

- hard spheres etc. – collisions
- “classical” MD – integration of the equations of motion
- Brownian (stochastic) dynamics, dissipative particle dynamics = MD + random forces

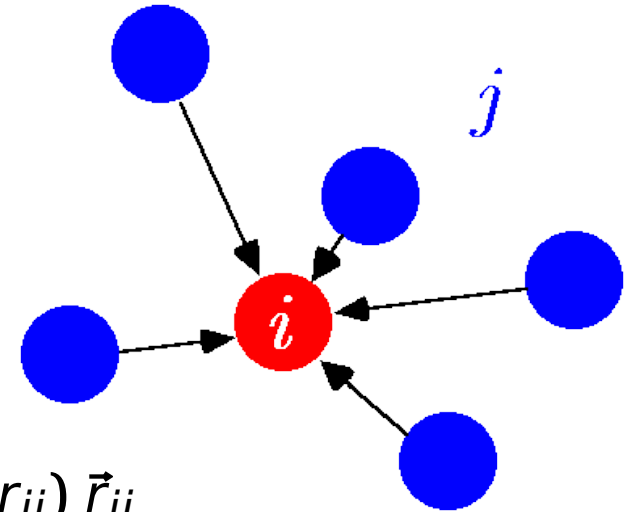
Forces:

$$\vec{f}_i = -\frac{\partial U(\vec{r}^N)}{\partial \vec{r}_i} \quad i = 1, \dots, N$$

Example – pair forces:

$$U = \sum_{i < j} u(r_{ij}) \Rightarrow \vec{f}_i = \sum_{\substack{j=1 \\ j \neq i}}^N \vec{f}_{ji} \equiv - \sum_{\substack{j=1 \\ j \neq i}}^N \frac{du(r_{ji})}{dr_{ji}} \frac{\partial r_{ji}}{\partial \vec{r}_i} = - \sum_{\substack{j=1 \\ j \neq i}}^N \frac{du(r_{ji})}{dr_{ji}} \frac{\vec{r}_{ji}}{r_{ji}}$$

Notation: $\vec{r}_{ij} = \vec{r}_j - \vec{r}_i$, $r_{ij} = |\vec{r}_{ij}|$



$$\frac{d^2 \vec{r}_i}{dt^2} = \ddot{\vec{r}}_i = \frac{\vec{f}_i}{m_i}, \quad i = 1, \dots, N$$

Method of finite differences, timestep h

Initial value problem: we know \vec{r} and $\dot{\vec{r}}$ at time t_0

Methods:

- Runge–Kutta: many evaluations of the right-hand side/step (costly!)
- Predictor-corrector: better, but ... (more below)
- Symplectic methods: good energy conservation
- Multiple timestep methods: as above, more timescales

Taylor expansion:

$$\begin{aligned}r(t-h) &= r(t) - h\dot{r}(t) + \frac{h^2}{2}\ddot{r}(t) - \dots && +1\times \\r(t) &= r(t) && -2\times \\r(t+h) &= r(t) + h\dot{r}(t) + \frac{h^2}{2}\ddot{r}(t) + \dots && +1\times\end{aligned}$$

⇒ numeric 2nd derivative: $\ddot{\vec{r}}_i(t) = \frac{\vec{f}_i(t)}{m_i} = \frac{\vec{r}_i(t-h) - 2\vec{r}_i(t) + \vec{r}_i(t+h)}{h^2} + \mathcal{O}(h^2)$

Verlet method: $\vec{r}_i(t+h) = 2\vec{r}_i(t) - \vec{r}_i(t-h) + h^2 \frac{\vec{f}_i(t)}{m_i}$

Initial values: $\vec{r}_i(t_0-h) = \vec{r}_i(t_0) - h\dot{\vec{r}}_i(t_0) + \frac{h^2}{2} \frac{\vec{f}_i(t_0)}{m_i} + \mathcal{O}(h^3)$

⊕ time-reversible (⇒ no energy drift); even symplectic

⊖ cannot use for $\ddot{r} = f(r, \dot{r})$ because $\dot{r}(t)$ is not known at time t

