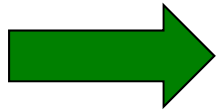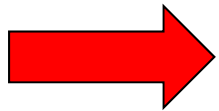# LECTURE 1

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COURSE OUTLINE

- **Some Concepts**
  - **Bond energy**
  - **Many body effects**
  - **Transferability**
  - **Reference state**
  - **Screening**

- **Models**
  - **Pair potentials**
  - **Embedded Atom Method (EAM)**
    - **theory**
    - **examples**
  - **Modified Embedded Atom Method (MEAM)**
    - **theory**
    - **examples**

- **Dislocation Motion**
  - **CREATOR**
  - **DYNAMO**
  - **XATOMS**
  - **Common Neighbor Analysis (CNA)**

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CONCEPT: BOND ENERGY

- **Every pair of atoms is connected by a bond (spring)**

- **The bond energy depends on the separation of the atoms**

- **The potential energy of a material is the sum of the bond energies**

CONCEPT: MANY BODY EFFECTS

- **All bonds are not equal**

- **The bond energy also depends on the local environment (coordination)**
  - **Coordination / bond length / bond energy are correlated (Pauling)**

CONCEPT: TRANSFERABILITY

- **The model will be accurate for all atomic environments**
    - **Volume (Nearest neighbor (1NN) distance)**
    - **Coordination (crystal structure - number of 1NN)**
    - **Defects or strain (loss of symmetry)**

CONCEPT: REFERENCE STATE (I)

- **Reference structure**
  - **A specific crystal structure**
  - **Properties of the reference structure can be obtained from experiment or first principles calculations**
    - **Energy vs. volume (1NN distance)**
    - **Elastic constants**
    - **Defect energies**
 - **Reference structures have high symmetry**

CONCEPT: REFERENCE STATE (II)

- **Reference path**
  - A specific path connecting 2 reference structures
  - Properties along the reference path can be obtained from first principles calculations
    - Energy vs. distance along path
  - Reference paths encompass low symmetry states
  - Coordination changes along a reference path

- **Incorporation of many reference states will facilitate transferability**

CONCEPT: SCREENING

- **Atomic interactions have a finite range**
  - **Radial screening**
    - at a cutoff distance the interactions go to zero (smoothly)
    - dependant on distance
    - independent of local geometry
    - at high compression - change in number of bonds
  - **Angular screening**
    - intervening atoms reduce interactions
    - dependent on local geometry
    - at high compression - number of bonds constant

