

Predictor-corrector type: knowledge of history is used to predict an approximate solution, which is made more accurate in the following step

- we do not want (otherwise good) methods that require several calculations of the r.h.s.
- a predictor without r.h.s. = polynomial, or equivalently a vector of derivatives:

$$R = \begin{pmatrix} \vec{r}_i \\ h\dot{\vec{r}}_i \\ \frac{h^2}{2!}\ddot{\vec{r}}_i \\ \frac{h^3}{3!}\dddot{\vec{r}}_i \end{pmatrix}$$

Predictor:

$$R(t+h)^{\text{pred}} = \begin{pmatrix} 1 & 1 & 1 & 1 \\ 0 & 1 & 2 & 3 \\ 0 & 0 & 1 & 3 \\ 0 & 0 & 0 & 1 \end{pmatrix} R(t)$$

The error of the predictor:

$$\vec{E}_i = \frac{h^2 \vec{f}_i(\vec{r}^N(t+h)^{\text{pred}})}{2 m_i} - \frac{h^2}{2} \vec{r}_i''(t+h)^{\text{pred}}$$

Corrector:

$$R(t+h) = R(t+h)^{\text{pred}} + \begin{pmatrix} a_0 \\ a_1 \\ a_2 \\ a_3 \end{pmatrix} E$$

Unknown constants determined from the **stability conditions**.

For a 1st order equation $y' = f(y)$:

$$E = hf(y(t+h)^{\text{pred}}) - hy'(t+h)^{\text{pred}}$$

equivalent to Adams–Bashforth

1st order:

M	a_0	a_1	a_2	a_3	a_4	a_5
2	1/2	1				
3	5/12	1	1/2			
4	3/8	1	3/4	1/6		
5	251/720	1	11/12	1/3	1/24	
6	95/288	1	25/24	35/72	5/48	1/120

2nd order:

M	a_0^a	a_0^b	a_1	a_2	a_3	a_4	a_5
3^c	0	0	1	1			
4	1/6	1/6	5/6	1	1/3		
5	19/120	19/90	3/4	1	1/2	1/12	
6	3/20	3/16	251/360	1	11/18	1/6	1/60

M = predictor length (local order $\mathcal{O}(h^M)$)

a suitable for a r.h.s. without \dot{r}

b suitable for a r.h.s. with \dot{r}

c velocity Verlet

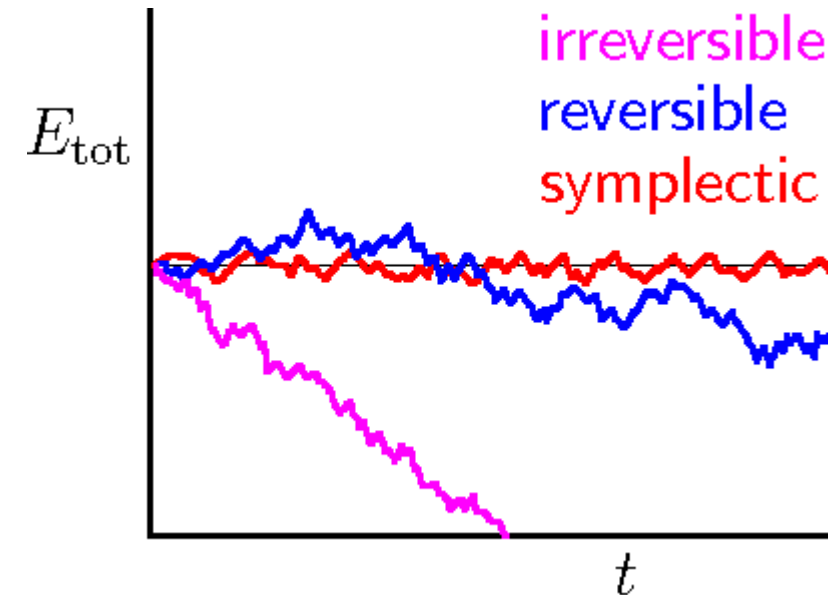
Verlet:

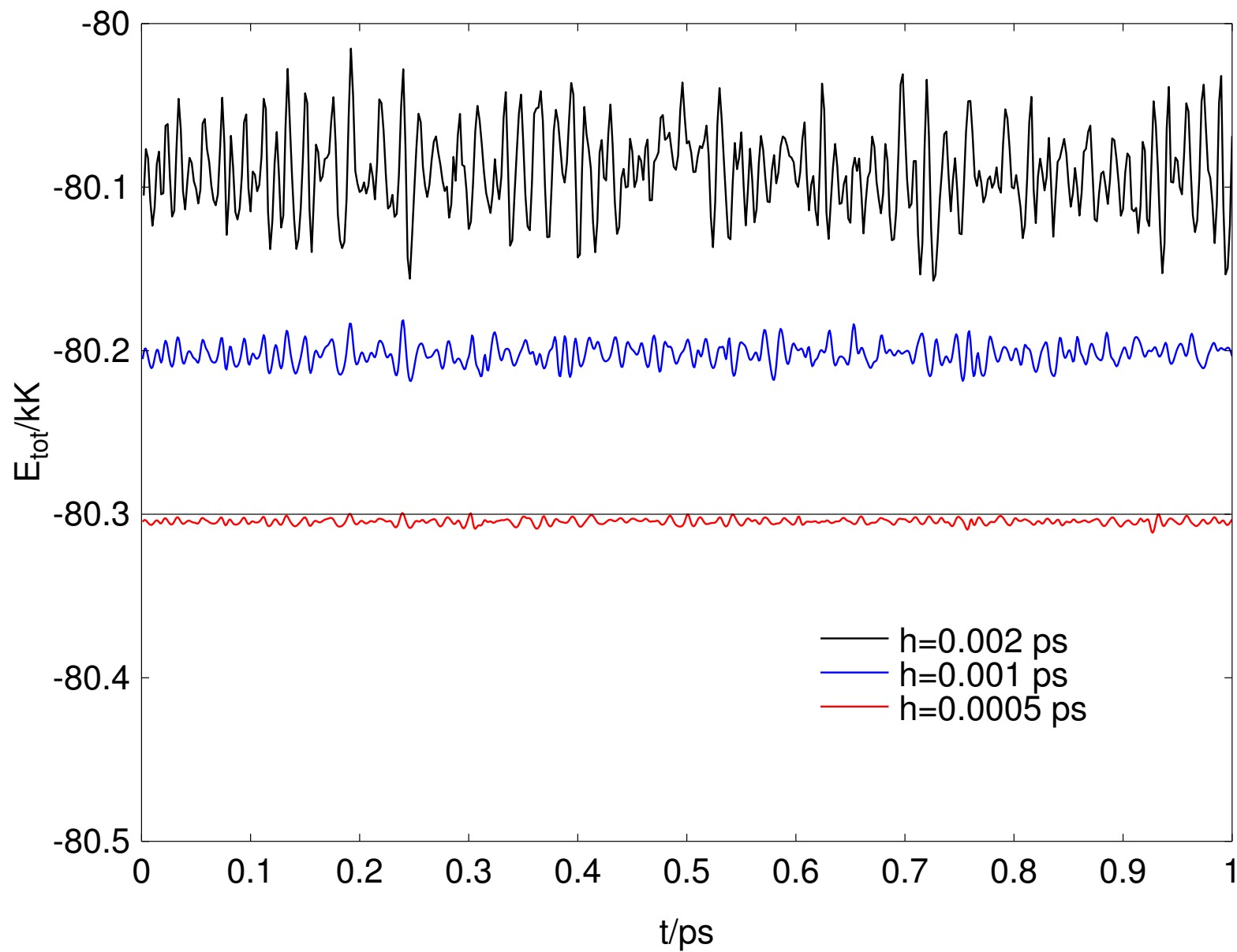
- ⊕ is time-reversible \Rightarrow no drift in the total (potential + kinetic) energy
- ⊕ is symplectic \Rightarrow error in the total energy is bound
- ⊕ is simple
- ⊖ low order (phase error)
- ⊖ (directly) not applicable to a r.h.s. containing velocities (equation $\ddot{r} = f(r, \dot{r})$: Nosé,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

