Introduction
- What is molecular dynamics (MD)? Examples of current research
- What will I learn in these lectures?

**Lecture 1: the theory behind molecular dynamics**
- Basic ideas & algorithms
- Brief introduction to the physics necessary to run & understand MD

**Lecture 2: total energy and force calculations**
- Quantum mechanical origin of atomic interactions
- Inter-atomic potentials: “averaging electrons out”

**Lecture 3: advanced techniques and mesodynamics**
- MD in under isothermal and isobaric conditions
- Coarse grain approaches and dynamics with implicit degrees of freedom
Lecture 2

MD = solve:

\[ \vec{F}_i = m_i \vec{a}_i \]

Forces from

\[ \vec{F}_i = -\vec{\nabla}_r V(r_j) \]

Today’s lecture

Topics:

• Quantum mechanical origin of bonding
  • How electrons lead to bonding between atoms

• Interatomic potentials or force fields
  • Average out electrons
  • Replace them with functions that describe how atoms interact
Classical mechanics

State of the system: \( \vec{r}(t), \vec{p}(t) \)

Energy:

\[
V = \frac{q_i q_j}{r} = -\frac{e^2}{r}
\]

\[
K = \frac{p^2}{2m} = \frac{1}{2}mv^2
\]

Ground state (minimum energy):

\[
r = 0
\]

\[
E = -\infty
\]

Atoms do not exist!!

Classical mechanics fails: quantum mechanics

State: wave function: \( \psi(\vec{r}) \)

Probability of finding the electron around \( r \):

\[
|\psi(\vec{r})|^2 = \psi(\vec{r})^* \psi(\vec{r})
\]

Observable \(\rightarrow\) operator

Position: \( \vec{r} \)

Momentum: \( \frac{\hbar}{i} \nabla \)

Energy: \( E = -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{r} \)

What one measures: expectation value

\[
\langle O \rangle = \int d^3r \psi^*(\vec{r})O(\vec{r})\psi(\vec{r})
\]
Why Quantum Mechanics?

- Ground state wave function
  - Function that minimizes the expectation value of the energy:

\[
\langle E \rangle = \int d^3 r \psi^* (\vec{r}) \left( -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{r} \right) \psi (\vec{r})
\]

Let's analyze two extreme cases:

**Very compact**

- Ground state: finite size
- **GOOD P.E.**
- BAD K.E.

**Very diffuse**

- **GOOD K.E.**
- BAD P.E.
The simplest molecule: $H_2^+$

Molecular wave function as linear combination of atomic orbitals (LCAO)

$$\psi_{\text{sym}}(\vec{r}) = \frac{1}{\sqrt{2}} (\psi_L(\vec{r}) + \psi_R(\vec{r}))$$

- K.E. good
- P.E. not so good
- Bonding

$$\psi_{\text{asym}}(\vec{r}) = \frac{1}{\sqrt{2}} (\psi_L(\vec{r}) - \psi_R(\vec{r}))$$

- K.E. not so good
- P.E. good
- Anti-bonding

Energy

Interatomic distance
Bonding in more complex molecules

<table>
<thead>
<tr>
<th>I A</th>
<th>II A</th>
<th>III A</th>
<th>IV A</th>
<th>VA</th>
<th>VIA</th>
<th>VII A</th>
<th>VIII A</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>He</td>
<td>B</td>
<td>C</td>
<td>N</td>
<td>O</td>
<td>F</td>
<td>Ne</td>
</tr>
<tr>
<td>Li</td>
<td>Be</td>
<td>Al</td>
<td>Si</td>
<td>P</td>
<td>S</td>
<td>Cl</td>
<td>Ar</td>
</tr>
<tr>
<td>Na</td>
<td>Mg</td>
<td>K</td>
<td>Ca</td>
<td>Sc</td>
<td>Ti</td>
<td>V</td>
<td>Cr</td>
</tr>
</tbody>
</table>

Energy vs. Inverse atomic distance

- **H₂**  Strong covalent bond
- **He₂**  Very weak bond
Bonding in oxygen

![H2O molecule diagram]

