Scientific Computing II

Molecular Dynamics Simulation

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Essentials from Continuum Mechanics

Molecular Dynamics – the Physical Model
- Quantum vs. Classical Mechanics
- Van der Waals Attraction
- Lennard Jones Potential

Molecular Dynamics – the Mathematical Model
- System of ODE
- Initial Conditions
- Computational Domain & Boundary Conditions
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1. Essentials from Continuum Mechanics for Fluids

- **fluid**:  
  - notion covering liquids and gases  
  - liquids: hardly compressible  
  - gases: volume depends on pressure  
  - small resistance to changes of form

- **continuum**:  
  - space, continuously filled with mass  
  - homogeneous  
  - subdivision into small fluid voxels with constant physical properties is possible  
  - idea valid on micro scale upward (where we consider continuous masses and not discrete particles)
Description of State

- consideration of a control volume $V_0$ (Eulerian perspective)
- description of the fluid’s state via
  - the velocity field $\vec{v}(\vec{x}, t)$ and two thermodynamical quantities, typically
    - the pressure $p(\vec{x}, t)$ and
    - the density $\rho(\vec{x}, t)$
- for incompressible fluids, the density $\rho$ is constant (if there are no chemical reactions)
Why Molecular Dynamics?

Example: channel flow at decreasing density, $Kn = \frac{\text{mean free path}}{\text{characteristic length}}$

$LBM \text{ Li et al.}$
$Present LBM: 2nd Order, VA$
$2nd Order Slip NS$
$Ohwada et al.$

→ continuum description only valid on coarse scale
→ other methods (Molecular Dynamics, Direct Simulation Monte Carlo, ...) required
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\[
\begin{align*}
\text{LBM Li et al.} & \quad \text{Present LBM: 2nd Order, VA} \\
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\end{align*}
\]

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Scope of Application

- Loschmidt number $2,687 \cdot 10^{19} \text{cm}^{-3}$: number of molecules in 1 cm$^3$ of an ideal gas
- Avogadro constant $6.0221415 \cdot 10^{23} \text{mol}^{-1}$: number of carbon-12 atoms in 12g of carbon-12, or number of molecules in 1 mol (1 mol, under normal conditions, taking a volume of 22.4 litres)
- Avogadro number: notion being used in different ways for both of the above constants, which depend on each other ($2,687 \cdot 10^{19} \text{cm}^{-3} \cdot 22.413996 \cdot 10^3 \text{cm}^3 \text{mol}^{-1} = 6.0221415 \cdot 10^{23} \text{mol}^{-1}$)
- Time steps for numerical simulations are typically in the order of femtoseconds ($1 \text{fs} := 10^{-15} \text{s}$)
Pour Me A Glass...

- assume we want to simulate all molecules in one glass (0.5l) of water for 1sec
- assume a time step of 1fs
- assume we only need one floating point operation per molecule in each time step

\[ \text{1.673} \cdot 10^{22} \text{ molecules} \]
\[ \text{10}^{15} \text{ timesteps} \]
\[ \text{1.673} \cdot 10^{37} \text{ operations} \]

Using SuperMUC, this means we need at least

- \[ \text{1.77} \cdot 10^{14} \text{ years} \]
- \[ 8.03 \cdot 10^{8} \text{ PB} \]

of memory assuming we need to store only 3+3 unknowns per molecule (position+velocity)

→ hence: scope of application is limited to micro- and nanoscale simulations (at least for the near future)
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2. Molecular Dynamics – the Physical Model

Quantum Mechanics – a “Tour de Force”

- particle dynamics described by the Schrödinger equation
- its solution (state or wave function $\psi$) only provides probability distributions for the particles’ (i.e. nuclei and electrons) position and momentum
- Heisenberg’s uncertainty principle: position and momentum cannot be measured with arbitrary accuracy simultaneously
- there are discrete values/units (for the energy of bonded electrons, e.g.)
- in general, no analytical solution available
Quantum Mechanics – a “Tour de Force” (2)

- high dimensional problems: dimensionality corresponds to number of nuclei and electrons

\[ \psi = \psi(R_1, \ldots, R_N, r_1, \ldots, r_K, t) \]

\( \psi \) - wave function
\( R \) - position of nucleus
\( r \) - position of electron
\( t \) - time