Gear: just opposite (excl. the simplest version identical to Verlet)

Notes:

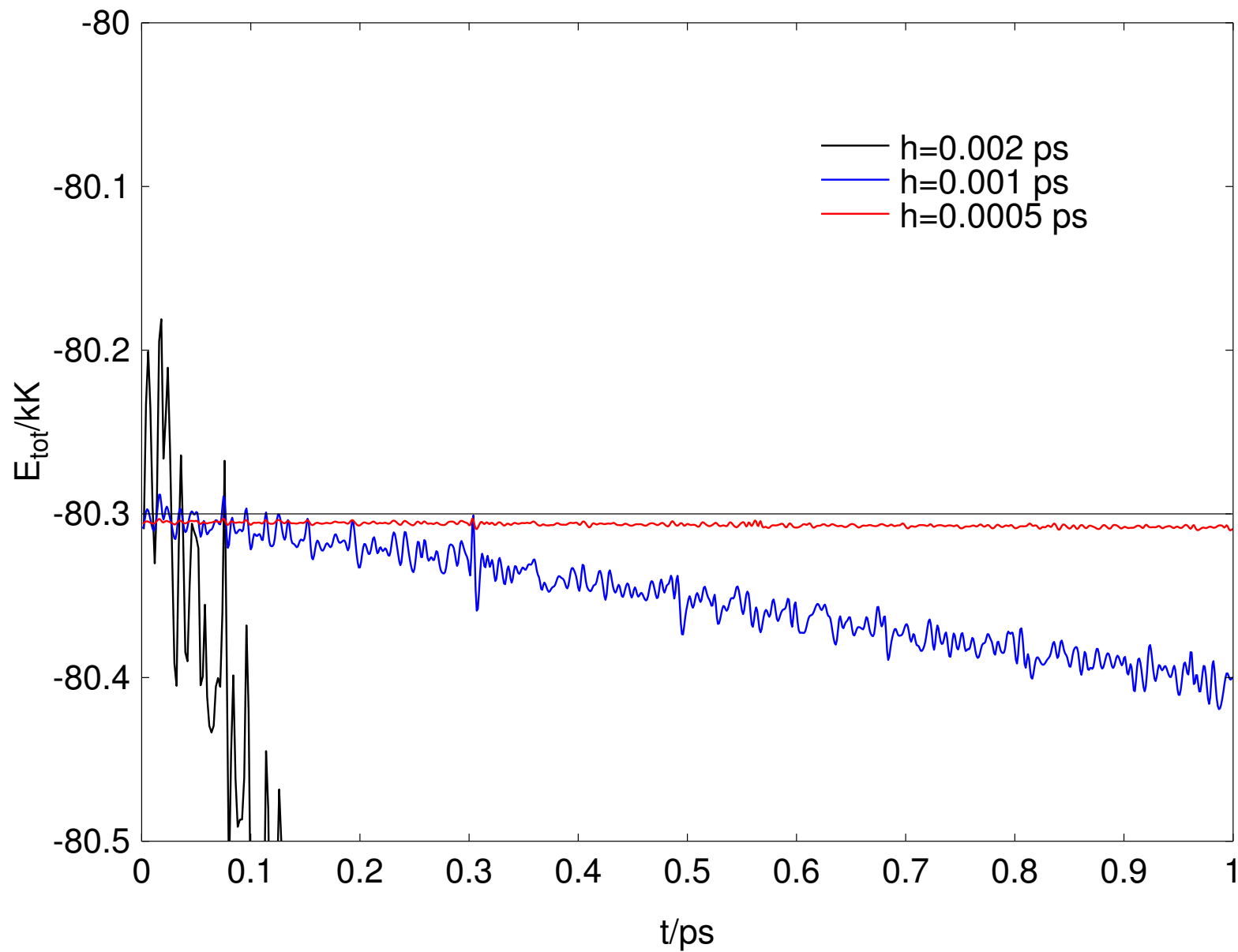
- a symplectic integerator preserves (with bounded accuracy) the phase space volume $d\vec{r}^N d\vec{p}^N$
- the quality of energy conservation helps us to set up the timestep h





