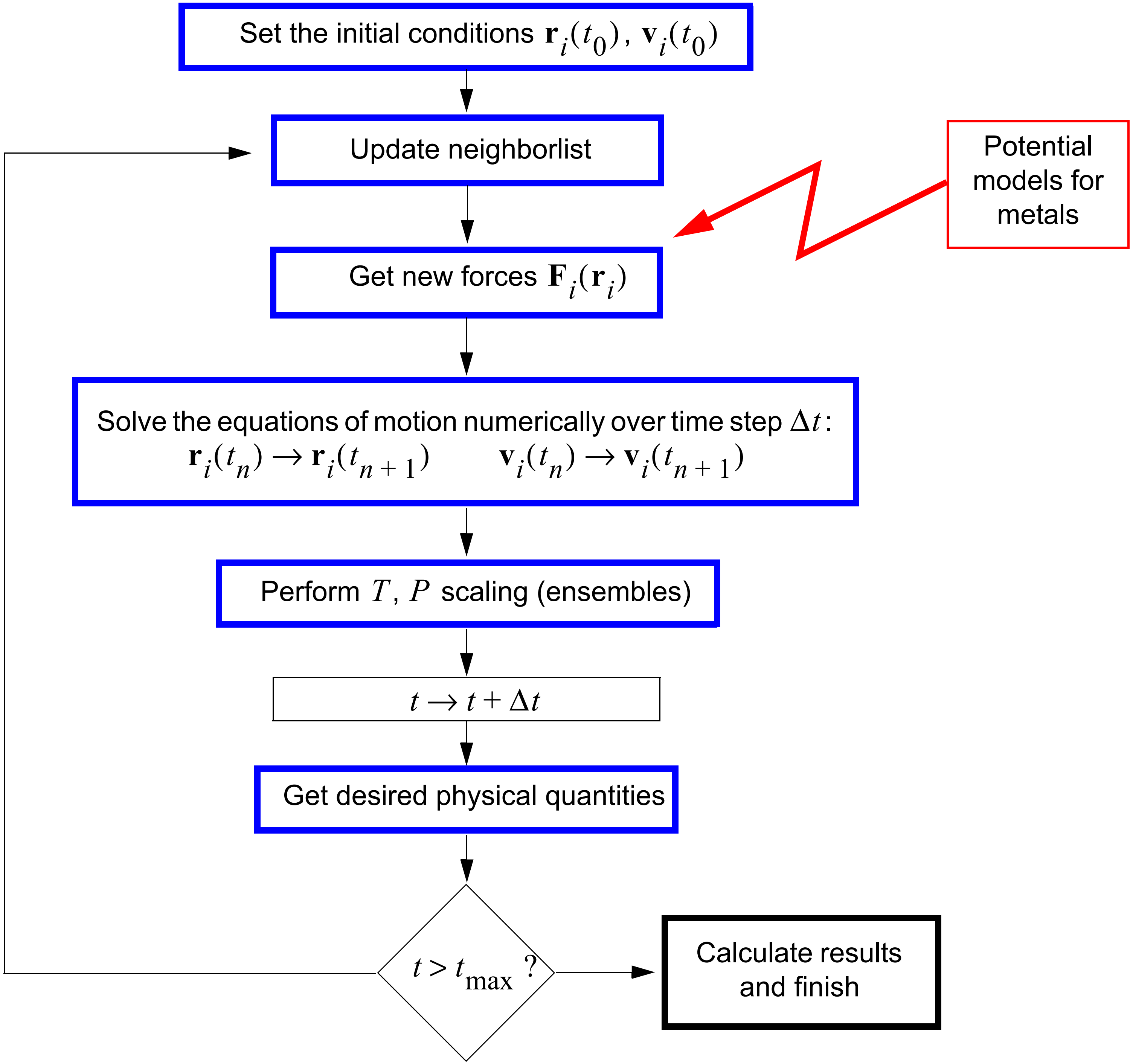


Set the initial conditions $\mathbf{r}_i(t_0)$, $\mathbf{v}_i(t_0)$

Update neighborlist

Get new forces $\mathbf{F}_i(\mathbf{r}_i)$

Potential models for metals

Solve the equations of motion numerically over time step Δt:

$$\mathbf{r}_i(t_n) \rightarrow \mathbf{r}_i(t_{n+1}) \qquad \mathbf{v}_i(t_n) \rightarrow \mathbf{v}_i(t_{n+1})$$

Perform T, P scaling (ensembles)

$t \rightarrow t + \Delta t$

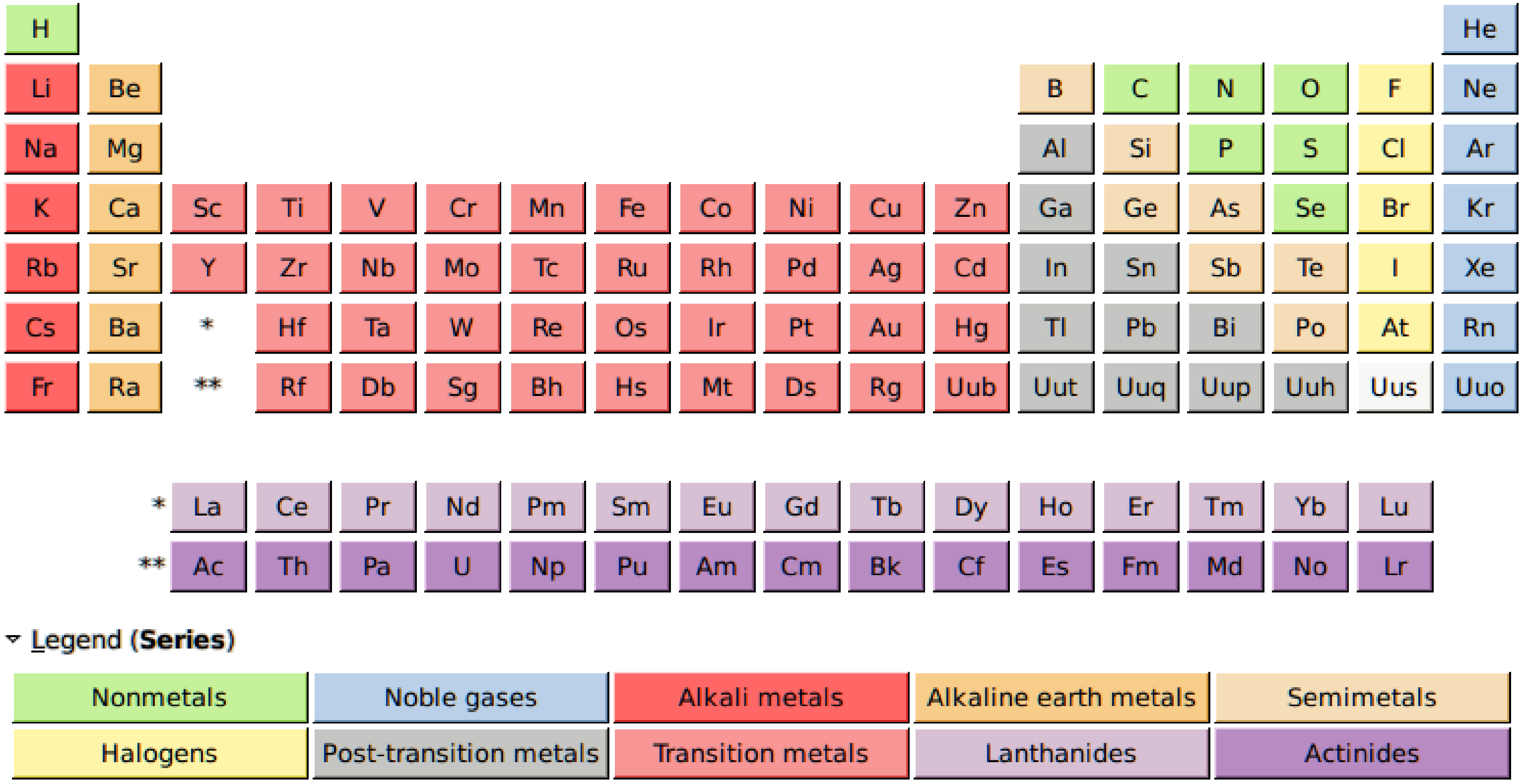
Get desired physical quantities

$t > t_{\max}$?

Calculate results and finish

Classical potentials for metals

- About 80 % of all elements are metals. The crystal structures of all the elements are distributed as follows:



H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	**	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub	Uut	Uuq	Uup	Uuh	Uus	Uuo
	*	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
	**	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

▿ Legend (**Series**)

Nonmetals	Noble gases	Alkali metals	Alkaline earth metals	Semimetals
Halogens	Post-transition metals	Transition metals	Lanthanides	Actinides

Program `gelemental`

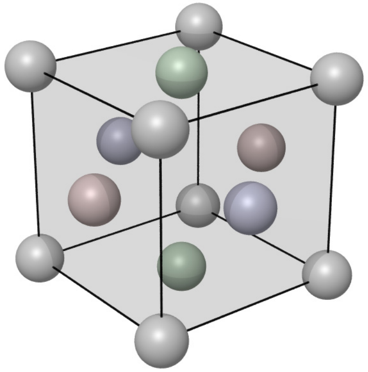
FCC 19 HCP 26 BCC 15 (quick counting from inside cover of Ashcroft&Mermin)

- If we can describe the FCC, HCP- and BCC structures with interatomic potentials, already some 60 % of all stable elements are described well at least with respect to the structure.