- **Necessary for computation to scale with the number of atoms**

A PAIR POTENTIAL REPRESENTS ONLY DISTANCE DEPENDENT BONDING

Different Strength

Same Strength

$\phi(R)$
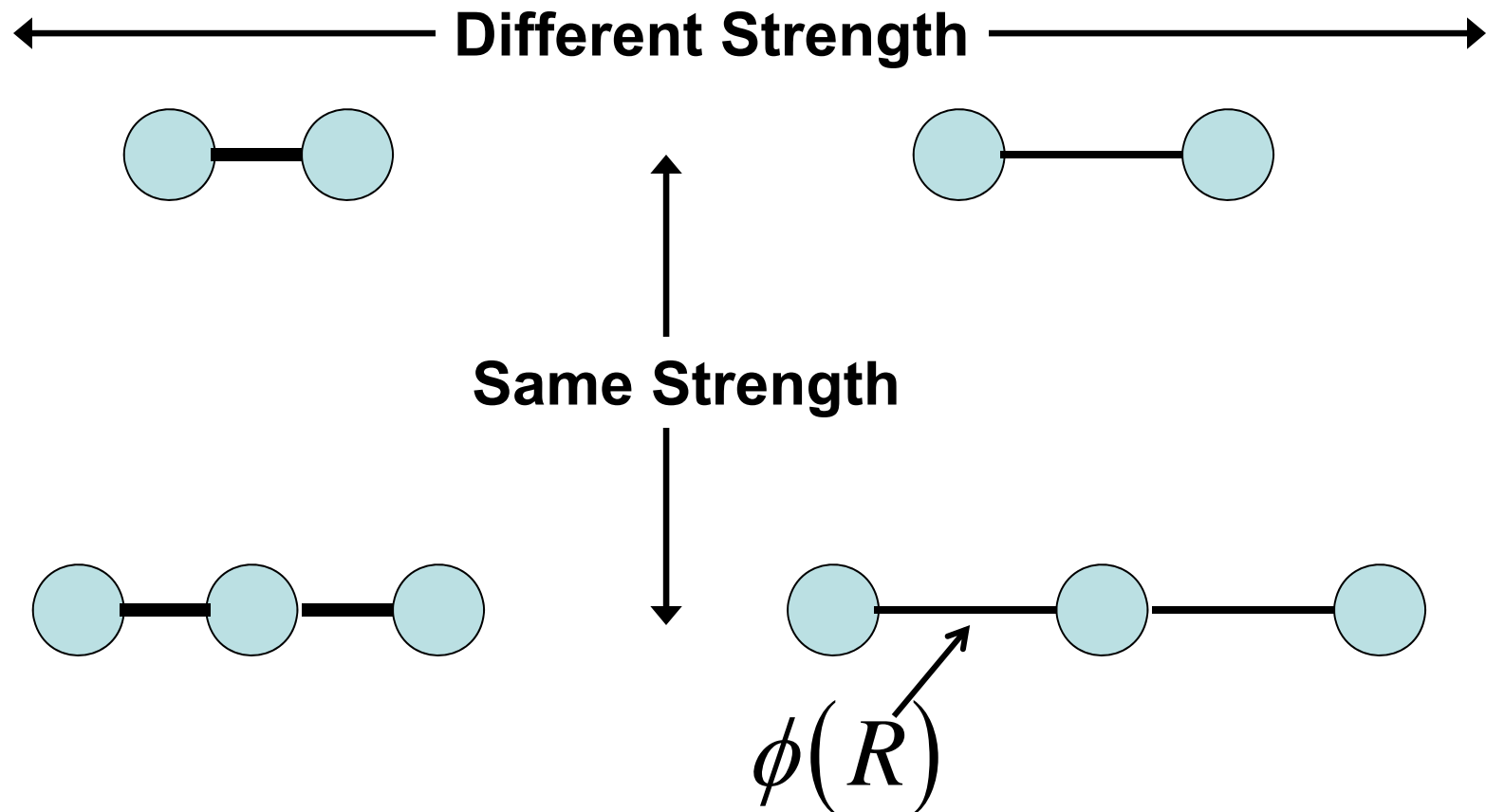
MODEL: PAIR POTENTIAL

Accuracy

- **Transferable**
  - **Volume**
  - **Coordination**
  - **Defects/strain**

Computation

- **Analytic or tabular**
- **Scales with number of atoms**
- **Parallel architecture**

potential energy

i: all atoms
j: neighbors of atom i

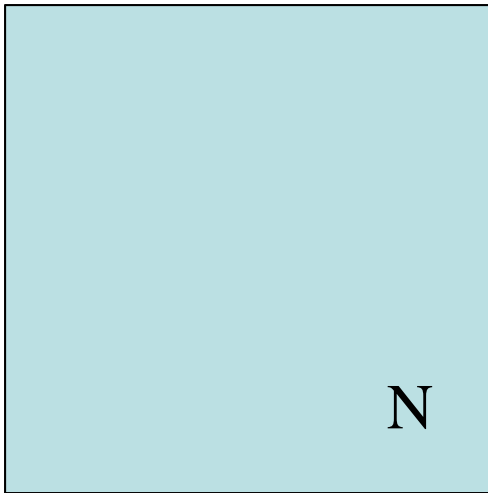$$U = \frac{1}{2}\sum_{i,j} \phi\left(R_{ij}\right) S\left(R_{ij}\right)$$

independent of environment

radial screening

SCREENING IS NECESSARY TO LIMIT COMPUTATIONAL TIME
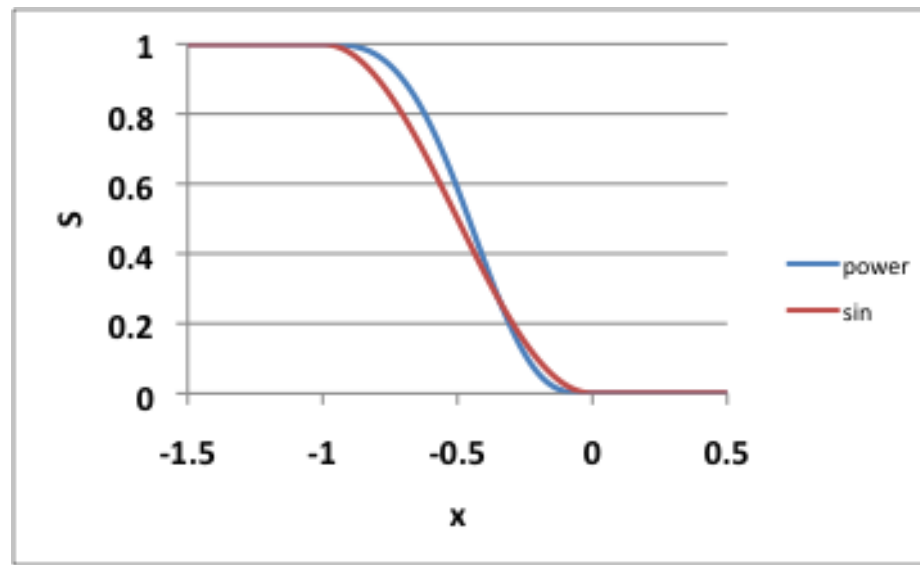
Computational time ~ N^2   **Computational time ~ nN**

