms. However,

in general the matrix exponential $\exp[(\mathbf{D}+\mathbf{N})\Delta t]$ is not equal the product of matrix exponentials of the individual terms. This is only true if the matrices commute. Here, the commutator is non-zero in general. We are therefore forced to *approximate* the matrix exponential by the product of matrix exponentials. Luckily, the Trotter expansion provides a way to do this without loosing the unitarian property of the operator, i.e. so that the resulting update equations will still be fully time-reversible. In fact,

$$\exp[(\mathbf{D}+\mathbf{N})\Delta t] \approx \exp[(\mathbf{N}/2+\mathbf{D}+\mathbf{N}/2)\Delta t] = e^{\mathbf{N}\Delta t/2} e^{\mathbf{D}\Delta t} e^{\mathbf{N}\Delta t/2} + O(\Delta t^3) \tag{63}$$

As in the original Trotter expansion, the factorization is exact up to and including terms of Δt^2. Since $\mathbf{D}$ is diagonal, the exponential acts directly on the components as

$$e^{\mathbf{D}\Delta t} = \begin{pmatrix} e^{\nu_{xx}\Delta t} & & \\ & e^{\nu_{yy}\Delta t} & \\ & & e^{\nu_{zz}\Delta t} \end{pmatrix}, \tag{64}$$

and since $\mathbf{N}$ is nilpotent 3×3, we have

$$e^{\mathbf{N}\Delta t/2} = 1 + \frac{\Delta t}{2}\mathbf{N} + \frac{\Delta t^2}{8}\mathbf{N}^2 \tag{65}$$

$$= \begin{pmatrix} 1 & \frac{\Delta}{2}t\,\nu_{xy} & \frac{\Delta t}{2}\,\nu_{xz} + \frac{\Delta t^2}{8}\nu_{xy}\nu_{yz} \\ & 1 & \frac{\Delta t}{2}\,\nu_{yz} \\ & & 1 \end{pmatrix}. \tag{66}$$

We can now calculate the product of matrix exponentials on the right hand side of Eq. (63). It is

$$e^{\mathbf{N}\Delta t/2} e^{\mathbf{D}\Delta t} e^{\mathbf{N}\Delta t/2} = \mathbf{A}(\nu_{\alpha\beta}\Delta t) \equiv \begin{pmatrix} a_{xx} & a_{xy} & a_{xz} \\ 0 & a_{yy} & a_{yz} \\ 0 & 0 & a_{zz}, \end{pmatrix} \tag{67}$$

where

$$\begin{aligned} a_{xx} &= e^{\nu_{xx}\Delta t} \\ a_{xy} &= \nu_{xy}\frac{\Delta t}{2}(e^{\nu_{xx}\Delta t} + e^{\nu_{yy}\Delta t}) \\ a_{xz} &= \nu_{xz}\frac{\Delta t}{2}(e^{\nu_{xx}\Delta t} + e^{\nu_{zz}\Delta t}) + \frac{\Delta t^2}{8}\nu_{xy}\nu_{yz}(e^{\nu_{xx}\Delta t} + 2e^{\nu_{yy}\Delta t} + e^{\nu_{zz}\Delta t}) \\ a_{yy} &= e^{\nu_{yy}\Delta t} \\ a_{yz} &= \nu_{yz}\frac{\Delta t}{2}(e^{\nu_{yy}\Delta t} + e^{\nu_{zz}\Delta t}) \\ a_{zz} &= e^{\nu_{zz}\Delta t}. \end{aligned} \tag{68}$$

In Eq. (61) also the integrated matrix exponential appears. The calculation of the latter is now straight forward with the help of Eqs. (67) & (74). With the help of the integrals

$$\begin{aligned} \int_0^{\Delta t} dt'\, e^{\alpha t'} &= \Delta t\, e^{\alpha\Delta t/2}\frac{\sinh(\alpha\Delta t/2)}{\alpha\Delta t/2} \\ &\equiv \Delta t\, e^{\alpha\Delta t/2} f(\alpha\Delta t/2) \qquad f(x) = \sinh(x)/x \end{aligned} \tag{69}$$

$$\begin{aligned}\int_0^{\Delta t} dt'\, t' e^{\alpha t'} &= \frac{\mathrm{d}}{\mathrm{d}\alpha}\int_0^{\Delta t} dt'\, e^{\alpha t'} = \frac{\mathrm{d}}{\mathrm{d}\alpha}\left[\Delta t\, e^{\alpha\Delta t/2}\frac{\sinh(\alpha\Delta t/2)}{\alpha\Delta t/2}\right] \\ &= \frac{\Delta t^2}{2} e^{\alpha\Delta t/2}\frac{\sinh(\alpha\Delta t/2)}{\alpha\Delta t/2}\left[1+\coth\alpha\Delta t/2 - \frac{1}{\alpha\Delta t/2}\right] \\ &\equiv \frac{\Delta t^2}{2} e^{\alpha\Delta t/2} f(\alpha\Delta t/2)\left[1+g(\alpha\Delta t/2)\right] \qquad g(x) = f'/f = \coth x - 1/x\end{aligned} \tag{70}$$