Identical trajectories: leap-frog, velocity Verlet, Gear ($m = 3$), Beeman

Leap-frog

velocity = displacement (change in position)
per unit time (h), a vector

$$\vec{v}(t + h/2) = \frac{\vec{r}(t + h) - \vec{r}(t)}{h}$$

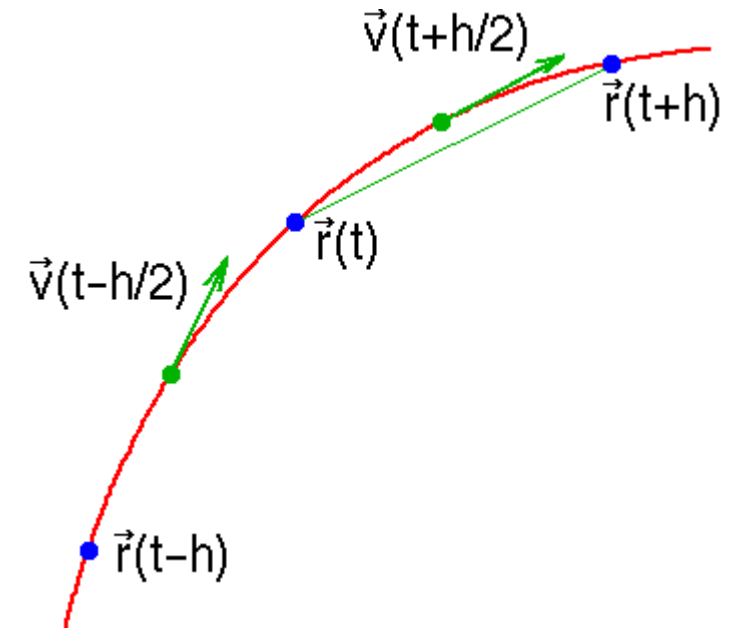
acceleration = change in velocity per unit time

$$\vec{a}(t) = \frac{\vec{v}(t + h/2) - \vec{v}(t - h/2)}{h} = \frac{\vec{f}}{m}$$

⇒

$$\left. \begin{aligned} \vec{v}(t + h/2) &:= \vec{v}(t - h/2) + \vec{a}(t)h \\ \vec{r}(t + h) &:= \vec{r}(t) + \vec{v}(t + h/2)h \\ t &:= t + h \end{aligned} \right\} \text{repeated}$$

- equivalent to Verlet (identical trajectory)
but: velocities at different time, different (by $\mathcal{O}(h^2)$) kinetic energy



Equivalence of Verlet and leap-frog

Leap-frog:

$$\left. \begin{aligned} v(t + h/2) &:= v(t - h/2) + a(t)h \\ r(t + h) &:= r(t) + v(t + h/2)h \\ t &:= t + h \end{aligned} \right\} \text{repeated}$$

2nd equation twice in 2 different times:

$$\begin{aligned} r(t + h) &= r(t) + v(t + h/2)h && \times + 1 \\ r(t) &= r(t - h) + v(t - h/2)h && \times - 1 \end{aligned}$$

Subtract both equations:

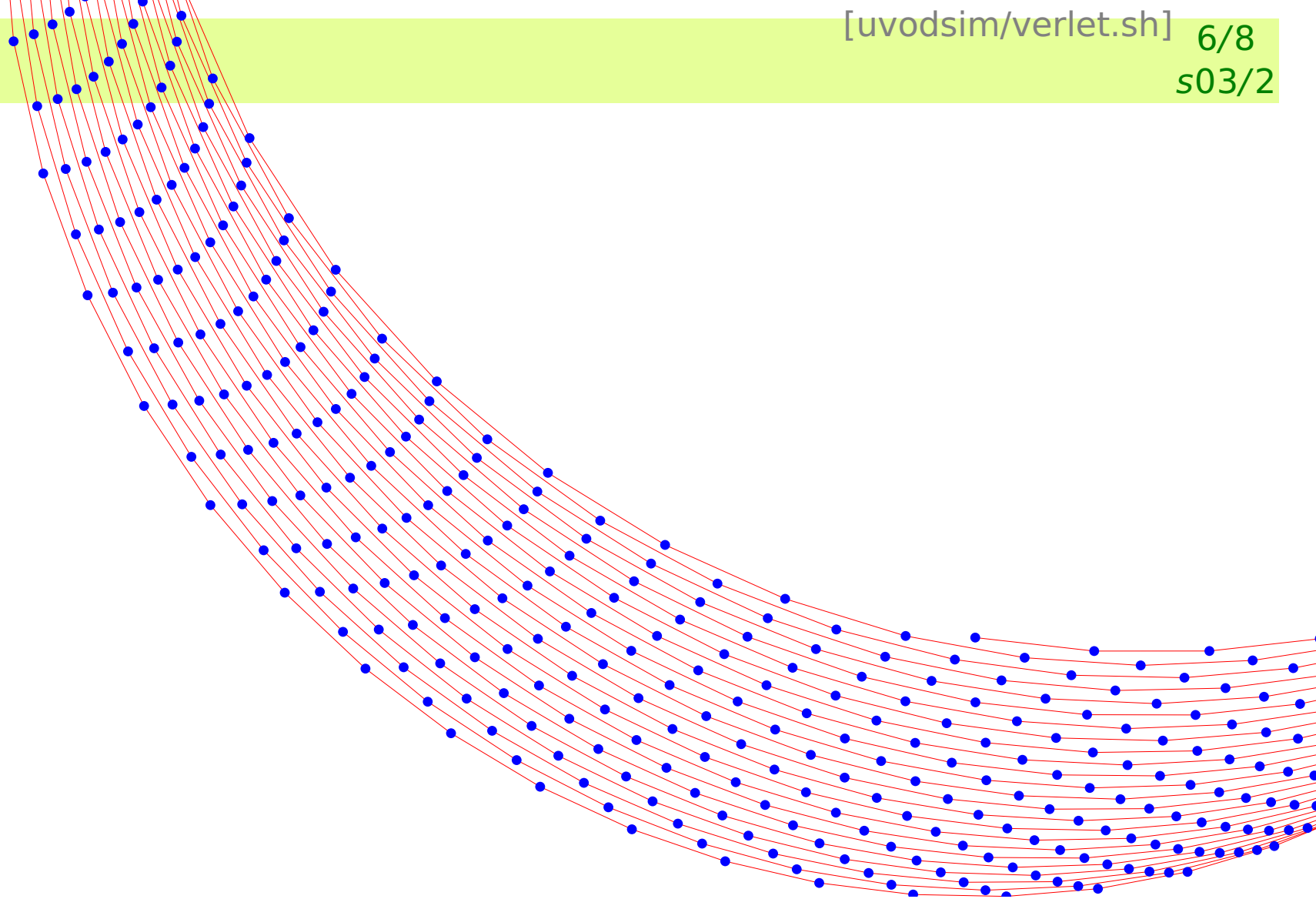
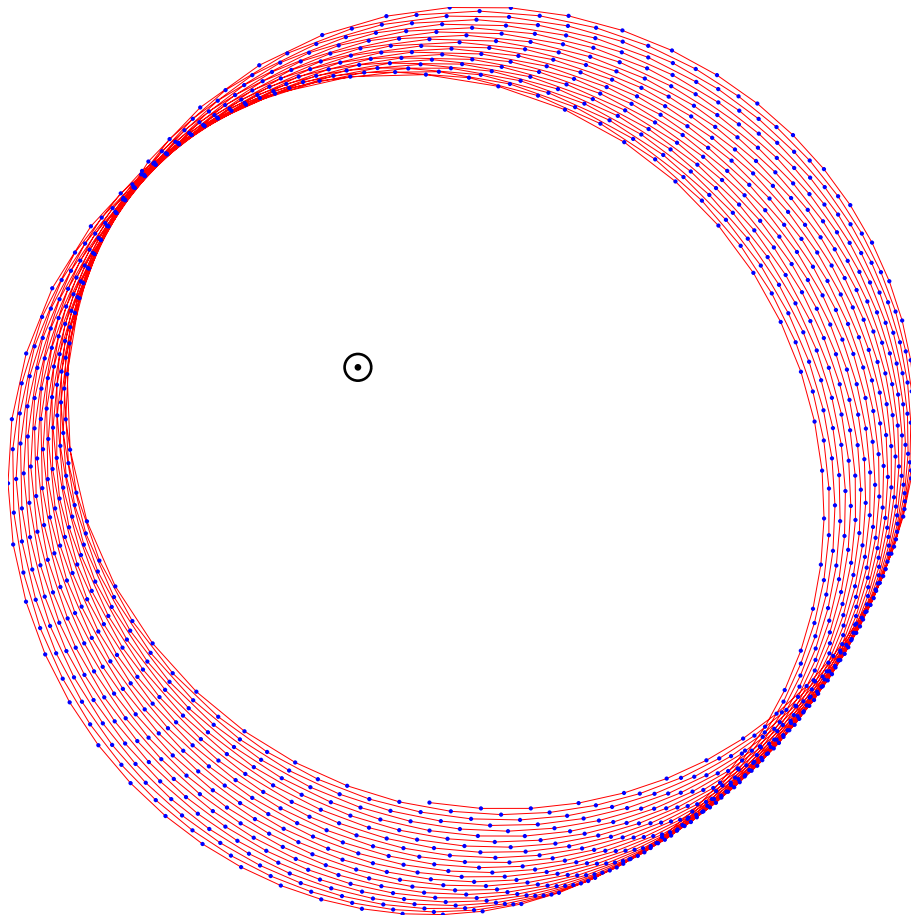
$$r(t + h) - r(t) = r(t) - r(t - h) + v(t + h/2)h - v(t - h/2)h$$