N

n

N
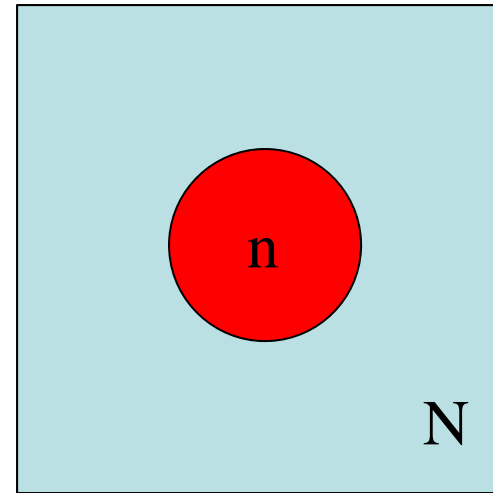
where N is the number of atoms in the computational cell and n is the number of interacting atoms

TYPICAL SCREENING FUNCTIONS

$$x = \frac{\left(R - R_c\right)}{\Delta r} \quad S = \begin{cases} 1 & x < -1 \\ \left[\sin\left(\frac{\pi x}{2}\right)\right]^2 \; or \left[\left\{1 - \left(1 + x\right)^3\right\}\right]^4 & -1 \le x \le 0 \\ 0 & x > 0 \end{cases}$$

A PAIR POTENTIAL HAS ONLY TWO INDEPENDENT ELASTIC CONSTANTS FOR A CUBIC MATERIAL

- A cubic material has 3 elastic constants (c_{11}, c_{12}, c_{44})

- A pair potential cannot reproduce real material elastic properties

- In equilibrium two elastic constants are related $c_{12}=c_{44}$

- The Cauchy discrepancy may be defined as $c_{12} / c_{44} - 1$

- For a way around this problem Baskes and Melius PRB 20, 1979 created "volume dependent" pair potentials, but these potentials don't work very well for non-uniform systems

REAL MATERIALS HAVE A CAUCHY DISCREPENCY

Solid	$C_{12}/C_{44} - 1$
Ar	0.1
Kr	0.0
Ni	0.2
Cu	0.6
Pd	1.5
Ag	1.0
Pt	2.3
Au	2.7

$$U = \frac{1}{2}\sum_{ij}\phi(R_{ij}) + F(V)$$

Volume

- **Volume dependent term needed to satisfy the Cauchy discrepancy**

- **How does one define volume for non-homogeneous systems?**

MODEL: LENNARD-JONES (LJ) POTENTIAL

- **Initially used to model rare gases**

- **Reference structure**
  - **diatomic**
  - **bond energy (E_0)**
  - **equilibrium bond distance (r_0)**

$$\phi(R) = 4\varepsilon_0\left[\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^{6}\right] = E_0\left[\left(\frac{r_0}{R}\right)^{12} - 2\left(\frac{r_0}{R}\right)^{6}\right]$$

MODEL: MORSE POTENTIAL

- **Convenient functional form for diatomic molecules**

- **Reference structure**
  - **diatomic**
  - **bond energy (E_0)**
  - **equilibrium bond distance (r_0)**
  - **force constant related to (α)**

$$\phi(R) = E_0 \left[e^{2\alpha(r_0 - R)} - 2e^{\alpha(r_0 - R)} \right]$$

SIMPLE ANALYTIC EXPRESSIONS FOR THE BULK MODULUS WITH LJ OR MORSE INTERACTIONS

For only nearest neighbor (1NN) interactions in an fcc crystal:

$$U = 6\phi(R)N \qquad \textcolor{red}{\textbf{remember double counting}}$$

$$r_e = r_0$$

$$K = \frac{1}{9V_e}\frac{\partial^2 E}{\partial(R/r_0)^2} = \begin{cases} 48\,E_0/\Omega_e & LJ \\ \left(4E_0/\Omega_e\right)\left(a^2 r_e^2/3\right) & Morse \end{cases}$$

where Ω_e is the volume per atom.

Thus for a Morse potential the experimental bulk modulus may be reproduced by an appropriate choice of the parameter α.

LET'S LOOK AT THE EXPERIMENTAL NUMBERS FOR Cu

E_c	3.54 eV
a_0	3.62 Å
K	0.875 eV/Å³
$E_0 = E_c/6$	0.59 eV
$r_0 = a_0 / \sqrt{2}$	2.56 Å
$\Omega_e = a_0^3 / 4$	11.86 Å³
$48E_0/\Omega_e$	2.388 eV/Å³

So the bulk modulus from a LJ potential (1NN model) is almost 3 times greater than experiment

LET'S LOOK AT THE EXPERIMENTAL NUMBERS FOR Cu

	Experiment	Pair Potential
E_c	3.54 eV	3.54 eV
E^f_{1V}	1.15 eV	3.54 eV
$E_{(100)}$	1.77 J/m^2	5.76 J/m^2
$\dfrac{E^f_{1V}}{r_e^2 E^f_{(100)}}$	1.6	1.5

- **vacancy formation energy and surface energy from a pair potential are about 3 times experiment**
- **ratio agrees quite well**

LJ PREDICTS A VERY HIGH MELTING POINT FOR Cu

	Experiment	LJ
$\dfrac{k_B T_m}{E_c}$	0.033	0.077

- **We take the MP for a LJ potential from the literature**
- **This MP ratio for all metals is ~ 1/30 in serious disagreement with the LJ potential**

HOW CAN WE IMPROVE THE ACCURACY AND TRANSFERABILITY OF PAIR POTENTIALS?