and

$$\begin{aligned}\int_0^{\Delta t} dt'\, t'^2 e^{\alpha t'} &= \frac{\mathrm{d}}{\mathrm{d}\alpha}\int_0^{\Delta t} dt'\, t' e^{\alpha t'} = \frac{\Delta t^3}{4} e^{\alpha\Delta t/2}[f(1+g) + fg' + f'(1+g)] \\ &= \frac{\Delta t^3}{4} e^{\alpha\Delta t/2} f(\alpha\Delta/2)\left\{g'(\alpha\Delta/2) + [1+g(\alpha\Delta/2)]^2\right\},\end{aligned} \tag{71}$$

where

$$g'(x) = \frac{\mathrm{d}}{\mathrm{d}x}(\coth x - 1/x) = \frac{1}{x^2} - \frac{1}{\sinh^2 x} \equiv h(x). \tag{72}$$

Note that the functions f, g and h have no singularity at the origin (singularities of individual terms cancel), i.e. they can be expanded as power series for small arguments for convenient evaluation in the numerical algorithm.

With the help of the above set of integrals, we can rewrite the time-integrated Eq. (67) as

$$\int_0^{\Delta} dt'\; e^{\mathbf{N}\Delta t/2} e^{\mathbf{D}\Delta t} e^{\mathbf{N}\Delta t/2} = \mathbf{B}(\nu_{\alpha\beta}\Delta t) \equiv \begin{pmatrix} b_{xx} & b_{xy} & b_{xz} \\ 0 & b_{yy} & b_{yz} \\ 0 & 0 & b_{zz}, \end{pmatrix} \tag{73}$$

where

$$\begin{aligned} b_{xx} =& \Delta t\, e^{\nu_{xx}\Delta t/2} f(\nu_{xx}\Delta t/2) \\ b_{xy} =& \frac{\Delta t^2}{4}\nu_{xy} B^{(1)}_{xy} \\ b_{xz} =& \frac{\Delta t^2}{4}\nu_{xz} B^{(1)}_{xz} + B_{xz} + \frac{\Delta t^2}{32}\nu_{xy}\nu_{yz}(B^{(2)}_{xx} + 2B^{(2)}_{yy} + B^{(2)}_{zz}) \\ b_{yy} =& \Delta t\, e^{\nu_{yy}\Delta t/2} f(\nu_{yy}\Delta t/2) \\ b_{yz} =& \frac{\Delta t^2}{4}\nu_{yz} B^{(1)}_{yz} \\ b_{zz} =& \Delta t\, e^{\nu_{zz}\Delta t/2} f(\nu_{zz}\Delta t/2). \end{aligned} \tag{74}$$

and where

$$\begin{aligned} B^{(1)}_{\alpha\beta} \equiv& \Big(e^{\nu_{\alpha\alpha}\Delta t/2} f(\nu_{\alpha\alpha}\Delta t/2)[1+g(\nu_{\alpha\alpha}\Delta t/2)] \\ &+ e^{\nu_{\beta\beta}\Delta t/2} f(\nu_{\beta\beta}\Delta t/2)[1+g(\nu_{\beta\beta}\Delta t/2)]\Big) \\ B^{(2)}_{\alpha} =& e^{\nu_{\alpha\alpha}\Delta t/2} f(\nu_{\alpha\alpha}\Delta t/2)\left\{h(\nu_{\alpha\alpha}\Delta t/2) + [1+g(\nu_{\alpha\alpha}\Delta t/2)]^2\right\} \end{aligned} \tag{75}$$

Together, Eqs. (67) & (73) determine the full solution of the position update equation Eq. (60).

iL_2**:** The action of $e^{iL_2\Delta t/2}$ on $\mathbf{v}_i(t)$ is described by the ODE

$$\dot{v}_{i,\alpha} = \frac{F_{i,\alpha}}{m_i} - \nu'_{\alpha\beta} v_{i,\beta}, \tag{76}$$

where $\nu'_{\alpha\beta} \equiv \nu_{\alpha\beta} + \delta_{\alpha\beta}(1/N_f)\mathrm{Tr}\nu_{\alpha\beta}$. The solution is again expressed in terms of matrix exponential, and the same solution as for the position update can be employed, when making the replacements $\nu \to -\nu'$ and $\Delta t \to \Delta t/2$.

