

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

N^2

← | | | | | | |

Force

$$\vec{F}_i = -\vec{\nabla}_i E = - \sum_{j \neq i}^N \frac{\partial V(\vec{R}_i - \vec{R}_j)}{\partial \vec{R}_i}$$

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

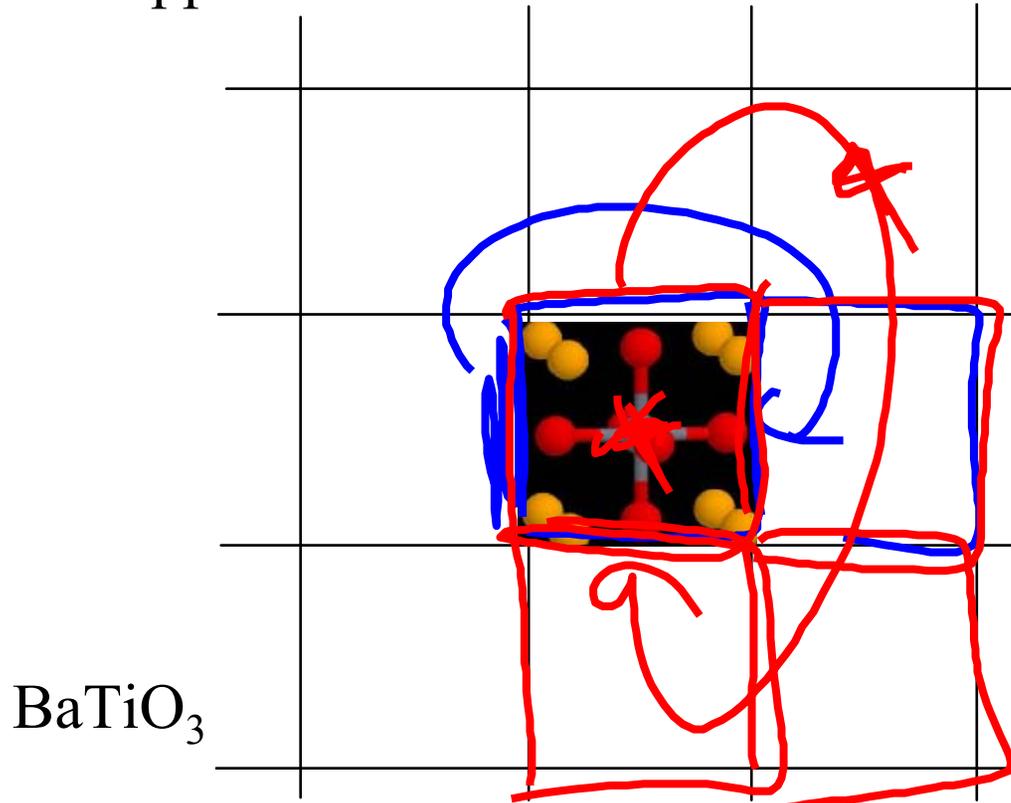
System sizes and Periodicity

Finite System (e.g. molecule or cluster)

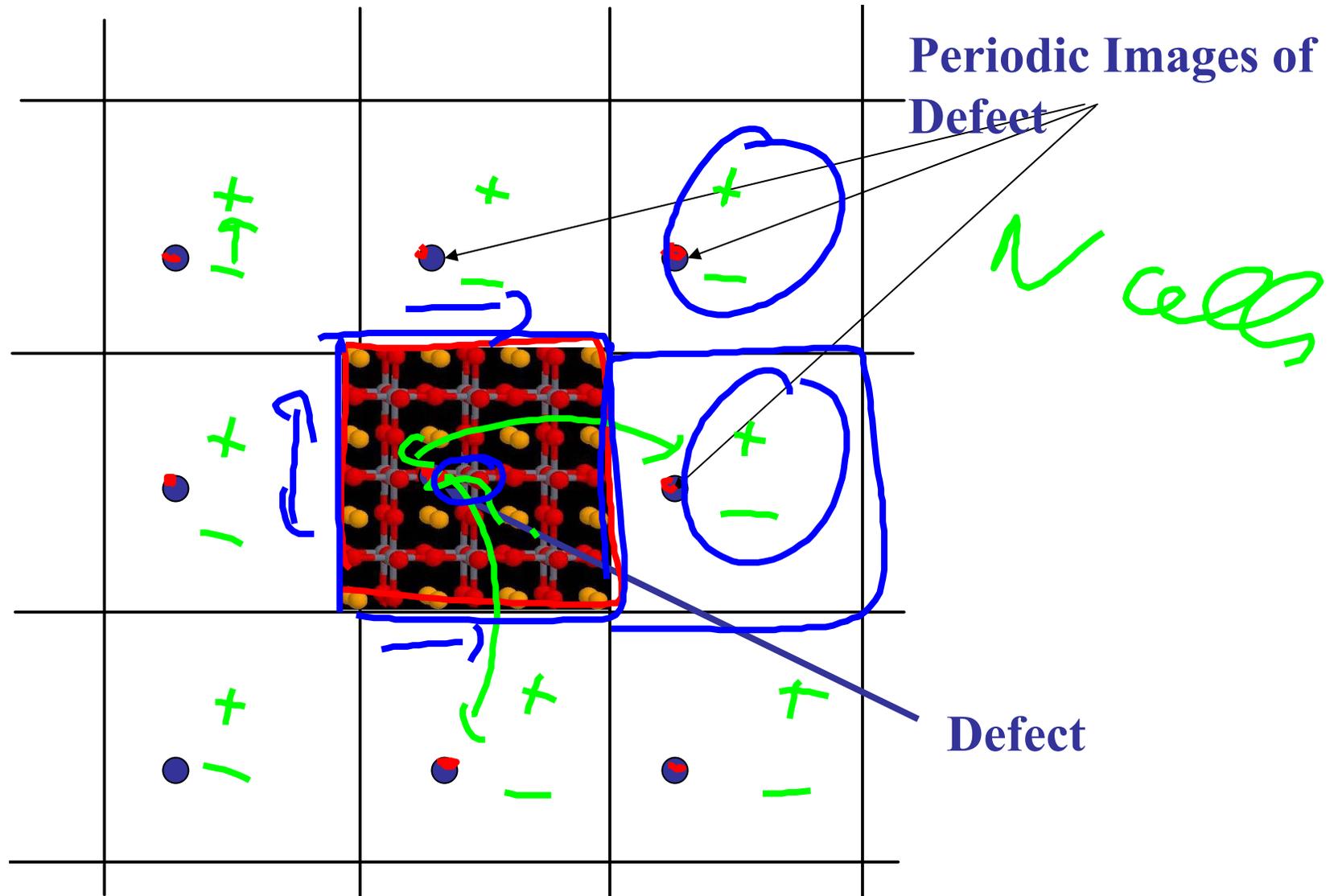
No problem; -> simply use all the atoms

Infinite System (e.g. solids/liquids)

