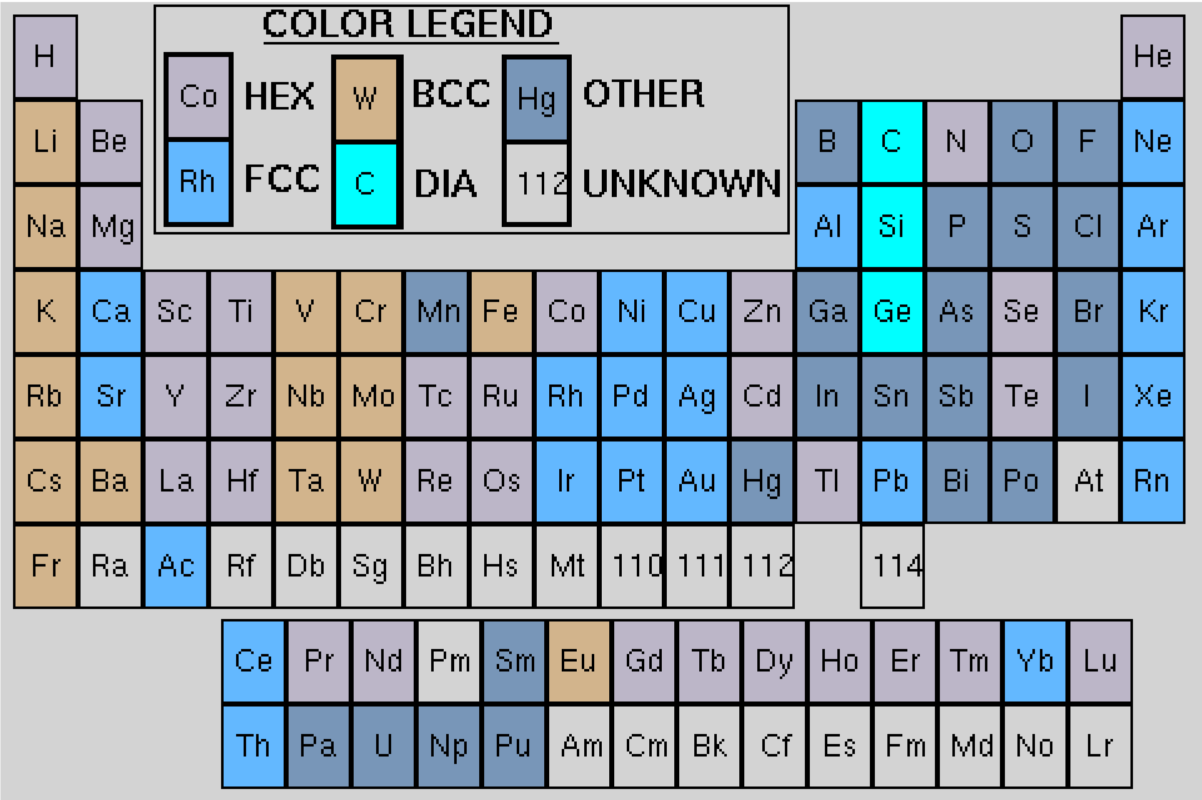
Classical potentials for metals

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

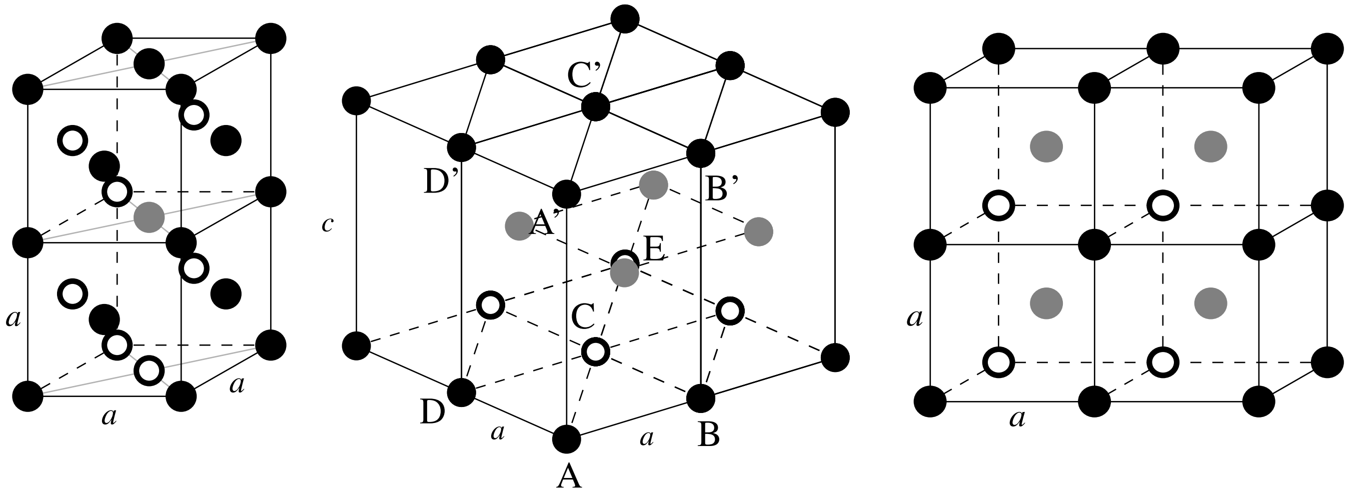


FCC	15
HCP	26
BCC	16
All other metals	13

So 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.

The crystal structures are as follows:

FCC (2 unit cells) **HCP (4 unit cells)** **BCC (4 unit cells)**



FCC	Face-Centered Cubic	close packed
HCP	Hexagonal Close-Packed	close packed
BCC	Body-Centered Cubic	not close packed

FCC: cubic unit cell, atoms at the corners of the cube and in the center of each side face
HCP: Unit cell formed by polyhedron bounded by atoms ABCDA’B’C’D’ in figure above. angle between x and y unit cell axes is 120^{o} . One atom at each corner of the unit cell, one (atom E) above the middle of the triangle ABC.
BCC: cubic unit cell, atoms at the corners of the cube and in the center of the cube

- FCC and HCP are both close packed, and can easily be stabilized with pair potentials (although getting the small HCP-FCC energy difference right is a bit tricky and requires a fairly long range for the potential). But as we discussed in lecture 5, there should be better models than pair potentials even for these.

- During this lecture we first go through the physical basis of some many-body potentials, then list a few common potentials and describe where they are applicable.

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

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

  where F is a function of the electron density, and Φ is a (usually purely repulsive) pair potential. The potential is sort of a generalization of the basic idea of DFT: that the 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, while in practice they are constructed purely by fitting.

