Reversible integrators

Tony Paxton

These notes describe how we implemented the Verlet algorithms in our tight binding codes. It's all taken from Martyna and Tuckerman.

Newton's equation of motion and the "velocity Verlet" algorithm

We have some N particles having positions $\{r\}$ and velocities $\{\dot{r}\}$. I will leave out the braces and suppress particle labels and vector notation. Newton's second law is

$$\ddot{r} = \frac{f}{m}$$

If we start at time t with known positions, velocities and forces, f, we can advance the coordinates to time $t + \delta t$ using a Taylor expansion exact to *second* order

$$r(t+\delta t) = r(t) + \dot{r}(t)\delta t + \frac{1}{2}\ddot{r}(t)\delta t^2 \tag{1}$$

$$r(t-\delta t) = r(t) - \dot{r}(t)\delta t + \frac{1}{2}\ddot{r}(t)\delta t^2 \tag{2}$$

Adding these together, we get

$$r(t+\delta t) + r(t-\delta t) = 2r(t) + \ddot{r}(t)\delta t^2 \tag{3}$$

This is called the "Verlet algorithm." It's inconvenient to carry two sets of positions (at t and $t-\delta t$) so we prefer the "velocity Verlet" algorithm which updates the positions and velocities like this:

$$r(t+\delta t) = r(t) + \dot{r}(t)\delta t + \frac{1}{2}\ddot{r}(t)\delta t^2$$

$$\dot{r}(t+\delta t) = \dot{r}(t) + \frac{1}{2}\left[\ddot{r}(t) + \ddot{r}(t+\delta t)\right]\delta t$$

We can show that these two algorithms generate identical trajectories. The Taylor expansion to second order of $r(t+2\delta t)$ is

$$r(t+2\delta t) = r(t+\delta t) + \dot{r}(t+\delta t)\delta t + \frac{1}{2}\ddot{r}(t+\delta t)\delta t^2$$

while (1) is

$$r(t) = r(t+\delta t) - \dot{r}(t)\delta t - \frac{1}{2}\ddot{r}(t)\delta t^2$$

adding these last two we get

$$r(t+2\delta t) + r(t) = 2r(t+\delta t) + \left[\dot{r}(t+\delta t) - \dot{r}(t)\right]\delta t + \frac{1}{2}\left[\ddot{r}(t+\delta t) - \dot{r}(t)\right]\delta t^2$$

The first quantity in brackets is

$$\dot{r}(t+\delta t) - \dot{r}(t) = \frac{1}{2}\left[\ddot{r}(t+\delta t) + \ddot{r}(t)\right]\delta t$$

and using (2) we end up with

$$r(t+2\delta t) + r(t) = 2r(t+\delta t) + \ddot{r}(t+\delta t)\delta t^2$$

which is the same as the Verlet algorithm (3).

You might think that the velocity Verlet is even less convenient because you'll need to retain the forces at time t and recompute them at time $t+\delta t$ before you can update the

velocities. But consider doing the following procedure, in which the symbols in boxes represent the actions that take you from left to right.

$$
\left.\begin{array}{l} r(t) \\ \dot{r}(t) \\ \ddot{r}(t) \end{array}\right\} \longrightarrow \boxed{\tfrac{1}{2}iL_v} \longrightarrow \begin{cases} r(t) \\ \dot{r}(t+\frac{1}{2}\delta t) = \dot{r}(t) + \frac{1}{2}\ddot{r}(t)\delta t \\ \ddot{r}(t) \end{cases} \qquad (4)
$$

$$
\left.\begin{array}{l} r(t) \\ \dot{r}(t+\frac{1}{2}\delta t) \\ \ddot{r}(t) \end{array}\right\} \longrightarrow \boxed{iL_r} \longrightarrow \begin{cases} r(t+\delta t) = r(t) + \dot{r}(t+\frac{1}{2}\delta t)\delta t \\ \dot{r}(t+\frac{1}{2}\delta t) \\ \ddot{r}(t) \end{cases}
$$

$$
\left.\begin{array}{l} r(t+\delta t) \\ \dot{r}(t+\frac{1}{2}\delta t) \\ \ddot{r}(t) \end{array}\right\} \longrightarrow \boxed{\tfrac{1}{2}iL_v} \longrightarrow \begin{cases} r(t+\delta t) \\ \dot{r}(t+\delta t) = \dot{r}(t+\frac{1}{2}\delta t) + \frac{1}{2}\ddot{r}(t+\delta t)\delta t \\ \ddot{r}(t+\delta t) \end{cases}
$$

$\uparrow$ *calculate force*

$r(t)$ and $\dot{r}(t)$ have been advanced like this:

$$
\begin{aligned}
r(t) \to r(t+\delta t) &= r(t) + \dot{r}(t+\tfrac{1}{2}\delta t)\delta t \\
&= r(t) + \dot{r}(t) + \tfrac{1}{2}\ddot{r}(t)\delta t^2 \qquad \text{using (4)} \\
\dot{r}(t) \to \dot{r}(t+\delta t) &= \dot{r}(t+\tfrac{1}{2}\delta t) + \tfrac{1}{2}\ddot{r}(t+\delta t)\delta t \\
&= \dot{r}(t) + \tfrac{1}{2}\left[\ddot{r}(t) + \ddot{r}(t+\delta t)\right]\delta t \qquad \text{using (4)}
\end{aligned}
$$

and this is the velocity Verlet algorithm exactly as described above. At the point indicated it is necessary to stop and recalculate the forces. This may be a nuisance if your program is not built around the molecular dynamics integrator; indeed the calculation of force may be the main focus of your program for example if it's a complex bandstructure program. But if you think of the "black box" $\boxed{\frac{1}{2}iL_v}$ as meaning this: "do nothing to the positions but advance the velocities by half a timestep," and you think of the "black box" $\boxed{iL_r}$ as meaning "do nothing to the velocities but advance the positions by δt," then you have

$$
\begin{aligned}
\boxed{iL_r} &: r \to r + \dot{r}\delta t \\
\boxed{\tfrac{1}{2}iL_v} &: \dot{r} \to \dot{r} + \tfrac{1}{2}\ddot{r}\delta t = \dot{r} + \tfrac{1}{2}(f/m)\delta t
\end{aligned}
$$

Once your bandstructure program has calculated forces for a given set of positions make the following sequence of updates to r and $\dot{r}$:

$$
\boxed{\tfrac{1}{2}iL_v} \longrightarrow \boxed{\tfrac{1}{2}iL_v} \longrightarrow \boxed{iL_r}
$$

$\uparrow$ *gather statistics*

You don't even have to worry about the time arguments to r and $\dot{r}$; just use the most recently updated values (you can throw away all previous values). However at each operation the times are not necessarily synchronised as seen from the top of the page. So be sure to gather statistics at a point where the times are aligned, as shown here.