Do not approximate as finite -> use Periodic Boundary Conditions



For defect calculation unit cell becomes a supercell



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

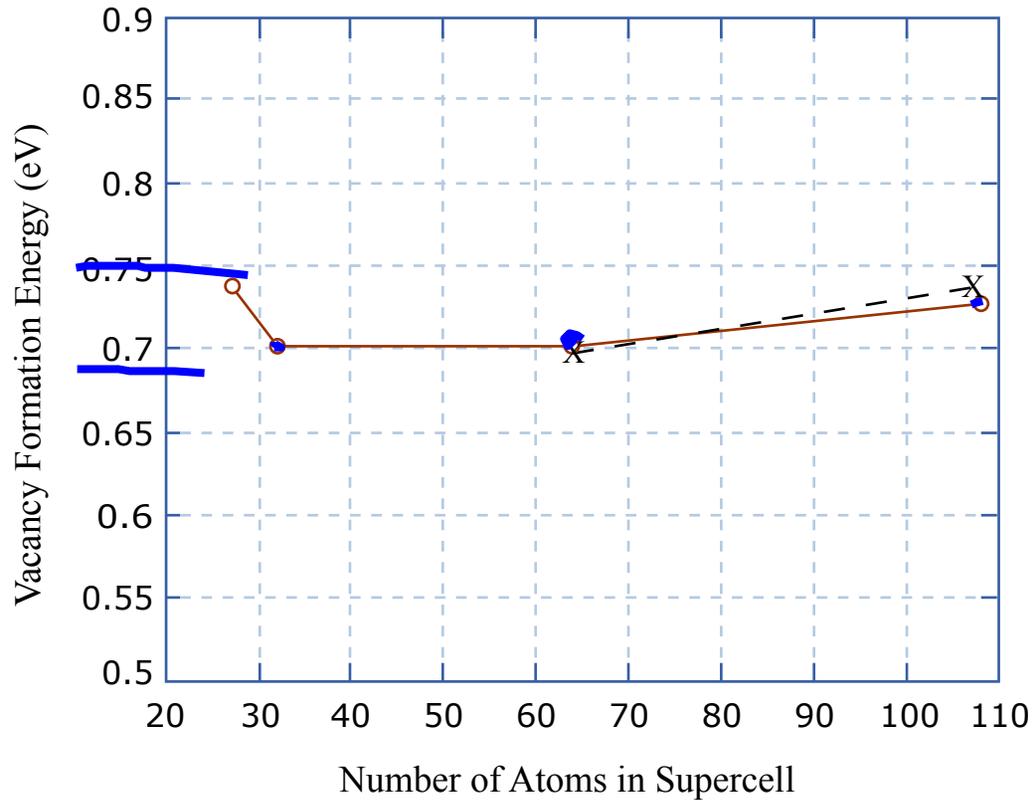


Figure by MIT OCW.

Limitations of Pair Potentials: Application to Physical Quantities

$$E_{coh} = C \sqrt{Z}$$

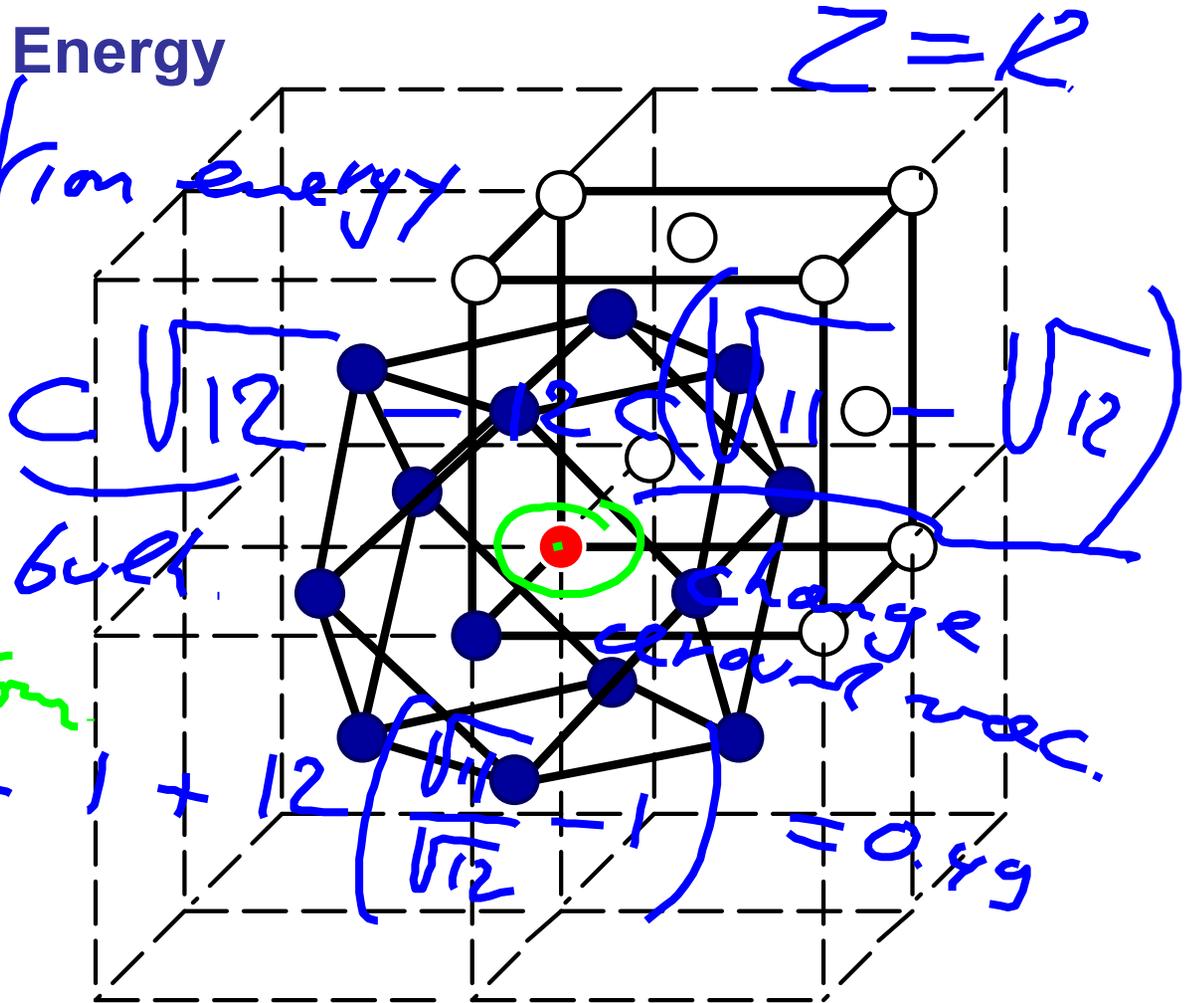
Vacancy Formation Energy

Vac. formation energy

$$\Delta E_{vac} = -12 E_{bond}$$

$$\Delta E_{vac} = -6 E_{bond}$$

$$\frac{\Delta E_{vac}}{\Delta E_{coh}} = 1 + 12 \left(\frac{V_{11}}{\sqrt{12}} - 1 \right) = 0.49$$