- **Bond distance**: 0.96 Å
- **Bond angle**: 104.5°

Bonding in nitrogen

<table>
<thead>
<tr>
<th>Compound</th>
<th>NH2</th>
<th>PH2</th>
<th>AsH2</th>
<th>SbH2</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Bond angle</strong></td>
<td>103.3°</td>
<td>91.7°</td>
<td>90.2°</td>
<td>90.3°</td>
</tr>
<tr>
<td>NH3</td>
<td>PH3</td>
<td>AsH3</td>
<td>SbH3</td>
<td></td>
</tr>
<tr>
<td><strong>Bond angle</strong></td>
<td>106.7°</td>
<td>93.3°</td>
<td>92.1°</td>
<td>91.6°</td>
</tr>
</tbody>
</table>

William Goddard, III, The nature of the chemical bond, Caltech. CRC Handbook, Bond lengths and angles in gas-phase molecules
Interatomic potentials: averaging electrons out

• Ab initio, electronic structure methods
  • Hartree Fock, Density Functional Theory
  • Quantum Monte Carlo
  • Very accurate but computationally intensive
    (applicable to small systems – 100s-1000s atoms)

• Interatomic potentials:

\[
V(\{r_i\}) = V_{\text{cov/met}}(\{r_i\}) + V_{\text{electr}}(\{r_i\}) + V_{\text{vdW}}(\{r_i\})
\]

Parameterized to describe specific materials
**Pair-wise potentials**

Simplest, non-trivial, function  
Sum of pair-wise terms

\[ V(\{r_i\}) = \sum_{i<j} \phi(|r_i - r_j|) \]

**Lennard-Jones (6-12)**

\[ \phi_{LJ}(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right] \]

Distance & energy

**Exponential-6**

\[ \phi_{\text{exp-6}}(r) = \varepsilon \left[ e^{-\gamma r} - Ar^{-6} \right] \]

**Morse**

\[ \phi_{\text{Morse}}(r) = \varepsilon \left[ \exp \left( \gamma \left( 1 - \frac{r}{r_0} \right) \right) - 2 \exp \left( \frac{\gamma}{2} \left( 1 - \frac{r}{r_0} \right) \right) \right] \]

Distance, energy, & curvature
Two-body potentials

Pair-wise interactions: \[ E(\{r_i\}) = \sum_{i<j} \phi(r_{ij}) \]

- Vacancy energy in Perfect crystal
- Coordination number \( Z \)
- Interactions: only first nearest neighbors

\[ E_{\text{xtal}}(N) = \frac{1}{2} NZE_0 \]

- Now let’s make a vacancy:

\[ E_{\text{vac}}(N - 1) = \frac{1}{2} NZE_0 - ZE_0 \]

\[ \varepsilon_{\text{vac}} = E_{\text{vac}}(N - 1) - \frac{N - 1}{N} E_{\text{xtal}}(N) = \frac{1}{2} NZE_0 - ZE_0 - \frac{1}{2} (N - 1)Z_0 = -\frac{1}{2} ZE_0 \]

Vacancy formation energy is equal to cohesive energy
Two-body potentials: limitations

- Two-body potentials: vacancy formation $\sim$ cohesive energy
- Metals: $\varepsilon_{\text{vac}} \sim 1/3 \ E_{\text{coh}}$

<table>
<thead>
<tr>
<th></th>
<th>$E_{\text{coh}}$ (eV)</th>
<th>$E_{\text{vac}}$ (eV)</th>
<th>$E_{\text{vac}}/E_{\text{coh}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>3.39</td>
<td>0.75</td>
<td>0.22</td>
</tr>
<tr>
<td>Ni</td>
<td>3.516</td>
<td>1.6</td>
<td>0.46</td>
</tr>
<tr>
<td>Cu</td>
<td>3.615</td>
<td>1.2</td>
<td>0.33</td>
</tr>
<tr>
<td>Ag</td>
<td>4.086</td>
<td>1.15</td>
<td>0.28</td>
</tr>
<tr>
<td>Pt</td>
<td>3.924</td>
<td>1.4</td>
<td>0.36</td>
</tr>
<tr>
<td>Au</td>
<td>4.079</td>
<td>0.95</td>
<td>0.23</td>
</tr>
</tbody>
</table>

- Two-body potentials and elastic constants: $c_{12} = c_{44}$
- Metals: $c_{12} > c_{44}$

- Pair potentials can only describe simple non-bond interactions
  - Closed-shell atoms (Ne, Ar, Kr, etc.)
  - Atoms that are fully coordinated (e.g. inter-molecular)

- Pauli repulsion at short distances
- London dispersion at longer distances

\[ \text{van der Waals} \]
More non-bond interactions: electrostatics

Difference in atomic electron affinity and ionization potential leads to charge transfer

