Atomistic Modeling of Materials
Introduction to the Course and Pair Potentials

3.320 Lecture 2 (2/3/05)
Practical Issues

Energy

\[ E = \frac{1}{2} \sum_{i,j \neq i}^{N} V(\vec{R}_i - \vec{R}_j) \]

Double summation: Number of operations proportional to \( N^2 \)

Force

\[ F_i = -\nabla_i E = - \sum_{j \neq i}^{N} \frac{\partial V(\vec{R}_i - \vec{R}_j)}{\partial \vec{R}_i} \]

Not feasible with million atom simulations -> use neighbor lists

Minimization

Standard schemes: Conjugate Gradient, Newton-Raphson, Line Minimizations (Using Force)

Typically at least scale as \( N^2 \)
Show movie of dislocation generation
System sizes and Periodicity

Finite System (e.g. molecule or cluster)
No problem; -> simply use all the atoms

Infinite System (e.g. solids/liquids)
Do not approximate as finite -> use Periodic Boundary Conditions

BaTiO$_3$
For defect calculation unit cell becomes a supercell

Periodic Images of Defect

Defect
How Large Should the Supercell Be?

Investigate Convergence!

Direct Interactions from Energy Expression (potential)

Indirect Interactions due to relaxation (elastic) -> typically much longer range.

For charged defects electrostatic interactions are long-ranged and special methods may be necessary.
Example: Calculating the vacancy formation energy in Al

![Graph showing vacancy formation energy vs number of atoms in supercell](image)

Figure by MIT OCW.
Limitations of Pair Potentials: Application to Physical Quantities

Vacancy Formation Energy
Some data for real systems

<table>
<thead>
<tr>
<th>Solid</th>
<th>C_{12}/C_{44}</th>
<th>E_{f}/E_{coh}</th>
<th>E_{coh}/kT_{m}</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pair Potential</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LJ</td>
<td>1.0</td>
<td>1.00</td>
<td>13</td>
</tr>
<tr>
<td><strong>Rare Gases</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ar</td>
<td>1.1</td>
<td>0.95</td>
<td>11</td>
</tr>
<tr>
<td>Kr</td>
<td>1.0</td>
<td>0.66</td>
<td>12</td>
</tr>
<tr>
<td><strong>FCC Metals</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>1.2</td>
<td>0.31</td>
<td>30</td>
</tr>
<tr>
<td>Cu</td>
<td>1.6</td>
<td>0.37</td>
<td>30</td>
</tr>
<tr>
<td>Pd</td>
<td>2.5</td>
<td>0.36</td>
<td>25</td>
</tr>
<tr>
<td>Ag</td>
<td>2.0</td>
<td>0.39</td>
<td>27</td>
</tr>
<tr>
<td>Pt</td>
<td>3.3</td>
<td>0.26</td>
<td>33</td>
</tr>
<tr>
<td>Au</td>
<td>3.7</td>
<td>0.23</td>
<td>34</td>
</tr>
</tbody>
</table>

Figure by MIT OCW.

Surface Relaxation

With potentials relaxation of surface plane is usually outwards, for metals experiments find that it is inwards.
Cauchy Problem

\[
\begin{pmatrix}
\sigma_{11} \\
\sigma_{22} \\
\sigma_{33} \\
\sigma_{12} \\
\sigma_{13} \\
\sigma_{23}
\end{pmatrix} =
\begin{pmatrix}
\varepsilon_{11} \\
\varepsilon_{22} \\
\varepsilon_{33} \\
\varepsilon_{12} \\
\varepsilon_{13} \\
\varepsilon_{23}
\end{pmatrix}
\cdot
C_{ij}
\]

For Potentials \( C_{12} = C_{44} \)
Crystal Structures

Pair Potentials can fundamentally not predict crystal structures in metals or covalent solids.

e.g. fcc - bcc energy difference can be shown to be “fourth moment” effect (i.e. it needs four-body interactions)
How to Fix Pair Potential Problem?

- Pair Potentials
- Pair Functionals
- Cluster Potentials
- Cluster Functionals

Many-Body

Non-Linearity
Effective Medium Theories: The Embedded Atom Method

Problem with potentials
Cohesive energy depends on number of bonds, but non-linearly

Solution

Write energy per atom as $E = f(\text{number of bonds})$ where $f$ is non-linear function

Energy Functionals

How to measure “number of bonds”

In Embedded Atom Method (EAM) proximity of other atoms is measured by the electron density they project on the central atom.
Atomic Electron Densities

Electron Density on Site $i$  

$$\rho_i = \sum_{j\neq i} f_j^a (R_i - R_j)$$

Atomic electron density of atom $j$

Clementi and Roetti Tables

Image removed for copyright reasons.

Clementi and Roetti [At. Data Nucl. Data Tables 14, 177 (1974).]
Clementi and Roetti Tables

Image removed for copyright reasons.