Some data for real systems

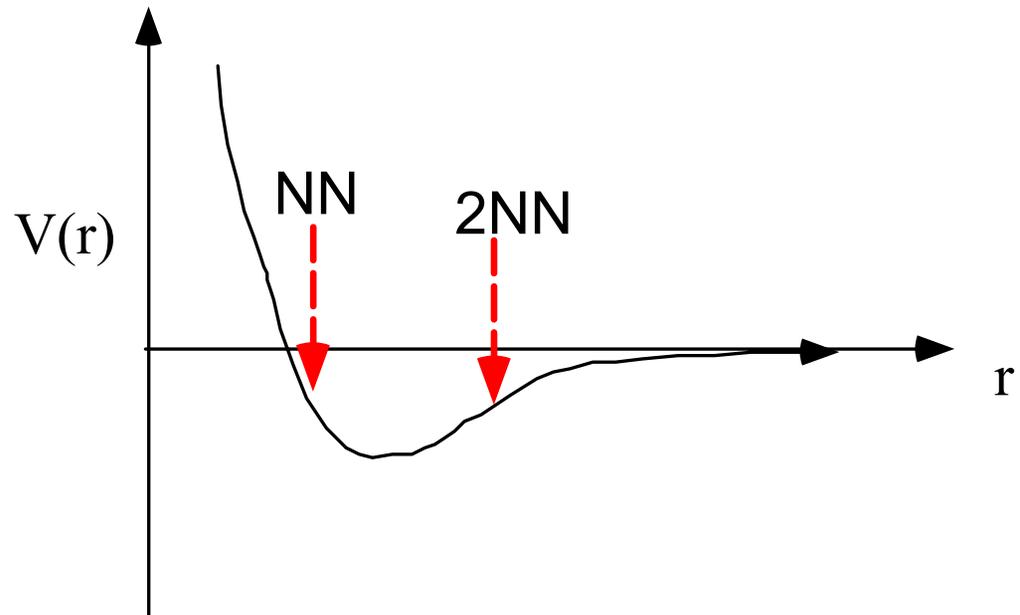
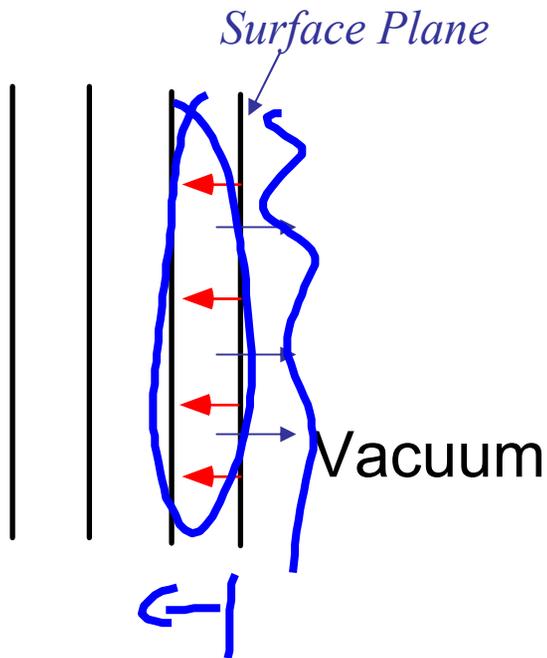
Solid	C_{12}/C_{44}	E_v^f/E_{coh}	E_{coh}/kT_m
Pair Potential LJ	1.0	1.00	13
Rare Gases Ar Kr	1.1 1.0	0.95 0.66	11 12
FCC Metals Ni Cu Pd Ag Pt Au	1.2 1.6 2.5 2.0 3.3 3.7	0.31 0.37 0.36 0.39 0.26 0.23	30 30 25 27 33 34

Figure by MIT OCW.

After Daw, M. S., S. M. Foiles, and M. I. Baskes. "The embedded-atom method: a review of theory and applications." *Materials Science Reports* **9**, 251 (1993).

Surface Relaxation

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



Cauchy Problem

$$\begin{pmatrix} \sigma_{11} \\ \sigma_{22} \\ \sigma_{33} \\ \sigma_{12} \\ \sigma_{13} \\ \sigma_{23} \end{pmatrix} = \mathbf{C}_{ij} \cdot \begin{pmatrix} \varepsilon_{11} \\ \varepsilon_{22} \\ \varepsilon_{33} \\ \varepsilon_{12} \\ \varepsilon_{13} \\ \varepsilon_{23} \end{pmatrix}$$

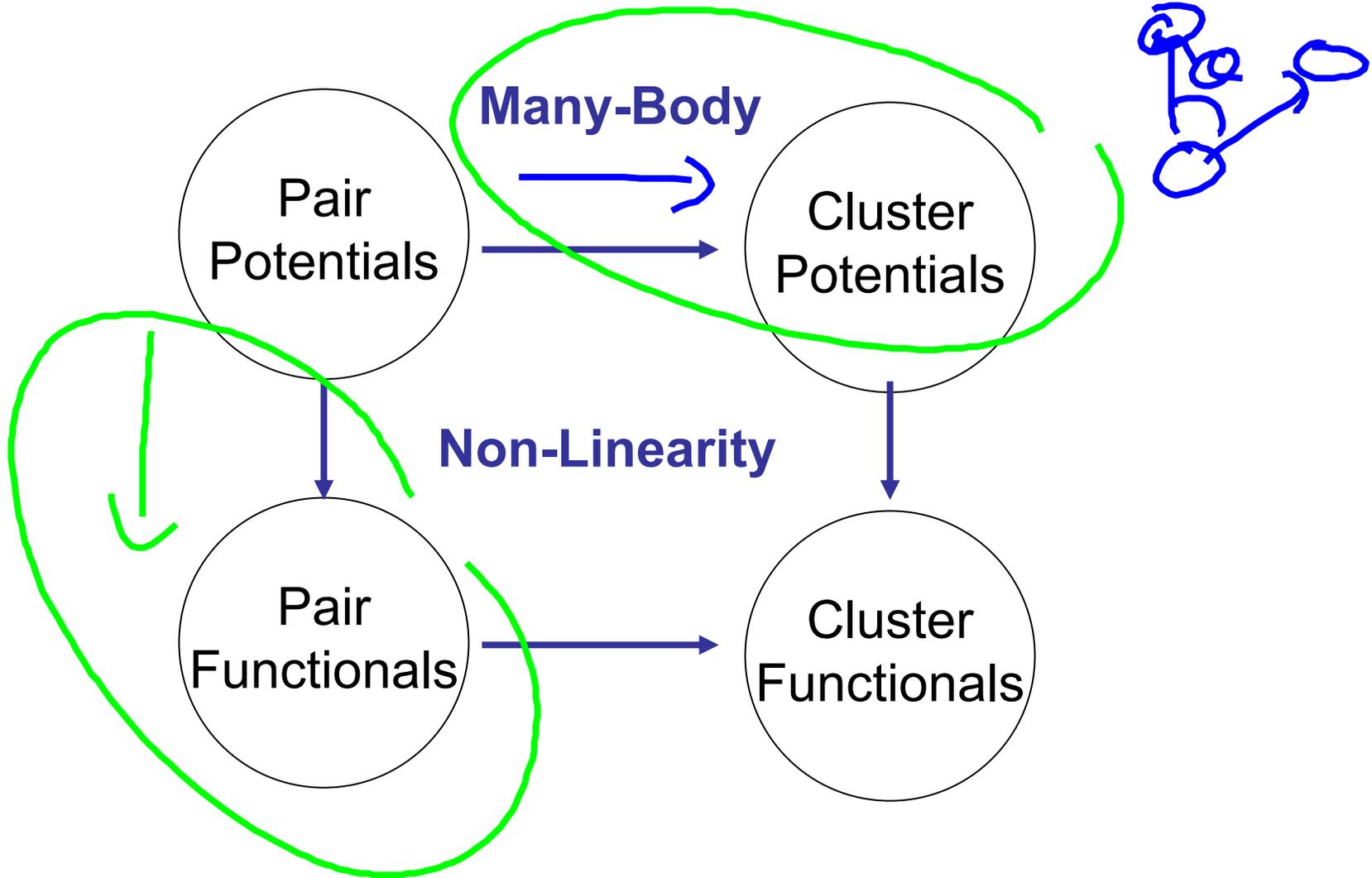
For Potentials $C_{12} = C_{44}$

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 ?



