Gear’s methods I

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

- Rarely used in special cases (rotations)
- 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:

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

Gear's metods II

The error of the predictor:

$$\vec{E}_i = \frac{h^2}{2}\frac{\vec{f}_i(\vec{r}^N(t+h)^{\text{pred}})}{m_i} - \frac{h^2}{2}\ddot{\vec{r}}_i(t+h)^{\text{pred}}$$

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

Gear’s metods I

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

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

[a] suitable for a r.h.s. without $\dot{\vec{r}}$

[b] suitable for a r.h.s. with $\dot{\vec{r}}$

[c] equivalent to velocity Verlet
(lower order, time-reversible)

2nd order:

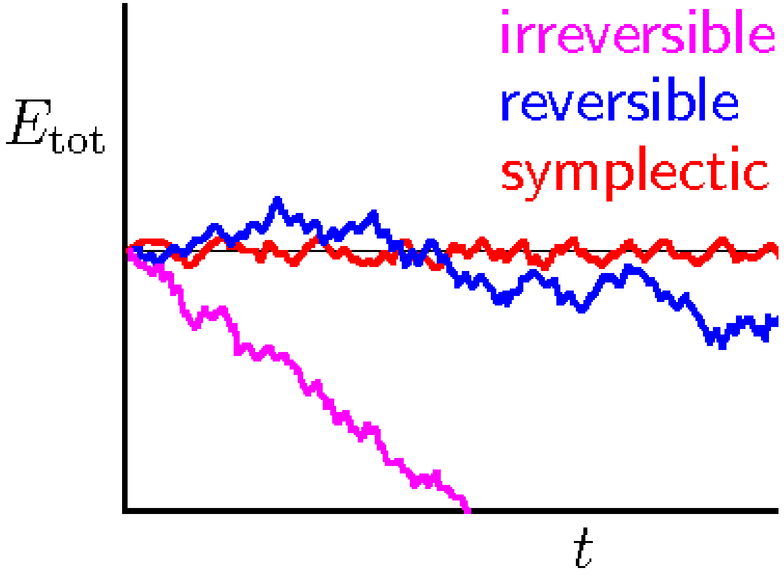
M	a_0 [a]	a_0 [b]	a_1	a_2	a_3	a_4	a_5
3[c]	0	0	1	1			
3	1/6	1/6	1	1			
4	1/6	1/6	5/6	1	1/3		
5	19/120	19/90	3/4	1	1/2	1/12	
6	3/20	3/16	251/360	1	11/18	1/6	1/60

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 so that the trajectory is accurate (in MD, usually not needed/does not matter)