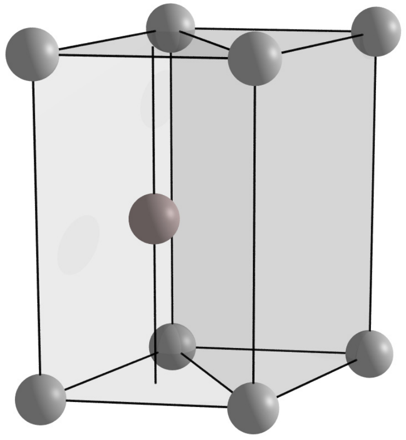
Classical potentials for metals

- The crystal structures are as follows:

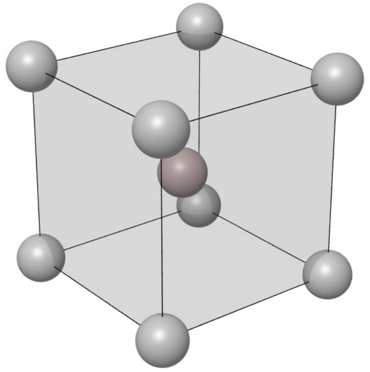
FCC



HCP



BCC



- FCC Face-Centered Cubic (close packed)
  atoms at the corners of the cube and in the center of each side face

  HCP Hexagonal Close-Packed (close packed)
  Angle between x and y unit cell axes is 120$^{\mathrm{o}}$.
  One atom at each corner of the unit cell,
  one (atom E) above the middle of the triangle ABC.

  BCC Body-Centered Cubic (not close packed)
  Cubic unit cell, atoms at the corners of the cube and in the center of the cube

  FCC and HCP are close packed $\Rightarrow$ can be stabilized with pair potentials (although getting the small HCP-FCC energy difference right is a bit tricky).

Effective medium theory

- The effective medium theory, EMT, is an approximation in which models based on density-functional theory are used to describe the properties of solids, usually metals.
  - Today there exist numerous many-body interatomic potentials which are based on EMT, in which the total energy is written in the form

$$E_{\text{tot}} = \sum_i F(n_i(\mathbf{R}_i)) + \frac{1}{2}\sum_{i,j} \Phi(\mathbf{R}_i - \mathbf{R}_j) \quad ,$$

    where F is a function of the electron density, and Φ is a (usually purely repulsive) pair potential.
  - Sort of a generalization of DFT: local electron density can be used to deduce the energy.

  - EMT can be used to directly derive a potential but many potentials only obtain the motivation of their functional form from EMT.

  - In EMT the real material is replaced by **jellium** which consists of
    1) a homogeneous electron gas, formed by the free electrons of the metal
    2) a constant positive background density (metal ions)

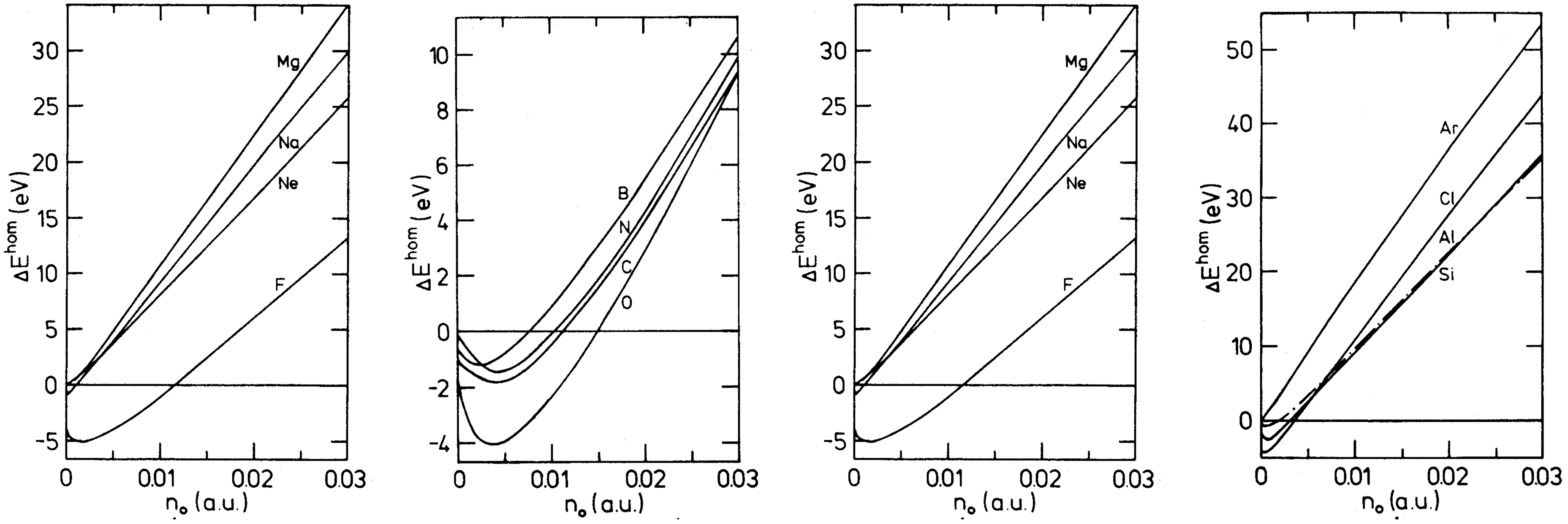
  - When an atom is 'embedded' into this medium in a position $\mathbf{r}$, the change in energy is as a first approximation

$$\Delta E(\mathbf{r}) = E_{\text{atom+jellium}} - (E_{\text{atom}} + E_{\text{jellium}}) \equiv \Delta E^{\text{hom}}(n_0(\mathbf{r})) \quad ,$$

    where $\Delta E^{\text{hom}}(n)$ is the **embedding energy** into a homogeneous electron gas with density n, and $n_0(\mathbf{r})$ is the electron density at $\mathbf{r}$.

Effective medium theory

- The embedding energy $\Delta E^{\text{hom}}(n)$ is a universal function of the electron density. Below is a list of examples [Puska, Nieminen, Manninen *Phys. Rev. B* **24** (1981) 3037].



- From the pictures we see that for noble gases $\Delta E^{\text{hom}}(n)$ is linear for all values of n, i.e. the closed electron shell only causes a repulsive interaction. (Some noble gases do have bonds, but this interaction derives from van der Waals effects which are not included in DFT/EMT).

- For other elements there is a minimum in the curves, which describes their propensity to form bonded materials.

Effective medium theory

- How do we get from this to the total energy of the whole system? [Manninen, *Phys. Rev. B* **34** (1986) 8486.]
  - The total energy of this "atoms in jellium" N-atom system is

    $$E^N_{\text{tot}} = E^N_R[n] \quad ,$$

    where n is the electron density of the ground state of the system.
  - The energy difference when an atom i is removed is

    $$\Delta E_i = E^N_{\text{tot}} - (E^{N-1}_{\text{tot}} + E_{\text{atom}}) = \Delta E_i[n_i] \quad ,$$

    where n_i is the electron density in the system *after* atom i has been removed.
  - **The idea of EMT** (motivated by DFT):

    Both E^N_{tot} and E^{N-1}_{tot} can be stated as a functional of the same electron density n_i.
  - The energy of the whole atom system can be stated as

    $$E_{\text{tot}} = E^{N-1}_{\text{tot}}[n_i] + \Delta E_i[n_i] + E_{\text{atom}}$$

Effective medium theory

- By removing more and more atoms, one at a time, we obtain for E_{tot}

$$E_{\mathrm{tot}} = NE_{\mathrm{atom}} + \sum_{i=1}^{N} \Delta E_i[n_{123\ldots i}] \quad .$$

  - Here $n_{123\ldots i}$ is an electron density in the system after atoms $1, 2, 3, \ldots, i$ all have been removed.
  - By rearranging the terms in the electron density this can be written as

$$\begin{aligned} E_{\mathrm{tot}} &= NE_{\mathrm{atom}} \\ &+ \sum_i \Delta E_i[n_i] \\ &+ \frac{1}{2}\sum_{ij} (\Delta E_j[n_{ij}] - \Delta E_j[n_j]) \\ &+ \frac{1}{6}\sum_{ijk} (\Delta E_k[n_{ijk}] - \Delta E_k[n_{ik}] - \Delta E_k[n_{jk}] - \Delta E_k[n_k]) \\ &+ \ldots \end{aligned}$$

In sums with many indices the terms with at least two same indices are left out.

  - Terms with distant atom pairs is are small, so the sums converge rapidly.

Effective medium theory

- The electron density $n_{123\ldots i}$ is approximated as a superposition of atom (or pseudo-atom) electron densities $n_{\mathrm{a}}(\mathbf{r})$

$$n_{123\ldots i}(\mathbf{r}) = \sum_{j=i+1}^{N} n_{\mathrm{a}}(\mathbf{r}_i - \mathbf{R}_j) \quad .$$

  - The atomic densities can be densities for free atoms or for atoms in the solid state where the surrounding compresses the electron shells.

- As mentioned above, in the first approximation

$$\Delta E_i[n_i] = \Delta E^{\mathrm{hom}}(n_i(\mathbf{R}_i)) \quad ,$$

  i.e. the functional is replaced by a function.

- By superposition the density n_{ij} is now

$$n_{ij}(\mathbf{R}_j) = n_j(\mathbf{R}_j) - n_{\mathrm{a}}(\mathbf{R}_j - \mathbf{R}_i) \quad .$$

- The embedding energy $\Delta E^{\mathrm{hom}}(n_{ij})$ can be calculated from $\Delta E^{\mathrm{hom}}(n_j)$ by developing it as a Taylor series

$$\Delta E^{\mathrm{hom}}(n_{ij}) = \Delta E^{\mathrm{hom}}(n_i) - n_{\mathrm{a}}(\mathbf{R}_i - \mathbf{R}_j)\frac{\partial \Delta E^{\mathrm{hom}}(n_j)}{\partial n_j} + \ldots \quad .$$

Effective medium theory

- If the same is done with the other terms in the expression (*), we find that the total energy:

$$E_{\mathrm{tot}} = \sum_{i=1}^{N} F^{\mathrm{hom}}(n_i(\mathbf{R}_i)) \quad ,$$

where

$$F^{\mathrm{hom}}(n) = E_{\mathrm{atom}} + \Delta E^{\mathrm{hom}}(n) - \frac{1}{2} n \frac{\partial \Delta E^{\mathrm{hom}}(n)}{\partial n} + \frac{1}{6} n^2 \frac{\partial^2 \Delta E^{\mathrm{hom}}(n)}{\partial n^2} \quad .$$

- Pair potential is completely missing!
- Can be used to some extent, but it is not completely satisfactory as it e.g. tends to lead to wrong values for the elastic constants [Daw, Baskes, *Phys. Rev. B* **29** (1984) 6443.]
- A better model is obtained by taking account of the electron density induced by an atom in the material

$$\Delta\rho(\mathbf{r}) = \Delta n(\mathbf{r}) - Z\delta(\mathbf{r})$$

and by considering the difference between the real external potential and the jellium external potential $\delta v^{\mathrm{ext}}(\mathbf{r})$.

