Scientific Computing II

Molecular Dynamics – Numerics

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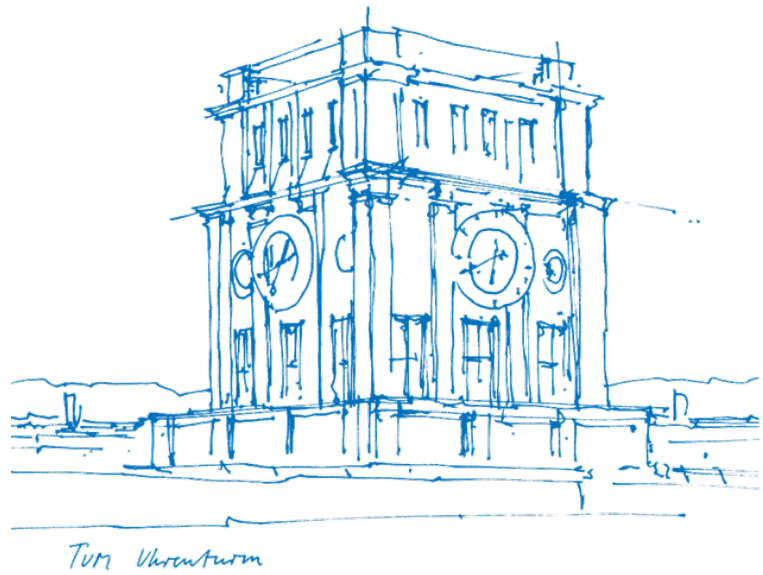


Recall: Molecular Dynamics – System of ODEs

- resulting force acting on a molecule: $\vec{F}_i = \sum_{j \neq i} \vec{F}_{ij}$
- acceleration of a molecule (Newton's 2nd law):

$$\ddot{\vec{r}}_i = \frac{\vec{F}_i}{m_i} = \frac{\sum_{j \neq i} \vec{F}_{ij}}{m_i} = -\frac{\sum_{j \neq i} \frac{\partial U(\vec{r}_i, \vec{r}_j)}{\partial |r_{ij}|}}{m_i}$$

- or, with acceleration $\vec{a}_i := \frac{1}{m_i} \vec{F}_i$: $\ddot{\vec{r}}_i = \vec{a}_i$,
  where $\vec{F}_i$ and $\vec{a}_i$ depend on all positions $\vec{r}_i$
- transfer to $2dN$ coupled ordinary differential equations of 1st order:

$$m_i \dot{\vec{r}}_i = \vec{p}_i \qquad \text{or} \qquad \dot{\vec{r}}_i = \vec{v}_i$$
$$\dot{\vec{p}}_i = \vec{F}_i \qquad\qquad \dot{\vec{v}}_i = \vec{F}_i / m_i = \vec{a}_i$$

Euler Time Stepping for MD

Explicit Euler Method:

- Taylor series expansion of the positions in time:

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

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

- neglecting terms of higher order of Δt, and 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:

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

Euler Time Stepping for MD (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:

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

- disadvantage for both schemes: do not conserve critical properties; lead to wrong long-term solutions (compare tutorial on circular motion); plus: low accuracy

Classical Störmer Verlet Method

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

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

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

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

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

- velocity can be estimated via

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

- disadvantage: needs to store two previous time steps

Crank Nicolson Method

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

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

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

- leads to Crank-Nicolson scheme for v:

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

- key disadvantage: implicit scheme, as $\vec{a}(t + \Delta t)$ depends on $\vec{r}(t + \Delta t)$; needs to solve non-linear system of equations