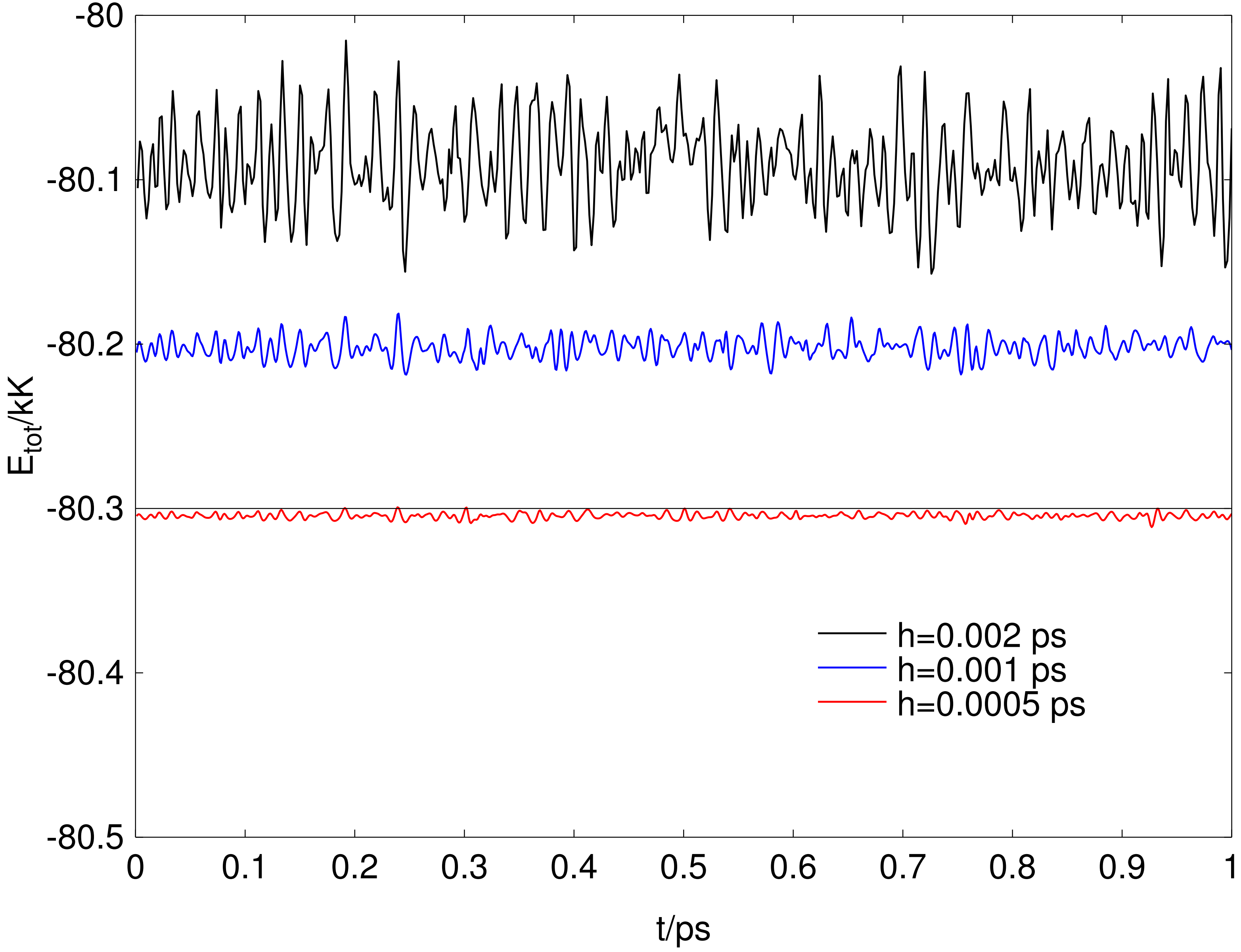
Gear and similar: just opposite



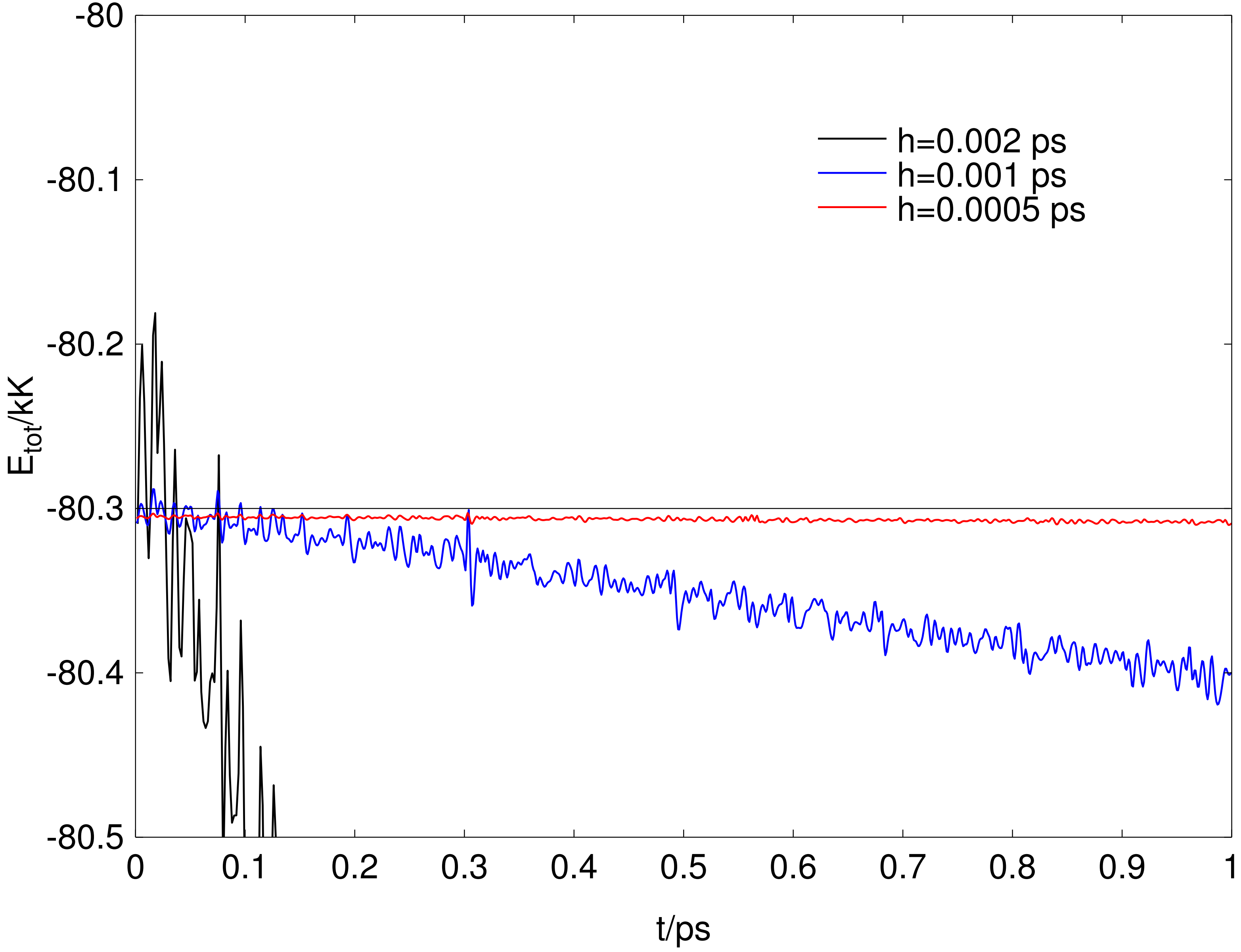
Notes:

- a symplectic integrator preserves (with bounded accuracy) the phase space volume $\mathrm{d}\vec{r}^N\mathrm{d}\vec{p}^N$
- 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

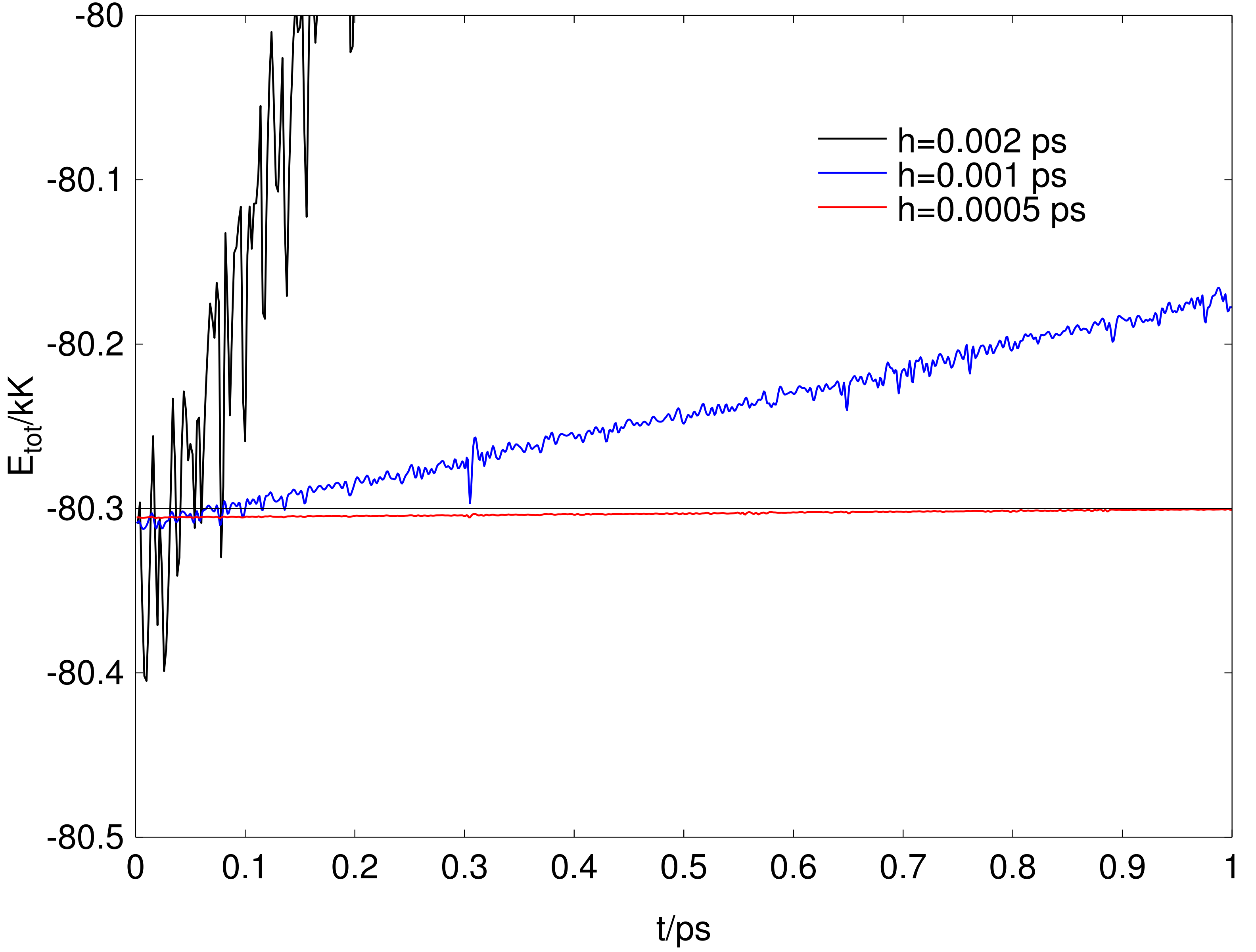
Energy conservation: Verlet



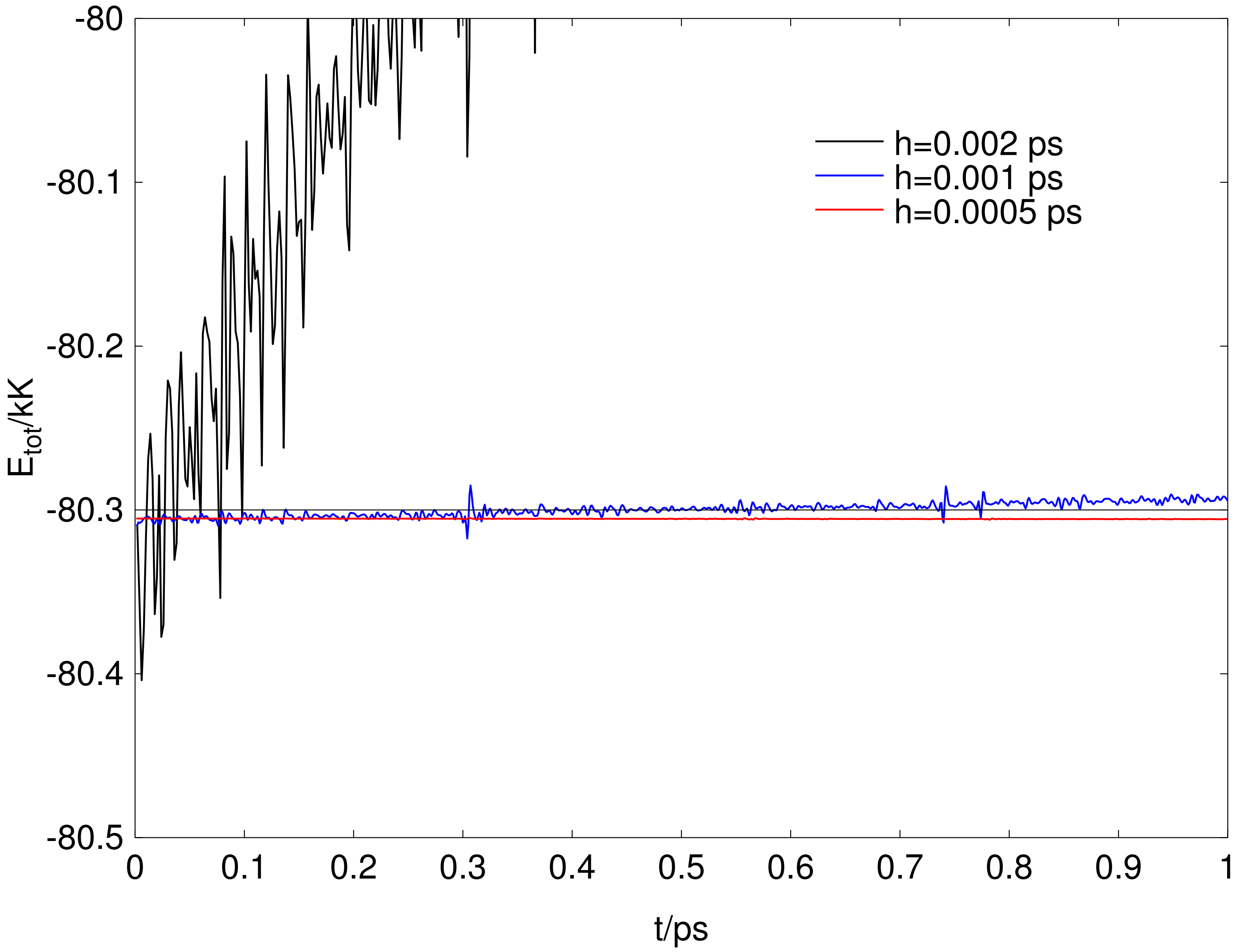
Energy conservation: Gear $M = 4$



Energy conservation: Gear $M = 5$



Energy conservation: Gear $M = 6$



Exercise

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 $K = 1$ a $m = 1$ and one of the following methods:

- Verlet
- velocity Verlet
- leap-frog
- Runge-Kutta 4th order for $y'' = f(x, y),\ y(x_0) = y_0,\ y'(x_0) = y'_0$:

$$\begin{aligned}
k_1 &= f(x_0, y_0, y'_0)\,,\\
k_2 &= f\left(x_0 + \frac{h}{2}, y_0 + \frac{1}{2}hy'_0 + \frac{h^2}{8}k_1, y'_0 + \frac{h}{2}k_1\right),\\
k_3 &= f\left(x_0 + \frac{h}{2}, y_0 + \frac{1}{2}hy'_0 + \frac{h^2}{8}k_2, y'_0 + \frac{h}{2}k_2\right),\\
