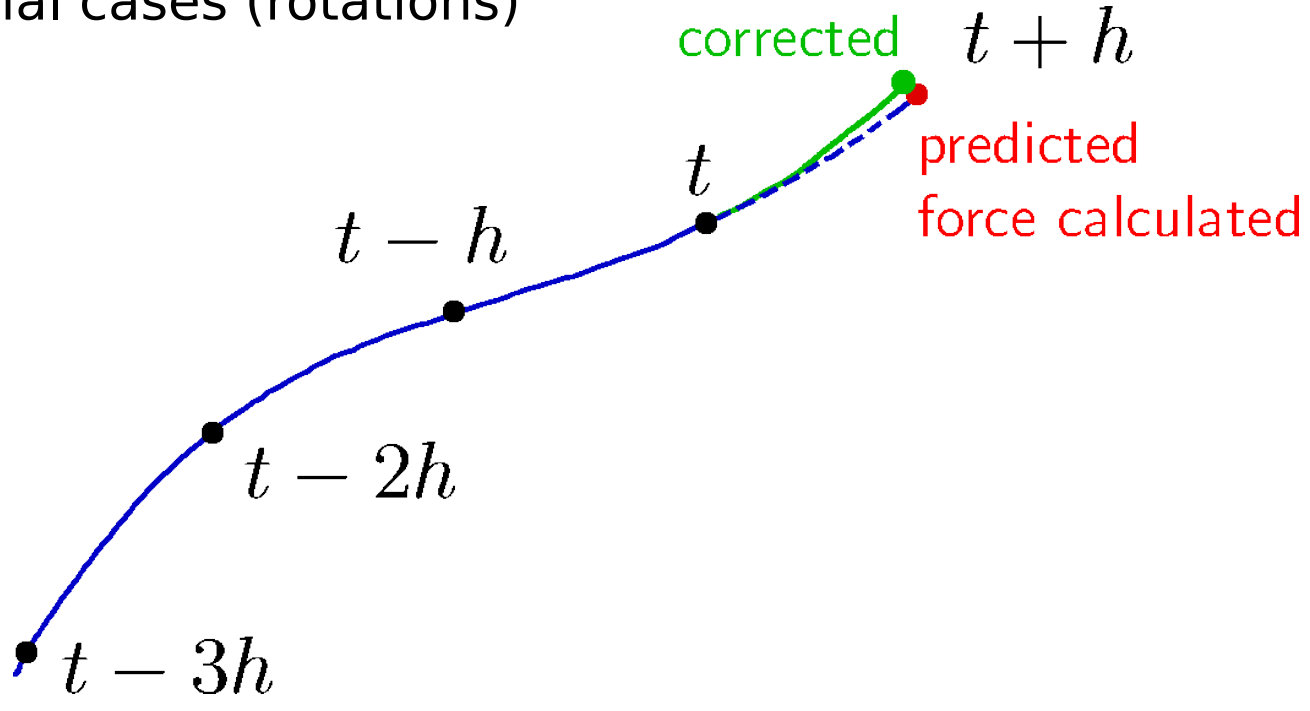
Gear methods

- **Predictor-corrector** type: knowledge of history is used to predict an approximate solution, which is made more accurate (and stable) in the following step
- Gear uses polynomial predictor = no additional costly evaluation of the right-hand side . . . but poor stability
- Methods are not time reversible* but have higher order
- Useful in special cases (rotations)



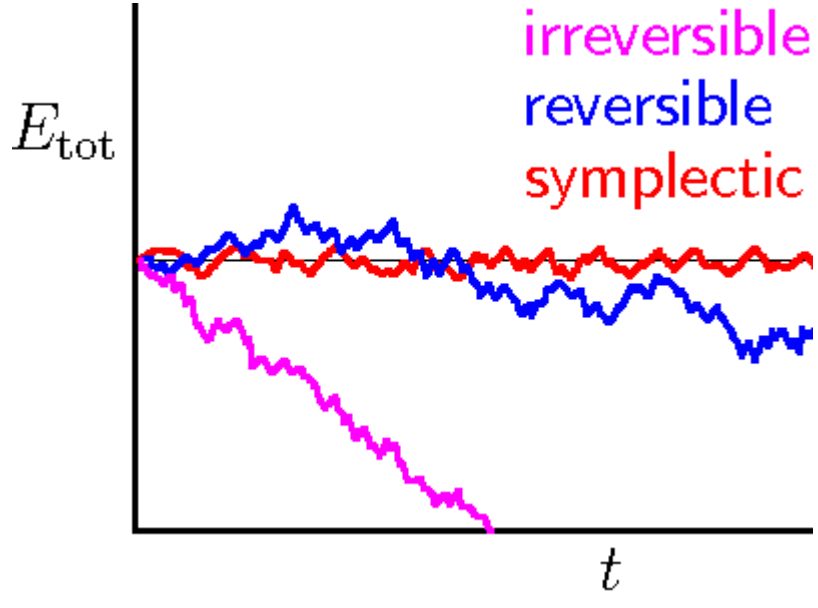
*Except one version of the simplest singular 2nd order method