- **Include many body effects**
  - the bond energy does not depend on just distance
  - the bond energy depends on the local environment

- **Daw and Baskes (PRL 1983) did that almost 3 decades ago and called the method the embedded atom method (EAM)**

# THE EMBEDDED ATOM METHOD YIELDS POTENTIALS THAT DEPEND UPON THE ENVIRONMENT

Basic Interaction

Pair Potential

EAM
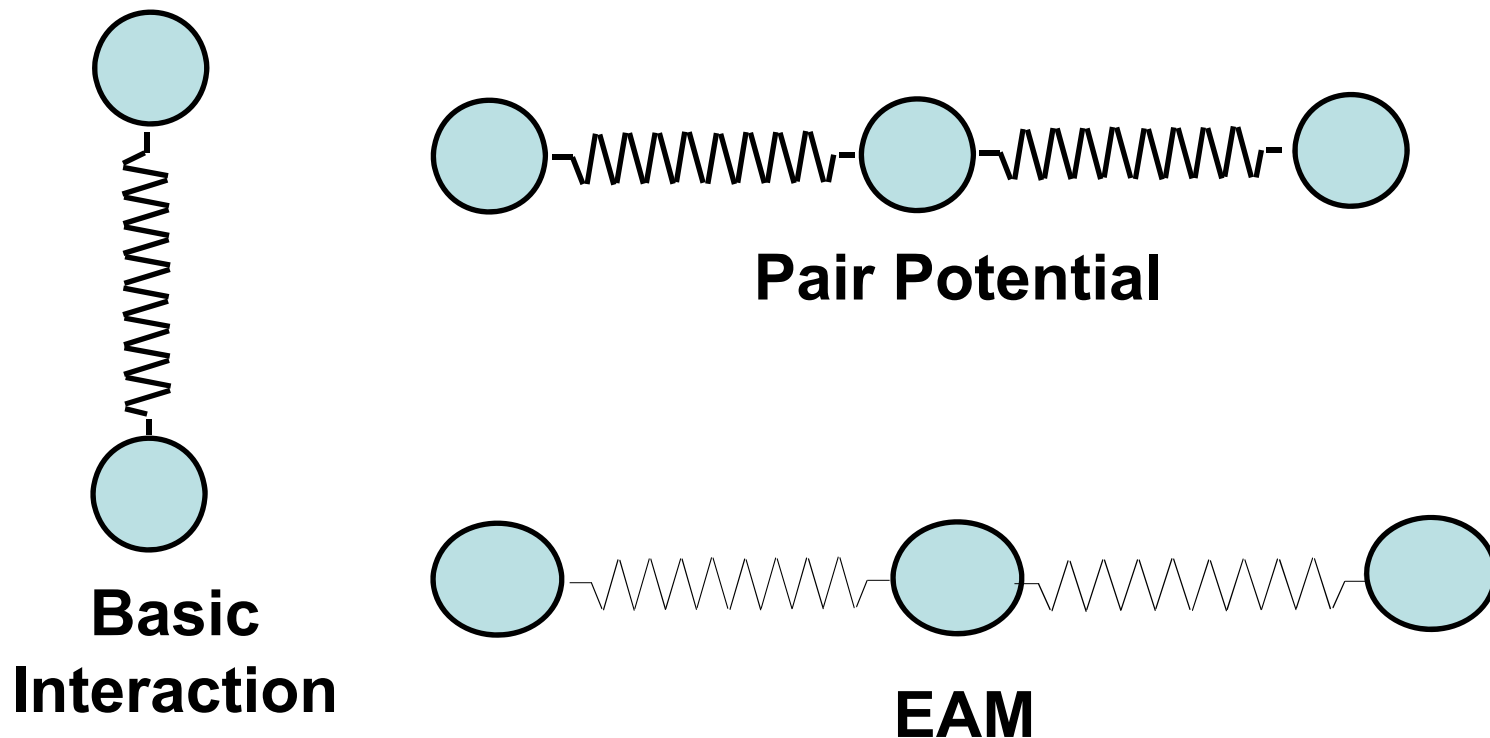
DENSITY FUNCTIONAL THEORY PROVES THAT THE ENERGY IS A FUNCTIONAL OF THE ELECTRON DENSITY