Effective Medium Theories: The Embedded Atom Method

Problem with potentials

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

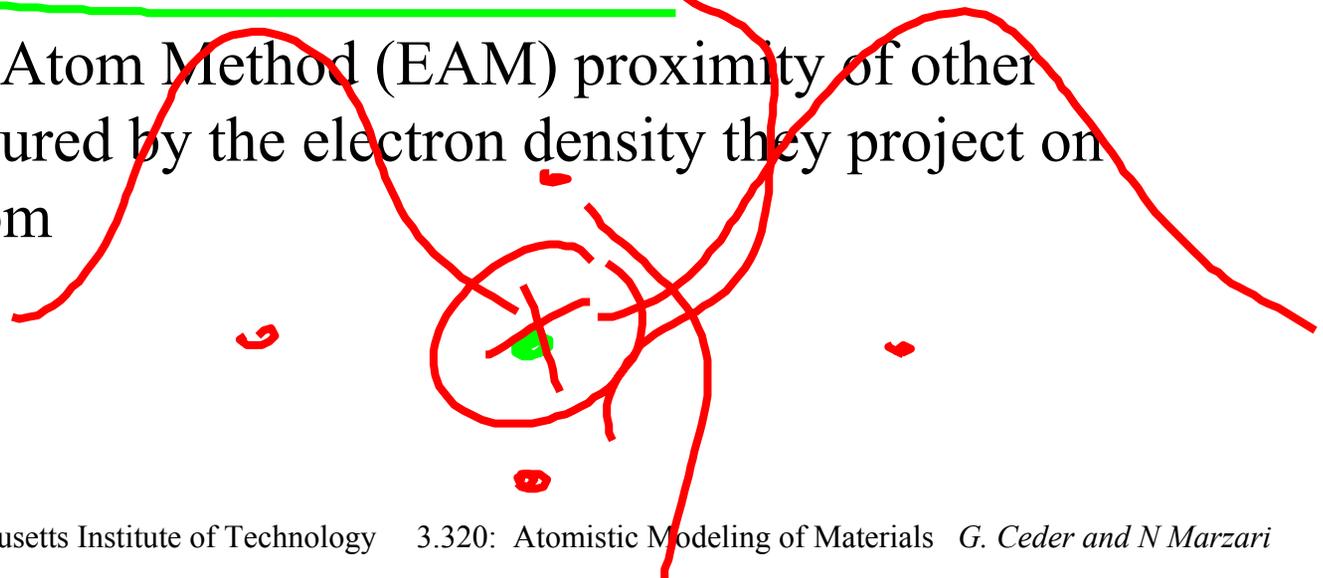
Solution

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”

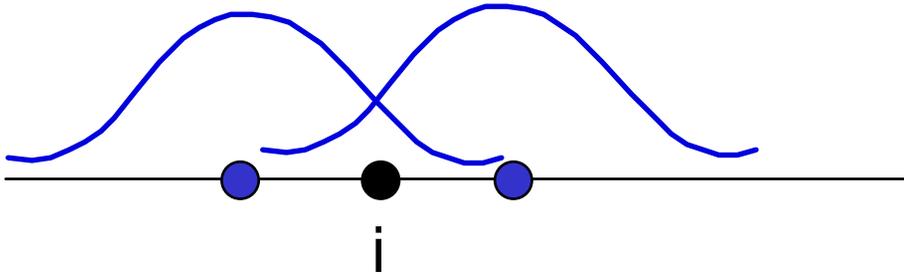
In Embedded Atom Method (EAM) proximity of other atoms is measured by the electron density they project on the central atom



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



Atomic densities are tabulated in E. Clementi and C. Roetti, *Atomic Data and Nuclear Data Tables*, Vol 14, p177 (1974).

