Introduction to Scientific Computing II

Molecular Dynamics Simulation (2)

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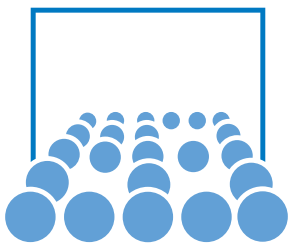

MD – Approximations and Discretization

- Time-Stepping for Molecular Dynamics
- Velocity Störmer Verlet Method
- Evaluation of Time Integration Methods

Short-Range Potentials

- Cut-Off Potentials
- Shifted Potentials

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MD – Approximations and Discretization

Explicit Euler Method:

- Taylor series expansion of the positions in time:

$$\vec{r}(t+\Delta t) = \vec{r}(t) + \Delta t \dot{\vec{r}}(t) + \frac{1}{2}\Delta t^2 \ddot{\vec{r}}(t) + \frac{\Delta t^i}{i!}\vec{r}^{(i)}(t) + \dots \quad (1)$$

  ($\dot{r}, \ddot{r}, r^{(i)}$: derivatives)

- approximation of (1), neglecting terms of higher order of Δt, as well as an analogous formulation of $\vec{v}(t) := \dot{\vec{r}}(t)$ with $\vec{a}(t) := \dot{\vec{v}}(t) = \ddot{\vec{r}}(t) = \frac{\vec{F}(t)}{m}$ leads to the explicit Euler method:

$$\vec{v}(t+\Delta t) \doteq \vec{v}(t) + \Delta t\, \vec{a}(t)$$
$$\vec{r}(t+\Delta t) \doteq \vec{r}(t) + \Delta t\, \vec{v}(t)$$

MD – Approximations and Discretization (cont.)

- explicit Euler method:

$$\vec{v}(t+\Delta t) \doteq \vec{v}(t) + \Delta t\, \vec{a}(t) \tag{2a}$$
$$\vec{r}(t+\Delta t) \doteq \vec{r}(t) + \Delta t\, \vec{v}(t) \tag{2b}$$

- similar for implicit Euler method
  $\rightarrow$ derivatives at the time step end:

$$\vec{v}(t+\Delta t) \doteq \vec{v}(t) + \Delta t\, \vec{a}(t+\Delta t) \tag{3a}$$
$$\vec{r}(t+\Delta t) \doteq \vec{r}(t) + \Delta t\, \vec{v}(t+\Delta t) \tag{3b}$$

- (2a) in (3b) $\Rightarrow \vec{r}(t+\Delta t) \doteq \vec{r}(t) + \Delta t \vec{v}(t) + \Delta t^2 \vec{a}(t)$

Störmer Verlet Method

- the Taylor series expansion in (1) can also be performed for $-\Delta t$: (Richardson extrapolation for $\delta = -1$)

$$\vec{r}(t-\Delta t) = \vec{r}(t) - \Delta t\dot{\vec{r}}(t) + \frac{1}{2}\Delta t^2\ddot{\vec{r}}(t) + \frac{(-\Delta t)^i}{i!}\vec{r}^{(i)}(t) + \ldots \quad (4)$$

- from (1) and (4) the classical Verlet algorithm can be derived:

$$\begin{aligned}\vec{r}(t+\Delta t) &= 2\vec{r}(t) - \vec{r}(t-\Delta t) + \Delta t^2\ddot{\vec{r}}(t) + \mathcal{O}(\Delta t^4) \\ &\approx 2\vec{r}(t) - \vec{r}(t-\Delta t) + \Delta t^2\vec{a}(t)\end{aligned} \quad (5)$$

  direct calculation of $\vec{r}(t+\Delta t)$ from $\vec{r}(t)$ and $\vec{F}(t)$

- the velocity can be estimated with

$$\vec{v}(t) = \dot{\vec{r}}(t) \doteq \frac{\vec{r}(t+\Delta t) - \vec{r}(t-\Delta t)}{2\Delta t} \quad (6)$$

Crank Nicolson Method

- explicit approximation (7a) for half step $[t, t + \frac{\Delta t}{2}]$ inserted into implicit approximation (7b) for half step $[t + \frac{\Delta t}{2}, t + \Delta t]$ gives for v (7c):

$$\vec{v}(t + \frac{\Delta t}{2}) = \vec{v}(t) + \frac{\Delta t}{2}\vec{a}(t) \tag{7a}$$

$$\vec{v}(t + \Delta t) = \vec{v}(t + \frac{\Delta t}{2}) + \frac{\Delta t}{2}\vec{a}(t + \Delta t) \tag{7b}$$

$$\vec{v}(t + \Delta t) = \vec{v}(t) + \frac{\Delta t}{2}\left(\vec{a}(t) + \vec{a}(t + \Delta t)\right) \tag{7c}$$

- alternative conversion to integral equation

$$\vec{v}(t + \Delta t) - \vec{v}(t) = \int_t^{t+\Delta t} \vec{a}(\tau)\, \mathrm{d}\tau$$

numerical integration with trapezoidal rule $\Rightarrow$ (7c)

