From Atoms to Materials: Predictive Theory and Simulations

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

Lecture 3.4: Potentials for Metals and Semiconductors

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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

End
Pair-wise potentials

Simplest, non-trivial, function

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

Lennard-Jones (6-12)

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

Lattice parameter & cohesive energy

Exponential-6

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

Morse

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

Lattice parameter, cohesive energy and bulk moduli
Two-body potentials: limitations

Pair-wise interactions: \[ E\left(\{R_i\}\right) = \sum_{i<j} \phi(R_{ij}) \]

We will calculate the vacancy formation energy

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

\[ E_{xtal}(N) = \frac{1}{2} NZE_0 \]
\[ E_{coh} = \frac{E_{xtal}(N)}{N} = \frac{1}{2} ZE_0 \]

• Now let’s create a vacancy:

\[ E_{vac}(N-1) = \frac{1}{2} NZE_0 - ZE_0 \]
Two-body potentials: limitations

\[ E_{\text{xtal}}(N) = \frac{1}{2} N Z E_0 \]

\[ E_{\text{vac}}(N-1) = \frac{1}{2} N Z E_0 - Z E_0 \]

Vacancy formation energy:

\[ \varepsilon_{\text{vac}} = E_{\text{vac}}(N-1) - \frac{N-1}{N} E_{\text{xtal}}(N) = \frac{1}{2} N Z E_0 - Z E_0 - \frac{1}{2} (N-1) Z E_0 = -\frac{1}{2} Z E_0 \]

Vacancy formation energy is equal (in magnitude) to cohesive energy
Two-body potentials: limitations

- Two-body potentials: vacancy formation \( \sim \) cohesive energy
- Metals: \( e_{\text{vac}} \sim \frac{1}{3} E_{\text{coh}} \)

<table>
<thead>
<tr>
<th></th>
<th>( E_{\text{coh}} ) (eV)</th>
<th>( E_{\text{vac}} ) (eV)</th>
<th>( \frac{E_{\text{vac}}}{E_{\text{coh}}} )</th>
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<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>
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<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 \( \{ \) van der Waals
Capturing many-body effects in metals

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

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

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

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
Directional bonding in semiconductors

Computer simulation of local order in condensed phases of silicon

Frank H. Stillinger and Thomas A. Weber
AT&T Bell Laboratories, Murray Hill, New Jersey 07974
(Received 7 November 1984)

\[ V(\{r_i\}) = \sum_{i<j} f_2(r_{ij}) + \sum_{i<j<k} f_3(r_i, r_j, r_k) \]

\[ f_2(r) = \begin{cases} A(Br^{-p} - r^{-q})\exp[(r-a)^{-1}], & r < a \\ 0, & r \geq a \end{cases} \]

\[ f_3(r_i, r_j, r_k) = h(r_{ij}, r_{ik}, \theta_{ijk}) + h(r_{ji}, r_{jk}, \theta_{ijk}) + h(r_{ki}, r_{kj}, \theta_{ijk}), \]

\[ h(r_{ij}, r_{ik}, \theta_{ijk}) = \lambda \exp[\gamma(r_{ij} - a)^{-1} + \gamma(r_{ik} - a)^{-1}] \times (\cos \theta_{ijk} + \frac{1}{2})^2; \]
Summary & additional reading

- Many-body and angular components important in the description of many materials

- When doing MD simulations always check the applicability and limitations of the interatomic potential

Embedded atom model:
- A. P. Sutton, J. Chen, Phil. Mag. Lett. 61, 139-146 (1990)

Bond-order potentials for covalent systems