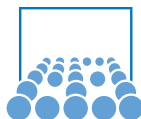


Introduction to Scientific Computing II

Molecular Dynamics Simulation (2)

Michael Bader – SCCS

Summer Term 2014



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:

$$\vec{v}(t + \Delta t) \doteq \vec{v}(t) + \Delta t \vec{a}(t) \quad (2a)$$

$$\vec{r}(t + \Delta t) \doteq \vec{r}(t) + \Delta t \vec{v}(t) \quad (2b)$$

- similar for implicit Euler method
→ derivatives at the time step end:

$$\vec{v}(t + \Delta t) \doteq \vec{v}(t) + \Delta t \vec{a}(t + \Delta t) \quad (3a)$$

$$\vec{r}(t + \Delta t) \doteq \vec{r}(t) + \Delta t \vec{v}(t + \Delta t) \quad (3b)$$

- (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 $-\Delta t$:

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

- 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):

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

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

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

- alternative: conversion to integral equation

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

numerical integration with trapezoidal rule \Rightarrow (7c)

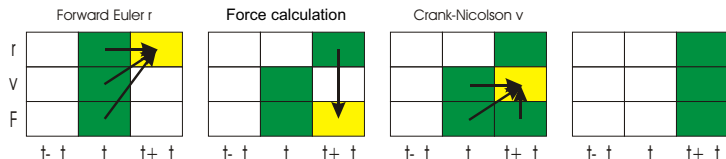
Velocity Störmer Verlet Method

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)

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

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



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} :

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

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} :

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

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

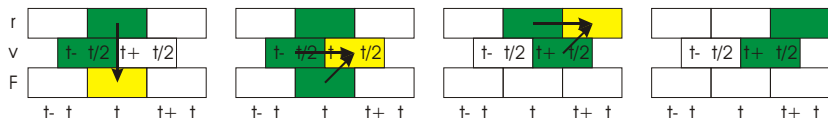
vectors \vec{v} and \vec{r} , as well as forces/accelerations \vec{a} may be updated in-place in each time step

Leapfrog Method

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

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

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



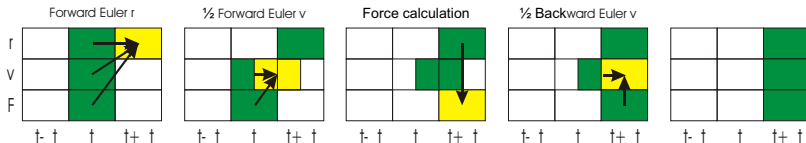
- exact arithmetic: Störmer Verlet, Velocity Störmer Verlet and Leapfrog Scheme are equivalent
- the latter two are more robust w.r.t. roundoff errors

Outlook: Dimensionless Velocity Störmer Verlet

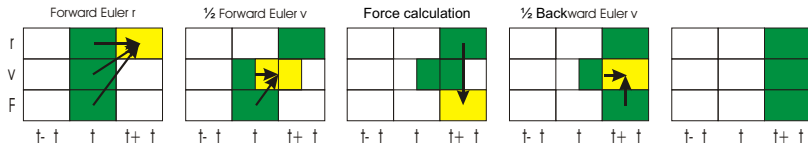
- remember dimensionless formulation:
 $(\vec{r} := \sigma \vec{r}^*, \vec{v} := \frac{\sigma}{\Delta t} \vec{v}^*, \Delta t^2 := \sigma^2 \frac{m}{\epsilon} \Delta t^{*2}, \ddot{\vec{r}} = \frac{1}{m} \vec{F} := \frac{1}{m} \frac{\epsilon}{\sigma} \vec{F}^*)$
- insert into Velocity Störmer Verlet Method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

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

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



Outlook: Dimensionless Velocity Störmer Verlet



Procedure:

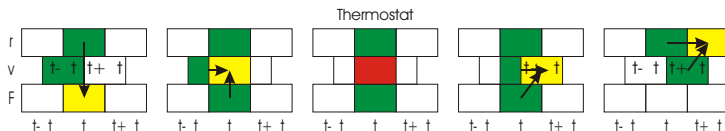
1. calculate new positions (10a),
partial velocity update: $+\frac{\Delta t^{*2}}{2} \vec{F}^*(t)$ in (10b)
 2. calculate new forces, accelerations (computationally intensive!)
 3. calculate new velocities: $+\frac{\Delta t^{*2}}{2} \vec{F}^*(t + \Delta t)$ in (10b)
- memory requirements: $3 \cdot 3N$

Outlook: Leapfrog Method with Thermostat

- Leapfrog method:

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

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



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

$$\vec{v}_{act}(t) = \vec{v}(t - \frac{\Delta t}{2}) + \frac{\Delta t}{2} \vec{a}(t) \quad (12a)$$

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

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

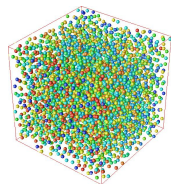
- time reversal for a closed system means
 - a turnaround of the velocities and also momentums; positions at the inversion point stay constant
 - traverse of a trajectory back in the direction of the origin
- demand for symmetry for time integration methods
 - + e.g. Verlet method
 - e.g. Euler method, 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

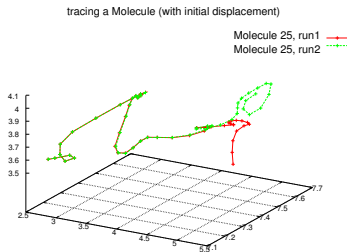
- Example of a simple system:
 - stable case:
jumping ball on a plane with slightly disturbed initial horizontal velocity \Rightarrow linear increase of the disturbance
 - instable case:
jumping ball on a sphere with slightly disturbed initial horizontal velocity \Rightarrow exponential increase of the 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

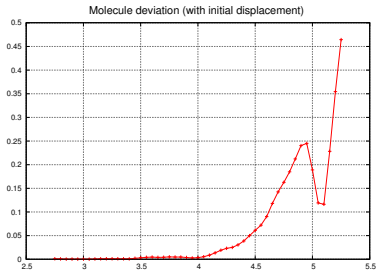
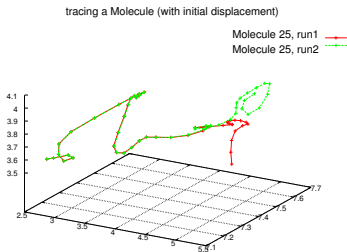


colours indicate
velocity



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!



MD – Approximations and Discretization

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Evaluation of Time Integration Methods

Short-Range Potentials

Cut-Off Potentials

Shifted Potentials

Short-Range Potential

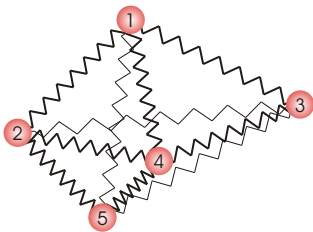
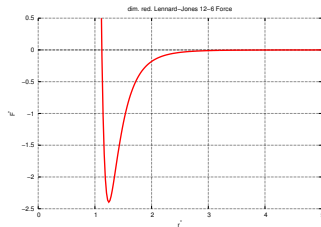
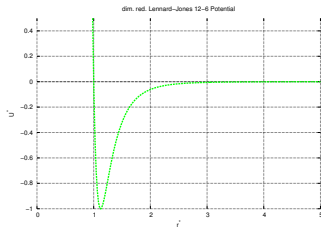
- choosing $m = 6$ (negative exponent in the LJ-potential) fast decay of potential and force
- for each molecule, an influence volume (closed sphere) with cut-off radius r_c can be assumed where every molecule outside this influence volume is neglected:

$$U_{LJ,r_c}^* (r_{ij}^*) = \begin{cases} 4 \left((r_{ij}^*)^{-6} - (r_{ij}^*)^{-3} \right) & \text{for } r_{ij}^* \leq r_c \\ 0 & \text{for } r_{ij}^* > r_c \end{cases} \quad (13a)$$

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

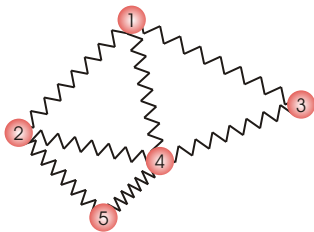
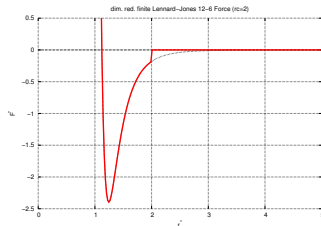
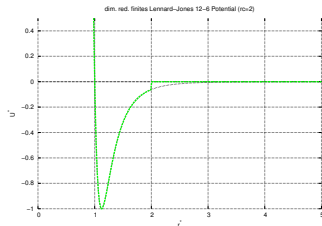
- consider only a subgraph of the interaction-graph