Using Liouville operators

We may assemble our particle positions into a vector Γ and ask how it evolves in time.

$$\begin{aligned}\dot{\Gamma} &= \dot{r}\,\frac{\partial \Gamma}{\partial r} \\ &= iL_r\,\Gamma\end{aligned}$$

which defines the *Liouville* operator

$$iL_r = \dot{r}\frac{\partial}{\partial r}$$

The differential equation $\dot{\Gamma} = iL_r\,\Gamma$ can be integrated from 0 to t,

$$\Gamma(r(t)) = \mathrm{e}^{iL_r\,t}\,\Gamma(r(0))$$

Now here's a nifty identity, (see Appendix for a proof)

$$\mathrm{e}^{a\,\partial/\partial x}\,\Gamma(x) = \Gamma(x+a)$$

And so, if we identify a with $\dot{r}(0)t$ and x with $r(0)$ we find that

$$\Gamma(r(t)) = \Gamma(r(0) + \dot{r}(0)\,t)$$

a simple shift of coordinates, exact however large t is. Compare this with "black box" $\boxed{iL_r}$.

Generally speaking the dynamics will depend on both positions *and* velocities so we need to enquire about the evolution of a vector Γ composed of all positions and velocities. Now we'll see that the equations of motion cannot be propagated without error. For a Hamiltonian system obeying Newton's law of motion, $\ddot{r} = f/m$, with $\dot{r} = p/m$ we have

$$\begin{aligned}\dot{\Gamma}(r,\dot{r}) = \dot{r}\,\frac{\partial \Gamma}{\partial r} + \ddot{r}\,\frac{\partial \Gamma}{\partial \dot{r}} &= \frac{p}{m}\,\frac{\partial \Gamma}{\partial r} + \frac{f}{m}\,\frac{\partial \Gamma}{\partial \dot{r}} \\ &= iL\,\Gamma\end{aligned}$$

and

$$iL = iL_r + iL_v$$

We cannot immediately integrate the differential equation by successive applications of $\mathrm{e}^{iL_r\,t}$ and $\mathrm{e}^{iL_v\,t}$ because

$$\mathrm{e}^{(iL_r+iL_v)\,t} \neq \mathrm{e}^{iL_r\,t}\;\mathrm{e}^{iL_v\,t}$$

since the operators $\partial/\partial r$ and $\partial/\partial\dot{r}$ do not commute (just as in quantum mechanics). So we use the "Trotter" identity

$$\begin{aligned}\mathrm{e}^{a+b} &= \lim_{p\to\infty}\left(\mathrm{e}^{a/2p}\,\mathrm{e}^{b/p}\,\mathrm{e}^{a/2p}\right)^p \\ &= \left(\mathrm{e}^{a/2p}\,\mathrm{e}^{b/p}\,\mathrm{e}^{a/2p}\right)^p\;\mathrm{e}^{\mathcal{O}(1/p^3)}.\end{aligned}$$

Identify a with iL_v, b with iL_r and $1/p$ with δt and we get

$$\mathrm{e}^{(iL_r+iL_v)\,\delta t} = \mathrm{e}^{\frac{1}{2}iL_v\,\delta t}\,\mathrm{e}^{iL_r\,\delta t}\,\mathrm{e}^{\frac{1}{2}iL_v\,\delta t} + \mathcal{O}(\delta t^3).$$

So to second order in the timestep δt the positions and velocities can be advanced exactly as at the top of page 2 with elementary shifts of the variables ($x \to x + \dot{x}\frac{1}{n}\delta t$) using the sequence

$$\boxed{\tfrac{1}{2}iL_v} \quad \longrightarrow \quad \boxed{iL_r} \quad \longrightarrow \quad \boxed{\tfrac{1}{2}iL_v}$$

This approach to the solution of an equation of motion by use of Liouville operators is very general and powerful. You can show that the dynamics are both (*i*) *reversible* and (*ii*) preserve volume in phase space. That is, they obey *Liouville's theorem* that the distribution of microstates in phase space is such that as the system evolves under Newton's equation their motion is that of an incomressible fluid. Clearly, the velocity Verlet is hereby shown to possess both these two properties.

The Nosé–Hoover thermostat

Hoover proposed a set of equations of motion appropriate to the canonical ensemble. The particles are subject to a velocity dependent force (like a viscous drag) that acts to maintain the temperature at some target, T_{ext}, by slowing them down or speeding them up.

The Nosé–Hoover equations of motion are

$$\begin{aligned} \ddot{r} &= \frac{f}{m} - \zeta\dot{r} \\ \dot{\zeta} \equiv G &= \frac{1}{Q}\left(\sum m\dot{r}^2 - N_f\, kT_{\text{ext}}\right) \\ &= \frac{1}{\tau_p^2}\left(\frac{T}{T_{\text{ext}}} - 1\right) \end{aligned}$$

Here, N_f is the number of degrees of freedom, usually $N_f = 3(N-1)$. ζ is the time-varying "viscosity" which acts to keep the temperature constant.† It is given an inertial "mass," $Q = N_f T_{\text{ext}} \tau_p^2$ by the user which corresponds to a time constant, or "relaxation time," τ_p. T is the instantaneous temperature. You can see that ζ varies most rapidly when the temperature deviates most from its target.

