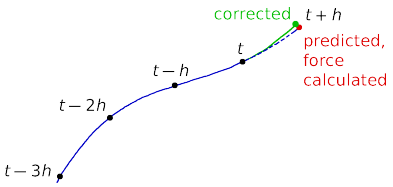
Gear's methods

- Are of **predictor-corrector** type: Knowledge of history (previous steps) is used to predict the approximate solution, which is corrected (and stabilized) in the following steps.
- Gear's method: polynomial predictor = no additional costly right-hand side evaluation of forces, but compromised stability.
- Not time-reversible* ⇒ drift in total energy
- Higher-order (3+).
- Rarely used in special cases (rotations).

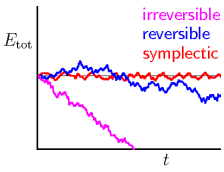


*except for the simplest second order methods

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)

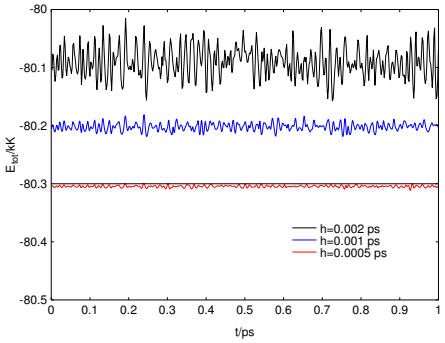


Gear, Runge-Kutta: most properties are opposite

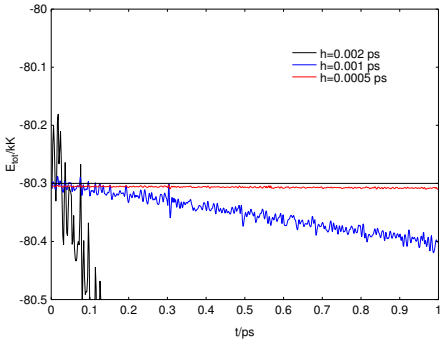
Notes:

- 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

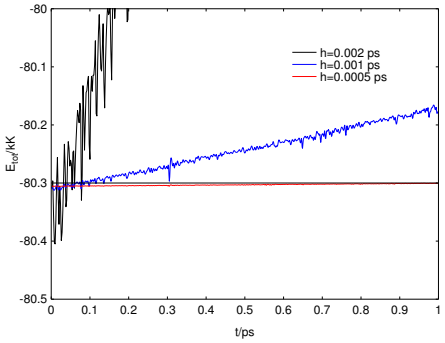
Energy conservation: Verlet



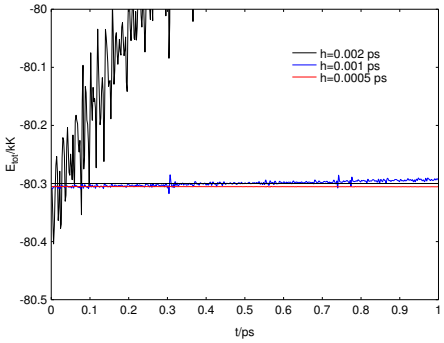
Energy conservation: Gear $M = 4$



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 $M = 4$

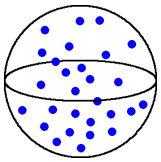
Try also the Hamilton equations of motion using:

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

Temperature

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

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



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

It is assumed that the conserved degrees of freedom are zero

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

Generally from the equipartition theorem:

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

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

* 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])

Nosé–Hoover thermostat

- one degree of freedom added: "position" s and "velocity" $\dot{s}$ ("piston of entropy")
- + kinetic energy $\frac{M_s}{2}\dot{s}^2$
- + potential energy $-fk_BT\ln s$

⋮

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

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

Thermostat time constant:

$$\tau = \sqrt{\frac{M_s}{fk_BT}}$$

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

Comparison of thermostats

Nosé–Hoover deterministic

- ⊕ canonical (except conserved quantites)
- ⊕ high quality
- ⊕ good for small systems (esp. Nosé–Hoover chain)
- ⊖ oscillations, decoupling (fine tuning of τ)
- ⊖ worse for start
- ⊖ equations of motion w. velocities

