

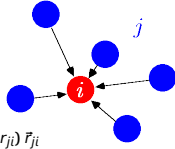
## Molecular dynamics

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- 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:

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

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

## Equivalence of Verlet and leap-frog

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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

## Newton's equations of motion

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

Method of finite differences, timestep  $h$

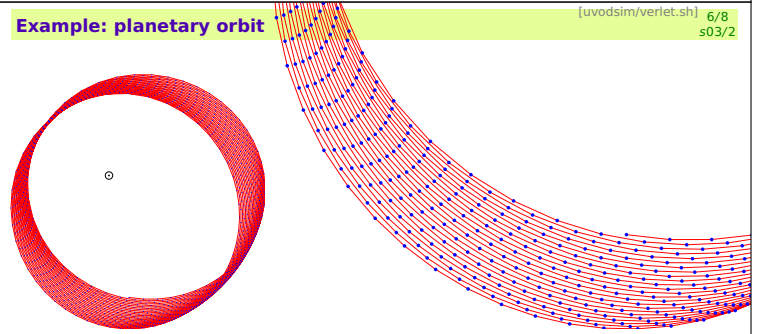
Initial value problem: we know  $\vec{r}$  and  $\dot{\vec{r}}$  at time  $t_0$

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

## Example: planetary orbit

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

## Verlet method

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Taylor expansion:

$$r(t-h) = r(t) - hr'(t) + \frac{h^2}{2}r''(t) - \dots \quad +1 \times$$

$$r(t) = r(t) \quad -2 \times$$

$$r(t+h) = r(t) + hr'(t) + \frac{h^2}{2}r''(t) + \dots \quad +1 \times$$

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

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

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

- ⊕ time-reversible ( $\Rightarrow$  no energy drift); even symplectic
- cannot use for  $\vec{r} = \vec{r}(t, \vec{r})$  because  $\dot{r}(t)$  is not known at time  $t$

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

## Verlet once again

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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**:

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

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

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

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

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

## Leap-frog

[start movies/leap-frog.mp4] 4/8  
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velocity = displacement (change in position)  
per unit time ( $h$ ), a vector

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

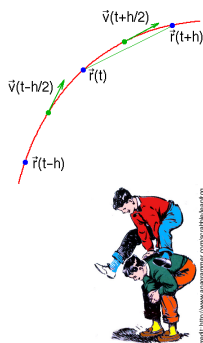
acceleration = change in velocity per unit time

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

$\Rightarrow$

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

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



## What is this good for?

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

- error  $\epsilon$  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  $h$