Nosé and Hoover introduce an additional variable s which has the meaning of a *scaling* of velocity and time, whose equation of motion is

$$\dot{s}/s = \zeta \equiv \dot{\xi}$$

where $\xi = \log s$. Now to integrate these equations of motion using Liouville operators, we note that our Γ is a vector

$$\Gamma = \Gamma(r, \dot{r}, \xi, \dot{\xi})$$

and so

$$\begin{aligned} \dot{\Gamma} &= \dot{r}\frac{\partial\Gamma}{\partial r} + \ddot{r}\frac{\partial\Gamma}{\partial\dot{r}} + \dot{\xi}\frac{\partial\Gamma}{\partial\xi} + \ddot{\xi}\frac{\partial\Gamma}{\partial\dot{\xi}} \\ &= \dot{r}\frac{\partial\Gamma}{\partial r} + \frac{f}{m}\frac{\partial\Gamma}{\partial\dot{r}} - \zeta\dot{r}\frac{\partial\Gamma}{\partial\dot{r}} + \zeta\frac{\partial\Gamma}{\partial\log s} + \dot{\zeta}\frac{\partial\Gamma}{\partial\zeta} \end{aligned}$$

† Sometimes ζ is written

$$\zeta = \dot{\xi} = \frac{p_\xi}{Q}$$

exposing ζ as the "velocity," p_ξ the "momentum" and Q the inertial "mass" of the thermostat.

from which we can write down the Liouville operator

$$iL = iL_r + iL_v + iL_{C_v} + iL_\xi + iL_G$$

This is the notation of Frenkel and Smit. There now follows a dictionary showing the five Liouville operators and the effects of $\mathrm{e}^{iL\frac{1}{n}\delta t}$ on one of the variables.

$$\begin{aligned}
iL_r &= \dot{r}\frac{\partial}{\partial r} \quad ; \quad \mathrm{e}^{iL_r\frac{1}{n}\delta t} = \boxed{\tfrac{1}{n}iL_r} : r \longrightarrow r + \dot{r}\,\tfrac{1}{n}\delta t \\
iL_v &= \frac{f}{m}\frac{\partial}{\partial \dot{r}} \quad ; \quad \mathrm{e}^{iL_v\frac{1}{n}\delta t} = \boxed{\tfrac{1}{n}iL_v} : \dot{r} \longrightarrow \dot{r} + (f/m)\,\tfrac{1}{n}\delta t \\
iL_{C_v} &= -\zeta\dot{r}\frac{\partial}{\partial \dot{r}} \quad ; \quad \mathrm{e}^{iL_{C_v}\frac{1}{n}\delta t} = \boxed{\tfrac{1}{n}iL_{C_v}} : \dot{r} \longrightarrow \dot{r}\,\mathrm{e}^{-\zeta\frac{1}{n}\delta t} \\
iL_\xi &= \zeta\frac{\partial}{\partial \log s} \quad ; \quad \mathrm{e}^{iL_\xi\frac{1}{n}\delta t} = \boxed{\tfrac{1}{n}iL_\xi} : \log s \longrightarrow \log s + \zeta\,\tfrac{1}{n}\delta t \\
iL_G &= G\frac{\partial}{\partial \zeta} \quad ; \quad \mathrm{e}^{iL_G\frac{1}{n}\delta t} = \boxed{\tfrac{1}{n}iL_G} : \zeta \longrightarrow \zeta + G\,\tfrac{1}{n}\delta t
\end{aligned}$$

The first two are familiar from the microcanonical ensemble, above. The third arises from the friction term in the equation of motion and this can be seen as a *scaling* of the velocities through the action of the thermostat. (Note we have used the second identity in the Appendix.) The fourth updates $\log s$ and the fifth updates ζ, it becomes larger or smaller (positive or negative) depending on G which measures the deviation from the target temperature.

The rest is easy. There is not a unique Trotter factorisation of iL but this is the one chosen usually. First write

$$\begin{aligned}
iL &= iL_r + iL_v + iL_{C_v} + iL_\xi + iL_G \\
&= iL_r + iL_v + iL_T
\end{aligned}$$

and employ the following Trotter factorisation

$$\mathrm{e}^{iL\delta t} = \mathrm{e}^{iL_T\frac{1}{2}\delta t}\,\mathrm{e}^{iL_v\frac{1}{2}\delta t}\,\mathrm{e}^{iL_r\,\delta t}\,\mathrm{e}^{iL_v\frac{1}{2}\delta t}\,\mathrm{e}^{iL_T\frac{1}{2}\delta t} + \mathcal{O}(\delta t^3)$$

Before giving details of how iL_T is dealt with, we'll treat it as a "black box," and show how a canonical NVT ensemble is worked into an MD program. In analogy with the microcanonical NVE ensemble described earlier, the following table shows the operators and time arguments of each variable before and after each factor is successively applied to the dynamical variables.

calculate force ↓

	$\boxed{\frac{1}{2}iL_T}$	$\longrightarrow$ $\boxed{\frac{1}{2}iL_v}$	$\longrightarrow$ $\boxed{iL_r}$	$\longrightarrow$ $\boxed{\frac{1}{2}iL_v}$	$\longrightarrow$ $\boxed{\frac{1}{2}iL_T}$	
r	$t-\delta t$	$t-\delta t$	$t-\delta t$	t	t	t
$\dot{r}$	$t-\delta t$	$t-\delta t$	$t-\frac{1}{2}\delta t$	$t-\frac{1}{2}\delta t$	t	t
$\ddot{r}$	$t-\delta t$	$t-\delta t$	$t-\delta t$	$t-\delta t \Vert t$	t	t
ζ	$t-\delta t$	$t-\frac{1}{2}\delta t$	$t-\frac{1}{2}\delta t$	$t-\frac{1}{2}\delta t$	$t-\frac{1}{2}\delta t$	t
$\log s$	$t-\delta t$	$t-\frac{1}{2}\delta t$	$t-\frac{1}{2}\delta t$	$t-\frac{1}{2}\delta t$	$t-\frac{1}{2}\delta t$	t

