Scientific Computing II

Molecular Dynamics Simulation – Modelling

Michael Bader – SCCS
Technical University of Munich

Summer 2017
Part I

Intro: Molecular Models for Fluid Mechanics?
Continuum Mechanics for Fluids

Fluid:
- term “fluid” covers liquids and gases
- liquids: hardly compressible
- gases: volume depends on pressure
- both: small resistance to changes of form

Continuum:
- “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)
Molecular Dynamics for Fluids?

N-Body Problem – Newton’s Laws of Motion:

- force on a molecule: \( \vec{F}_i = \sum_{j \neq i} \vec{F}_{ij} \)
- leads to acceleration (Newton’s 2nd Law):

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

- system of \( dN \) ODE (2nd order)
  \( (N: \text{number of molecules}, \ d: \text{dimension}), \)
- reformulated into a system of \( 2dN \) 1st-order ODEs:

\[
\begin{align*}
\vec{p}_i &: = m_i \dot{\vec{r}}_i \\
\dot{\vec{p}}_i &= \vec{F}_i
\end{align*}
\]
Continuum vs. Molecular Dynamics

Compare Simulation Results for a (Micro-/Nano-)Channel Flow

For various Knudsen numbers: $Kn = \frac{\text{mean free path}}{\text{characteristic length}}$

→ continuum description only valid on coarse scale
→ other methods (Molecular Dynamics, Direct Simulation Monte Carlo, ...) required
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 C$_{12}$ atoms in 12g of C$_{12}$
  - number of molecules in 1 mol of a substance
    - (1 mol of ideal gas, under normal conditions, takes a volume of 22.4 litres)
- “**Avogadro number**”:
  - notion 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 1 second
- assume a time step of 1 fs
- assume we only need one floating point operation per molecule in each time step

→ $1.673 \cdot 10^{22}$ molecules (biggest MD simulation: $4 \cdot 10^{12}$ molecules)
→ $10^{15}$ timesteps
→ $1.673 \cdot 10^{37}$ operations

Using SuperMUC, this means we need at least
- $1.77 \cdot 10^{14}$ years for the computations
- $8.03 \cdot 10^8$ PB of memory assuming we need to store only 3+3 unknowns per molecule (position+velocity)

Scope of application thus limited to micro- and nanoscale simulations (at least for the near future)
Part II

Molecular Dynamics – the Physical Model
Classical Molecular Dynamics

- Quantum mechanics: Schrödinger equation, probability distributions, etc.
  → too difficult for $N$-body settings, where $N$ is large
  → use other approaches, such as Density Functional Theory (DFT)
- approximation via “classical” Molecular Dynamics
  → based on Newton’s equations of motion: $\ddot{r}_i = m_i \ddot{r}_i$
- molecules are modelled as particles (simplest case: point masses)
- there are interactions (forces) between molecules
- multibody potential functions describe the potential energy of the system; the velocities of the molecules (kinetic energy) are a composition of
  - Brownian motion (high velocities, no macroscopic movement)
  - flow velocity (for fluids)
- 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:

$$U := \sum_{i=1}^{N} U_1(r_i) + \sum_{i=1}^{N} \sum_{j=i+1}^{N} U_2(r_i, r_j) + \sum_{i=1}^{N} \sum_{j=i+1}^{N} \sum_{k=j+1}^{N} U_3(r_i, r_j, r_k) + \ldots$$

there are $\binom{N}{n} = \frac{N!}{n!(N-n)!} \in \mathcal{O}(N^n)$ $n$-body potentials $U_n$,
particulary $N$ one-body and $\frac{1}{2}N(N-1)$ two-body potentials

- force $\vec{F} = -\text{grad}U$
Forces vs. Potentials

- some potentials from mechanics:
  - harmonic potential (Hooke’s law): \( U_{\text{harm}} (r_{ij}) = \frac{1}{2} k (r_{ij} - r_0)^2 \)
    potential energy of a spring with length \( r_0 \), stretched/clinched to a length \( r_{ij} \)
  - gravitational potential: \( U_{\text{grav}} (r_{ij}) = -g \frac{m_i m_j}{r_{ij}} \)
    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 sphere potential: \( U_{HS}(r_{ij}) = \begin{cases} \infty & \forall r_{ij} \leq d \\ 0 & \forall r_{ij} > d \end{cases} \)  
  \( \rightsquigarrow \) force: Dirac function

