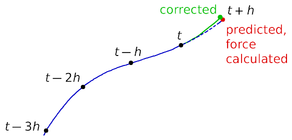
Gear's methods I

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.
- Without r.h.s. ⇒ predictor= polynomial, 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:

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

Gear's metods II

The error of the predictor:

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

Corrector:

$$R(t+h) = R(t+h)^{\rm pred} + \begin{pmatrix} \alpha_0 \\ \alpha_1 \\ \alpha_2 \\ \alpha_3 \end{pmatrix} E$$

Unknown constants determined from the **stability conditions**.

For a 1st order equation $y' = f(y)$:

$$E = hf(y(t+h)^{\rm pred}) - hy'(t+h)^{\rm pred}$$

equivalent to Adams–Bashforth

Gear's metods – coefficients

1st order equation:

M	α_0	α_1	α_2	α_3	α_4	α_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

2nd order equation:

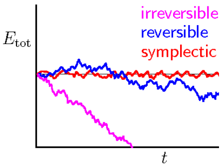
M	α_0 [a]	α_0 [b]	α_0 [c]	α_1	α_1 [c]	α_2	α_3	α_4	α_5
3[d]	1/6	1/6	0	1	1	1			
4	1/6	1/6	0	5/6	2/3	1	1/3		
5	19/120	19/90	1/12	3/4	3/4	1	1/2	1/12	
6	3/20	3/16	1/30	251/360	23/36	1	11/18	1/6	1/60

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] better energy conservation
[d] $\alpha_0 = 0, \alpha_1 = \alpha_2 = 1$: equivalent to velocity Verlet (lower order, time-reversible)

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)

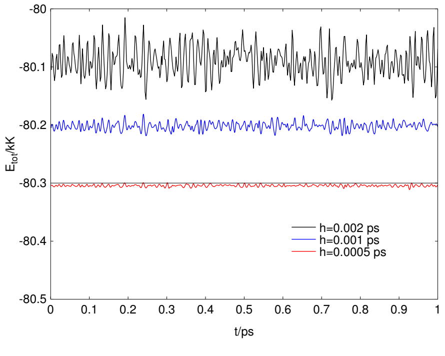


Gear, Runge-Kutta: most properties are opposite

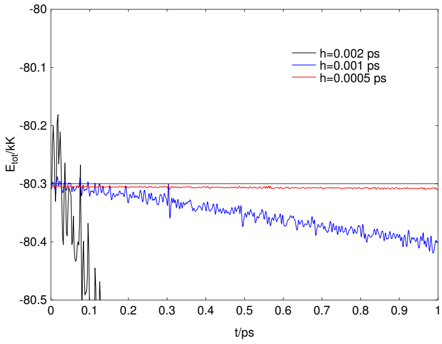
Notes:

- a symplectic integrator 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

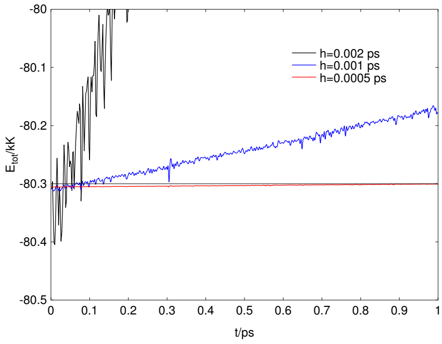
Energy conservation: Verlet



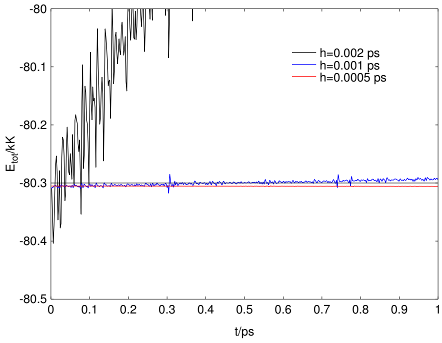
Energy conservation: Gear $M = 4$



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

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

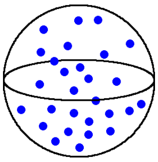
Exercise II

- 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.
- $T_\text{tr} \ne T_\text{rot+in}$ 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: $\vec{v}_{i,\text{new}} = \vec{v}_i(T/T_\text{kin})^{1/2}$
- *Berendsen (friction): $\vec{v}_{i,\text{new}} = \vec{v}_i(T/T_\text{kin})^q$, $q < 1/2$,

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

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 velocities of particles are drawn from the Maxwell–Boltzmann distribution, $\boldsymbol{\pi}(\dot{x}_i) = \exp(-\dot{x}^2/2\sigma^2)/\sigma\sqrt{2\pi}$, $\sigma^2 = k_\text{B}T/m_i$
- 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 $-fk_\text{B}T\ln s$

⋮

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:

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

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

Comparison of thermostats

simolant -I6 -N50 -Pbc=2,T=.48,tau=0.1,rho=0.1,block=1,method=5

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

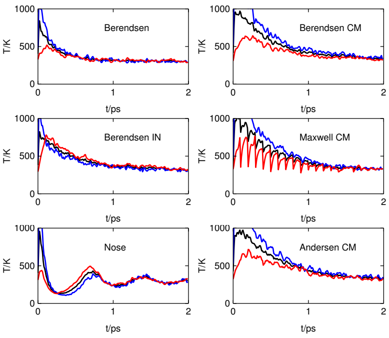
- ⊕ canonical (incl. conserved quantities)
- ⊕ exponential relaxation
- also center-of-mass and total momentum sampled
- ⊖ kinetics lost
- ⊖ problematic with constrained dynamics