insert for the difference of velocities:

$$r(t + h) - 2r(t) + r(t - h) = h[v(t + h/2) - v(t - h/2)] = a(t)h^2 = \frac{f(t)}{m}h^2$$

which is the Verlet method

Example: planetary orbit



- energy is well conserved
- perihelion precession $\mathcal{O}(h^2)$
- harmonic oscillator: frequency shifted $\mathcal{O}(h^2)$

By methods of theoretical mechanics:

- expressing the position and momentum propagators in operator form
- some tricks to overcome their noncommutativity

we can derive the **velocity Verlet**:

$$r(t+h) = r(t) + v(t)h + \frac{f(t)h^2}{m} \frac{1}{2}$$
$$v(t+h) = v(t) + \frac{f(t) + f(t+h)h}{m} \frac{1}{2}$$

The same trajectory as Verlet with $v(t) = \frac{r(t+h) - r(t-h)}{2h} \dots$

kinetic energy differs from leap-frog by $\mathcal{O}(h^2)$

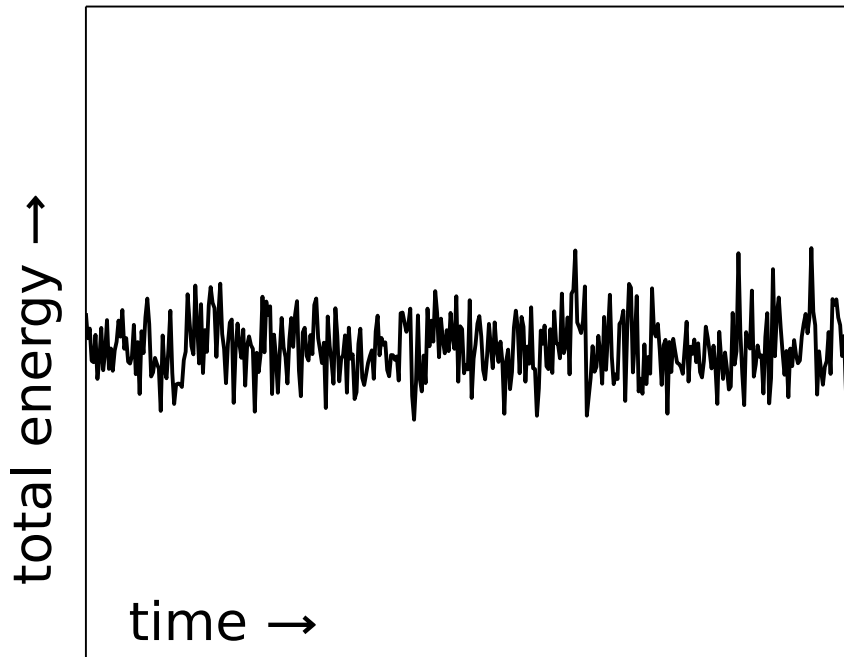
... but we can also learn a lot about energy conservation

What is this good for?

