How to model chemical interactions

Lecture 5

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## Content overview

### I. Particle and continuum methods

1. Atoms, molecules, chemistry
2. Continuum modeling approaches and solution approaches
3. Statistical mechanics
4. Molecular dynamics, Monte Carlo
5. Visualization and data analysis
6. Mechanical properties – application: how things fail (and how to prevent it)
7. Multi-scale modeling paradigm
8. Biological systems (simulation in biophysics) – how proteins work and how to model them

### II. Quantum mechanical methods

1. It’s A Quantum World: The Theory of Quantum Mechanics
2. Quantum Mechanics: Practice Makes Perfect
3. The Many-Body Problem: From Many-Body to Single-Particle
4. Quantum modeling of materials
5. From Atoms to Solids
6. Basic properties of materials
7. Advanced properties of materials
8. What else can we do?
Overview: Material covered so far…

- **Lecture 1:** Broad introduction to IM/S

- **Lecture 2:** Introduction to atomistic and continuum modeling (multi-scale modeling paradigm, difference between continuum and atomistic approach, case study: diffusion)

- **Lecture 3:** Basic statistical mechanics – property calculation I (property calculation: microscopic states vs. macroscopic properties, ensembles, probability density and partition function)

- **Lecture 4:** Property calculation II (advanced property calculation, introduction to chemical interactions, Monte Carlo method)

- **Lecture 5:** How to model chemical interactions
Lecture 5: How to model chemical interactions

Outline:
1. Monte-Carlo (MC) approach: Metropolis-Hastings algorithm
2. How to model chemical interactions
   2.1 Pair potentials
   2.2 How to model metals: Multi-body potentials

Goals of today’s lecture:
- Get to know basic methods to model chemical bonds (starting with simple “pair potentials”)
- Learn how to identify parameters for models of chemical bonds (for pair potentials)
- Limitations of pair potentials – and other, alternative methods
1. Monte-Carlo (MC) approach: Metropolis-Hastings algorithm
Averaging over the ensemble

\[ A_{\text{macro}} \neq \frac{1}{3}(A_1 + A_2 + A_3) \]
Averaging over the ensemble

Instead, we must average with proper weights that represent the probability of a system in a particular microscopic state!

\( A_{\text{macro}} \neq \frac{1}{3}(A_1 + A_2 + A_3) \)

\( A_{\text{macro}} = \rho_1 A_1 + \rho_2 A_2 + \rho_3 A_3 = \rho_1(r_1, p_1)A_1(r_1, p_1) + \rho_2(r_2, p_2)A_2(r_2, p_2) + \rho_3(r_3, p_3)A_3(r_3, p_3) \)

Probability to find system in state \( C_1 \)
How to solve…

\[ < A > = \int_{p} \int_{r} A(p, r) \rho(p, r) dr dp \]

**Probability density distribution**

E.g.: 

\[ T(p) = \frac{1}{3} \frac{1}{Nk_B} \sum_{i=1}^{N} \frac{m_i^2 \vec{v}_i^2}{m_i} = A(p) \]

Virtually impossible to carry out analytically

Must know all possible configurations

**Therefore:** Require numerical simulation

Molecular dynamics OR Monte Carlo
Monte Carlo scheme

Method to carry out integration over “domain”

Want:

\[
A = \int_{\Omega} f(\vec{x}) d\Omega
\]

E.g.: Area of circle (= \(\pi/4\) exact solution)

\[
A_c = \frac{\pi d^2}{4} \quad A_c = \frac{\pi}{4}
\]

\[\pi = 4 A_c\]
Monte Carlo scheme for integration

- **Step 1**: Pick random point $\vec{x}_i$ in $\Omega$
- **Step 2**: Accept/reject point based on criterion (e.g. if inside or outside of circle and if in area not yet counted)
- **Step 3**: If accepted, add $f(\vec{x}_i) = 1$ to the total sum

$$A_C = \int_{\Omega} f(\vec{x}) d\Omega$$
$$A_C = \frac{\pi}{16}$$

$N_A$: Attempts made

$$A_C = \frac{1}{N_A} \sum_i f(\vec{x}_i)$$

Courtesy of John H. Mathews. Used with permission.
How to apply to ensemble average?