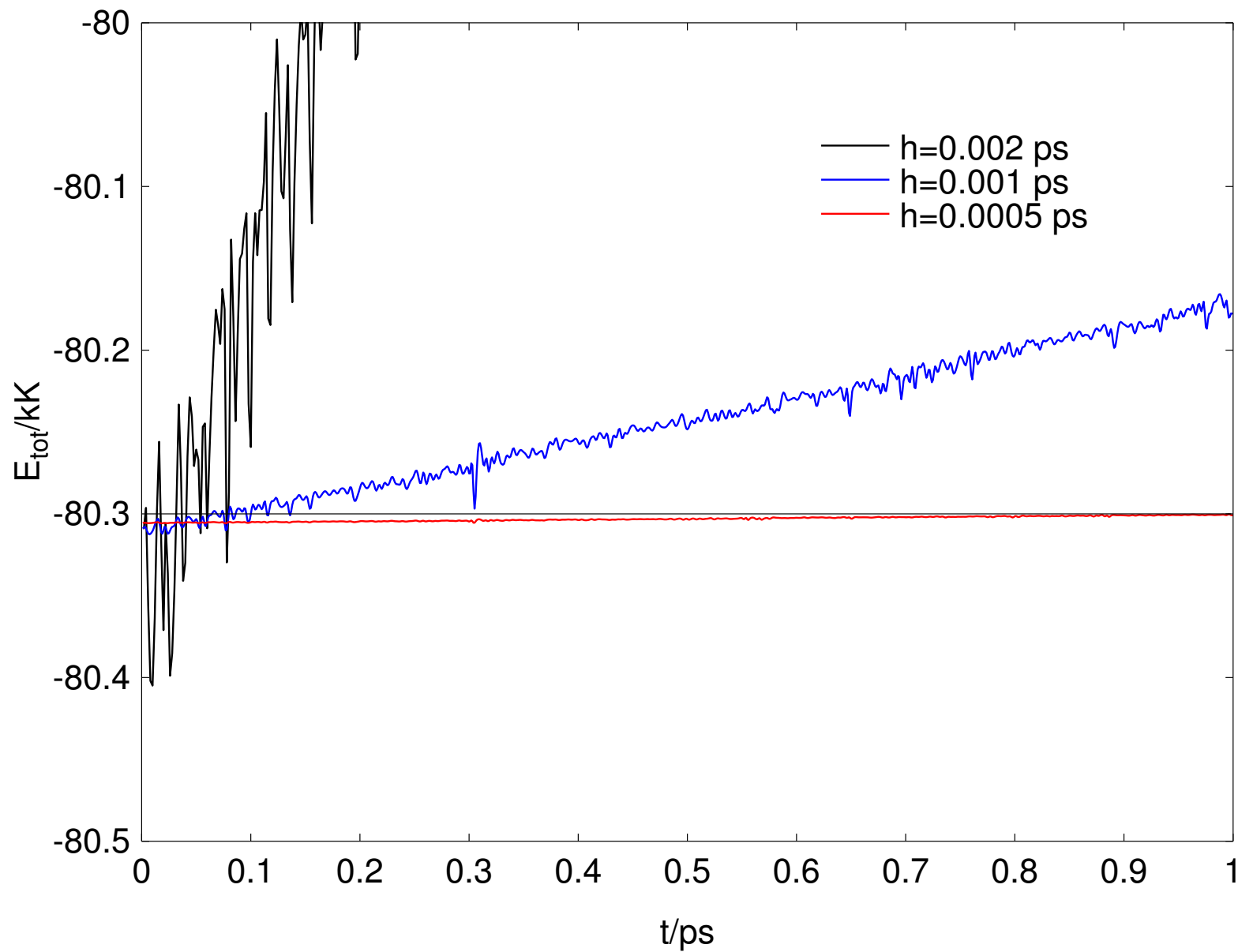
Energy conservation: Gear $M = 4$

+ 6/16
s04/2



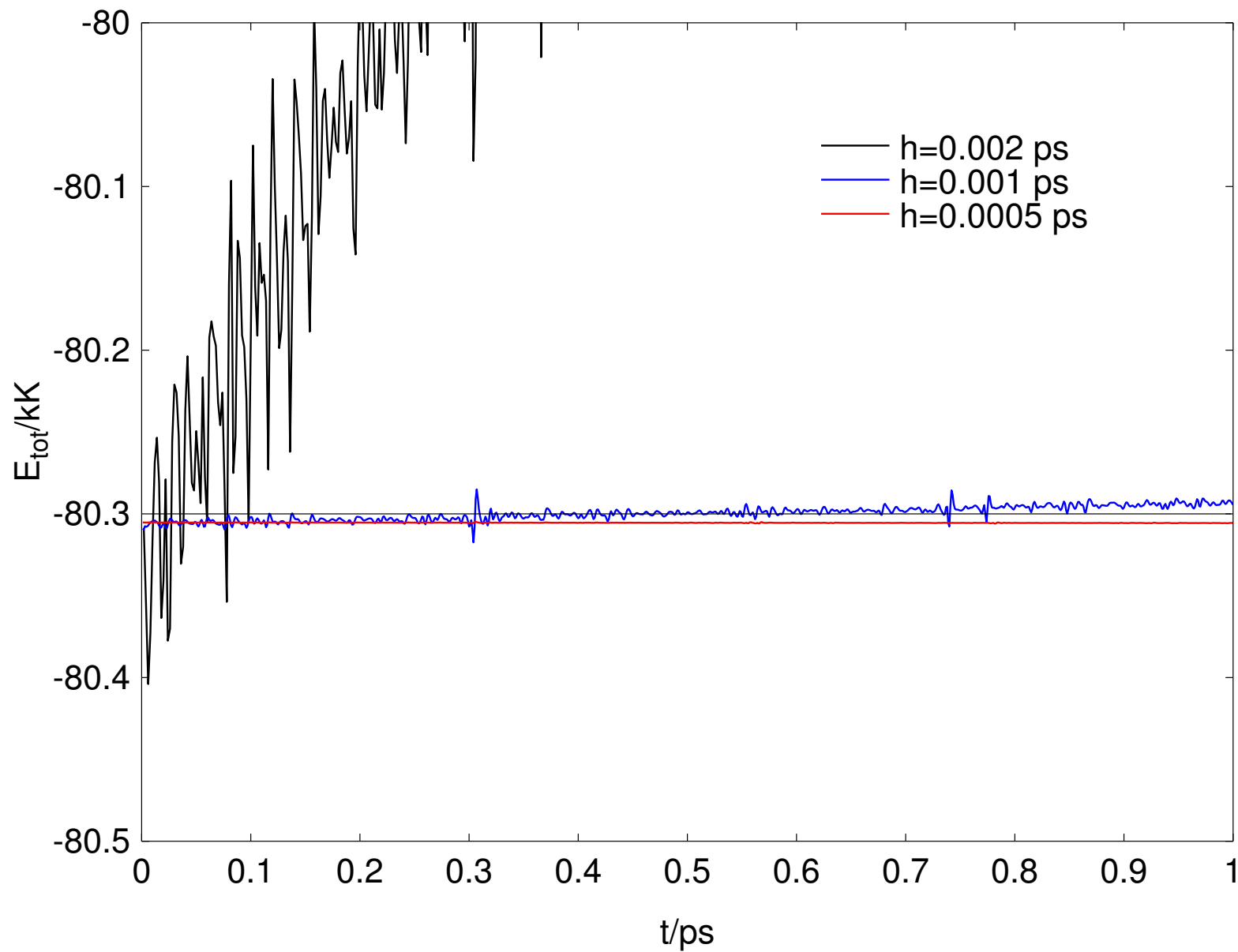
Energy conservation: Gear $M = 5$

+ 7/16
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Energy conservation: Gear $M = 6$

