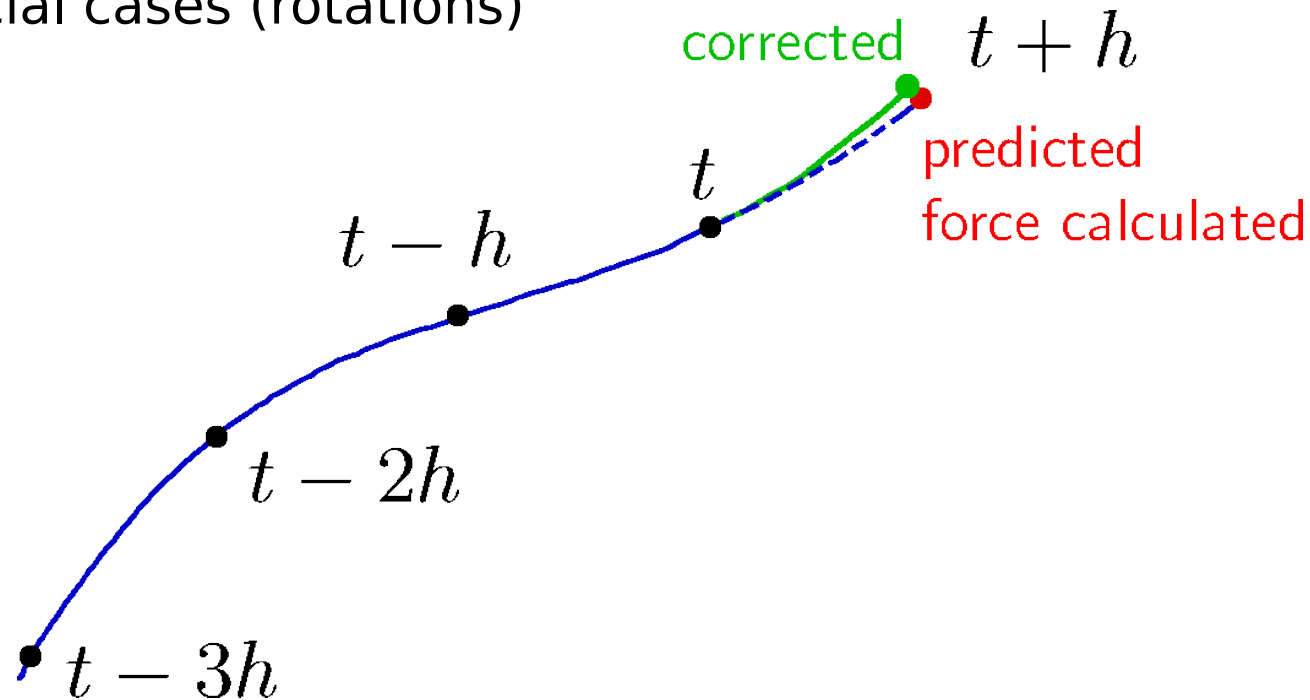


Gear methods

- **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

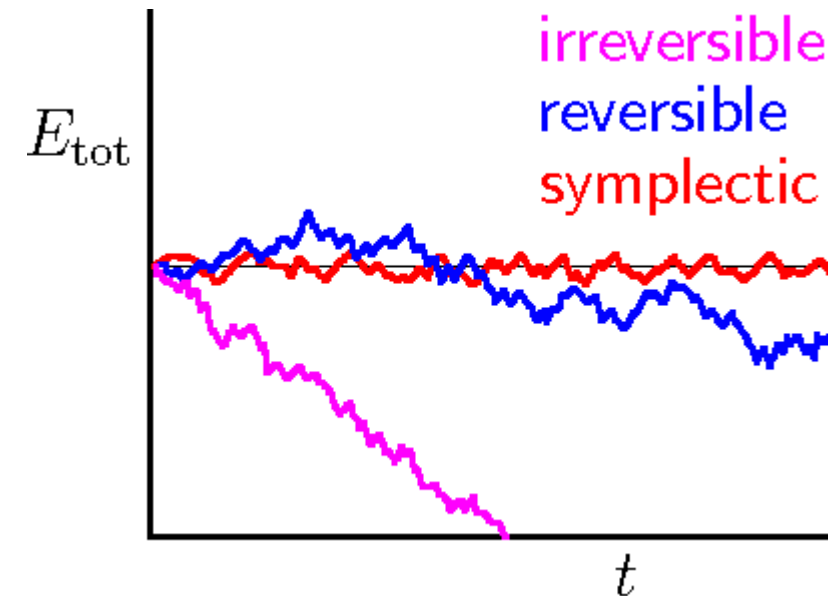
Verlet:

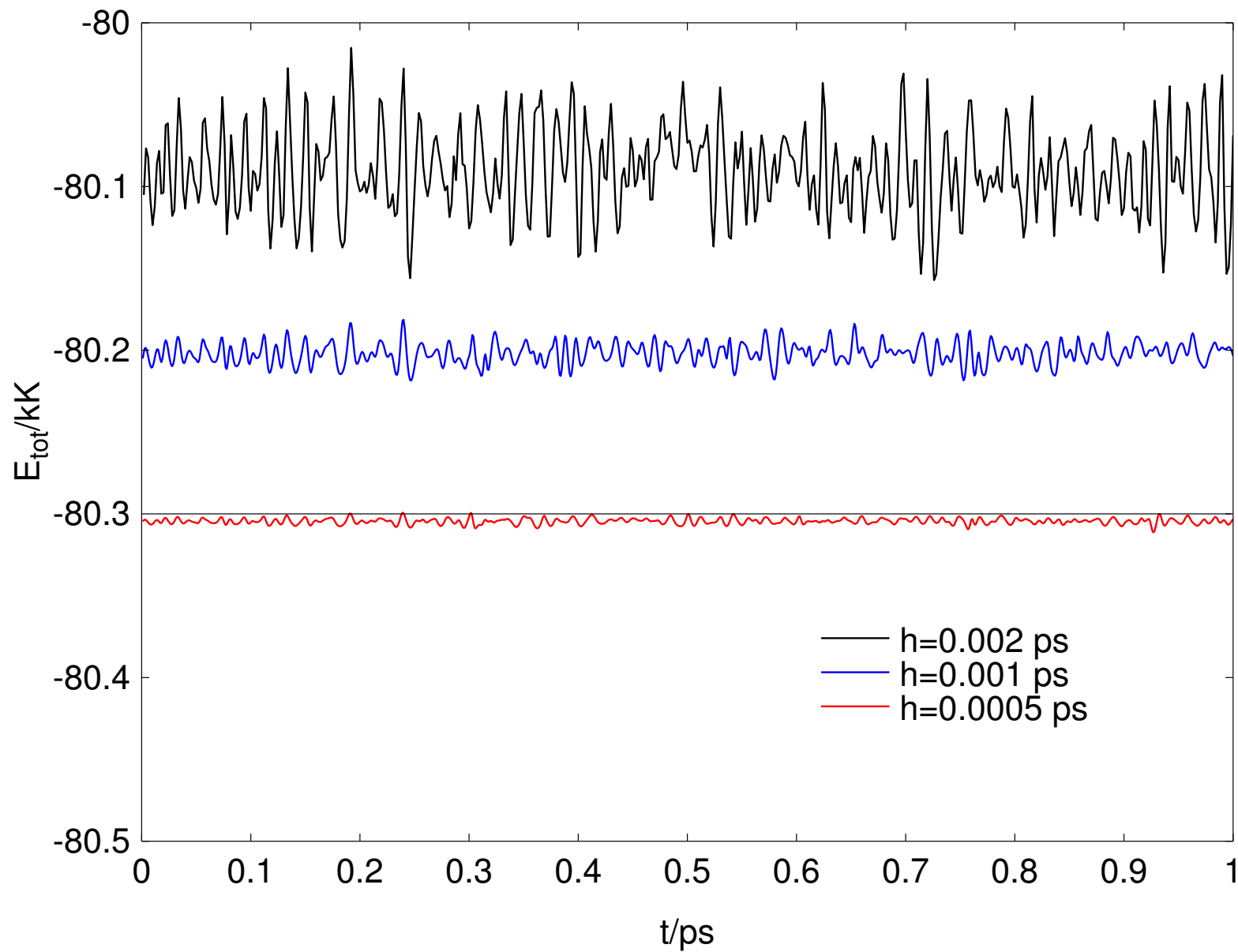
- ⊕ is time-reversible \Rightarrow no drift in the total (potential + kinetic) energy
- ⊕ is symplectic \Rightarrow error in the total energy is bound
- ⊕ is simple
- ⊖ low order (phase error)
- ⊖ (directly) not applicable to a r.h.s. containing velocities (equation $\ddot{r} = f(r, \dot{r})$: Nosé–Hoover,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