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

Thermostats: Application to water

start simul/spce/spce250.plb

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



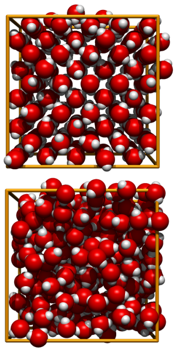
$\tau = 0.1$ ps

T:

— total

— center-of-mass

— rotations



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:

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

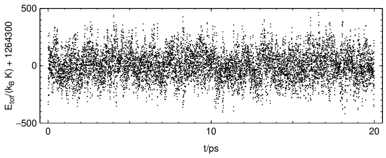
$$\text{Var}\,E_\text{tot} = N_\text{f}\sigma_\text{f}^2$$

$\sigma_\text{f} \propto h^2$
(Verlet is 2nd order)

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

$\sigma_\text{f}/k_\text{B} \lessapprox$ (a few)$10^{-3}T$, at ambient temperature: $\sigma_\text{f}/k_\text{B} \lessapprox 1$ K

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



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

$N_\text{f} = 6 \times 267 - 3 = 1599 \quad \Rightarrow \quad \sigma_\text{f}/k_\text{B} = \sigma(E_\text{tot})/\sqrt{N_\text{f}} = 3.1\,\text{K} \gtrapprox 1\,\%T$: $h = 2$ fs is rather inaccurate

For $h = 1$ fs, the expected $\sigma_\text{f}/k_\text{B} = 3.1\,\text{K} \times (1\,\text{fs}/2\,\text{fs})^2 \approx 0.78$ K: $h = 1$ fs is acceptable

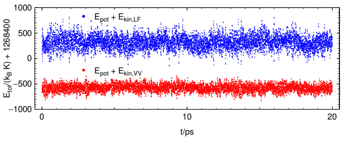
More about the kinetic energy in the Verlet-like integrators

- 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 $\lesssim 0.1\,\%$, LF $= 0.3\,\%$
- Relative error of diffusivity: VV $= 2.8\,\%$, LF $\lesssim 0.5\,\%$

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 $\text{kg}\,\text{m}^{-3}$:
  σ_f are calculated in NVE (10^4 steps) and are divided by k_B
  ΔT is calculated in NVT (see previous slide)

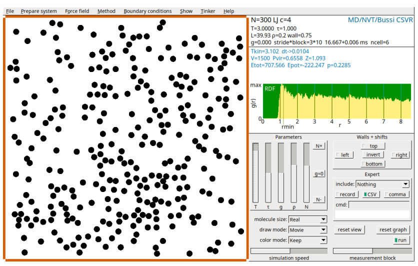
	real masses				H=5, O=8 g/mol	
h [fs]	$\sigma_\text{f,VV}$ [K]	$\sigma_\text{f,LF}$ [K]	ΔT_VV [K]	ΔT_LF [K]	$\sigma_\text{f,VV}$ [K]	$\sigma_\text{f,LF}$ [K]
1	0.44	0.74	0.58	−0.29	0.17	0.31
2	1.80	3.11	2.36	−1.14	0.65	1.19
3	3.94	7.17			1.45	2.81
4	7.32	12.8			2.64	5.02
5					4.20	7.87

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

Try molecular dynamics yourself: SIMOLANT

Installation of SIMOLANT (Windows):

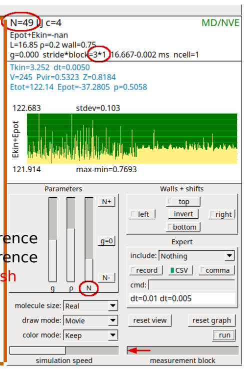
- Google 🔍 simolant or use the following links:
  - https://github.com/kolafaj/SIMOLANT → executables
  - http://old.vscht.cz/fch/software/simolant
- Download `simolant-win.zip`
- Create a folder
  and unpack SIMOLANT there.
  Do not run directly from
  `simolant-win.zip`
  – help would not work,
  –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



N=300 LJ c=4 MD/NVT/Bussi CSVR
T=3.0000 τ=1.000
L=39.93 ρ=0.2 wall=0.75
g=0.000 stride*block=3*10 16.667+0.006 ms ncell=6
Tkin=3.102 dt->0.0104
V=1500 Pvir=0.6558 Z=1.093
Etot=707.566 Epot=-222.247 p=0.2285
include: Nothing
cmd:
molecule size: Real
draw mode: Movie
color mode: Keep

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)



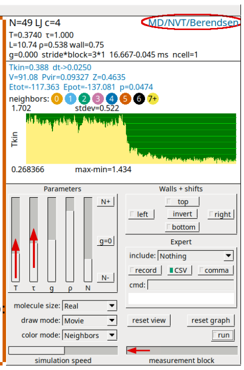
```
N=49 LJ c=4                                    MD/NVE
Epot+Ekin=-nan
L=16.85 ρ=0.2 wall=0.75
g=0.000  stride*block=3*1  16.667-0.002 ms  ncell=1
Tkin=3.252  dt=0.0050
V=245  Pvir=0.5323  Z=0.8184
Etot=122.14  Epot=-37.2805  p=0.5058
```

cmd: dt=0.01 dt=0.005

molecule size: Real
draw mode: Movie
color mode: Keep

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



```
N=49 LJ c=4                          MD/NVT/Berendsen
T=0.3740  τ=1.000
L=10.74 ρ=0.538 wall=0.75
g=0.000  stride*block=3*1  16.667-0.045 ms  ncell=1
Tkin=0.388  dt->0.0250
V=91.08  Pvir=0.09327  Z=0.4635
Etot=-117.363  Epot=-137.081  p=0.0474
```

molecule size: Real
draw mode: Movie
color mode: Neighbors