k_4 &= f\left(x_0 + h, y_0 + hy'_0 + \frac{h^2}{2}k_3, y'_0 + hk_3\right),\\
y_1 = y(x_0 + h) &= y_0 + hy'_0 + \frac{h^2}{6}(k_1 + k_2 + k_3)\,,\\
y'_1 = y'(x_0 + h) &= y'_0 + \frac{h}{6}(k_1 + 2k_2 + 2k_3 + k_4)\,.
\end{aligned}$$

Exercise II

- 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:

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

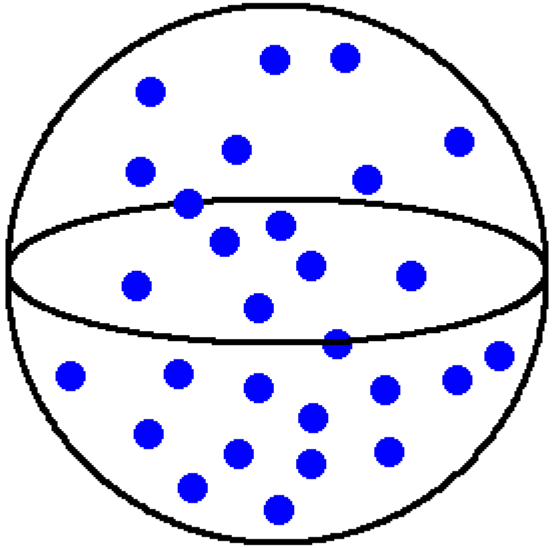
  $$y(t+h) = y(t) + \frac{h}{12}[23f(t) - 16f(t-h) + 5f(t-2h)]$$

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

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

Temperature

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



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

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

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:

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

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, . . .).