$iL_{g,1}$**:** The action of this operator is described by

$$\dot{h}_{\alpha\beta} = \nu_{\alpha\gamma} h_{\gamma\beta} \tag{77}$$

with matrix exponential solution

$$h_{\alpha\beta}(\Delta t) = \left[e^{\nu_{\alpha\beta}\Delta t}\right]_{\alpha\gamma} h_{\gamma\beta}(0). \tag{78}$$

Since its effect amounts to a rescaling of the initial value, this operator is also called a scaling operator. The same matrix for the exponential can be used as for rescaling the positions in Eq. (67).

$iL_{g,2}$**:** The RHS of Eq. (53) does not depend on ν_α, so this operator amounts to a translation [Eq. (9)],

$$\nu_{\alpha\beta}(\Delta t/2) = \nu_{\alpha\beta}(0) + \frac{\Delta t}{2W}\left[(\det \mathbf{h})\,(P_{\alpha\beta} - \delta_{\alpha\beta}P) + \delta_{\alpha\beta}\frac{1}{N_f}\sum_i m_i \mathbf{v}_i^2\right] \tag{79}$$

$iL_{T,1}$**:** The operator $e^{iL_{T,1}\Delta t/2}$ again acts on $\mathbf{v_i}$ as a scaling operator,

$$\mathbf{v}_i(\Delta t/2) = e^{\xi\Delta t/2}\mathbf{v}_i(0) \tag{80}$$

$iL_{T,2}$**:** The operator $e^{iL_{T,2}\Delta t/4}$ is a translation,

$$\xi(\Delta t/4) = \xi(0) + \frac{\Delta t}{4\tau_T^2}\left(\frac{\sum_i m_i \mathbf{v}_i^2}{N_f k_B T} - 1\right) \tag{81}$$

$iL_{T,3}$: Finally, the same holds for $e^{iL_{T,3}\Delta t/2}$:

$$\eta(\Delta t/2) = \eta(0) + \frac{\Delta t}{2}\xi \tag{82}$$

For reference, we now compile all above steps into the final update equations, using

Eqs. (58) & (59):