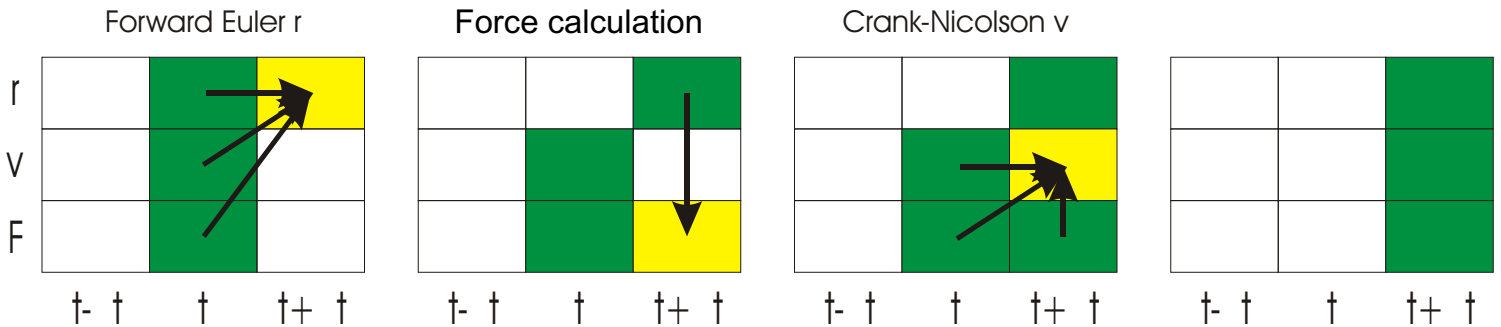
Velocity Störmer Verlet Method

The velocity Störmer Verlet method is a composition of a

- Taylor series expansion of 2nd order for the positions (1)
- and a Crank Nicolson method for the velocities (7c)

$$\vec{r}(t+\Delta t) = \vec{r}(t) + \Delta t \vec{v}(t) + \frac{\Delta t^2}{2}\vec{a}(t) \tag{8a}$$

$$\vec{v}(t+\Delta t) = \vec{v}(t) + \frac{\Delta t}{2}\left(\vec{a}(t) + \vec{a}(t+\Delta t)\right) \tag{8b}$$



memory requirements: $(3+1)\cdot 3N$ (3+1 vector fields)

update of $v(t+\Delta t)$ requires $v(t)$, $r(t+\Delta t)$ and $F(t+\Delta t)$, but also $F(t)$

Velocity Störmer Verlet – Implementation

- reformulate equation for positions $\vec{r}$:

$$\begin{aligned}\vec{r}(t+\Delta t) &= \vec{r}(t) + \Delta t\vec{v}(t) + \frac{\Delta t^2}{2}\vec{a}(t) \\ &= \vec{r}(t) + \Delta t\left(\vec{v}(t) + \frac{\Delta t}{2}\vec{a}(t)\right)\end{aligned}$$

  contains half an Euler time step for $\vec{v}$

- similar for the velocities $\vec{v}$:

$$\begin{aligned}\vec{v}(t+\Delta t) &= \vec{v}(t) + \frac{\Delta t}{2}\left(\vec{a}(t) + \vec{a}(t+\Delta t)\right) \\ &= \left(\vec{v}(t) + \frac{\Delta t}{2}\vec{a}(t)\right) + \frac{\Delta t}{2}\vec{a}(t+\Delta t)\end{aligned}$$

  reuses the result of the half Euler time step for $\vec{v}$

Velocity Störmer Verlet – Implementation (2)

1. compute half an Euler time step for $\vec{v}$

$$\vec{v}(t + \frac{\Delta t}{2}) = \vec{v}(t) + \frac{\Delta t}{2}\vec{a}(t)$$

2. update positions $\vec{r}$:

$$\vec{r}(t + \Delta t) = \vec{r}(t) + \Delta t\vec{v}(t + \frac{\Delta t}{2})$$

3. calculate forces $\vec{a}(t + \Delta t)$ from positions $\vec{r}(t + \Delta t)$
4. update the velocities $\vec{v}$:

$$\vec{v}(t + \Delta t) = \vec{v}(t) + \frac{\Delta t}{2}\vec{a}(t + \Delta t)$$

Note: memory requirements: $3 \cdot 3N$ (3 vector fields)

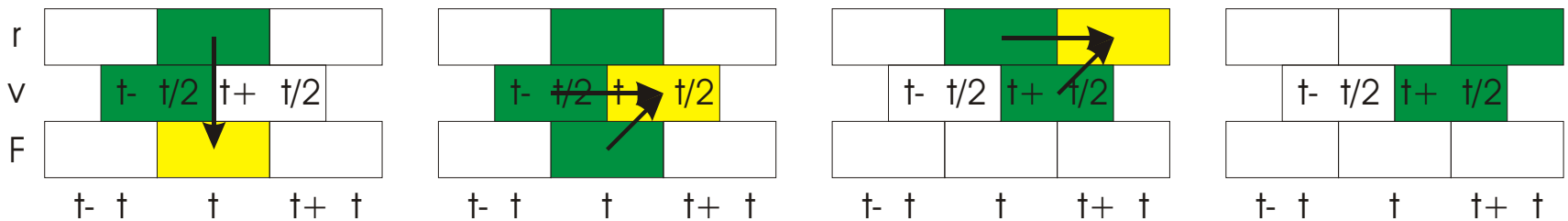
vectors $\vec{v}$ and $\vec{r}$, as well as forces/accelerations $\vec{a}$ may be updated in-place in each time step

Leapfrog Method

- combine steps 4 (from previous time step) and 1 to a single step
- velocity calculation thus shifted by a half time step:

$$\vec{v}(t + \frac{\Delta t}{2}) = \vec{v}(t - \frac{\Delta t}{2}) + \Delta t\, \vec{a}(t) \tag{9a}$$

$$\vec{r}(t + \Delta t) = \vec{r}(t) + \Delta t\, \vec{v}(t + \frac{\Delta t}{2}) \tag{9b}$$



