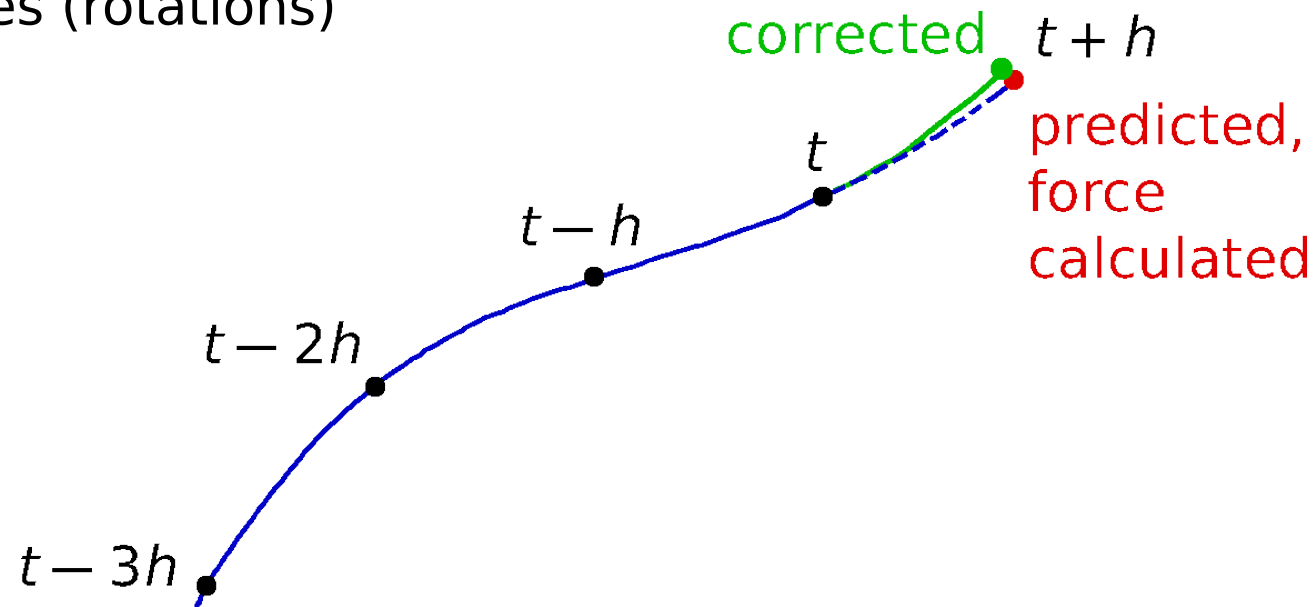


Gear's methods

- **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

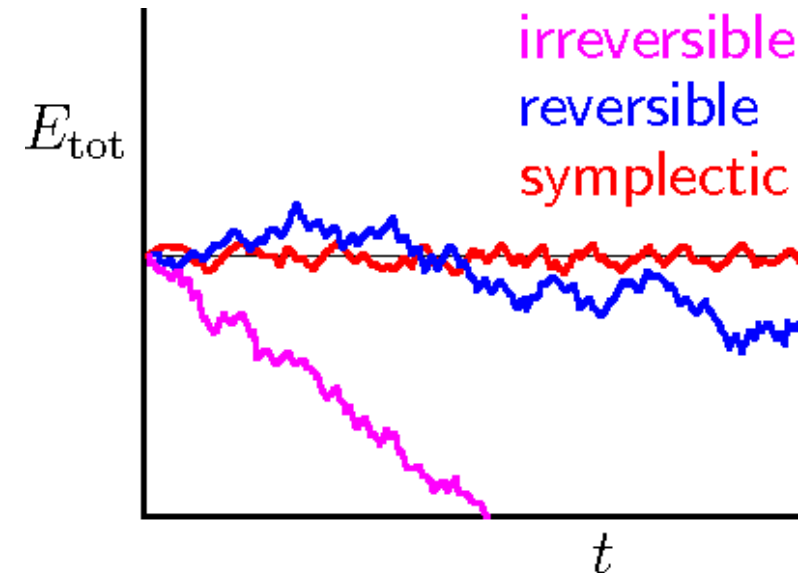
Verlet:

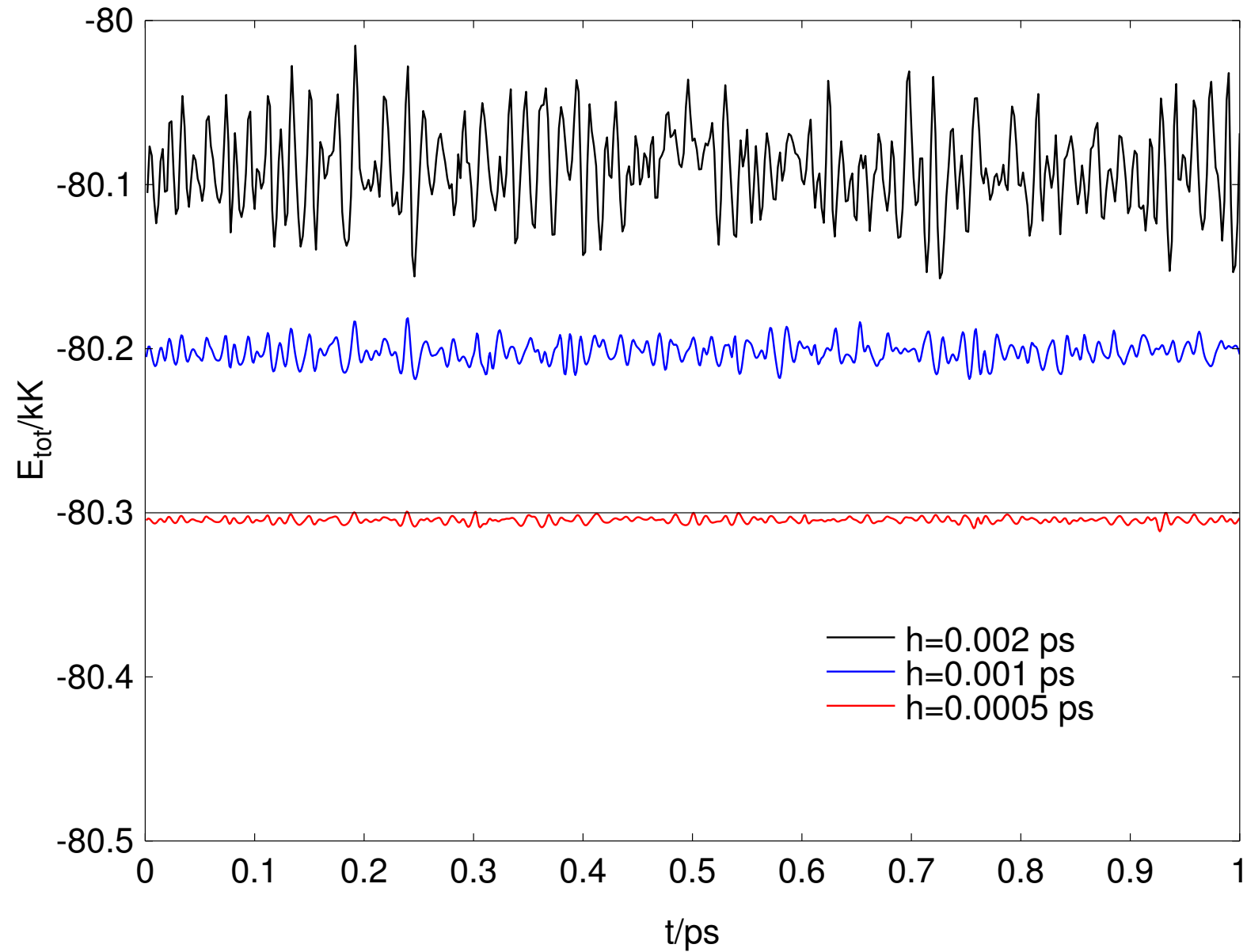
- ⊕ is time-reversible \Rightarrow no drift in the total (potential + kinetic) energy
- ⊕ is symplectic \Rightarrow error in the total energy is bound
- ⊕ is simple
- ⊖ low order (phase error)
- ⊖ (directly) not applicable to a r.h.s. containing velocities (equation $\ddot{r} = f(r, \dot{r})$: Nosé–Hoover,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

