An overview of integration schemes for molecular dynamics simulations

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In this overview, I will present some more or less widely used integration schemes for molecular dynamics simulations. It's essentially a 'cocktail' of undergrad mechanics and undergrad numerics using a smart 'recipe'. After deriving very simple schemes, I will sketch some general concepts for devising more accurate integrators. These notes are an excerpt from some of Burkhard Dünweg's lecture notes [1, 2] and my diploma thesis [3].

1 A bit of theory

1.1 Equations of motion of classical mechanics

The Lagrangian equation of motion for a Hamiltonian system of particles is

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_i}\right) - \frac{\partial L}{\partial q_i} = 0, \tag{1}$$

where q_i and $\dot{q}_i$ are generalized coordinates and velocities, respectively, and the Lagrange function is given in terms of the kinetic energy K and the potential U:

$$L = K - U. \tag{2}$$

Using Cartesian coordinates $\mathbf{r}_i$ and the usual definition of the kinetic energy

$$K = \frac{1}{2}\sum_i m_i \dot{\mathbf{r}}_i^2 \tag{3}$$

and forces $\mathbf{f}_i$

$$\mathbf{f}_i = \nabla_{\mathbf{r}_i} L = -\nabla_{\mathbf{r}_i} U, \tag{4}$$

the Euler-Lagrange equation (1) yields Newton's equation of motion

$$m_i \ddot{\mathbf{r}}_i - \mathbf{f}_i = 0. \tag{5}$$

Introducing generalized momenta p_i conjugate to the coordinates

$$p_i = \frac{\partial L}{\partial \dot{q}_i}, \tag{6}$$

we can define the Hamiltonian for the system

$$H = \sum_i \dot{q}_i p_i - L. \tag{7}$$

If the potential does not depend on the velocities $\dot{q}_i$ and the time t, the Hamiltonian resembles the energy. The Hamiltonian equations of motion are

$$\begin{aligned} \dot{q}_i &= \frac{\partial H}{\partial p_i}, \\ \dot{p}_i &= -\frac{\partial H}{\partial q_i}. \end{aligned} \tag{8}$$

For Cartesian coordinates we get

$$\begin{aligned} \dot{\mathbf{r}}_i &= \frac{\mathbf{p}_i}{m_i}, \\ \dot{\mathbf{p}}_i &= \mathbf{f}_i. \end{aligned} \tag{9}$$

While (5) is a system of $3N$ second-order differential equations, (9) is a system of $6N$ first order differential equations. Both systems are equivalent but they can lead to different discrete algorithms for their solution. The Euler algorithm introduced later uses the first order system while the Verlet algorithm uses the second order system.

1.2 Liouville's equation

Let $\mathbf{\Gamma} = \{\mathbf{r}_i, \mathbf{p}_i\}$ be the phase-space formed by all positions and momenta. It contains all information about the microscopic state of the system. A trajectory in phase-space is denoted by $\mathbf{\Gamma}(t)$ and the phase-space density is denoted by $\rho(\mathbf{\Gamma}; t)$. We introduce the *Liouville operator* $\mathcal{L}$

$$i\mathcal{L} = \sum_i \left(\dot{\mathbf{r}}_i \frac{\partial}{\partial \mathbf{r}_i} + \dot{\mathbf{p}}_i \frac{\partial}{\partial \mathbf{p}_i} \right). \tag{10}$$

For an observable $A(\mathbf{\Gamma})$ in phase-space the time evolution is

$$\frac{d}{dt} A(\mathbf{\Gamma}) = \sum_i \left(\frac{\partial A}{\partial \mathbf{r}_i} \dot{\mathbf{r}}_i + \frac{\partial A}{\partial \mathbf{p}_i} \dot{\mathbf{p}}_i \right) = i\mathcal{L} A(\mathbf{\Gamma}), \tag{11}$$

With this notation, from the equations of motion follows immediately *Liouville's theorem*

$$\nabla_{\mathbf{\Gamma}} \dot{\mathbf{\Gamma}} = 0, \tag{12}$$

which implies the *continuity equation* for the phase-space density

$$\frac{\partial \rho}{\partial t} + \nabla_{\mathbf{\Gamma}} \left(\rho \dot{\mathbf{\Gamma}} \right) = 0. \tag{13}$$

As a consequence, the phase-space density along a trajectory is conserved

$$\frac{d}{dt}\rho(\mathbf{\Gamma};t) = 0. \tag{14}$$

Application of the chain rule yields *Liouville's equation*

$$\frac{\partial}{\partial t}\rho(\mathbf{\Gamma};t) + i\mathcal{L}\rho(\mathbf{\Gamma};t) = 0. \tag{15}$$

Liouville's equation is the basis for deriving symplectic integrators.

