Molecular dynamics

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

Forces:

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

Example—pair forces:

$$U = \sum_{i<j} u(r_{ij})$$

$\Rightarrow$

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

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

Newton's equations of motion

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

Method of finite differences, timestep h

Initial value problem: 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

Verlet method

Taylor ⇒:
$$\ddot{\vec{r}}_i(t) = \frac{\vec{r}_i(t-h) - 2\vec{r}_i(t) + \vec{r}_i(t+h)}{h^2} + O(h^2)$$

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

- ⊕ time-reversible (⇒ no energy drift); even symplectic
- ⊖ cannot use for $\ddot{r} = f(r, \dot{r})$: $\dot{r}(t)$ unknown at time t

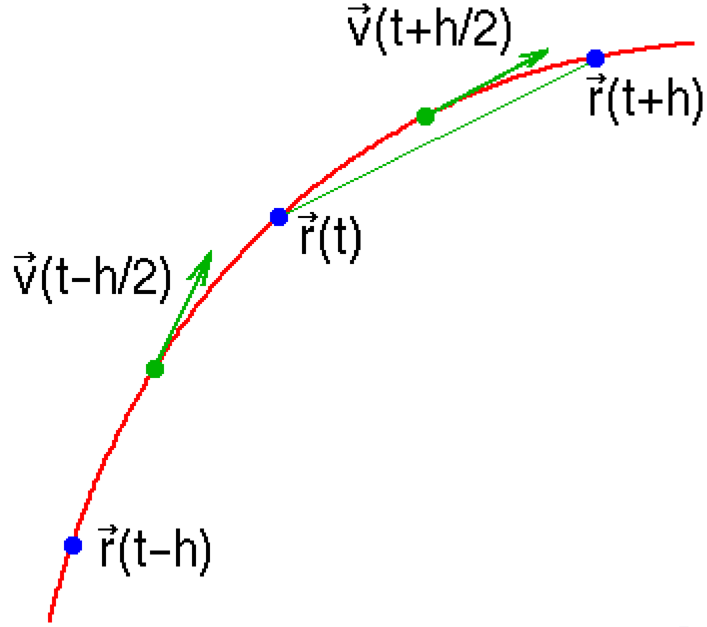
Identical trajectories (not necessarily velocities) given by:

- leap-frog (nest slide)
- velocity Verlet (see later this talk)
- Gear ($m = 3$) (next talk)
- 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