$$
\begin{aligned}
\text{step 1:} \quad \nu_{\alpha\beta}(t) \to \nu_{\alpha\beta}(t+\Delta t/2) =& \nu_{\alpha\beta}(t) \\
&+ \frac{\Delta t}{2W}\left[(\det \mathbf{h})\,(P_{\alpha\beta}(t) - \delta_{\alpha\beta}P) + \delta_{\alpha\beta}\frac{1}{N_f}\sum_i m_i \mathbf{v}_i^2(t)\right] \\
\text{step 2a:} \quad \xi(t) \to \xi(t+\Delta t/4) =& \xi(t) + \frac{\Delta t}{4\tau_T^2}\left(\frac{\sum_i m_i \mathbf{v}_i^2(t)}{N_f k_B T} - 1\right) \\
\text{step 2b:} \quad \eta(t) \to \eta(t+\Delta t/2) =& \eta(t) + \frac{\Delta t}{2}\xi(t+\Delta t/4) \\
\text{step 2c:} \quad \mathbf{v}_i(t) \to \mathbf{v}_i' =& \mathbf{v}_i(0)\, e^{-\xi(t+\Delta t/4)\Delta t/2} \\
\text{step 2d:} \quad \xi(t+\Delta t/4) \to \xi(t+\Delta t/2) =& \xi(t+\Delta t/4) + \frac{\Delta t}{4\tau_T^2}\left(\frac{\sum_i m_i \mathbf{v}_i'^2}{N_f k_B T} - 1\right) \\
\text{step 3:} \quad v_{i,\alpha}' \to v_{i,\alpha}(t+\Delta t/2) =& A_{\alpha\beta}[-\nu'(t+\Delta t/2)_{\alpha\beta}\Delta t/2]\, v_{i,\beta}' \\
&+ B_{\alpha\beta}(-\nu'(t+\Delta t/2)_{\alpha\beta}\Delta t/2]\frac{F_{i,\beta}(t)}{2m_i} \\
\text{step 4:} \quad r_{i,\alpha}(t) \to r_{i,\alpha}(t+\Delta t) =& A_{\alpha\beta}[\nu(t+\Delta t/2)_{\alpha\beta}\Delta t] r_{i,\beta} \\
&+ B_{\alpha\beta}[\nu(t+\Delta t/2)_{\alpha\beta}\Delta t] v_{i,\beta}(t+\Delta t/2) \\
\text{step 5:} \quad h_{\alpha\beta}(t) \to h_{\alpha\beta}(t+\Delta t) =& A_{\alpha\gamma}[\nu_{\alpha\beta}(t+\Delta t/2)\Delta t] h_{\gamma\beta}(t) \\
\text{step 6:} \quad v_{i,\alpha}(t+\Delta t/2) \to v_{i,\alpha}'' =& A_{\alpha\beta}[-\nu'(t+\Delta t/2)_{\alpha\beta}\Delta t/2]\, v_{i,\beta}(t+\Delta t/2) \\
&+ B_{\alpha\beta}(-\nu'(t+\Delta t/2)_{\alpha\beta}\Delta t/2]\frac{F_{i,\beta}(t+\Delta t)}{2m_i} \\
\text{step 7a:} \quad \xi(t+\Delta t/2) \to \xi(t+3\Delta t/4) =& \xi(t+\Delta t/2) + \frac{\Delta t}{4\tau_T^2}\left(\frac{\sum_i m_i \mathbf{v}_i''^2}{N_f k_B T} - 1\right) \\
\text{step 7b:} \quad \eta(t+\Delta t/2) \to \eta(t+\Delta t) =& \eta(t+\Delta t/2) + \frac{\Delta t}{2}\xi(t+3\Delta t/4) \\
\text{step 7c:} \quad \mathbf{v}_i'' \to \mathbf{v}_i(t+\Delta t) =& \mathbf{v}_i''\, e^{-\xi(t+3\Delta t/4)\Delta t/2} \\
\text{step 7d:} \quad \xi(t+3\Delta t/4) \to \xi(t+\Delta t) =& \xi(t+3\Delta t/4) + \frac{\Delta t}{4\tau_T^2}\left(\frac{\sum_i m_i \mathbf{v}_i^2(t+\Delta t)}{N_f k_B T} - 1\right) \\
\text{step 8:} \quad \nu_{\alpha\beta}(t+\Delta t/2) \to \nu_{\alpha\beta}(t+\Delta t) =& \nu_{\alpha\beta}(t+\Delta t/2) \\
&+ \frac{\Delta t}{2W}\Big[(\det \mathbf{h})\Big(P_{\alpha\beta}(t+\Delta t) - \delta_{\alpha\beta}P\Big) \\
&+ \delta_{\alpha\beta}\frac{1}{N_f}\sum_i m_i \mathbf{v}_i^2(t+\Delta t)\Big]
\end{aligned}
$$

The functions f, g and h which occur in the matrices $\mathbf{A}$ and $\mathbf{B}$ are approximated using the Taylor series,

$$f(x) = \frac{\sinh(x)}{x} \approx \sum_{n=0}^{5} a_{2n} x^{2n} \tag{83}$$

with $a_0 = 1$, $a_2 = 1/6$, $a_4 = 1/120$, $a_6 = 1/5040$, $a_8 = 1/362880$, and $a_{10} = 319916800$,

$$g(x) = \coth x - 1/x \approx \sum_{n=0}^{4} b_{2n+1} x^{2n+1} \tag{84}$$

with $b_1 = 1/3$, $b_3 = -1/45$, $b_5 = 1/945$, $b_7 = -1/4725$ and $b_9 = -1/93555$, and

$$h(x) = \frac{1}{x^2} - \frac{1}{sinh^2 x} \approx \sum_{n=0}^{5} c_{2n} x^{2n}, \tag{85}$$

with $c_0 = 1/3$, $c_2 = -1/15$, $c_4 = 2/189$, $c_6 = -1/675$, $c_8 = 2/10395$ and $c_10 = -1382/58046625$.

2.2.3 Verification of the geometric property of the integrator

The above update scheme is explictly reversible. We show in the following that it also strictly preserves the phase-space measure of Sec. 2.1.2.

For every of the above update steps, the change in phase space volume is given by the Jacobian of the mapping. In steps $i = 1, 2, 7$ and 8, only one quantity $X_{j,i} \to X_{j,i+1}$ is updated (uncoupled update) and all the other quantities stay the same, this implies that the Jacobian is of the form

$$J_i = \left| \frac{\partial X_{j,i+1}}{\partial X_{,i}} \right| = \left| \det \begin{pmatrix} 1 & & & & & & & \\ & \ddots & & & & & & \\ & & 1 & & & & & \\ * & \cdots & * & a & * & \cdots & * & \\ & & & & 1 & & & \\ & & & & & \ddots & & \\ & & & & & & 1 & \end{pmatrix} \right|, \tag{86}$$

where only non-zero matrix elements are explictly shown. The above determinant can be shown to evaluate to $J_{i,j} = |a|$, where a is the diagonal element. If the update equation is of the form $X_{j,i+1} = aX_{j,i} + b$, the diagonal element is the prefactor of the quantity x_i. E.g. for step 1, we have $J_{i,1} = 1$.