2 Simple integration schemes

I will focus on Verlet-like algorithms (in contrast to Gear predictor-corrector algorithms). A discretization of the equations of motion can be obtained by Taylor expansion:

$$\mathbf{r}_i(t + \Delta t) = \mathbf{r}_i(t) + \Delta t\ \mathbf{v}_i(t) + \frac{\Delta t^2}{2m_i}\ \mathbf{f}_i(t) + \frac{\Delta t^3}{3!}\ \dddot{\mathbf{r}}_i(t) + \mathcal{O}(\Delta t^4) \tag{16}$$

$$\mathbf{v}_i(t + \Delta t) = \mathbf{v}_i(t) + \frac{\Delta t}{m_i}\ \mathbf{f}_i(t) + \frac{\Delta t^2}{2}\ \ddot{\mathbf{v}}_i(t) + \frac{\Delta t^3}{3!}\ \dddot{\mathbf{v}}_i(t) + \mathcal{O}(\Delta t^4). \tag{17}$$

2.0.1 Euler algorithm

Perhaps the most simple integration scheme based on equations (16) and (17) is realized by the Euler algorithm. The trajectory is calculated according to

$$\mathbf{r}_i(t + \Delta t) = \mathbf{r}_i(t) + \Delta t\ \mathbf{v}_i(t) + \frac{\Delta t^2}{2m_i}\mathbf{f}_i(t) + \mathcal{O}(\Delta t^3)$$

$$\mathbf{v}_i(t + \Delta t) = \mathbf{v}_i(t) + \frac{\Delta t}{m_i}\ \mathbf{f}_i(t) + \mathcal{O}(\Delta t^2) \tag{18}$$

The Euler algorithm is neither time-reversible nor phase-space preserving and hence rather unfavorable. Nevertheless, the Euler scheme can be used to integrate other equations of motion, e.g. the Boltzmann equation.

2.0.2 Verlet algorithm

If we solve the second order system (5) based on the current positions $\mathbf{r}_i(t)$ and forces $\mathbf{f}_i(t)$ and the previous positions $\mathbf{r}_i(t - \Delta t)$, we get the Verlet algorithm. The derivation is straightforward:

$$\mathbf{r}_i(t - \Delta t) = \mathbf{r}_i(t) - \Delta t\ \mathbf{v}_i(t) + \frac{\Delta t^2}{2m_i}\ \mathbf{f}_i(t) - \frac{\Delta t^3}{3!}\ \dddot{\mathbf{r}}_i(t) + \mathcal{O}(\Delta t^4). \tag{19}$$

The updating equation for the positions is obtained by adding (16) and (19), and for the velocities by subtracting them, respectively:

$$\mathbf{r}_i(t + \Delta t) = 2\mathbf{r}_i(t) - \mathbf{r}_i(t - \Delta t) + \frac{\Delta t^2}{m_i}\mathbf{f}_i(t) + \mathcal{O}(\Delta t^4),$$

$$\mathbf{v}_i(t) = \frac{\mathbf{r}_i(t + \Delta t) - \mathbf{r}_i(t - \Delta t)}{2\Delta t} + \mathcal{O}(\Delta t^3). \tag{20}$$

The velocities are actually not needed to compute the trajectories, but they are useful for calculating observables like the kinetic energy. However, in the Verlet scheme the velocities $\mathbf{v}(t)$ are only available once $\mathbf{r}(t + \Delta t)$ has been calculated, i.e. one time step later. Moreover, the updating of positions according to (20) gives rise to numerical imprecision because a small term of order Δt^2 is added to a difference of $\mathcal{O}(1)$-terms.