- Similar method can be used to apply to integrate the ensemble average

\[
< A > = \int_\mathbb{R} \int_\mathbb{R} A(p,r) \rho(p,r) drdp
\]

\[
\rho(p,r) = \frac{1}{Q} \exp \left[ - \frac{H(p,r)}{k_B T} \right]
\]

To be computationally more effective, need more complex iteration scheme (replace “random sampling” by “importance sampling”)

> Computationally inefficient: If states are created “randomly” that have low probability….

\[
< A > = \sum_{i=1}^{N_A} \frac{A \exp\left(- \frac{H(r_A, p_A)}{k_B T}\right)}{\sum_{i=1}^{N_A} \exp\left(- \frac{H(r_A, p_A)}{k_B T}\right)}
\]
Challenge: sampling specific types of distributions

- We want to
  - Integrate a sharply-peaked function
  - Use Monte Carlo with uniformly-distributed random numbers (e.g. here from -1 to 1)

\[
f(x) = \exp\left(-\left(100x\right)^{12}\right)
\]

\[
A = \int_{-1}^{1} f(x)dx
\]
Challenge: sampling specific types of distributions

- We want to
  - Integrate a sharply-peaked function
  - Use Monte Carlo with uniformly-distributed random numbers (e.g. here from -1 to 1)

- What happens?
  - Very few points contribute to the integral (~9%)
  - Poor computational efficiency/convergence

- Solution: use a different distribution of random numbers to sample "importance sampling"

\[ f(x) = \exp\left(-\left(100x\right)^{12}\right) \]

\[ A = \int_{-1}^{1} f(x)dx \]
**Importance sampling**

- **Core concept:** Picking states with a biased probability: Importance sampling (sampling the “correct” way…)

\[
\langle A \rangle = \int \int A(p, r) \rho(p, r) dr dp \quad \rho(p, r) = \frac{1}{Q} \exp \left[- \frac{H(p, r)}{k_B T} \right]
\]
Importance sampling

- **Core concept:** Picking states with a biased probability: Importance sampling (sampling the “correct” way…)

\[
< A >= \int \int_A \rho(p,r) dr dp \quad \rho(p,r) = \frac{1}{Q} \exp\left[-\frac{H(p,r)}{k_B T}\right]
\]

**Notice:** Probability (and thus importance) related to energy of state
Importance sampling: Metropolis algorithm

- Leads to an appropriate “chain” of states, visiting each state with **correct probability**

- Concept:
  - Pick random initial state
  - Move to trial states
  - Accept trial state with certain probability (based on knowledge about behavior of system, *i.e.*, energy states)

Metropolis-Hastings Algorithm

Concept: Generate set of random microscopic configurations
Accept or reject with certain scheme

State $A$

State $B$

Random move to new state $B$
Metropolis-Hastings Algorithm: \( NVT \)

Have: State \( A \) (initial state) + energy function \( H(A) \)

Step 1: Generate new state \( B \) (random move)
Metropolis-Hastings Algorithm: \textit{NVT}

Have: State \( A \) (initial state) + energy function \( H(A) \)

Step 1: Generate new state \( B \) (random move)

Step 2: if \( H(B) < H(A) \) then \( a = 1 \) else \( a = 0 \) endif \( a = \text{true}[1]/\text{false}[0] \) for acceptance

Draw random number \( 0 < p < 1 \)

“Downhill” moves always accepted
Metropolis-Hastings Algorithm: \textit{NVT}

Have: State $A$ (initial state) + energy function $H(A)$

Step 1: Generate new state $B$ (random move)

Step 2: if $H(B) < H(A)$ then $a = 1$
else

“Downhill” moves always accepted, uphill moves with finite (“thermal”) probability

Draw random number $0 < p < 1$

if $p < \exp\left[-\frac{H(B) - H(A)}{k_B T}\right]$ then $a = 1$
else $a = 0$
endif

$a = \text{true}[1]/\text{false}[0]$ for acceptance
Metropolis-Hastings Algorithm: \textit{NVT}

Have: State $A$ (initial state) + energy function $H(A)$

Step 1: Generate new state $B$ (random move)

Step 2: if $H(B) < H(A)$ then $a = 1$ \hspace{1cm} $a = \text{true}[1]/\text{false}[0]$ for acceptance
else

