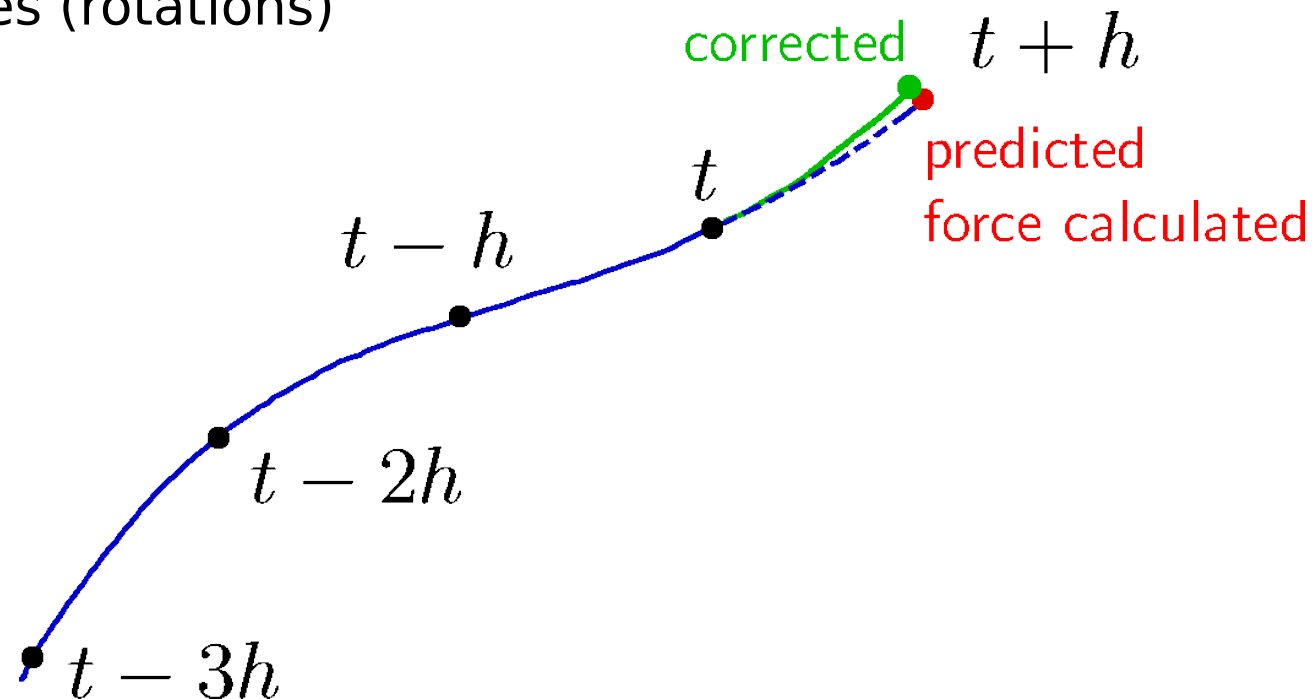


Gear's methods

- **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's methods use a 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 equivalent to Verlet

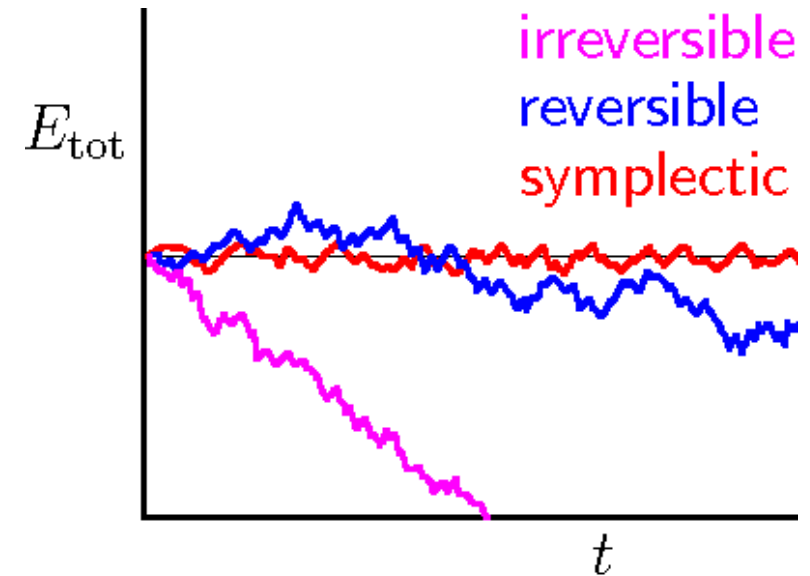
Verlet:

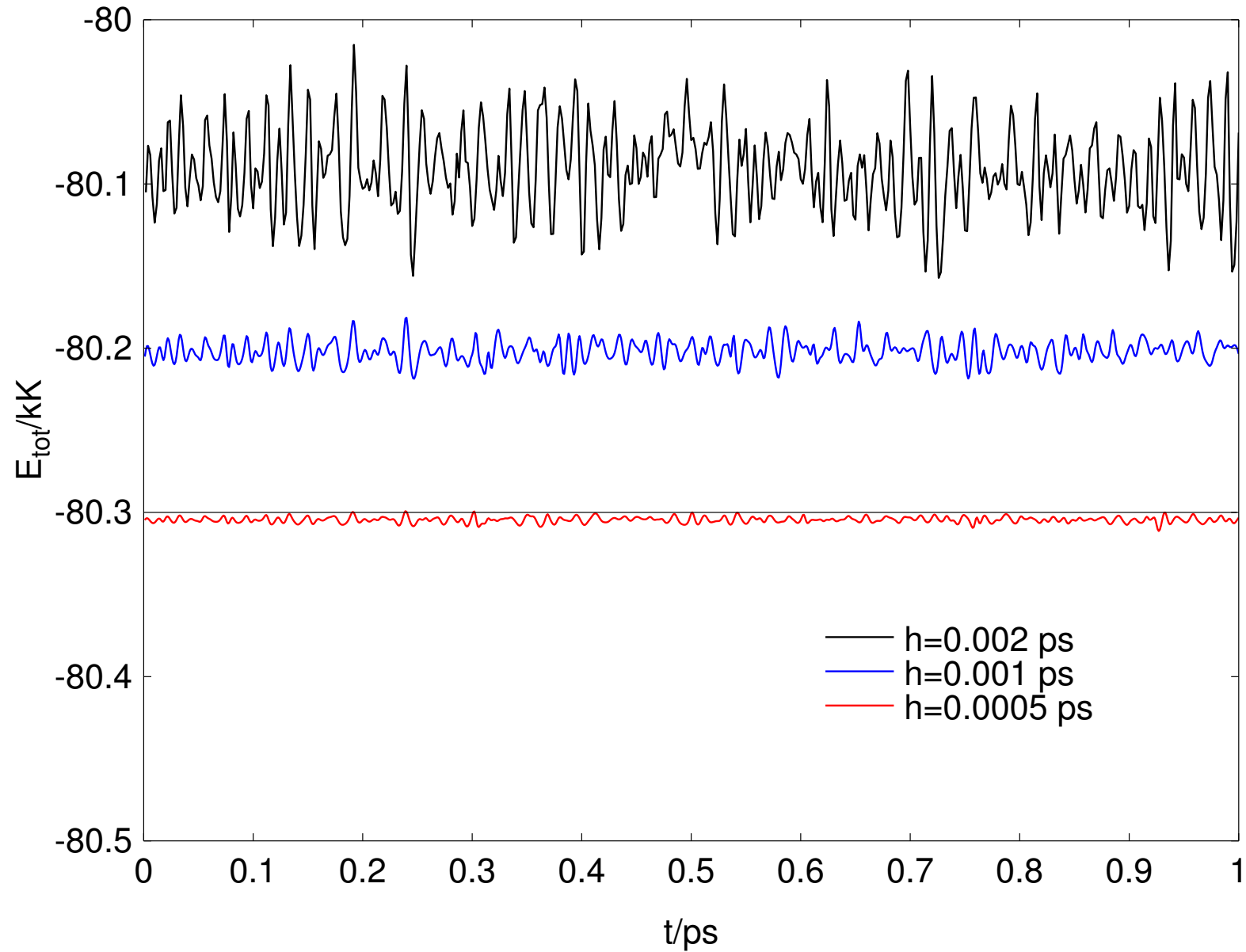
- ⊕ is time-reversible \Rightarrow no drift in the total (potential + kinetic) energy
- ⊕ is symplectic \Rightarrow error in the total energy is bound
- ⊕ is simple
- ⊖ low order (phase error)
- ⊖ (directly) not applicable to a r.h.s. containing velocities (equation $\ddot{r} = f(r, \dot{r})$: Nosé–Hoover,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