Effective medium theory

- By using perturbation theory one obtains

$$\Delta E^{(1)}(\mathbf{R}_i) = \int d\mathbf{r}\Delta\rho(\mathbf{r}-\mathbf{R}_i)\delta v^{\mathrm{ext}}(\mathbf{r}) \quad ,$$

which can also be written as

$$\Delta E^{(1)}(\mathbf{R}_i) = \int d\mathbf{r}\Delta\rho(\mathbf{r}-\mathbf{R}_i)\phi(\mathbf{r}) \quad ,$$

where $\phi(\mathbf{r})$ is the electrostatic potential of the system (without the potential of the embedded atom).

- By the superposition principle this can be stated as a sum over single-atom potentials:

$$\Delta E^{(1)}(\mathbf{R}_i) = \sum_{i \neq j} \int d\mathbf{r} d\mathbf{r}' \frac{\Delta\rho(\mathbf{r}-\mathbf{R}_i)\Delta\rho(\mathbf{r}'-\mathbf{R}_j)}{|\mathbf{r}-\mathbf{r}'|}$$

- By using instead of the electron density at a point some average over the electron density in a region the model can also be improved. One suitable average is

$$\bar{n}_i(\mathbf{R}_i) = -\frac{1}{\alpha}\int d\mathbf{r} d\mathbf{r}' n_i(\mathbf{r})\frac{\Delta\rho_i(\mathbf{r}'-\mathbf{R}_i)}{|\mathbf{r}-\mathbf{r}'|} \quad ,$$

where

$$\alpha = -\int d\mathbf{r} d\mathbf{r}' \frac{\Delta\rho_i(\mathbf{r}'-\mathbf{R}_i)}{|\mathbf{r}-\mathbf{r}'|} \quad .$$

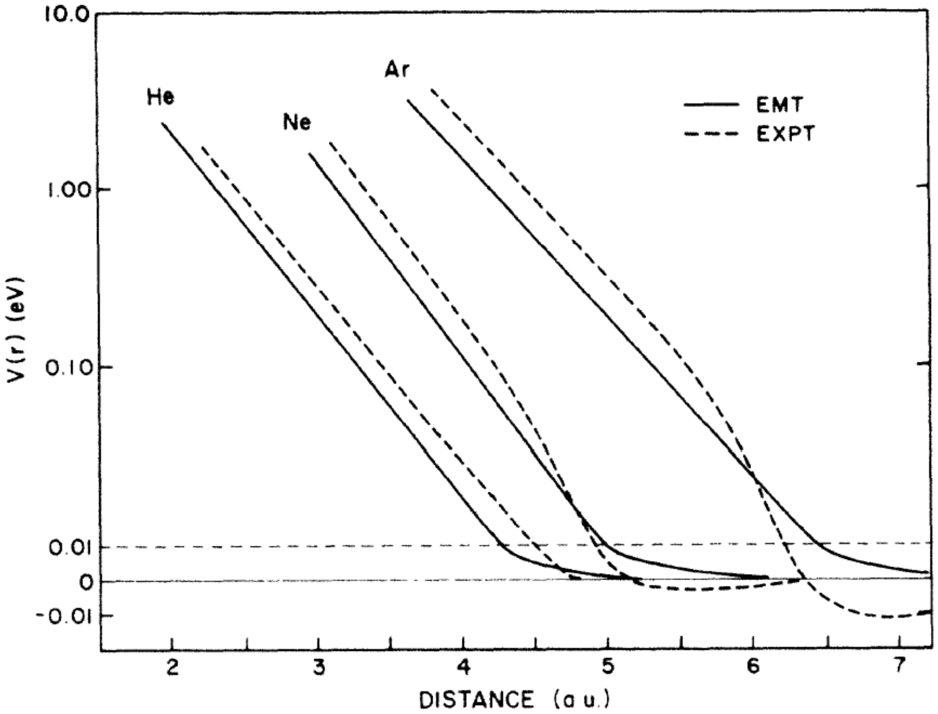
Effective medium theory

- Now the total energy of the system is of the form

$$E_{\text{tot}} = \sum_i F^{\text{hom}}(\bar{n}(\mathbf{R}_i)) + \frac{1}{2}\sum_{i \neq j}\int d\mathbf{r}\,d\mathbf{r}'\frac{\Delta\rho(\mathbf{r}-\mathbf{R}_i)\Delta\rho(\mathbf{r}'-\mathbf{R}_j)}{|\mathbf{r}-\mathbf{r}'|} \quad .$$

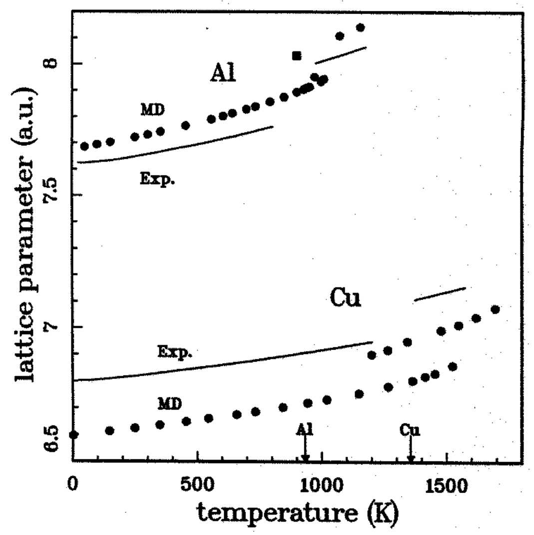
  - A density-dependent term and a pair potential term!
  - Changes in the single-electron states in the system ⇒ correction term $\Delta E_{1\text{el}}$.
    - Affects things mostly in the case of transition metals (unfilled d shell)

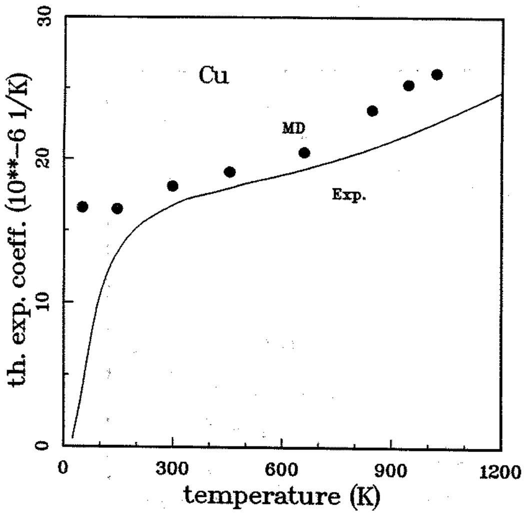
- As an example measured and simulated potentials for a few metals:



Effective medium theory

- As an example of an application to metals the properties of Al and Cu studied by constant pressure MD:





Embedded-Atom Method (EAM)

- The **EAM** method [Daw, Foiles and Baskes, *Mat. Sci. Rep.* **9** (1993) 251] is based on the same ideas as EMT.
  - The functional form has been deduced primarily semi-empirically and in part by fitting.
  - Despite its poorer physical motivation EAM usually works as well or better than EMT.
- The EAM total energy is written in the form

$$E_{\mathrm{tot}} = \sum_i F_i(\rho_i) + \frac{1}{2}\sum_{ij} V_{ij}(r_{ij}) \quad \text{(EAM 1)}$$

where

$\rho_i = \sum_{j \neq i} \rho_j^{\mathrm{a}}(r_{ij})$ is the electron density at atom i,

$\rho_j^{\mathrm{a}}(r)$ is the electron density of atom j and

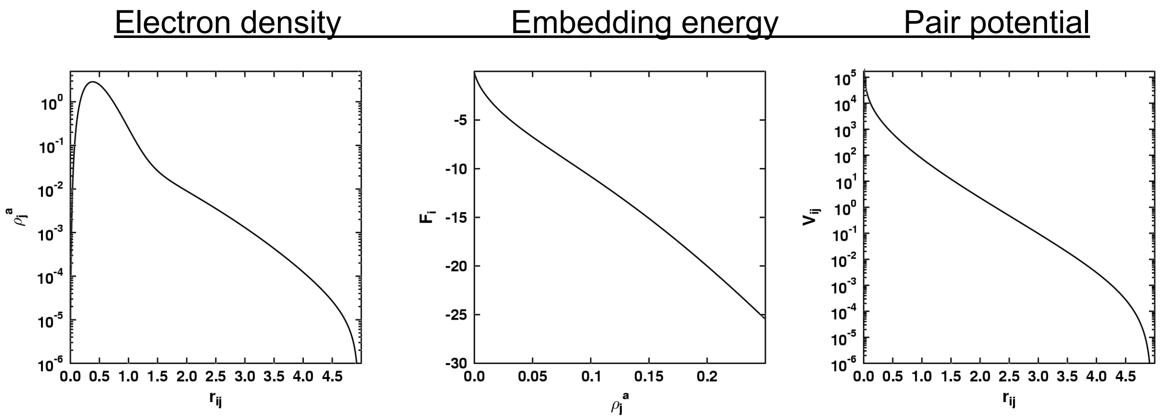
F_i is the embedding function.

Embedded-Atom Method (EAM)

- This resembles a lot the EMT total energy, the main difference being that the argument of F_i is the electron density in a given point.
  - Note that the embedding function F_i is universal in the sense that a same function can be used to embed the atom to different materials; material dependence only comes through the argument ρ.
  - Daw, Baskes and Foiles obtained the functions F_i and V_{ij} by fitting experimental results (lattice parameter, elastic constants, cohesive energy, vacancy formation energy and difference between fcc- and bcc- structures).