Draw random number $0 < p < 1$

if $p < \exp\left[-\frac{H(B) - H(A)}{k_B T}\right]$ then $a = 1$
else

$a = 0$
endif
endif

Step 3: if $a = 1$ then accept state $B$
endif

\hspace{1cm} $a=$ variable either 0 or 1
\hspace{1cm} (used to detect acceptance of state $B$ when $a=1$)
Metropolis-Hastings Algorithm: NVT

Have: State \( A \) (initial state) + energy function \( H(A) \)

Step 1: Generate new state \( B \) (random move)

Step 2: if \( H(B) < H(A) \) then \( a = 1 \) else

Draw random number \( 0 < p < 1 \)

if \( p < \exp \left[ -\frac{H(B) - H(A)}{k_B T} \right] \) then \( a = 1 \) else \( a = 0 \) endif

endif

Step 3: if \( a = 1 \) then accept state \( B \)

endif

repeat \( N_A \) times

\[
< A > = \frac{1}{N_A} \sum_{i=1}^{N_A} A(i)
\]
Arrhenius law - explanation

Consider two states, $A$ and $B$

State $B$ has higher energy than state $A$

Otherwise accepted anyway!


Arrhenius law - explanation

\[ H(B) > H(A) \]

\[ H(B) - H(A) \]

Energy difference between states \( A \) and \( B \) ("uphill")

\[
\exp\left[-\frac{H(B) - H(A)}{k_BT}\right]
\]

Probability of success of overcoming the barrier at temperature \( T \)
Arrhenius law - explanation

\[ \exp \left[- \frac{H(B) - H(A)}{k_B T} \right] \]

Probability of success of overcoming the barrier

Random number \(0 < p < 1\)
(equal probability to draw any number between 0 and 1)

Acceptance if:

\[ p < \exp \left[- \frac{H(B) - H(A)}{k_B T} \right] \]

E.g. when \(\exp(\ldots) = 0.8\) most choices for \(p\) will be below, that is, higher chance for acceptance

Play "1D darts"
Summary: Metropolis-Hastings Algorithm

Have: State $A$ (initial state) + energy function $H(A)$

Step 1: Generate new state $B$ (random move)

Step 2: if $H(B) < H(A)$ then $a = 1$
   else Draw random number $0 < p < 1$
   if $p < \exp\left[-\frac{H(B) - H(A)}{k_BT}\right]$ then $a = 1$
   else $a = 0$
   endif
endif

Step 3: if $a = 1$ then accept state $B$
endif

repeat $N_A$ times

Summary:

\[ < A > = \frac{1}{N_A} \sum_{i=1}^{N_A} A(i) \]
Summary: MC scheme

Have achieved:

\[
< A > = \int \int A(p, r) \rho(p, r) dr dp \quad \leftrightarrow \quad < A > = \frac{1}{N_A} \sum_{i=1}^{N_A} A_i
\]

Note:
- Do not need forces between atoms (for accelerations)
- Only valid for equilibrium processes
Property calculation with MC: example

Averaging leads to “correct” thermodynamic property

Error in Monte Carlo decreases as $\sqrt{N_A}$
Complex moves

- Move sets can be adapted for other cases, e.g. not just move of particles but also rotations of side chains (=rotamers), torsions, etc.

E.g. application in protein folding problem when we’d like to determine the 3D folded structure of a protein in thermal equilibrium

After: R.J. Sadus
Possible Monte Carlo moves

- Trial moves
  - Rigid body translation
  - Rigid body rotation
  - Internal conformational changes (soft vs. stiff modes)
  - Titration/electronic states
  - …

- Questions:
  - How “big” a move should we take?
  - Move one particle or many?

Image by MIT OpenCourseWare.
Monte Carlo moves

- How “big” a move should we take?
  - **Smaller moves:** better acceptance rate, slower sampling
  - **Bigger moves:** faster sampling, poorer acceptance rate

- Move one particle or many?
  - Possible to achieve more efficient sampling with *correct* multi-particle moves
  - One-particle moves must choose particles at random
2. How to model chemical interactions
Atomic interactions – different types of chemical bonds

- **Primary bonds ("strong")**
  - Ionic (ceramics, quartz, feldspar - **rocks**)
  - Covalent (**silicon**)
  - Metallic (copper, nickel, **gold**, silver) (high melting point, 1000-5,000K)

- **Secondary bonds ("weak")**
  - Van der Waals (**wax**, low melting point)
  - Hydrogen bonds (proteins, **spider silk**) (melting point 100-500K)
Atomic interactions – different types of chemical bonds