- hence, numerical solution is possible for rather small systems only

- therefore, various (simplifying and approximating) approaches such as density functional method or Hartree-Fock approach or ab-initio Molecular Dynamics
Classical Molecular Dynamics

- Quantum mechanics $\xrightarrow{\text{approximation}}$ classical Molecular Dynamics
- classical Molecular Dynamics is based on Newton's equations of motion
- molecules are modelled as particles; simplest case: point masses
- there are interactions between molecules
- multibody potential functions describe the potential energy of the system; the velocities of the molecules (kinetic energy) are a composition of
  - the Brownian motion (high velocities, no macroscopic movement),
  - flow velocity (for fluids)
- ab-initio Molecular Dynamics uses quantum mechanical calculations to determine the potential hypersurface, apart from semi-empirical potential functions (cf. Car Parrinello Molecular Dynamics (CPMD) methods)
- total energy is constant $\leftrightarrow$ energy conservation
Fundamental Interactions

- Classification of the fundamental interactions:
  - strong nuclear force
  - electromagnetic force
  - weak nuclear force
  - gravity

- Interaction $\rightarrow$ potential energy

- The total potential of $N$ particles is the sum of multibody potentials:
  $$ U := \sum_{0<i<N} U_1(r_i) + \sum_{0<i<N} \sum_{i<j<N} U_2(r_i, r_j) $$
  $$ + \sum_{0<i<N} \sum_{i<j<N} \sum_{j<k<N} U_3(r_i, r_j, r_k) + \ldots $$
  - There are $\binom{N}{n} = \frac{N!}{n!(N-n)!} \in \mathcal{O}(N^n)$ $n$-body potentials $U_n$, particularly $N$ one-body and $\frac{1}{2}N(N-1)$ two-body potentials

- Force $\vec{F} = -\text{grad}U$
Van der Waals Attraction: So Small, So Important...
Van der Waals Attraction

- intermolecular, electrostatic interactions
- electron motion in the atomic hull may result in a temporary asymmetric charge distribution in the atom (i.e. more electrons (or negative charge, resp.) on one side of the atom than on the opposite one)
- charge displacement $\Rightarrow$ temporary dipole
- a temporary dipole
  - attracts another temporary dipole
  - induces an opposite dipole moment for a non-dipole atom and attracts it
- dipole moments are very small and the resulting electric attraction forces (van der Waals or London dispersion forces) are weak and act in a short range only
- atoms have to be very close to attract each other, for a long distance the two dipole partial charges cancel each other
- high temperature (kinetic energy) breaks van der Waals bonds
Well-Known Potentials

- some potentials from mechanics:
  - harmonic potential (Hooke’s law): $U_{harm}(r_{ij}) = \frac{1}{2} k (r_{ij} - r_0)^2$; potential energy of a spring with length $r_0$, stretched/clinched to a length $r_{ij}$
  - gravitational potential: $U_{grav}(r_{ij}) = -g \frac{m_i m_j}{r_{ij}}$; potential energy caused by a mass attraction of two bodies (planets, e.g.)
- the resulting force is $\vec{F}_{ij} = -\nabla U(r_{ij}) = -\frac{\partial U}{\partial r_{ij}}$
  integration of the force over the displacement results in the energy or a potential difference
- Newton’s 3rd law (actio=reactio): $\vec{F}_{ij} = -\vec{F}_{ji}$
Intermolecular Two-Body Potentials: Hard Vs. Soft Spheres

hard sphere potentials
- hard sphere
- Square–well
- Sutherland

soft sphere potentials
- soft sphere
- Lennard–Jones
- van der Waals

potential U vs. distance r
Intermolecular Two-Body Potentials

- hard sphere potential: \( U_{HS}(r_{ij}) = \begin{cases} \infty & \forall r_{ij} \leq d \\ 0 & \forall r_{ij} > d \end{cases} \)
  
  Force: Dirac Funktion

- soft sphere potential: \( U_{SS}(r_{ij}) = \epsilon \left( \frac{\sigma}{r_{ij}} \right)^n \)

- Square-well potential: \( U_{SW}(r_{ij}) = \begin{cases} \infty & \forall r_{ij} \leq d_1 \\ -\epsilon & \forall d_1 < r_{ij} < d_2 \\ 0 & \forall r_{ij} \geq d_2 \end{cases} \)