Gear: and similar: just opposite

Notes:

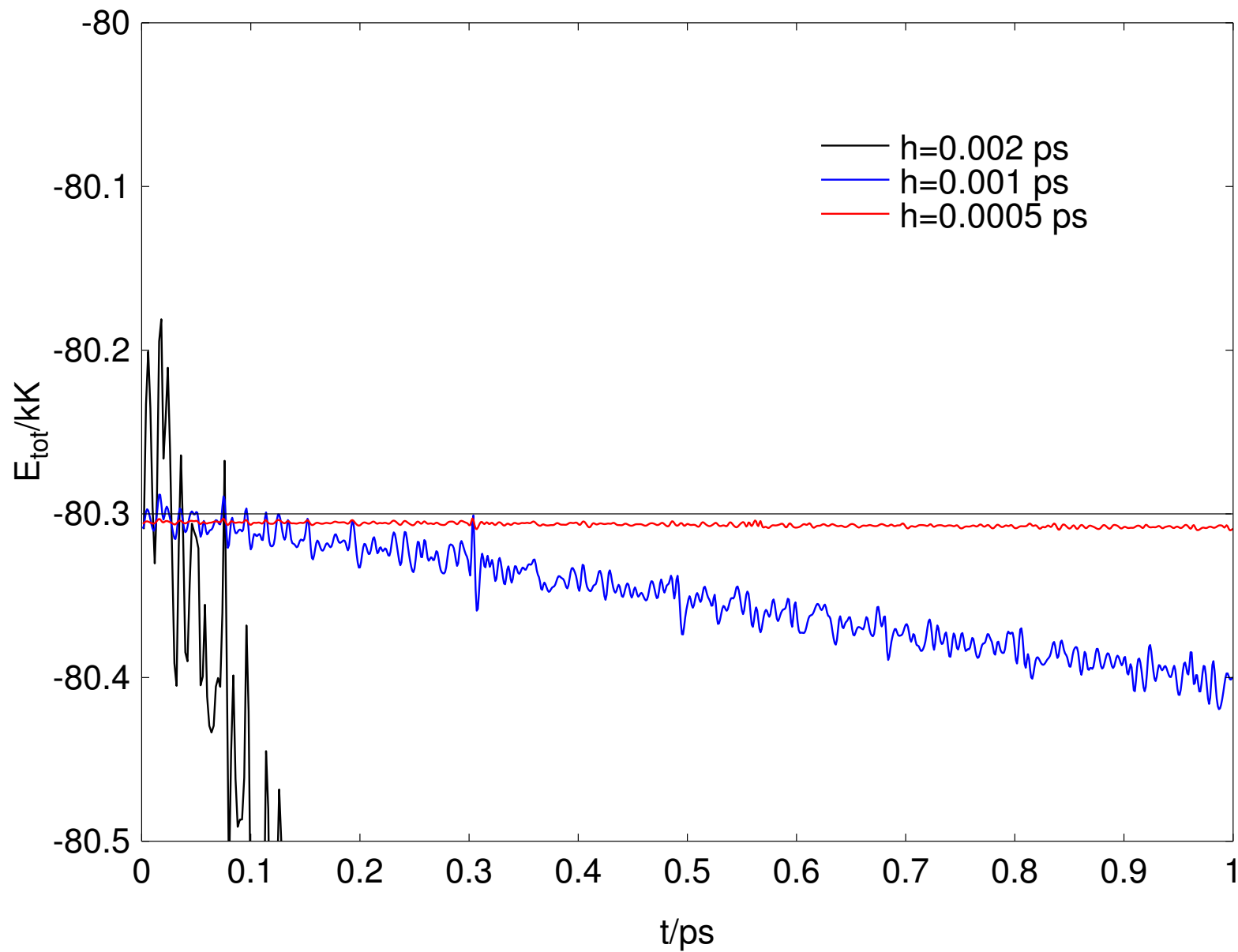
- a symplectic integerator preserves (with bounded accuracy) the phase space volume $d\vec{r}^N d\vec{p}^N$
- the quality of energy conservation helps us to set up the timestep h