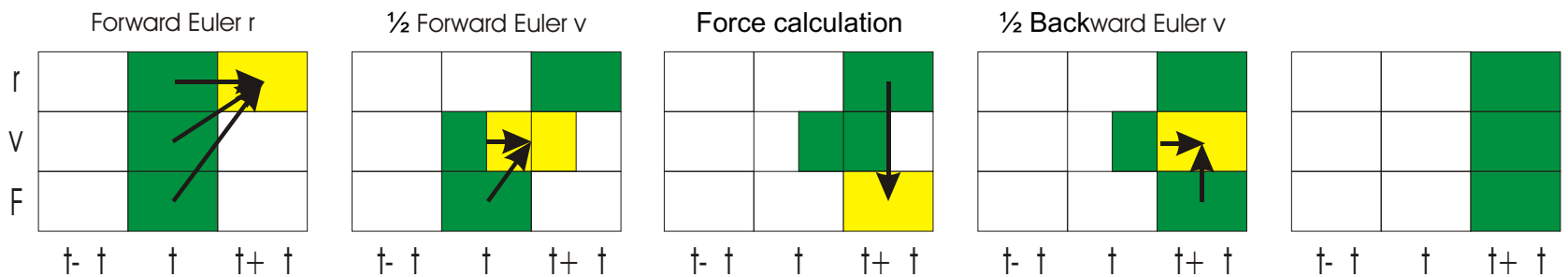
- exact arithmetic: Störmer Verlet, Velocity Störmer Verlet and Leapfrog schemes are equivalent
- the latter two are more robust w.r.t. roundoff errors

Outlook: Dimensionless Velocity Störmer Verlet

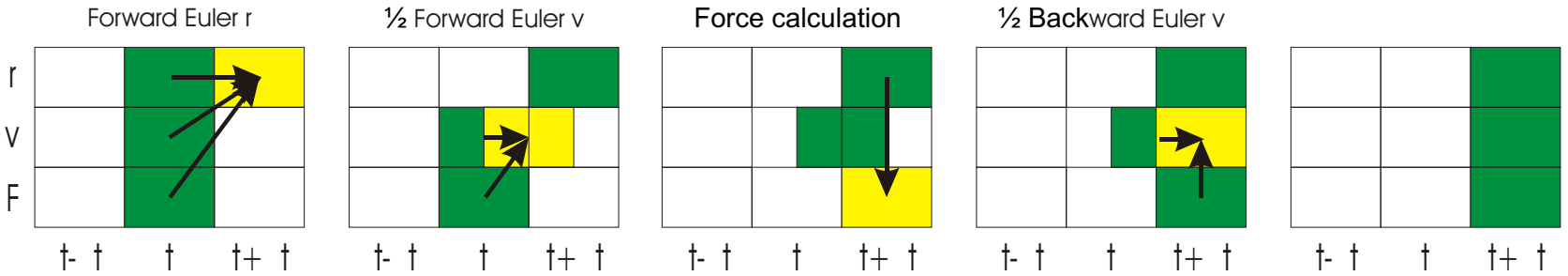
- remember dimensionless formulation:
  $(\vec{r} := \sigma \vec{r}^*,\ \vec{v} := \frac{\sigma}{\Delta t}\vec{v}^*,\ \Delta t^2 := \sigma^2 \frac{m}{\epsilon}\Delta t^{*2},\ \ddot{\vec{r}} = \frac{1}{m}\vec{F} := \frac{1}{m}\frac{\epsilon}{\sigma}\vec{F}^*)$
- insert into Velocity Störmer Verlet Method to get:.

$$\vec{r}^*(t+\Delta t) = \vec{r}^*(t) + \vec{v}^*(t) + \frac{\Delta t^{*2}}{2}\vec{F}^*(t) \tag{10a}$$

$$\vec{v}^*(t+\Delta t) = \vec{v}^*(t) + \frac{\Delta t^{*2}}{2}\vec{F}^*(t) + \frac{\Delta t^{*2}}{2}\vec{F}^*(t+\Delta t) \tag{10b}$$



Outlook: Dimensionless Velocity Störmer Verlet



Procedure:

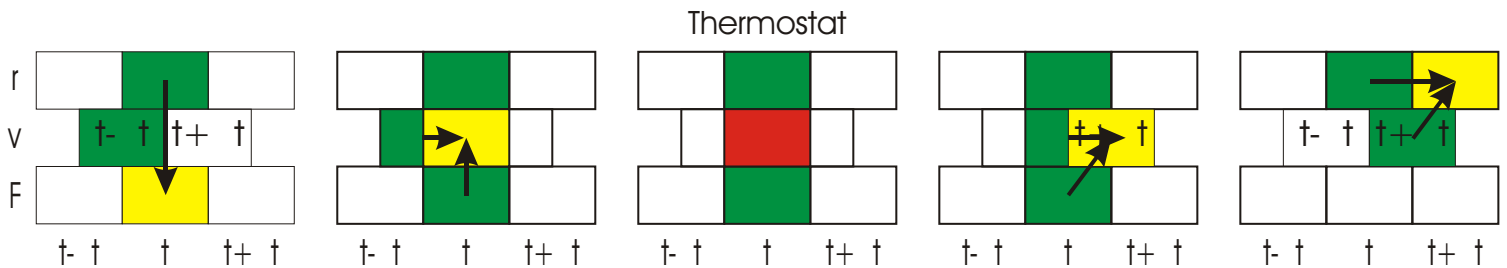
1. calculate new positions (10a),
   partial velocity update: $+\frac{\Delta t^{*2}}{2}\vec{F}^{*}(t)$ in (10b)
2. calculate new forces, accelerations (computationally intensive!)
3. calculate new velocities: $+\frac{\Delta t^{*2}}{2}\vec{F}^{*}(t+\Delta t)$ in (10b)

$\rightarrow$ memory requirements: $3 \cdot 3N$

Outlook: Leapfrog Method with Thermostat

- Leapfrog method:

$$\vec{v}(t + \tfrac{\Delta t}{2}) = \vec{v}(t - \tfrac{\Delta t}{2}) + \Delta t\, \vec{a}(t)$$
$$\vec{r}(t + \Delta t) = \vec{r}(t) + \Delta t\, \vec{v}(t + \tfrac{\Delta t}{2})$$



- intermediate step may be introduced for the thermostat $\vec{v}(t) := \frac{1}{2}\left(\vec{v}(t + \frac{\Delta t}{2}) + \vec{v}(t - \frac{\Delta t}{2})\right)$ to synchronize velocity:

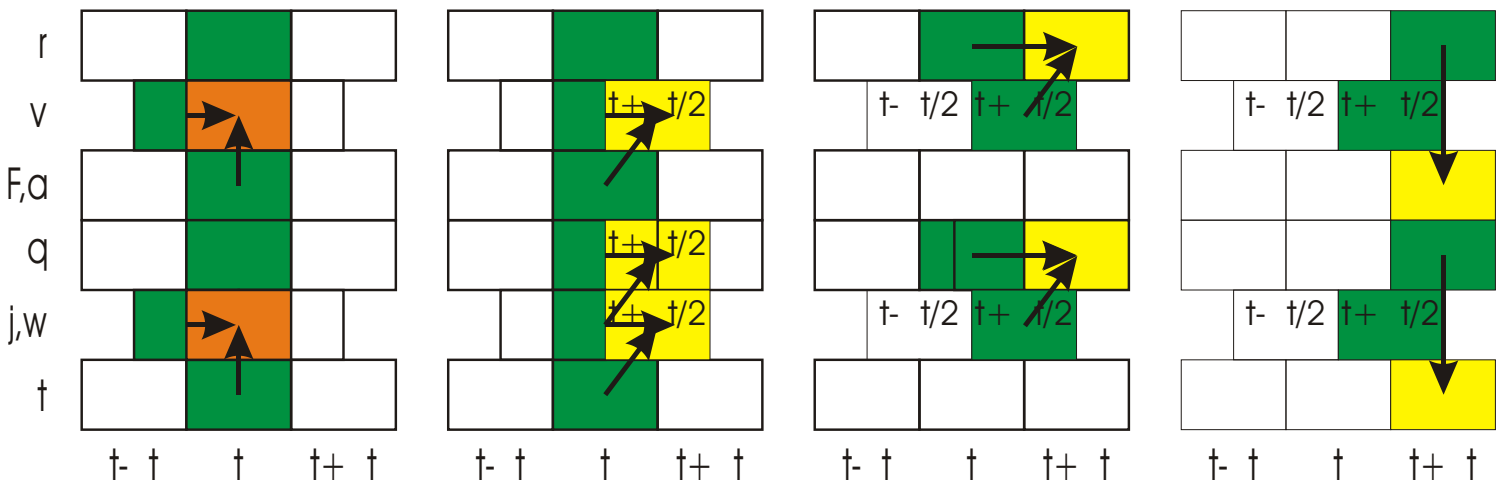
$$\vec{v}_{act}(t) = \vec{v}(t - \tfrac{\Delta t}{2}) + \tfrac{\Delta t}{2}\vec{a}(t) \qquad (12a)$$
$$\vec{v}(t + \tfrac{\Delta t}{2}) = (2\beta - 1)\vec{v}_{act}(t) + \tfrac{\Delta t}{2}\vec{a}(t) \qquad (12b)$$

Outlook: Multistep, Predictor Corrector Methods

- Multistep methods:
  - results are stored for several time steps, which define a (polynomial) interpolant
  - use the interpolant (extrapolation) for the integration
  - initialization with single-step-methods
  - increased memory requirements caused by storage of data of previous steps' data!
- Predictor Corrector methods:
  1. explicit method to determine predictor values for $t + \Delta t$
  2. implicit method uses predictor values instead of the unknown ones for $t + \Delta t$
  3. increased computational effort!
  4. quality of the predictor step caused by the complex chaotic behaviour is often not very good

Outlook: Multi-Centered Molecules

- besides position *r* and velocities *v*, orientations *q* and angular velocities *w* have to be calculated
- candidate: explicit or implicit version of the Fincham Leapfrog rotational algorithm
  - *r*,*v*,*F* using classical Leapfrog method
  - additional orientation *q*, angular velocity *w* as well as angular momentum *j*



Evaluation of Time Integration Methods

- accuracy (not of great importance)
- stability
- conservation
  - of phase space density (symplectic)
  - of energy
  - of momentum (especially with PBC (Periodic Boundary Conditions))
- reversibility of time
- use of resources:
  - computational effort (number of force evaluations)
  - maximum time step size
  - memory usage

Reversibility of Time

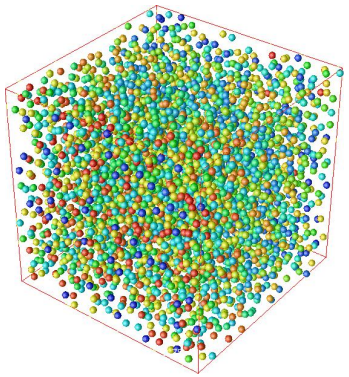
- time reversal for a closed system means
  - a turnaround of the velocities and also momentums; positions at the inversion point stay constant
  - traverse of a trajectory back in the direction of the origin
- demand for symmetry for time integration methods
  - \+ e.g. Verlet method
  - \- e.g. Euler method, Predictor Corrector methods
- contradiction with
  - the H-theorem (increase of entropy, irreversible processes)? (Loschmidt objection)
  - the second theorem of thermodynamics?
  - reversibility in theory only for a very short time
- Lyapunov instability $\Rightarrow$ Kolmogorov entropy