Comparison of methods

Verlet:

- ⊕ is time-reversible ⇒ no drift in the total (potential + kinetic) energy
- ⊕ is symplectic ⇒ error in the total energy is bound
- ⊕ is simple
- ⊖ low order (phase error)
- ⊖ (directly) not applicable to a r.h.s. containing velocities (equation $\ddot{r} = f(r, \dot{r})$: Nosé–Hoover, rotations)
- ⊖ difficult change of the timestep

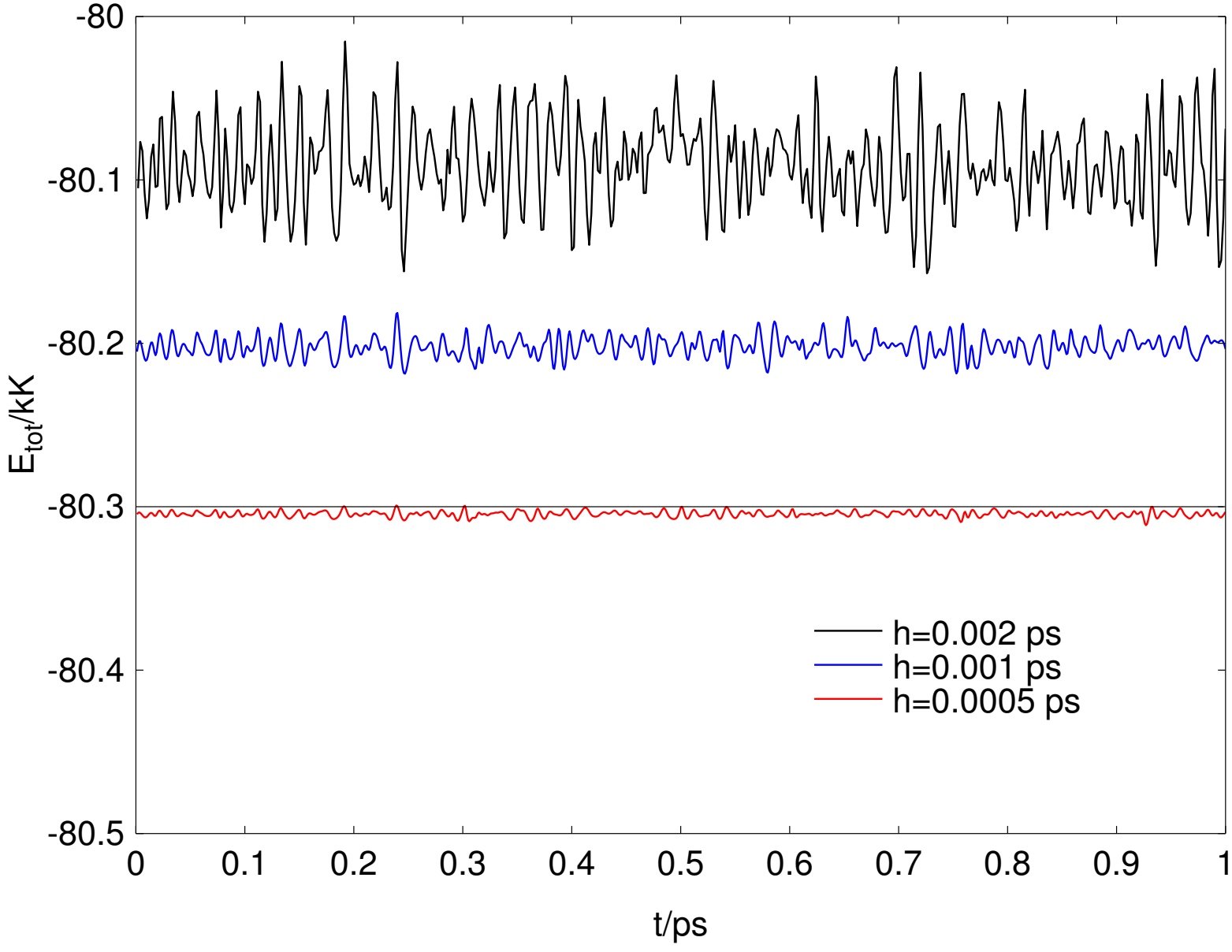
Gear: and similar: just opposite



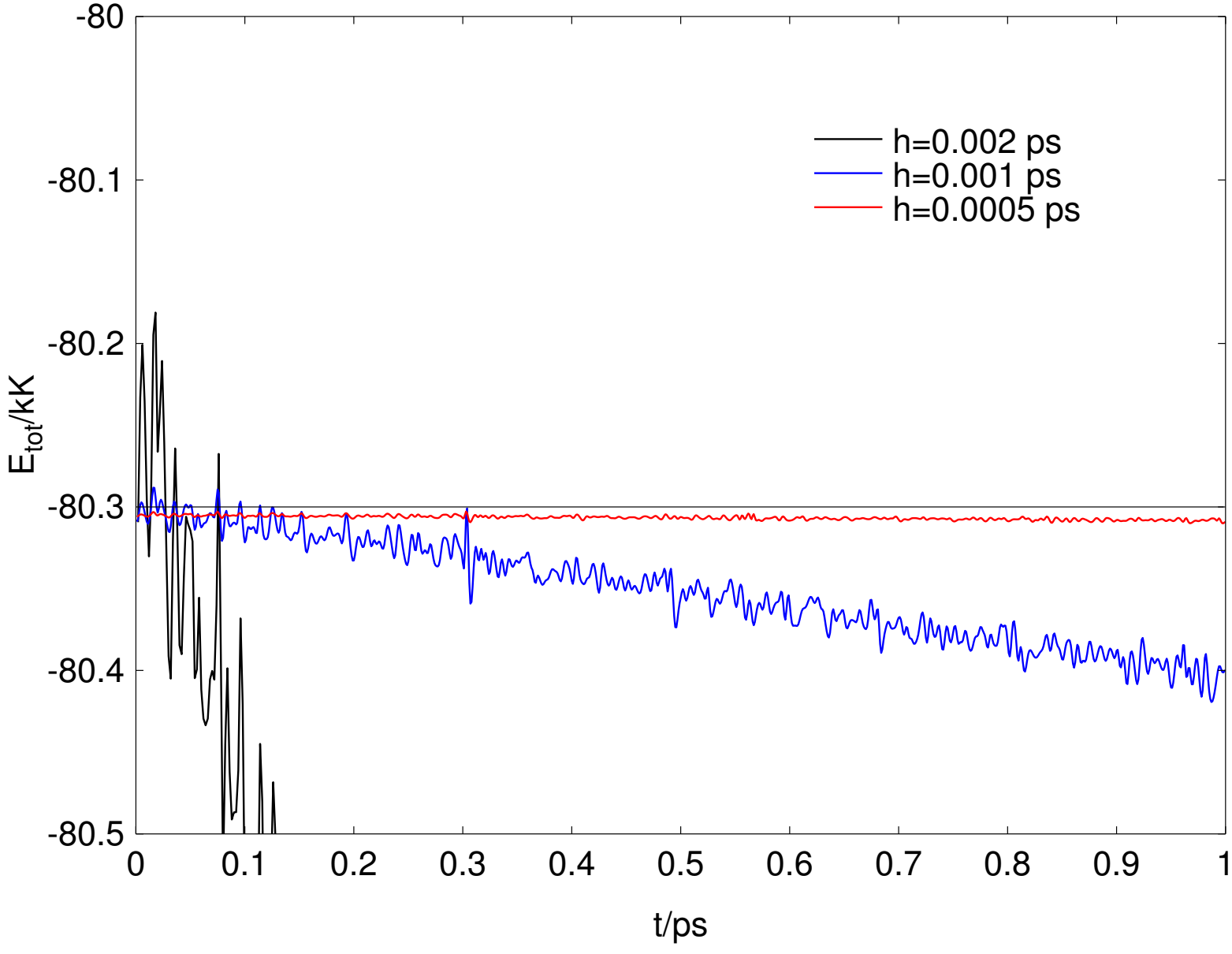
Notes:

- a symplectic integerator preserves (with bounded accuracy) the phase space volume $\mathrm{d}\vec{r}^N \mathrm{d}\vec{p}^N$
- the quality of energy conservation helps us to set up the timestep h