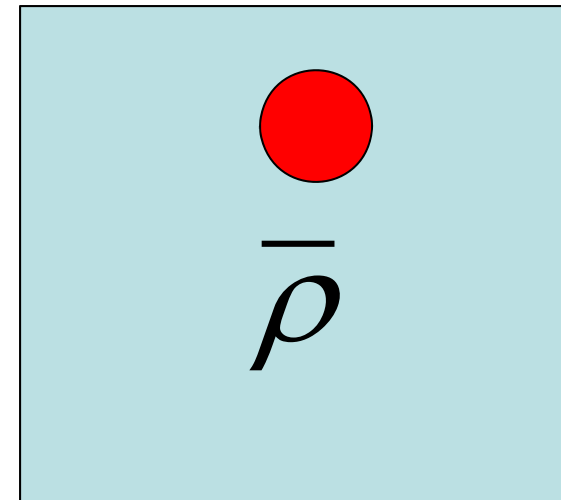$$U = f\left[\rho(\vec{R})\right]$$

unknown functional

electron density

If we know the electron density everywhere, then the potential energy is determined

AN ATOM IS EMBEDDED INTO A HOMOGENEOUS ELECTRON GAS

$\overline{\rho}$

$\overline{\rho}$
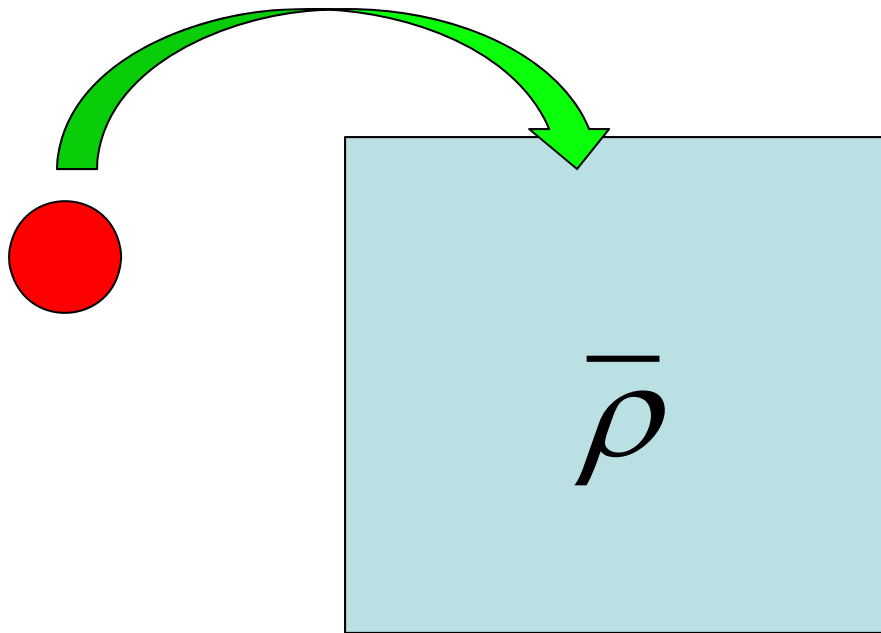
homogeneous electron gas

homogeneous electron gas

$$\Delta U = F(\overline{\rho})$$

embedding function

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# THE ELECTRON DENSITY IN A CRYSTAL IS NOT HOMOGENEOUS

- **Replace the background electron density by the electron density at an atom**

- **Supplement the embedding energy by a repulsive pair potential to represent core-core interactions**

homogeneous
electron gas

inhomogeneous
electron gas
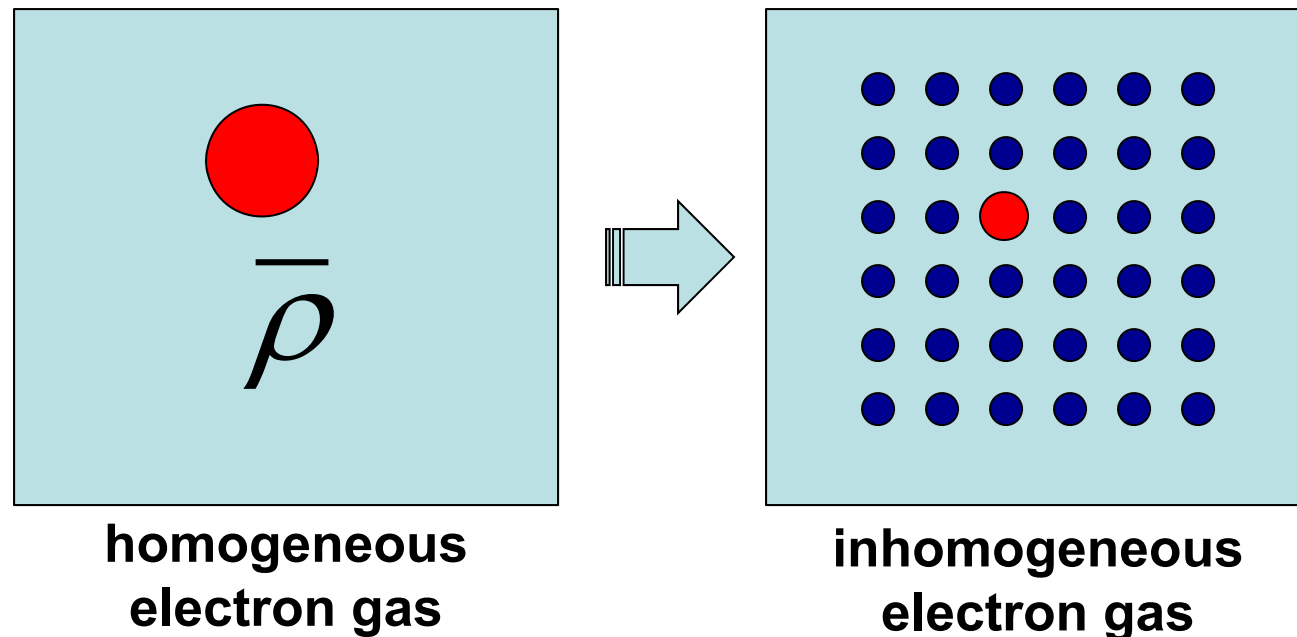
BACKGROUND ELECTRON DENSITY IS A SIMPLE LINEAR SUPERPOSITION