Note where the force is calculated to update $\dot{r}$, indicated by the bars, '$\|$'. It may not be convenient to break off the algorithm at that point to return to the force calculation, so a more practical sequence of operators may be

$$\boxed{\tfrac{1}{2}iL_v} \longrightarrow \boxed{\tfrac{1}{2}iL_T} \longrightarrow \boxed{\tfrac{1}{2}iL_T} \longrightarrow \boxed{\tfrac{1}{2}iL_v} \longrightarrow \boxed{iL_r}$$

which can be entered for a given set of positions and forces and completed ready for the next set. It's understood in that case that the positions and forces correspond to one time, the velocities and the friction are half a timestep behind. This means that statistics must be gathered after a step at which all quantities are in synchrony. It's not necessary to keep explicit track of the time for each dynamical variable at each Liouville operation; it is a *fundamental property* of the scheme that each operator takes current values; all values may be overwritten as they are updated.

Finally, the details of the action of the "black box" $\boxed{\tfrac{1}{2}iL_T}$ can be revealed. The following Trotter factorisation is made,

$$\mathrm{e}^{iL_T\,\frac{1}{2}\delta t} = \mathrm{e}^{iL_G\,\frac{1}{4}\delta t}\,\mathrm{e}^{iL_\xi\,\frac{1}{2}\delta t}\,\mathrm{e}^{iL_{C_v}\,\frac{1}{2}\delta t}\,\mathrm{e}^{iL_G\,\frac{1}{4}\delta t} + \mathcal{O}(\delta t^3)$$

Using the "dictionary" at the top of page 5, we can write down the updating operations that amount to an application of the "black box"

$$\boxed{\tfrac{1}{2}iL_T} \;=\; \boxed{\tfrac{1}{4}iL_G} \longrightarrow \boxed{\tfrac{1}{2}iL_\xi} \longrightarrow \boxed{\tfrac{1}{2}iL_{C_v}} \longrightarrow \boxed{\tfrac{1}{4}iL_G}$$

on the vector $\Gamma(r,\dot{r},\xi,\dot{\xi}) = \Gamma(r,\dot{r},\log s,\zeta)$:

$$\begin{aligned}
\zeta &\longrightarrow \zeta + G\,\tfrac{1}{4}\delta t \\
\dot{r} &\longrightarrow \dot{r}\mathrm{e}^{-\zeta\,\frac{1}{2}\delta t} \qquad\qquad \textit{recalculate kinetic energy} \\
\log s &\longrightarrow \log s + \zeta\,\tfrac{1}{2}\delta t \\
\zeta &\longrightarrow \zeta + G\,\tfrac{1}{4}\delta t
\end{aligned}$$

Note that the thermostat does not affect the particle coordinates but it does scale the velocities without advancing them in time. Following this scaling the kinetic energy must be recalculated in order to update G before the next application of $\boxed{\tfrac{1}{4}iL_G}$.

Since the NVE ensemble follows Hamilton's equations of motion the total energy $H_{\mathrm{NVE}} = K + V$ (kinetic plus potential energy) must be conserved. Therefore this is the quantity to watch as the dynamics evolve to confirm the "health" of the MD simulation. The NPT ensemble is a non Hamiltonian system, nevertheless there is a conserved quantity which must be monitored over the simulation.

$$\begin{aligned}
H_{\mathrm{NVT}} &= K + V + N_f kT \log s + \frac{1}{2}Q\zeta^2 \\
&= K + V + N_f kT\left(\log s + \frac{1}{2}\tau_p^2\zeta^2\right)
\end{aligned}$$

Since we think of ζ as the "velocity" and Q as the inertial "mass" of the thermostat, the last term is a kind of fake kinetic energy belonging to the thermostat. The term $LkT\log s$ is the "potential energy" associated with the thermostat. The equation of motion for the scaling factor s, namely $\dot{s}/s = \zeta$ is ancillary in the sense that the two Nosé–Hoover

equations on page 4 are sufficient to determine the dynamics. But it is useful to update $\log s$ during the dynamics, since

$$\log s = \int^t \zeta(t)\,\delta t \approx \sum \zeta(t)\,\delta t$$

so by accumulating the viscosity ζ over the dynamics, its value can be compared with the current value of $\log s$ as a further check on the health of the simulation.

Isothermal–isobaric NPT ensemble

For this we need to calculate the internal pressure, P_{int} as well as the forces.

$$P_{\text{int}} = \frac{1}{3\Omega}\left(NkT + \mathcal{W}\right)$$

where Ω is the instantaneous volume, T the instantaneous temperature, and

$$\mathcal{W} = \sum_{ij} \mathbf{r}_{ij} \cdot \mathbf{f}_{ij}$$

is the "internal virial." Here,

$$NkT = 2K = \sum mv^2$$

is twice the kinetic energy. In the NPT ensemble it is necessary to distinguish the velocities, v, from the quantities $\dot{r}$ which include a contribution from the changing volume,

$$\dot{r} = \frac{p}{m} + \frac{p_\varepsilon}{W} r = v + v_\varepsilon r$$

Here, v_ε and $W = NT_{\text{ext}}\tau_b^2$ are the "velocity" and inertial "mass" of the barostat (see the footnote on page 4). The "mass" is introduced by the user through a relaxation time, τ_b.