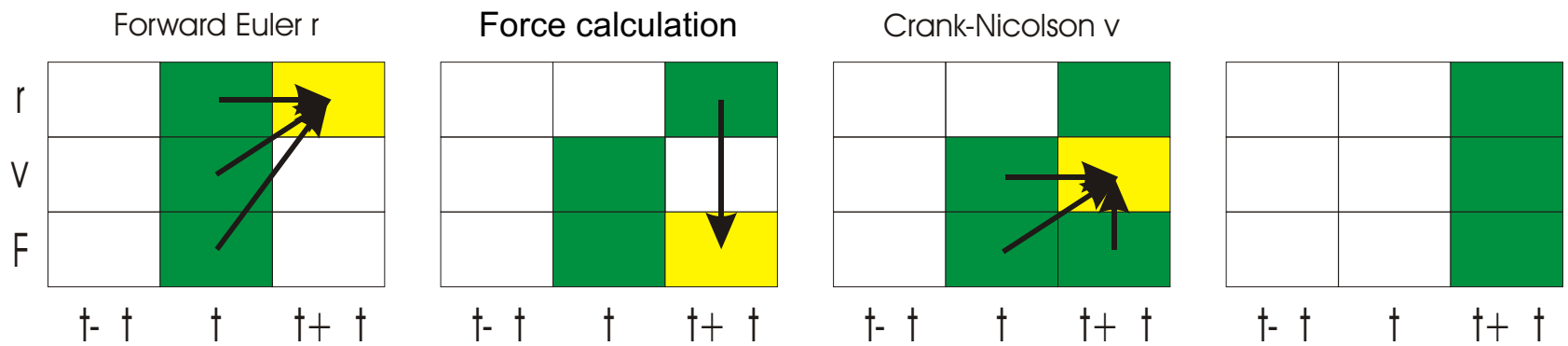
Velocity Störmer Verlet Method

The Velocity Störmer Verlet method is a composition of a

- Taylor series expansion of 2nd order for the positions, as in Eq. (1)
- and a Crank Nicolson method for the velocities, as in Eq. (8)

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

$$\vec{v}(t+\Delta t) = \vec{v}(t) + \frac{\Delta t}{2}\left(\vec{a}(t) + \vec{a}(t+\Delta t)\right) \tag{9b}$$



Memory requirement: $(3+1) \cdot 3N$ (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 $\vec{v}$

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

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

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

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

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

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

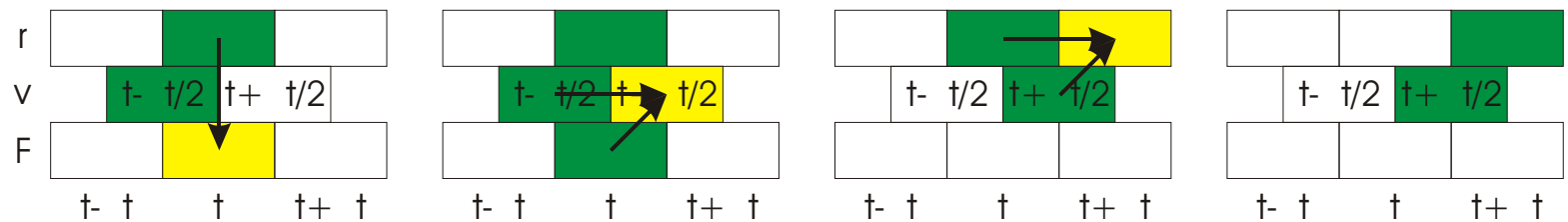
vectors $\vec{v}$ and $\vec{r}$, as well as forces/accelerations $\vec{a}$ may be updated in-place in each time step

Leapfrog Method

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

$$\vec{v}(t + \tfrac{\Delta t}{2}) = \vec{v}(t - \tfrac{\Delta t}{2}) + \Delta t\, \vec{a}(t) \tag{10a}$$

$$\vec{r}(t + \Delta t) = \vec{r}(t) + \Delta t\, \vec{v}(t + \tfrac{\Delta t}{2}) \tag{10b}$$



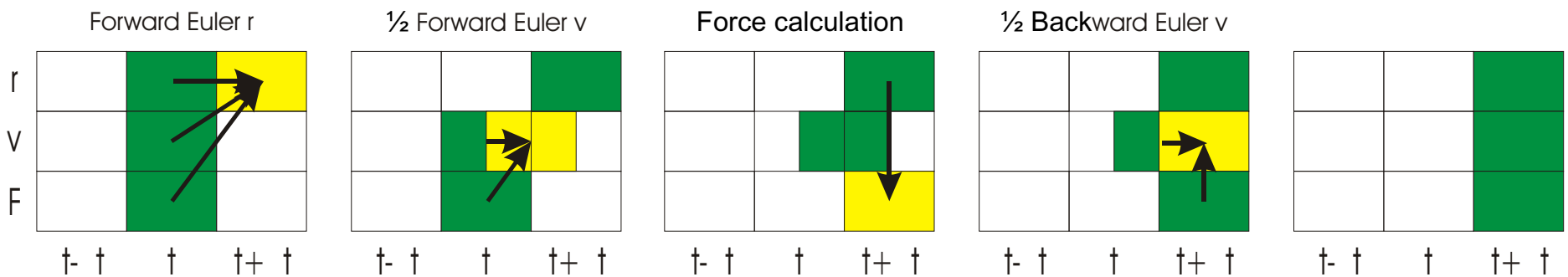
- exact arithmetic: Störmer Verlet, Velocity Störmer Verlet and Leapfrog Scheme are equivalent
- the latter two are more robust w.r.t. roundoff errors

