HOW TO DEVELOP MODIFIED EMBEDDED ATOM METHOD POTENTIALS

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OUTLINE

- Modified EAM (MEAM)
- Single Element
- Alloys

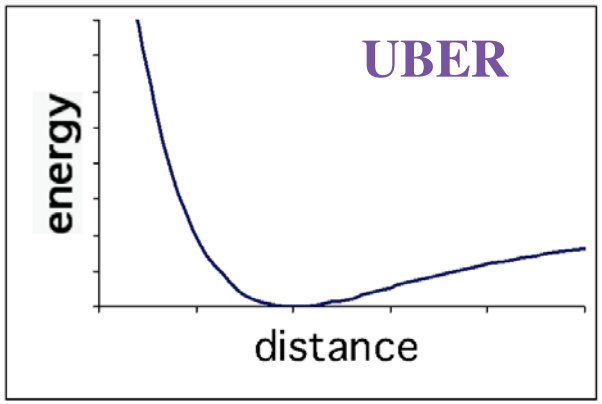
THE EMBEDDED ATOM METHOD IS SEMI-EMPIRICAL

embedding energy

host electron density

pair interaction

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



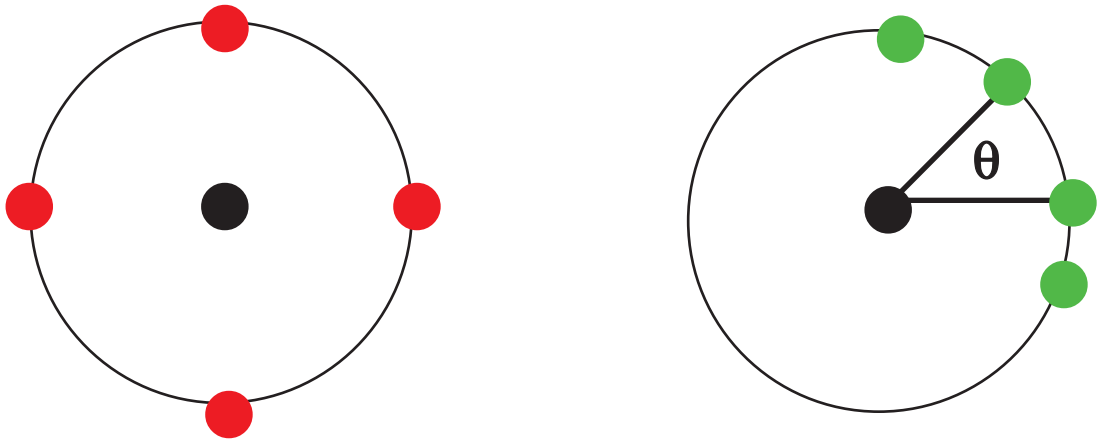
$\bar{\rho}$ is obtained from a linear superposition of atomic densities

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)

COMPLEX MATERIALS REQUIRE THE ADDITION OF ANGULAR FORCES

- EAM uses a linear superposition of spherically averaged electron densities
- MEAM allows the background electron density to depend on the local symmetry



$$\rho_k^{(l)2} = \sum_i \rho_l(R_{ik}) \sum_j \rho_l(R_{kj}) P_l^0\left(\cos(\theta_{ikj})\right)$$

MODIFIED EMBEDDED ATOM METHOD (MEAM)

Universal Binding Energy Relationship
UBER

$$E^u(R) = -E_c\left(1 + a^* + \delta a^{*3}\frac{r_e}{R}\right)e^{-a^*}$$

$$a^* = \alpha\left(\frac{R}{r_e} - 1\right) \qquad \alpha^2 = \frac{9\Omega B}{E_c}$$

Background Electron Density

$$\bar{\rho} = \rho^{(0)}\cdot\sqrt{1+\Gamma}$$

$$\Gamma = \sum_{l=1}^{3} t^{(l)}\left(\rho^{(l)}/\rho^{(0)}\right)^2$$

$$\rho_k^{(l)2} = \sum_i \rho_l(R_{ik})\sum_j \rho_l(R_{kj})P_l^0\left(\cos(\theta_{ikj})\right)$$

