Potentials, periodicity

Lecture 2
1/23/18
Survey responses

Your knowledge of Linux
Answered: 16  Skipped: 0

Familiarity with linear algebra
Answered: 16  Skipped: 0

Experience with Python
Answered: 16  Skipped: 0

Familiarity with thermodynamics and statistical mechanics
Answered: 16  Skipped: 0

Comfort level with quantum mechanics concepts
Answered: 16  Skipped: 0
Topic requests

DFT (10), Molecular dynamics (7), Monte Carlo (5)
Machine Learning (4), High-throughput, Databases (4)

NEB, phonons, Non-equilibrium MD, DFT+U, TD DFT, GW/BSE, QMC

Renewable energy, batteries, defects and surfaces, ferroelectrics, catalysis, polymers, solutions, ion transport,

Note: AP295 Introduction to Quantum Theory of Solids (Tue, Thu 10-11:30 Pierce 209)
Pair potential forms

Morse potential

\[ V(r) = D \left[ 1 - e^{-\alpha(r-r_0)} \right]^2 \]

Born-Mayer/Buckingham

\[ V(r) = A e^{-Br} - \frac{C}{r^6} - \frac{D}{r^8} \]
How far from equilibrium can you go?

Even simple harmonic models do well close to equilibrium

Vibrational frequency is determined by the curvature at equilibrium

\[
V = V_o + \sum_i \left( \frac{\partial V}{\partial x_i} \right) x_i + \frac{1}{2} \sum_{i,j} \left( \frac{\partial^2 V}{\partial x_i \partial x_j} \right) x_i x_j + ...
\]

\[
V \approx \frac{1}{2} k (x - x_o)^2
\]

Total energy

\[
E = E_0 + \frac{1}{2} \sum_{i \neq j} V(\overrightarrow{R_i} - \overrightarrow{R_j})
\]
Potential energy surface

Total energy as a function of degrees of freedom
Structure is “relaxed” when all forces (and stresses) are zero

\[ \vec{F}_i = -\frac{1}{2} \sum_{i \neq j} \nabla_i V(r_{ij}) \]
Can use a variety of optimization algorithms

**Gradient descent**
Simple but may slow down near minimum

**Conjugate gradient**
more iterations, quite robust

**Newton’s method (or BFGS)**
fewer iterations but not guaranteed to work

Can mix methods during optimization
Optimization finds only local minimum

• Can have multiple minima and saddle points
• Optimization only looks for the nearest minimum
• Complex systems (large molecules) may require explicit sampling of configurations
• Monte Carlo and genetic algorithm approaches

Periodic boundary conditions

How to represent an infinite crystal in a finite simulation
Periodic boundary conditions

Space is translationally invariant, unit cell definition is arbitrary
Defects in crystals

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Defects in crystals
Vacancy formation energy

- Energy to remove an atom from a site and putting it to the bulk
- Note: need to conserve the number \((n-1)\) of atoms

\[
E_{\text{vacancy}} = E_{n-1 \text{ atoms}}(n \text{ sites}) - \frac{n-1}{n} E_{n \text{ atoms}}(n \text{ sites})
\]

perfect crystal
Strain fields are long-range
Surface energy

• There are two surfaces in the simulation

• Convergence issues:
  • how many layers in the slab
  • how much vacuum

• Hint: no need to relax the cell parameters to approximate bulk
How large should supercell be?

• Always check size convergence!

• **Factors that affect supercell convergence**
  
  • Direct interactions: interatomic potentials
  
  • Indirect elastic interactions due to relaxations → long range.
  