These are the Jacobians J_i for the uncoupled update steps $i = 1, 2, 7$ and 8

$$J_1 = 1 \qquad J_2 = e^{-N_f \xi(t+\Delta t/4)\Delta t/2} \tag{87}$$

$$J_7 = e^{-N_f \xi(t+3\Delta t/4)\Delta t/2} \qquad J_8 = 1, \tag{88}$$

where J_2 results from step 2c and J_7 results from step 7c.The product of these Jacobians is

$$J_1 J_2 J_7 J_8 = e^{-N_f [\xi(t+\Delta t/4) - \xi(t+3\Delta t/4)]\Delta t/2} \tag{89}$$

Substituting steps 2b & 7b, we arrive at

$$J_1 J_2 J_7 J_8 = e^{-N_f [\eta(t+\Delta t) - \eta(t)]} \tag{90}$$

In steps $3, 4, 5$ and 6 several variables are updated simultaneously. The above theorem about the determinant of the Jacobian generalizes to this case. Only the diagonal element a has to be replaced by a matrix A, which is the Jacobian sub-matrix of the variables that are actually updated simultaneously. Consequently, for step 5 we need to evaluate a determinant of the 6×6 matrix with rows and columns labeled by xx, xy, xz, yy, yz and zz, with explicit form

$$\mathbf{C} = \begin{pmatrix} a_{xx} & 0 & 0 & 0 & 0 & 0 \\ 0 & a_{xx} & 0 & a_{xy} & 0 & 0 \\ 0 & 0 & a_{xx} & 0 & a_{xy} & a_{xz} \\ 0 & 0 & 0 & a_{yy} & 0 & 0 \\ 0 & 0 & 0 & 0 & a_{yy} & a_{yz} \\ 0 & 0 & 0 & 0 & 0 & a_{zz} \end{pmatrix} \tag{91}$$

with $a_{\alpha\beta}$ defined in Eq. (67). Due to the upper triangular form of this matrix, only the diagonal elements are relevant and the determinant is given by their product. Hence,

$$J_5 = a_{xx}^3(\nu\Delta t)a_{yy}^2(\nu'\Delta t)a_{zz}(\nu'\Delta t) \tag{92}$$

$$= e^{\Delta t \mathrm{Tr}\,\nu + \Delta t\sum_{i=1}^3 (d-i)\nu_{ii}}. \tag{93}$$

For steps $3, 4$ and 6 similar calculations (with a 3×3 Jacobian) yield

$$J_3 = J_6 = |\det \mathbf{A}(-\nu'\Delta t/2)|^N = e^{-N\Delta t\,\mathrm{Tr}\,\nu'/2} = e^{-N\Delta t\,\mathrm{Tr}\,\nu/2 - \Delta t \mathrm{Tr}\,\nu/2} \tag{94}$$

$$J_4 = |\det \mathbf{A}(\nu\Delta t)|^N = e^{N\Delta t \mathrm{Tr}\,\nu}. \tag{95}$$

Together,

$$J_3J_4J_5J_6 = e^{\Delta t\,\sum_{i=1}^3 (d-i)\nu_{ii}} = \frac{h_{xx}^2(t+\Delta t)h_{yy}(t+\Delta t)}{h_{xx}^2(t)h_{yy}(t)} \tag{96}$$

where we used

$$e^{\nu_{ii}\Delta t} = \frac{h_{ii}(t+\Delta t)}{h_{ii}(t)}. \tag{97}$$

Combining Eqs. (90) and Eq. (96) we find the total Jacobian of the transformation $X(t)\to X(t+\Delta t)$,

$$J = \left[e^{N_f[\eta(t+\Delta t)-\eta(t)]}\frac{h_{xx}^2(t)h_{yy}(t)}{h_{xx}^2(t+\Delta t)h_{yy}(t+\Delta t)}\right]^{-1} \tag{98}$$

which, for $d=3$ is precisely is the per time-step Jacobian that cancels the measure given by Eqs. (27) and (48), as required by the Liouville equation. Thus, the integrator is measure-preserving. We remark that it is easy to 'destroy' the latter property be reordering the equations, e.g. by combining the velocity updates in steps 2c and 3, and 6 and 7c (though the integrator would still be time-reversible).