Clementi and Roetti [At. Data Nucl. Data Tables 14, 177 (1974).]
The Embedding Function

Can be represented either analytically or in Table form

\[
F(\rho) = F_0 \left[ \frac{n}{n-m} \left( \frac{\rho}{\rho_e} \right)^m - \frac{m}{n-m} \left( \frac{\rho}{\rho_e} \right)^n \right] + F_1 \left( \frac{\rho}{\rho_e} \right)
\]

\[
F(\rho) = \left[ 1 - \ln \left( \frac{\rho}{\rho_e} \right)^n \right] \left( \frac{\rho}{\rho_e} \right)^n
\]

More typically, embedding function is tabulated so as to give an exact fit to the equation of state (Energy versus volume)
Convexity of the Embedding Function


Figure by MIT OCW.
The complete energy expression: Embedding energy + pair potential

\[ E_{coh} = \sum_{\text{atoms } i} F_i \left( \sum_{j \neq i} f(r_{ij}) \right) + \frac{1}{2} \sum_i \sum_{j \neq i} V(r_{ij}) \]

**Embedding energy**

Pair potential can have any form, often screened electrostatic used

\[ \phi_{AB}(r) = \frac{q_A(r)q_B(r)}{r} \]

with \( q(r) = q_0 (1 + \beta r^\nu) e^{-\alpha r} \)
EAM: The Physical Concept

Bonding energy (embedding 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
EAM is similar to many other effective medium theories. Other theories differ in the “non-linearity” used or the measure of “embedding density”

- Glue model (Ercollesi, Tosatti and Parrinello)
- Finnis Sinclair Potentials
- Equivalent Crystal Models (Smith and Banerjee)

EAM is similar to Pair Potentials in computational intensity

\[
E_{coh} = \sum_{\text{atoms } i} F_i \left( \sum_{j \neq i} f(r_{ij}) \right) + \frac{1}{2} \sum_{i} \sum_{j \neq i} V(r_{ij})
\]
Typical Data to fit EAM parameters to

Pure metal properties used to determine the functions: equilibrium lattice constants, sublimation energy, bulk modulus, elastic constants, and vacancy-formation energy. Where two numbers are given, the top number is the value calculated with these functions and the lower number is the experimental value.

<table>
<thead>
<tr>
<th></th>
<th>Cu</th>
<th>Ag</th>
<th>Au</th>
<th>Ni</th>
<th>Pd</th>
<th>Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a_0(\text{Å}))</td>
<td>3.615</td>
<td>4.09</td>
<td>4.08</td>
<td>3.52</td>
<td>3.89</td>
<td>3.92</td>
</tr>
<tr>
<td>(E_{\text{sub}}(\text{eV}))</td>
<td>3.54</td>
<td>2.85</td>
<td>3.93</td>
<td>4.45</td>
<td>3.91</td>
<td>5.77</td>
</tr>
<tr>
<td>(B(\text{ergs/cm}^3))</td>
<td>1.38</td>
<td>1.04</td>
<td>1.67</td>
<td>1.804</td>
<td>1.95</td>
<td>2.83</td>
</tr>
<tr>
<td>(C_{11}(\text{ergs/cm}^3))</td>
<td>1.67</td>
<td>1.29</td>
<td>1.83</td>
<td>2.33</td>
<td>2.18</td>
<td>3.03</td>
</tr>
<tr>
<td></td>
<td>1.70</td>
<td>1.24</td>
<td>1.86</td>
<td>2.465</td>
<td>2.341</td>
<td>3.47</td>
</tr>
<tr>
<td>(C_{12}(\text{ergs/cm}^3))</td>
<td>1.24</td>
<td>0.91</td>
<td>1.59</td>
<td>1.54</td>
<td>1.84</td>
<td>2.73</td>
</tr>
<tr>
<td></td>
<td>1.225</td>
<td>0.934</td>
<td>1.57</td>
<td>1.473</td>
<td>1.76</td>
<td>2.51</td>
</tr>
<tr>
<td>(C_{44}(\text{ergs/cm}^3))</td>
<td>0.76</td>
<td>0.57</td>
<td>0.45</td>
<td>1.28</td>
<td>0.65</td>
<td>0.68</td>
</tr>
<tr>
<td></td>
<td>0.758</td>
<td>0.461</td>
<td>0.42</td>
<td>1.247</td>
<td>0.712</td>
<td>0.765</td>
</tr>
<tr>
<td>(E_{u}^{f}(\text{eV}))</td>
<td>1.28</td>
<td>0.97</td>
<td>1.03</td>
<td>1.63</td>
<td>1.44</td>
<td>1.68</td>
</tr>
<tr>
<td></td>
<td>1.3</td>
<td>1.1</td>
<td>0.9</td>
<td>1.6</td>
<td>1.4</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Figure by MIT OCW.
Some results: Linear Thermal Expansion (10^{-6}/K)