Dimensionless Velocity Störmer Verlet

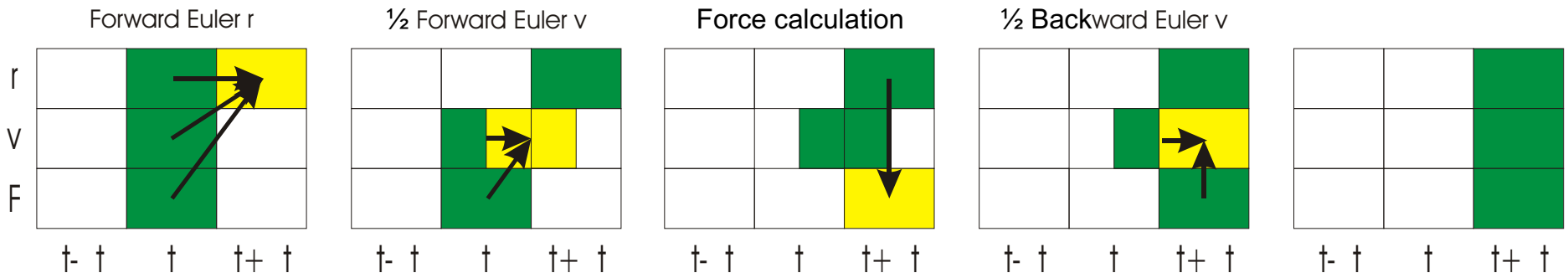
- remember dimensionless formulation:
  $(\vec{r} := \sigma \vec{r}^*,\ \vec{v} := \frac{\sigma}{\Delta t}\vec{v}^*,\ \Delta t^2 := \sigma^2 \frac{m}{\epsilon}\Delta t^{*2},\ \ddot{\vec{r}} = \frac{1}{m}\vec{F} := \frac{1}{m}\frac{\epsilon}{\sigma}\vec{F}^*)$
- insert into Velocity Störmer Verlet Method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

$$\vec{r}^*(t+\Delta t) = \vec{r}^*(t) + \vec{v}^*(t) + \frac{\Delta t^{*2}}{2}\vec{F}^*(t) \tag{11a}$$

$$\vec{v}^*(t+\Delta t) = \vec{v}^*(t) + \frac{\Delta t^{*2}}{2}\vec{F}^*(t) + \frac{\Delta t^{*2}}{2}\vec{F}^*(t+\Delta t) \tag{11b}$$



Dimensionless Velocity Störmer Verlet (2)



Procedure:

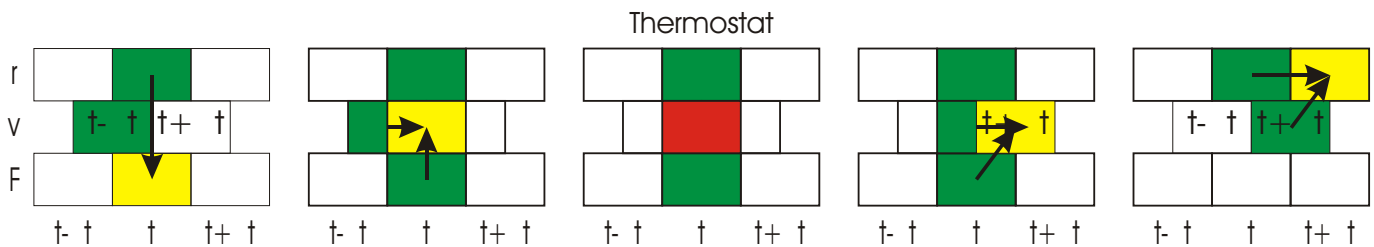
1. calculate new positions (11a),
   partial velocity update: $+\frac{\Delta t^{*2}}{2}\vec{F}^{*}(t)$ in (11b)
2. calculate new forces, accelerations (computationally intensive!)
3. calculate new velocities: $+\frac{\Delta t^{*2}}{2}\vec{F}^{*}(t+\Delta t)$ in (11b)