Lyapunov Instability

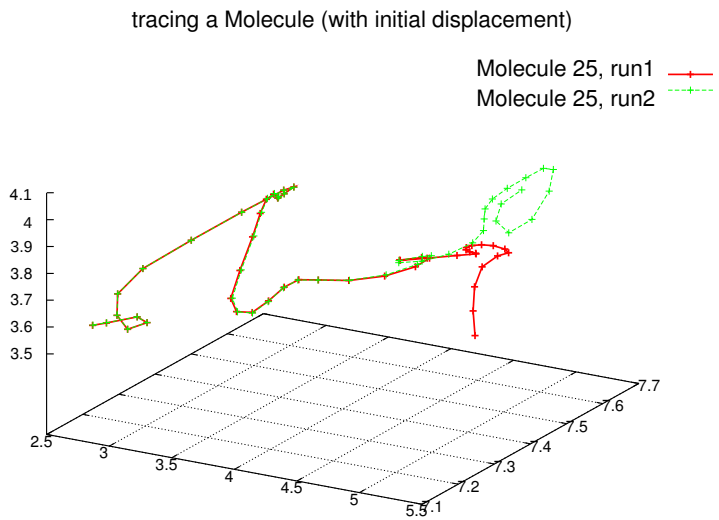
- Example of a simple system:
  - stable case:
    jumping ball on a plane with slightly disturbed initial horizontal velocity $\Rightarrow$ linear increase of the disturbance
  - instable case:
    jumping ball on a sphere with slightly disturbed initial horizontal velocity $\Rightarrow$ exponential increase of the disturbance (Lyapunov exponent)
- for the instable case, small disturbances result in large changes: chaotic behaviour (butterfly $\Rightarrow$ hurricane?)
- non-linear differential equations are often dynamically instable

Lyapunov Instability: A Numerical Experiment

- setup of 4000 fcc atoms
- for a second setup, the position of a single atom was changed with a displacement of 0.001
- trace the movement of the atom in both setups

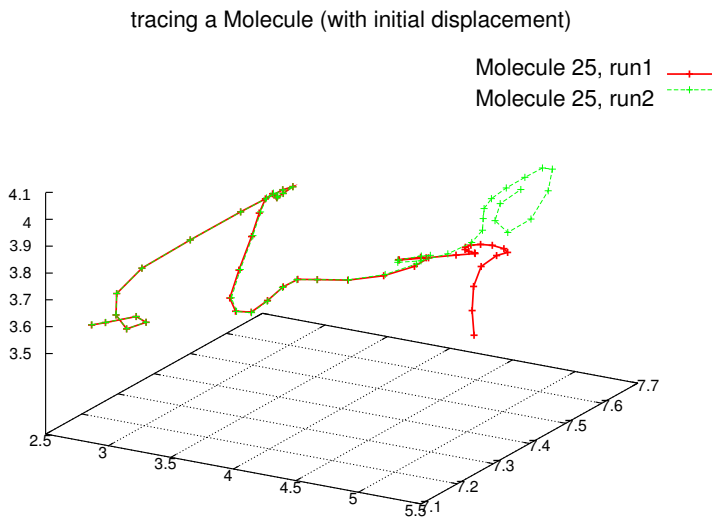


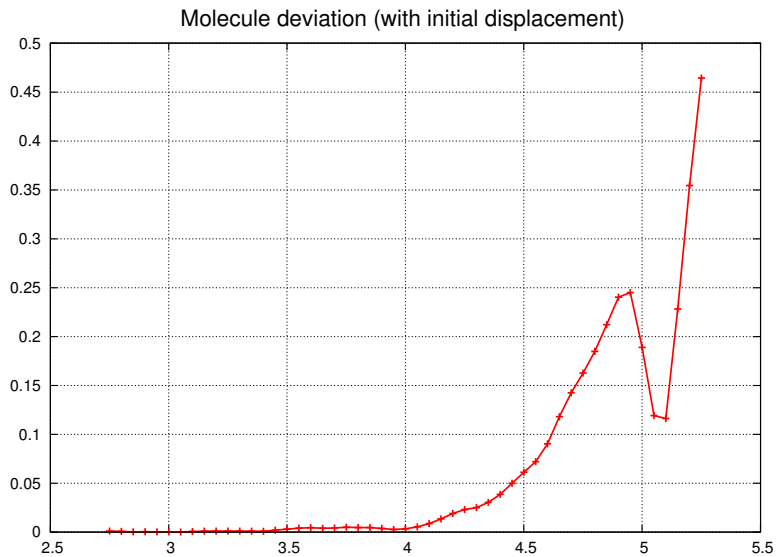
colours indicate velocity



Lyapunov Instability: A Numerical Experiment

- calculation of the trajectories: badly conditioned problem; a small change of the initial position of a molecule may result in a distance to the comparable original position, after some time, in the magnitude of the whole domain!
- there are also conserved quantities for which numerical simulations make sense!





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Short-Range Potential

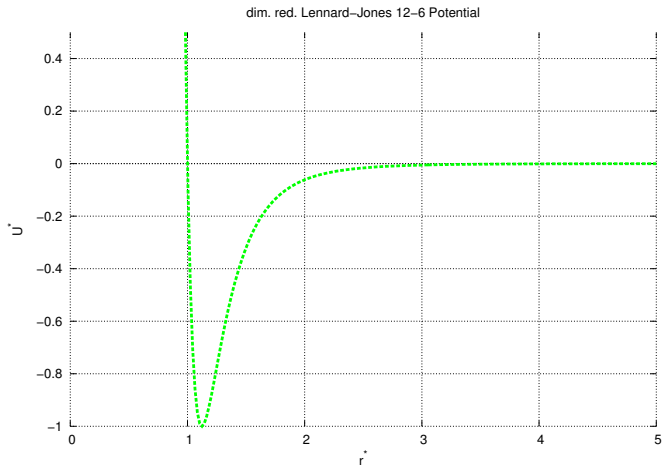
- choosing $m = 6$ (negative exponent in the LJ-potential)
  fast decay of potential and force
- for each molecule, an influence volume (closed sphere) with cut-off radius r_c can be assumed where every molecule outside this influence volume is neglected:

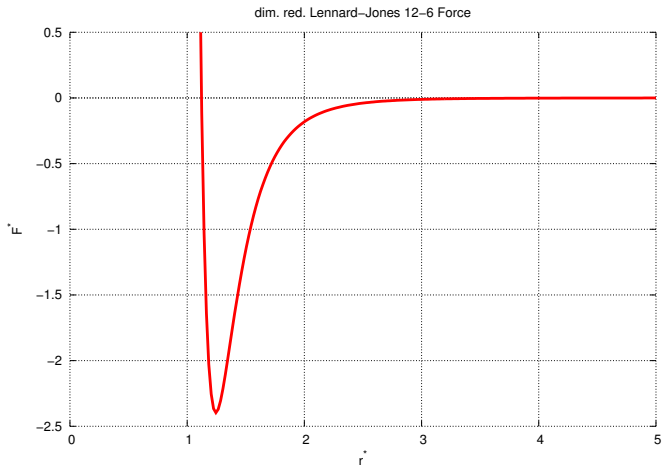
$$U^*_{LJ,r_c}\left(r^*_{ij}\right) = \begin{cases} 4\left(\left(r^{*2}_{ij}\right)^{-6} - \left(r^{*2}_{ij}\right)^{-3}\right) & \text{for } r^*_{ij} \leq r_c \\ 0 & \text{for } r^*_{ij} > r_c \end{cases} \tag{13a}$$

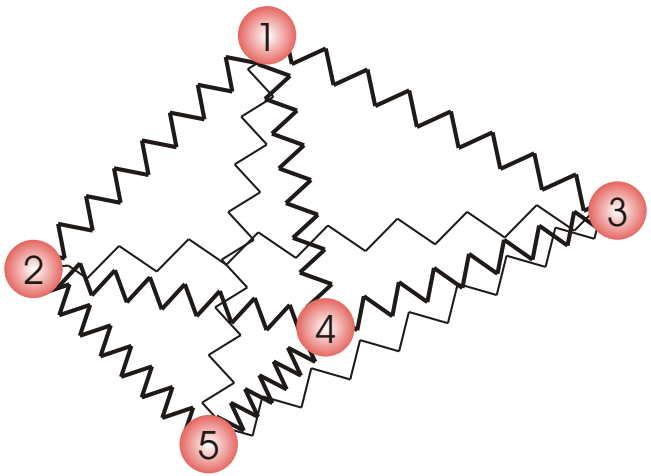
$$\vec{F}^*_{ij,r_c}\left(\vec{r}^*_{ij}\right) = \begin{cases} 24\left(2\left(r^{*2}_{ij}\right)^{-6} - \left(r^{*2}_{ij}\right)^{-3}\right)\frac{\vec{r}^*_{ij}}{r^{*2}_{ij}} & \text{for } r^*_{ij} \leq r_c \\ 0 & \text{for } r^*_{ij} > r_c \end{cases} \tag{13b}$$

- consider only a subgraph of the interaction-graph

Short-Range Interactions – Force Matrix



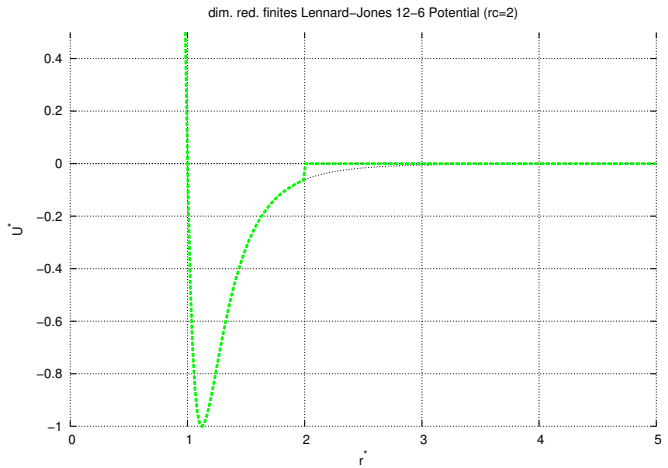


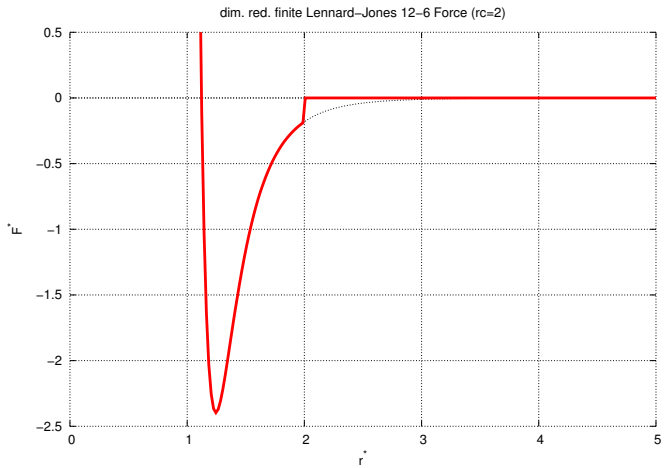


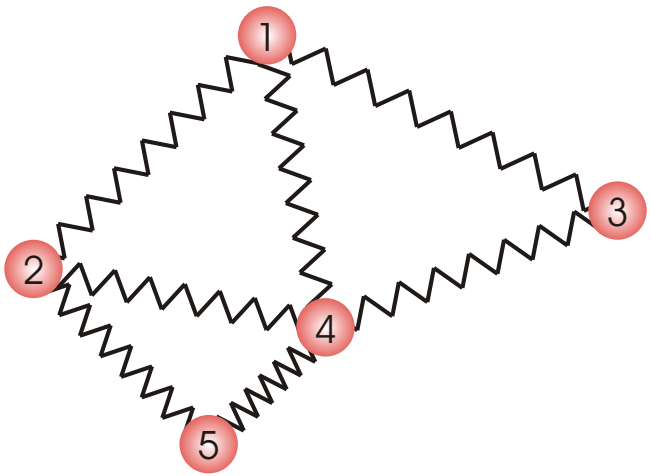
F_{ij} Force matrix/Interaction-graph

-	F_{12}	F_{13}	F_{14}	F_{15}
$-F_{12}$	-	F_{23}	F_{24}	F_{25}
$-F_{13}$	$-F_{23}$	-	F_{34}	F_{35}
$-F_{14}$	$-F_{24}$	$-F_{34}$	-	F_{45}
$-F_{15}$	$-F_{25}$	$-F_{35}$	$-F_{45}$	-