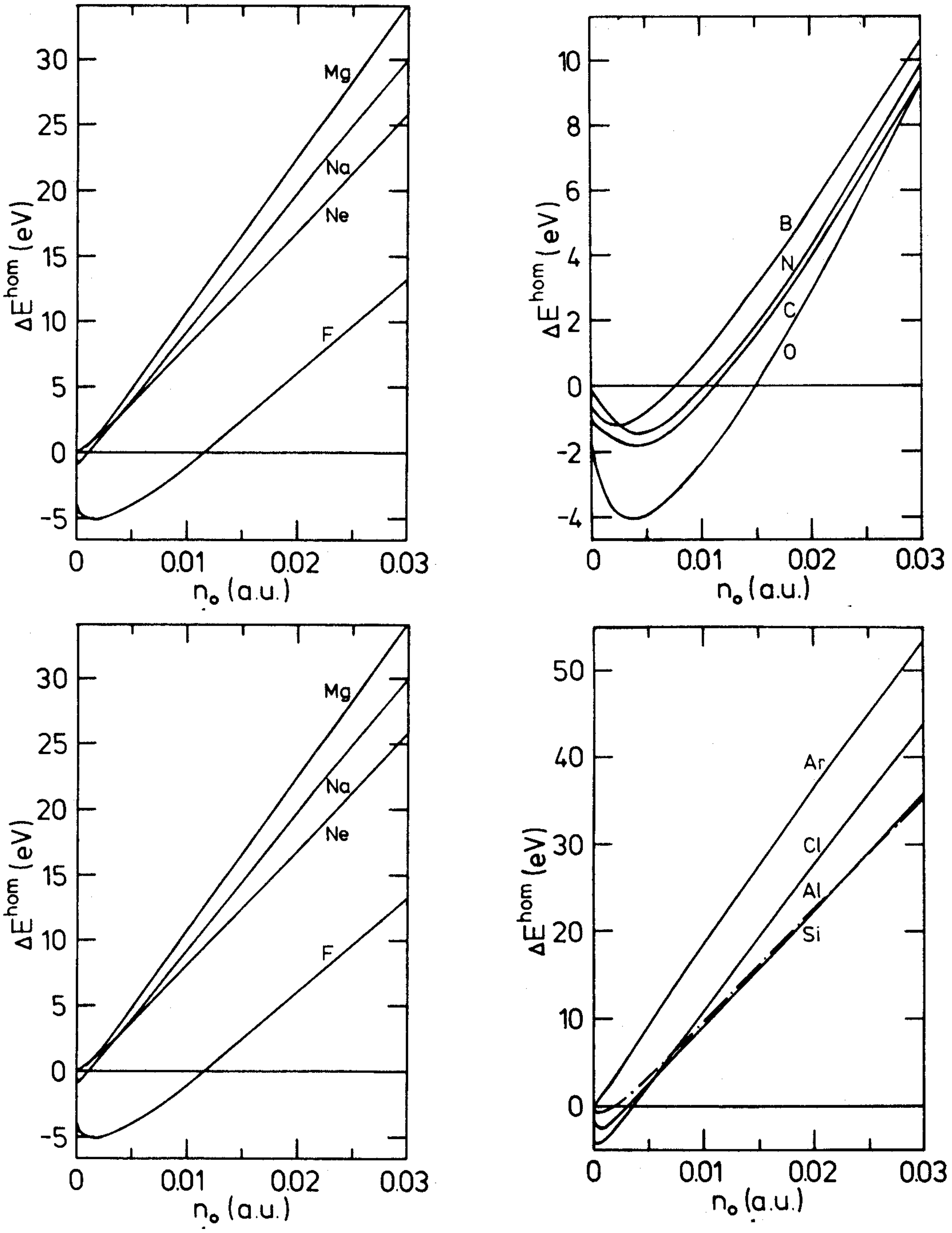
- In EMT the real material is imagined to be replaced by *jellium* (the name derives from “jelly”) which consists of a homogeneous electron gas, formed by the free electrons of the metal. The metal ions are imagined to be replaced by a constant positive background density.

- 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 $\mathbf{r}$.

- The embedding energy $\Delta E^{\mathrm{hom}}(n)$ 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 $\Delta E^{\mathrm{hom}}(n)$ 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.

- 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

$$E_{\mathrm{tot}}^{N} = E_{R}^{N}[n] \quad ,$$

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

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

where n_i is the electron density in the system *after* atom i has been removed. The idea in EMT is that both E_{tot}^{N} and E_{tot}^{N-1} can be stated as a functional of the same electron density n_i. This is motivated by DFT.

- The energy of the whole atom system can be stated as

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