2.0.3 Leap-frog algorithm

To obtain both the positions and velocities from readily available quantities, the leap-frog scheme can be applied. The updating equations are:

$$
\begin{aligned}
\mathbf{v}_i(t + \frac{\Delta t}{2}) &= \mathbf{v}_i(t - \frac{\Delta t}{2}) + \frac{\Delta t}{m_i}\, \mathbf{f}_i(t), \\
\mathbf{r}_i(t + \Delta t) &= \mathbf{r}_i(t) + \Delta t\, \mathbf{v}_i(t + \frac{\Delta t}{2}).
\end{aligned}
\tag{21}
$$

The velocities are updated at half time steps and 'leap' ahead the positions. The current velocities can be obtained from

$$
\mathbf{v}_i(t) = \frac{\mathbf{v}_i(t - \frac{\Delta t}{2}) + \mathbf{v}_i(\Delta t + \frac{\Delta t}{2})}{2}.
\tag{22}
$$

Numerical imprecision is minimized in the leap-frog scheme. However, the velocities are still not accessible in an ad-hoc manner.

2.0.4 Velocity-Verlet algorithm

An algorithm that yields the positions, velocities and forces at the same time is given by the Velocity-Verlet scheme. The positions and velocities are updated according to

$$
\begin{aligned}
\mathbf{r}_i(t + \Delta t) &= \mathbf{r}_i(t) + \Delta t\, \mathbf{v}_i(t) + \frac{\Delta t^2}{m_i}\, \mathbf{f}_i(t) + \mathcal{O}(\Delta t^3), \\
\mathbf{v}_i(t + \Delta t) &= \mathbf{v}(t) + \frac{\Delta t}{2m_i}\, (\mathbf{f}_i(t) + \mathbf{f}_i(t + \Delta t)) + \mathcal{O}(\Delta t^3).
\end{aligned}
\tag{23}
$$

The Velocity-Verlet scheme is algebraically equivalent to the original Verlet algorithm. Equations (20) can be derived from (23) by elimination of the velocities in the position update. Despite its simplicity the Velocity-Verlet algorithm is very stable and has become the perhaps most widely used Molecular Dynamics algorithm. The Velocity-Verlet scheme is a *symplectic integrator*, i.e. it preserves the volume in phase-space.

3 Splitting methods

3.1 The Trotter expansion

We can formally integrate the equation of motion for an observable to obtain

$$
A(t) = \exp\left(i\mathcal{L}t\right) A(0).
\tag{24}
$$

The Liouville operator can be split into a position part and a momentum part:

$$i\mathcal{L} = i\mathcal{L}_{\mathbf{r}} + i\mathcal{L}_{\mathbf{p}}, \tag{25}$$

where

$$i\mathcal{L}_{\mathbf{r}} = \sum_i \dot{\mathbf{r}}_i \frac{\partial}{\partial \mathbf{r}_i} \qquad i\mathcal{L}_{\mathbf{p}} = \sum_i \dot{\mathbf{p}}_i \frac{\partial}{\partial \mathbf{p}_i}. \tag{26}$$

These operators yield shifts of coordinates and momenta, respectively. To use $i\mathcal{L}_{\mathbf{r}}$ and $i\mathcal{L}_{\mathbf{p}}$ in equation (24) we write the *Trotter expansion* of the Liouville operator

$$e^{i(\mathcal{L}_{\mathbf{r}} + \mathcal{L}_{\mathbf{p}})\Delta t} = e^{i\frac{\Delta t}{2}\mathcal{L}_{\mathbf{p}}} \; e^{i\Delta t \mathcal{L}_{\mathbf{r}}} \; e^{i\frac{\Delta t}{2}\mathcal{L}_{\mathbf{p}}} + \mathcal{O}(\Delta t^3). \tag{27}$$