- **Primary bonds (“strong”)**
  - Ionic (ceramics, quartz, feldspar - **rocks**)
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    (high melting point, 1000-5,000K)

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  - Van der Waals (**wax**, low melting point)
  - Hydrogen bonds (proteins, **spider silk**)
    (melting point 100-500K)

- Ionic: Non-directional (point charges interacting)
- Covalent: Directional (bond angles, torsions matter)
- Metallic: Non-directional (electron gas concept)

*Difference of material properties originates from different atomic interactions*
Types of bonding (illustrations)

- **Ionic bonding**: Covalent bonds are characterized by the sharing of electrons between atoms. In ionic bonding, there are charged ions formed by the transfer of electrons.

- **Hydrogen bonding**: Involves the interaction between a hydrogen atom and a highly electronegative atom (like oxygen or nitrogen) with a partially negative charge.

- **Covalent bonding**: Electron density is localized between two atoms.

- **Metallic bonding**: Electron density is delocalized throughout the material, contributing to its metallic properties.

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Wax

Soft, deformable, does not break under deformation

Rocks

Quite brittle (breaks e.g. during earthquake)

Image courtesy of Wikimedia Commons.
Rocks and sand on Mars

What are the properties and composition of extraterrestrial rocks?

Image courtesy of NASA.
Gold

Very “soft” metal, deformable, high density
Silicon

Rather brittle – shatters into many pieces if dropped

Image courtesy of NASA.
Spider web

Very extensible, deformation, yet very strong (similar to steel)

Image courtesy of U.S. Fish and Wildlife Service.
Tree’s leaf

Very deformable under bending (wind loads), but breaks easily under tear.
Particularly intriguing...brittle or ductile?

Glass Polymers Ice...

BRITTLE

DUCTILE

Copper, Gold

Shear load

Image courtesy of quinn.anya. License: CC-BY.

Image by MIT OpenCourseWare.
Outline

- Goal: model chemical bonds with the objective to enable force calculation (see lecture 2, basic MD algorithm) or energy calculation (see lecture 4/5, MC)

- Two-step approach:
  1. Define energy landscape, i.e. defines how distance between particles controls the energy stored in the bond
  2. Then take derivatives to obtain forces, to be used in the MD algorithm

"Modeling and simulation" paradigm:
- First, develop mathematical expressions (modeling)
- Second, use model in numerical solution (simulation, =MD)
Models for atomic interactions

- Define interatomic potentials that describe the energy of a set of atoms as a function of their coordinates $r$:

\[
U_{total} = U_{total}(r) \quad \text{Depends on position of all other atoms}
\]

\[
r = \{\vec{r}_j\} \quad j = 1..N
\]
Models for atomic interactions

- Define interatomic potentials that describe the energy of a set of atoms as a function of their coordinates $r$: 

$$
U_{\text{total}} = U_{\text{total}}(r)
$$

- Change of potential energy due to change of position of particle $i$ (“gradient”):

$$
\nabla_{\vec{r}_i} = \left( \frac{\partial}{\partial r_{1,i}}, \frac{\partial}{\partial r_{2,i}}, \frac{\partial}{\partial r_{3,i}} \right)
$$

- Depends on position of all other atoms

$$
r = \{\vec{r}_j\} \quad j = 1..N
$$

$U_{\text{total}}$ depends on position of all other atoms.
2.1 Pair potentials
Pair potentials: energy calculation

**Simple approximation:** Total energy is sum over the energy of all pairs of atoms in the system

\[ E = \sum_{i,j} E_{ij} \]

where \( E_{ij} \) is the energy of pair \( i \) and \( j \), and \( r_{ij} \) is the distance between particles \( i \) and \( j \).
Pair potentials: energy calculation

**Simple approximation:** Total energy is sum over the energy of all pairs of atoms in the system.

\[
\text{Total energy} = \sum_{i \neq j} \phi(r_{ij})
\]

where \( r_{ij} \) is the distance between particles \( i \) and \( j \).

\[ r_{ij} = \text{distance between particles } i \text{ and } j \]

\( \phi(r_{ij}) \) is the pair-wise interaction potential energy for each bond.
Pair potentials: energy calculation