The Nosé–Hoover equations of motion, modified by Martyna *et al.*, are

$$\begin{aligned}
\dot{p} &= f - \zeta p - \left(1 + \frac{3}{N_f}\right) v_\varepsilon p \\
\dot{\zeta} &= \frac{1}{Q}\left(2K - (N_f + 1)kT + W v_\varepsilon^2\right) \\
&= G \\
\dot{v}_\varepsilon &= \frac{1}{W}\left(3\Omega\left(P_{\text{int}} - P_{\text{ext}}\right) + \frac{3}{N_f} 2K - \zeta W v_\varepsilon\right) \\
&= G_\varepsilon - \zeta v_\varepsilon \\
\dot{\Omega} &= 3 v_\varepsilon \Omega
\end{aligned}$$

The volume dilatation is $3\varepsilon = \log \Omega/\Omega_0$, where Ω_0 is the volume at $t = 0$. The "velocity" associated with the change of volume is $\dot{\varepsilon} = v_\varepsilon$. Although these are complicated equations of motion, they can be integrated using Liouville operators. A phase space vector is

$$\Gamma = \Gamma(r, p, \xi, \dot{\xi}, \varepsilon, \dot{\varepsilon}) = \Gamma(r, p, \log s, \zeta, \varepsilon, \dot{\varepsilon})$$

and so the Liouville operator is

$$\begin{aligned}
iL &= \dot{r}\,\frac{\partial}{\partial r} + \dot{p}\,\frac{\partial}{\partial p} + \dot{\xi}\,\frac{\partial}{\partial \xi} + \ddot{\xi}\,\frac{\partial}{\partial \dot{\xi}} + \dot{\varepsilon}\,\frac{\partial}{\partial \varepsilon} + \ddot{\varepsilon}\,\frac{\partial}{\partial \dot{\varepsilon}} \\
&= v\,\frac{\partial}{\partial r} + v_\varepsilon r\,\frac{\partial}{\partial r} + \dot{v}\,\frac{\partial}{\partial v} - \zeta p\,\frac{\partial}{\partial p} - \left(1+\frac{3}{N_f}\right) v_\varepsilon\,\frac{\partial}{\partial p} \\
&\qquad + iL_\xi + iL_G + v_\varepsilon\,\frac{\partial}{\partial \varepsilon} + (G_\varepsilon - \zeta v_\varepsilon)\,\frac{\partial}{\partial v_\varepsilon} \\
&= \left[(v + v_\varepsilon r)\,\frac{\partial}{\partial r} + v_\varepsilon\,\frac{\partial}{\partial \varepsilon}\right] + \dot{v}\,\frac{\partial}{\partial v} + iL_{C_v} + iL_\xi + iL_G \\
&\qquad - \left(1+\frac{3}{N_f}\right) v_\varepsilon p\,\frac{\partial}{\partial p} + (G_\varepsilon - \zeta v_\varepsilon)\,\frac{\partial}{\partial v_\varepsilon} \\
&= iL_r + iL_v + iL_{TP}
\end{aligned}$$

Note that in the context of the NPT ensemble, iL_r is the operator in the square brackets above. We deal with this later. Moreover iL_G is not the same as in the NVT ensemble, since the definition of G is modified by coupling to the barostat. Otherwise we proceed as before. First we write

$$iL_{TP} = iL_{C_v} + iL_\xi + iL_G + iL_{\nu\varepsilon} + iL_{G_\varepsilon}$$

and create a "dictionary" as in the case of the NVT ensemble.

$$\begin{aligned}
iL_{C_v} &= -\left(\zeta + \left(1+\frac{3}{N_f}\right) v_\varepsilon\right) v\frac{\partial}{\partial v} \;\; ; \qquad \mathrm{e}^{iL_{C_v}\frac{1}{n}\delta t} = \boxed{\tfrac{1}{n} iL_{C_v}} : v \longrightarrow v\,\mathrm{e}^{-\left(\zeta + \left(1+(3/N_f)\right)v_\varepsilon\right)\frac{1}{n}\delta t} \\
iL_\xi &= \zeta\frac{\partial}{\partial \log s} \qquad\qquad ; \qquad \mathrm{e}^{iL_\xi\frac{1}{n}\delta t} = \boxed{\tfrac{1}{n} iL_\xi} : \log s \longrightarrow \log s + \zeta\,\tfrac{1}{n}\delta t \\
iL_{G_\varepsilon} &= G_\varepsilon\frac{\partial}{\partial v_\varepsilon} \qquad\qquad ; \qquad \mathrm{e}^{iL_G\frac{1}{n}\delta t} = \boxed{\tfrac{1}{n} iL_{G_\varepsilon}} : v_\varepsilon \longrightarrow v_\varepsilon + G_\varepsilon\,\tfrac{1}{n}\delta t \\
iL_{\nu\varepsilon} &= -\zeta v_\varepsilon\frac{\partial}{\partial v_\varepsilon} \qquad\qquad ; \qquad \mathrm{e}^{iL_{\nu\varepsilon}\frac{1}{n}\delta t} = \boxed{\tfrac{1}{n} iL_{\nu\varepsilon}} : v_\varepsilon \longrightarrow v_\varepsilon\,\mathrm{e}^{\zeta\,\frac{1}{n}\delta t} \\
iL_G &= G\frac{\partial}{\partial \zeta} \qquad\qquad ; \qquad \mathrm{e}^{iL_G\frac{1}{n}\delta t} = \boxed{\tfrac{1}{n} iL_G} : \zeta \longrightarrow \zeta + G\,\tfrac{1}{n}\delta t
\end{aligned}$$

The following Trotter factorisations are made.

$$\begin{aligned}
\mathrm{e}^{iL\delta t} &= \mathrm{e}^{iL_{TP}\frac{1}{2}\delta t}\,\mathrm{e}^{iL_v\frac{1}{2}\delta t}\,\mathrm{e}^{iL_r\,\delta t}\,\mathrm{e}^{iL_v\frac{1}{2}\delta t}\,\mathrm{e}^{iL_{TP}\frac{1}{2}\delta t} \\
\mathrm{e}^{iL_{TP}\frac{1}{2}\delta t} &= \mathrm{e}^{iL_G\frac{1}{4}\delta t} && (5.6) \\
&\quad \times \left(\mathrm{e}^{iL_{\nu\varepsilon}\frac{1}{8}\delta t}\,\mathrm{e}^{iL_{G_\varepsilon}\frac{1}{4}\delta t}\,\mathrm{e}^{iL_{\nu\varepsilon}\frac{1}{8}\delta t}\right) && (5.5) \\
&\quad \times \mathrm{e}^{iL_\xi\frac{1}{2}\delta t} && (5.4) \\
&\quad \times \mathrm{e}^{iL_{C_v}\frac{1}{2}\delta t} && (5.3) \\
&\quad \times \left(\mathrm{e}^{iL_{\nu\varepsilon}\frac{1}{8}\delta t}\,\mathrm{e}^{iL_{G_\varepsilon}\frac{1}{4}\delta t}\,\mathrm{e}^{iL_{\nu\varepsilon}\frac{1}{8}\delta t}\right) && (5.2) \\
&\quad \times \mathrm{e}^{iL_G\frac{1}{4}\delta t} && (5.1)
\end{aligned}$$

