Introduction to Scientific Computing II

Molecular Dynamics Simulation (2)

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Summer Term 2012
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
MD – Approximations and Discretization

Time-Stepping for Molecular Dynamics
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Short-Range Potentials
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Explicit Euler Method:

• Taylor series expansion of the positions in time:

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

(\vec{r}, \vec{\dot{r}}, \vec{r}^{(i)}: \text{derivatives})

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

\[ \vec{v}(t + \Delta t) \equiv \vec{v}(t) + \Delta t \vec{a}(t) \]
\[ \vec{r}(t + \Delta t) \equiv \vec{r}(t) + \Delta t \vec{v}(t) \]
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
  \[\rightarrow\] 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 $-\Delta t$: (Richardson extrapolation for $\delta = -1$)

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

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

$$\vec{r}(t + \Delta t) = 2\vec{r}(t) - \vec{r}(t - \Delta t) + \Delta t^2 \ddot{\vec{r}}(t) + \mathcal{O}(\Delta t^4)$$

$$\approx 2\vec{r}(t) - \vec{r}(t - \Delta t) + \Delta t^2 \vec{a}(t)$$

(5)

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

- the velocity can be estimated with

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

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

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

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

- 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 $\vec{r}$:

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

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

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

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

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

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

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:

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

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

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

• remember dimensionless formulation:
  \((\vec{r} := \sigma \vec{r}^*, \vec{v} := \sigma \frac{\Delta t}{\epsilon} \vec{v}^*, \Delta t^2 := \frac{\sigma^2 m}{\epsilon} \Delta t^* \Delta t, \vec{r} = \frac{1}{m} \vec{F} := \frac{1}{m} \frac{\epsilon}{\sigma} \vec{F}^*)\)

• insert into Velocity Störmer Verlet Method to get:

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

\[
\vec{v}^*(t + \Delta t) = \vec{v}^*(t) + \frac{\Delta t^*}{2} \vec{F}^*(t) + \frac{\Delta t^*}{2} \vec{F}^*(t + \Delta t) \tag{10b}
\]
Outlook: Dimensionless Velocity Störmer Verlet

Procedure:

1. calculate new positions (10a),
   partial velocity update: \( +\frac{\Delta t^*}{2} \vec{F}^*(t) \) in (10b)

2. calculate new forces, accelerations (computationally intensive!)

3. calculate new velocities: \( +\frac{\Delta t^*}{2} \vec{F}^*(t + \Delta t) \) 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

\[
\vec{v}(t) := \frac{1}{2} \left( \vec{v}(t + \frac{\Delta t}{2}) + \vec{v}(t - \frac{\Delta t}{2}) \right)
\]

to synchronize velocity:

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

\[
\vec{v}(t + \frac{\Delta t}{2}) = (2\beta - 1)\vec{v}_{act}(t) + \frac{\Delta t}{2} \vec{a}(t) \quad (12b)
\]
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
  - unstable case: jumping ball on a sphere with slightly disturbed initial horizontal velocity $\Rightarrow$ exponential increase of the disturbance (Lyapunov exponent)
- for the unstable case, small disturbances result in large changes: chaotic behaviour (butterfly $\Rightarrow$ hurricane?)
- non-linear differential equations are often dynamically unstable
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

Tracing a molecule (with initial displacement)
Molecule 25, run 1
Molecule 25, run 2

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 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:

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

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

- consider only a subgraph of the interaction-graph
Short-Range Interactions – Force Matrix

\[ F_{ij} \]

Force matrix/Interaction-graph

\[
\begin{align*}
- & & F_{12} & & F_{13} & & F_{14} & & F_{15} \\
- F_{12} & - & - & & F_{23} & & F_{24} & & F_{25} \\
- F_{13} & - F_{23} & - & - & - & & F_{34} & & F_{35} \\
- F_{14} & - F_{24} & - F_{34} & - & - & - & - & & F_{45} \\
- F_{15} & - F_{25} & - F_{35} & - F_{45} & - & - & - & - & -
\end{align*}
\]
Sparse Force Matrix with Cut-Off Potentials

**Force matrix/Interaction-graph**

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<th>$F_{12}$</th>
<th>$F_{13}$</th>
<th>$F_{14}$</th>
<th>$F_{24}$</th>
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Cut-Off Potentials – Summary

- fast decay of force contributions with increasing distance → dense force matrix with $O(n^2)$, 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 $O(N^2)$ to $O(N)$
- todo: efficient implementation to identify the close neighbours
Shifted Potentials

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

\[ \vec{F}_{ij, r_c}^{*} (\vec{r}_{ij}^{*}) = \begin{cases} 
\vec{F}_{ij}^{*} (r_{ij}^{*}) & \text{for } r_{ij}^{*} \leq r_{c}^{*} \\
0 & \text{for } r_{ij}^{*} > r_{c}^{*}
\end{cases} \]
• additionally, constant additive term for the potential
  ⇒ continuous potential
  reduced error for the overall potential
Shifted Potentials

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

\[ F_{ij,rc,shifted}^* (r_{ij}) = \begin{cases} F_{ij}^* (r_{ij}) - F_{LJ}^* (r_*) & \text{for } r_{ij} \leq r_* \\ 0 & \text{for } r_{ij} > r_* \end{cases} \]
Shifted Potentials

- additionally, constant additive term for the potential
  \[ \Rightarrow \text{continuous potential} \]
- additionally, linear additive term for the potential
  \[ \Rightarrow \text{continuous force} \]
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 homogeneous distribution are a prerequisite

- physical values in the calculated volume can be approximately extrapolated