3 Stability analysis

In this section, we perform some tests of effectiveness and stability of the integrator. We simulate a system of $N = 20,000$ particles at a volume fraction of $\phi = 0.2$ with a Lennard-Jones (LJ) potential, cut off at $r_c = 2.5$, with $\epsilon = \sigma = 1$. The pressure and temperature set points are $P = 2$ and $T = 1$, with barostat and thermostat time constants $\tau_T = \tau_P = 0.5$. We use cubic box symmetry. To avoid numerical problems related to the discontinuity of the potential and the force at the cut-off, we employ XPLOR smoothing of the potential between $r_{\mathrm{on}} = 1.5\sigma$ and r_c. The simulations were performed using single floating-point precision on Tesla M2090 GPUs with a modified version of HOOMD-blue implementing the above update scheme (class `TwoStepNPTMTK`).

We first show a basic verification of the effectiveness of the integrator in equilibrating towards the target values of the temperature and the pressure. Fig. 1 (left) demonstrates that the system quickly equilibrates within 10,000 time steps, and that the temperature T (blue curve) and pressure P (red curve) fluctuate around their target values thereafter. The right panel of Fig. 1 shows the initial evolution of the conserved quantity H and the volume V for the first 10,000 time steps. It is evident that while the volume exhibits large initial flucutations of about 50% of its equilibrium value until the system reaches its equilibrium density, the conserved quantity stays essentially constant on the scale of the plot.

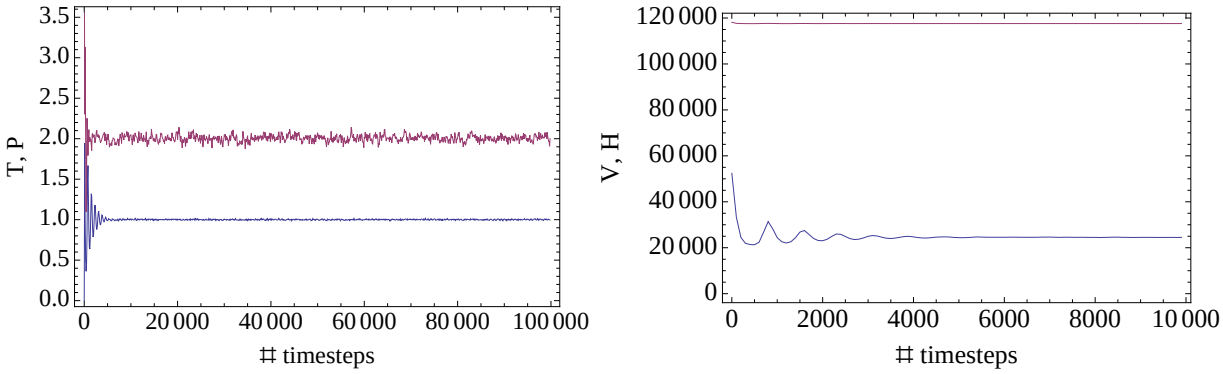

Figure 1: *Left:* Plot of the trajectories of temperature T (blue curve) and pressure T as a function of the number simulation steps. *Right:* Plot of the initial trajectories for the volume V (blue curve) and the conserved quantity H as a function of the number of simulation steps.

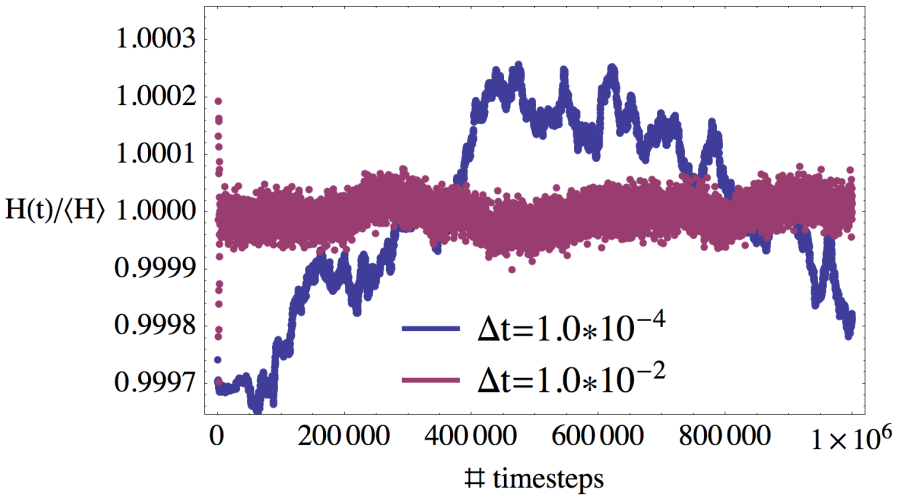

Figure 2: Example trajectories of the conserved quantity $H/\langle H(t)\rangle$ normalized by the time-average, for two NPT-simulation runs of a N=20,000 LJ particle system in cubic symmetry for two different time steps $\Delta t = 10^{-4}$ (blue curve) and $\Delta t = 10^{-2}$ (red curve). The trajectory corresponding to the smaller time step exhibits larger fluctuations, due to numerical instabilities.