$$\rho_l = e^{-b^*}S \qquad b^* = \beta^{(l)}\left(\frac{R}{r_e} - 1\right)$$

Embedding Function

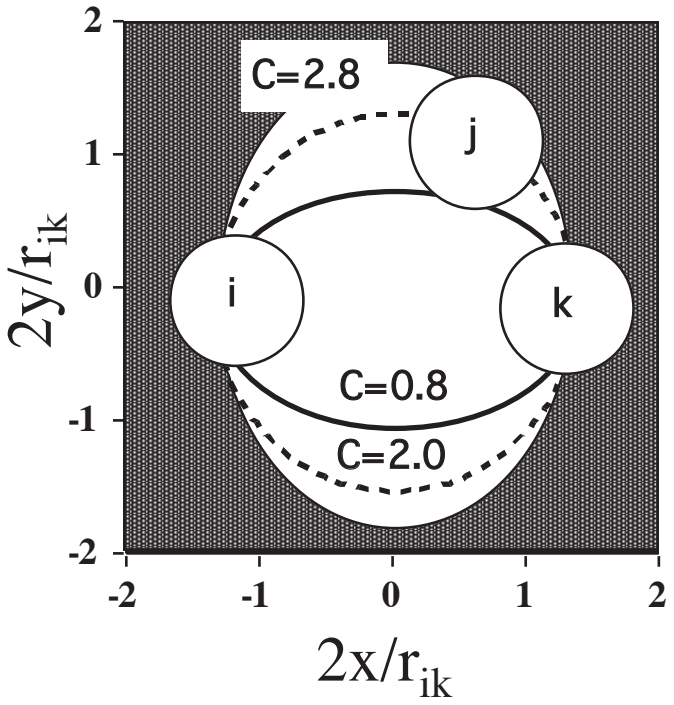
$$F(\bar{\rho}) = AE_c\bar{\rho}\ln\bar{\rho}$$

Pair Potential

$$\phi(R) = \frac{2}{Z}\left\{E^u(R) - F(\bar{\rho}^0(R))\right\}S$$

12 parameters + angular screening for the pair potential and electron densities

CONCEPT OF THE SCREENING ELLIPSE LEADS TO A SIMPLE SCREENING MODEL



screening ellipse defined by C

$$x^2 + \frac{1}{C} y^2 = \left(\frac{1}{2} r_{ik}\right)^2$$

$$X_{ij} = \left(\frac{r_{ij}}{r_{ik}}\right)^2 \qquad C = \frac{2\left(X_{ij} + X_{jk}\right) - \left(X_{ij} - X_{jk}\right)^2 - 1}{1 - \left(X_{ij} - X_{jk}\right)^2}$$

C_{min} and C_{max} set limits of screening

$$S_{ijk} = \begin{cases} 0 & C \le C_{\min} \\ f\left(\frac{C - C_{\min}}{C_{\max} - C_{\min}}\right) & C_{\min} < C < C_{\max} \\ 1 & C \ge C_{\max} \end{cases}$$

$$S_{ik} = \prod_{j \neq i,k} S_{ijk}$$

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

RECIPE FOR SINGLE ELEMENT

- **Choose Reference Structure**
- **Assemble Data Base**
- **Associate/Fit Parameters with Data Base**
- **Validate**
- **Iterate**

CHOOSE REFERENCE STRUCTURE

- **Simple Crystal Structure**
  - **fcc**
  - **bcc**
  - **hcp**
  - **diamond cubic**
- **Usually Equilibrium Ground State**
- **Must Have Data**
- **Relevant to Simulations**

ASSEMBLE DATA BASE

- **Experiment (reference structure)**
  - **Cohesive energy**
  - **Lattice constant**
  - **Elastic constants**

  } calibration

  - **Vacancy formation energy**
  - **Stacking fault energy**
  - **Thermal expansion**

  } validation

  - **Other phases**
- **First Principles (reference structure)**
  - **Energy vs. volume**
  - **Other phase relative energies**
  - **Transformation path**

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ASSOCIATE/FIT PARAMETERS WITH DATA BASE (I)

- **UEOS**
  - **Cohesive energy (E_c)**
  - **Lattice constant (r_e)**
  - **Bulk modulus (α)**
  - **Thermal expansion (δ)**
- **Partial Electron Density Weights**
  - **Vacancy formation energy (t_1)**
  - **Shear elastic constants (t_2)**
  - **Stacking fault energy (t_3)**

ASSOCIATE/FIT PARAMETERS WITH DATA BASE (II)

- **Embedding Energy Strength (A)**
  - **Energy of other phases**
- **Atomic Electron Density Decay**
  - **Energy of other phases (β_0)**
  - **Surface relaxation (β_1)**
  - **Shear elastic constants (β_2)**
  - **c/a (β_3)**
- **Angular Screening**
  - **Energy of other phases**
  - **Shear elastic constants**