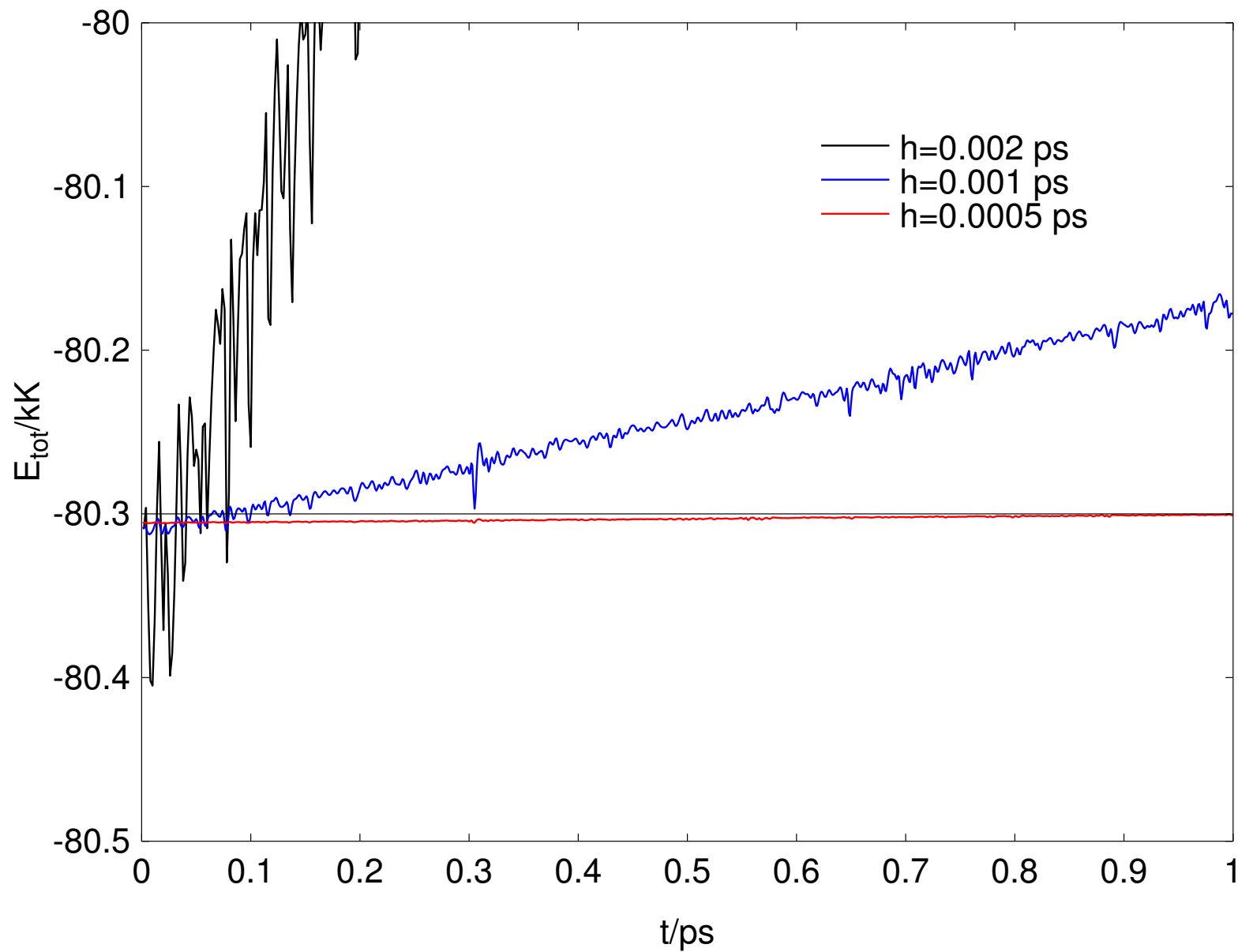
Energy conservation: Gear $M = 4$

+ 4/14
s04/2



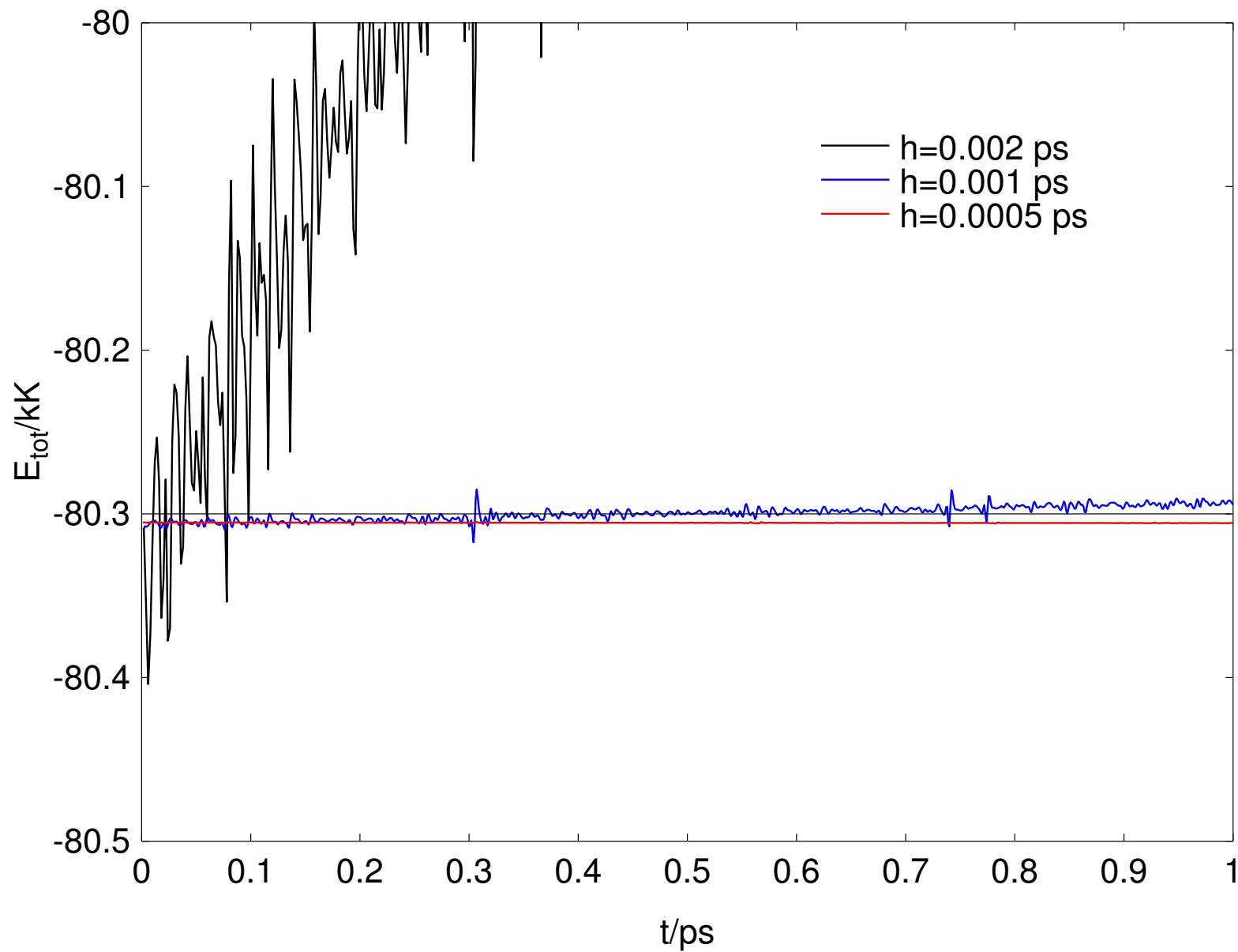
Energy conservation: Gear $M = 5$

+ 5/14
s04/2



Energy conservation: Gear $M = 6$

+ 6/14
s04/2



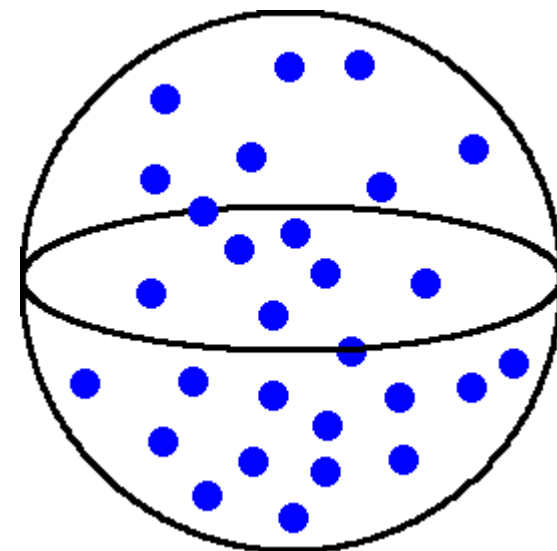
The temperature is **measured** in the standard (microcanonical) MD.