- Sutherland potential: \( U_{Su}(r_{ij}) = \begin{cases} \infty & \forall r_{ij} \leq d \\ -\epsilon / r_{ij}^6 & \forall r_{ij} > d \end{cases} \)

- Lennard Jones potential

- van der Waals potential \( U_W(r_{ij}) = -4\epsilon\sigma^6 \left( \frac{1}{r_{ij}} \right)^6 \)

- Coulomb potential: \( U_C(r_{ij}) = \frac{1}{4\pi\varepsilon_0} \frac{q_i q_j}{r_{ij}} \)

\( \varepsilon = \) energy parameter
\( \sigma = \) length parameter (corresponds to atom diameter, cmp. van der Waals radius)
Lennard Jones Potential

- Lennard Jones potential: \( U_{LJ}(r_{ij}) = \alpha \epsilon \left( \left( \frac{\sigma}{r_{ij}} \right)^n - \left( \frac{\sigma}{r_{ij}} \right)^m \right) \)
  
  with \( n > m \) and \( \alpha = \frac{1}{n-m} \left( \frac{n^n}{m^m} \right)^\frac{1}{n-m} \)
  
- continuous and differentiable (\( C^\infty \)), since \( r_{ij} > 0 \)
Lennard Jones Potential (2)

LJ 12-6 potential

\[ U_{LJ}(r_{ij}) = 4\epsilon \left( \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6 \right) \]

- \( m = 6 \): van der Waals attraction (van der Waals potential)
- \( n = 12 \): Pauli repulsion (soft sphere potential): heuristic
- application: simulation of inert gases (e.g. Argon)
- force between 2 molecules:
  \[ F_{ij} = -\frac{\partial U(r_{ij})}{\partial r_{ij}} = \frac{24\epsilon}{r_{ij}} \left( 2 \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6 \right) \]
- very fast fade away \( \Rightarrow \) short range \((m = 6 > 3 = d \text{ dimension})\)
# LJ Atom-Interaction Parameters

<table>
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<tr>
<th>atom</th>
<th>$\epsilon$</th>
<th>$\sigma$</th>
</tr>
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<tr>
<td></td>
<td>[$1.38066 \cdot 10^{-23} \text{ J}$]</td>
<td>[10$^{-1}$ nm]</td>
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<tr>
<td>H</td>
<td>8.6</td>
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<tr>
<td>Kr</td>
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<td>3.83</td>
</tr>
</tbody>
</table>

$\epsilon$ = energy parameter  
$\sigma$ = length parameter (cmp. van der Waals radius)  
→ parameter fitting to real world experiments

*Boltzmann-constant: $k_B := 1.38066 \cdot 10^{-23} \frac{\text{J}}{\text{K}}$  
$10^{-1} \text{nm} = 1 \AA$ (Ångstöm)
Dimensionsless Formulation

using reference values such as $\sigma$, $\epsilon$, reduced forms of the equations can be derived and implemented $\rightarrow$ transformation of the problem

- position, distance
  \[ \vec{r}^* := \frac{1}{\sigma} \vec{r} \]  
  \[ \text{(1a)} \]

- time
  \[ t^* := \frac{1}{\sigma} \sqrt{\frac{\epsilon}{m}} t \]
  \[ \text{(1b)} \]

- velocity
  \[ \vec{v}^* := \frac{\Delta t}{\sigma} \vec{v} \]
  \[ \text{(1c)} \]
Dimensionsless Formulation (2)

- **potential** (atom-interaction parameters are eliminated!): \( U^* := \frac{U}{\epsilon} \)

\[
U_{LJ}^* (r_{ij}) := \frac{U_{LJ} (r_{ij})}{\epsilon} = 4 \left( (r_{ij}^*)^{-6} - (r_{ij}^*)^{-3} \right)
\]

(2a)

\[
U_{kin}^* := \frac{U_{kin}}{\epsilon} = \frac{1}{\epsilon} \frac{mv^2}{2} = \frac{v^*^2}{2\Delta t^*^2}
\]

(2b)

- **force**

\[
\vec{F}_{ij}^* := \frac{\vec{F}_{ij} \sigma}{\epsilon} = 24 \left( 2 (r_{ij}^*)^{-6} - (r_{ij}^*)^{-3} \right) \frac{\vec{r}_{ij}^*}{r_{ij}^*^2}
\]