Gear: and similar: just opposite

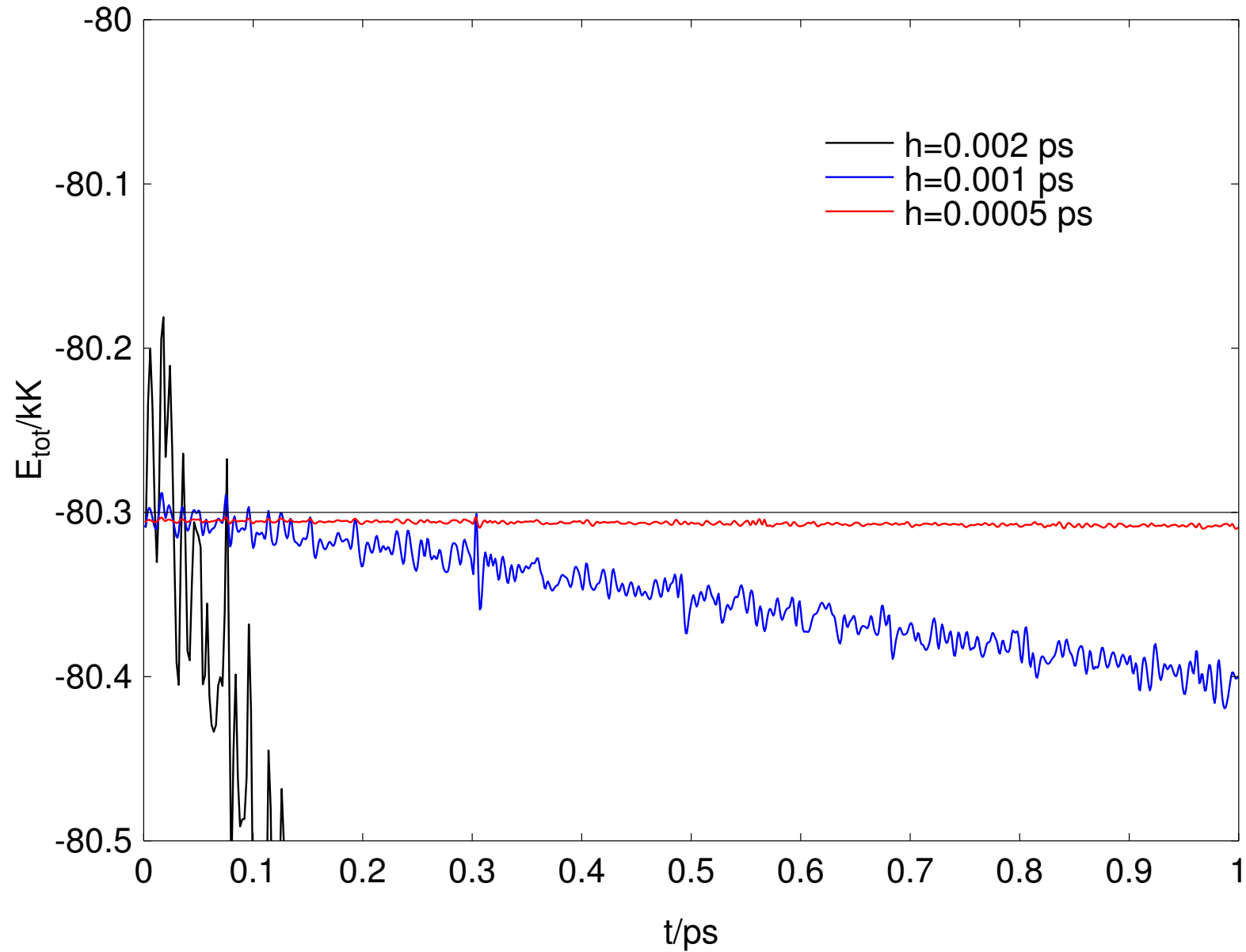
Notes:

- a symplectic integrator preserves (with bounded accuracy) the phase space volume $d\vec{r}^N d\vec{p}^N$
- is a subset of geometric integrators preserving flow of phase-space volume
- the quality of energy conservation helps us to set up the timestep h

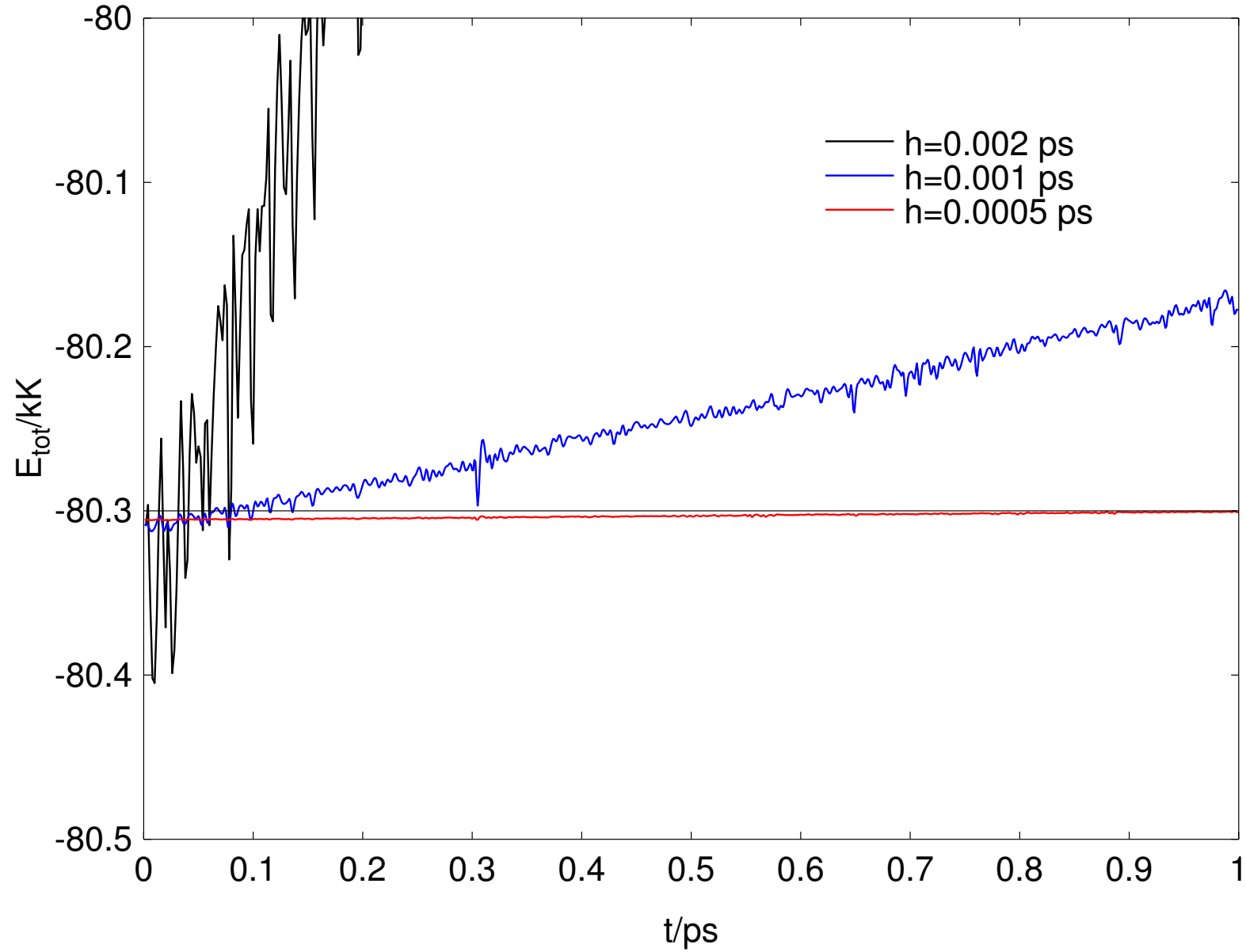




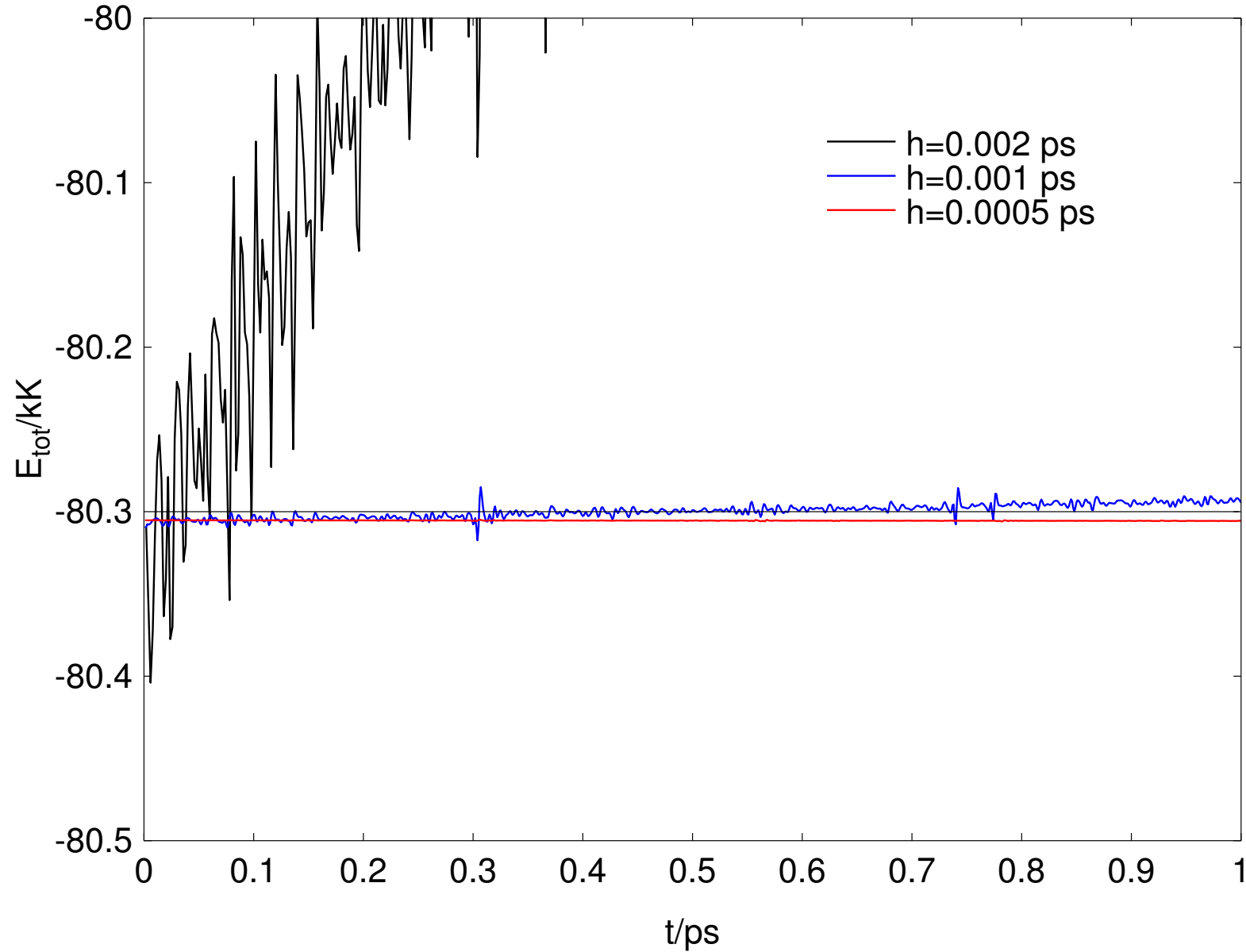
Energy conservation: Gear $M = 4$



Energy conservation: Gear $M = 5$



Energy conservation: Gear $M = 6$



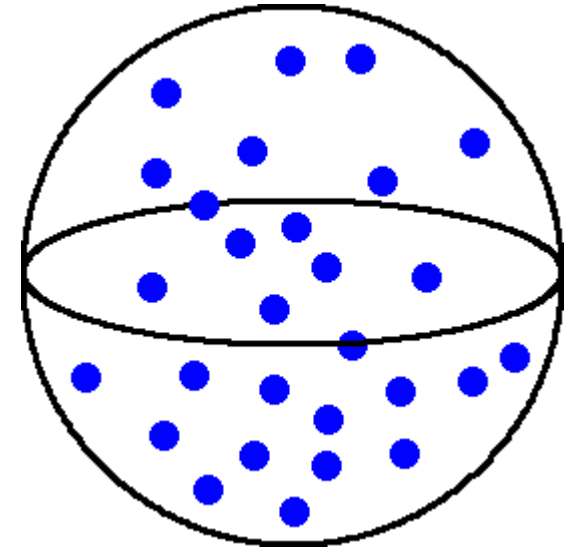
The temperature is **measured** in the standard (microcanonical) MD.

$$T = \left\langle \frac{E_{\text{kin}}}{\frac{1}{2}k_B f} \right\rangle = \langle T_{\text{kin}} \rangle$$