Now as in the NVT ensemble, having calculated forces for a given set of positions, the following sequence of operations is performed.

$$\boxed{\tfrac{1}{2} iL_v} \longrightarrow \boxed{\tfrac{1}{2} iL_{TP}} \longrightarrow \boxed{\tfrac{1}{2} iL_{TP}} \longrightarrow \boxed{\tfrac{1}{2} iL_v} \longrightarrow \boxed{iL_r}$$

The updating of dynamical variables by the operator $\mathrm{e}^{iL_{TP}\frac{1}{2}\delta t}$ is actually quite simple. The steps 1–5 above require the following sequence of updates.

$$\begin{aligned}
(5.1) \quad &: \quad \zeta \longrightarrow \zeta + G\,\tfrac{1}{4}\delta t \\
(5.2) \quad &: \quad v_\varepsilon \longrightarrow v_\varepsilon\,\mathrm{e}^{-\zeta\frac{1}{4}\delta t} + G_\varepsilon\,\mathrm{e}^{-\zeta\frac{1}{8}\delta t}\,\tfrac{1}{4}\delta t \\
(5.3) \quad &: \quad v \longrightarrow v\,\mathrm{e}^{-\left(\zeta+\left(1+(3/N_f)\right)v_\varepsilon\right)\frac{1}{2}\delta t} \qquad \textit{recalculate kinetic energy} \\
(5.4) \quad &: \quad \log s \longrightarrow \log s + \zeta\,\tfrac{1}{2}\delta t \\
(5.5) \quad &: \quad v_\varepsilon \longrightarrow v_\varepsilon\,\mathrm{e}^{-\zeta\frac{1}{4}\delta t} + G_\varepsilon\,\mathrm{e}^{-\zeta\frac{1}{8}\delta t}\,\tfrac{1}{4}\delta t \\
(5.6) \quad &: \quad \zeta \longrightarrow \zeta + G\,\tfrac{1}{4}\delta t
\end{aligned}$$

It is quite easy to verify, using the dictionary, that the sequence of operations (5.2) lead to the result given here. Again, note that as long as the steps are carried out in the proper order each dynamical variable can be overwritten with its updated value; no previous values need to be retained. It's very important to remember to recalculate the kinetic energy once the velocities has been scaled by (5.3) and the values of G and G_ε updated before carrying out steps (5.5) and (5.6).

It remains to specify the operator of the modified $\mathrm{e}^{iL_v\,\delta t}$ in the NPT ensemble.

$$iL_v = \left[(v + v_\varepsilon r)\,\frac{\partial}{\partial r} + v_\varepsilon\,\frac{\partial}{\partial \varepsilon}\right]$$

The second component results in a simple shift of the strain, ε; the first is not found using the dictionary, instead its action is regarded as equivalent to solving the differential equation

$$\dot{r} = v + v_\varepsilon r$$

at constant v and v_ε. If the initial positions are those at time t then the solution at time $t + \delta t$ is

$$\begin{aligned}
r(t+\delta t) = r(t)\mathrm{e}^{v_\varepsilon(t)\,\delta t} + \mathrm{e}^{\frac{1}{2}v_\varepsilon(t)\,\delta t}\sinh\left(\tfrac{1}{2}v_\varepsilon(t)\,\delta t\right)\frac{\mathrm{e}^{\frac{1}{2}v_\varepsilon(t)\,\delta t}}{\frac{1}{2}v_\varepsilon(t)\,\delta t} \\
\times\left(v(t)\delta t + \tfrac{1}{2}\frac{f(t)}{m}\delta t^2\right)
\end{aligned}$$

We recognise the last line as $v(t+\frac{1}{2}\delta t)\delta t$ which is exactly the velocity we need; as can be seen from the table at the end of page 5, on entry to $\boxed{iL_r}$ the velocity is half a timestep ahead of the position coordinate. So, in summary we add this to the dictionary:

$$iL_r = \dot{r}\frac{\partial}{\partial r} \qquad ; \qquad \mathrm{e}^{iL_r\delta t} = \boxed{iL_r} : \begin{aligned} r &\longrightarrow r\,\mathrm{e}^{2t_\varepsilon} + v\,\mathrm{e}^{t_\varepsilon}\frac{\sinh t_\varepsilon}{t_\varepsilon}\,\delta t \\ \varepsilon &\longrightarrow \varepsilon + v_\varepsilon\delta t \end{aligned}$$

where, $t_\varepsilon = \frac{1}{2}v_\varepsilon\delta t$. To avoid the case that $t_\varepsilon \to 0$, it's safer to employ a Maclaurin expansion of the fraction $(\sinh t/t = \sum(1/\,(2n+1)!)\,t^{2n})$. The purpose of ε is to provide a scaling of the lattice constant and particle coordinates, $\Omega = \Omega_0\,\mathrm{e}^{3\varepsilon}$ is the volume scaling, lengths having a value a_0 at $t = 0$ are scaled using $a = a_0\,\mathrm{e}^{\varepsilon}$ on exit from $\boxed{iL_r}$.

The conserved quantity in the NPT ensemble is

$$H_{\mathrm{NPT}} = K + V + \left(N_f + 1\right)kT\log s + \frac{1}{2}\frac{p_\varepsilon^2}{W} + \frac{1}{2}\frac{p_\xi^2}{Q} + P_{\mathrm{ext}}\Omega$$

See the footnote on page 4. Here we have two fake kinetic energies associated with the "velocities" and inertial "masses" of the thermostat and the barostat.