(2c)
Multi-Centered Molecules

- molecules can be composed with multiple LJ-centers
  → rigid bodies without internal degrees of freedom
- additionally: orientation (quaternions), angular velocity
- additionally: moment of inertia (principal axes transformation)
- calculation of the interactions between each center of one molecule to each center of the other
- resulting force (sum) acts at the center of gravity, additional calculation of torque
Multi-Centered Molecules (2)

- MBS (Multi Body System) point of view: instead of moving multi-centered molecules, there is a holonomically constrained motion of atoms (for a constraint to be holonomic it can be expressible as a function $f(r, v, t) = 0$)
- advantage: better approximation of unsymmetric molecules
- there is not necessarily one LJ center for each atom
Mixtures of Fluids

- simulation of various components (molecule types)
- modified Lorentz-Berthelot rules for interaction of molecules of different types

\[
\sigma_{AB} := \frac{\sigma_A + \sigma_B}{2} \tag{3a}
\]
\[
\varepsilon_{AB} := \xi \sqrt{\varepsilon_A \varepsilon_B} \tag{3b}
\]

with \( \xi \approx 1 \)

e.g. \( N_2 + O_2 \rightarrow \xi = 1.007, \ O_2 + CO_2 \rightarrow \xi = 0.979 \ldots \)
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3. Molecular Dynamics – the Mathematical Model

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):

\[
\ddot{\vec{r}}_i = \frac{\vec{F}_i}{m_i} = \frac{\sum_{j \neq i} \vec{F}_{ij}}{m_i} = -\frac{\sum_{j \neq i} \frac{\partial U(\vec{r}_i, \vec{r}_j)}{\partial |\vec{r}_{ij}|}}{m_i} \tag{4}
\]

- system of \( dN \) coupled ordinary differential equations of 2nd order transferable (as compared to Hamilton formalism) to \( 2dN \) coupled ordinary differential equations of 1st order (\( N \): number of molecules, \( d \): dimension), e.g. independent variables \( q := r \) and \( p \) with

\[
\dot{\vec{p}}_i := m_i \dot{\vec{r}}_i \tag{5a}
\]
\[
\dot{\vec{p}}_i = \vec{F}_i \tag{5b}
\]
Initial Conditions

Initial Value Problem:
position of the molecules and velocities have to be given;
initial configuration e.g.:
- molecules in crystal lattice (body-/face-centered cell)
- initial velocity
  - random direction
  - absolute value dependent of the temperature (normal distribution or uniform), e.g.
  \[
  \frac{d}{2} N k_B T = \frac{1}{2} \sum_{i=1}^{N} m v_i^2 \quad \text{with} \quad v_i := v_0
  \]
  \[
  \Rightarrow v_0 := \sqrt{\frac{d k_B T}{m}} \quad \text{resp.} \quad v^*_0 := \sqrt{dT^* \Delta t^*}
  \]

Time discretisation: \( t := t_0 + i \cdot \Delta t \)
\( \rightarrow \) time integration procedure
NVT-Ensemble, Thermostat

statistical (thermodynamics) ensemble: set of possible states a system might be in

- for the simulation of a (canonical) NVT-ensemble, the following values have to be kept constant:
  - \( N \): number of molecules
  - \( V \): volume
  - \( T \): temperature
- a thermostat regulates and controls the temperature (the kinetic energy), which is fluctuating in a simulation
- the kinetic energy is specified by the velocity of the molecules:
  \[
  E_{\text{kin}} = \frac{1}{2} \sum_i m_i \vec{v}_i^2
  \]
- the temperature is defined by
  \[
  T = \frac{2}{dN k_B} E_{\text{kin}}
  \]
  \((N: \text{number of molecules, } k_B: \text{Boltzmann-constant})\)
- simple method: isokinetic (velocity) scaling
  \[
  v_{\text{corr}} := \beta v_{\text{act}} \text{ mit } \beta = \sqrt{\frac{T_{\text{ref}}}{T_{\text{act}}}}
  \]
- further methods e.g. Berendsen-, Nosé-Hoover-thermostat
Boundary Conditions

- Periodic Boundary Conditions (PBC):
  - modelling an infinite space, built from identical cells
  ⇒ domain with torus topology
Computational Domain

- Minimum Image Convention (MIC):
  - with PBC, each molecule and the associated interactions exist several times
  - with MIC, only interactions between the closest representants of a molecule are taken into consideration