$\rightarrow$ 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:

$$\vec{v}_{act}(t) = \vec{v}(t - \tfrac{\Delta t}{2}) + \tfrac{\Delta t}{2}\vec{a}(t) \tag{13a}$$
$$\vec{v}(t + \tfrac{\Delta t}{2}) = (2\beta - 1)\vec{v}_{act}(t) + \tfrac{\Delta t}{2}\vec{a}(t) \tag{13b}$$

Evaluation of Time Integration Methods

Evaluation criteria:

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

Reversibility of Time

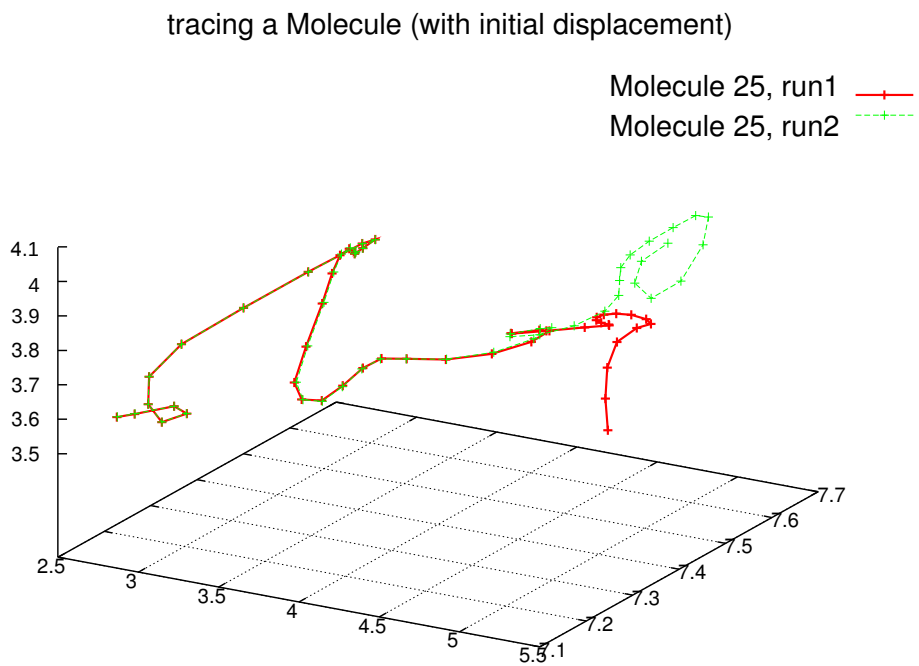
- time reversal for a closed system means
  - a turnaround of the velocities and also momentums; positions at the inversion point stay constant
  - traverse of a trajectory back in the direction of the origin
- demand for symmetry for time integration methods
  - $+$ satisfied by Verlet method, e.g.
  - $-$ not satisfied by, e.g., Euler method, Predictor Corrector methods (also not by standard Runge-Kutta methods)
- contradiction with
  - the H-theorem (increase of entropy, irreversible processes)? (Loschmidt's paradox)
  - the second theorem of thermodynamics?
  - reversibility in theory only for a very short time
- Lyapunov instability $\Rightarrow$ Kolmogorov entropy

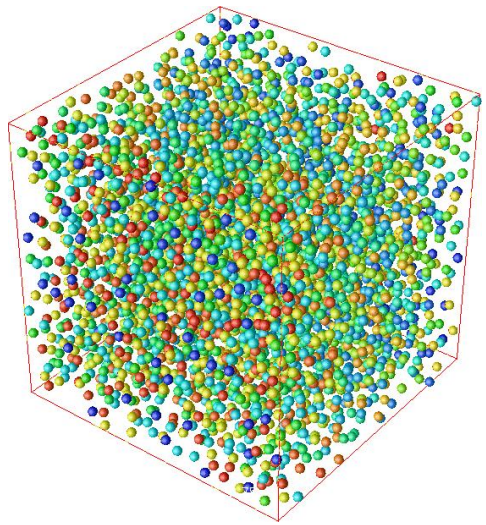
Lyapunov Instability

- Basic question: how does a model behave with slightly disturbed initial condition?
- 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 leading to a 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 displaced by 0.001
- this atom is traced in both setups





colours indicate velocity

Lyapunov Instability: A Numerical Experiment

- Calculation of the trajectories $\rightarrow$ 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!
- Thus: do not target at simulation of individual trajectories
  $\rightarrow$ numerical simulation of the behaviour of the system is wanted!