Berendsen deterministic

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

Bussi et al. (CSVR) stochastic

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

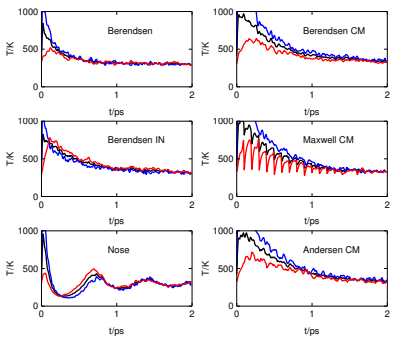
Maxwell–Boltzmann, Langevin etc. stochastic

- ⊕ canonical (incl. conserved quantities)
- ⊕ exponential relaxation
- ● also center-of-mass and total momentum sampled
- ⊖ kinetics lost
- ⊖ problematic with constrained dynamics

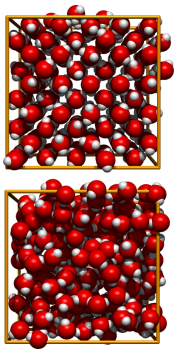
for me: Show flying icecube simolant: max. speed + select Berendsen thermostat

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



Energy conservation error and timestep: NVE

Variance of $E_{\text{tot}} = E_{\text{kin}} + E_{\text{pot}} \approx$ sum of N_f independent random contribution:

$E_{\text{pot}} \equiv U(\vec{r}^N)$

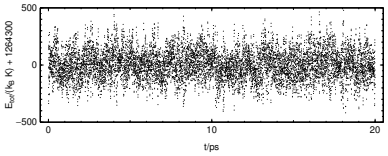
$$\text{Var}\, E_{\text{tot}} = N_f\sigma_f^2$$

$\sigma_f \propto h^2$
(Verlet is 2nd order)

N_f = number of degrees of freedom
σ_f = "standard deviation of the total energy per a degree of freedom"

$\sigma_f/k_B \lessapprox$ (a few)$10^{-3}T$, at ambient temperature: $\sigma_f/k_B \lessapprox 1$ K

Example: 267 SPC/E water molecules, Ewald summation, NVE $h = 2$ fs, 10000 time steps, SHAKE, $T \approx 298$ K, $\rho = 997$ kg m^{-3}, leap-frog kinetic energy (see next page):



$\Rightarrow\quad \sigma(E_{\text{tot}}) = \sqrt{\text{Var}\,(E_{\text{tot}})} = k_B \cdot 126$ K.

$N_f = 6 \times 267 - 3 = 1599 \quad\Rightarrow\quad \sigma_f/k_B = \sigma(E_{\text{tot}})/\sqrt{N_f} = 3.1\,\text{K} \lessapprox 1\,\%T$: $h = 2$ fs is rather inaccurate
For $h = 1$ fs, the expected $\sigma_f/k_B = 3.1\,\text{K} \times (1\,\text{fs}/2\,\text{fs})^2 \approx 0.78$ K: $h = 1$ fs is acceptable

More about the kinetic energy in the Verlet-like integrators

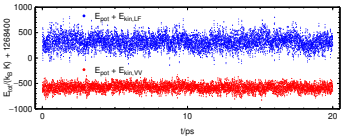
- Velocity-Verlet (VV) kinetic energy (naturally available in the VV version of the integrator):

$$E_{\text{kin,VV}} = \sum_i \frac{m_i}{2} v_i(t)^2 = \sum_i \frac{m_i}{2}\left[\frac{\vec{r}(t+h) - \vec{r}(t-h)}{2h}\right]^2$$

- Leap-frog (LF) kinetic energy (naturally available in the LF version of the integrator):

$$E_{\text{kin,LF}} = \sum_i \frac{m_i}{4}\left\{v(t-h/2)^2 + v(t+h/2)^2\right\} = \sum_i \frac{m_i}{4}\left\{\left[\frac{\vec{r}(t) - \vec{r}(t-h)}{h}\right]^2 + \left[\frac{\vec{r}(t+h) - \vec{r}(t)}{h}\right]^2\right\}$$

- The VV and LF trajectories are identical.
- T_{kin} depends on the kinetic energy formula, E_{kin}.
- Static quantities do not depend.
- The error in $E_{\text{tot}} = E_{\text{pot}} + E_{\text{kin}}$ is smaller for VV.
- The values of kinetic quantities using velocities may depend on the velocity formula.
- With some thermostats (Nosé–Hoover, Berendsen, Bussi CSVR), both static and kinetic quantities do depend on the velocity/kinetic energy formula through E_{kin}.