Embedded-Atom Method (EAM)

- Here is an example of all the terms in the original Foiles Cu EAM potential:



- Let’s compare the expression above with the general expression for a many-body potential given earlier:

$$V = \sum_{i} V_1(\boldsymbol{r}_i) + \sum_{i,j} V_2(\boldsymbol{r}_i, \boldsymbol{r}_j) + \sum_{i,j,k} V_3(\boldsymbol{r_i}, \boldsymbol{r_j}, \boldsymbol{r_k}) + \dots$$

  - V_{ij} is clearly a pair potential V_2 . But what is the embedding term?
  - The embedding term is easiest to understand as a pair potential whose strength is affected by the local environment: an **environment-dependent pair potential**.
  - It can not be directly written in the form shown above.
  - Maybe, by Taylor expansion, it could be done. (Haven’t tried it.) In that case the series in the above-mentioned would be infinite.

Embedded-Atom Method (EAM)

- The pair potential is further interpreted as

$$V_{ij}(r) = \frac{1}{4\pi\varepsilon_0}\frac{Z_i^a(r)Z_j^a(r)}{r}$$

where the $Z_i^a(r)$ are effective screened charges of the nuclei of atom type α.

  - This has the advantage that if instead of V_{ij} the $Z_i^a(r)$ are used as the starting point in evaluating the potential, forming the EAM potential for an alloy is straightforward:
    - The mixed V_{ij} is given by the equation above, and since $\rho_j^{\mathrm{a}}(r)$ only depends on the type of atom j and F_i on the type of atom i, the embedding term can also be evaluated directly for the mixture.

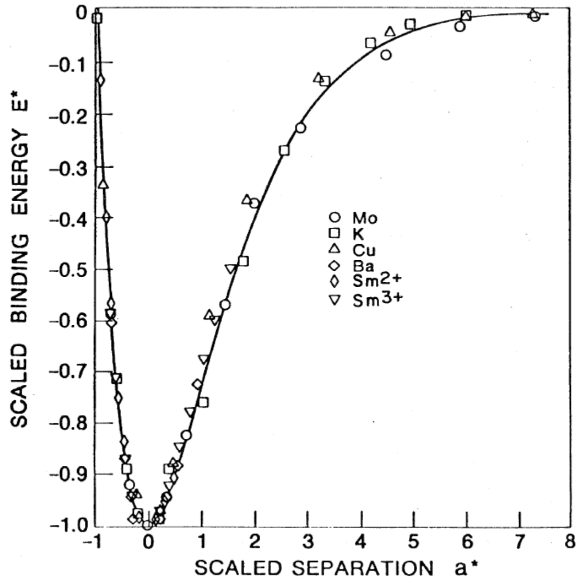
- The electron densities $\rho_j^{\mathrm{a}}(r)$ are obtained from modified HF electron densities for the outermost electrons of the material.

- In many cases the embedding function $F(\rho)$ is obtained by fitting to universal binding energy relation [Rose *et al.*, *Phys. Rev. B* **29** (1984) 2963.]:

$$E(a^*) = -E_{\mathrm{coh}}f(a^*)$$

$$f(a^*) = (1 + a^*)e^{-a^*}$$

$$a^* = \left(\frac{a}{a_0} - 1\right)\left(\frac{E_{\mathrm{coh}}}{9B\Omega}\right)^{-1/2}$$, B = bulk modulus, Ω = atomic volume



Embedded-Atom Method (EAM)

- So in practice the EAM potential has three 1-dimensional functions.
  - In analytical form or a set of points to be used with spline interpolation
  - The standard “Universal 3” format for elemental EAM potentials of Daw, Baskes and Foiles looks like:

```
Arbitrary comment line
Z1 m a latticename
nrho drho nr dr rcut
((nr points of F(rho) data))
((nr points of Z(r) data, V(r)=1/(4 pi epsilon_0) Z(r)^2/r))
((nrho points of rho data))
```

where `Z1` is the atomic number, m the mass and `a` the lattice constant.

  - A real example (Foiles Cu potential):

```
Cu functions (universal 3)
29      63.550         3.6150    FCC
500 5.0100200400801306e-04 500 1.0000000000000009e-02  4.9499999999999886e+00
0.
-3.1561636903424350e-01
-5.2324876182494506e-01
```

and so on, with 1497 more data points.

  - The advantage of using a code which reads this format is that any potential which can be given in the functional form (EAM 1) can then be made into a set of spline points and read into the code without any modifications necessary in the code itself.

Embedded-Atom Method (EAM)

- Non-uniqueness of EAM-like potentials: Note that in EAM-like potentials the division of the energy into the pair potential and embedding term is not unique.
  - In the formalism (EAM 1) one obtains the same total potential energy for any configuration with the transformation

    $$\begin{cases} V_{ij}(r) = V_{ij}(r) + 2\lambda\rho_j(r_{ij}) \\ F(\rho_i) = F(\rho_i) - \lambda\rho_i \end{cases}$$

    , where λ is an arbitrary real number.

- Forces in EAM (embedding part; force on atom k):

$$\mathbf{F}_k = -\nabla_k \sum_i F(\rho_i) = -\nabla_k \sum_i F\left(\sum_{j \neq i} \rho(r_{ij})\right)$$

$$= -\nabla_k F\left(\sum_{j \neq k} \rho(r_{kj})\right) - \nabla_k \sum_{i \neq k} F\left(\sum_{j \neq i} \rho(r_{ij})\right)$$

$$= -F'(\rho_k) \sum_{j \neq k} \rho'(r_{kj})\hat{\mathbf{r}}_{kj} - \sum_{i \neq k} F'(\rho_i)\rho'(r_{ik})\hat{\mathbf{r}}_{ki}$$

$$= -\sum_{i \neq k} [F'(\rho_k) + F'(\rho_i)]\rho'(r_{ik})\hat{\mathbf{r}}_{ki}$$

Glue models

- Like EAM but physical interpretation of the functions more or less thrown away
- For instance Ercolessi *et al.* gold potential: [*Phys. Rev. Lett.* **57** (1986) 719 , *Phil.Mag. A* **58** (1988) 213.]
  - Nearest neighbors only
  - Functions are usually polynomials
- In here instead of an embedding function a 'glue function' U is used, which depends on the atomic coordination

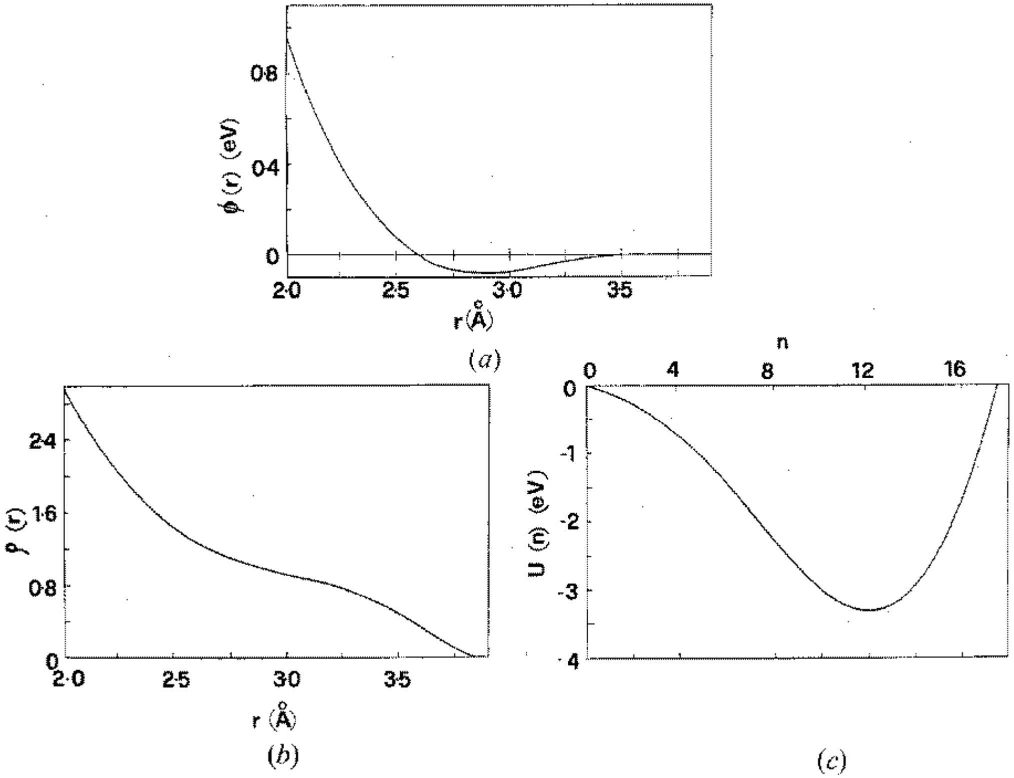
$$E_{\text{tot}} = \frac{1}{2}\sum_{i \neq j} \phi(r_{ij}) + \sum_{i} U(n_i) \quad ,$$

where

$$n_i = \sum_{i \neq j} \rho(r_{ij}) \quad .$$

Glue models

- Example: glue model for Au



The three functions $\phi(r)$ (*a*), $\rho(r)$ (*b*) and $U(n)$ (*c*) optimized for Au.

- Note that here the pair potential is no longer purely repulsive (Non-uniqueness of EAM-like potentials!)