  • Long-range electrostatic interactions need special corrections*

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Metals: delocalized electrons

QM: Cohesive energy is nonlinear in coordination
Bonds get weaker as more atoms are added to central atom

For pair potentials:  \( E_{coh} \propto Z \)

For metals*:  \( E_{coh} \propto \sqrt{Z} \)

Covalent systems have many-atom nature of bonding
Delocalization lowers the kinetic energy of the electrons

*Sutton and Balluffi, *Interfaces in crystalline materials*, 1995
Failure for metals

Pair potentials $E_{coh} \approx \frac{E_{bond}}{2} = \frac{cZ}{2}$

$E_{vac} \approx ZE_{bond} - E_{coh} = E_{coh}$

This is in contradiction with experiment

<table>
<thead>
<tr>
<th>Property</th>
<th>Cu</th>
<th>Ag</th>
<th>Pt</th>
<th>Au</th>
<th>LJ</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_c/k_BT_m$</td>
<td>30</td>
<td>28</td>
<td>33</td>
<td>33</td>
<td>13</td>
</tr>
<tr>
<td>$E_v/E_c$</td>
<td>0.33</td>
<td>0.36</td>
<td>0.26</td>
<td>0.25</td>
<td>~1</td>
</tr>
<tr>
<td>$C_{12}/C_{44}$</td>
<td>1.5</td>
<td>1.9</td>
<td>3.3</td>
<td>3.7</td>
<td>1</td>
</tr>
</tbody>
</table>
Bond strength depends on coordination

Quantum mechanical calculations for Al

Many-atom interactions in solids

By Volker Heine, I. J. Robertson and M. C. Payne
Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, U.K.

Table 2. Calculated formation energy $U$ of various structures spanning a range of coordinated numbers

<table>
<thead>
<tr>
<th>structure</th>
<th>coordination</th>
<th>energy (atom eV)</th>
<th>$U$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>atom</td>
<td>0</td>
<td>$-54.95$</td>
<td>$0$</td>
</tr>
<tr>
<td>line</td>
<td>2</td>
<td>$-56.28$</td>
<td>$-1.33$</td>
</tr>
<tr>
<td>graphite mesh</td>
<td>3</td>
<td>$-56.05$</td>
<td>$-2.00$</td>
</tr>
<tr>
<td>diamond</td>
<td>4</td>
<td>$-57.42$</td>
<td>$-2.47$</td>
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<tr>
<td>square mesh</td>
<td>4</td>
<td>$-57.29$</td>
<td>$-2.34$</td>
</tr>
<tr>
<td>square bilayer</td>
<td>5</td>
<td>$-57.64$</td>
<td>$-2.69$</td>
</tr>
<tr>
<td>simple cubic</td>
<td>6</td>
<td>$-57.91$</td>
<td>$-2.96$</td>
</tr>
<tr>
<td>triangular mesh</td>
<td>6</td>
<td>$-57.49$</td>
<td>$-2.54$</td>
</tr>
<tr>
<td>vacancy lattice</td>
<td>8</td>
<td>$-58.10$</td>
<td>$-3.15$</td>
</tr>
<tr>
<td>face centred cubic</td>
<td>12</td>
<td>$-58.31$</td>
<td>$-3.36$</td>
</tr>
</tbody>
</table>

Need a bond energy that is non-linear in coordination
Bonds become weaker as environment is more crowded
Embedded Atom Method

• Make bond energy nonlinear on the number and distance of surrounding atoms
• Electron density as a measure of the local environment

\[ E_{coh} = \sum_i F_i(\rho_i) + \frac{1}{2} \sum_{i\neq j} V(r_{ij}) \]

embedding energy  pair potential

electron density from neighbors

\[ \rho_i = \sum_{i\neq j} f(r_{ij}) \]
Typical EAM functions (Zr metal)

EAM interaction

Density function

Embedding function

Illustrated using the Zr EAM potential

Figures from materialsdesign.com
Surface relaxation

How will the surface outer layer relax?
Pair potentials predict: same (or outwards)
EAM correctly predicts: inwards
Bonds with lower coordination are stronger
### Typical EAM results