If we apply the single terms of this expansion to the positions and momenta, we get

$$\begin{aligned}
e^{i\frac{\Delta t}{2}\mathcal{L}_{\mathbf{p}}} \; \mathbf{r}_i &= \mathbf{r}_i & e^{i\frac{\Delta t}{2}\mathcal{L}_{\mathbf{p}}} \; \mathbf{p}_i &= \mathbf{p}_i + \frac{\Delta t}{2}\dot{\mathbf{p}}_i \\
e^{i\Delta t \mathcal{L}_{\mathbf{r}}} \; \mathbf{r}_i &= \mathbf{r}_i + \Delta t \; \dot{\mathbf{r}}_i & e^{i\Delta t \mathcal{L}_{\mathbf{r}}} \; \mathbf{p}_i &= \mathbf{p}_i.
\end{aligned} \tag{28}$$

Altogether we obtain

$$\begin{aligned}
e^{i\frac{\Delta t}{2}\mathcal{L}_{\mathbf{p}}} \; e^{i\Delta t \mathcal{L}_{\mathbf{r}}} \; e^{i\frac{\Delta t}{2}\mathcal{L}_{\mathbf{p}}} \; \mathbf{r}_i(t) &= \mathbf{r}_i(t) + \Delta t \; \dot{\mathbf{r}}(\frac{\Delta t}{2}) \\
&= \mathbf{r}_i(t) + \Delta t \; \mathbf{v}_i(t) + \frac{\Delta t^2}{2m_i}\mathbf{f}_i(t) \\
e^{i\frac{\Delta t}{2}\mathcal{L}_{\mathbf{p}}} \; e^{i\Delta t \mathcal{L}_{\mathbf{r}}} \; e^{i\frac{\Delta t}{2}\mathcal{L}_{\mathbf{p}}} \; \mathbf{p}_i(t) &= \mathbf{p}_i(t) + \frac{\Delta t}{2}\left(\dot{\mathbf{p}}_i(t) + \dot{\mathbf{p}}_i(t + \Delta t)\right) \\
&= \mathbf{p}_i(t) + \frac{\Delta t}{2}\left(\mathbf{f}_i(t) + \mathbf{f}_i(t + \Delta t)\right).
\end{aligned} \tag{29}$$

This yields exactly the updating equations (23) of the Velocity-Verlet algorithm. The operators $\mathcal{L}_{\mathbf{r}}$ and $\mathcal{L}_{\mathbf{p}}$ are hermitian, thus $e^{i\frac{\Delta t}{2}\mathcal{L}_{\mathbf{p}}} \; e^{i\Delta t \mathcal{L}_{\mathbf{r}}} \; e^{i\frac{\Delta t}{2}\mathcal{L}_{\mathbf{p}}}$ is a unitary operator, which implies that the volume in phase-space is preserved. Time-reversibility is satisfied because the equations are symmetric with respect to future and past coordinates. The Trotter expansion (27) is correct up to terms of order Δt^3. Due to the deviations, the true Hamiltonian H of the system is not strictly conserved. However, under certain conditions it can be shown that some kind of pseudo-Hamiltonian is conserved. This explains the absence of energy drift and is the reason for the good stability of the Velocity-Verlet scheme.

3.2 Integrator for Langevin thermostat

Now we consider the Langevin equations of motion

$$\frac{d}{dt}\mathbf{r}_i = \frac{1}{m_i}\mathbf{p}_i, \tag{30}$$

$$\frac{d}{dt}\mathbf{p}_i = \mathbf{F}_i - \gamma_i\left[\frac{1}{m_i}\mathbf{p}_i - \mathbf{u}_i\right] + \mathbf{f}_i, \tag{31}$$

where $\mathbf{u}_i$ is the solvent velocity in case of coupling to a lattice Boltzmann fluid, while $\mathbf{u}_i = 0$ in case of the standard Langevin thermostat. $\mathbf{F}_i$ is the conservative deterministic force, which (as before) depends only on the positions of the particles. The fluctuation–dissipation relation reads

$$
\begin{aligned}
\langle f_{i\alpha} \rangle &= 0, \quad (32) \\
\langle f_{i\alpha}(t) f_{j\beta}(t') \rangle &= 2\gamma_i k_B T \delta_{ij} \delta_{\alpha\beta} \delta(t - t'). \quad (33)
\end{aligned}
$$