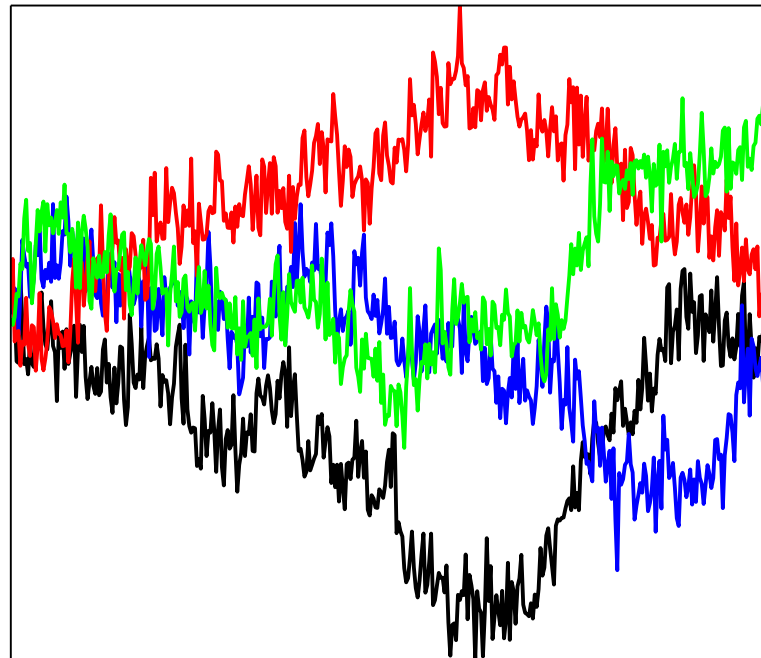
$$\exp(i\hat{L}_p h/2) \exp(i\hat{L}_r h) \exp(i\hat{L}_p h/2) = \exp(i\hat{L}h + \epsilon)$$

- error ϵ can be estimated ($\propto h^3$)
- we can calculate a “perturbed Hamiltonian” (error $\mathcal{O}(h^3)$ per step, $\mathcal{O}(h^2)$ globally), exactly constant with the Verlet method
i.e., Verlet is **symplectic** \Rightarrow error is bound
(time reversibility \Rightarrow only error $\propto t^{1/2}$)
- multiple-timestep methods and higher-order methods

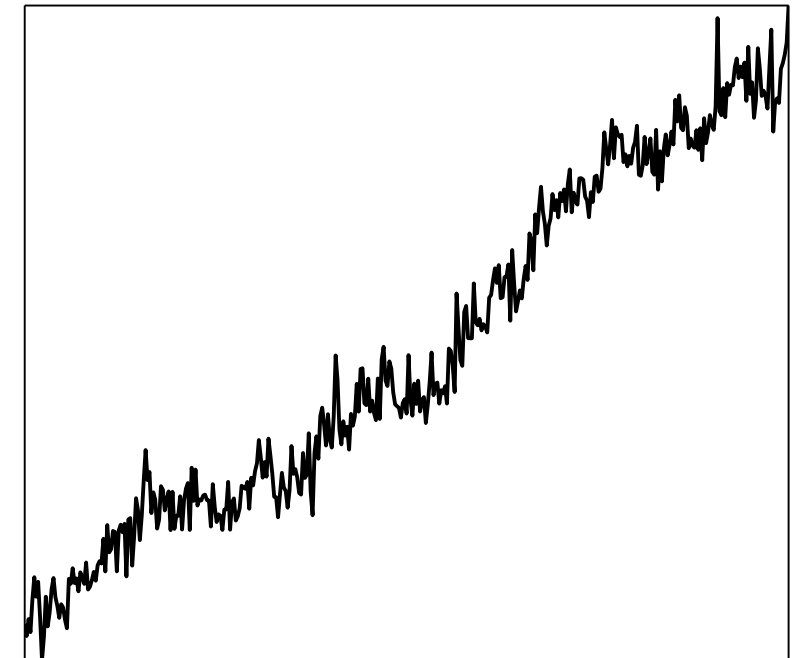
energy conservation error is used to set the timestep h



symplectic



reversible



irreversible