VALIDATE (I –Reference Phase)

- **Thermal properties**
  - **Expansion**
  - **Specific heat**
- **Surfaces**
  - **Energy**
  - **Relaxation**
  - **Reconstruction**
- **Point defects**
  - **Vacancy mobility**
  - **Interstitial**
    - **Formation energy**
    - **Geometry**
    - **Migration energy**

VALIDATE (II – Other Phases)

- Liquid
  - Heat of fusion
  - Density
  - Melting point
- Solid
  - Relative stability
  - Lattice constants
  - Internal relaxation
  - Elastic constants
  - Transformation paths

EXPERIMENTAL DATA BASE FOR FE

Cohesive Energy (eV)	4.29
α Lattice Constant (300K) (Å)	2.866
Bulk Modulus (GPa)	167
C_{44} (GPa)	117
C' (GPa)	47.5
$\alpha \rightarrow \gamma$ Transformation Temperature (P=0) (K)	1185
$\gamma \rightarrow \delta$ TransformationTemperature (P=0) (K)	1657
$\alpha \rightarrow \varepsilon$ Transformation Pressure (0K) (GPa)	6-15
Vacancy Formation Energy (eV)	1.7
Thermal Expansion (500K) $\mu m \cdot m^{-1} \cdot K^{-1}$	14.4

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MEAM PARAMETERS ARE CORRELATED WITH PHYSICAL PROPERTIES

Physical Property	MEAM Parameter
Cohesive Energy	E_c
α Lattice Constant	r_e
Bulk Modulus	α
Thermal Expansion (500K)	δ
C_{44}	t_2, β_2
C'	t_2, β_2
$\alpha \rightarrow \gamma$ Transformation Temperature (P=0)	A, β_0, C_{min}
$\gamma \rightarrow \delta$ TransformationTemperature (P=0)	A, β_0, C_{min}
$\alpha \rightarrow \varepsilon$ Transformation Pressure (0K)	t_3, β_3
Vacancy Formation Energy	t_1, β_1

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MEAM PARAMETERS FOR FE

E_c (eV)	4.29	α	5.0729
r_e (Å)	2.469	δ	0.3
A	0.6	β_0	4.045
t_1	-1.6	β_1	2
t_2	12	β_2	0.8
t_3	-0.05	β_3	1
C_{max}	1.9	C_{min}	0.7

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MEAM REPRODUCES DATA BASE EXTREMELY WELL FOR IRON

Physical Property	Experiment	MEAM
Cohesive Energy (eV)	4.29	4.29
α Lattice Constant (300K) (Å)	2.866	2.866
Bulk Modulus (GPa)	167	170
C_{44} (GPa)	117	116
C' (GPa)	47.5	49
$\alpha \rightarrow \gamma$ Transformation Temperature (P=0) (K)	1185	1175
$\gamma \rightarrow \delta$ TransformationTemperature (P=0) (K)	1657	1750
$\alpha \rightarrow \varepsilon$ Transformation Pressure (0K) (GPa)	6-15	11
Vacancy Formation Energy (eV)	1.7	1.7
Thermal Expansion (500K) $\mu m \cdot m^{-1} \cdot K^{-1}$	14.4	14.3

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RECIPE FOR A BINARY SYSTEM

- **Choose Reference Structure**
- **Assemble Data Base**
- **Associate/Fit Parameters with Data Base**
- **Validate**
- **Iterate**

CHOOSE REFERENCE STRUCTURE

- Simple Crystal Structure
  - Preferably with 1NN of opposite type
  - B1 (rock salt –NaCl)
- Equilibrium Ground State if Simple
- Must Have Data
- Relevant to Simulations
  - stoichiometry
  - Structure
- Derive Analytic Expression for Cross Pair Potential

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ASSEMBLE DATA BASE

- **Experiment or First Principles (reference structure)**
  - **Cohesive energy**
  - **Lattice constant**
  - **Elastic constants**
  - **Thermal expansion**
- **Other Phases**
  - **Cohesive energy**

ASSOCIATE/FIT PARAMETERS WITH DATA BASE

- **UEOS (reference structure)**
  - **Cohesive energy (E_c)**
  - **Lattice constant (r_e)**
  - **Bulk modulus (α)**
  - **Thermal expansion (δ)**
- **Electron Density Scaling**
  - **Elastic constants (ρ^a_0)**
  - **Other cohesive energies (ρ^a_0, C_{min}, C_{max})**