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

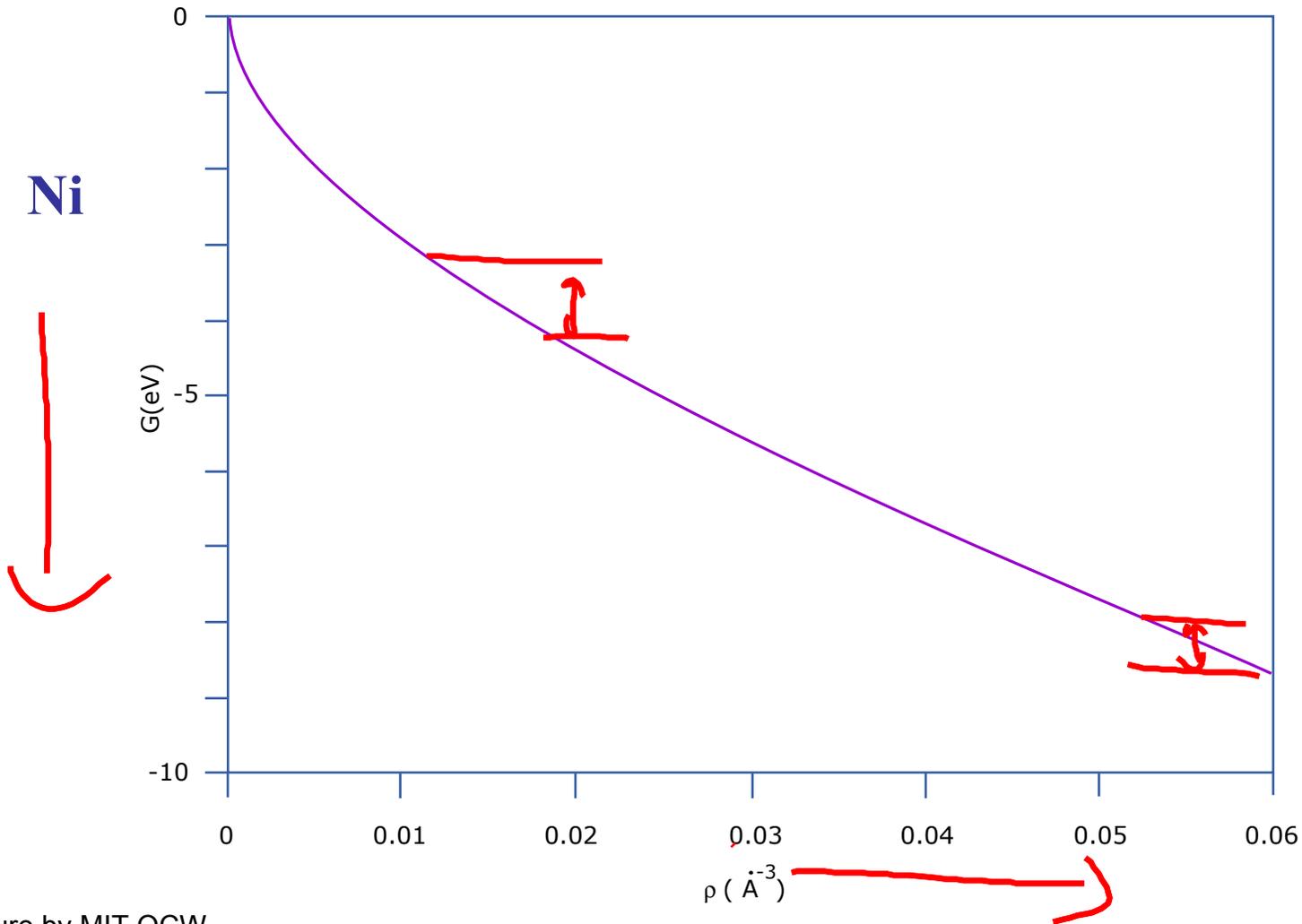


Figure by MIT OCW.

Source: Daw, M. S., Foiles, S. M. & Baskes, M. I. The embedded-atom method: a review of theory and applications. *Materials Science Reports* **9**, 251 (1993).

The complete energy expression: Embedding energy + pair potential

$$\rightarrow E_{coh} = \underbrace{\sum_{\text{atoms } i} F_i \left(\sum_{j \neq i} f(r_{ij}) \right)}_{\text{Embedding energy}} + \underbrace{\frac{1}{2} \sum_i \sum_{j \neq i} V(r_{ij})}_{\text{Pair Potential}}$$

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

$$\frac{\partial^2 \psi}{\partial x^2}$$

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

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

Typical Data to fit EAM parameters to

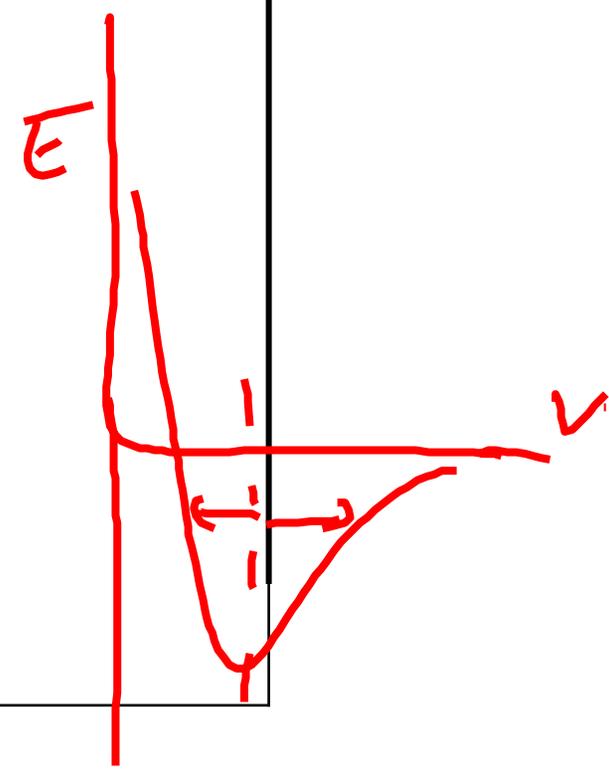
Pure metal properties used to determine the functions: equilibrium lattice constants, sublimation energy, bulk modulus, elastic constants, and vacancy-formation energy. Where two numbers are given, the top number is the value calculated with these functions and the lower number is the experimental value.

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

Figure by MIT OCW.

Some results: Linear Thermal Expansion ($10^{-6}/\text{K}$)

Element	EAM	Experiment
Cu	16.4	16.7
Ag	21.1	19.2
Au	12.9	14.1
Ni	14.1	12.7
Pd	10.9	11.5
Pt	7.8	8.95



data from Daw, M. S., Foiles, S. M. & Baskes, M. I. The embedded-atom method: a review of theory and applications. *Materials Science Reports* **9**, 251 (1993).

Some results: Activation Energy for Self Diffusion (in eV)

Element	EAM	Experiment
Cu	2.02	2.07
Ag	1.74	1.78
Au	1.69	1.74
Ni	2.81	2.88
Pd	2.41	< 2.76
Pt	2.63	2.66

data from Elsevier from Daw, M. S., Foiles, S. M. & Baskes, M. I. The embedded-atom method: a review of theory and applications. *Materials Science Reports* **9**, 251 (1993).

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.

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

Relaxation of the top-layer spacing Δz_{12} , and of the second-layer spacing Δz_{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.

Face	Cu	Ag	Au	Ni	Pd	Pt
(100) Δz_{12}	-0.03	-0.04	-0.13	-0.00	-0.09	-0.14
Δz_{23}	-0.01	-0.00	0.01	-0.00	-0.00	0.01
(110) Δz_{12}	-0.06	-0.07	-0.22	-0.03	-0.16	-0.24
Δz_{23}	0.00	0.01	0.03	0.00	-0.02	0.04
(111) Δz_{12}	-0.03	-0.03	-0.10	-0.01	-0.07	-0.11
Δz_{23}	-0.00	0.00	0.02	0.00	0.01	0.02

Tables by MIT OCW.

After Daw, M. S., S. M. Foiles, and M. I., Baskes. "The embedded-atom method: a review of theory and applications." *Materials Science Reports* **9**, 251 (1993).