Constant temperature in MD: methods

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

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)

canonical stochastic:

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

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

Comparison of thermostats

```
simolant -H.1 -I9 -N50 -Pbc=2,T=.5,tau=0.1,rho=0.1
```

Nosé–Hoover

- ⊕ canonical (except conserved quantites)
- ⊕ 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 quantites)
- ⊕ 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

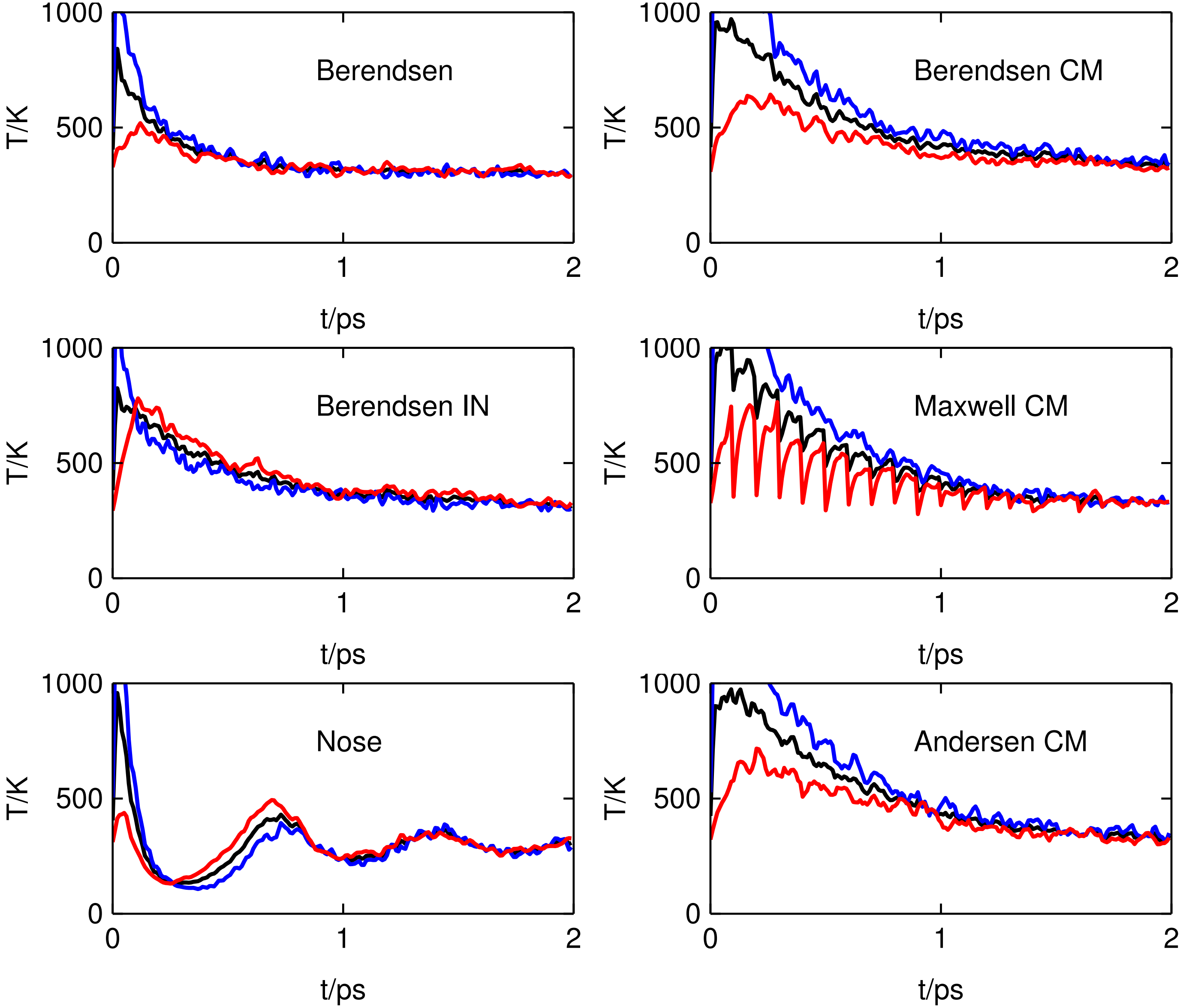
- ⊖ kinetics lost
- ⊖ problematic with constrained dynamics

