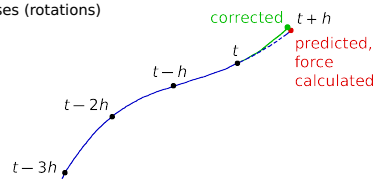
Gear's methods

- **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)

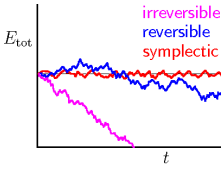


*Except one version of the simplest singular 2nd order method equivalent to Verlet

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)

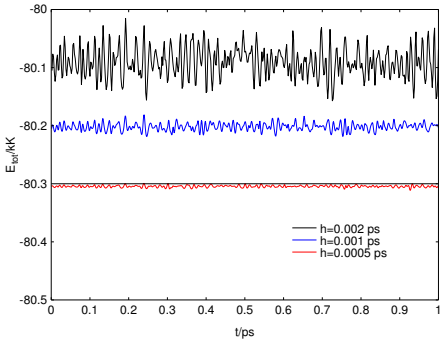


Gear and similar: just opposite

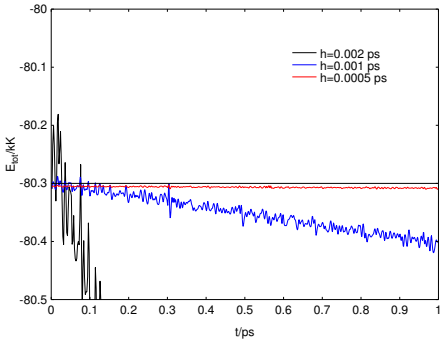
Notes:

- a symplectic 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

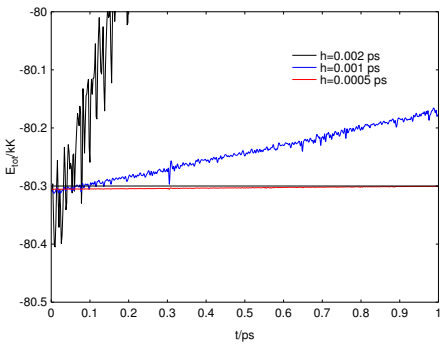
Energy conservation: Verlet



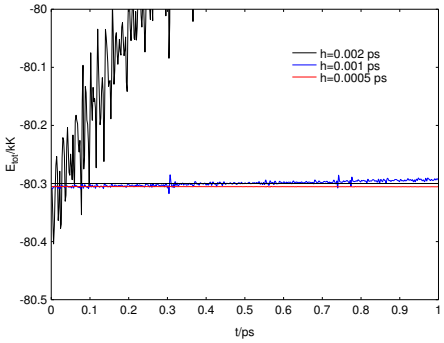
Energy conservation: Gear $M = 4$



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 $y'' = f(x, y),\ y(x_0) = y_0,\ y'(x_0) = y'_0$:

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

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

Exercise II

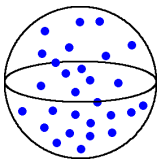
- Beeman: $r(t+h) = r(t) + v(t)h + \frac{4f(t)-f(t-h)}{6m}h^2$
  $v(t+h) = v(t) + \frac{2f(t+h)+5f(t)-f(t-h)}{6m}h$
- Gear 2nd order $M = 4$

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:
  $y(t+h) = y(t) + \frac{h}{2}[3f(t) - f(t-h)]$
  $y(t+h) = y(t) + \frac{h}{12}[23f(t) - 16f(t-h) + 5f(t-2h)]$
  $y(t+h) = y(t) + \frac{h}{24}[55f(t) - 59f(t-h) + 37f(t-2h) - 9f(t-3h)]$
- Runge-Kutta 4th order (for the 1st order differential equation)

Temperature

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



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

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

It is assumed that the conserved degrees of freedom are zero

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

Generally from the equipartition theorem:

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

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:

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

Constant temperature in MD: methods

not canonical: (do not give the canonical ensemble)

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

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

* 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 ⇒ canonical ensemble. Problem: tricks needed with Verlet (r.h.s. depends on velocities)

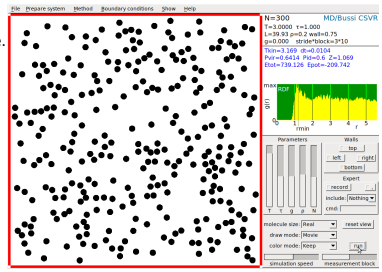
canonical stochastic:

- 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])

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



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 $-fk_{\mathrm{B}}T\ln s$

⋮

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

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

Thermostat time constant:

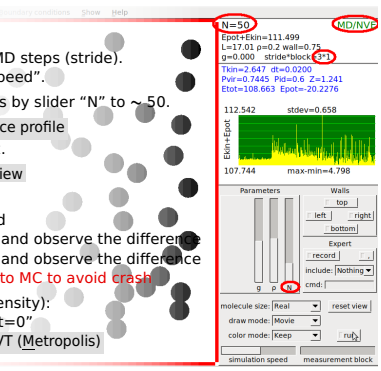
$$\tau = \sqrt{\frac{M_s}{fk_{\mathrm{B}}T}}$$

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

Energy conservation

show/thermostats.sh

- 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)



Comparison of thermostats

simolant -H.1 -l9 -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.

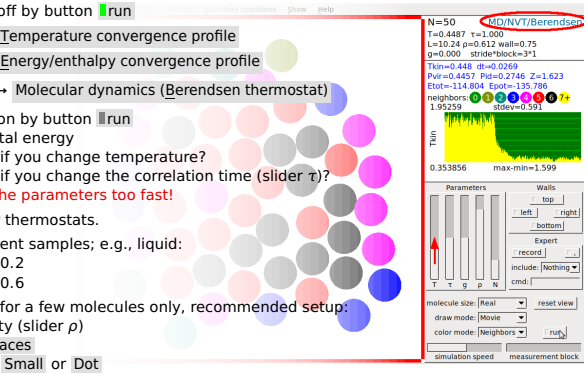
- ⊕ canonical (incl. conserved quantities)
- ⊕ exponential relaxation
- ⊖ kinetics lost
- ⊖ problematic with constrained dynamics

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

Try thermostats by yourself

show/thermostats.sh

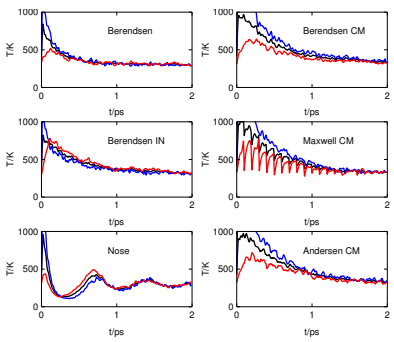
- Turn simulation off by button run
- Menu: Show → Temperature convergence profile
  or optionally Energy/enthalpy convergence profile
- Menu: Method → Molecular dynamics (Berendsen thermostat)
- Turn simulation on by button run
  – observe the total energy
  – what happens if you change temperature?
  – 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



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