Some results: Phonon Dispersion for fcc Cu

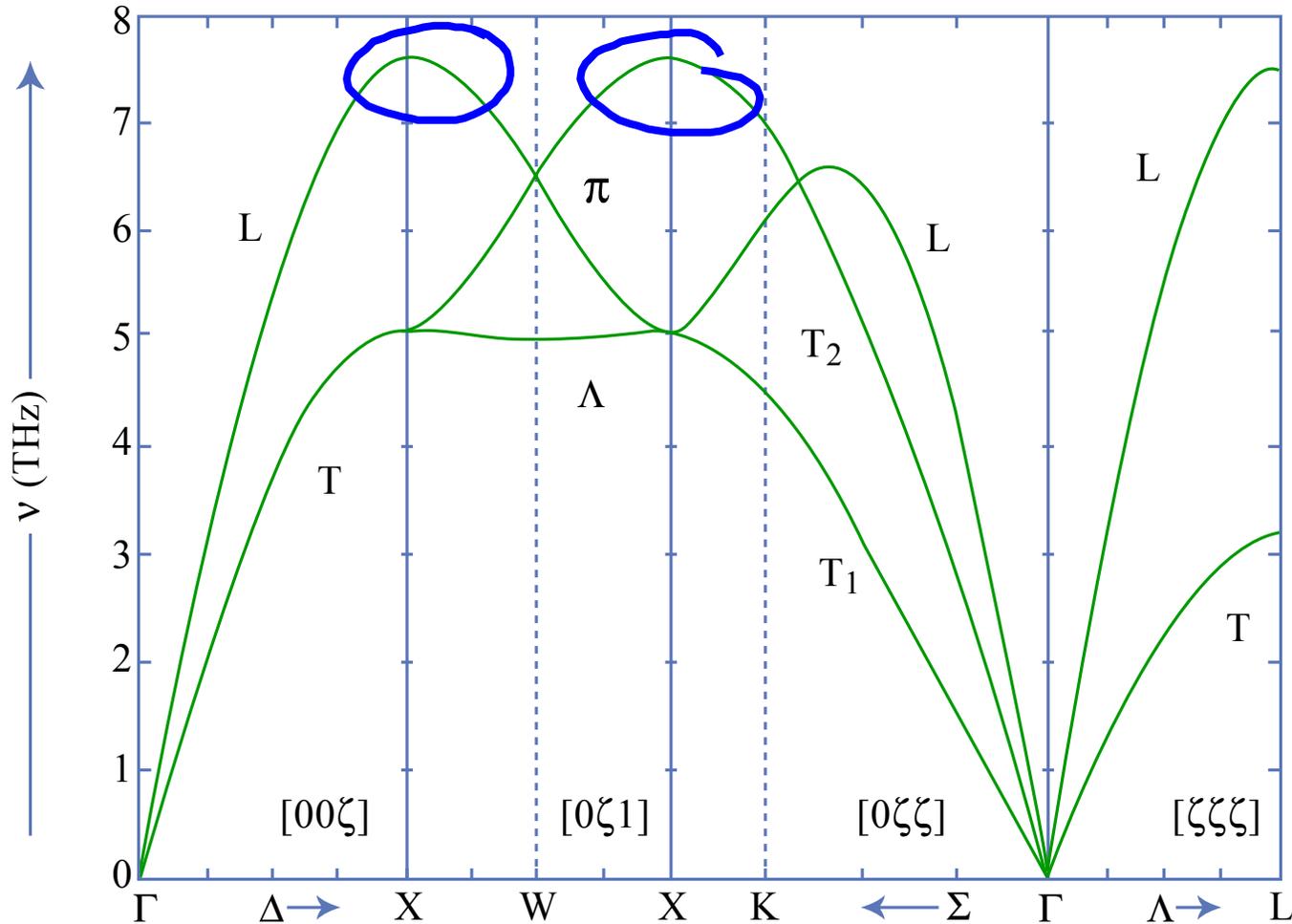


Figure by MIT OCW.

After Daw, M. S., S. M. Foiles, and M. I. Baskes. "The embedded-atom method: a review of theory and applications." *Materials Science Reports* **9**, 251 (1993).

Some results: Melting Points

Element	EAM		Experiment
Cu	1340	↔	1358
Ag	1170	↔	1234
Au	1090		1338
Ni	1740		1726
Pd	1390		1825
Pt	1480		2045

data from Elsevier from Daw, M. S., Foiles, S. M. & Baskes, M. I. The embedded-atom method: a review of theory and applications. *Materials Science Reports* **9**, 251 (1993).

Some results: Structure of Liquid Ag at 1270 K

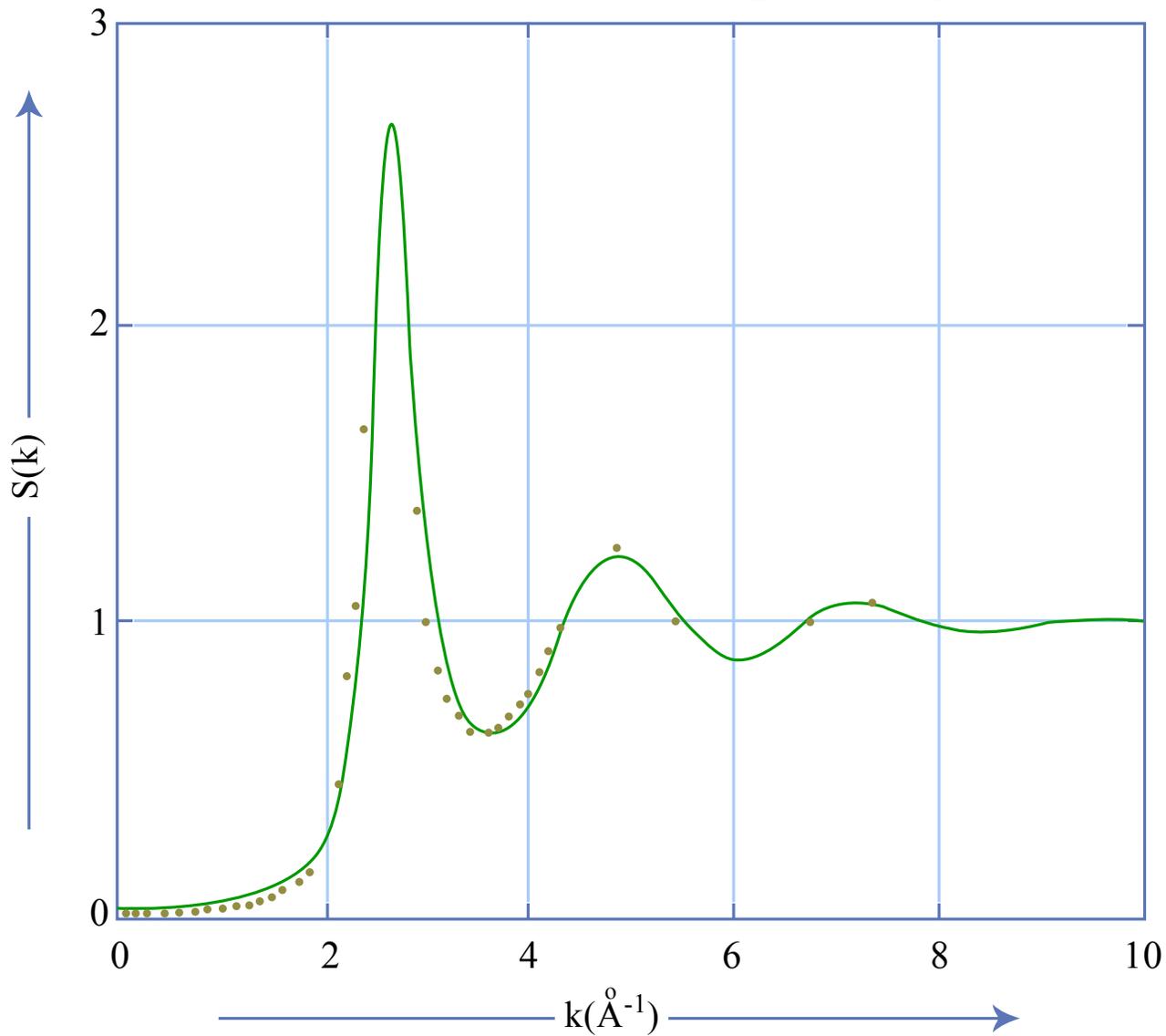


Figure by MIT OCW.

After Daw, M. S., S. M. Foiles, and M. I., Baskes. "The embedded-atom method: a review of theory and applications." *Materials Science Reports* **9**, 251 (1993).

Some results: Grain Boundary in Al

Image removed for copyright reasons.

Source: Daw, M. S., Foiles, S. M. and M. I. Baskes. "The embedded-atom method: a review of theory and applications." *Materials Science Reports* 9, 251 (1993).