In order to derive a Verlet-like algorithm, we rewrite the equations of motion using the Fokker-Planck picture (Kramers-Moyal expansion, cf. [1]):

$$
\partial_t \rho(\mathbf{\Gamma}; t) = (\mathcal{L}_1 + \mathcal{L}_2 + \mathcal{L}_3 + \mathcal{L}_4) \rho(\mathbf{\Gamma}; t) \quad (34)
$$

with

$$
\mathcal{L}_1 = -\sum_i \frac{\partial}{\partial \mathbf{r}_i} \cdot \frac{\mathbf{p}_i}{m_i}, \quad (35)
$$

$$
\mathcal{L}_2 = -\sum_i \frac{\partial}{\partial \mathbf{p}_i} \cdot \mathbf{F}_i, \quad (36)
$$

$$
\mathcal{L}_3 = \sum_i \gamma_i \frac{\partial}{\partial \mathbf{p}_i} \cdot \left[\frac{1}{m_i} \mathbf{p}_i - \mathbf{u}_i \right], \quad (37)
$$

$$
\mathcal{L}_4 = k_B T \sum_i \gamma_i \frac{\partial^2}{\partial \mathbf{p}_i^2}, \quad (38)
$$

which describe conservative real–space, conservative momentum–space, dissipative, and stochastic propagation, respectively. Now we can again use the Trotter expansion

$$
\begin{aligned}
&\exp\left[(\mathcal{L}_1 + \mathcal{L}_2 + \mathcal{L}_3 + \mathcal{L}_4) \Delta t \right] \quad (39) \\
&= \exp\left[\mathcal{L}_1 \Delta t / 2 \right] \exp\left[(\mathcal{L}_2 + \mathcal{L}_3 + \mathcal{L}_4) \Delta t \right] \exp\left[\mathcal{L}_1 \Delta t / 2 \right] + O(\Delta t^3),
\end{aligned}
$$

Observing that $\mathcal{L}_1$ contains only derivatives with respect to the particle positions and $\mathcal{L}_2 + \mathcal{L}_3 + \mathcal{L}_4$ contains only derivatives with respect to the momenta, we thus get an $\mathcal{O}(h^3)$-algorithm that subsequently shifts positions for $\Delta t / 2$, momenta for Δt and positions again for $\Delta t / 2$.

For this sequence, the solutions of the equations of motion can be found *exactly*. The position update is trivially given by

$$
\mathbf{r}_i(t + \frac{\Delta t}{2}) = \mathbf{r}_i(t) + \frac{\Delta t}{2} \frac{\mathbf{p}_i(t)}{m_i}. \quad (40)
$$

The momentum update is given by exactly solving the Langevin equation

$$
\frac{d}{dt} \mathbf{p}_i = \mathbf{F}_i - \gamma_i \left[\frac{1}{m_i} \mathbf{p}_i - \mathbf{u}_i \right] + \mathbf{f}_i \quad (41)
$$

for *constant* $\mathbf{F}_i$, $\mathbf{u}_i$. This is the main task which will allow us to construct the second–order updating scheme.

Mathematically, Eq. (41) is nothing but the well–known problem of Brownian motion in a harmonic potential (Ornstein–Uhlenbeck process). However, the solution shall be worked out here for the convenience of the reader. We first re–write the equation as

$$\left(\frac{d}{dt} + \frac{\gamma_i}{m_i}\right) \mathbf{p}_i = \boldsymbol{\phi}_i + \mathbf{f}_i, \tag{42}$$

where we have introduced the abbreviation

$$\boldsymbol{\phi}_i = \mathbf{F}_i + \gamma_i \mathbf{u}_i, \tag{43}$$

and consider the right hand side as an inhomogeneity. The solution of the homogeneous equation is

$$\mathbf{p}_i(t) = \exp\left(-\frac{\gamma_i}{m_i}t\right) \mathbf{p}_i(0). \tag{44}$$

Variation of constants tells us that for the full problem we should use the ansatz

$$\mathbf{p}_i(t) = \exp\left(-\frac{\gamma_i}{m_i}t\right) \boldsymbol{\pi}_i(t). \tag{45}$$

The Langevin equation for $\boldsymbol{\pi}_i$ then reads

$$\frac{d}{dt}\boldsymbol{\pi}_i = \exp\left(+\frac{\gamma_i}{m_i}t\right) (\boldsymbol{\phi}_i + \mathbf{f}_i). \tag{46}$$