Gear and similar: just opposite

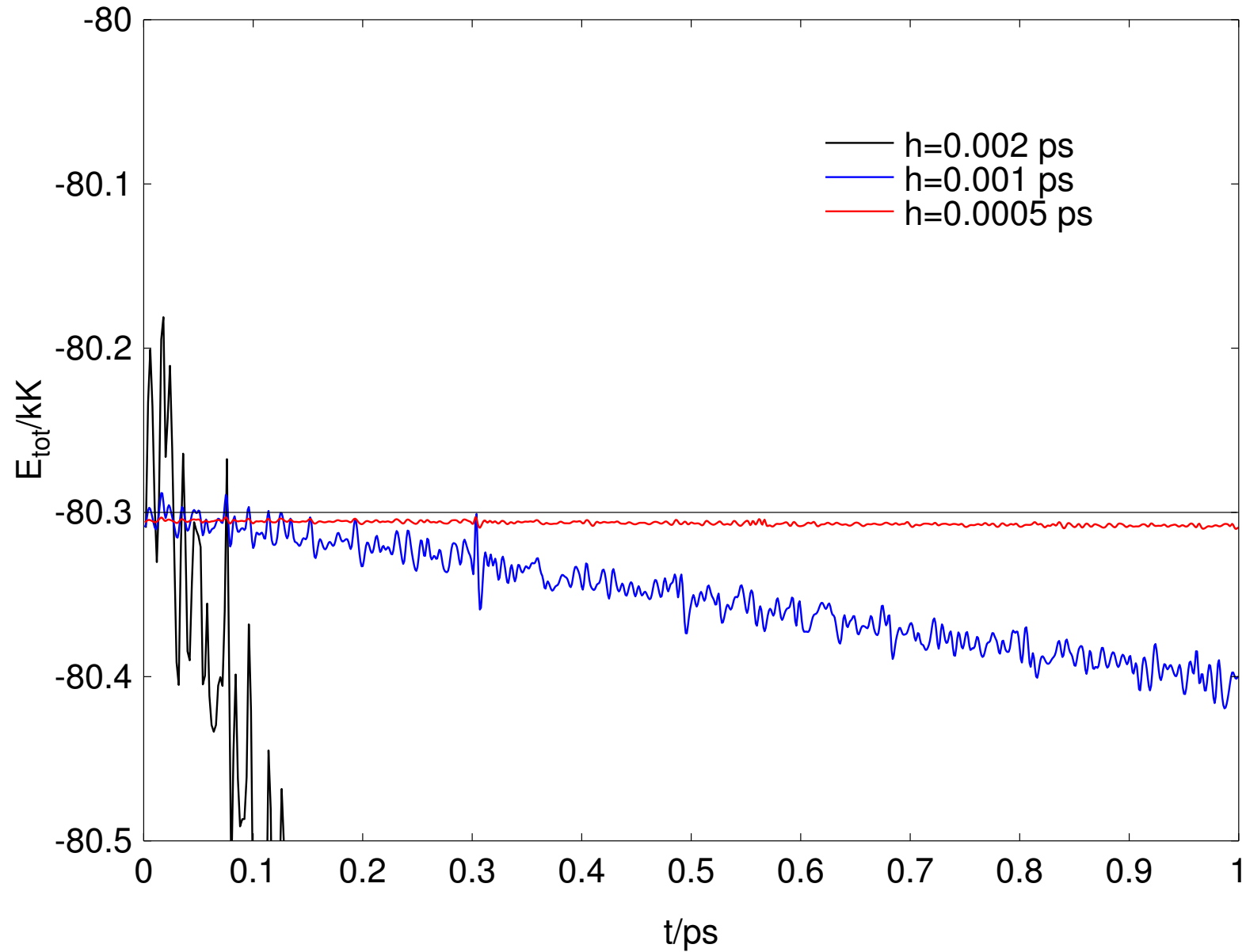
Notes:

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

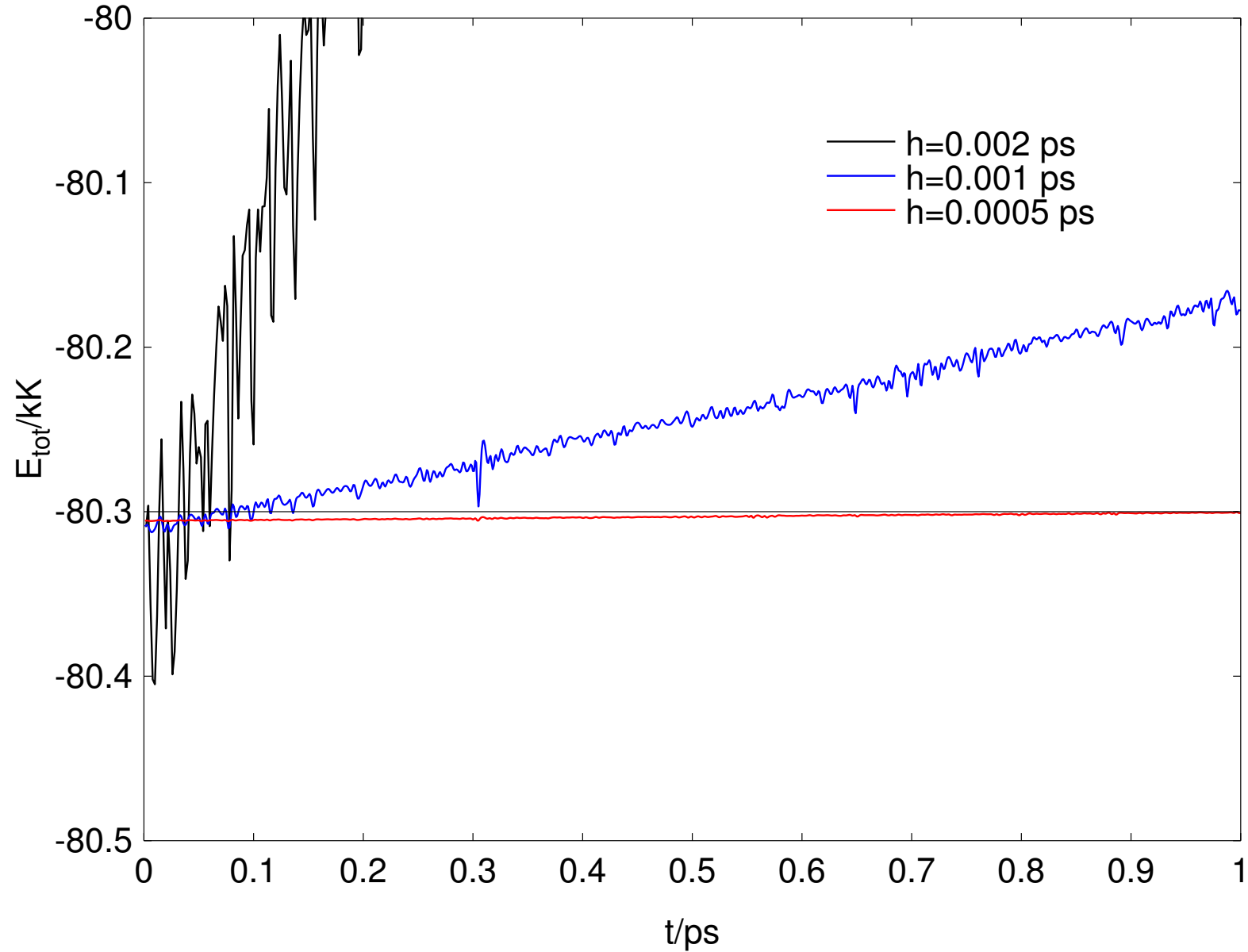




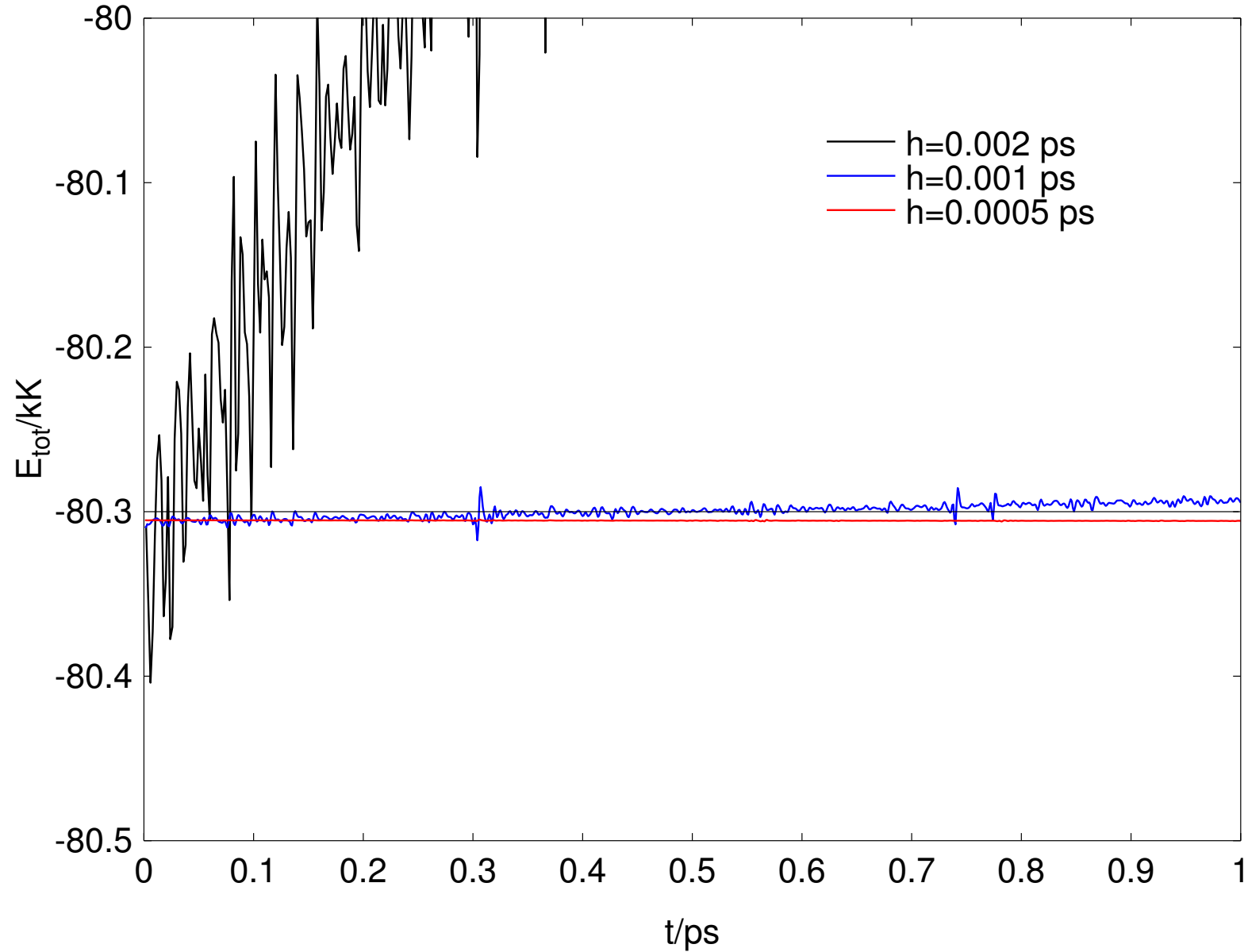
Energy conservation: Gear $M = 4$



Energy conservation: Gear $M = 5$



Energy conservation: Gear $M = 6$



Write a computer program for a numerical integration of the Newton's equations for a harmonic oscillator with the force constant K ($f(x) = -Kx$). Use $K = 1$ and $m = 1$ and one of the following methods:

- Verlet
- velocity Verlet
- leap-frog

● Runge-Kutta 4th order for $y'' = f(x, y)$, $y(x_0) = y_0$, $y'(x_0) = y'_0$:

$$k_1 = f(x_0, y_0, y'_0),$$

$$k_2 = f\left(x_0 + \frac{h}{2}, y_0 + \frac{1}{2}hy'_0 + \frac{h^2}{8}k_1, y'_0 + \frac{h}{2}k_1\right),$$

$$k_3 = f\left(x_0 + \frac{h}{2}, y_0 + \frac{1}{2}hy'_0 + \frac{h^2}{8}k_2, y'_0 + \frac{h}{2}k_2\right),$$

$$k_4 = f\left(x_0 + h, y_0 + hy'_0 + \frac{h^2}{2}k_3, y'_0 + hk_3\right),$$

$$y_1 = y(x_0 + h) = y_0 + hy'_0 + \frac{h^2}{6}(k_1 + k_2 + k_3),$$

$$y'_1 = y'(x_0 + h) = y'_0 + \frac{h}{6}(k_1 + 2k_2 + 2k_3 + k_4).$$

● Beeman: $r(t + h) = r(t) + v(t)h + \frac{4f(t) - f(t-h)}{6m}h^2$
 $v(t + h) = v(t) + \frac{2f(t+h) + 5f(t) - f(t-h)}{6m}h$

● Gear 2nd order $M = 4$

Try also the Hamilton equations of motion using:

● Gear 1st order

● Euler for $y' = f(y)$: $y(t + h) = y(t) + f(t)h$ (where $f(t) = f(y(t))$)

● Adams-Bashforth various orders:

$$y(t + h) = y(t) + \frac{h}{2}[3f(t)h - f(t - h)]$$

$$y(t + h) = y(t) + \frac{h}{12}[23f(t) - 16f(t - h) + 5f(t - 2h)]$$

$$y(t + h) = y(t) + \frac{h}{24}[55f(t) - 59f(t - h) + 37f(t - 2h) - 9f(t - 3h)]$$

● Runge-Kutta 4th order (for the 1st order differential equation)

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

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

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

It is assumed that the conserved degrees of freedom are zero

Example: molecules in a spherical cavity: $f_{\text{conserve}} = 1_{\text{energy}} + 3_{\text{rotations}}$

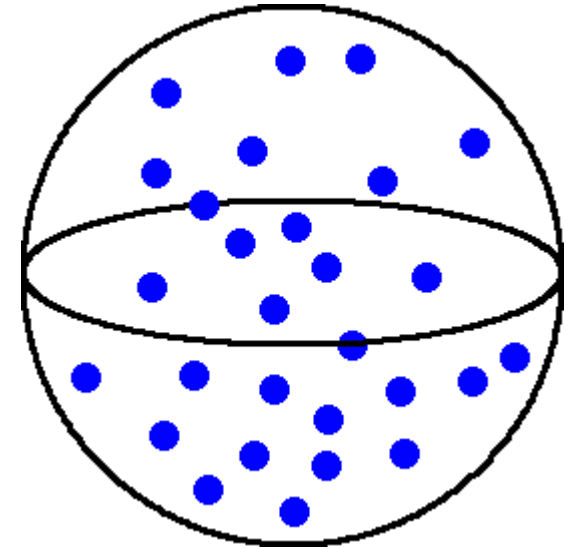
Generally from the equipartition theorem:

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

where p is any component of any momentum vector and q the canonically conjugate coordinate

Equipartition: 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.

● $T_{\text{tr}} \neq T_{\text{rot+in}}$ 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: $\ddot{\vec{r}}_i = \frac{\vec{f}_i}{m_i} - \eta(T_{\text{kin}} - T)\dot{\vec{r}}_i$, $\eta = \frac{q}{Th}$

* do not sample the center-of-mass in the periodic boundary conditions

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)

canonical stochastic:

- Maxwell–Boltzmann: once a while the velocities of particles are drawn from the Maxwell–Boltzmann distribution, $\pi(\dot{x}_i) = \exp(-\dot{x}_i^2/2\sigma^2)/\sigma\sqrt{2\pi}$, $\sigma^2 = k_B T/m_i$
- Andersen: randomly visit particles (usually better)
- Langevin: small random force added to all particles at every step
- *Canonical sampling through velocity rescaling (CSVR [Bussi, Donadio, Parrinello])

● 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

Comparison of thermostats

Nosé–Hoover

- ⊕ canonical (except conserved quantities)
- ⊕ high quality
- ⊕ good also for small systems (Nosé–Hoover 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

Bussi et al. (CSVR)

- ⊕ canonical (except conserved quantities)
- ⊕ exponential relaxation (i.e., good also for start)
- ⊖ sometimes (crystals) less accurate than Nosé–Hoover