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

Thermostats: application to water

start simul/spce/spce250.plb

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



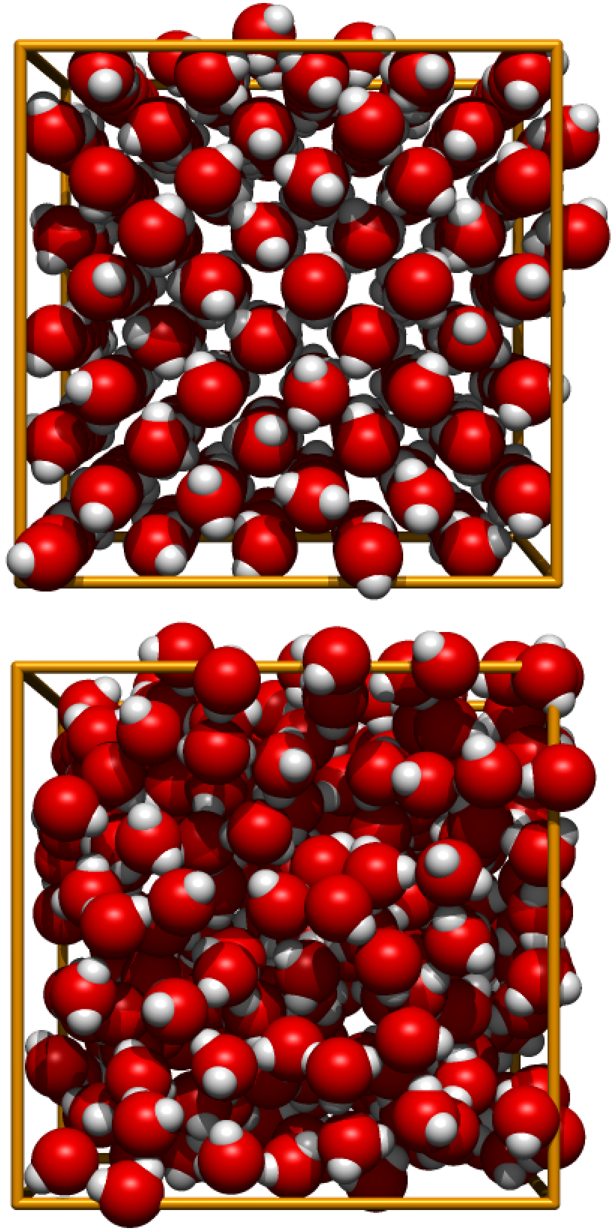
$\tau = 0.1$ ps

T:

— total

— center-of-mass

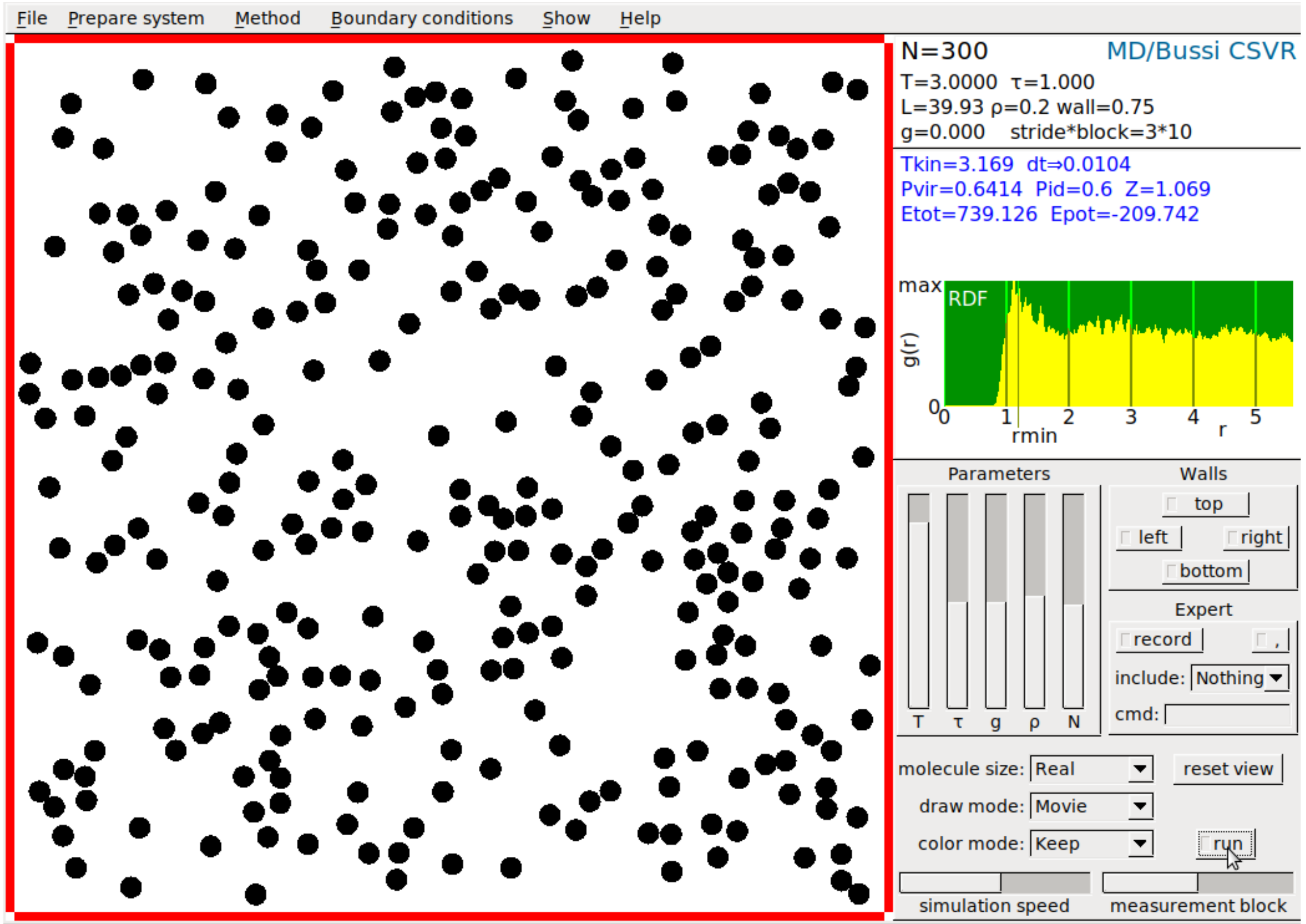
— rotations



SIMOLANT: Try molecular dynamics by yourself

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

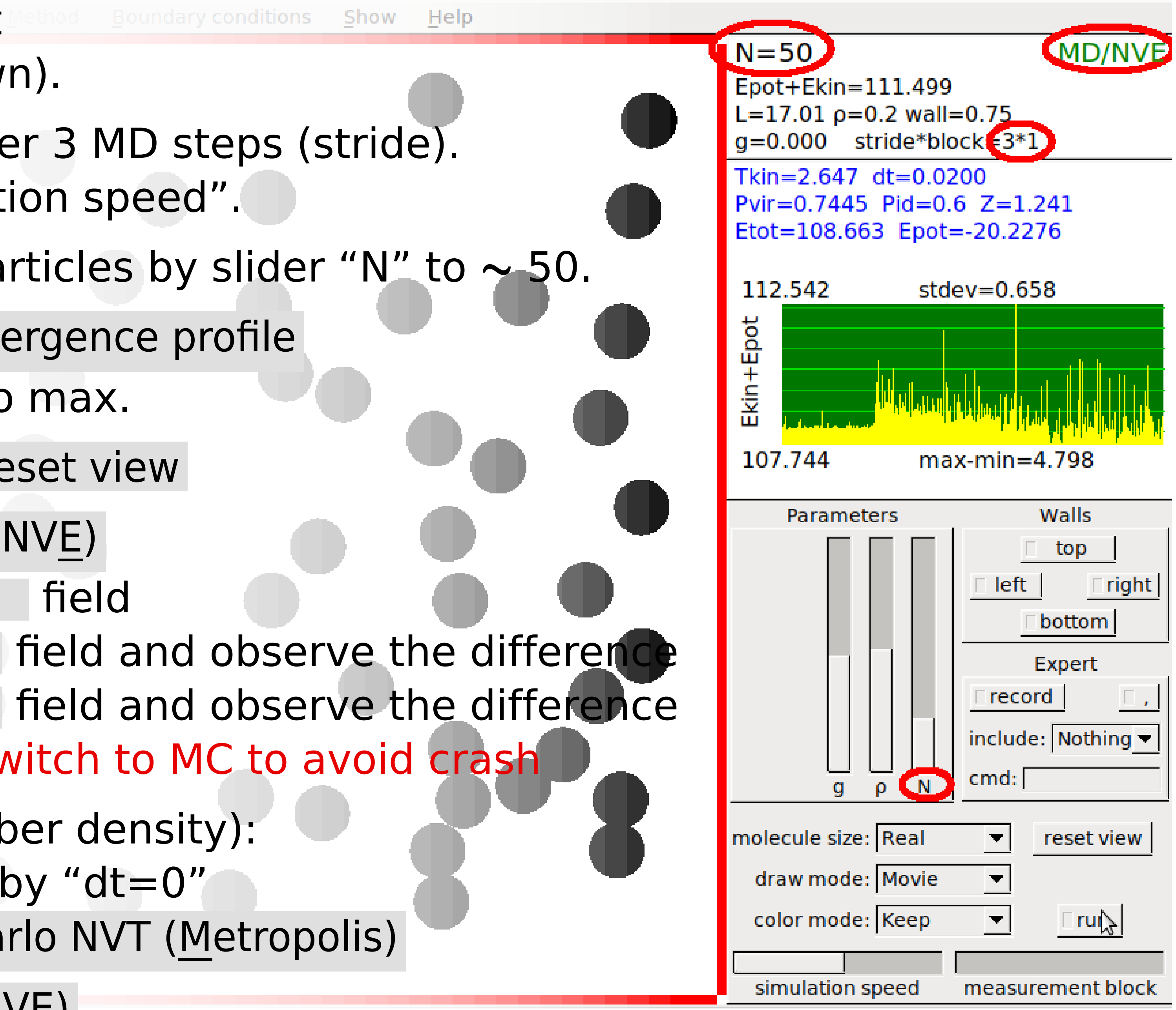


```
N=300                MD/Bussi CSVR
T=3.0000  τ=1.000
L=39.93 ρ=0.2 wall=0.75
g=0.000   stride*block=3*10
Tkin=3.169  dt⇒0.0104
Pvir=0.6414  Pid=0.6  Z=1.069
Etot=739.126  Epot=-209.742
```

include: Nothing
cmd:
molecule size: Real
draw mode: Movie
color mode: Keep

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) (ρ = rho = 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)