Taking into account that $\boldsymbol{\phi}_i$ is constant, we can straightforwardly integrate this one time step to find

$$\boldsymbol{\pi}_i(\Delta t) = \boldsymbol{\pi}_i(0) + \frac{m_i}{\gamma_i} \left[\exp\left(+\frac{\gamma_i}{m_i}\Delta t\right) - 1\right] \boldsymbol{\phi}_i + \int_0^{\Delta t} dt \exp\left(+\frac{\gamma_i}{m_i}t\right) \mathbf{f}_i(t), \tag{47}$$

or

$$\begin{aligned}
\mathbf{p}_i(\Delta t) &= \exp\left(-\frac{\gamma_i}{m_i}\Delta t\right) \mathbf{p}_i(0) \\
&+ \frac{m_i}{\gamma_i} \left[1 - \exp\left(-\frac{\gamma_i}{m_i}\Delta t\right)\right] \boldsymbol{\phi}_i \\
&+ \int_0^{\Delta t} \exp\left(-\frac{\gamma_i}{m_i}(\Delta t - t)\right) \mathbf{f}_i(t).
\end{aligned} \tag{48}$$

Since this is a linear operator acting on the Gaussian white noise, we find that the $\mathbf{p}_i(\Delta t)$ must be Gaussian random variables. We characterize these by calculating their first two moments, taking into account the fluctuation–dissipation relation for the noise:

$$\langle \mathbf{p}_i(\Delta t) \rangle = \exp\left(-\frac{\gamma_i}{m_i}\Delta t\right) \mathbf{p}_i(0) + \frac{m_i}{\gamma_i} \left[1 - \exp\left(-\frac{\gamma_i}{m_i}\Delta t\right)\right] \boldsymbol{\phi}_i, \tag{49}$$

$$\langle [p_{i\alpha}(\Delta t) - \langle p_{i\alpha}(\Delta t)\rangle] [p_{j\beta}(\Delta t) - \langle p_{j\beta}(\Delta t)\rangle]\rangle \tag{50}$$
$$= m_i k_B T \left[1 - \exp\left(-2\frac{\gamma_i}{m_i}\Delta t\right)\right] \delta_{ij}\delta_{\alpha\beta}.$$

Thus, the update of momenta can be written as

$$\mathbf{p}_i(\Delta t) = d_i(\Delta t)\mathbf{p}_i(0) + q_i(\Delta t)\boldsymbol{\phi}_i + \sigma_i(\Delta t)\boldsymbol{\zeta}_i, \tag{51}$$

where we have introduced the parameters

$$d_i(\Delta t) = \exp\left(-\frac{\gamma_i}{m_i}\Delta t\right), \tag{52}$$

$$q_i(\Delta t) = \frac{m_i}{\gamma_i}\left[1 - \exp\left(-\frac{\gamma_i}{m_i}\Delta t\right)\right], \tag{53}$$

$$\sigma_i(\Delta t) = \sqrt{m_i k_B T \left[1 - \exp\left(-2\frac{\gamma_i}{m_i}\Delta t\right)\right]}, \tag{54}$$

which can be calculated at the beginning of the simulation. The random variables $\boldsymbol{\zeta}_{i\alpha}$ are mutually uncorrelated, Gaussian, and have zero mean and unit variance. Taylor-expanding the exponentials we recover the Velocity-Verlet scheme, which shows that this is only first order in Δt for Langevin dynamics.

3.3 Integrator for Anderson barostat

The Anderson barostat is based on the following Lagrangian [4, 5]

$$L = \sum_i \frac{L^2}{2} m_i \dot{\mathbf{s}}_i^2 - \sum_{i<j} U_{ij} + \frac{1}{2}Q\dot{V}^2 - PV, \tag{55}$$

where m_i is the mass of particle i, $\mathbf{s}_i$ are the scaled coordinates, U_{ij} is the potential between particles i and j, and Q is the mass associated to the piston.