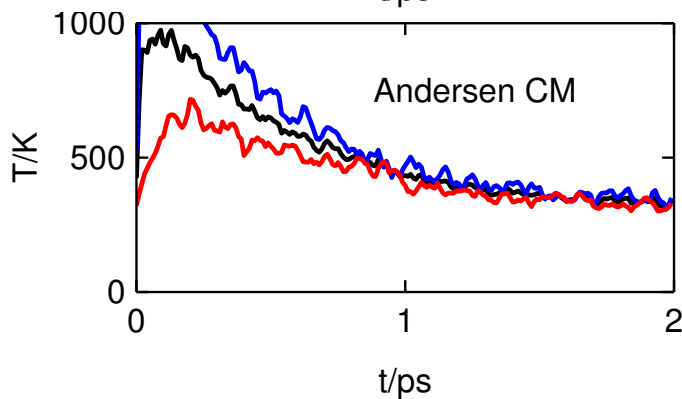
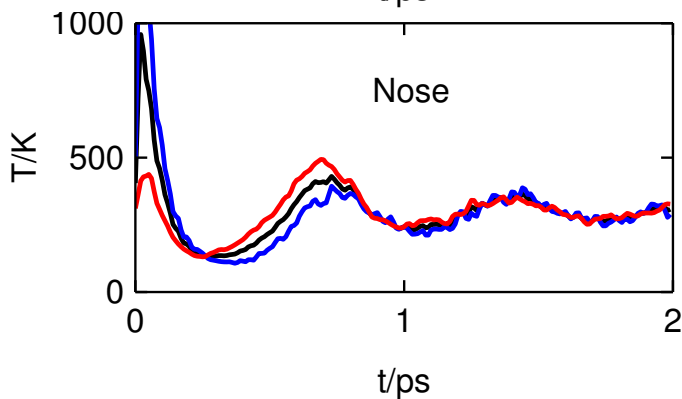
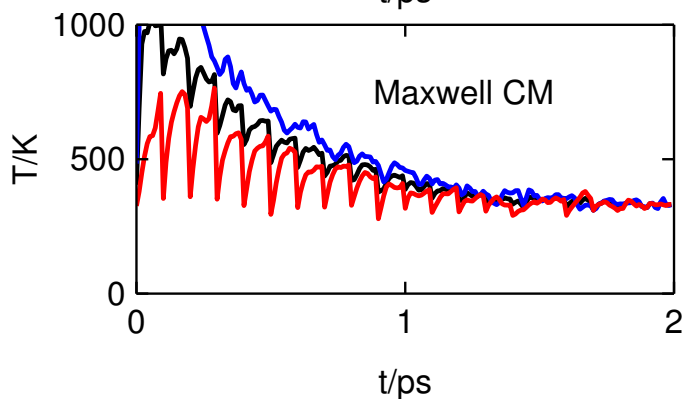
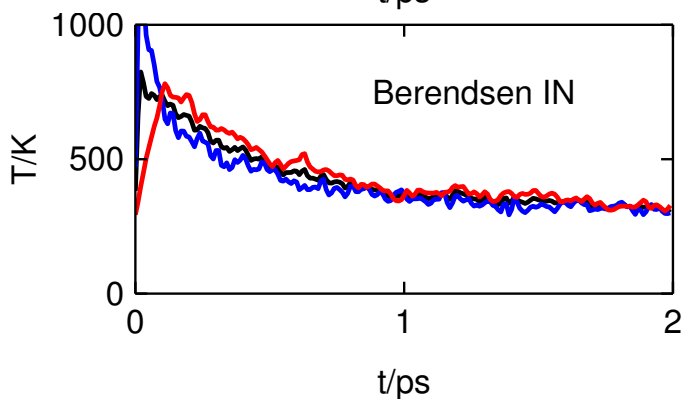
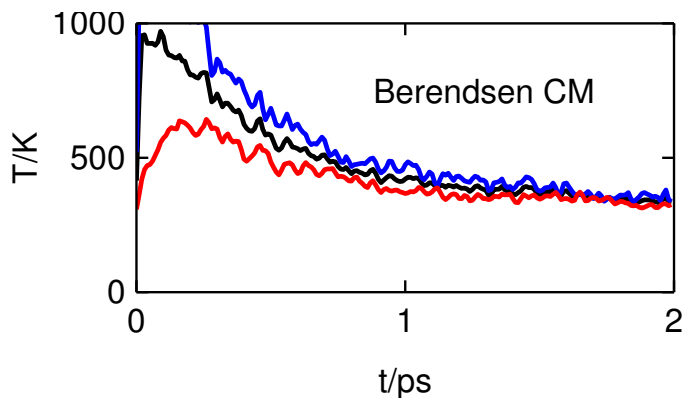
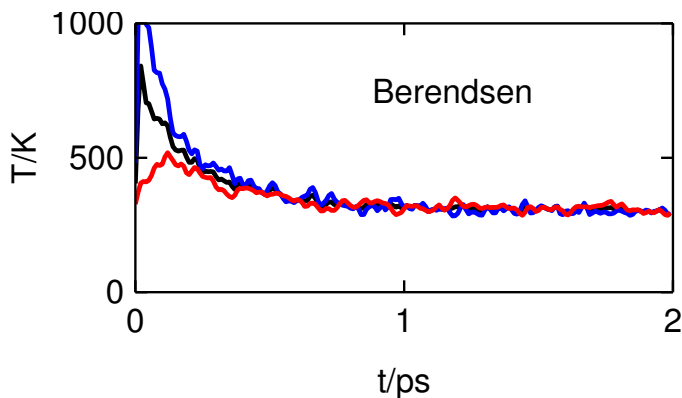
Maxwell–Boltzmann, Langevin etc.