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

$$\frac{\partial E}{\partial R_{ij}}$$

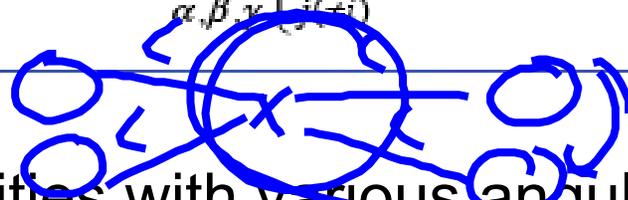
$$s \ (l=0) \quad \rho_i^{(0)} = \sum_{j(\neq i)} \rho_j^{a(0)}(R_{ij})$$

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

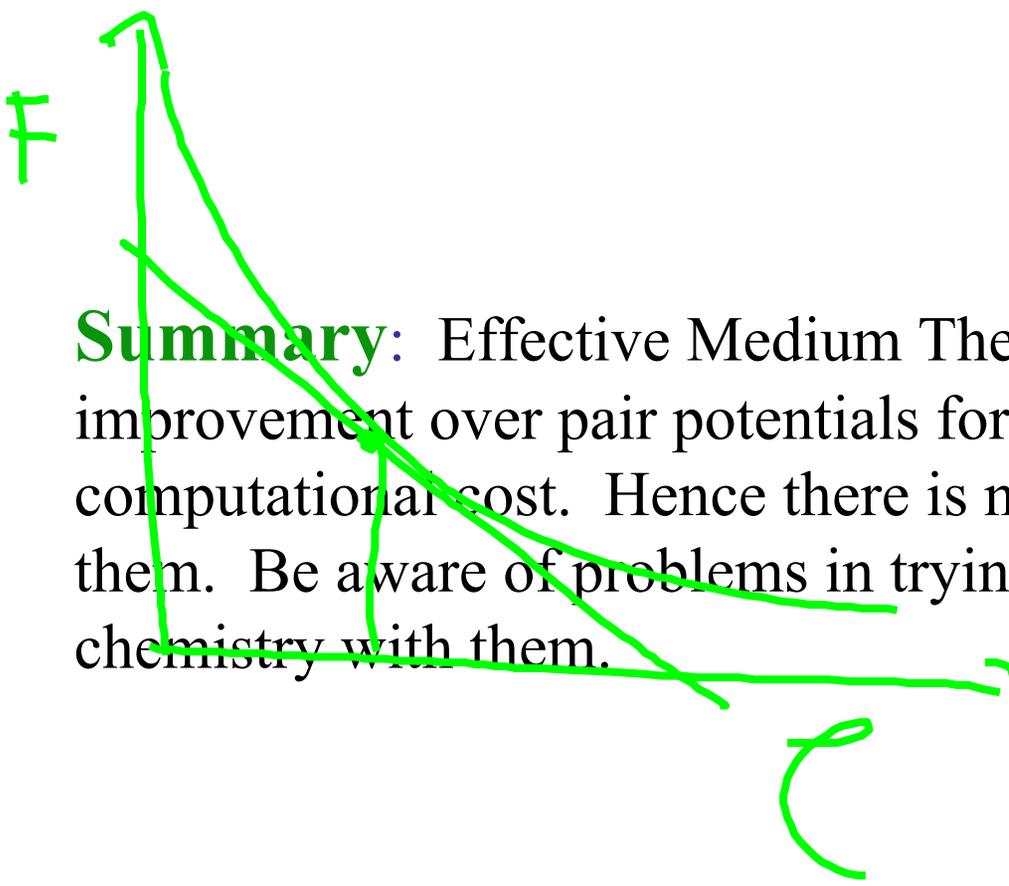
$x_{ij}^{\alpha} = R_{ij}^{\alpha} / R_{ij}$

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

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



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.