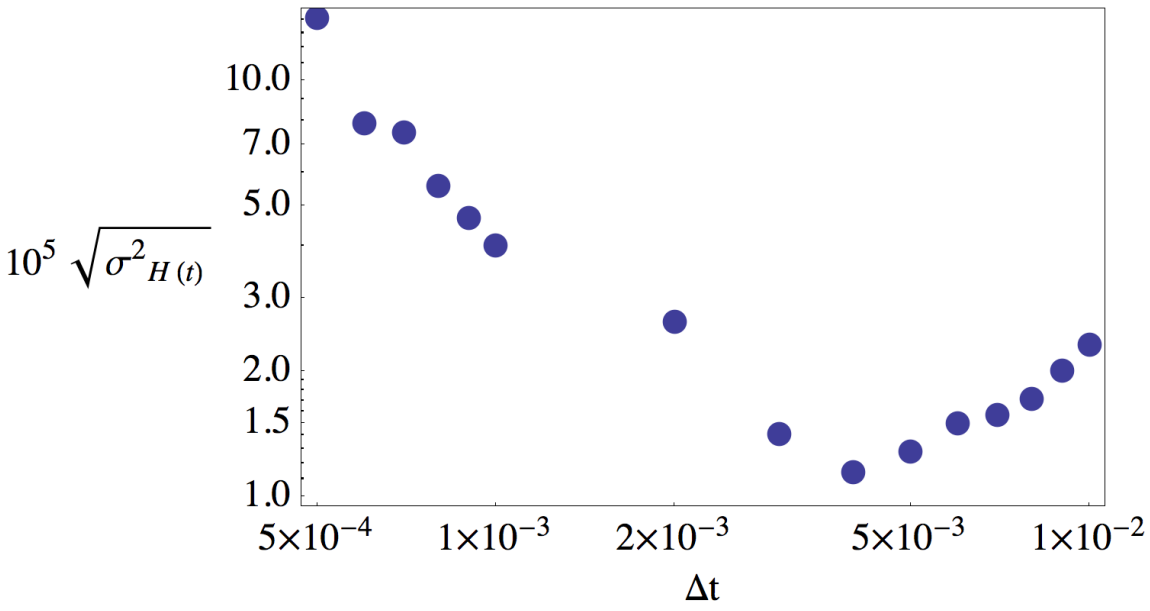

Figure 3: Standard deviation σ of the conserved quantity $H(t)$ vs. time step Δt in double-logarithmic representation, determined over the length of a simulation run of $N = 10^6$ time steps after subtraction of a linear drift term from the trajectories $H(t)$. The fluctuations are minimal for $\Delta t = 0.004$.

We now analyze the stability of the integrator in more detail by means of actual trajectories of the conserved quantity H. Fig. 2 shows two different example trajectories of the normalized conserved quantity $H(t)$ [Eq. (23)] for two values of the time step Δt. Remarkably, the trajcectory corresponding two the larger time step exhibits less 'motion', and the fluctuations occur within a band that explores a narrower range of values of of H. Since the ideal discretization error in the reversible update scheme scales as Δt^3 [cf. Eq. (3)], we suspect that the apparently increased error at the smaller time step must be due to numerical instabilities. This is plausible, given that the simulations were run at single floating-point precision.

The trajectories exhibit non-negligible drift, even over a comparatively short run of 10^6 time steps (see below). We therefore subtracted a drift term from the trajectory, which we determined by fitting the latter to a linear function. Then we calculated the standard deviation of the fluctuations of the conserved quantity. The results are shown in Fig. 3. We observe that the dependence of the magnitude σ of the fluctuations on the time step Δt is clearly non-monotonic. If the fluctuations were explained solely by discretization error, we would expect them to increase as Δt increases. This, however, is only the case for $\Delta t \gtrsim 0.004 = \Delta t_0$. Below this threshold, the fluctuations increase even as Δt decreases. This is consistent with our earlier finding of larger errors for small Δt and we conclude that the algorithm is unstable at $\Delta t \lesssim \Delta t_0$. Conversely, the simulation will ultimately blow up at too large values of Δt, so that $\Delta t = \Delta t_0$ appears to constitute an optimal choice if one is interested in long-term stability.