Sparse Force Matrix with Cut-Off Potentials







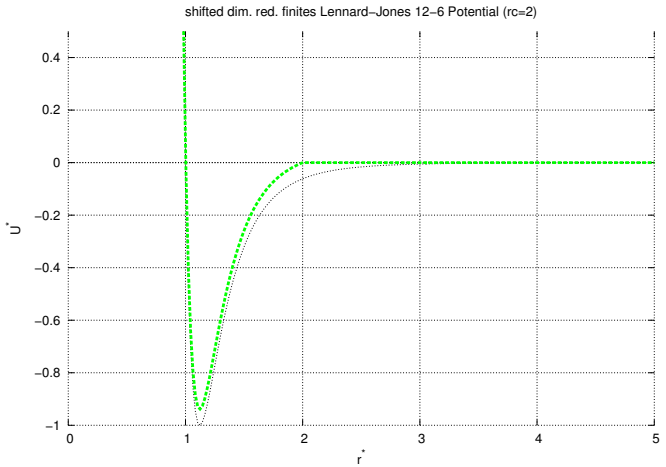
F_{ij} Force matrix/Interaction-graph

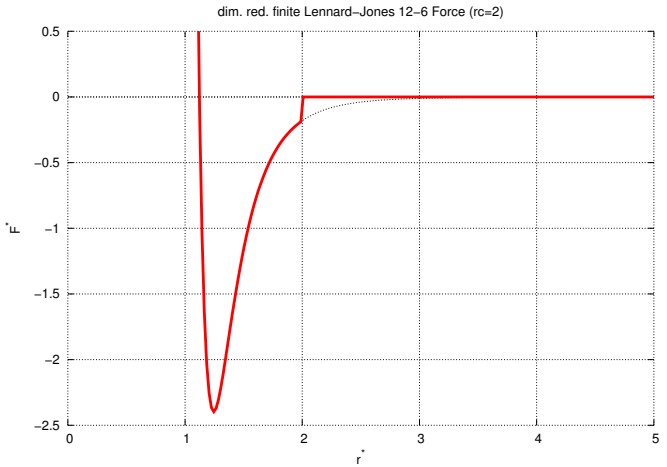
-	F_{12}	F_{13}	F_{14}	0
$-F_{12}$	-	0	F_{24}	F_{25}
$-F_{13}$	0	-	F_{34}	0
$-F_{14}$	$-F_{24}$	$-F_{34}$	-	F_{45}
0	$-F_{25}$	0	$-F_{45}$	-

Cut-Off Potentials – Summary

- fast decay of force contributions with increasing distance $\rightarrow$ dense force matrix with $\mathcal{O}(n^2)$, but mostly very small, entries
- with cut-off: force matrix is sparse (and anti-symmetric)
- only small (constant) number of molecules fits into the cut-off radius
- cut-off radius thus leads to a reduction of the computational effort
- complexity of entire force calculation thus reduce from $\mathcal{O}\left(N^2\right)$ to $\mathcal{O}(N)$
- todo: efficient implementation to identify the close neighbours

Shifted Potentials

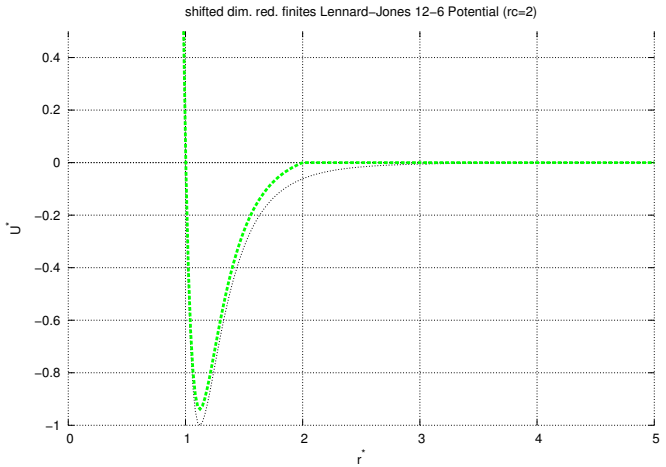


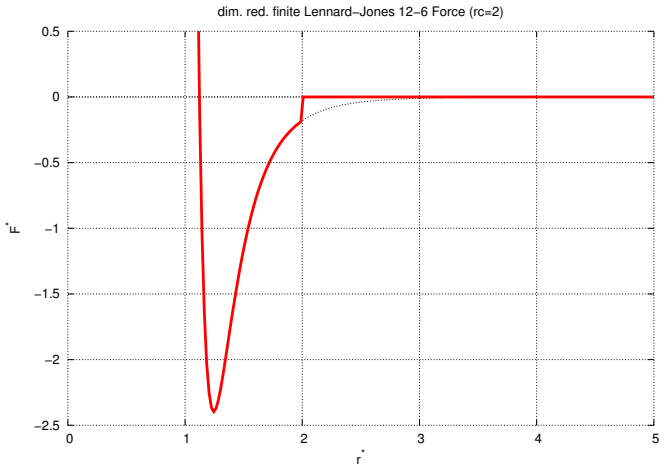


$$U^*_{LJ,r_c,shifted}\left(r^*_{ij}\right) = \begin{cases} U^*_{LJ}\left(r^*_{ij}\right) - U^*_{LJ}\left(r^*_c\right) & \text{for } r^*_{ij} \leq r^*_c \\ 0 & \text{for } r^*_{ij} > r^*_c \end{cases}$$

$$\vec{F}^*_{ij,r_c}\left(\vec{r}^*_{ij}\right) = \begin{cases} \vec{F}^*_{ij}\left(r^*_{ij}\right) & \text{for } r^*_{ij} \leq r^*_c \\ 0 & \text{for } r^*_{ij} > r^*_c \end{cases}$$