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

Example: molecules in a spherical cavity:

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



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

not canonical (do not give the canonical ensemble)

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

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

canonical deterministic:

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

canonical stochastic:

- Maxwell–Boltzmann: once a while the velocities of particles are drawn from the Maxwell–Boltzmann distribution, $\pi(\dot{x}_i) = \exp(-\dot{x}^2/2\sigma^2)/\sigma\sqrt{2\pi}, \sigma^2 = k_B T/m_i$
- 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: $E_{\text{kin}} = \text{const}$, canonical in the configurational space only

● one degree of freedom added: “position” s and “velocity” \dot{s}

● + kinetic energy $\frac{M_s}{2}\dot{s}^2$

● + potential energy $-fk_B T \ln s$

⋮

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

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

Thermostat time constant:

$$\tau = \sqrt{\frac{M_s}{fk_B T}}$$

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

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

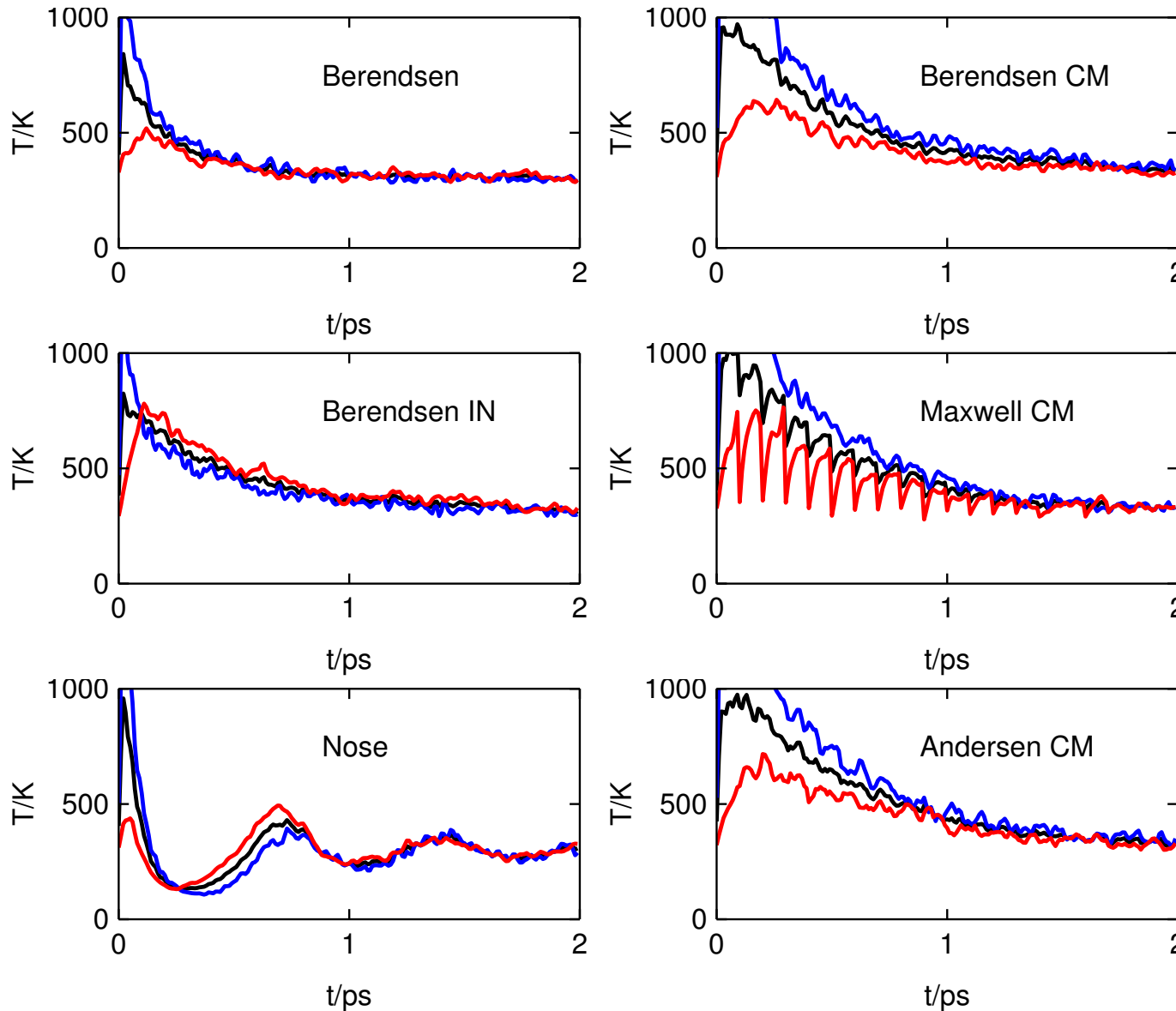
- ⊕ simple
- ⊕ exponential relaxation (i.e., good also for start)
- ⊖ flying icecube
- ⊖ not canonical
- ⊖ poor for small systems