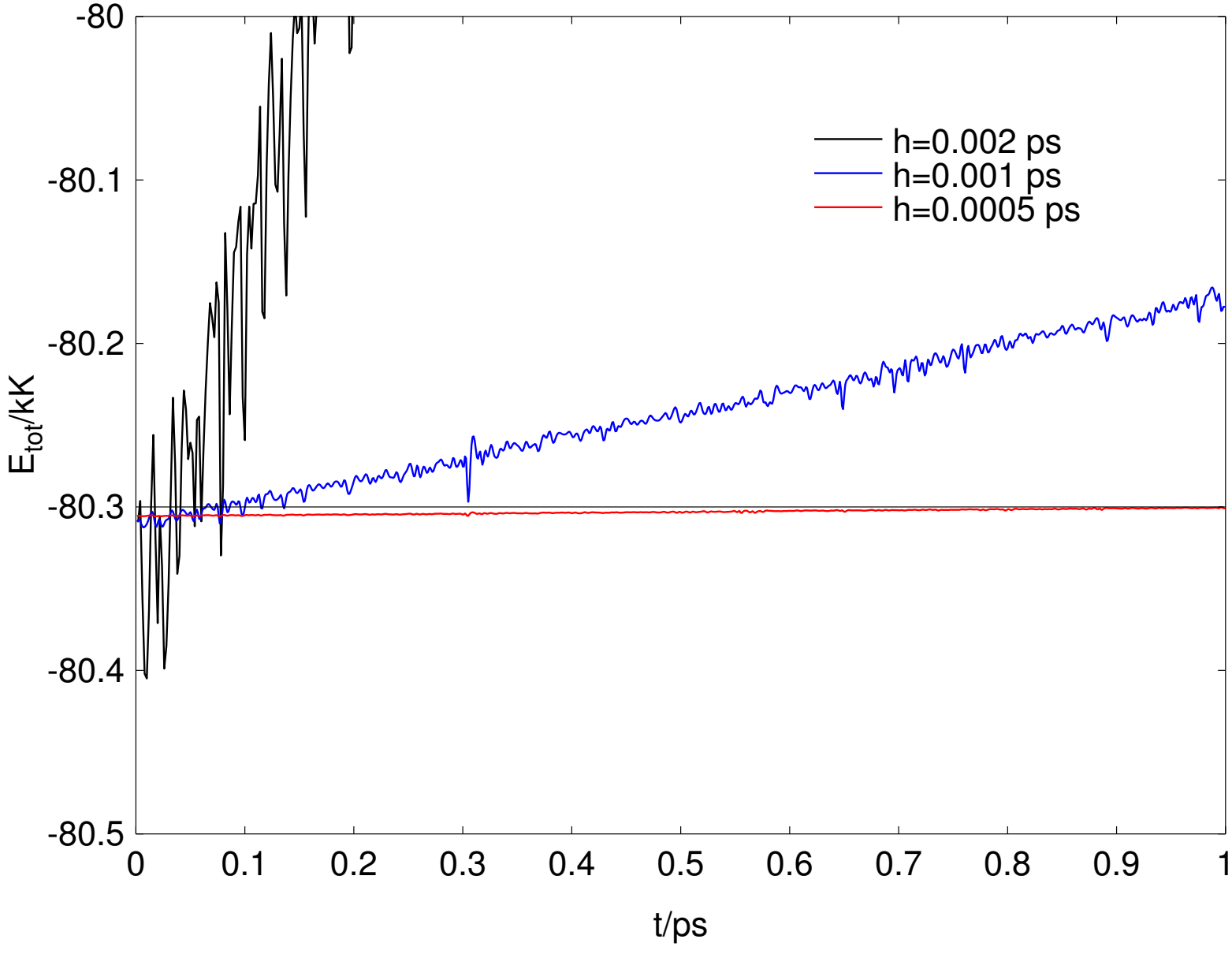
Energy conservation: Verlet



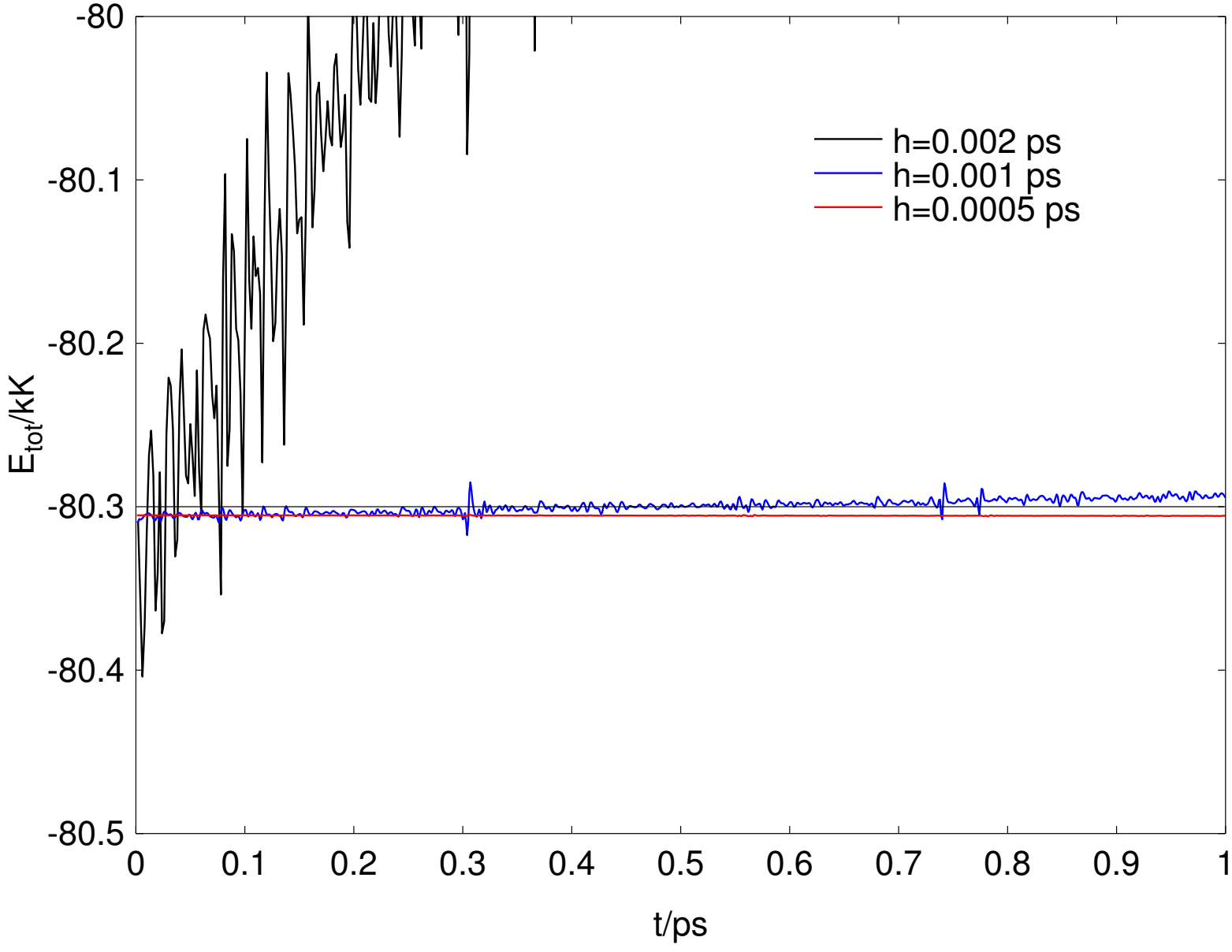
Energy conservation: Gear $M = 4$



Energy conservation: Gear $M = 5$



Energy conservation: Gear $M = 6$



Temperature

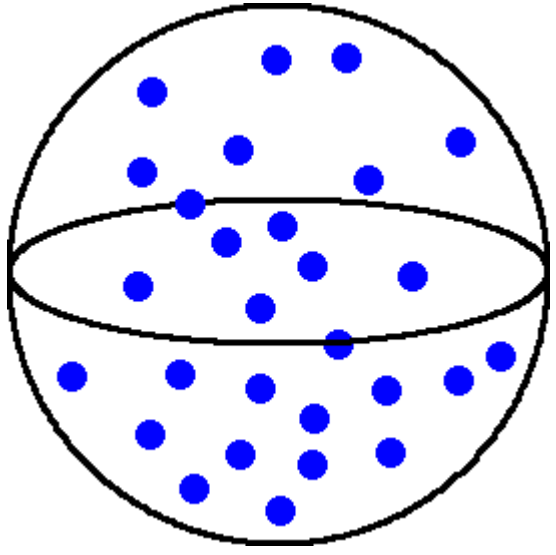
The temperature is **measured** in the standard (microcanonical) MD.

$$T = \left\langle \frac{E_{\mathrm{kin}}}{\frac{1}{2}k_{\mathrm{B}}f} \right\rangle = \langle T_{\mathrm{kin}} \rangle$$

$f = 3N - f_{\mathrm{conserved}} \approx 3N$

Example: molecules in a spherical cavity:

$$f_{\mathrm{conserve}} = 1_{\mathrm{energy}} + 3_{\mathrm{rotations}}$$



NOTE: the averaged kinetic temperature should not depend on (a subset of) the degrees of freedom used. Typically, one may easily separate:

- T_{tr} from the velocities of the centers of mass
- $T_{\mathrm{rot+in}}$ from rotations and internal degrees of freedom.
- disagreement $T_{\mathrm{tr}} \neq T_{\mathrm{rot+in}}$ indicates various problems (bad equilibration, too long timestep, . . .).

Constant temperature in MD: methods

