From Atoms to Materials: Predictive Theory and Simulations

Week 3: Dynamics of Atoms – Classical Mechanics and MD Simulations

Lecture 3.1: What is “Molecular Dynamics”? 

Ale Strachan
strachan@purdue.edu
School of Materials Engineering &
Birck Nanotechnology Center
Purdue University
West Lafayette, Indiana USA
Quantum mechanics:

• A group of atoms can be fully described by their wavefunction
• The time evolution of this wavefunction is given by the Schrödinger equation

\[ i\hbar \frac{d}{dt} \Psi(r,t) = H\Psi(r,t) \]

Too complex to be solved even with supercomputers

Electrons:
Time independent Schrödinger Eq.

\[ H\psi = E\psi \]

Ions:
Classical (Newton’s) mechanics

\[ F = ma \]
Ab initio Molecular dynamics

Initial conditions
\[ \{ R_i \} \quad \{ V_i \} \]

Compute energy & forces
\[ H \psi = E \psi \]
\[ F_i = -\nabla_{R_i} E(\{ R_i \}) \]

Integrate Eqs. of Motion
\[ R_i(t) \rightarrow R_i(t + \Delta t) \]
\[ V_i(t) \rightarrow V_i(t + \Delta t) \]
What is molecular dynamics?

Follow the dynamics (motion) of all the atoms in your material

Numerically solve classical equations of motion (Newton’s):

Approximation

\[
\vec{F}_i = m_i \vec{A}_i \quad \text{or} \quad \begin{cases} 
\dot{\vec{R}}_i = \frac{\vec{P}_i}{M_i} = \frac{\partial \vec{R}_i}{\partial t} \\
\dot{\vec{P}}_i = \vec{F}_i = \frac{\partial \vec{F}_i}{\partial t}
\end{cases}
\]

Forces on atoms come from the interaction with other atoms:

\[
\vec{F}_i = -\nabla_{R_i} V(\{R_j\})
\]

Approximated (in almost all cases)

Total potential energy
- Eigenvalue in the time-independent Schrodinger Eq.
- An empirical potential energy function
Classical mechanics: Hamilton’s picture

William Hamilton reformulation of classical mechanics (1800’s)

Hamiltonian:

\[ H(\{R_i\},\{P_i\}) = \sum_{i=1}^{3N} \frac{P_i(t)^2}{2m_i} + V(\{R_i(t)\}) \]

\( i \) denotes atom and Cartesian component (x, y, or z)

Equations of motion can be derived from the Hamiltonian:

\[ \dot{R}_i = \frac{\partial H}{\partial P_i} \]

\[ \dot{P}_i = -\frac{\partial H}{\partial R_i} \]

• These equations can only be solved analytically for very few cases
• MD solves the dynamics of many atoms (billions in supercomputers)
Classical mechanics: conserved quantities

\[ H(\{R_i\},\{P_i\}) = V(\{R_i(t)\}) + \sum_{i=1}^{3N} \frac{P_i(t)^2}{2m_i} \]

Let's calculate the time derivative of the Hamiltonian:

\[ \frac{dH}{dt} = \sum_{i=1}^{3N} \left( \frac{\partial H}{\partial R_i} \dot{R}_i + \frac{\partial H}{\partial P_i} \dot{P}_i \right) \]

Using the equations of motion we get:

\[ \frac{dH}{dt} = \sum_{i=1}^{3N} \left( \frac{\partial H}{\partial R_i} \frac{\partial H}{\partial P_i} + \frac{\partial H}{\partial P_i} \frac{\partial H}{\partial R_i} \right) = 0 \]

Total energy is conserved

Other constants of motion are:

- Linear momentum: \[ \vec{P} = \sum \vec{P}_i \]
- Angular momentum: \[ \vec{L} = \sum \vec{r}_i \times \vec{P}_i \]
Sample MD simulations
Structure of a minimalist MD code

1. **Initial conditions**
   
   \[ \{ R_i(0), V_i(0) \} \]

2. **Calculate forces at current time** \([F_i(t)]\) from \([R_i(t)]\)

3. **Integrate equations of motion**
   
   \[ R(t) \rightarrow R(t+\Delta t) \]
   \[ V(t) \rightarrow V(t+\Delta t) \]
   \[ t \rightarrow t+\Delta t \]

4. **Save properties**

5. **Output files**

6. **Done?**
   
   - **Yes**
   - **No**

7. **End**
Integrating the equations of motion

\[ \dot{R}_i = \frac{\ddot{P}_i}{M_i} = \frac{\ddot{R}_i(t + \Delta t) - \ddot{R}_i(t)}{\Delta t} \]

\[ \dot{P}_i = \vec{F}_i = \frac{\ddot{P}_i(t + \Delta t) - \ddot{P}_i(t)}{\Delta t} \]

\[ R_i(t + \Delta) = R_i(t) + \frac{P_i(t)}{M_i} \Delta t \]

Euler method

Verlet algorithm: Taylor expansion of positions with time

\[ R_i(t + \Delta t) = R_i(t) + \dot{R}_i(t) \Delta t + \frac{1}{2} \ddot{R}_i(t) \Delta t^2 + \frac{1}{6} \dddot{R}_i(t) \Delta t^3 + O(\Delta t^4) \]

\[ R_i(t - \Delta t) = R_i(t) - \dot{R}_i(t) \Delta t + \frac{1}{2} \ddot{R}_i(t) \Delta t^2 - \frac{1}{6} \dddot{R}_i(t) \Delta t^3 + O(\Delta t^4) \]

Sum two equations:

\[ R_i(t + \Delta t) = 2R_i(t) - R_i(t - \Delta t) + \dot{R}_i(t) \Delta t^2 + O(\Delta t^4) \]
MD simulations

Initial conditions
\[ [R_i(0), V_i(0)] \]

Calculate forces at current
time \[ [F_i(t)] \] from \[ R_i(t) \]

Integrate equations of motion
\[ R(t) \rightarrow R(t+\Delta t) \]
\[ V(t) \rightarrow V(t+\Delta t) \]
\[ t \rightarrow t+\Delta t \]

Save properties

Output files

Done?

No

Y

End