- 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

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

Here in sums with many indices the terms with at least two same indices are left out. In each sum the terms in which some atom pair is far from each other are small, so the sums converge rapidly.

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

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

- 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

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

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

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

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

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

where

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

- So in this simple expression a pair potential is completely missing. It 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 $\delta v^{\mathrm{ext}}(\mathbf{r})$. 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

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

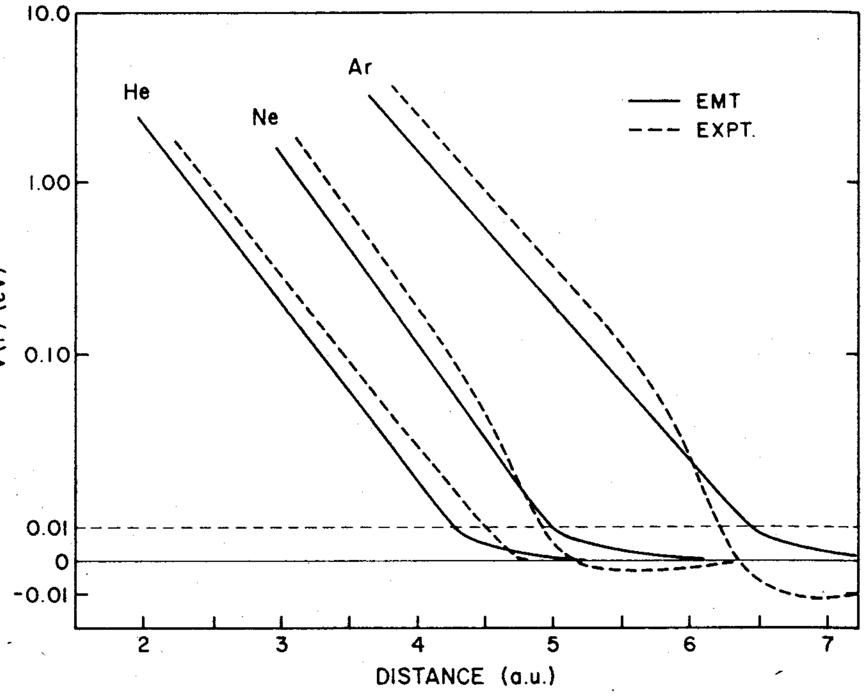
- Now the total energy of the system is of the form