not canonical (do not give the canonical ensemble)

- velocity rescaling: $\vec{v}_{i,\mathrm{new}} = \vec{v}_i (T/T_{\mathrm{kin}})^{1/2}$
- Berendsen (friction): $\vec{v}_{i,\mathrm{new}} = \vec{v}_i (T/T_{\mathrm{kin}})^{q}$, $q < 1/2$,

  is equivalent to: $\ddot{\vec{r}}_i = \dfrac{\vec{f}_i}{m_i} - \eta(T_{\mathrm{kin}} - T)\dot{\vec{r}}_i,\ \eta = \dfrac{q}{Th}$

canonical deterministic:

- Nosé–Hoover: one (or more) degrees of freedom added, averaging it ⇒ canonical ensemble. Problem: tricks needed with Verlet (r.h.s. depends on velocities)
- Modified Berendsen

canonical stochastic:

- Maxwell–Boltzmann: once a while the velocties of particles are drawn from the Maxwell–Boltzmann distribution, $\pi(\dot{x}_i) = \exp(-\dot{x}^2/2\sigma^2)/\sigma\sqrt{2\pi},\ \sigma^2 = k_{\mathrm{B}}T/m_i$
- Andersen: randomly visit particles (usually better)
- Langevin: small random force added to all particles at every step
- Canonical sampling through velocity rescaling (Bussi, Donadio, Parrinello)
- Gaussian rescaling: $E_{\mathrm{kin}} = \mathrm{const}$, canonical in the configurational space only