ELASTIC CONSTANT RELATIONSHIPS

- From continuum anisotropic elasticity theory we know

$$U == \frac{1}{2}\int C_{ijkl}\varepsilon_{ij}\varepsilon_{kl}dV = \frac{1}{2}C_{ijkl}\varepsilon_{ij}\varepsilon_{kl}V$$

$$u = \frac{U}{N} = \frac{1}{2}C_{ijkl}\varepsilon_{ij}\varepsilon_{kl}\frac{V}{N} = \frac{1}{2}C_{ijkl}\varepsilon_{ij}\varepsilon_{kl}\Omega \Rightarrow C_{ijkl} = \frac{\partial^2 u}{\partial\varepsilon_{ij}\partial\varepsilon_{kl}}\frac{2}{\Omega}$$

$$\sigma_{ij} = C_{ijkl}\varepsilon_{kl} \Rightarrow C_{ijkl} = \frac{\partial\sigma_{ij}}{\partial\varepsilon_{kl}}$$

- Sum over repeated indices

HOW TO CALCULATE ELASTIC CONSTANTS

- **Consider these states of strain (ε=0.001) applied to the equilibrium structure**
  - **for B $\varepsilon_x=\varepsilon_y=\varepsilon_z=\varepsilon$, $\varepsilon_{xy}=\varepsilon_{xz}=\varepsilon_{yz}=0$, e.g., scale=1±ε, 1±ε, 1±ε**
  - **for C' $\varepsilon_x=-\varepsilon_y=\varepsilon$, $\varepsilon_z=\varepsilon_{xy}=\varepsilon_{xz}=\varepsilon_{yz}=0$, e.g., scale=1±ε,1-(±ε),1**
  - **for C_{44} $\varepsilon_{xz}=\varepsilon$, $\varepsilon_x=\varepsilon_y=\varepsilon_z=\varepsilon_{xy}=\varepsilon_{yz}=0$, e.g., shear=±ε**
- **We can calculate the elastic constants in each state**

$$B=\frac{1}{3}\left(C_{11}+C_{12}\right)=\frac{1}{9\Omega}\frac{\partial^2 u}{\partial\varepsilon^2}=\frac{\sigma_{xx}}{3\varepsilon}$$

$$C'=\frac{1}{2}\left(C_{11}-C_{12}\right)=\frac{1}{4\Omega}\frac{\partial^2 u}{\partial\varepsilon^2}=\frac{\sigma_{xx}}{2\varepsilon}$$

$$C_{44}=\frac{1}{4\Omega}\frac{\partial^2 u}{\partial\varepsilon^2}=\left|\frac{\sigma_{xz}}{2\varepsilon}\right|$$

- **Extra credit – derive these relationships**

HOW TO CALCULATE ELASTIC CONSTANTS

- **Energy method**
  - **Calculate u" numerically using potential energies from eam88**

$$\frac{\partial^2 u}{\partial \varepsilon^2} = \frac{u(1+\varepsilon)+u(1-\varepsilon)-2u(1)}{\varepsilon^2}$$

- **Stress method**
  - **The stress tensor σ may be obtained from the stress tensor in eam88**

$$\sigma = -\frac{\partial U}{N\Omega}$$

total volume of computational cell

- **sx 0.48880E-06 -0.10482E-13 0.53647E-14** xx xy xz
- **sy -0.10482E-13 0.48880E-06 -0.20132E-13** yx yy yz
- **sz 0.53647E-14 -0.20132E-13 0.48880E-06** zx zy zz

VALIDATE (I –Reference Phase)

- **Thermal properties**
  - **Expansion**
  - **Specific heat**
- **Surfaces**
  - **Energy**
  - **Relaxation**
  - **Reconstruction**
  - **Segregation**