- ⊕ canonical (incl. conserved quantities)
- ⊕ exponential relaxation
- ⊖ kinetics lost
- ⊖ problematic with constrained dynamics

for me: Show flying icecube simolant: max. speed + select Berendsen thermostat

Thermostats: application to water

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



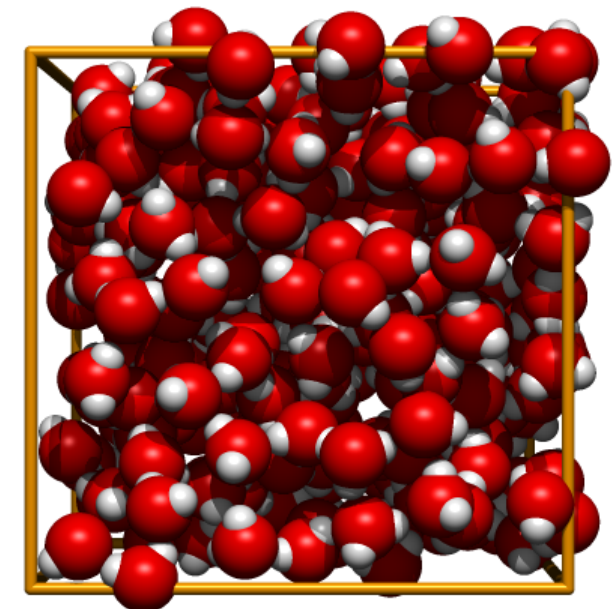
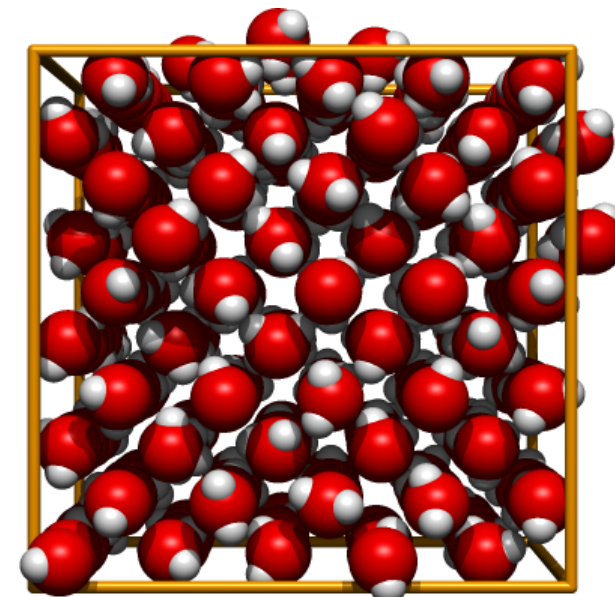
$\tau = 0.1$ ps

T :