Nosé–Hoover thermostat

- one degree of freedom added: “position” s and “velocity” $\dot{s}$
- + kinetic energy $\frac{M_s}{2}\dot{s}^2$
- + potential energy $-f k_\mathrm{B} T \ln s$

⋮

Equations of motion ($\xi = \ln s$):

$$\begin{aligned} \ddot{\vec{r}}_i &= \frac{\vec{f}_i}{m_i} - \dot{\vec{r}}_i \dot{\xi} \\ \ddot{\xi} &= \left(\frac{T_\mathrm{kin}}{T} - 1 \right) \tau^{-2} \end{aligned}$$

Thermostat time constant:

$$\tau = \sqrt{\frac{M_s}{f k_\mathrm{B} T}}$$

Provided that the system is ergodic, it can be proven that we get the canonical ensemble

Thermostats

Nosé–Hoover

- ⊕ canonical
- ⊕ high quality
- ⊕ good also for small systems (N-H chain)
- ⊖ oscillations, decoupling (fine tuning of τ)
- ⊖ worse for start
- ⊖ equations of motion w. velocities

Berendsen

- ⊕ simple
- ⊕ exponential relaxation (i.e., good also for start)
- ⊖ flying icecube
- ⊖ not canonical
- ⊖ poor for small systems

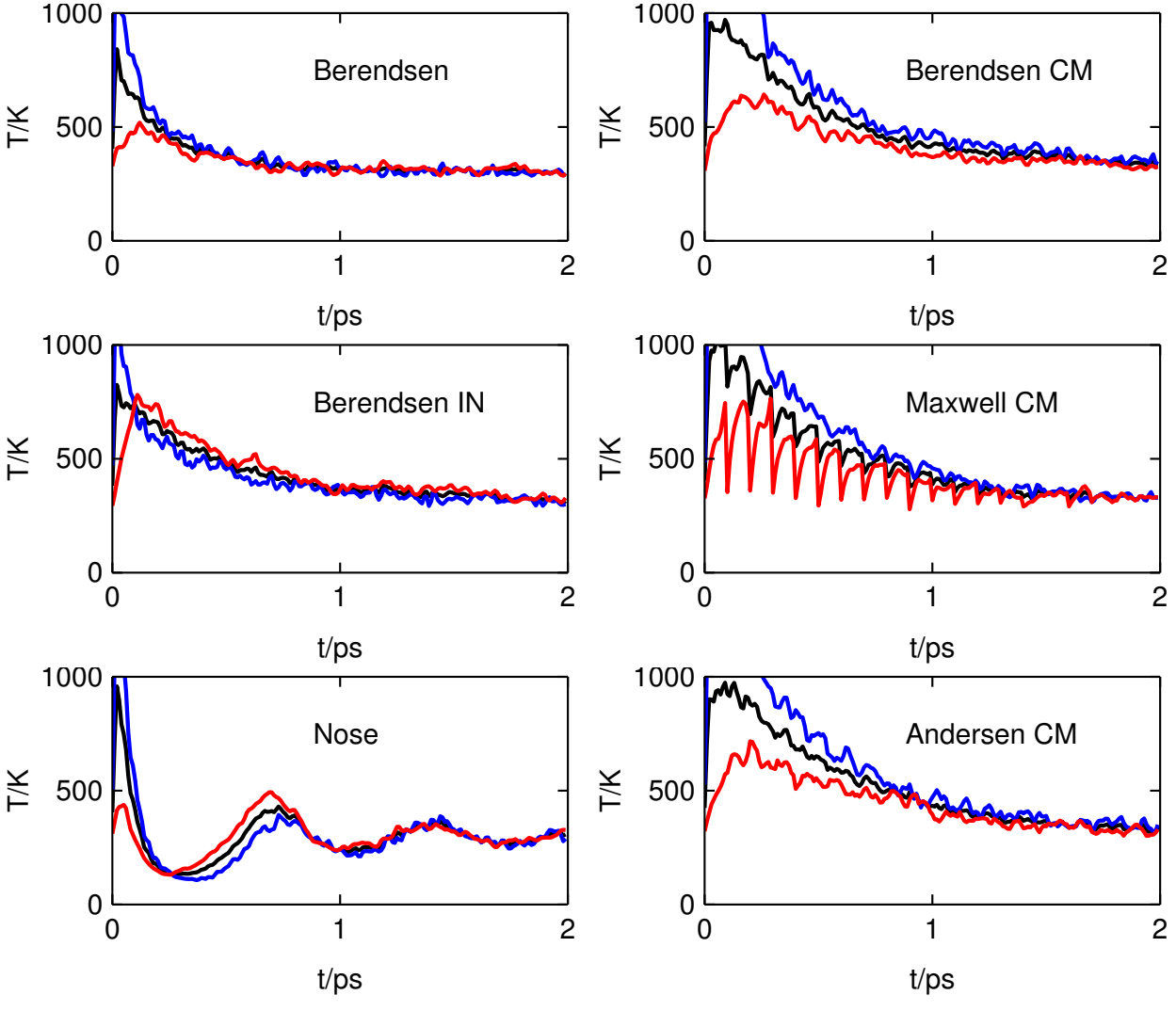
Maxwell–Boltzmann etc.