Glue models

- A few properties of the potential:

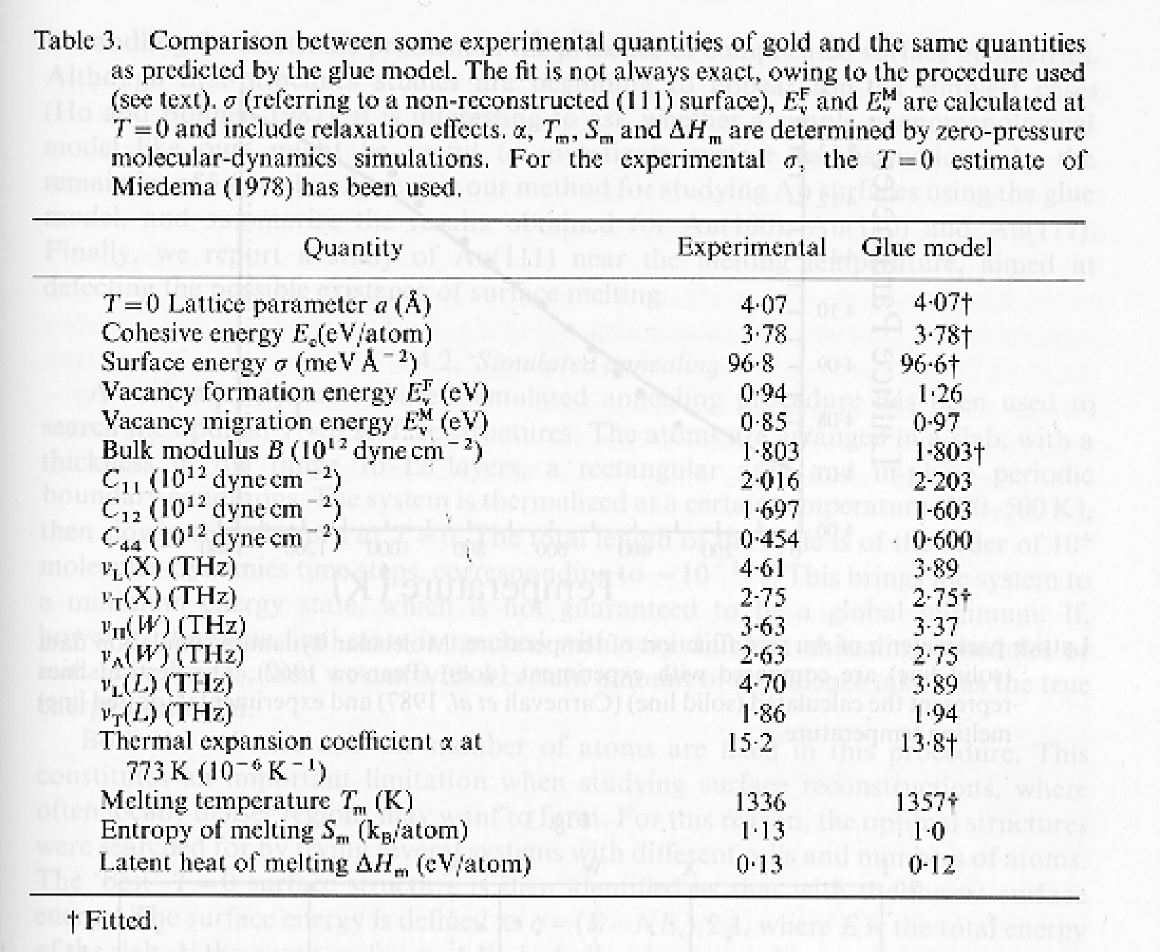
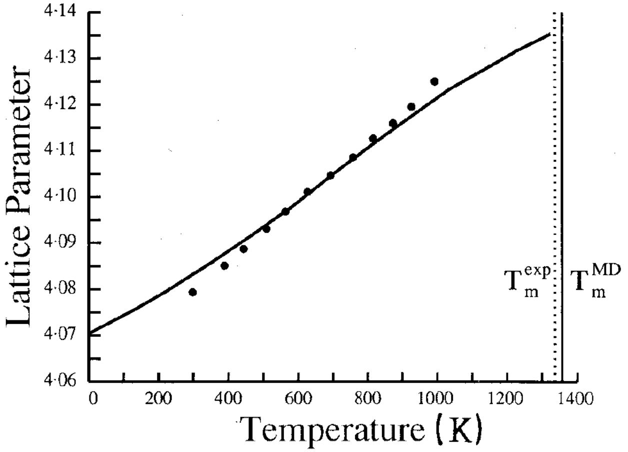


Table 3. Comparison between some experimental quantities of gold and the same quantities as predicted by the glue model. The fit is not always exact, owing to the procedure used (see text). σ (referring to a non-reconstructed (111) surface), E_v^F and E_v^M are calculated at $T=0$ and include relaxation effects. α, T_m, S_m and ΔH_m are determined by zero-pressure molecular-dynamics simulations. For the experimental σ, the $T=0$ estimate of Miedema (1978) has been used.

Quantity	Experimental	Glue model
$T=0$ Lattice parameter a (Å)	4·07	4·07†
Cohesive energy E_c(eV/atom)	3·78	3·78†
Surface energy σ (meV Å^{-2})	96·8	96·6†
Vacancy formation energy E_v^F (eV)	0·94	1·26
Vacancy migration energy E_v^M (eV)	0·85	0·97
Bulk modulus B (10^{12} dyne cm^{-2})	1·803	1·803†
C_{11} (10^{12} dyne cm^{-2})	2·016	2·203
C_{12} (10^{12} dyne cm^{-2})	1·697	1·603
C_{44} (10^{12} dyne cm^{-2})	0·454	0·600
$\nu_L(X)$ (THz)	4·61	3·89
$\nu_T(X)$ (THz)	2·75	2·75†
$\nu_{II}(W)$ (THz)	3·63	3·37
$\nu_A(W)$ (THz)	2·63	2·75
$\nu_L(L)$ (THz)	4·70	3·89
$\nu_T(L)$ (THz)	1·86	1·94
Thermal expansion coefficient α at 773 K (10^{-6} K^{-1})	15·2	13·8†
Melting temperature T_m (K)	1336	1357†
Entropy of melting S_m (k_B/atom)	1·13	1·0
Latent heat of melting ΔH_m (eV/atom)	0·13	0·12

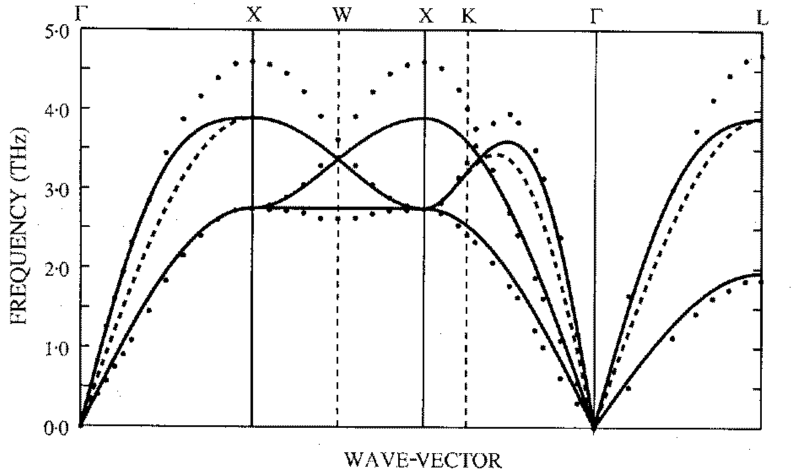
† Fitted.

- Thermal expansion from MD simulations



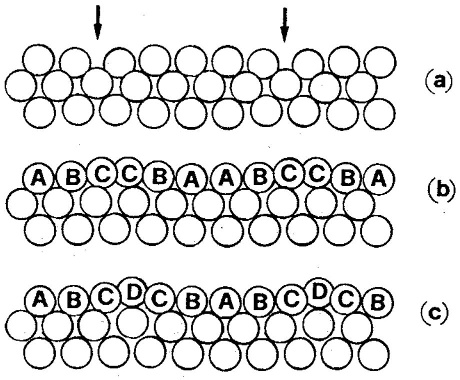
Glue models

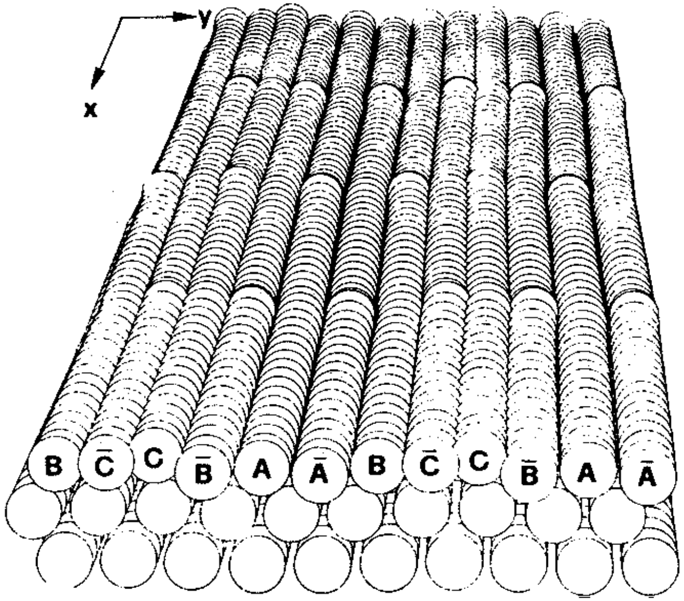
- Phonon dispersion relation:



points: experiment
solid line: with glue function
dashed line: without glue function

- Gold (100) surface reconstruction





Rosato group potentials

- The group of Rosato *et al.* (first ones by Cleri and Rosato) has formulated a large group of potentials based on the second-moment approximation of the tight-binding Hamiltonian (TB-SMA). [Cleri and Rosato, Phys. Rev. B **48** (1993) 22]:
  - The method starts from the knowledge that a large set of properties of transition metals can be derived purely from the density of states of the outermost *d* electrons:
  - The second moment of the density of states is μ_2 , and experimentally it has been found that the cohesive energy of metals is roughly proportional to the width of the density of states, which in the second-moment approximation is simply $\sqrt{\mu_2}$.
  - When only the ddσ, ddπ and ddδ orbitals are taken into account, the band-energy of atom i can according to the model be written as:

$$E_B^i = -\sqrt{\sum_j \xi^2 \exp\left[-2q\left(\frac{r_{ij}}{r_0} - 1\right)\right]}$$

which only depends on the distance and which formally is exactly the same as the $F(\rho)$ part of the EAM potentials (with the square root operation being the embedding function F).

Rosato group potentials

- In addition the model has a repulsive Born-Mayer-term:

$$E_R^i = \sum_j A \exp\left[-p\left(\frac{r_{ij}}{r_0} - 1\right)\right]$$

so the total energy of the system becomes

$$E_c = \sum_i (E_R^i + E_B^i)$$

- Here r_0 is the equilibrium distance between atoms, and A, ξ, p and q are fitted parameters. Despite its simple functional form, the model can be used to describe quite well elastic, defect and melting properties of a wide range of FCC- and HCP-metals.

- Later work in the Rosato group has given also extensions to alloys, e.g. [Mazzone *et al.*, Phys. Rev. B **55** (1997) 837].