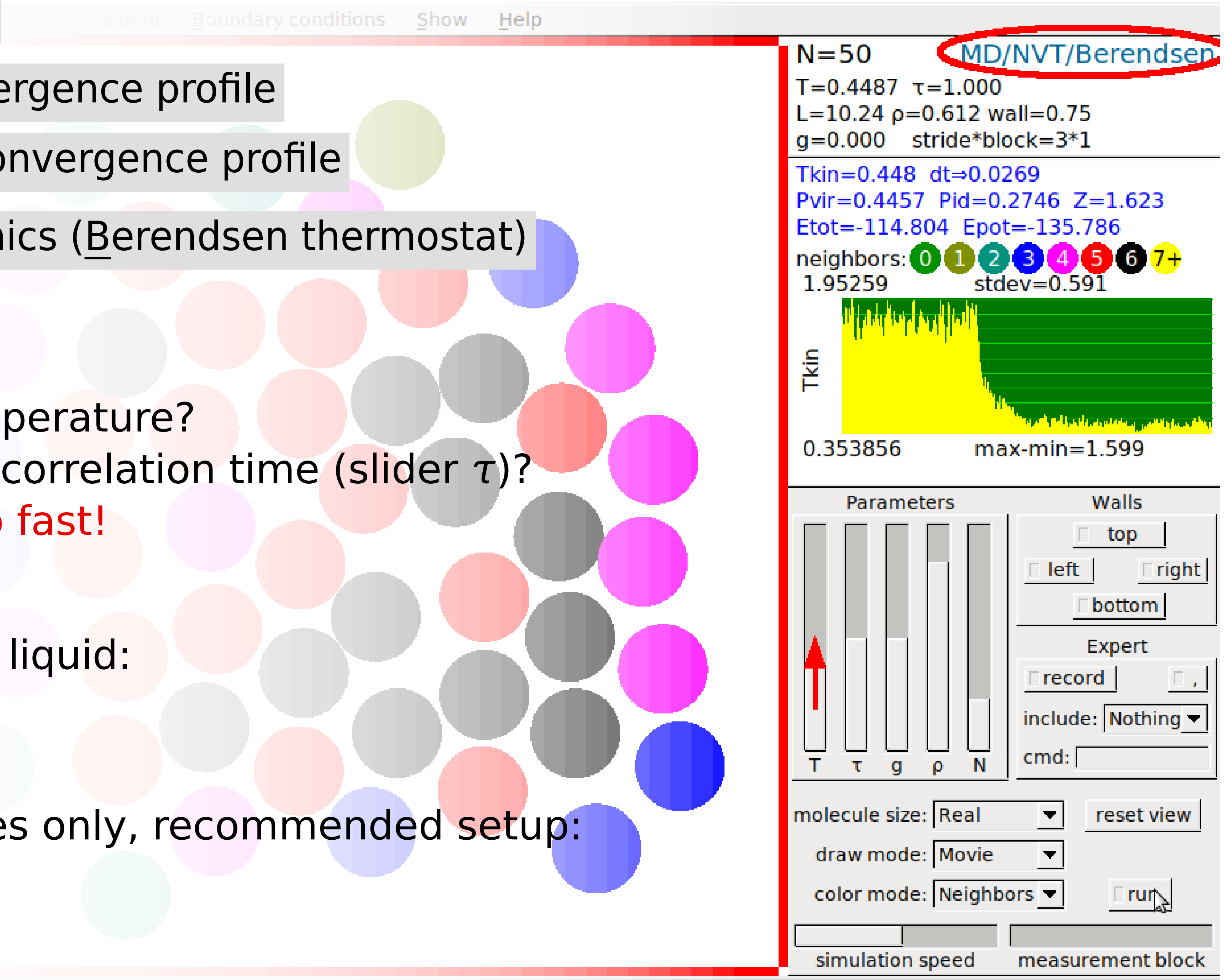


```
N=50                                   MD/NVE
Epot+Ekin=111.499
L=17.01 ρ=0.2 wall=0.75
g=0.000   stride*block=3*1
Tkin=2.647  dt=0.0200
Pvir=0.7445  Pid=0.6  Z=1.241
Etot=108.663  Epot=-20.2276
```

include: Nothing
cmd:
molecule size: Real
draw mode: Movie
color mode: Keep

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



N=50 MD/NVT/Berendsen
T=0.4487 τ=1.000
L=10.24 ρ=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+

include: Nothing
cmd:
molecule size: Real
draw mode: Movie
color mode: Neighbors