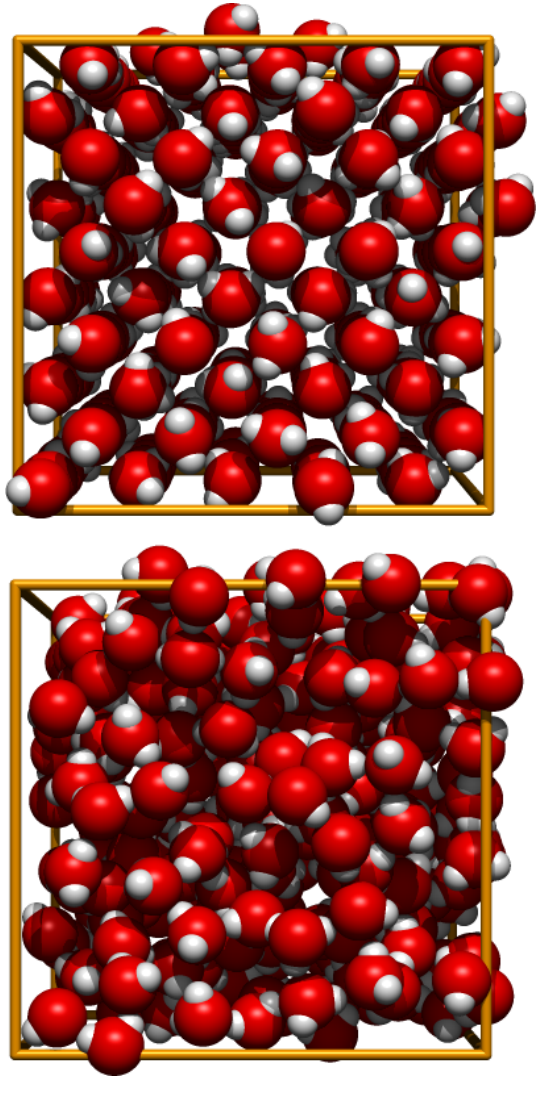
- ⊕ canonical
- ⊕ exponential relaxation
- ⊖ kinetics lost
- ⊖ problematic with constrained dynamics

for me:
Show flying icecube simolant: periodic b.c., τ = min, lower ρ, max. speed
old simolant: periodic b.c., N=100, L=40, hot key '=', tau=0.2

Thermostats: application to water

250 molecules of SPC/E water started from an fcc lattice of randomly oriented molecules, $\tau = 0.1$ ps