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

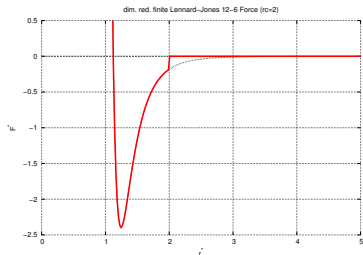
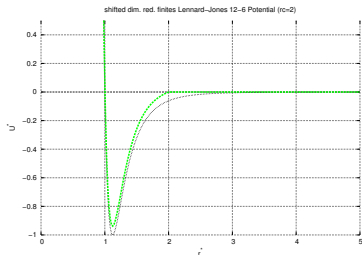


F_{ij}	Force matrix/Interaction-graph			
-	F_{12}	F_{13}	F_{14}	0
$-F_{12}$	-	0	F_{24}	F_{25}
$-F_{13}$	0	-	F_{34}	0
$-F_{14}$	$-F_{24}$	$-F_{34}$	-	F_{45}
0	$-F_{25}$	0	$-F_{45}$	-

Cut-Off Potentials – Summary

- fast decay of force contributions with increasing distance
→ 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 $\mathcal{O}(N^2)$ to $\mathcal{O}(N)$
- todo: efficient implementation to identify the close neighbours

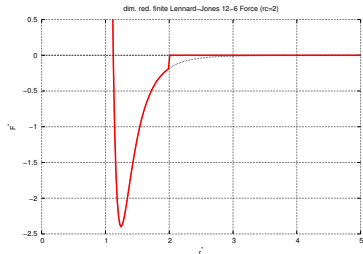
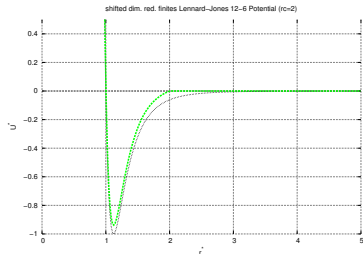
Shifted Potentials



$$U_{LJ,r_c,shifted}^*(r_{ij}^*) = \begin{cases} U_{LJ}^*(r_{ij}^*) - U_{LJ}^*(r_c^*) & \text{for } r_{ij}^* \leq r_c^* \\ 0 & \text{for } r_{ij}^* > r_c^* \end{cases}$$

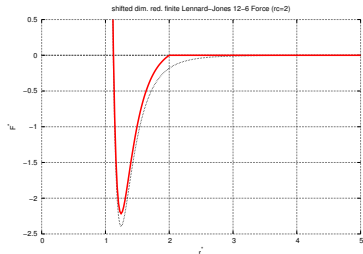
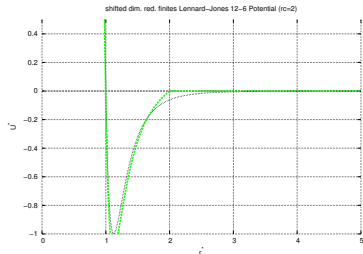
$$\vec{F}_{ij,r_c}^*(\vec{r}_{ij}^*) = \begin{cases} \vec{F}_{ij}^*(\vec{r}_{ij}^*) & \text{for } r_{ij}^* \leq r_c^* \\ 0 & \text{for } r_{ij}^* > r_c^* \end{cases}$$

Shifted Potentials



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

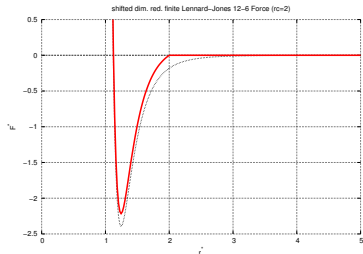
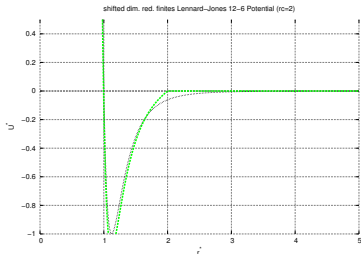
Shifted Potentials



$$U_{LJ,r_c,shifted}^*(r_{ij}^*) = \begin{cases} U_{LJ}^*(r_{ij}^*) - U_{LJ}^*(r_c^*) - F_{LJ}^*(r_c^*)(r_{ij}^* - r_c^*) & \text{for } r_{ij}^* \leq r_c^* \\ 0 & \text{for } r_{ij}^* > r_c^* \end{cases}$$

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

Shifted Potentials



- additionally, constant additive term for the potential
⇒ continuous potential
- additionally, linear additive term for the potential
⇒ continuous force

Cut-Off Corrections

- due to the cut-off radius, the calculation of
 - the potential energy
 - the pressureneglects some addends with small absolute values
⇒ (small) errors
- cut-off correction tries to correct this error
- constant density and a homogeneous distribution are a prerequisite
- physical values in the calculated volume can be approximately extrapolated