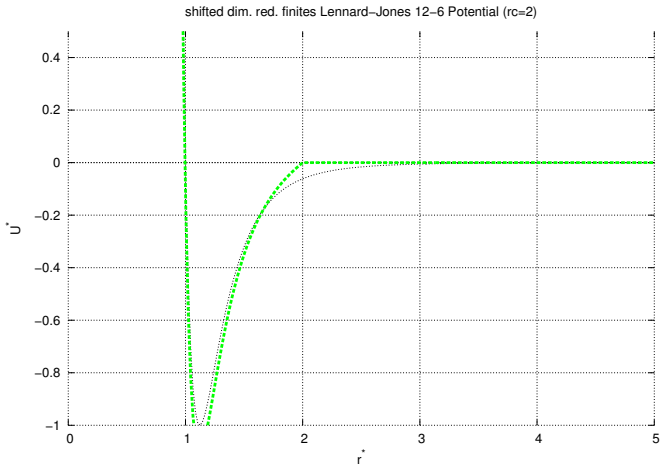
Shifted Potentials

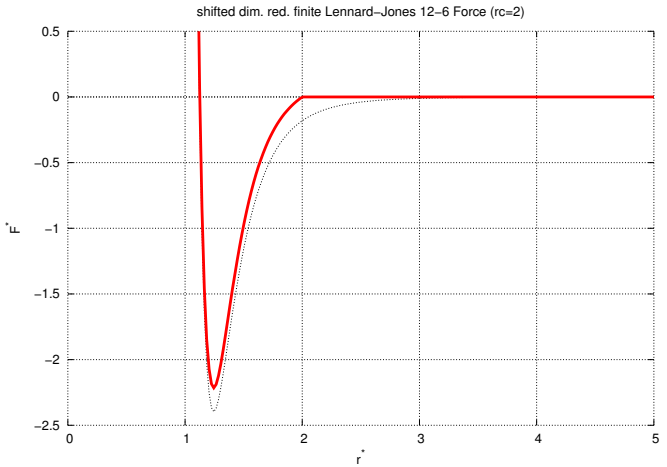




- additionally, constant additive term for the potential
  $\Rightarrow$ continuous potential
  reduced error for the overall potential

Shifted Potentials

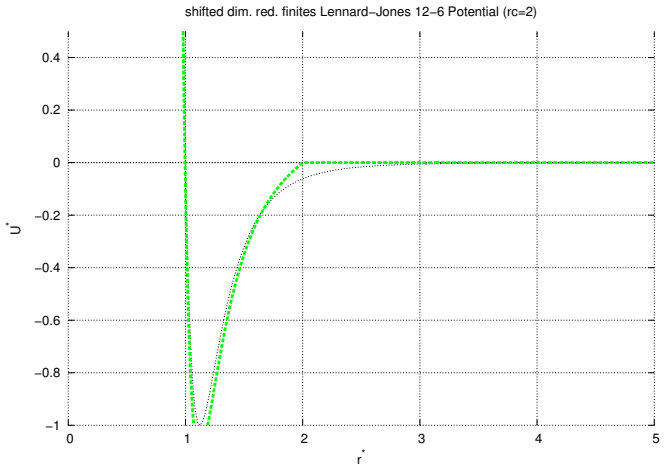


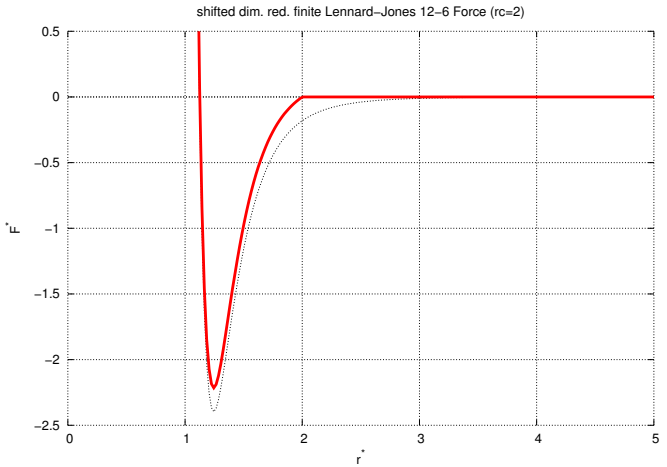


$$U^*_{LJ,r_c,shifted}\left(r^*_{ij}\right) = \begin{cases} U^*_{LJ}\left(r^*_{ij}\right) - U^*_{LJ}\left(r^*_c\right) - F^*_{LJ}\left(r^*_c\right)\left(r^*_{ij} - r^*_c\right) & \text{for } r^*_{ij} \leq \\ 0 & \text{for } r^*_{ij} > \end{cases}$$

$$\vec{F}^*_{ij,r_c,shifted}\left(r^*_{ij}\right) = \begin{cases} \vec{F}^*_{ij}\left(r^*_{ij}\right) - F^*_{LJ}\left(r^*_c\right) & \text{for } r^*_{ij} \leq r^*_c \\ 0 & \text{for } r^*_{ij} > r^*_c \end{cases}$$

Shifted Potentials





- additionally, constant additive term for the potential
  $\Rightarrow$ continuous potential
- additionally, linear additive term for the potential
  $\Rightarrow$ continuous force

Cut-Off Corrections

- due to the cut-off radius, the calculation of
  - the potential energy
  - the pressure

  neglects some addends with small absolute values
  $\Rightarrow$ (small) errors
- cut-off correction tries to correct this error
- constant density and a homogeneus distribution are a prerequisite
- physical values in the calculated volume can be approximately extrapolated