+ 8/16
s04/2



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:

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

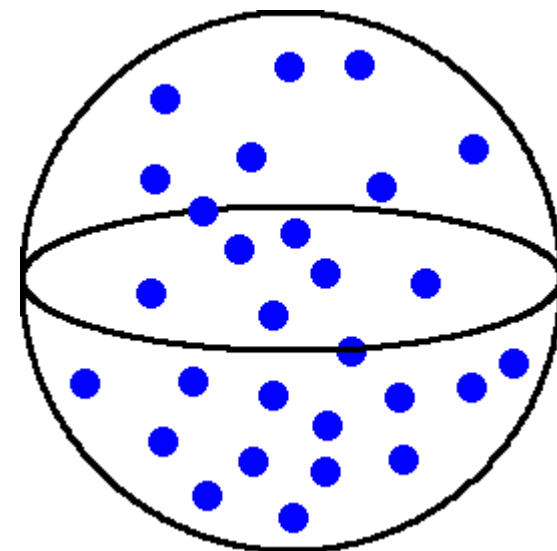
Generally from the equipartition theorem:

$$\left\langle p \frac{\partial \mathcal{H}}{\partial p} \right\rangle = k_B T$$

where p is any component of any momentum (vector)

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, ...).



Constant temperature in MD: methods

- canonical (yields an [almost] accurate canonical ensemble):

- Maxwell–Boltzmann

$$p(\dot{x}_i) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{\dot{x}^2}{2\sigma^2}\right), \quad \sigma^2 = \langle \dot{x}_i^2 \rangle = \frac{k_B T}{m_i}$$

once a while all particles

- Andersen: randomly visit particles (usually better)
- Langevin: small random force added to all particles at every step
- Canonical Sampling through the Velocity Rescaling (Bussi)
- Nosé–Hoover: one (or more) degrees of freedom added, averaging of it (them) \Rightarrow canonical ensemble
problem: more tricks needed with Verlet (r.h.s. depends on velocities)
- Modified Berendsen
- Gaussian rescaling: $E_{\text{kin}} = \text{const}$, canonical in the config. space only

- approximate

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

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

● 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 ($\xi = \ln s$):

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

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

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.