Electrostatic energy:
Assuming point charges:

\[ V_{elec} = C_{unit} \sum_{i<j} \frac{q_i q_j}{r_{ij}} \]

How to obtain atomic charges?
• Formal charge
• Dipole moment or polarization
• From electronic structure calculations
• Self-consistently charge equilibration
Electrostatics and periodic boundary conditions

Coulomb interaction decays very slowly

\[ V_{elec} = C_{\text{unit}} \sum_{i<j} \frac{q_i q_j}{r_{ij}} \]

With periodic boundary conditions (infinite system):
• The Coulomb sum is conditionally convergent:
  • Result depends on the order of the summands
  • Result depends on charge arrangement on the surface
• Need to use special sum techniques and boundary conditions
  • Ewald method [part of the sum in real space and part in reciprocal Fourier space]
  • Particle-mesh Ewald and other techniques

Electrostatics: shielding

• Charge distributions are not point-like

Short distances: Shielded Coulomb

Long interatomic distances: 1/r

Some molecular potentials use exclusions
No Coulomb for:
• Bonded atoms
• 1-3 (atoms separated by two covalent bonds)
• 1-4 (atoms separated by three covalent bonds)
Metallic and covalent interactions

\[ V(\{r_i\}) = V_{\text{cov/met}}(\{r_i\}) + V_{\text{electr}}(\{r_i\}) + V_{\text{vdW}}(\{r_i\}) \]
Capturing many-body effects in metals

Embedded atom model (EAM)
Mike Baskes and collaborators 1980’s + other groups

\[ V = \sum_{i<j} \phi(r_{ij}) + \sum_i F(\rho_i) \]

Two-body potential
Embedding energy:
Energy to embed atom \(i\) in the electronic density \(\rho_i\)

\[ \rho_i = \sum_{j \neq i} f(r_{ij}) \]

Local electronic density
around atoms \(i\) contributed from nearby atoms

Accurate description of:
• Environment dependence of bonding in metals (vacancy and surfaces)
• Elastic constants and plastic deformation
• Phase transformations (melting & solid-solid)
• Alloys

Not very accurate for:
• Cases where bonding is highly directional
EAM potentials: parameterization

- Fit parameters based on experimental data
  - Lattice parameter, elastic constants, vacancy & surface energy
- Use of \textit{ab initio} data enables the incorporation of more information

EAM potential for Tantalum

\textbf{bcc phase}

\textbf{fcc phase}

\textbf{A15 phase}

\begin{itemize}
  \item \textbf{Circles: QM}
  \item \textbf{Lines: FF (qEAM)}
\end{itemize}

**EAM potentials: parameterization**

- Large deformations
  - Shear transformation in the twinning mode (ideal strength)

\[
a = \frac{1}{2}[11-1] + s[-111] \\
b = \frac{1}{2}[111] + s[-111] \\
c = \frac{1}{2}[111]
\]

<table>
<thead>
<tr>
<th>vol</th>
<th>qEAM FF</th>
<th>DFT-GGA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E (eV)</td>
<td>(\tau) (GPa)</td>
</tr>
<tr>
<td>18.36</td>
<td>0.188</td>
<td>7.14</td>
</tr>
<tr>
<td>17.618</td>
<td>0.2</td>
<td>8</td>
</tr>
<tr>
<td>15.144</td>
<td>0.26</td>
<td>12.05</td>
</tr>
<tr>
<td>10.91</td>
<td>0.43</td>
<td>28.2</td>
</tr>
</tbody>
</table>

DFT-data from:

- Vacancy and surface formation energies
 Thermal expansion

From isothermal and isobaric MD runs
2-phase MD simulation

Melting at ambient pressure
- Simulation: 3150±50 K (4%)
- Experiment: 3290±50 K

Experiment shock melting
Brown and Shaner (1984)
Temperature for Hugoniot

Cohen ab initio Hugoniot
Using exper. pressure

Free electrons

Band electrons

Pressure (GPa)

Temperature (K)

Strachan et al. MSMSE (2004)
Covalent interactions

Interaction between atoms separated by chemical bonds

Bond stretch: \[ \phi_{bond}(r) = \begin{cases} \frac{1}{2} k_{ij} (r - r_{ij}^0)^2 \\ Morse, L - J \end{cases} \]