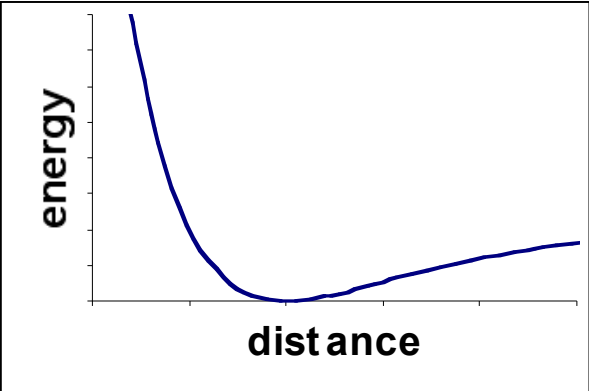$$\overline{\rho}_i = \sum_j \rho_j^a \left(R_{ij} \right)$$

spherically averaged atomic density from first principles calculations
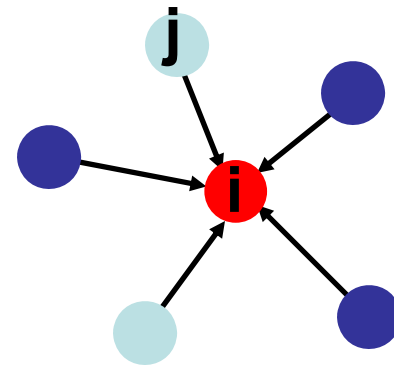
- atom j is a neighbor of atom i
- do not include atom i in the sum

THE EMBEDDED ATOM METHOD IS SEMI-EMPIRICAL

embedding energy   **background electron density**   **pair interaction**

$$E = \sum_i \left(F_i(\bar{\rho}_i) \ + \ \frac{1}{2}\sum_{j \neq i} \phi_{ij}(R_{ij}) \right)$$

energy vs. distance

$\bar{\rho}$ is obtained from a linear superposition of atomic densities

F and ϕ are obtained by fitting to the following properties:

Universal Binding Energy Relationship (UBER)

(lattice constant, bulk modulus, cohesive energy)

Shear moduli

Vacancy formation energy

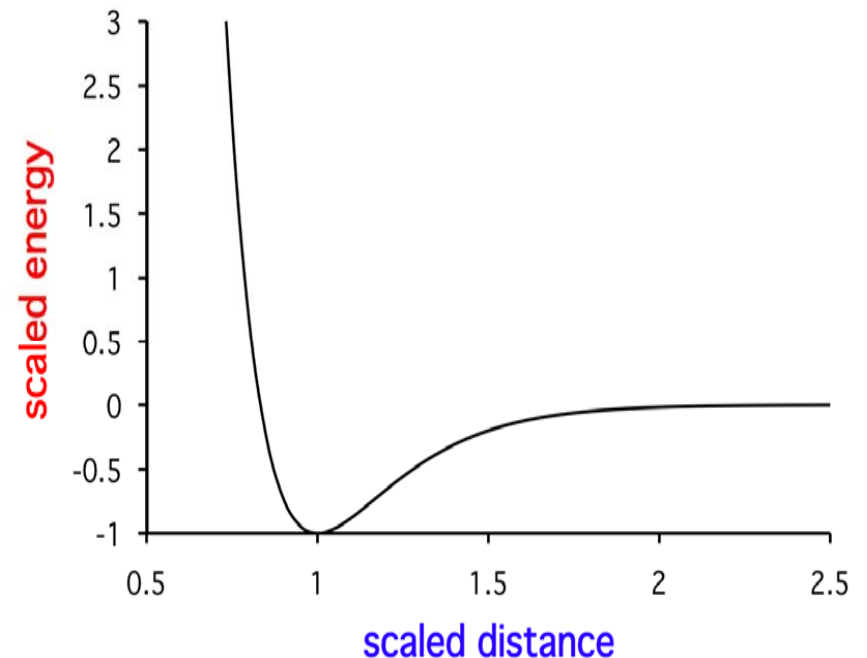Structural energy differences (hcp/fcc, bcc/fcc)