Appendix

We can prove

$$\mathrm{e}^{a\,\partial/\partial x}\,f(x) = f(x+a)$$

for constant a as follows.

$$\mathrm{e}^{a\,\partial/\partial x}\,f(x) = \sum_{n=0}^{\infty} \frac{1}{n!}\,a^n\,\frac{\partial^n}{\partial x^n}\,f(x)$$

by the expansion of the exponential, while

$$f(x+a) = \sum_{n=0}^{\infty} \frac{1}{n!}\,a^n\,\frac{\partial^n}{\partial x^n}\,f(x)$$

by Taylor's theorem.

A related identity is

$$\mathrm{e}^{ax\,\partial/\partial x}\,f(x) = f\left(x\mathrm{e}^{a}\right)$$

We can prove this using the previous identity. Let c be a constant and let g and f be functions of a variable, q. Then

$$\begin{aligned}\mathrm{e}^{c\,\partial/\partial g}\,f(q) &= \mathrm{e}^{c\,\partial/\partial g}\,f\left\{g^{-1}\left[g(q)\right]\right\}\\ &= f\left\{g^{-1}\left[g(q)+c\right]\right\}\end{aligned}$$

Now $ax\,\partial/\partial x = a\,\partial/\partial \log x$, so making the making the substitution $u = \log x$

$$\begin{aligned}\mathrm{e}^{a\,\partial/\partial u}\,f(x) &= \mathrm{e}^{a\,\partial/\partial u}\,f\left(e^{\log x}\right)\\ &= f\left(\mathrm{e}^{\log x + a}\right)\\ &= f(x\mathrm{e}^{a})\end{aligned}$$

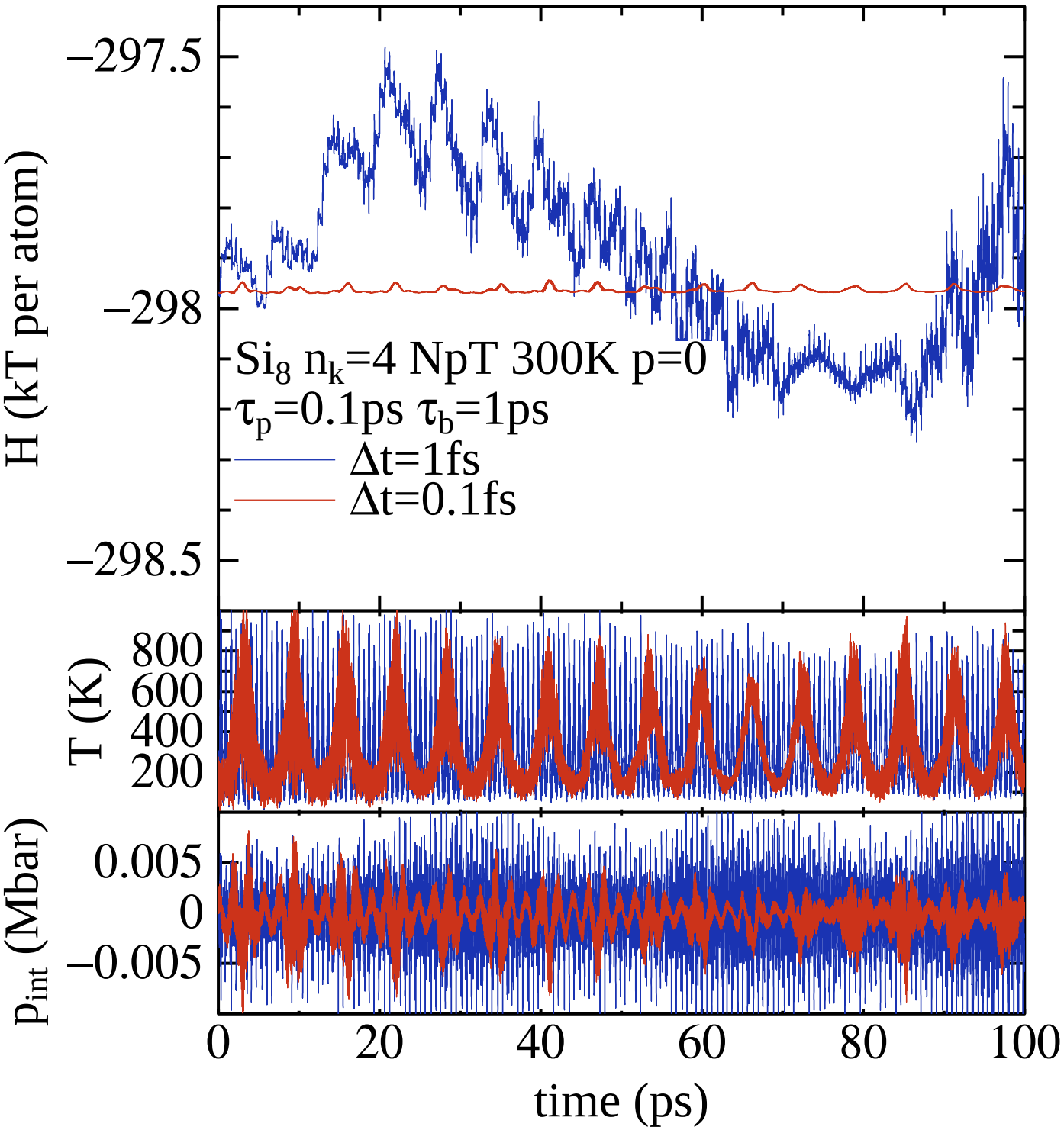
You can make up some further identities. For example, for a, β, γ all constants,