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

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

Example: molecules in a spherical cavity:

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



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

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

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

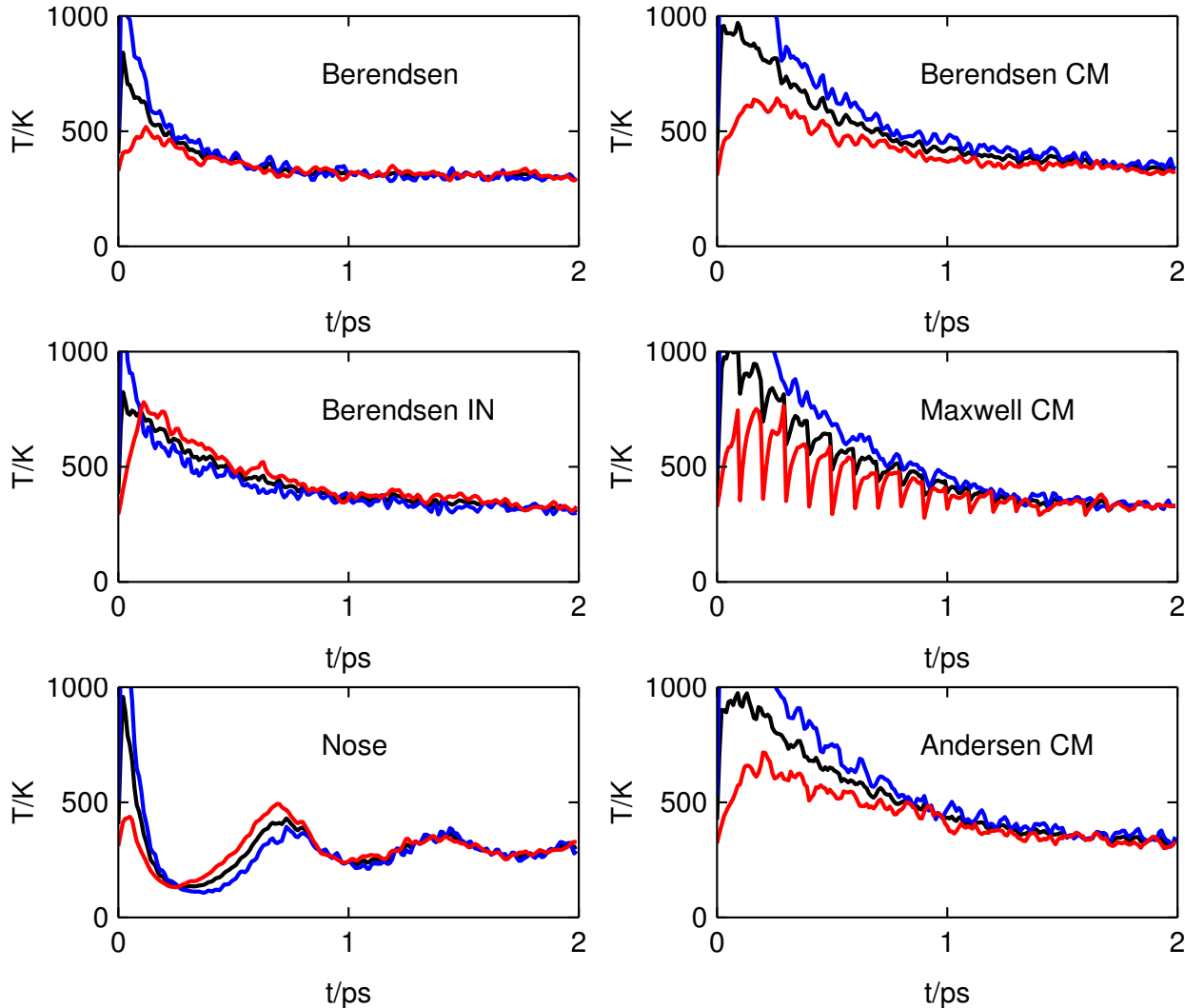
- kinetics lost
- problematic with constrained dynamics

for me:

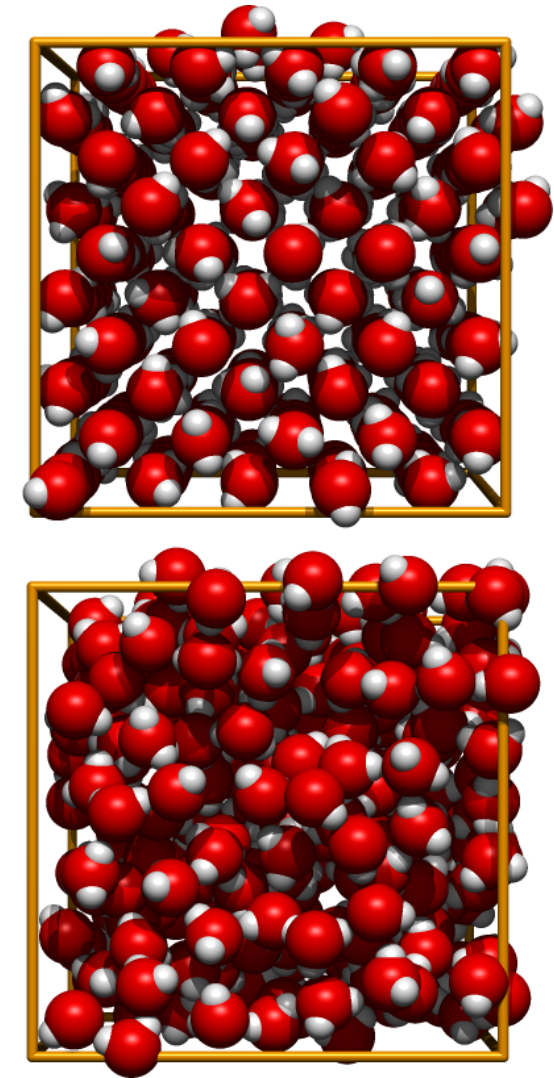
Show flying icecube simolant: periodic b.c., $\tau = \min$, lower ρ , max. speed
old simolant: periodic b.c., $N=100$, $L=40$, hot key '=' , $\tau=0.2$

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

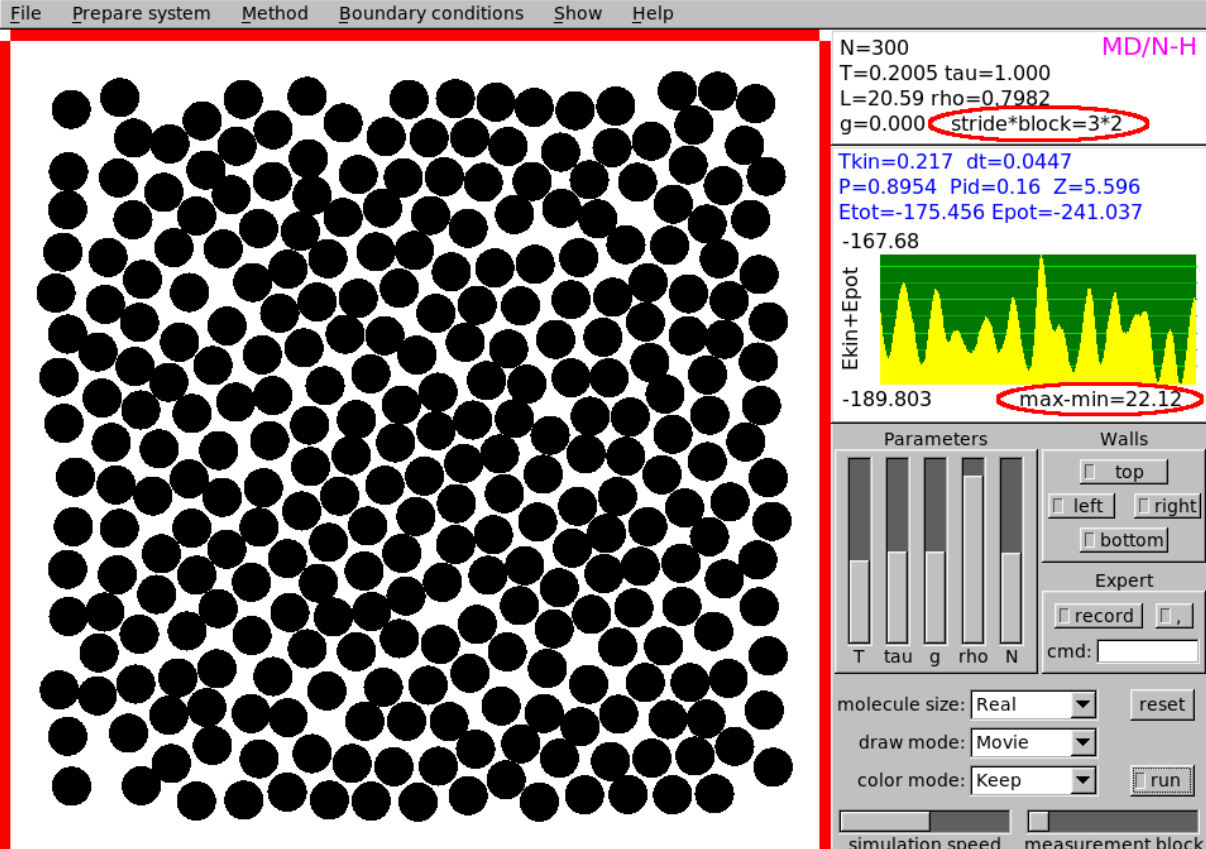
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Installation of SIMOLANT (Windows):