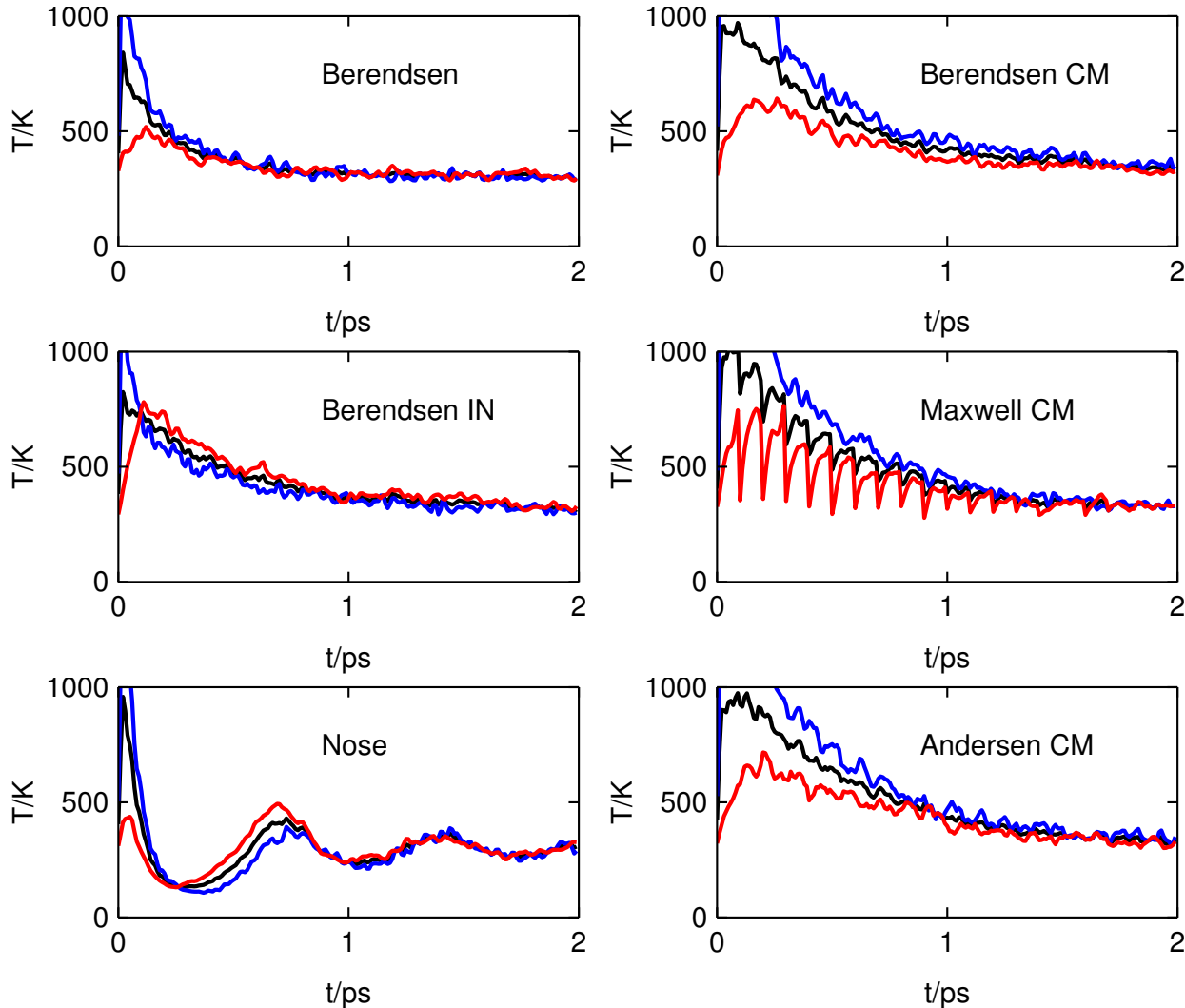
- + canonical
- + exponential relaxation
- kinetics lost
- problematic with constrained dynamics

for me:

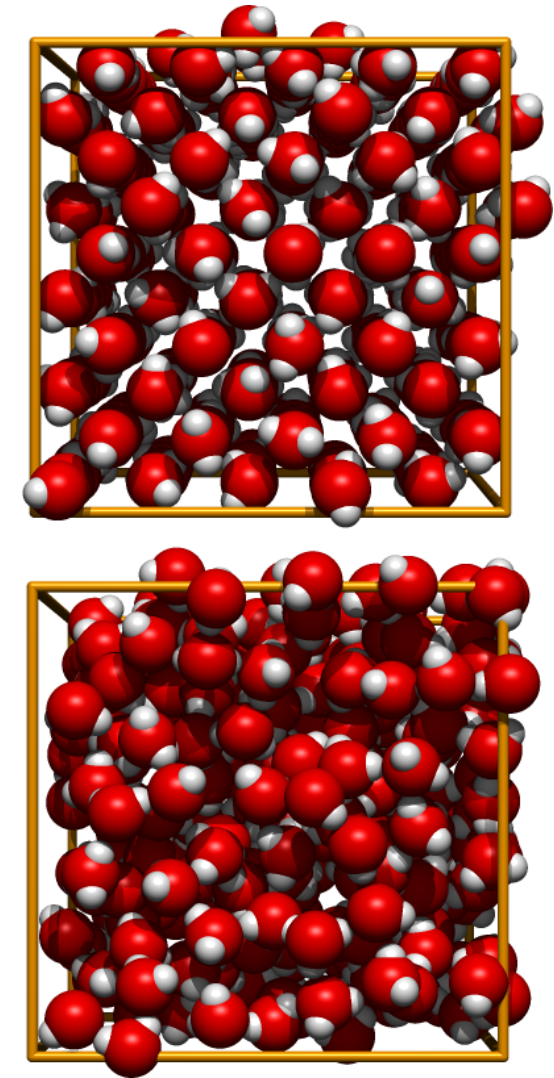
Show flying icecube simolant: periodic b.c., $\tau = \min$, lower ρ , max. speed
old simolant: periodic b.c., $N=100$, $L=40$, hot key '=' , $\tau=0.2$