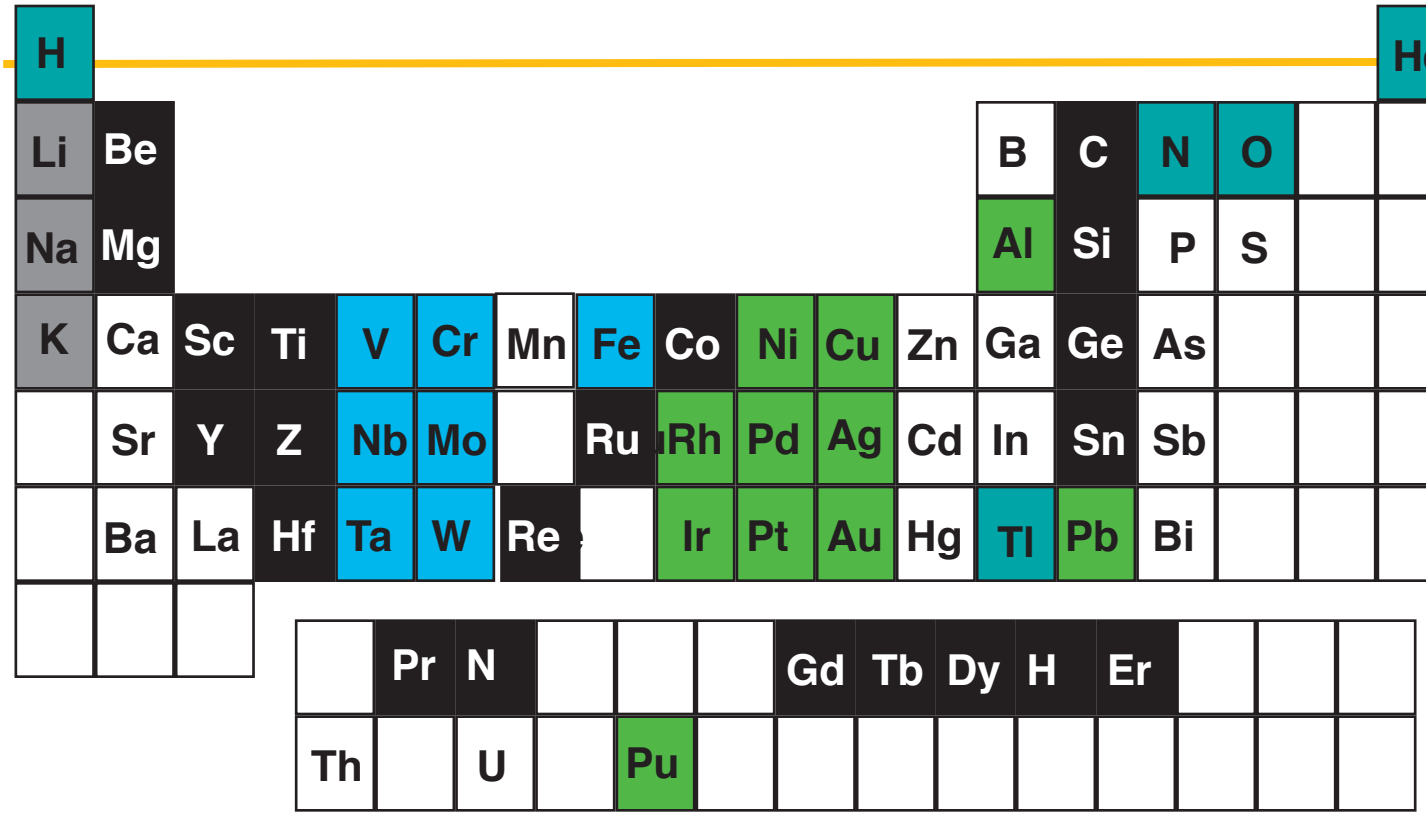
VALIDATE (II –Reference Phase)

- **Point defects**
  - **Vacancy (on A and B sub-lattices) mobility**
  - **Interstitial**
    - **Formation energy**
    - **Geometry**
    - **Migration energy**

VALIDATE (III – Other Phases)

- Liquid
  - Heat of fusion
  - Density
  - Melting point
- Solid
  - Relative stability
  - Lattice constants
  - Internal relaxation
  - Elastic constants
  - Transformation paths
  - Dilute heats of solution
  - Short range order

CURRENTLY DEVELOPED MEAM FUNCTIONS COVER MOST OF THE PERIODIC TABLE



Impurities

ISSUES FOR MULTI-COMPONENT SYSTEMS

- There are a limited number of free parameters for multi-components
  - For AB choose ρ^{aB}_0
  - For AC choose ρ^{aC}_0
  - There is no ρ to choose for BC
- There are $C_{min}(A,B,C)$ and $C_{max}(A,B,C)$ to choose
  - All combinations of A, B, C

TAKE AWAY

- **MEAM is Parameterized to Facilitate Relatively Easy Function Determination**
- **MEAM Can Quantitatively Reproduce the Fe Data Base Including Phase Transformations**