**Simple approximation:** Total energy is sum over the energy of all pairs of atoms in the system

\[
U_i = \sum_{j=1}^{N} \phi(r_{ij})
\]

\[r_{ij} = \text{distance between particles } i \text{ and } j\]

\[\phi(r_{ij}) = \text{Pairwise interaction potential energy for each bond}\]
Overview - pair potentials: total energy calculation

**Simple approximation:** Total energy is sum over the energy of all pairs of atoms in the system

\[ U_{\text{total}} = \frac{1}{2} \sum_{i=1, i \neq j}^{N} \sum_{j=1}^{N} \phi(r_{ij}) \]

Pair wise interaction potential

\[ \phi(r_{ij}) \]

Pair wise summation of bond energies

Energy of atom \( i \)

\[ U_i = \sum_{j=1}^{N} \phi(r_{ij}) \]

Avoid double counting

\[ r_{ij} = \text{distance between particles } i \text{ and } j \]
Example: calculation of total energy

two “loops” over pairs of all particles

\[ U_{total} = \frac{1}{2} \sum_{i=1, i \neq j}^{N} \sum_{j=1}^{N} \phi(r_{ij}) \]

with \( \phi_{ij} = \phi(r_{ij}) \)

\[ U_{total} = \frac{1}{2} \left( \phi_{12} + \phi_{13} + \phi_{14} + \phi_{1N} \ldots + \phi_{21} + \phi_{23} + \ldots + \phi_{2N} + \ldots + \phi_{N-1,N} \right) \]
Interatomic pair potentials: examples

\[ \phi(r_{ij}) = D \exp\left(-2\alpha(r_{ij} - r_0)\right) - 2D \exp\left(-\alpha(r_{ij} - r_0)\right) \]
Morse potential

\[ \phi(r_{ij}) = 4\varepsilon \left[ \left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6} \right] \]
Lennard-Jones 12:6 potential
(excellent model for noble Gases, Ar, Ne, Xe..)

\[ \phi(r_{ij}) = A \exp\left(-\frac{r_{ij}}{\sigma}\right) - C\left(\frac{\sigma}{r_{ij}}\right)^6 \]
Buckingham potential

\[ \phi(r_{ij}) = a_0 + \frac{1}{2}k(r_{ij} - r_0)^2 \]
Harmonic approximation
(no bond breaking)
How to use a pair potential, e.g. LJ
Force calculation – pair potential

Forces on particles can be calculated by taking derivatives from the potential function & by considering all pairs of atoms

Start with force magnitude (STEP 1): Negative derivative of potential energy with respect to atomic distance

\[ F = -\frac{d \phi(r)}{d r} \bigg|_{r=r_{ij}} = -\frac{d \phi(r_{ij})}{d r_{ij}} = -\phi'(r_{ij}) \]
Force calculation – pair potential

Forces on particles can be calculated by taking derivatives from the potential function & by considering all pairs of atoms.

Start with **force magnitude (STEP 1):** Negative derivative of potential energy with respect to atomic distance

\[
F = -\frac{d\phi(r)}{dr} \bigg|_{r=r_{ij}} = -\frac{d\phi(r_{ij})}{dr_{ij}} = -\phi'(r_{ij})
\]

Calculate **force vector (STEP 2):**

Component \( i \) of vector \( \vec{r}_{ij} \)

\[
f_i = F \frac{x_i}{r_{ij}} \quad f = f_i \hat{e}_i
\]

\[
r_{ij} = |\vec{r}_{ij}|
\]
What can we do with this potential?
Bending a copper wire until it breaks
A closer look

http://www2.ijs.si/~goran/sd96/e6sem1y.gif

Courtesy of Goran Drazic. Used with permission.
Case study: plasticity in a micrometer crystal of copper

Simulation details

- 1,000,000,000 atoms (0.3 micrometer side length)
- 12:6 Lennard-Jones ductile material, for copper
- Visualization using energy filtering method (only show high energy atoms)

Image by MIT OpenCourseWare. After Buehler, et al., 2005.