- <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`.



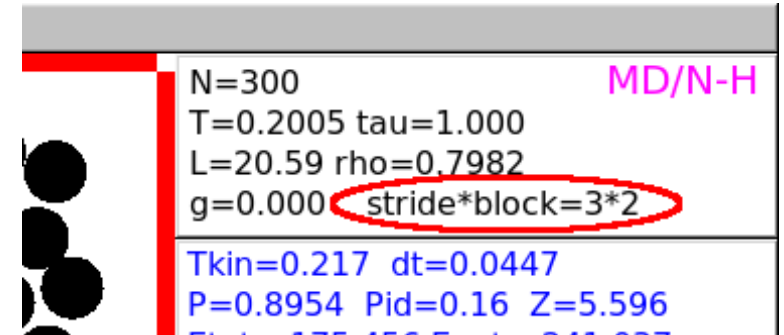
The screenshot displays the SIMOLANT software interface. The main window shows a 2D visualization of a molecular system, represented by black circles (atoms) arranged in a disordered pattern. The interface includes a menu bar with options: File, Prepare system, Method, Boundary conditions, Show, Help. On the right side, there is a control panel with the following information:

- System parameters: $N=300$, $T=0.2005$, $\tau=1.000$, $L=20.59$, $\rho=0.7982$, $g=0.000$. A red circle highlights the parameter `stride*block=3*2`.
- Simulation parameters: $T_{kin}=0.217$, $dt=0.0447$, $P=0.8954$, $P_{id}=0.16$, $Z=5.596$, $E_{tot}=-175.456$, $E_{pot}=-241.037$, -167.68 .
- A graph showing $E_{kin}+E_{pot}$ vs time, with a red circle highlighting `max-min=22.12`.
- Parameters: T, τ , g, ρ , N.
- Walls: top, left, right, bottom.
- Expert: record, cmd: [input field].
- molecule size: Real (dropdown), reset.
- draw mode: Movie (dropdown).
- color mode: Keep (dropdown), run.
- simulation speed and measurement block sliders.

Watch energy conservation by yourself

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- 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. On the right, a white box contains simulation parameters. The text is as follows: 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 this, there is a horizontal line, followed by Tkin=0.217 dt=0.0447, and P=0.8954 Pid=0.16 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)

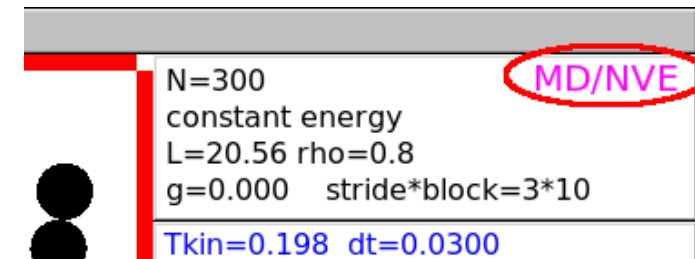
– write “dt=0.01” to the cmd: field

– 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. On the right, a white box contains simulation parameters. The text is as follows: N=300, constant energy, L=20.56 rho=0.8, g=0.000, and stride*block=3*10 (circled in red). Below this, there is a horizontal line, followed by Tkin=0.198 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 ”: $\rho \approx 0.6$