- 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: \( U_{Su}(r_{ij}) = \begin{cases} \infty & \forall r_{ij} \leq d \\ -\epsilon \frac{1}{r_{ij}^6} & \forall r_{ij} > d \end{cases} \)

- Lennard-Jones potential

- van der Waals potential: \( U_{W}(r_{ij}) = -4\epsilon \sigma^6 \left( \frac{1}{r_{ij}} \right)^6 \)
  \( \epsilon = \) energy parameter
  \( \sigma = \) length parameter (rel. to atom diameter, cmp. van der Waals radius)

- Coulomb potential: \( U_{\text{col}}(r_{ij}) = \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{r_{ij}} \)
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
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 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
Lennard-Jones Potential

- general Lennard-Jones potential:
  \[ U_{LJ}(r_{ij}) = \alpha \varepsilon \left( \left( \frac{\sigma}{r_{ij}} \right)^n - \left( \frac{\sigma}{r_{ij}} \right)^m \right) \]
  with \( n > m \) and \( \alpha = \frac{1}{n-m} \left( \frac{m^n}{m^m} \right)^{\frac{1}{n-m}} \)

- LJ-12-6 potential
  \[ U_{LJ}(r_{ij}) = 4\varepsilon \left( \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6 \right) \]
  - \( m = 6 \): van der Waals attraction (matches van der Waals potential)
  - \( n = 12 \): Pauli repulsion (soft sphere potential) \( \Rightarrow \) purely heuristic

- application: simulation of ideal gases (e.g. Argon)

- force between 2 molecules:
  \[ F_{ij} = -\frac{\partial U(r_{ij})}{\partial r_{ij}} = \frac{24\varepsilon}{r_{ij}} \left( 2 \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6 \right) \]
  - very fast decay \( \Rightarrow \) short range \( (m = 6 > 3 = d \ \text{dimension}) \)
## LJ Atom-Interaction Parameters

<table>
<thead>
<tr>
<th>atom</th>
<th>(\epsilon)</th>
<th>(\sigma)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>8.6</td>
<td>2.81</td>
</tr>
<tr>
<td>He</td>
<td>10.2</td>
<td>2.28</td>
</tr>
<tr>
<td>C</td>
<td>51.2</td>
<td>3.35</td>
</tr>
<tr>
<td>N</td>
<td>37.3</td>
<td>3.31</td>
</tr>
<tr>
<td>O</td>
<td>61.6</td>
<td>2.95</td>
</tr>
<tr>
<td>F</td>
<td>52.8</td>
<td>2.83</td>
</tr>
<tr>
<td>Ne</td>
<td>47.0</td>
<td>2.72</td>
</tr>
<tr>
<td>S</td>
<td>183.0</td>
<td>3.52</td>
</tr>
<tr>
<td>Cl</td>
<td>173.5</td>
<td>3.35</td>
</tr>
<tr>
<td>Ar</td>
<td>119.8</td>
<td>3.41</td>
</tr>
<tr>
<td>Br</td>
<td>257.2</td>
<td>3.54</td>
</tr>
<tr>
<td>Kr</td>
<td>164.0</td>
<td>3.83</td>
</tr>
</tbody>
</table>

\(\epsilon\) = energy parameter  
\(\sigma\) = length parameter  
(cmp. van der Waals radius)

→ parameter fitting to match experiments

---

\(^a\)Boltzmann-constant: \(k_B := 1.38066 \cdot 10^{-23} \text{ J} \cdot \text{K}^{-1}\)  
\(^b\)10\(^{-1}\) nm = 1 Å (Ångstöm)
Dimensionless Formulation

“Dimensionless”: use reference values such as \( \sigma, \epsilon, \ldots \) to derive equations in which quantities no longer carry any dimensional units (m/s, kg, etc.)