Generic features of atomic bonding: "repulsion vs. attraction"
A simulation with 1,000,000,000 particles
Lennard-Jones - copper

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Strengthening caused by hindering dislocation motion
If too difficult, ductile modes break down and material becomes brittle
Parameters for Morse potential

(for reference)
Morse potential parameters for various metals

\[ \phi(r_{ij}) = D \exp\left(-2\alpha(r_{ij} - r_0)\right) - 2D \exp\left(-\alpha(r_{ij} - r_0)\right) \]

### Morse Potential Parameters for 16 Metals

<table>
<thead>
<tr>
<th>Metal</th>
<th>( \alpha a_0 )</th>
<th>( \beta )</th>
<th>( L \times 10^{-22} ) (eV)</th>
<th>( \alpha ) (A(^{-1}))</th>
<th>( r_0 ) (A)</th>
<th>D (eV)</th>
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<tbody>
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<td>1.1836</td>
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<td>12.667</td>
<td>1.4199</td>
<td>2.780</td>
<td>0.4205</td>
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<td>10.330</td>
<td>1.3588</td>
<td>2.866</td>
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<td>Al</td>
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<td>44.17</td>
<td>8.144</td>
<td>1.1646</td>
<td>3.253</td>
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<tr>
<td>Ca</td>
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<td>4.888</td>
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<td>Sr</td>
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<td>0.73776</td>
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<td>Mo</td>
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<td>13.297</td>
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<td>Fe</td>
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<td>0.4174</td>
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<tr>
<td>Ba</td>
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<td>4.266</td>
<td>0.65698</td>
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<td>K</td>
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<td>1.634</td>
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<td>Na</td>
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<td>0.58993</td>
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<td>Cs</td>
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<td>Rb</td>
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<td>1.399</td>
<td>0.42981</td>
<td>7.207</td>
<td>0.04644</td>
</tr>
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</table>


Image by MIT OpenCourseWare.
Morse potential: **application example** (nanowire)


Further Morse potential parameters:

<table>
<thead>
<tr>
<th>Material</th>
<th>Crystal structure</th>
<th>Dissociation energy, (D) (eV)</th>
<th>Equilibrium radius, (r_o) (Å)</th>
<th>(\alpha)-parameter (Å(^{-1}))</th>
<th>Lattice constant (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium</td>
<td>FCC</td>
<td>0.2703</td>
<td>3.253</td>
<td>1.1650</td>
<td>4.05</td>
</tr>
<tr>
<td>Copper</td>
<td>FCC</td>
<td>0.3429</td>
<td>2.866</td>
<td>1.3590</td>
<td>3.62</td>
</tr>
<tr>
<td>Nickel</td>
<td>FCC</td>
<td>0.4205</td>
<td>2.780</td>
<td>1.4199</td>
<td>3.52</td>
</tr>
<tr>
<td>Iron</td>
<td>BCC</td>
<td>0.4172</td>
<td>2.845</td>
<td>1.3890</td>
<td>2.87</td>
</tr>
<tr>
<td>Chromium</td>
<td>BCC</td>
<td>0.4414</td>
<td>2.754</td>
<td>1.5721</td>
<td>2.89</td>
</tr>
<tr>
<td>Tungsten</td>
<td>BCC</td>
<td>0.9906</td>
<td>3.032</td>
<td>1.4116</td>
<td>3.17</td>
</tr>
</tbody>
</table>

Cutoff-radius: saving time
Cutoff radius

\[ U_i = \sum_{j=1}^{N_{\text{neigh}}} \phi(r_{ij}) \]

Cutoff radius = considering interactions only to a certain distance
Basis: Force contribution negligible (slope)
Derivative of LJ potential ~ force

Beyond cutoff: Changes in energy (and thus forces) small
Putting it all together…
MD updating scheme: Complete

(1) Updating method (integration scheme)

\[ r_i(t_0 + \Delta t) = -r_i(t_0 - \Delta t) + 2r_i(t_0)\Delta t + a_i(t_0)(\Delta t)^2 + ... \]

Positions at \( t_0 - \Delta t \)

Positions at \( t_0 \)

Accelerations at \( t_0 \)

(2) Obtain accelerations from forces

\[ f_i = ma_i \]
\[ a_i = f_i / m \]

(3) Obtain forces from potential

\[ F = -\frac{d\phi(r)}{dr} \]
\[ f_i = F \frac{x_i}{r} \]

Potential

\[ \phi(r) = 4\varepsilon \left( \left[ \frac{\sigma}{r} \right]^{12} - \left[ \frac{\sigma}{r} \right]^{6} \right) \]
2.2 How to model metals: Multi-body potentials

**Pair potential**: Total energy sum of all pairs of bonds
Individual bond contribution does not depend on other atoms
“all bonds are the same”

\[
U_{\text{total}} = \frac{1}{2} \sum_{i=1,i\neq j}^{N} \sum_{j=1}^{N} \phi(r_{ij})
\]

Is this a good assumption?
Are all bonds the same? - valency in hydrocarbons

All bonds are not the same!