Maxwell-Boltzmann etc.

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

Thermostats: application to water

2 ps trajectory started from 250 randomly oriented SPC/E water molecules at fcc lattice



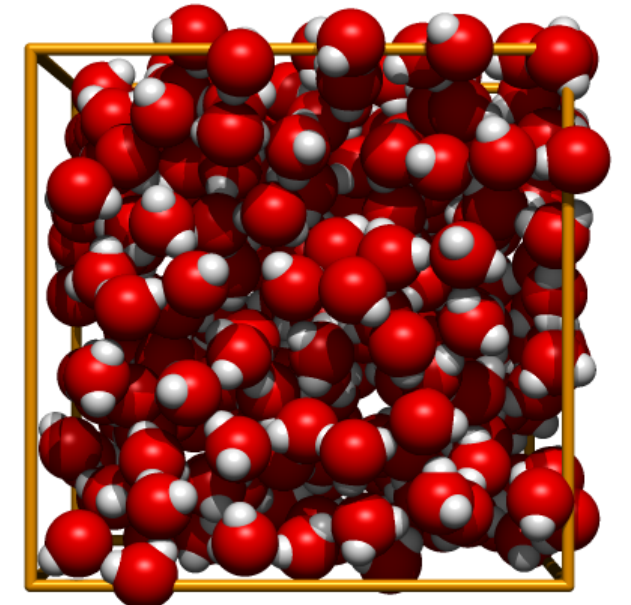
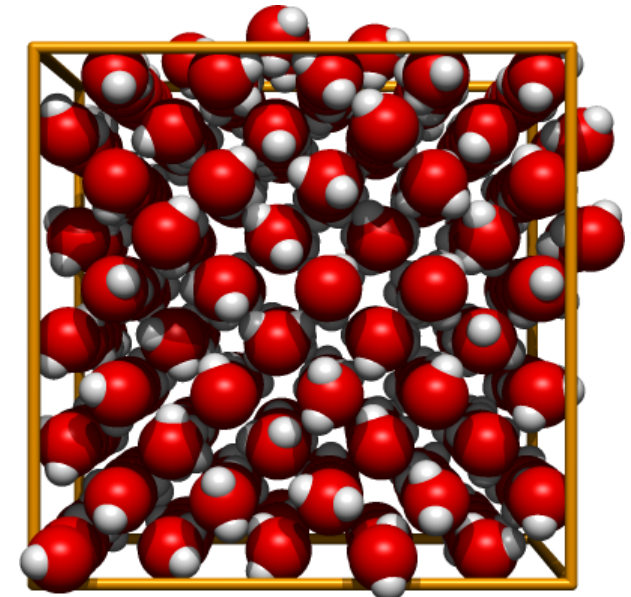
$\tau = 0.1$ ps