Re-scaling to dimensionless quantities:

- position, distance
  \[
  \vec{r}^* := \frac{1}{\sigma} \vec{r} \quad (3a)
  \]

- time
  \[
  t^* := \frac{1}{\sigma} \sqrt{\frac{\epsilon}{m}} t \quad (3b)
  \]

- velocity
  \[
  \vec{v}^* := \frac{\Delta t}{\sigma} \vec{v} \quad (3c)
  \]
Dimensionless Formulation (2)

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

\[
U^*_LJ (r_{ij}) := \frac{U_{LJ} (r_{ij})}{\epsilon} = 4 \left( \left( \frac{r_{ij}^*}{2} \right)^{-6} - \left( \frac{r_{ij}^*}{2} \right)^{-3} \right) \tag{4a}
\]

\[
U^*_{kin} := \frac{U_{kin}}{\epsilon} = \frac{1}{\epsilon} \frac{mv^2}{2} = \frac{v^*}{2\Delta t^*} \tag{4b}
\]

- force

\[
\vec{F}_{ij}^* := \frac{\vec{F}_{ij}^*}{\epsilon} = 24 \left( 2 \left( \frac{r_{ij}^*}{2} \right)^{-6} - \left( \frac{r_{ij}^*}{2} \right)^{-3} \right) \frac{\vec{r}_{ij}^*}{r_{ij}^*} \tag{4c}
\]
Outlook: Multi-Centered Molecules

- molecules composed of multiple LJ-centers (rigid bodies without internal degrees of freedom)
- additionally: orientation (quarternions), 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
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):

\[
\ddot{\vec{r}}_i = \frac{\vec{F}_i}{m_i} = \frac{\sum_{j \neq i} \vec{F}_{ij}}{m_i} = -\frac{\sum_{j \neq i} \frac{\partial U(\vec{r}_i, \vec{r}_j)}{\partial |\vec{r}_{ij}|}}{m_i}
\]  \( (5) \)

- system of \( dN \) coupled ordinary differential equations of 2nd order  
  \( (N: \) number of molecules, \( d: \) dimension)  
- transferable to \( 2dN \) coupled ordinary differential equations of 1st order,  
  e.g. by introducing velocity \( \vec{v} := \dot{\vec{r}} \) (“derivative” variable),  
  or (even better) momentum \( \vec{p} \):

\[
\begin{align*}
\vec{p}_i &:= m_i \dot{\vec{r}}_i \quad \text{(6a)} \\
\ddot{\vec{p}}_i &= \vec{F}_i \quad \text{(6b)}
\end{align*}
\]
Initial Conditions

**Initial Value Problem:**
Molecule positions and velocities have to be given:

- place molecules as in a crystal lattice (body-/-face-centered cell)
- choose initial velocity to match temperature:

\[
\frac{d}{2} N k_B T = \frac{1}{2} \sum_{i=1}^{N} m v_i^2 \quad \text{with} \quad v_i := v_0
\]

- set velocities according to normal or uniform distribution around

\[
v_0 := \sqrt{\frac{d k_B T}{m}} \quad \text{resp.} \quad v_0^* := \sqrt{d T^* \Delta t^*}
\]

and with random direction
NVT Ensemble, Thermostat

- statistical (thermodynamics) “ensemble”: system in equilibrium, described by a set of macroscopically observable variables
- for the simulation of a (canonical) NVT ensemble, the following values have to be kept constant:
  - \( N \): number of molecules
  - \( V \): volume
  - \( T \): temperature
- thermostat regulates and controls the temperature (the kinetic energy), which is fluctuating in a simulation
- kinetic energy specified by the velocity of the molecules: \( E_{\text{kin}} = \frac{1}{2} \sum_i m_i \vec{v}_i^2 \)
- temperature is defined by \( T = \frac{2}{dNk_B} E_{\text{kin}} \) \((k_B: \text{Boltzmann constant})\)
- simple method: isokinetic (velocity) scaling
  \( \vec{v}_{\text{corr}} := \beta \vec{v}_{\text{act}} \) with \( \beta = \sqrt{\frac{T_{\text{ref}}}{T_{\text{act}}}} \)
- further methods exists, e.g. Berendsen or Nosé-Hoover thermostat
Periodic Boundary Conditions

- replicate simulated box periodically in all dimensions
- models an infinite space, built from identical cells
  ⇒ domain with torus topology