Angle bending: \[ \phi_{angle}(\theta) = \begin{cases} \frac{1}{2} k_{ijk} (\theta - \theta_{ijk}^0)^2 \\ \frac{1}{2} \frac{k_{ijk}}{\sin^2 \theta_{ijk}^0} \left[ \cos \theta - \cos \theta_{ijk}^0 \right]^2 \end{cases} \]
Covalent interactions

Torsion bending (dihedral angles)

$$\phi_{\text{torsions}}(\varphi) = k_{ijkl} \left[ 1 - \cos(n_{jk}(\varphi - \varphi_{jk}^0)) \right]$$

**Ethylene (planar)**

- $sp^2$ hybridization
  - Equilibrium at $0^\circ$ & $180^\circ$
  - Maxima at: $90^\circ$ & $270^\circ$
  - High torsional barrier
    - Rotating around C-C bond breaks the PI bond

**Ethane (staggered)**

- $sp^3$ hybridization
  - Equilibrium at $60^\circ$, $180^\circ$, & $300^\circ$
  - Maxima at: $0^\circ$, $120^\circ$, & $240^\circ$
  - Low torsional barrier
    - Dominated by vdW between H
Atom types in molecular force fields

• Element alone is not enough to determine the interactions
  • E.g.: sp3 carbon and sp2 carbon behave differently

• In traditional molecular force fields the user specifies force field types to establish the character of the atom
  • Force field types & connectivities need to be determined prior to MD simulation
  • FF types and connectivities are kept fixed during run

Widely used force fields for molecular simulations:


**Features:**

- Interactions should depend only on element and environment
  - No force field types
  - Partial charges should depend on environment
- No pre-determined connectivities
  - Bonds should be determined based on geometry
  - Bonds can be broken and formed

\[
V(\{r_i\}) = V_{\text{cov}}(\{r_i\}) + V_{\text{elect}}(\{r_i\}) + V_{\text{vdW}}(\{r_i\})
\]
Reactive force fields: covalent interactions

Bond distance $\rightarrow$ bond order $\rightarrow$ bond energy

- Bond stretch, angle, & torsion terms depend on bond orders involved
  - E.g. distinguish between sp$^2$ and sp$^3$ carbon
- As a bond order goes to zero all terms involving also tend to zero
  - Bond orders are pre-factors for all covalent terms
- Over-coordination penalty
  - Limit the number of bonds an atom can make

van Duin & Goddard, Caltech
Partial atomic charges should be allowed to change as chemical reactions occur.

Charge equilibration enables the calculation of partial charges based on atomic positions.

- Minimize the total electrostatic energy for fixed atomic positions

\[ V_{\text{elec}} = \sum_{i<j} q_i q_j J(r_{ij}) + \sum_i \left( \chi_i q_i + \frac{1}{2} H_i q_i^2 \right) \]

- Interactions (shielded Coulomb)
- Atomic terms (electron affinity and ionization potential)


**Reactive force fields: key developments**

- **Reactive Empirical Bond Order (REBO):**

- **AI-REBO:**

- **ReaxFF:**
Reactive force fields: parameterization

ReaxFF (Adri van Duin and Bill Goddard @ Caltech)

Bond breaking

H₃C-NH₂ dissociation

Energy (kcal/mol) vs. Bond distance (Å)

Angle bending

H₂N-O-NH₂ angle

Energy (kcal/mol) vs. Angle (degrees)

Torsion bending

H₂C=NH torsion angle

Energy (kcal/mol) vs. Angle (degrees)

- Bond breaking curves for all bonds
- Angle and torsion bending
- Gas phase reactions
- Crystalline data
- 100s chemical reactions
- 1000s equilibrium structures
Reactive force fields: parameterization

ReaxFF (Adri van Duin and Bill Goddard @ Caltech)

- Unimolecular decomposition pathways of RDX
- QM vs. ReaxFF

Reactive force fields: applications

Shock decomposition

32 RDX molecules on 32 RDX molecules

\[ \pm u_p \]


Thermal decomposition

Constant temperature & density

Interatomic potentials: summary

• Ab initio electronic structure calculations
  • Very accurate but computationally intensive

• Parameterize “first principled-based interatomic potentials”
  • Equations of state for various crystals, elastic constants
  • Chemical reactions
  • Defect structure and energies

• Enable predictive simulations
  • Validate approach for well characterize materials
  • Use it to predict the behavior of new materials or devices
Question 1
Question 2
Question 3
Question 4
Question 5
Question 6
Question 7
Question 8