- One practical caveat about the Cleri-Rosato potentials: at least in some of their papers they have been sloppy with factors of 1/2 and minus signs, you may have to correct these yourself.

Finnis-Sinclair potentials

- One more important group of EAM-like potentials are the so called Finnis-Sinclair potentials [*Phil.Mag. A* **50** (1984) 45; for an improvement see *Phil. Mag. A* **56** (1987) 15]. They model transition metals based on ideas derived from the tight binding method.

  - The form of a Finnis-Sinclair-potential is

$$E_{\text{tot}} = \frac{1}{2}\sum_{i \neq j} \phi(r_{ij}) - A\sum_{i} \sqrt{n_i} \quad ,$$

where

$$n_i = \sum_{i \neq j} \rho(r_{ij}) \quad .$$

i.e. this is the same functional form as in EAM where the embedding function is simply $F(n_i) = -A\sqrt{n_i}$. The square root function can be motivated by the tight-binding model, as in the Rosato potentials.

  - The potential parameters are obtained purely by fitting to experimental data.

Vacancy formation energy revisited

See e.g. Rob Phillips, *Crystals, Defects and Microstructures*.

- Definition of the formation energy:

$$E^{\mathrm{f}}_{\mathrm{vac}} = E_{\mathrm{tot}}(\mathrm{vacancy}, N) - E_{\mathrm{tot}}(\mathrm{perfect}, N)$$

- EAM-type potential

$$E_{\mathrm{tot}} = \sum_i F(\rho_i) + \frac{1}{2}\sum_{ij} V(r_{ij}),$$

$$\rho_i = \sum_{j \neq i} \rho^{\mathrm{a}}(r_{ij})$$

Remember pair potentials:

$$E_{\mathrm{tot}}(\mathrm{vacancy}, N) = \frac{1}{2}[(N-12)12\phi + 12(12-1)\phi] = 6(N-1)\phi$$

$$E_{\mathrm{tot}}(\mathrm{perfect}, N) = \frac{1}{2}N12\phi = 6N\phi$$

$$\Rightarrow E^{\mathrm{f}}_{\mathrm{vac}} = -6\phi = -E_{\mathrm{coh}}/\mathrm{atom}$$

- Perfect fcc lattice atoms, only NN interaction, equilibrium bond length r_0:

$$E_{\mathrm{tot}}(\mathrm{perfect}, N) = NF(12\rho_0) + \frac{1}{2}12N\phi = NF(12\rho_0) + 6N\phi$$

$$E_{\mathrm{tot}}(\mathrm{vacancy}, N) = (N-12)F(12\rho_0) + 12F(11\rho_0) + \frac{1}{2}[(N-12)12\phi + 12 \times 11\phi],$$

where $\rho_0 = \rho^{\mathrm{a}}(r_0)$, $\phi = V(r_0)$

$$\Rightarrow E^{\mathrm{f}}_{\mathrm{vac}} = 12[F(11\rho_0) - F(12\rho_0)] - 6\phi$$

Vacancy formation energy revisited

- Note that now cohesion energy per atom is

$$E_{\mathrm{coh}} = \frac{E_{\mathrm{tot}}(\mathrm{perfect}, N)}{N} = F(12\rho_0) + 6\phi \Rightarrow 6\phi = E_{\mathrm{coh}} - F(12\rho_0)$$

- Substitute 6ϕ in expression for $E^{\mathrm{f}}_{\mathrm{vac}}$

$$\Rightarrow \quad E^{\mathrm{f}}_{\mathrm{vac}} = 12F(11\rho_0) - 11F(12\rho_0) - E_{\mathrm{coh}}$$

NOTE: Pure pair potential means that $F(\rho) = \alpha\rho$, i.e. linearity $\Rightarrow$

$$E^{\mathrm{f}}_{\mathrm{vac}} = 12(11\alpha\rho_0) - 11(12\alpha\rho_0) - E_{\mathrm{coh}} = -E_{\mathrm{coh}}$$

Element	$\lvert E_{\mathrm{coh}}\rvert$ (eV)	$E^{\mathrm{t}}_{\mathrm{vac}}$ (eV)
V	5.31	2.1 ± 0.2
Nb	7.57	2.6 ± 0.3
W	8.90	4.0 ± 0.2

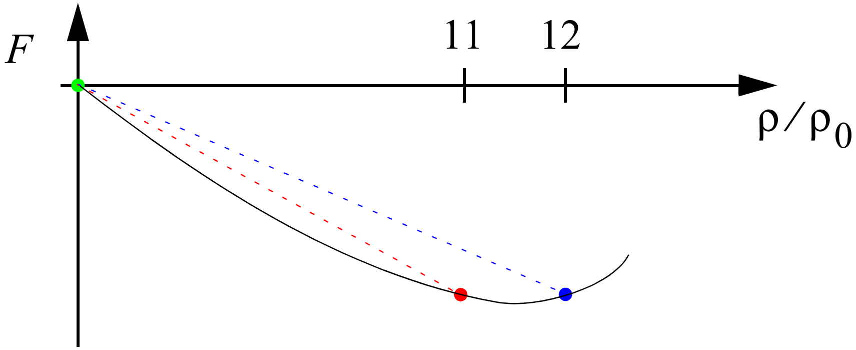
Typically for metals
$E_{\mathrm{vac}}/E_{\mathrm{coh}} = 0.2\ldots0.4$

Vacancy formation energy revisited

- So now we at least have $E_{\mathrm{vac}}^{\mathrm{f}} \neq -E_{\mathrm{coh}}$
- To have $E_{\mathrm{vac}}^{\mathrm{f}} < -E_{\mathrm{coh}}$ requires

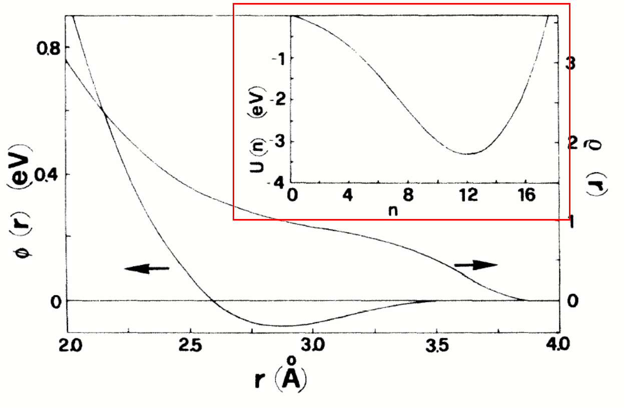
$$12F(11\rho_0) - 11F(12\rho_0) < 0 \Rightarrow \frac{F(11\rho_0)}{11} < \frac{F(12\rho_0)}{12},$$

i.e. positive curvature $\frac{d^2F}{d\rho^2} > 0$:

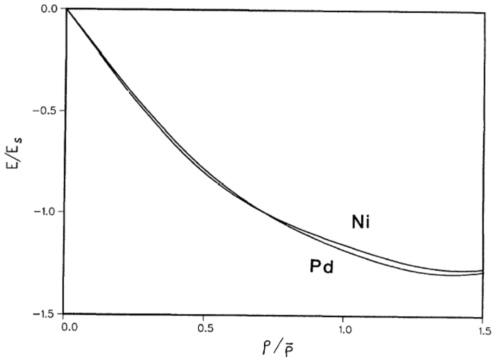


Vacancy formation energy revisited

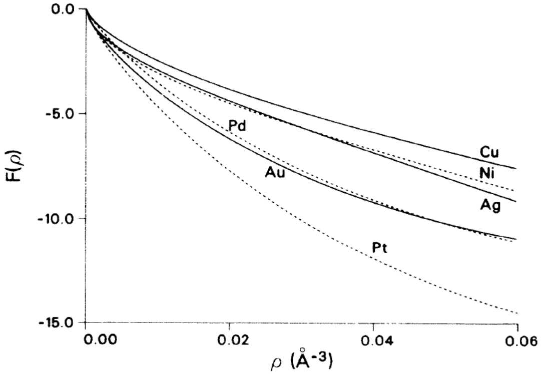
- Glue model for Au



Daw & Baskes for Ni, Pd



Foiles *et al.*



Some EAM-like potentials

- Below are listed some EAM potentials. It is impossible to list all of them, so this is just a list of some common ones.

- **FCC metals**
- **“Original” EAM**-potentials [S. M. Foiles, Phys. Rev. B **32** (1985) 3409; *ibid.* **33** (1986) 7983]:
  - Good potentials for Ni, Cu, Pd, Ag, Pt, Au and all dilute alloys of these. Good in many ways, surfaces the most commonly mentioned shortcoming. But surfaces tend to be a problem for most EAM potentials
  - Decent potential for Al.
  - Very widely used and tested, and almost no fatal shortcomings have been reported, so these can be used with good confidence.

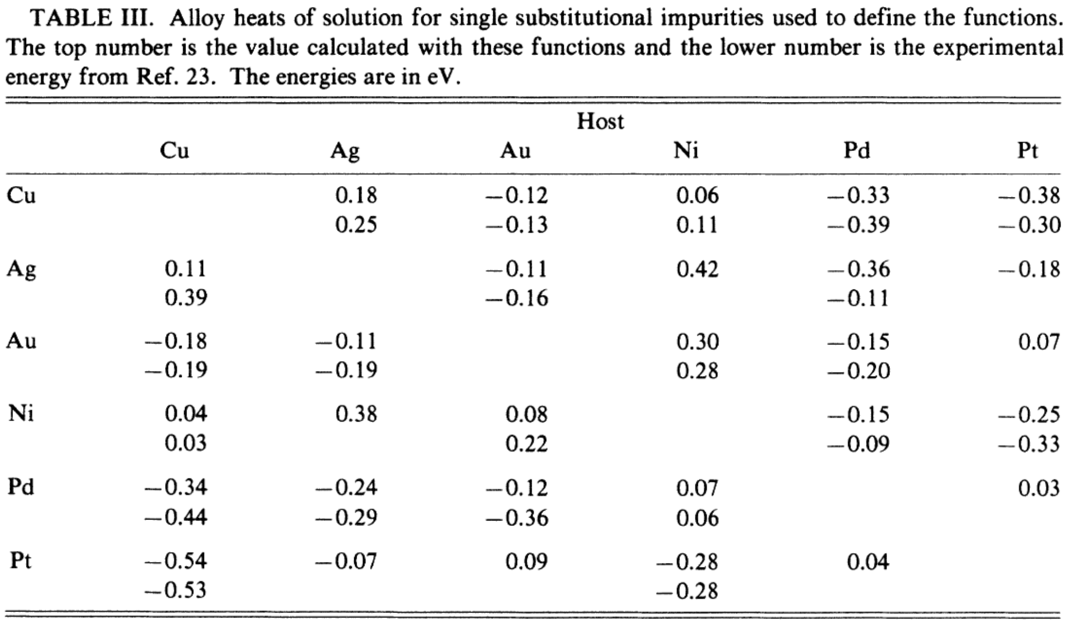


TABLE III. Alloy heats of solution for single substitutional impurities used to define the functions. The top number is the value calculated with these functions and the lower number is the experimental energy from Ref. 23. The energies are in eV.