Adding another H is not favored

Ethane C₂H₆
(stable configuration)
Are all bonds the same? – metallic systems

Pair potentials: All bonds are equal!
Reality: Have environment effects; it matters that there is a free surface!

Bonds depend on the environment!
Are all bonds the same?

Bonding energy of red atom in \[ \text{graph} \] is six times bonding energy in \[ \text{graph} \]

This is in contradiction with both experiments and more accurate quantum mechanical calculations on many materials

Bonding energy of atom \( i \)

\[
U_i = \sum_{j=1}^{N} \phi(r_{ij})
\]

After: G. Ceder
Are all bonds the same?

Bonding energy of red atom in is six times bonding energy in

This is in contradiction with both experiments and more accurate quantum mechanical calculations on many materials

For pair potentials $\sim Z$

For metals $\sim \sqrt{Z}$

Bonds get “weaker” as more atoms are added to central atom

After: G. Ceder
Bond strength depends on coordination

energy per bond

Nickel

$\sim Z$ pair potential

$\sim \sqrt{Z}$

Transferability of pair potentials

- Pair potentials have limited **transferability**: Parameters determined for molecules cannot be used for crystals, parameters for specific types of crystals cannot be used to describe range of crystal structures.

- E.g. difference between FCC and BCC cannot be captured using a pair potential.
Metallic bonding: multi-body effects

- Need to consider more details of chemical bonding to understand environmental effects

Delocalized valence electrons moving between nuclei generate a binding force to hold the atoms together: **Electron gas model** *(positive ions in a sea of electrons)*

*Mostly non-directional bonding, but the bond strength indeed depends on the environment of an atom, precisely the electron density imposed by other atoms*
Concept: include electron density effects

Each atom features a particular distribution of electron density
Concept: include electron density effects

Electron density at atom $i$ $\rho_i = \sum_{j=1}^{N_{\text{neigh}}} \pi_{\rho,j}(r_{ij})$

Contribution to electron density at site $i$ due to electron density of atom $j$ evaluated at correct distance ($r_{ij}$)
Concept: include electron density effects

\[ \phi_i = \sum_{j=1..N_{\text{neigh}}} \frac{1}{2} \phi(r_{ij}) + F(\rho_i) \]

Embedding term \( F \)
(how local electron density contributes to potential energy)

Electron density at atom \( i \)
\[ \rho_i = \sum_{j=1..N_{\text{neigh}}} \pi_{\rho,j}(r_{ij}) \]

\( \pi_{\rho,j}(r_{ij}) \)

Atomic electron density of atom \( j \)
Embedded-atom method (EAM)

Atomic energy

\[ \phi_i = \sum_{j=1 \ldots N_{\text{neigh}}} \frac{1}{2} \phi(r_{ij}) + F(\rho_i) \]

Pair potential energy

Embedding energy as a function of electron density

Total energy

\[ U_{\text{total}} = \sum_{i=1}^{N} \phi_i \]

\( \rho_i \) Electron density at atom \( i \) based on a “pair potential”:

\[ \rho_i = \sum_{j=1 \ldots N_{\text{neigh}}} \pi_{\rho,j}(r_{ij}) \]

First proposed by Finnis, Sinclair, Daw, Baskes et al. (1980s)
Physical concept: EAM potential

- Describes bonding energy due to electron delocalization

  As electrons get more states to spread out over their kinetic energy decreases

- When an impurity is put into a metal its energy is lowered because the electrons from the impurity can delocalize into the solid.

- The embedding density (electron density at the embedding site) is a measure of the number of states available to delocalize onto.

- Inherently **MANY BODY** effect!
Effective pair interactions

Can describe differences between bulk and surface

See also: Daw, Foiles, Baskes, *Mat. Science Reports*, 1993
Summary: EAM method

- State of the art approach to model metals
- Very good potentials available for Ni, Cu, Al since late 1990s, 2000s
- Numerically efficient, can treat billions of particles
- Not much more expensive than pair potential (approximately three times), but describes physics much better

- Strongly recommended for use!