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

So the energy has a density-dependent term and a pair potential term.

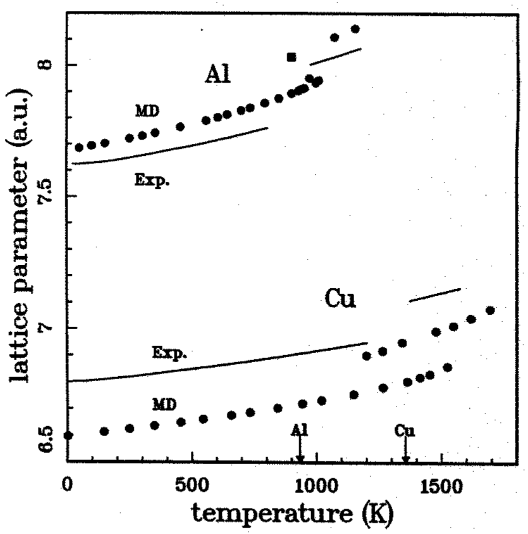
It is also possible to take into account changes in the single-electron states in the system, which gives a correction term $\Delta E_{1\text{el}}$. This affects things mostly in the case of transition metals, in which the partially filled d-shell electrons have a crucial role on the bonding.

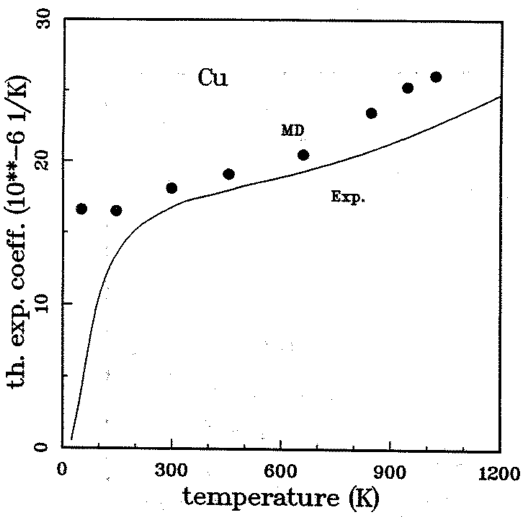
- As an example measured and simulated potentials for a few metals:



Note that EMT/DFT does not reproduce at all the attractive part of the potential, which does exist in the experiments.

- 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 basic form of the potential is practically the same as in EMT, but the functional form has been deduced primarily semi-empirically and in part by fitting., and not by direct derivation as in EMT. Despite its poorer physical motivation EAM usually works as well or better than EMT, and various EAM potentials are very popular for describing a wide range of materials.

- The EAM total energy is written in the form

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

  where

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

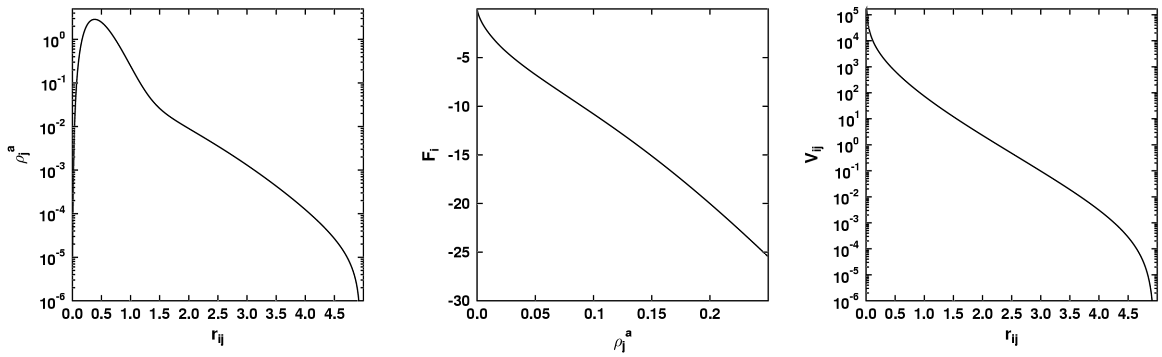
  $\rho_j^{\mathrm{a}}(r)$ is the electron density of atom j and