T :

— total

— center-of-mass

— rotations



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

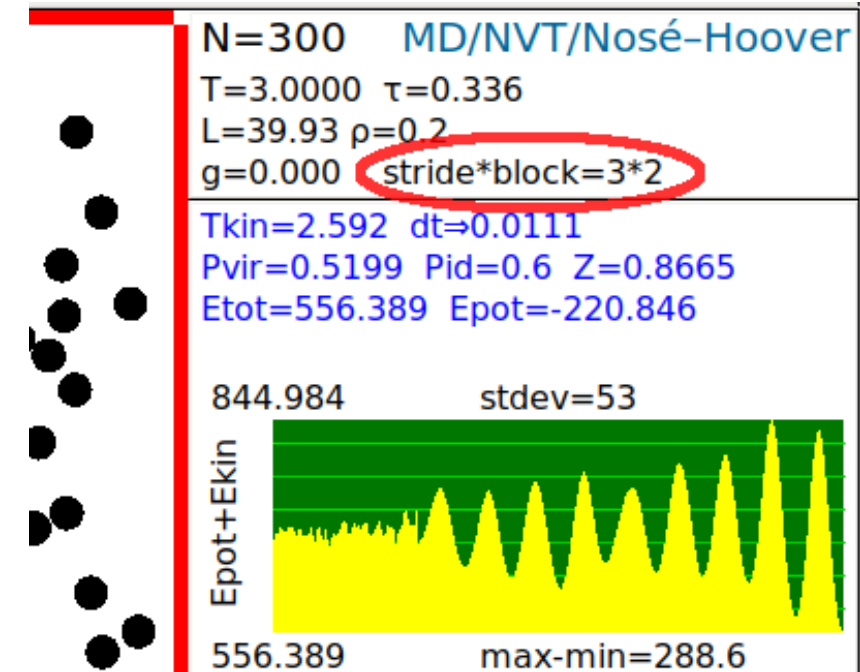
● Run `simolant.exe`.

● Also supported: linux, MacOS

The screenshot displays the SIMOLANT software interface. The main window shows a simulation of a system of particles, represented by black circles, arranged in a roughly rectangular shape. The interface includes a menu bar at the top with options: File, Prepare system, Method, Boundary conditions, Show, Help. On the right side, there is a panel with simulation parameters and a graph. The parameters are: N=300, T=0.2005, tau=1.000, L=20.59, rho=0.7982, g=0.000, and stride*block=3*2. The graph shows Ekin+Epot vs time, with a maximum value of 22.12 and a minimum value of -189.803. Below the graph, there are sections for Parameters (T, tau, g, rho, N), Walls (top, left, right, bottom), Expert (record, cmd:), molecule size (Real), draw mode (Movie), and color mode (Keep). At the bottom, there are buttons for simulation speed and measurement block.

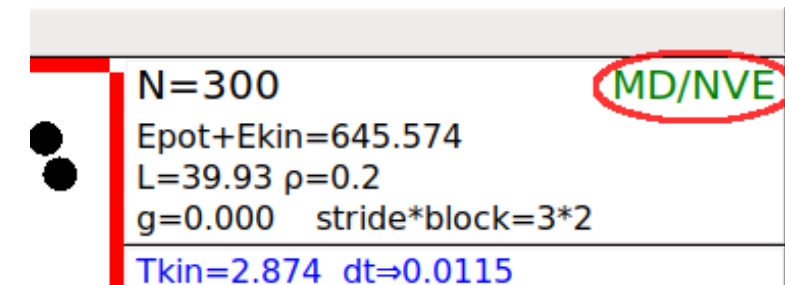
Energy conservation

- 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 slow, decrease # of particles by slider “N”
- Menu: Show → Integral of motion convergence profile



The time development of energy is always scaled from min to max.

- If needed, 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

- Turn simulation off by button `■ run`
- Menu: `Ⓢ` → `Ⓔ` Energy/enthalpy convergence profile
- Menu: `Ⓜ` → `Ⓜ` Molecular dynamics (`Ⓕ` Berendsen thermostat)
- Turn simulation on by button `■ run`
- Menu: `Ⓜ` → `Ⓜ` 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 ”: $\rho \approx 0.6$