Velocity-Verlet vs. leap-frog with thermostat

- SPC/E water at ambient conditions
  Thermostat Nosé–Hoover + TRVP, temperature from $E_{\text{kin,VV}}$ or $E_{\text{kin,LF}}$
  Convergence $h \to 0$ ($h = 2$ fs, 1 fs, 0.5 fs) is analyzed

For liquid argon and green quantities, LF ⟷ VV

VV converges faster for:

- E_{tot}
- pressure
- parameters of distribution T_{kin}: variance (slightly), kurtosis (much).

LF converges faster for:

- potential energy
- diffusivity (from $\langle r^2 \rangle$)
- equipartition error $\Delta T = T_{\text{translation}} - T_{\text{rotation}}$

Extremes, for $h = 2$ fs:

- Relative error of density: VV ≤ 0.1 %, LF = 0.3 %
- Relative error of diffusivity: VV = 2.8 %, LF ≤ 0.5 %

Sources: original calculations and Kolafa, Lísal 2011

Mass repartioning, equipartition error

- *Mass repartitioning* (mass equalization) allows for a longer time step.
  The ensemble averages of static quantities are unchanged.
  Kinetic quantities (relaxation time, diffusivity, viscosity,...) are affected, though.
- Equipartition error: $\Delta T = T_{\text{translations}} - T_{\text{rest (rotations)}}$, good for small molecules.
- Tests for water SPC/E, 25 °C, 997 kg m^{-3}:
  σ_f are calculated in NVE (10^4 steps) and are divided by k_B
  ΔT is calculated in NVT (see previous slide)

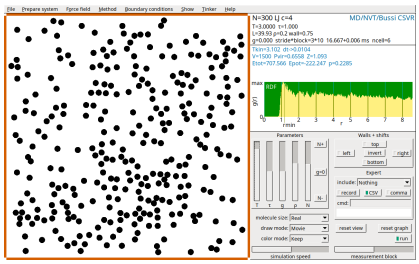
h	real masses				H=5, O=8 g/mol	
	$\sigma_{f,VV}$	$\sigma_{f,LF}$	ΔT_{VV}	ΔT_{LF}	$\sigma_{f,VV}$	$\sigma_{f,LF}$
[fs]	[K]	[K]	[K]	[K]	[K]	[K]
1	0.44	0.74	0.58	−0.29	0.17	0.31
2	1.80	3.11	2.36	−1.14	0.65	1.19
3	3.94	7.17			1.45	2.81
4	7.32	12.8			2.64	5.02
5					4.20	7.87

Water with equalized masses and $h = 2$ fs is acceptable.

Try molecular dynamics yourself: SIMOLANT

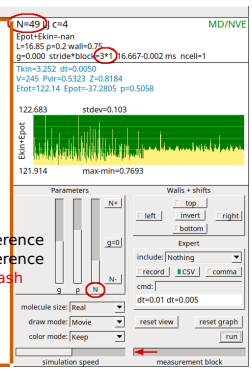
Installation of SIMOLANT (Windows):

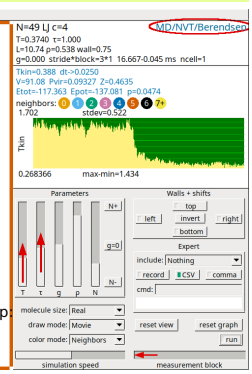
- Google simolant or use the following links:
  – https://github.com/kolafaj/SIMOLANT → executables
  – http://old.vscht.cz/fch/software/simolant
- Download `simolant-win.zip`
- Create a folder
  and unpack SIMOLANT there.
  Do not run directly from
  `simolant-win.zip`
  – help would not work,
  – you would not find saved files.
- Run `simolant.exe`
- Also available for:
  – linux
  – MacOS (compilation needed)



Hands-on: Energy conservation

- Slider "measurement block" to the left
  (1 point shown = 1 calculated value).
- The default is one energy calculated per 3 MD steps (stride)
  This can be changed by slider "simulation speed".
- To be faster, 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, observe the difference
  – write "dt=0.02" to the cmd: field, 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)



Hands-on: Thermostats

- 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: run
  – observe the total energy
  – what happens if you change temperature (slider T)?
  – what if you change the thermostat time constant (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