  F_i is the embedding function.

- 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. 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).

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

Electron density　　Embedding energy　　Pair potential



- To digress from the main discussion for a moment, 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. So an EAM potential can be understood as an **environment-dependent pair potential,** although it could also be rewritten in an explicit three-body potential form:

$$\begin{aligned} E_{\text{tot}} &= \sum_i F_i\left(\sum_{j \neq i} \rho_j^{\text{a}}(r_{ij})\right) + \frac{1}{2}\sum_{ij} V_{ij}(r_{ij}) && \text{2-body form} \\ &= \sum_{ij} \delta_{ij} F_i\left(\sum_{k \neq i} \rho_k^{\text{a}}(r_{ik})\right) + \frac{1}{2}\sum_{ij} V_{ij}(r_{ij}) && \text{3-body form} \end{aligned}$$

where δ_{ij} is the Kronecker delta. But using the 3-body form would of be ridiculously inefficient and hence never done in practice.

- The pair potential is further interpreted as

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

where the $Z^a(r)$ are effective screened charges of the nuclei of atom type a. This has the advantage that if instead of V_{ij} the $Z^a(r)$ 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 $\rho_j^{\text{a}}(r)$ 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 $\rho_j^{\text{a}}(r)$ are obtained from modified HF electron densities for the outermost electrons of the material.

- So in practice the EAM potential has three 1-dimensional functions. These can of course have an analytical form, but many authors, including Daw, Baskes and Foiles, only give the data as a set of points and then use spline interpolation [Numerical Recipes] to get each term efficiently.

  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.

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.

Glue models

- In the so called glue models the function form and the practical evaluation of the potential is exactly as in EAM, but the derivation is partly based on DFT.

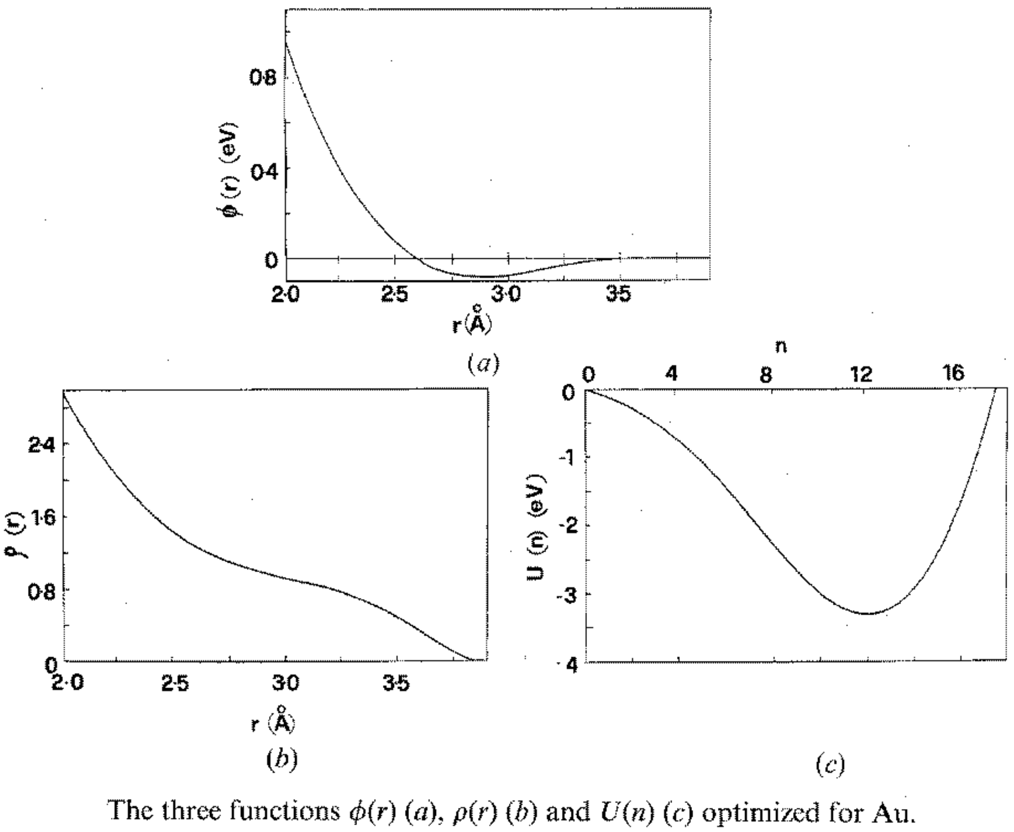
- For instance Ercolessi *et al.* gold potential: [*Phys. Rev. Lett.* **57** (1986) 719 , *Phil.Mag. A* **58** (1988) 213.]

