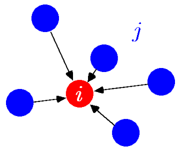
Molecular dynamics

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

Forces are needed:

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



Example – pair forces:

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

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

Newton’s equations of motion

$$\frac{\mathrm{d}^2\vec{r}_i}{\mathrm{d}t^2} = \ddot{\vec{r}}_i = \frac{\vec{f}_i}{m_i}, \qquad i = 1,\ldots,N$$

Method of finite differences, timestep h

Initial value problem: $\vec{r}$ and $\dot{\vec{r}}$ at time t_0 are known

Methods:

- Runge–Kutta: many evaluations of the right-hand side/step (costly!)
- Predictor–corrector: a bit better, rarely used
- Verlet and clones (symplectic = good energy conservation)
- Multiple timestep methods: more timescales (usually symplectic)
- Geometric integrators (symplectic)

Verlet method

Taylor expansion:

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

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

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

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

- ⊕ time-reversible ($\Rightarrow$ 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 (vector)

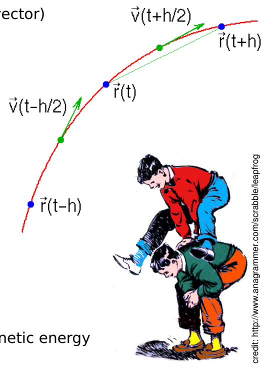
$$\vec{v}(t+h/2) = \frac{\vec{r}(t+h) - \vec{r}(t)}{h}$$

acceleration = change in velocity per unit time

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

$\Rightarrow$

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



- equivalent to Verlet (identical trajectory)
  but: velocities at different time, a bit 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:

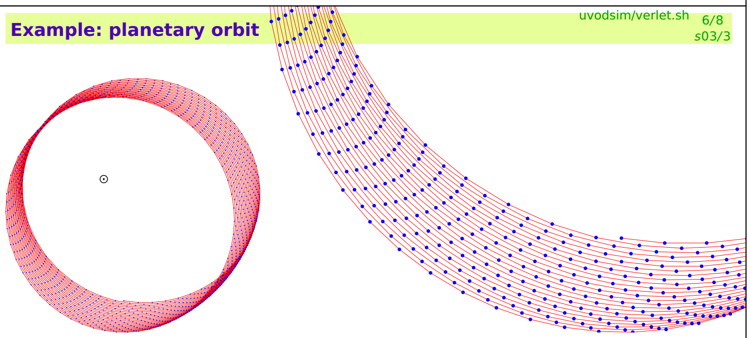
$$r(t+h) - r(t) = r(t) - r(t-h) + v(t+h/2)h - v(t-h/2)h$$

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 $\mathcal{O}(h^2)$

Verlet once again

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**:

$$\begin{aligned} r(t+h) &= r(t) + v(t)h + \frac{f(t)}{m}\frac{h^2}{2} \\ v(t+h) &= v(t) + \frac{f(t)+f(t+h)}{m}\frac{h}{2} \end{aligned}$$

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

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

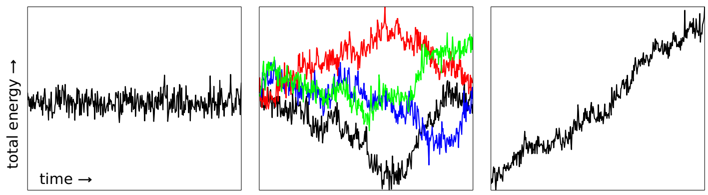
. . . but we can also learn a lot about energy conservation

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