UBER EXTENDS EQUILIBRIUM BEHAVIOR

$$U_u(R) = -E_c(1 + a^*)e^{-a^*}$$

$$a^* = \alpha(R/r_e - 1)$$

$$\alpha = \sqrt{\frac{9K\Omega_e}{E_c}}$$

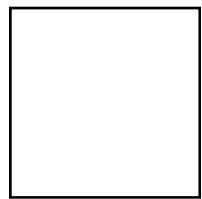**atomic volume and 1NN distance
are related for any crystal structure**
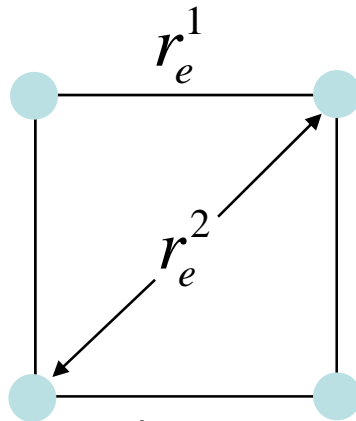
EMBEDDING FUNCTION COMES FROM HOMOGENEOUS DEFORMATION

$$U_u\left(\lambda r_e^1\right) = F\left(\overline{\rho}(\lambda)\right) + \tfrac{1}{2}\sum_n N_n \phi\left(\lambda r_e^n\right)$$

$$F\left(\overline{\rho}(\lambda)\right) = U_u\left(\lambda r_e^1\right) - \tfrac{1}{2}\sum_n N_n \phi\left(\lambda r_e^n\right)$$

$$\overline{\rho}(\lambda) = \sum_n N_n \rho^a\left(\lambda r_e^n\right)$$

r_e^1

r_e^2
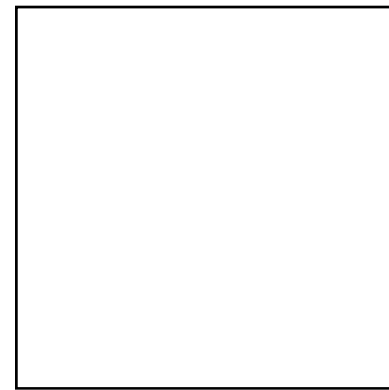
$\lambda = 0.6$ $\lambda = 1$ $\lambda = 1.2$

A FUNCTIONAL FORM IS CHOSEN FOR THE PAIR POTENTIAL

- **For the initial EAM functions:**

$$\phi_{ij}\left(R_{ij}\right) = \frac{Z_i\left(R_{ij}\right)Z_j\left(R_{ij}\right)}{R_{ij}}$$

- **various forms for Z have been chosen**
  - cubic splines
  - $Z_i\left(R\right) = Z_{0i}\left(1 + c_{1i}R^{c_{3i}}\right)e^{-c_{2i}R}$

- **other functional forms have been used**

FUNCTIONS HAVE A RADIAL CUTOFF

$$g(R) \longrightarrow \begin{cases} g(R) & R \leq R_{min} \\ g(R)S\left(\dfrac{R - R_{max}}{R_{max} - R_{min}}\right) & R_{min} < R < R_{max} \\ 0 & R \geq R_{max} \end{cases}$$

$$g = \phi, \rho^{a}$$

$S(x)$ **goes from 1 to 0 smoothly**

EMBEDDED ATOM METHOD SUMMARY

- **Based on Density Functional Theory**
  - **Gives one a warm feeling that *maybe* results are reliable**
  - **Experience shows it is reliable**

- **Fit to "Real" Material Properties**
  - **Experiment**
  - **First principles**