			Host			
	Cu	Ag	Au	Ni	Pd	Pt
Cu		0.18 0.25	−0.12 −0.13	0.06 0.11	−0.33 −0.39	−0.38 −0.30
Ag	0.11 0.39		−0.11 −0.16	0.42	−0.36 −0.11	−0.18
Au	−0.18 −0.19	−0.11 −0.19		0.30 0.28	−0.15 −0.20	0.07
Ni	0.04 0.03	0.38	0.08 0.22		−0.15 −0.09	−0.25 −0.33
Pd	−0.34 −0.44	−0.24 −0.29	−0.12 −0.36	0.07 0.06		0.03
Pt	−0.54 −0.53	−0.07	0.09	−0.28 −0.28	0.04	

Foiles *et al.*, *Phys. Rev. B* **33** (1986) 7983.

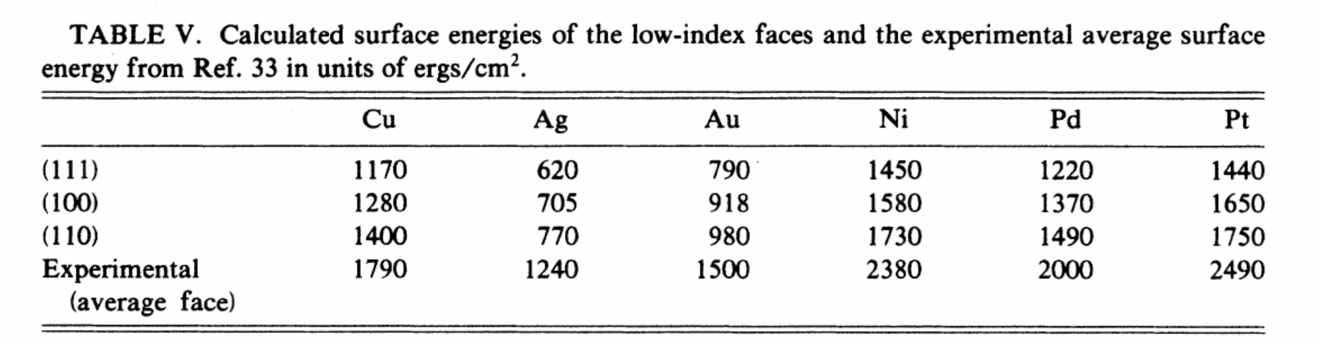


TABLE V. Calculated surface energies of the low-index faces and the experimental average surface energy from Ref. 33 in units of ergs/cm^2.

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

Some EAM-like potentials

- Glue potentials: [Ercolessi, Adams: Europhys. Lett. 26 (1994) 583]: good potentials at least for Au and Al.

- [Cai and Ye, Phys. Rev. B **54** (1996) 8398]: Alternative EAM potentials for Al, Ag, Au, Cu, Ni, Pd and Pt. May be better than original EAM in particular for alloys and surfaces.

- [Johnson, Phys. Rev. B **37** (1988) 3924]: Analytical EAM model for most FCC metals

- [Sabochick, Lam, Phys. Rev. B **43** (1991) 5243]: Potential for Cu, Ti and their compounds

- [Zhou, Johnson, Wadley, Phys. Rev. B 69 (2004) 144113]: EAM potentials for numerous metals that can be mixed for a huge number of alloys using a special mixing rule.

Some EAM-like potentials

- The Cu part of this potential seems to be very good for point defects
  [Nordlund and Averback, Phys. Rev. Lett. 80 (1998) 4201] (see on the right).
- [Voter and Chen, Mat. Res. Soc. Symp. Proc. **82** (1989) 175]: NiAl system potentials
- Cleri-Rosato parameters (see above) for FCC metals exist at least for Ni, Cu, Rh, Pd, Ag, Ir, Pt, Au, Al and Pb.
- [Ackland and Vitek, Phys. Rev. B **41** (1990) 10324]: EAM potentials for Cu, Ag, Au and alloys. Improvements in [Deng and Bacon, Phys. Rev. B **48** (1993) 10022].

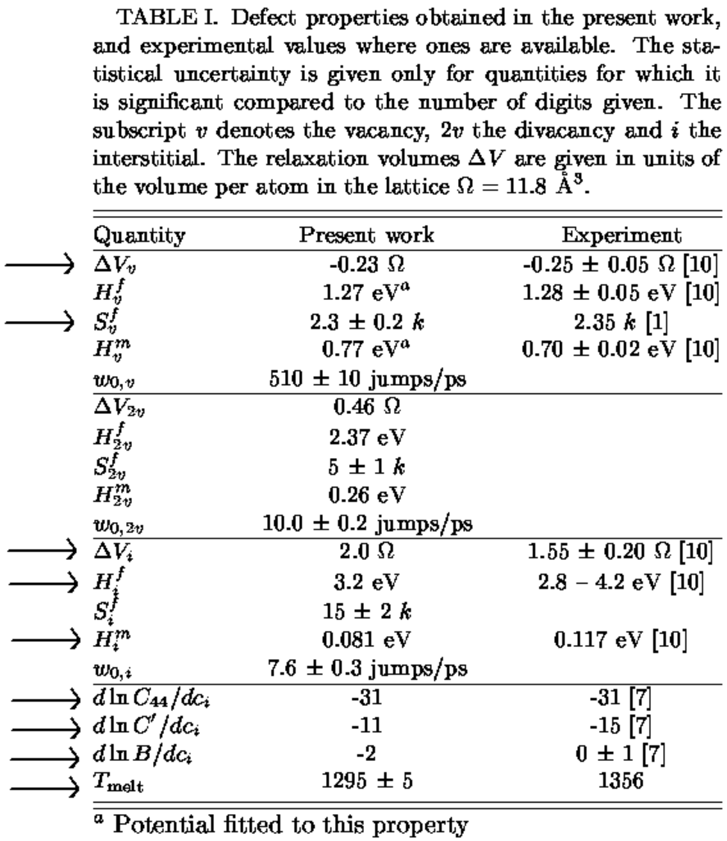


TABLE I. Defect properties obtained in the present work, and experimental values where ones are available. The statistical uncertainty is given only for quantities for which it is significant compared to the number of digits given. The subscript v denotes the vacancy, $2v$ the divacancy and i the interstitial. The relaxation volumes ΔV are given in units of the volume per atom in the lattice $\Omega = 11.8$ Å^3.

Quantity	Present work	Experiment
ΔV_v	-0.23 Ω	-0.25 ± 0.05 Ω [10]
H_v^f	1.27 eV^a	1.28 ± 0.05 eV [10]
S_v^f	2.3 ± 0.2 k	2.35 k [1]
H_v^m	0.77 eV^a	0.70 ± 0.02 eV [10]
$w_{0,v}$	510 ± 10 jumps/ps	
ΔV_{2v}	0.46 Ω	
H_{2v}^f	2.37 eV	
S_{2v}^f	5 ± 1 k	
H_{2v}^m	0.26 eV	
$w_{0,2v}$	10.0 ± 0.2 jumps/ps	
ΔV_i	2.0 Ω	1.55 ± 0.20 Ω [10]
H_i^f	3.2 eV	2.8 – 4.2 eV [10]
S_i^f	15 ± 2 k	
H_i^m	0.081 eV	0.117 eV [10]
$w_{0,i}$	7.6 ± 0.3 jumps/ps	
$d \ln C_{44}/dc_i$	-31	-31 [7]
$d \ln C'/dc_i$	-11	-15 [7]
$d \ln B/dc_i$	-2	0 ± 1 [7]
T_{melt}	1295 ± 5	1356

[a] Potential fitted to this property

Some EAM-like potentials

- **HCP-metals**

- Compared to both FCC and BCC metals, the HCP metals have been studied relatively little, both experimentally and with simulations.
- In fitting potentials for an HCP one should take care to ensure that the HCP phase is lower in energy than the FCC phase, and that one can obtain the required c/a ratio (which experimentally seldom equals exactly $\sqrt{8/3}$, which is the “ideal” value calculated for close packing of hard spheres)
- In addition there are 5 elastic constants, rather than 3 as in cubic metals.

- Pasianot and Savino [Phys. Rev. B **45** (1992) 12704] have made EAM-like potentials for HCP-metals Hf, Ti, Mg and Co. But they also showed that an EAM-like model **can not** reproduce all elastic constants correctly for those HCP metals which have

$$c_{13} - c_{44} < 0 \quad \text{or} \quad \frac{1}{2}(3c_{12} - c_{11}) < c_{13} - c_{44}$$

  - Such metals are e.g. Be, Y, Zr, Cd and Zn.

- Cleri and Rosato (see above) derive parameters for the HCP metals Ti, Zr, Co, Cd, Zn and Mg.

- Oh and Johnson [J. Mater. Res. **3** (1988) 471] have also put their fingers here, for the HCP metals Mg, Ti and Zr.

Some EAM-like potentials

- **BCC-metals**

- When one constructs potentials for BCC metals, one has to take into account that the BCC structure is not closed packed. A pair potential would most likely make the BCC phase unstable compared to FCC and HCP, unless carefully constructed. Or one can attain unwanted effects such as a negative thermal expansion.