<table>
<thead>
<tr>
<th>Element</th>
<th>EAM</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>16.4</td>
<td>16.7</td>
</tr>
<tr>
<td>Ag</td>
<td>21.1</td>
<td>19.2</td>
</tr>
<tr>
<td>Au</td>
<td>12.9</td>
<td>14.1</td>
</tr>
<tr>
<td>Ni</td>
<td>14.1</td>
<td>12.7</td>
</tr>
<tr>
<td>Pd</td>
<td>10.9</td>
<td>11.5</td>
</tr>
<tr>
<td>Pt</td>
<td>7.8</td>
<td>8.95</td>
</tr>
</tbody>
</table>

Some results: 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>

Some results: Surface Energy and Relaxation

Calculated surface energies of the low-index faces and the experimental average surface energy in units of erg/cm². The theoretical results are from Foiles et al.

<table>
<thead>
<tr>
<th>Face</th>
<th>Cu</th>
<th>Ag</th>
<th>Au</th>
<th>Ni</th>
<th>Pd</th>
<th>Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>(100)</td>
<td>1280</td>
<td>705</td>
<td>918</td>
<td>1580</td>
<td>1370</td>
<td>1650</td>
</tr>
<tr>
<td>(110)</td>
<td>1400</td>
<td>770</td>
<td>980</td>
<td>1730</td>
<td>1490</td>
<td>1750</td>
</tr>
<tr>
<td>(111)</td>
<td>1170</td>
<td>620</td>
<td>790</td>
<td>1450</td>
<td>1220</td>
<td>1440</td>
</tr>
<tr>
<td>Experimental (average face)</td>
<td>1790</td>
<td>1240</td>
<td>1500</td>
<td>2380</td>
<td>2000</td>
<td>2490</td>
</tr>
</tbody>
</table>

Relaxation of the top-layer spacing $\Delta z_{12}$, and of the second-layer spacing $\Delta z_{23}$, for the low-index faces. For the sake of comparison, these values are calculated for unreconstructed geometries. Distances are expressed in Å. From Foiles et al.

<table>
<thead>
<tr>
<th>Face</th>
<th>$\Delta z_{12}$</th>
<th>$\Delta z_{23}$</th>
<th>Cu</th>
<th>Ag</th>
<th>Au</th>
<th>Ni</th>
<th>Pd</th>
<th>Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>(100)</td>
<td>$\Delta z_{12}$</td>
<td>$\Delta z_{23}$</td>
<td>-0.03</td>
<td>-0.04</td>
<td>-0.13</td>
<td>-0.00</td>
<td>-0.09</td>
<td>-0.14</td>
</tr>
<tr>
<td></td>
<td>$\Delta z_{12}$</td>
<td>$\Delta z_{23}$</td>
<td>-0.01</td>
<td>-0.00</td>
<td>0.01</td>
<td>-0.00</td>
<td>-0.00</td>
<td>0.01</td>
</tr>
<tr>
<td>(110)</td>
<td>$\Delta z_{12}$</td>
<td>$\Delta z_{23}$</td>
<td>-0.06</td>
<td>-0.07</td>
<td>-0.22</td>
<td>-0.03</td>
<td>-0.16</td>
<td>-0.24</td>
</tr>
<tr>
<td></td>
<td>$\Delta z_{12}$</td>
<td>$\Delta z_{23}$</td>
<td>0.00</td>
<td>0.01</td>
<td>0.03</td>
<td>0.00</td>
<td>-0.02</td>
<td>0.04</td>
</tr>
<tr>
<td>(111)</td>
<td>$\Delta z_{12}$</td>
<td>$\Delta z_{23}$</td>
<td>-0.03</td>
<td>-0.03</td>
<td>-0.10</td>
<td>-0.01</td>
<td>-0.07</td>
<td>-0.11</td>
</tr>
<tr>
<td></td>
<td>$\Delta z_{12}$</td>
<td>$\Delta z_{23}$</td>
<td>-0.00</td>
<td>0.00</td>
<td>0.02</td>
<td>0.00</td>
<td>0.01</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Tables by MIT OCW.