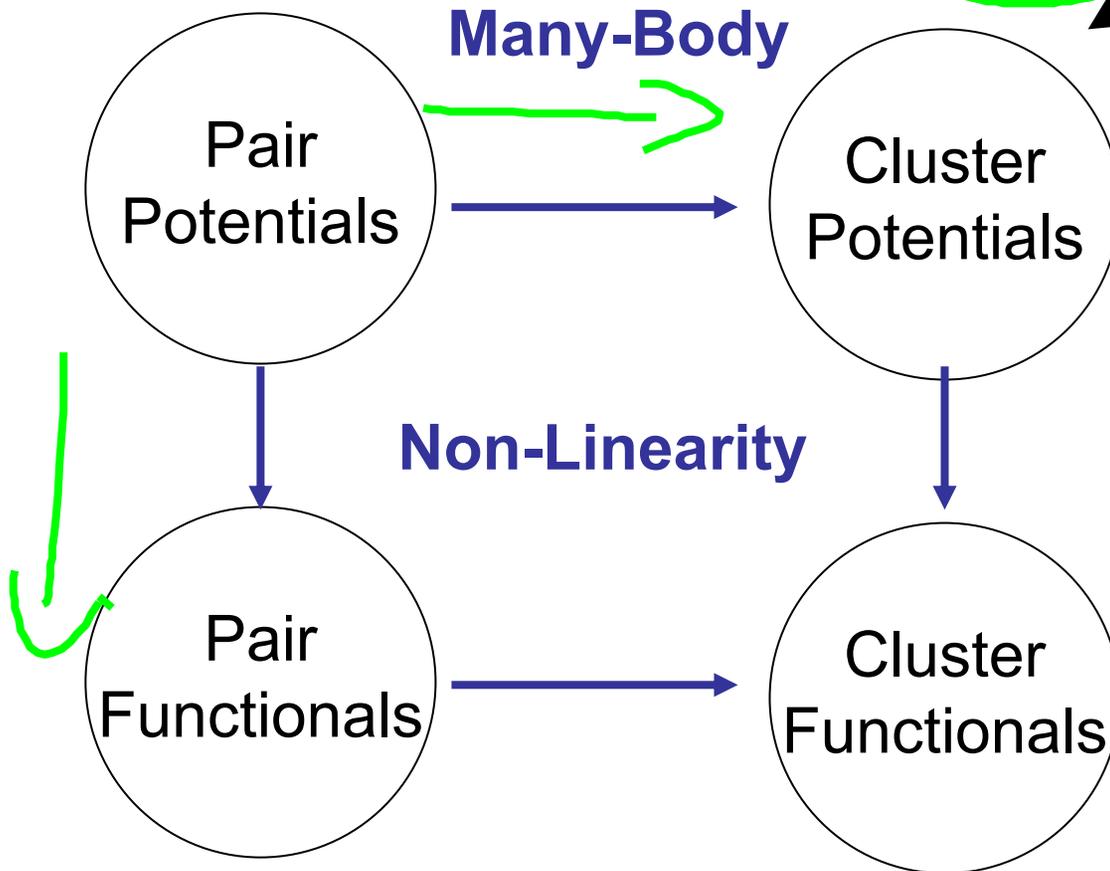
Resources for Embedded Atom Method

Some useful lecture notes and examples

<http://www.ide.titech.ac.jp/~takahak/EAMers/>

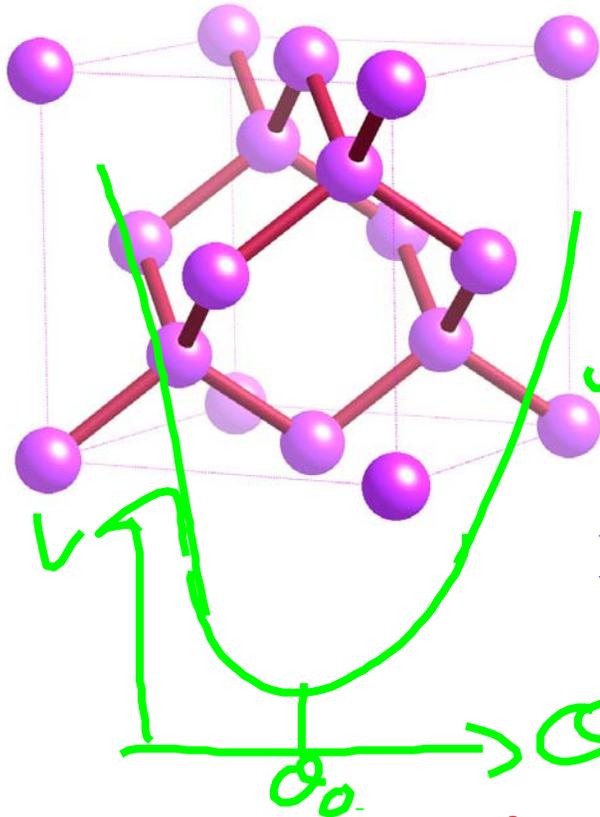
The other option: Many Body Potentials

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



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

$$K(\theta - \theta_0)^2$$

$$K(\cos\theta + 1/3)^2$$

Note: Now need N^3 operations for evaluating potential

Stillinger Webber Potential for Si

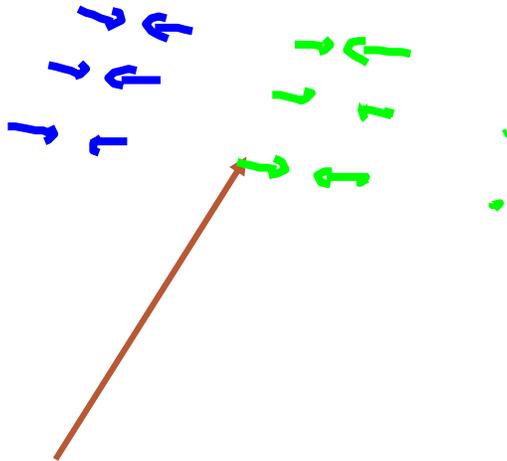
$$V_3 = \lambda \exp \left[\gamma (r_{ij} - a)^{-1} + \gamma (r_{ik} - a)^{-1} \right] \left[\cos \theta_{ijk} + \frac{1}{3} \right]^2$$

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

Surface Reconstruction for Si

unreconstructed Si(100)

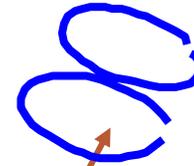
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Si surface atoms are bonded to 2 atoms below

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

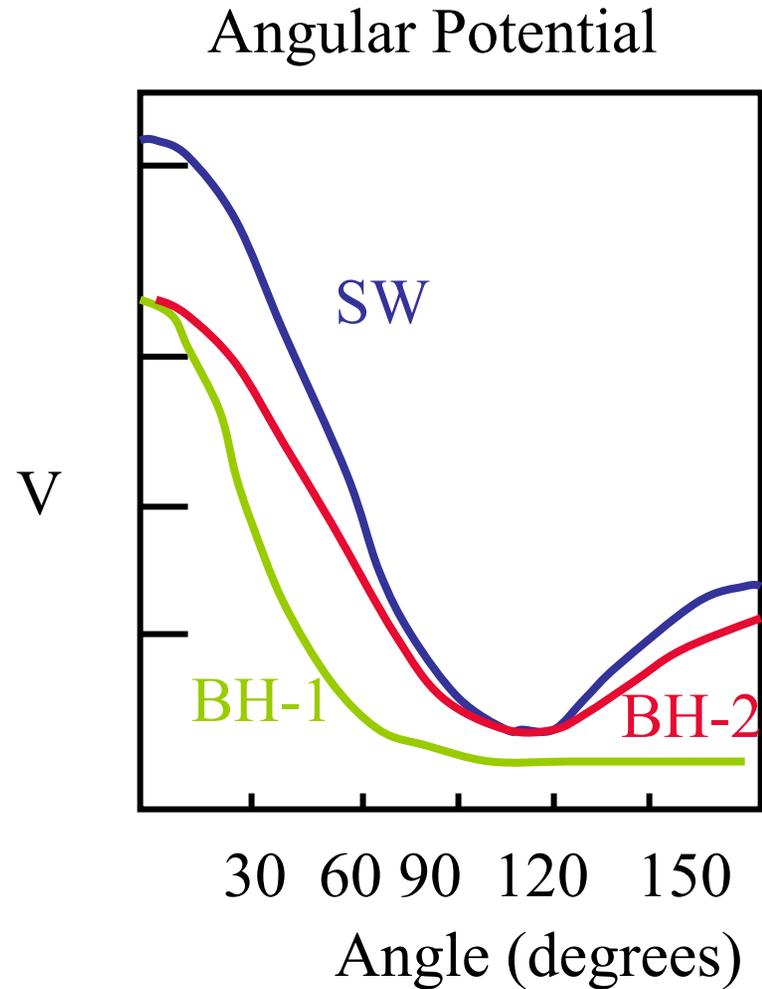
Surface Reconstruction for Si

Diagram removed for
copyright reasons.

7x7 reconstruction for Si(100) is not reproduced

A multitude of potentials for Si

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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.

See for example: Nurminen et al. *Physical Review B* **67** 035405 (2003).

Image removed for copyright reasons.

References for Si Potentials

1) Keating:

P.N.Keating,Phys.Rev. 145,637(1966)

Valid only for small deviations from the ideal diamond lattice sites.

Used for elastic constants and phonon properties.

2) Stillinger-Weber:

F.H.Stillinger and T.A. Weber, Phys. Rev. B 31, 5262 (1985) 2 and 3 body terms. Fitted to stable crystal structure, reasonable melting temperature and $g(r)$ in the liquid.

3) Tersoff:

J. Tersoff, Physical Review B, vol.38, (no.14):9902-5 (1988) pair functional. gets good elastic properties, stable crystal structures, liquid properties.

4) Biswas-Hamann

R. Biswas and D.R. Hamann, Phys.Rev.Lett. 55,2001(1985)

R. Biswas and D.R. Hamann, Phys.Rev.B 36, 6434 (1987)

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

M.I.Baskes, Phys.Rev.Lett. 59,2666(1987)

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 Pearson, Takai, Halicioglu and Tiller, J.Cryst.Growth 70,33(1984)

o Dodson, Phys.Rev.B 35,2795(1987)

o Khor and Das Sarma, Several articles in PRB 1988-89.

o Chelikowsky, J.R.; Phillips, J.C.; Kamal, M.; Stauss, M., Phys Rev Lett 62, 292(1989)

A comparison between 6 of these potentials can be found in Balamane, H.; Halicioglu, T.; Tiller, W.A. Comparative study of silicon empirical interatomic potentials. Physical Review B 46,2250 (1992)

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)