- In BCC metals the Finnis-Sinclair potentials (see above) have been much used. Originally they were formulated at least for Fe, V, Nb, Ta, Mo and W. In the five latter ones serious problems were later found, which were corrected in [Ackland and Thetford, Phil. Mag. A **56** (1987) 15].

- Johnson and Oh [J. Mater. Res. **4** (1989) 1195] have been active in BCC as well. They derived potentials at least for Li, Na, K, V, Nb, Ta, Cr, Mo, W and Fe.

- But in BCC metals one should take into account the recent theoretical work which showes that in them 4-body interactions can have an important role, and these can of course not be described well by EAM-like potentials [J. A. Moriarty, Phys. Rev. B **42** (1990) 1609].
  - Moriarty has developed 4-body potentials at least for a few metals [e.g. Phys. Rev. B **49** (1994) 12431]. These have shown for instance that the migration energies of the Finnis-Sinclair model are probably 3-15 times too large [Phys. Rev. B **54** (1996) 6941].

Some EAM-like potentials

- **Metal-hydrogen potentials**

- Finally, we mention that it is possible to construct a somewhat sensible EAM-like potential for metal-hydrogen interactions. Of course these can not describe delocalized hydrogen in metals, but they can still reproduce well e.g. the cohesive and migration energy of hydrogen in solid metals and hydrogen on solid surfaces.

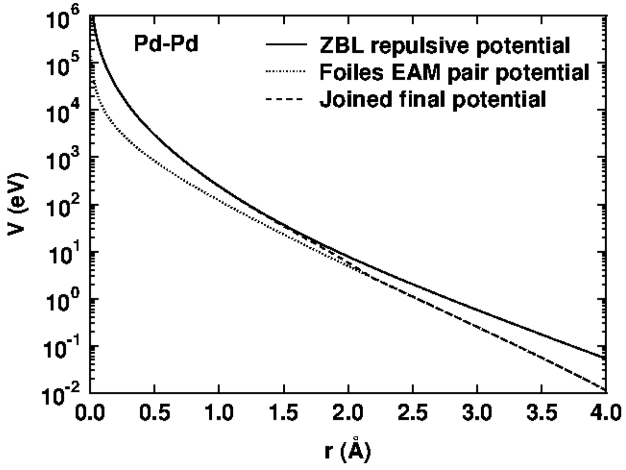
- Just one example: [Rice *et al.*, J. Chem. Phys. **92** (1990) 775]; EAM potential for Ni-H.

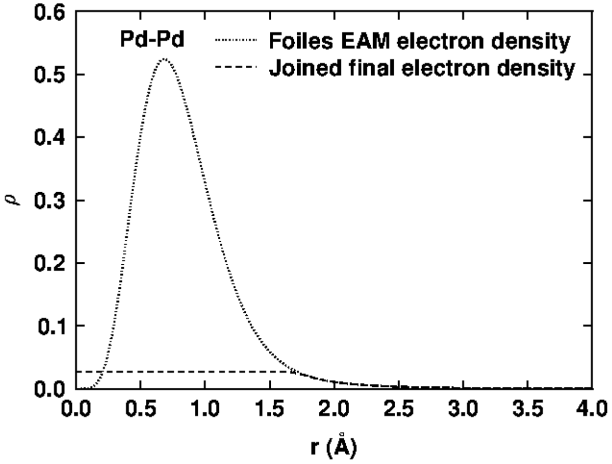
Fitting a repulsive potential to EAM models.

- When one wants to describe high-energy processes (E_{kin} > 10 eV) one almost always has to modify the repulsive part of the potential. One can for instance use the so called ZBL universal potential for this, which describes the repulsive part with ~ 10 % accuracy for all material combinations, or even better an accurate potential derived from *ab initio* - calculations.

- A special feature for EAM-like potentials is that one still has to remember that the electron density has to be set to a constant value in the same r range where the high-energy repulsive potential is fit to the pair potential part.

- Example: fitting the Foiles Pd-potential to the ZBL repulsive potential. With the same fit also the high-pressure properties and melting point of the potential was obtained almost exactly right, whereas the properties of the interstitial atom became worse. [Nordlund *et al.*, Phys. Rev. B **57** (1998) 13965].



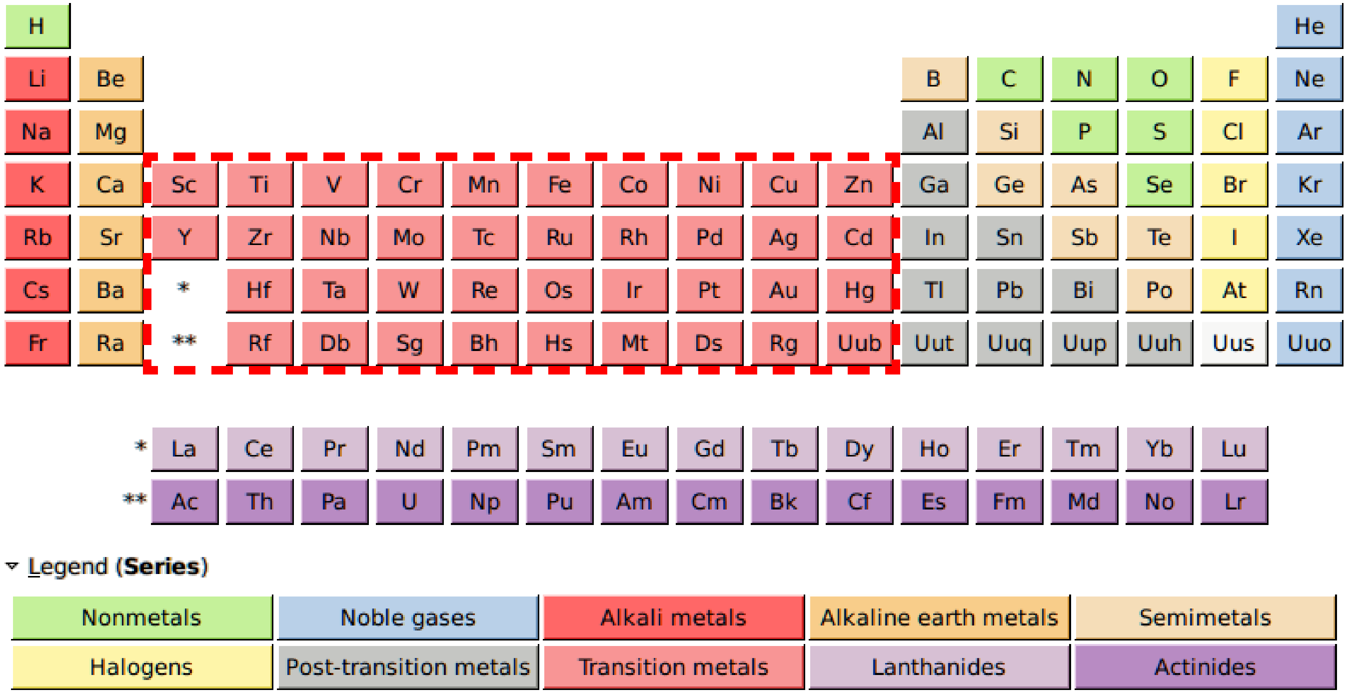


Two-band EAM model

- EAM is often used to model transition metals:
  - Their bonding is characterized by the free-electron-like s orbital and the narrow d orbital.
  - In the original EAM potential the effect of these two orbitals was taken into account by assuming the electron density be a sum of contributions from s and d shells:

$$\rho^{a}(r) = n_s\rho_s(r) + n_d\rho_d(r) .$$

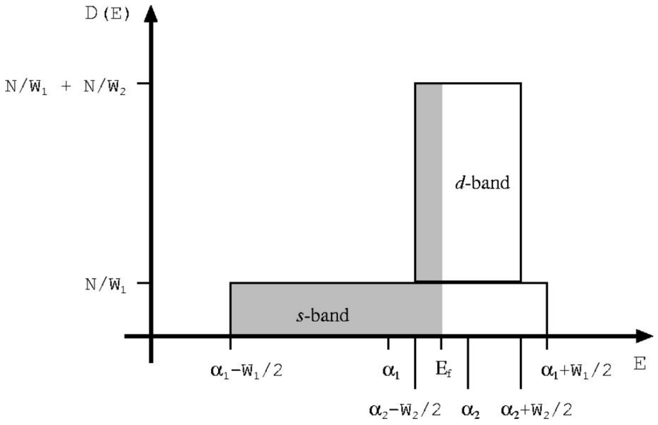
  - The ‘occupations’ n_s and n_d were obtained by e.g. fitting to H heat of solution or such.



H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	**	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub	Uut	Uuq	Uup	Uuh	Uus	Uuo
	*	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
	**	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

▿ Legend (**Series**)

Nonmetals	Noble gases	Alkali metals	Alkaline earth metals	Semimetals
Halogens	Post-transition metals	Transition metals	Lanthanides	Actinides



G.J.Ackland, S.K.Reed, *Phys. Rev.* **B 67** (2003) 174108.

Two-band EAM model

- In the two-band EAM model the s and d orbitals (or bands) are explicitely taken into account.
  - Energy of atom i is written as

$$E_i = F_d(\rho_{i,d}) + F_s(\rho_{i,s}) + \frac{1}{2}\sum_j V(r_{ij}),$$

where $\rho_{i,b} = \sum_j \phi_b(r_{ij})$ is the electron density contribution from band b.

  - The original formulation of the EAM model in the form of fitting the s band density
  - A two-band EAM potential has been developed for elemental caesium [G.J.Ackland et al., *Phys. Rev. B* **67** (2003) 174108.] and for the binary alloy FeCr [P.Olsson et al., *Phys. Rev. B* **72** (2005) 214119.]
  - For many transition metals the cohesion is determined mainly by the d band but the s band affects the elastic properties by providing repulsion.
  - On the other hand for alkali and alkaline-earth metals are normally close-packed metals with bonding determined by the s electrons.
    - However, at large pressures electrons are transferred to d band which is — although higher in energy — more compact, allowing lower atomic volumes.
  - With these models the isostructural transition of Cs and the thermodynamical properties of Fe-Cr alloy were reasonably described.