Some results: Phonon Dispersion for fcc Cu

Some results: Melting Points

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

Some results: Structure of Liquid Ag at 1270 K


Figure by MIT OCW.
Some results: Grain Boundary in Al


Image removed for copyright reasons.
Issues and Problems with EAM

**Bonding is Spherical:** Limitation in early transition metals and covalent systems $\rightarrow$ MEAM

**Potential is not unique:** Some part of the energy can be divided arbitrarily between pair potential and embedding function. *Note that the linear part of the embedding function is equivalent to a pair potential*

**Limitations in Alloys:** In elements, any error arising from using the atomic electron density is absorbed when the Embedding function $F$ is fitted. In A-B alloys $F$ has to work for electron density from both A and B
Modified Embedded Atom Method (MEAM) to address problem of spherical charge density

\[ s \ (l=0) \quad \rho_i^{(0)} = \sum_{j\neq i} \rho_j^{(0)}(R_{ij}) \]

\[ p \ (l=1) \quad \left( \rho_i^{(1)} \right)^2 = \sum_{\alpha} \left( \sum_{j\neq i} x_{ij}^{\alpha} \rho_j^{(1)}(R_{ij}) \right)^2 \quad x_{ij}^{\alpha} = R_{ij}^{\alpha} / R_{ij} \]

\[ d \ (l=2) \quad \left( \rho_i^{(2)} \right)^2 = \sum_{\alpha,\beta} \left( \sum_{j\neq i} x_{ij}^{\alpha} x_{ij}^{\beta} \rho_j^{(2)}(R_{ij}) \right)^2 \quad - \frac{1}{3} \left( \sum_{j\neq i} \rho_j^{(2)}(R_{ij}) \right)^2 \]

\[ f \ (l=3) \quad \left( \rho_i^{(3)} \right)^2 = \sum_{\alpha,\beta,\gamma} \left( \sum_{j\neq i} x_{ij}^{\alpha} x_{ij}^{\beta} x_{ij}^{\gamma} \rho_j^{(3)}(R_{ij}) \right)^2 \]

Take densities with various angular momenta
**Summary**: Effective Medium Theories are a significant improvement over pair potentials for metals, at almost no computational cost. Hence there is no reason NOT to use them. Be aware of problems in trying to do too much subtle chemistry with them.
Resources for Embedded Atom Method

Some useful lecture notes and examples

http://www.ide.titech.ac.jp/~takahak/EAMers/
The other option: Many Body Potentials

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

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

Triplet coordinate \( R_i, R_j, R_k \) can be replaced with \( (R_k-R_i), (R_j-R_i), \theta_{ijk} \)

Possible Choices

\[ K(\theta - \theta_o)^2 \]
\[ K \left( \cos \theta + \frac{1}{3} \right)^2 \]

Note: Now need \( N^3 \) operations for evaluating potential
Stillinger Webber Potential for Si

\[ V_3 = \lambda \exp \left[ \gamma (r_{ij} - a)^{-1} + \gamma (r_{ik} - a)^{-1} \right] \cos \theta_{ijk} + \frac{1}{3} \right]^2 \]

\[ V_2 = A \left[ Br^{-p} - r^{-q} \right] \exp \left[ (r - a)^{-1} \right] \]
Surface Reconstruction for Si

unreconstructed Si(100)

Diagram removed for copyright reasons.

Si surface atoms are bonded to 2 atoms below

2x1 reconstruction
for Si(100)

Diagram removed for copyright reasons.

Si surface atoms are bonded to 2 atoms below and one on surface → dimer formation on surface
Surface Reconstruction for Si

Diagram removed for copyright reasons.

7x7 reconstruction for Si(100) is not reproduced
A multitude of potentials for Si

Graph removed for copyright reasons.
Comparison between potentials

While most potentials give similar static properties (since they are usually fitted to static properties) they often result in different dynamics.

References for Si Potentials

1) Keating:
Valid only for small deviations from the ideal diamond lattice sites.
Used for elastic constants and phonon properties.

2) Stillinger-Weber:

3) Tersoff:

4) Biswas-Hamann
Rather complicated to evaluate. Two versions. The first is longer ranged than the second. The old one is better at bulk metallic Si phases and high pressure transitions of Si. The new one does better for layered and interstitial structures.

5) Embedded Atom
Modification of the EAM of metals to deal with covalent bonding, including
and angle-dependent electron density to model the effects of bond bending.
Fitted to Si lattice constant, sublimation energy and elastic constants.
Reproduces well the LDA structural geometries and energies.

6) Kaxiras-Pandey Kaxiras, E.; Pandey, K.C., Physical Review B vol. 38,
12736 (1988)
2 and 3 body fitted to self diffusion paths in pure silicon. Suited for molecular dynamics simulations of atomic processes in Si.

Others:
o Khor and Das Sarma, Several articles in PRB 1988-89.
o Chelikowsky, J.R.; Phillips, J.C.; Kamal, M.; Stauss, M.,
A comparison between 6 of these potentials can be found in
For a review and comparison of valence force field potentials (i.e., potentials that only describe small displacements from the ideal sites, like the Keating potential), see Stoneham, A.M.; Torres, V.T.B.; Masri, P.M.; Schober, H.R.
Philosophical Magazine A 58, 93 (1988)
**************************************************************************

2/3/05 Massachusetts Institute of Technology 3.320: Atomistic Modeling of Materials G. Ceder and N Marzari