**Melting points**

<table>
<thead>
<tr>
<th>Element</th>
<th>EAM</th>
<th>Experiment</th>
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<tbody>
<tr>
<td>Cu</td>
<td>1340</td>
<td>1358</td>
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<tr>
<td>Ag</td>
<td>1170</td>
<td>1234</td>
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<tr>
<td>Au</td>
<td>1090</td>
<td>1338</td>
</tr>
<tr>
<td>Ni</td>
<td>1740</td>
<td>1726</td>
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<tr>
<td>Pd</td>
<td>1390</td>
<td>1825</td>
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<tr>
<td>Pt</td>
<td>1480</td>
<td>2045</td>
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</table>

**Activation Energy for Self Diffusion (in eV)**

<table>
<thead>
<tr>
<th>Element</th>
<th>EAM</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>2.02</td>
<td>2.07</td>
</tr>
<tr>
<td>Ag</td>
<td>1.74</td>
<td>1.78</td>
</tr>
<tr>
<td>Au</td>
<td>1.69</td>
<td>1.74</td>
</tr>
<tr>
<td>Ni</td>
<td>2.81</td>
<td>2.88</td>
</tr>
<tr>
<td>Pd</td>
<td>2.41</td>
<td>&lt; 2.76</td>
</tr>
<tr>
<td>Pt</td>
<td>2.63</td>
<td>2.66</td>
</tr>
</tbody>
</table>

Typical EAM results

Remarkable agreement with DFT and experiment

Figure from https://sites.google.com/site/eampotentials/Ni
EAM advantages

• EAM deals well with different coordination environments – e.g. grain boundaries, vacancies, even cracks
  • Pair potentials have no chance if coordination is not known
  • Close to equilibrium, where coordination / density stays the same, pair potentials in metals may be ok

• Low computational cost, similar to pair potentials
  • A much better approximation for metallic systems

• Variants of EAM ideas: Glue model, Finnis-Sinclair potentials
EAM limitations

- Bonding is spherical, embedding energy is independent of the angle (considered in Modified EAM)
- **Potential is not unique:** Some energy can be divided arbitrarily between pair potential and embedding function.
  - Linear part of the embedding function is equivalent to a pair potential

- For $n$-component alloy need $n(n+1)/2$ pairwise interaction functions and $n$ embedding functions.
  - Models may not be compatible

\[ E_i = F_\alpha \left( \sum_{j \neq i} \rho_\beta(r_{ij}) \right) + \frac{1}{2} \sum_{j \neq i} \phi_{\alpha\beta}(r_{ij}) \]
Directional bonding in Silicon

- 4 electrons centered on each atom
- Repulsion between sp³ orbitals leads to angular dependence
- Very hard to stabilize diamond cubic structure with pair potentials
- Need 3-body interactions
- An atom needs to know more about its neighbors’ distances and directions
3-body potentials

Add a term depending on the positions of three atoms

\[ E = E_0 + \frac{1}{2} \sum_{i \neq j} V(\vec{R}_i, \vec{R}_j) + \frac{1}{3!} \sum_{i \neq j \neq k} V(\vec{R}_i, \vec{R}_j, \vec{R}_k) \]

or two distances and an angle

\[ V(\vec{R}_i, \vec{R}_j, \vec{R}_k) \rightarrow V(\vec{R}_i - \vec{R}_j, \vec{R}_i - \vec{R}_k, \theta_{ijk}) \]

angular dependence can be included explicitly

\[ K(\theta - \theta_0)^2 \quad \text{or} \quad K(\cos \theta + 1/3)^2 \]
Stillinger-Weber potential for Si

One of many choices for Si potential

\[
E = \sum_i \sum_{j > i} \phi_2(r_{ij}) + \sum_i \sum_{j \neq i} \sum_k \phi_3(r_{ij}, r_{ik}, \theta_{ijk})
\]

2-body \[
\phi_2(r_{ij}) = A_{ij} \varepsilon_{ij} \left[ B_{ij} \left( \frac{\sigma_{ij}}{r_{ij}} \right)^p - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^q \right] \exp \left( \frac{\sigma_{ij}}{r_{ij} - a_{ij} \sigma_{ij}} \right)
\]