see simul/spce/water.*

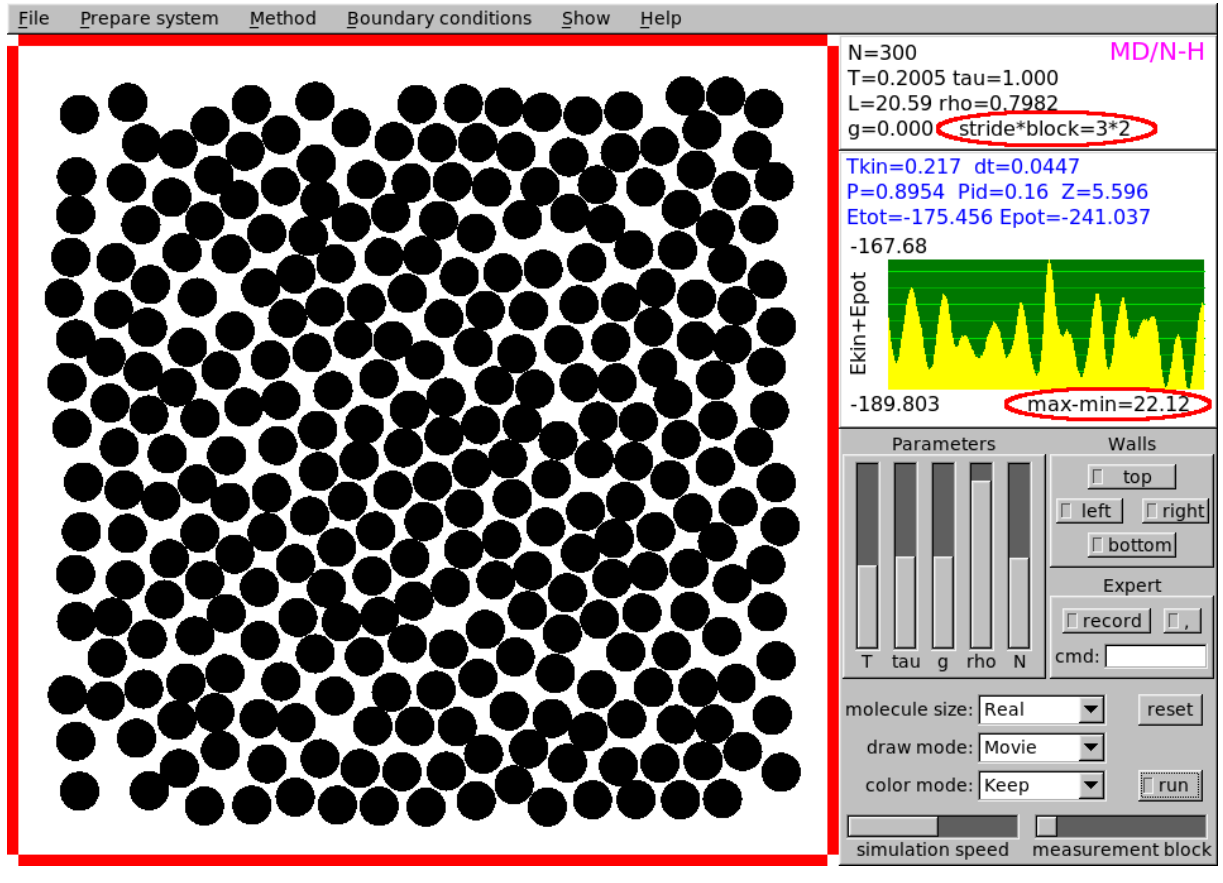
T: — total — center-of-mass — rotations

Try molecular dynamics by yourself

Installation of SIMOLANT (Windows):

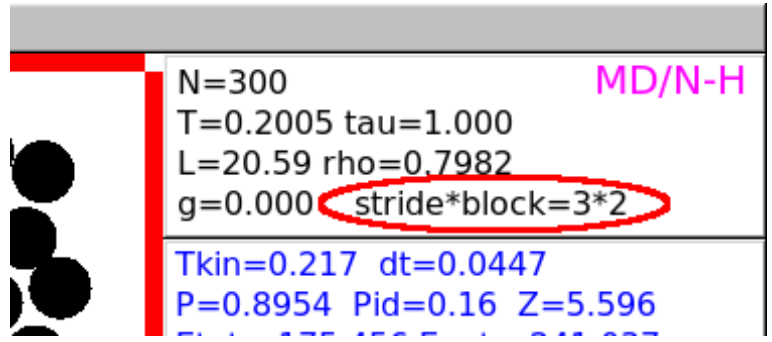
- http://old.vscht.cz/fch/software/simolant
- Download `simolant-win32.zip`
- Create a folder and unpack SIMOLANT there.

  Do not run directly from `simolant-win32.zip`
  – help would not work
  – you could not find saved files
- Run `simolant.exe`.



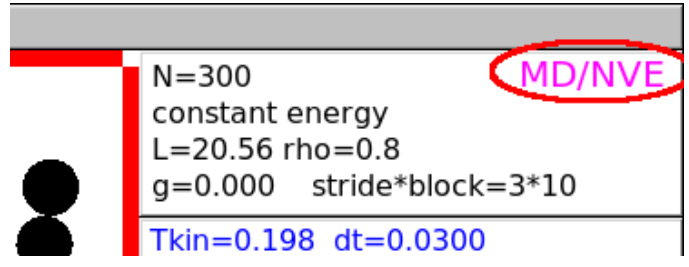
Watch energy conservation by yourself

- Slider “measurement block” to the left (1–3 values averaged per 1 point shown)
- The default is one energy calculated per 3 MD steps (stride). This can be changed by slider “simulation speed”.



- if still too slow, decrease the number of particles by slider “N”
- Menu: Show → Energy convergence profile
  The time development of energy is always scaled from minimum to maximum:
  Note the value of max-min reported
  Reset the graph by button reset

- Menu: Method → Molecular dynamics (NVE)
  – write “dt=0.01” to the cmd: [ ] field
  – write “dt=0.02” to the cmd: [ ] field
  and observe the difference
  – for too long dt, the simulation will switch to MC to avoid crash
  – do not forget to return the default (automatic setup) by “dt=0”



Try thermostats by yourself

- Menu: Method → Molecular dynamics (Berendsen thermostat)
  – observe the total energy
  – what happens if you change temperature?
  – what happens if you change the correlation time (slider τ)?
  Do not change the parameters too fast!
- Repeat for other thermostats.
- Repeat for different samples; e.g., liquid:
  slider "T": $T \approx 0.2$
  slider "ρ": $\rho \approx 0.6$