Fig. 4 shows the trajectory of the conserved quantity in one simulation with $\Delta t = 0.005$ over an interval of 10^7 time steps. It can be seen that the sign of the drift is negative in this case, and that the relative magnitude of the drift is about 0.1% over this length of the simulation. We suspect that the drift is a consequence of round-off errors incurred by single-precision floating point arithmetics. Short simulations of 10^6

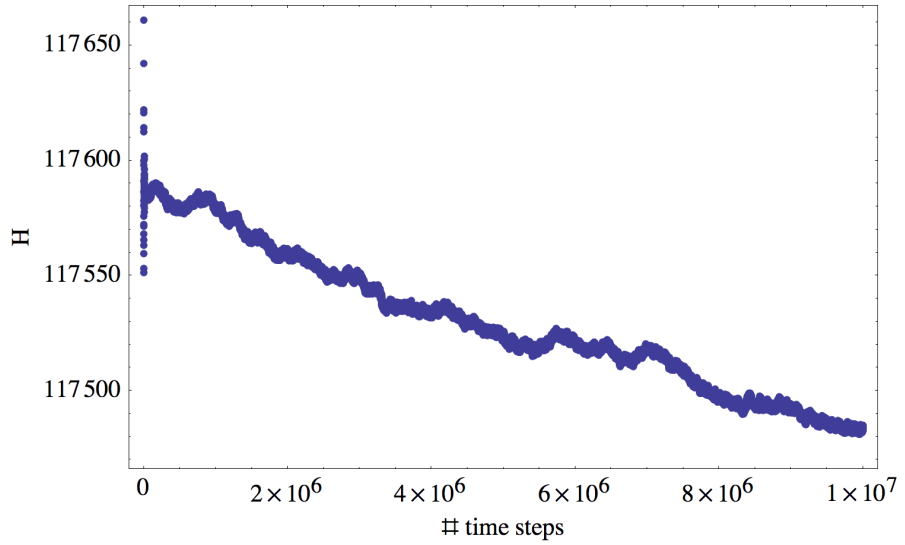

Figure 4: Evolution of the conserved quantity for a simulation with $\Delta t = 0.005$, showing the drift over 10^7 time steps.

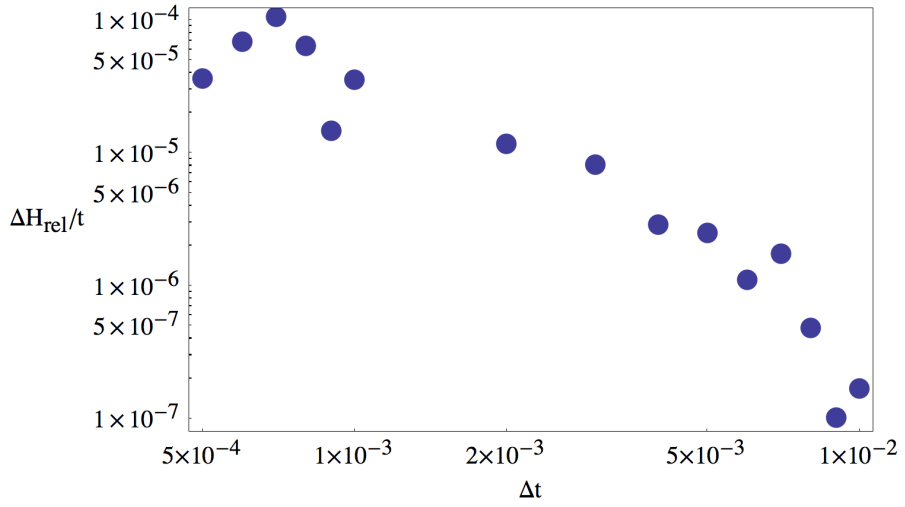

Figure 5: Value of the relative drift $\Delta H_{\mathrm{rel}}/t$ of the conserved quantity H per Lennard-Jones time, as a function of the simulation time step Δt (double-logarithmic representation).

time steps corroborate this hypothesis. Fig. 5 shows the relative magnitude of the drift per unit Lennard-Jones time as a function of the time step. For increasing time step Δt the drift velocity decreases. This is consistent with the expectation that the importance of round-off errors vs. discretization errors decreases with increasing time step.

4 Conclusion

We have derived the equations of motion of integration in the anisotropic NPT ensemble. We presented an explicitly reversible and measure-preserving update scheme. We analyzed the stability of the integrator as implemented on the GPU in HOOMD-blue and found that the NPT-integrator behaves as expected, but that too small time steps can cause numerical problems at single-precision. It would be interesting to see whether the stability at small time steps improves with double-precision arithmetics.

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