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

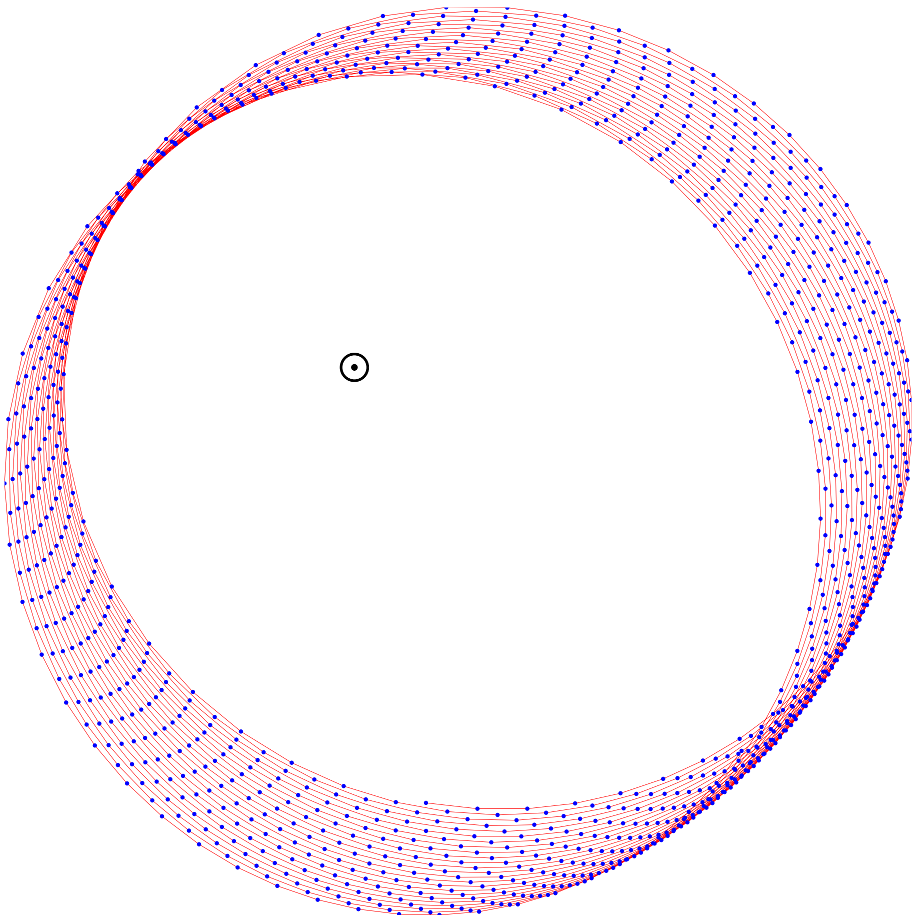
⇒

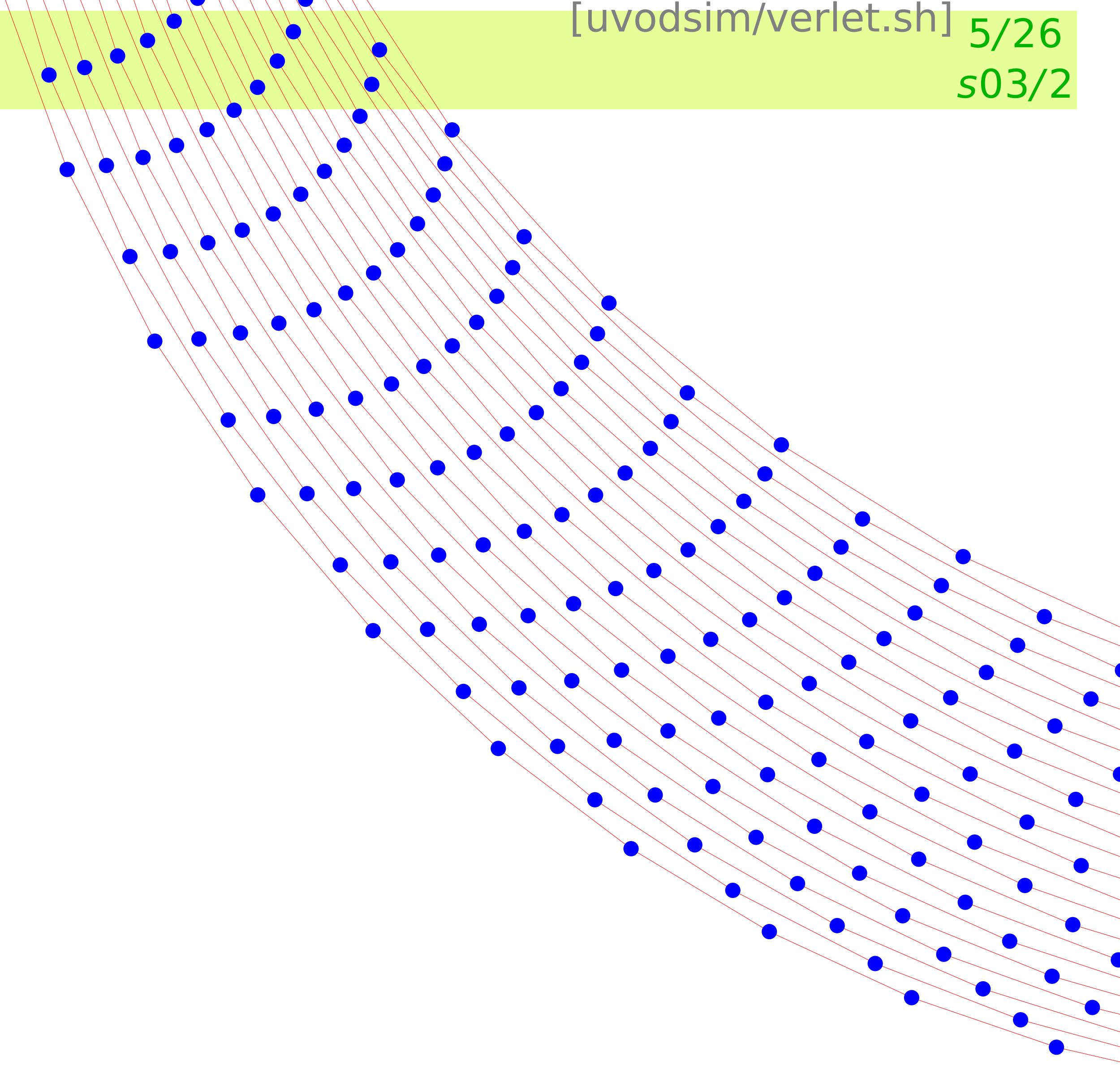
$$\left.\begin{aligned} \vec{v}(t+h/2) &:= \vec{v}(t-h/2) + \vec{a}(t)h \\ \vec{r}(t+h) &:= \vec{r}(t) + \vec{v}(t+h/2)h \\ t &:= t+h \end{aligned}\right\} \text{repeated}$$

credit: http://www.anagrammer.com/scrabble/leapfrog

- equivalent to Verlet
  but: velocities

Example: planetary motion





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 $v(t) = \dfrac{r(t+h) - r(t-h)}{2h}$

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

But we can also learn a lot about energy conservation ...
see the next slide

What is this complicated derivation 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 $\propto h^3$ per step, or $\propto h^2$ in a finite interval), exactly constant with the Verlet method
  i.e., Verlet is **symplectic** ⇒ error is constant
  (time reversibility ⇒ only error $\propto t^{1/2}$)
- higher-order methods
- multiple-timestep methods

Behavior of integrators →