— total

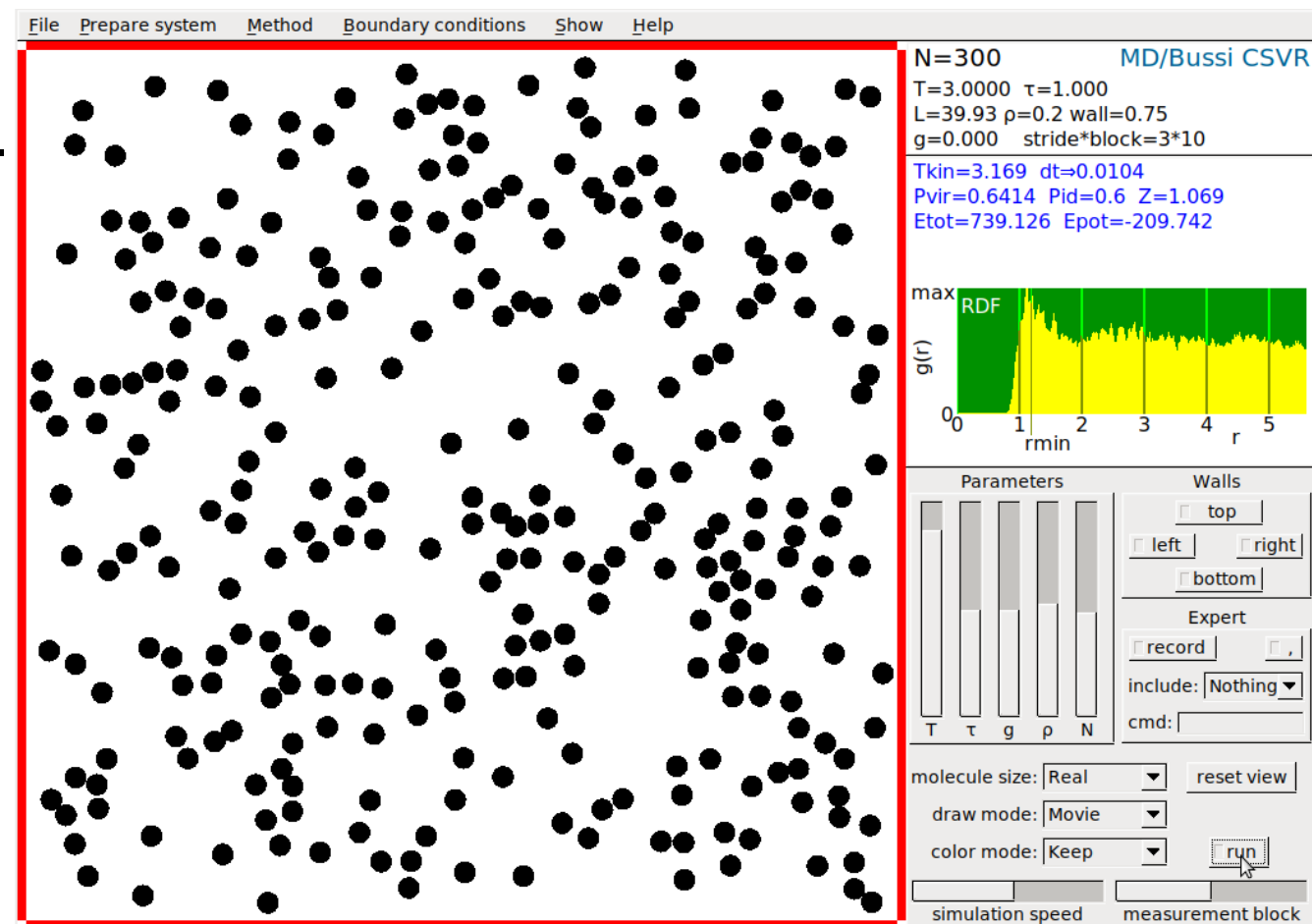
— center-of-mass

— rotations



Installation of SIMOLANT (Windows):

- <http://old.vscht.cz/fch/software/simolant>
or [Google](#) 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



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”.
- For faster simulation, decrease # of particles by slider “N” to ~ 50 .
- Menu: Show → Integral of motion convergence profile
The graph is always scaled from min to max.
- If needed, reset the graph by button reset view
- Menu: Method → Molecular dynamics (NVE)
 - write “dt=0.005” to the cmd: field
 - write “dt=0.01” to the cmd: field and observe the difference
 - write “dt=0.02” to the cmd: field and observe the difference
 - **for too long dt, the simulation may switch to MC to avoid crash**
- Try to change (T, ρ, N) ($\rho = \text{rho} = \text{number density}$):
 - return the default (automatic setup) by “dt=0”
 - switch the method to (e.g.) Monte Carlo NVT (Metropolis)
 - switch back to Molecular dynamics (NVE)

N=50 MD/NVE
 Epot+Ekin=111.499
 L=17.01 ρ =0.2 wall=0.75
 g=0.000 stride*block=3*1
 Tkin=2.647 dt=0.0200
 Pvir=0.7445 Pid=0.6 Z=1.241
 Etot=108.663 Epot=-20.2276
 112.542 stdev=0.658
 Ekin+Epot
 107.744 max-min=4.798
 Parameters Walls
 g ρ N
 top
 left right
 bottom
 Expert
 record
 include: Nothing
 cmd:
 molecule size: Real reset view
 draw mode: Movie
 color mode: Keep run
 simulation speed measurement block

Try thermostats by yourself

- Turn simulation off by button **run**
- Menu: **Show** → **Temperature convergence profile**
or optionally **Energy/enthalpy convergence profile**
- Menu: **Method** → **Molecular dynamics (Berendsen thermostat)**
- Turn simulation on by button **run**
 - 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 ”: $\rho \approx 0.6$
- Try thermostats for a few molecules only, recommended setup:
 - very low density (slider ρ)
 - draw mode: **Traces**
 - molecule size: **Small** or **Dot**

Method Boundary conditions Show Help

N=50 **MD/NVT/Berendsen**
 T=0.4487 $\tau=1.000$
 L=10.24 $\rho=0.612$ wall=0.75
 g=0.000 stride*block=3*1

Tkin=0.448 dt=0.0269
 Pvir=0.4457 Pid=0.2746 Z=1.623
 Etot=-114.804 Epot=-135.786

neighbors: 0 1 2 3 4 5 6 7+
 1.95259 stdev=0.591

Tkin
 0.353856 max-min=1.599

Parameters Walls
 T τ g ρ N
 top
 left right
 bottom
 Expert
 record ,
 include: Nothing
 cmd:

molecule size: Real reset view
 draw mode: Movie
 color mode: Neighbors **run**

simulation speed measurement block