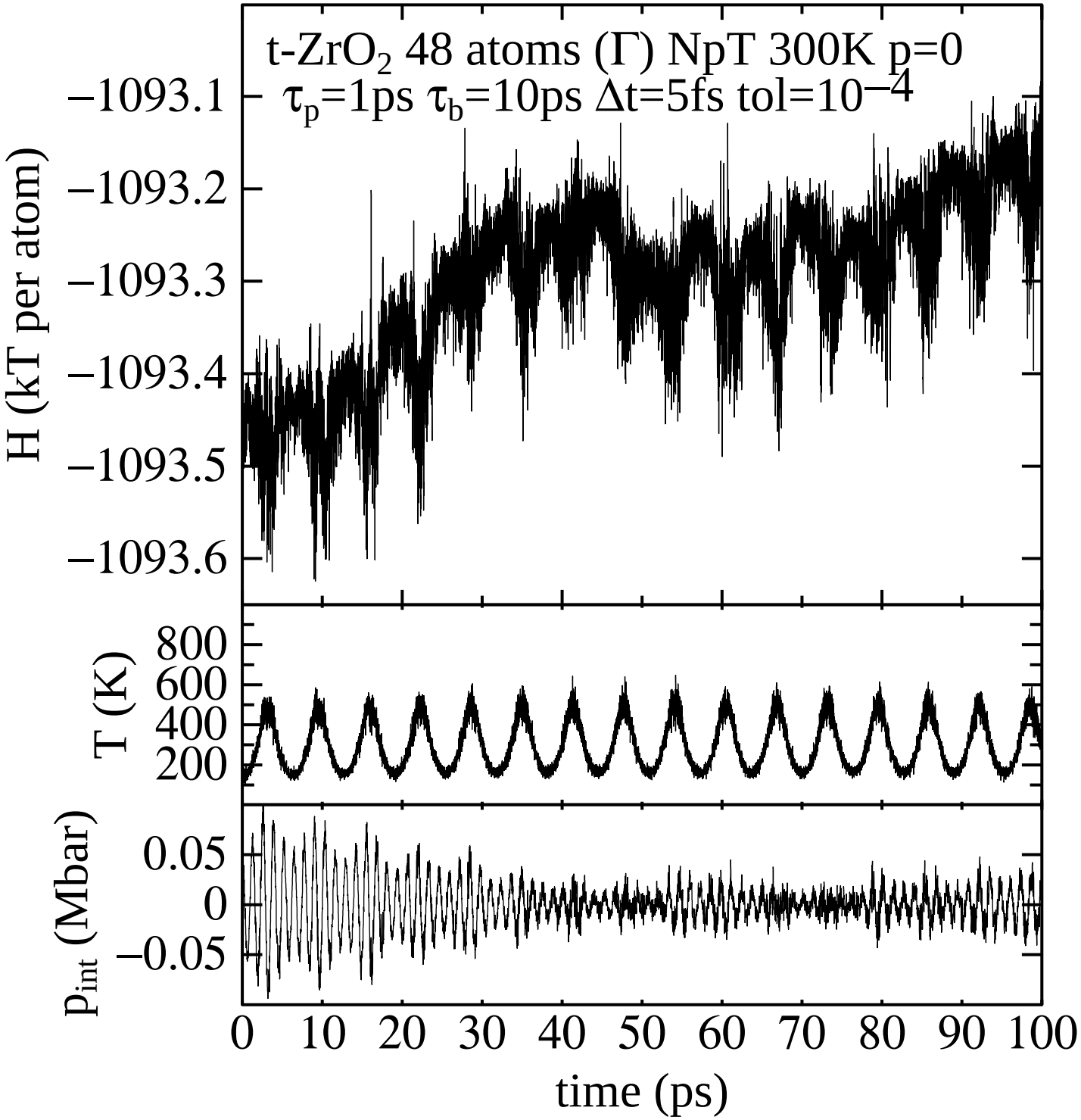
$$\mathrm{e}^{a\,\partial/\partial x}\,f(\beta x) = f\left(\beta\left(x+a\right)\right)$$

$$\mathrm{e}^{ax\,\partial/\partial x}\,f(\beta x+\gamma) = f\left(\mathrm{e}^{a}\left(\beta+\gamma-a\gamma\right)\right)$$

Bibliography

1. Shuichi Nosé, "A unified formulation of the constant temperature molecular dynamics methods," *J. Chem. Phys.*, **81**, 511–9 (1984)
2. William G. Hoover, "Canonical dynamics: equilibrium phase-space distributions," *Phys. Rev. A*, **31**, 1695–7 (1985)
3. M. P. Allen and D. J. Tildesley, "Computer simulation of liquids," (Oxford, Clarendon Press) 1987
4. Glenn J. Martyna, Douglas J. Tobias and Michael L. Klein, "Constant pressure molecular dynamics algorithms," *J. Chem. Phys.*, **101**, 4177–4189 (1994)
5. Glenn J. Martyna, Mark E. Tuckerman, Douglas J. Tobias and Michael L. Klein, "Explicit reversible integrators for extended system dynamics," *Mol. Phys.*, **87**, 1117–1157 (1996)
6. Daan Frenkel and Berend Smit, "Understanding molecular simulations: from algorithms to applications," (San Diego, Academic Press) 1996
7. Mark E. Tuckerman, José Alejandre, Roberto López-Rendón, Andrea L. Jochim and Glenn J. Martyna, "A Liouville-operator derived measure-preserving integrator for molecular dynamics simulations in the isothermal–isobaric ensemble," *J. Phys. A:Math. Gen.*, **39**, 5629–5651 (2006)
8. Mark E. Tuckerman, G25.2651: Statistical Mechanics, (New York University) `http://www.nyu.edu/classes/tuckerman/stat.mech/index.html`


H (kT per atom)
−297.5
−298
−298.5
Si8 nk=4 NpT 300K p=0
τp=0.1ps τb=1ps
Δt=1fs
Δt=0.1fs
T (K)
800
600
400
200
pint (Mbar)
0.005
0
−0.005
0
20
40
60
80
100
time (ps)


t-ZrO2 48 atoms (Γ) NpT 300K p=0
τp=1ps τb=10ps Δt=5fs tol=10−4
H (kT per atom)
−1093.1
−1093.2
−1093.3
−1093.4
−1093.5
−1093.6
T (K)
800
600
400
200
pint (Mbar)
0.05
0
−0.05
0
10
20
30
40
50
60
70
80
90
100
time (ps)