Legendre transformation yields the Hamiltonian

$$H = \sum_i \frac{1}{2L^2 m_i}\boldsymbol{\pi}_i^2 + \sum_{i<j} U_{ij} + \frac{1}{2Q}\Pi_V^2 + PV \tag{56}$$

and the equations of motion are

$$\dot{\mathbf{s}}_i = \frac{1}{L^2 m_i}\boldsymbol{\pi}_i \tag{57}$$

$$\dot{\boldsymbol{\pi}}_i = L\mathbf{f}_i \tag{58}$$

$$\dot{V} = \frac{1}{Q}\Pi_V \tag{59}$$

$$\dot{\Pi}_V = \frac{1}{3V}\sum_{i<j}\mathbf{f}_{ij}\mathbf{s}_{ij} + \frac{1}{3L^2 V}\sum_i \frac{1}{m_i}\boldsymbol{\pi}_i^2 - P \tag{60}$$

Again, we use the Fokker-Planck picture to apply the Trotter expansion, where the splitting of the operators is

$$
i\mathcal{L}_1 = -\sum_i L\mathbf{f}_i \frac{\partial}{\partial \boldsymbol{\pi}_i}, \tag{61}
$$

$$
i\mathcal{L}_2 = -\left(\frac{1}{3V} \sum_{i<j} \mathbf{f}_{ij}\mathbf{s}_{ij} + \frac{1}{3L^2V} \sum_i \frac{1}{m_i}\boldsymbol{\pi}_i^2 - P \right) \frac{\partial}{\partial \Pi_v}, \tag{62}
$$

$$
i\mathcal{L}_3 = -\frac{\Pi_v}{Q} \frac{\partial}{\partial V}, \tag{63}
$$

$$
i\mathcal{L}_4 = -\sum_i \frac{\boldsymbol{\pi}_i}{L^2 m_i} \frac{\partial}{\partial \mathbf{s}_i}. \tag{64}
$$

With this, we arrive at the following algorithm:

1. $\mathbf{p}_i' = \mathbf{p}_i(t) + \frac{\Delta t}{2}\mathbf{f}_i(t)$

2. $\Pi_V(t + \frac{\Delta t}{2}) = \Pi_v(t) + \frac{\Delta t}{2} \left(\frac{1}{3V(t)} \sum_{i<j} \mathbf{f}_{ij}(t)\mathbf{r}_{ij}(t) + \frac{1}{3V(t)} \sum_i \frac{1}{m_i}\mathbf{p}_i'^2 - P \right)$

3. $V(t + \frac{\Delta t}{2}) = V(t) + \frac{\Delta t}{2Q}\Pi_V(t + \frac{\Delta t}{2})$

4. $\mathbf{r}_i' = \mathbf{r}_i(t) + \Delta t \frac{L^2(t)}{L^2(t+\Delta t/2)} \frac{\mathbf{p}_i'}{m_i}$

5. $V(t + \Delta t) = V(t + \frac{\Delta t}{2}) + \frac{\Delta t}{2Q}\Pi_V(t + \frac{\Delta t}{2})$
   $\mathbf{r}_i(t + \Delta t) = \frac{L(t+\Delta t)}{L(t)}\mathbf{r}_i'$
   $\mathbf{p}_i'' = \frac{L(t)}{L(t+\Delta t)}\mathbf{p}_i'$

6. $\Pi_v(t+\Delta t) = \Pi_V(t+\frac{\Delta t}{2}) + \frac{\Delta t}{2} \left(\frac{1}{3V(t+\Delta t)} \sum_{i<j} \mathbf{f}_{ij}(t + \Delta t)\mathbf{r}_{ij}(t + \Delta t) + \frac{1}{3V(t+\Delta t)} \sum_i \frac{1}{m_i}\mathbf{p}_i''^2 - P \right)$

7. $\mathbf{p}_i(t + \Delta t) = \mathbf{p}_i'' + \frac{\Delta t}{2}\mathbf{f}_i(t + \Delta t)$

It is straightforward to extend this algorithm with noise and friction in order to integrate the Langevin equations of motion for the NPT ensemble.

References and further reading

The material presented here just summarizes the basics of integration methods, which every simulator should be familiar with in my view. If you want to know more, take a look into the literature or ask the experts in the group (e.g. Burkhard, Berk, Matej, Torsten and others).

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