3-body \[
\phi_3(r_{ij}, r_{ik}, \theta_{ijk}) = \lambda_{ijk} \varepsilon_{ijk} \left[ \cos \theta_{ijk} - \cos \theta_{0ijk} \right]^2 \exp \left( \frac{\gamma_{ij} \sigma_{ij}}{r_{ij} - a_{ij} \sigma_{ij}} \right) \exp \left( \frac{\gamma_{ik} \sigma_{ik}}{r_{ik} - a_{ik} \sigma_{ik}} \right)
\]

Smoothly vanishing beyond a cutoff distance
Favors tetrahedral coordination
Describes the Si (100) surface reconstruction
But not the (111) surface
High-pressure phases not well described
Coordination in liquid is a bit too low
Tersoff potential for semiconductors

Strength of bond depends on environment
Similar to “glue model” in metals – use coordination to adjust bond energy
Bond order potential: focus on orbital charge, not atoms

\[
V = \frac{1}{2} \sum_{i \neq j} f_c(r_{ij}) \left[ \phi_R(r_{ij}) + B(g_{ij})\phi_A(r_{ij}) \right]
\]

**Idea:** Bond \( ij \) is weakened by presence of other bonds \( ik \) with atom \( i \)

\[
g_{ij} = \sum_k f_c(r_{ik}) g(\theta_{ijk}) f(r_{ij} - r_{ik})
\]

Lots of parameters to fit
Charged ion interactions

In ionic compounds long-range Coulomb interaction dominates ~1/r
examples: NaCl, MgO, Li₂S

Neutral particles with dipoles interact as ~1/r³
examples: water, HCl

Higher order multipoles decay more rapidly

\[ E_{\text{Coulomb}} = \frac{1}{2} \sum_{i,j} \frac{q_i q_j}{\varepsilon r_{ij}} \]
Computing energies

\[
E = \sum_{i,j} A e^{-B r_{ij}} - \frac{C}{r_{ij}^6} + \frac{q_i q_j}{\varepsilon r_{ij}}
\]

All particles interact with all particles, \( N^2 \) scaling

Tricky to cutoff at long distance

Dielectric screening can reduce interactions

\[
U = \frac{1}{2} \int \rho(r)V(r)d^3r
\]
Issues with point charges

Anions (e.g. O, S) have a lot of electrons, are polarizable
Electrostatic fields in crystals tends to compress anions expand cations
$O^{2-}$ is not bound in free space
  Size and shape of electron cloud depends on environment
  Partial charges also depend on local environment

Polarization depends on the environment symmetry
Need more terms for quadrupole effects
Charge transfer, oxidation state changes...
Shell models

Treat polarization as a spring-shell model
Cores and shells on different ions interact via long-range Coulomb potential
Shell-shell includes short-range LJ-interaction

\[ Q_{ion} = Q_C + Q_S \]

\[ E = E_0 + \frac{Q_C^2}{2r_C} + \frac{Q_S^2}{2r_S} + \frac{2Q_C Q_S}{r_C + r_S} + V(|2r_S|) + 2K|r_C - r_S|^2 \]

Can fit to polarizability of single atoms
Shell model in PbTiO$_3$ ferroelectric

Charge equilibration scheme (QEq)

Charges can transfer from one atom to another (e.g. NaCl)

Use electronegativity and electronic hardness of each atom

\[ \chi = \frac{\text{IP} + \text{EA}}{2} \approx \frac{\partial E}{\partial Q} \]
\[ \eta = \text{IP} - \text{EA} \approx \frac{\partial^2 E}{\partial Q^2} \]

\[ E = \sum_i \left( q_i \chi_i + \frac{q_i^2}{2} \eta_i \right) + \sum_{i \neq j} q_i q_j J_{ij} \]

Self-consistently minimize the total electrostatic energy

Charges will rearrange depending on local configurations

Can describe surfaces, defects etc.

Design potential for H$_2$O

- Single molecule close to equilibrium
- What about liquid water?

![Calculated physical properties of the water models](http://www1.lsbu.ac.uk/water/water_models.html)