Thermostats: application to water

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



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



see simul/spce/water.*

Try molecular dynamics by yourself

14/16
s04/2

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

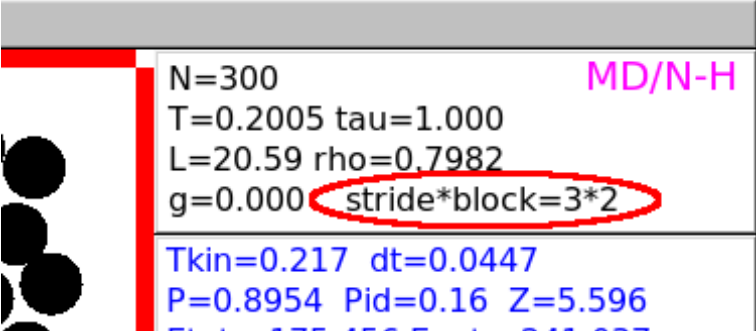
- Run `simolant.exe`.

The screenshot displays the SIMOLANT software interface. The main window shows a simulation of particles (black circles) in a container. The interface includes a menu bar (File, Prepare system, Method, Boundary conditions, Show, Help) and a right-hand control panel. The control panel displays simulation parameters: N=300, T=0.2005, tau=1.000, L=20.59, rho=0.7982, g=0.000, and MD/N-H. A red circle highlights the parameter `stride*block=3*2`. Below the parameters is a graph of `Ekin+Epot` vs time, with a red circle highlighting `max-min=22.12`. The control panel also features a 'Parameters' section with sliders for T, tau, g, rho, and N; a 'Walls' section with buttons for top, left, right, and bottom; an 'Expert' section with 'record' and 'cmd:' fields; and a 'molecule size' section with a dropdown set to 'Real' and a 'reset' button. At the bottom, there are 'draw mode' (set to 'Movie') and 'color mode' (set to 'Keep') dropdowns, and a 'run' button. A 'simulation speed' and 'measurement block' slider is also present.

Watch energy conservation by yourself

15/16
s04/2

- 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”.



A screenshot of a simulation control panel. On the left, there are three black circular sliders. The main panel displays the following parameters: N=300, T=0.2005 tau=1.000, L=20.59 rho=0.7982, g=0.000, and stride*block=3*2 (circled in red). Below a horizontal line, it shows Tkin=0.217 dt=0.0447, P=0.8954, Pid=0.16, and Z=5.596. The label 'MD/N-H' is in the top right corner.

- 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)

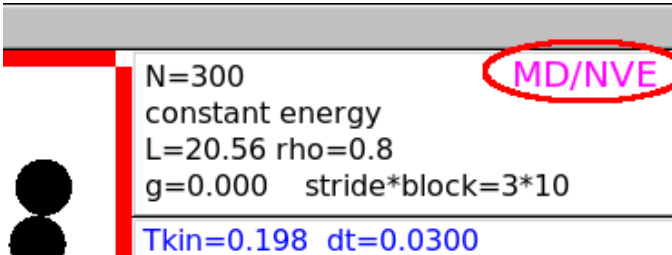
– write “dt=0.01” to the cmd: field

– 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”



A screenshot of a simulation control panel. On the left, there are two black circular sliders. The main panel displays the following parameters: N=300, constant energy, L=20.56 rho=0.8, g=0.000, and stride*block=3*10 (circled in red). Below a horizontal line, it shows Tkin=0.198 and dt=0.0300. The label 'MD/NVE' is in the top right corner.

- 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 ”: $\rho \approx 0.6$