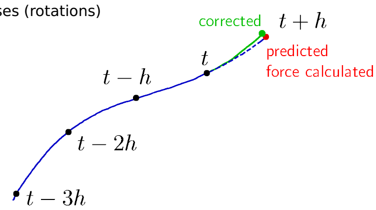
Gear's methods

- **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)



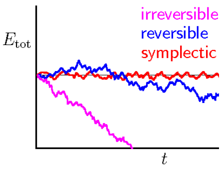
*Except one version of the simplest singular 2nd order method equivalent to Verlet

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 $\ddot{\vec r} = f(r, \dot r)$: Nosé–Hoover, rotations)
- ⊖ difficult change of the timestep

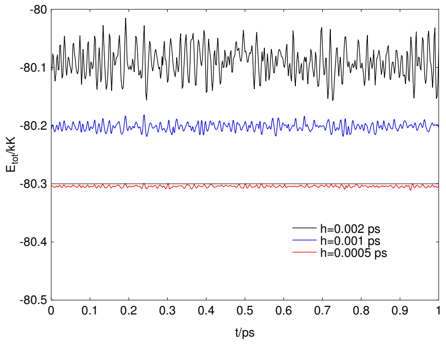
Gear: and similar: just opposite



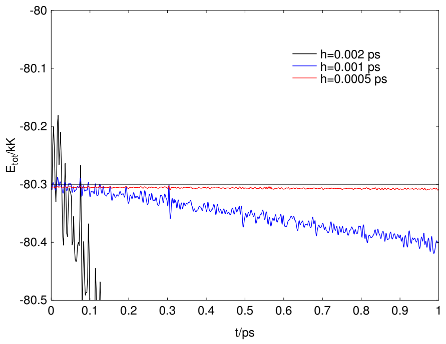
Notes:

- 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 flow of phase-space volume
- the quality of energy conservation helps us to set up the timestep h

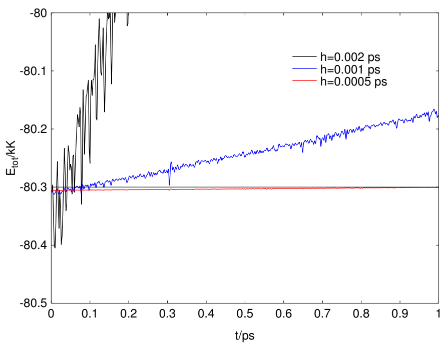
Energy conservation: Verlet



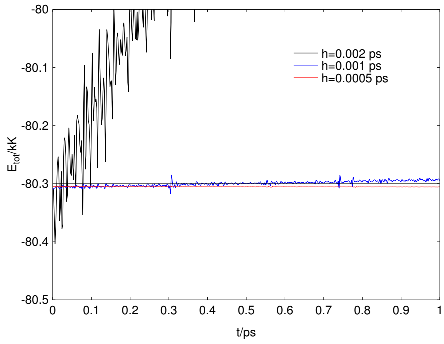
Energy conservation: Gear $M = 4$



Energy conservation: Gear $M = 5$



Energy conservation: Gear $M = 6$



Temperature

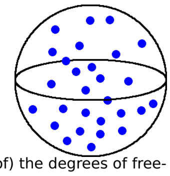
The temperature is **measured** in the standard (microcanonical) MD.

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

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

Example: molecules in a spherical cavity:

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



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
- $T_\mathrm{rot+in}$ from rotations and internal degrees of freedom.
- disagreement $T_\mathrm{tr} \neq T_\mathrm{rot+in}$ 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: $\ddot{\vec r}_i = \frac{\vec f_i}{m_i} - \eta (T_\mathrm{kin} - T) \dot{\vec r}_i$, $\eta = \frac{q}{Th}$

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)
- Modified Berendsen

canonical stochastic:

- Maxwell–Boltzmann: once a while the velocties of particles are drawn from the Maxwell–Boltzmann distribution, $\pi(\dot x_i) = \exp(-\dot x^2/2\sigma^2)/\sigma\sqrt{2\pi}$, $\sigma^2 = k_\mathrm{B} T/m_i$
- Andersen: randomly visit particles (usually better)
- Langevin: small random force added to all particles at every step
- Canonical sampling through velocity rescaling (Bussi, Donadio, Parrinello)
- Gaussian rescaling: $E_\mathrm{kin} = \mathrm{const}$, canonical in the configurational space only

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 ($\xi = \ln s$):

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

Thermostat time constant:

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

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

Thermostats

Nosé–Hoover

⊕ canonical	⊖ oscillations, decoupling (fine tuning of τ)
⊕ high quality	⊖ worse for start
⊕ good also for small systems (N-H chain)	⊖ equations of motion w. velocities

Berendsen

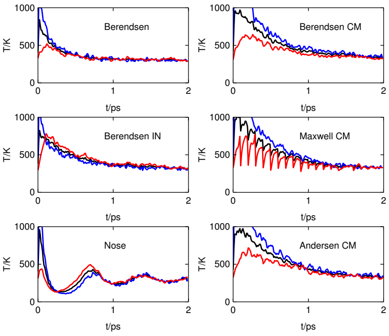
⊕ simple	⊖ flying icecube
⊕ exponential relaxation (i.e., good also for start)	⊖ not canonical
	⊖ poor for small systems

Maxwell–Boltzmann etc.

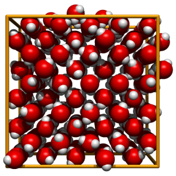
⊕ canonical	⊖ kinetics lost
⊕ exponential relaxation	⊖ problematic with constrained dynamics

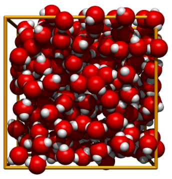
Thermostats: application to water

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



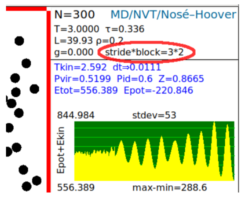
$\tau = 0.1$ ps
T:
— total
— center-of-mass
— rotations





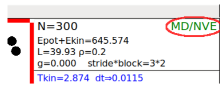
Energy conservation

- 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".
- If slow, decrease # of particles by slider "N"
- Menu:
  Show → Integral of motion convergence profile



The time development of energy is always scaled from min to max.

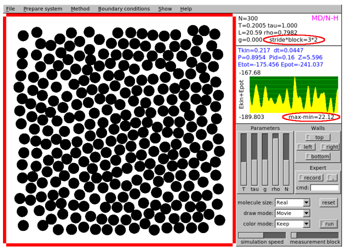
- If needed, reset the graph by button reset
- Menu: Method → Molecular dynamics (NVE)
  – write "dt=0.01" to the cmd: field
  – write "dt=0.02" to the cmd: field
  and observe the difference
  – for too long dt, the simulation will switch to MC to avoid crash
  – do not forget to return the default (automatic setup) by "dt=0"



SIMOLANT: Try molecular dynamics by yourself

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`.
- Also supported: linux, MacOS



Try thermostats by yourself

- Turn simulation off by button run
- Menu: Show → Energy/enthalpy convergence profile
- Menu: Method → Molecular dynamics (Berendsen thermostat)
- Turn simulation on by button run
- 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": $\rho \approx 0.6$