- **Equivalent in Computer Time to Pair Potential Methods**

- **Includes "Many Body" Interactions**

- **Predictive - Once the fitting is done, there are no more knobs.**

MODEL: EAM

Accuracy

- **Transferable**
  - **Volume**
  - **Coordination**
  - **Defects/strain**

Computation

- **Analytic or tabular**
- **Scales with number of atoms**
- **Parallel architecture**
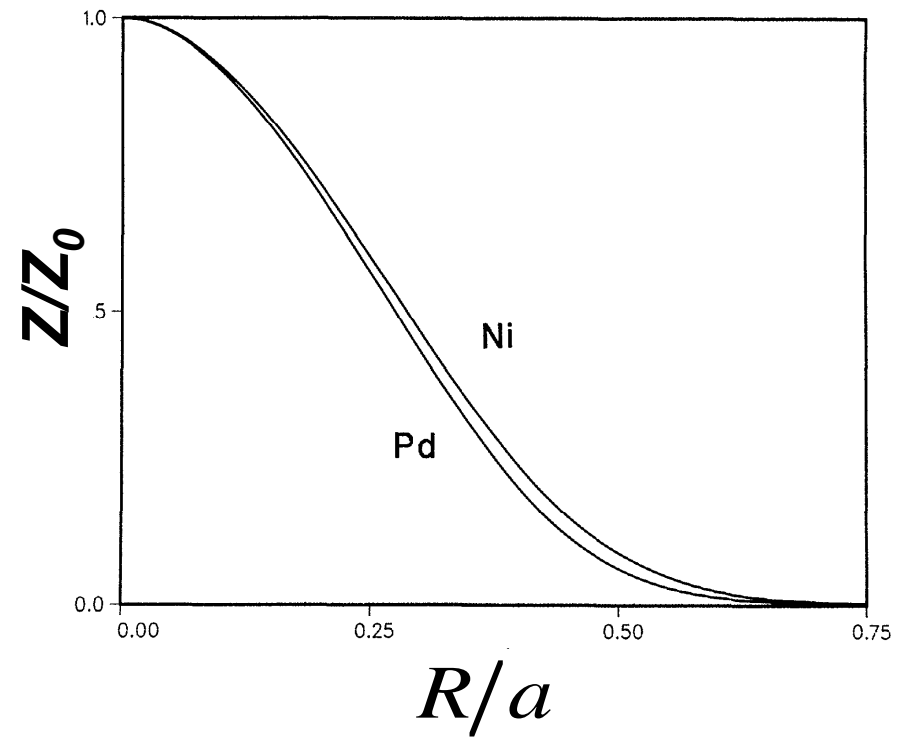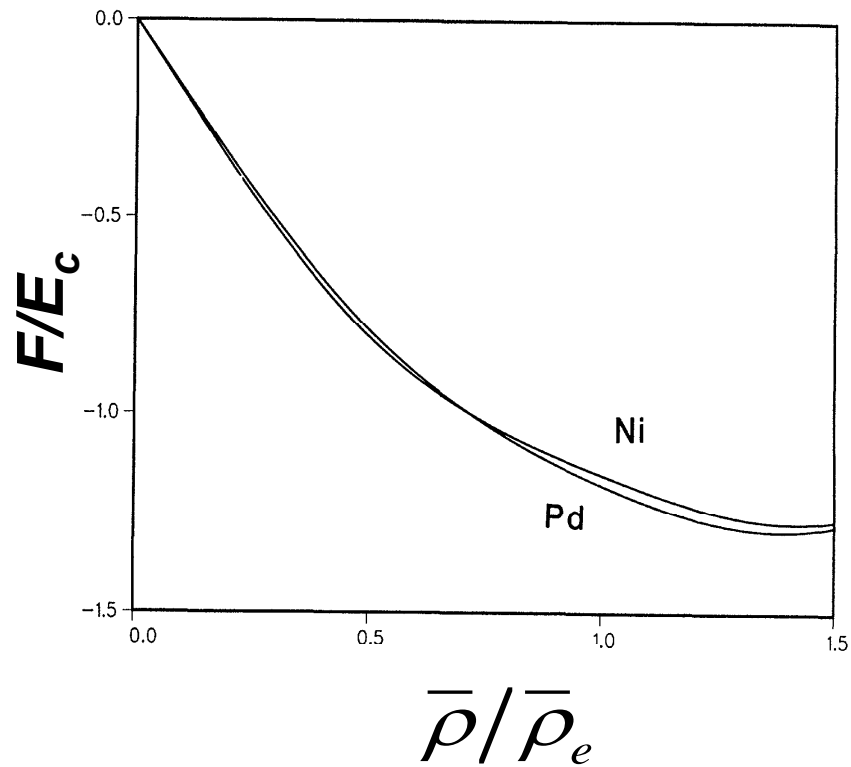
i: all atoms
j: neighbors of atom i

$$U = \sum_i F\left(\bar{\rho}_i\right) + \frac{1}{2} \sum_{i,j} \phi\left(R_{ij}\right) S\left(R_{ij}\right)$$

$$\bar{\rho}_i = \sum_i \rho^a\left(R_{ij}\right) S\left(R_{ij}\right)$$

radial screening

depends on environment

EAM FUNCTIONS ARE SIMPLE

EAM CAN REPRESENT ONLY A POSITIVE CAUCHY DISCREPANCY

- **We know from experiment that as coordination increases the bond energy goes down and the bond length increases**
  - **A diatomic always has a shorter bond length and stronger bond energy than a crystalline solid**
- **The EAM formalism shows that $F''>0$ reproduces this behavior**
- **The Cauchy discrepancy is proportional to F''**
- **Hence the Cauchy discrepancy in EAM is greater than zero**

LET'S COMPARE EAM TO EXPERIMENT FOR Cu

	Experiment	EAM
E_c	3.54 eV	3.54 eV
r_e	2.56 Å	2.56 Å
K	0.875 eV/Å^3	0.875 eV/Å^3
c_{44}	0.48 eV/Å^3	0.48 eV/Å^3
c_{12}/c_{44}-1	0.62	0.63
E^f_{1V}	1.3 eV	1.28 eV
$E_{(100)}$	1.77 J/m^2	1.28 J/m^2
Cu_2 bond energy	1.84 eV	1.22 eV
Cu_2 bond length	2.22 Å	2.15 Å