- 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

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



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.

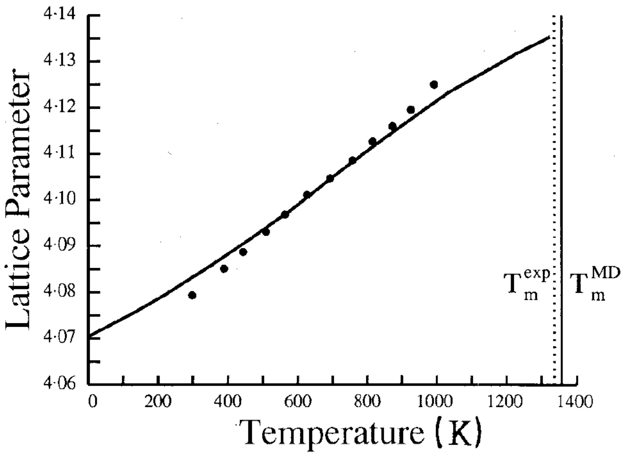
A few properties of the potential:

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
ν_L(X) (THz)	4·61	3·89
ν_T(X) (THz)	2·75	2·75†
ν_{II}(W) (THz)	3·63	3·37
ν_A(W) (THz)	2·63	2·75
ν_L(L) (THz)	4·70	3·89
ν_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

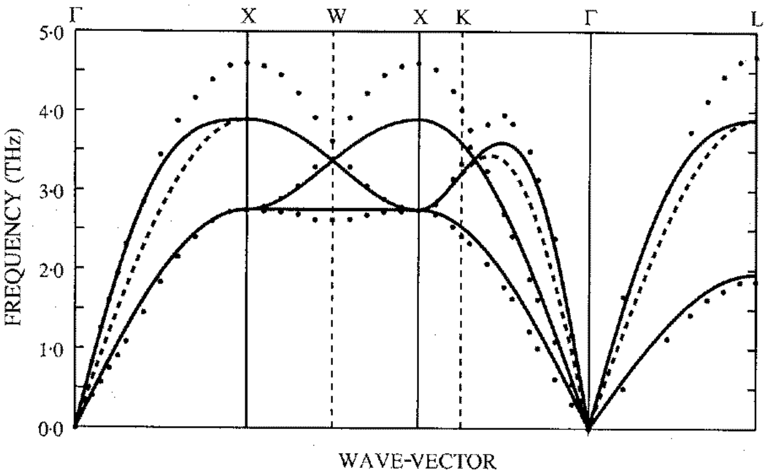
† Fitted.

Lattice parameter from MD simulations:

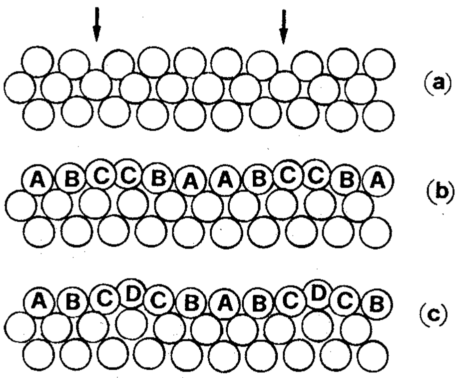


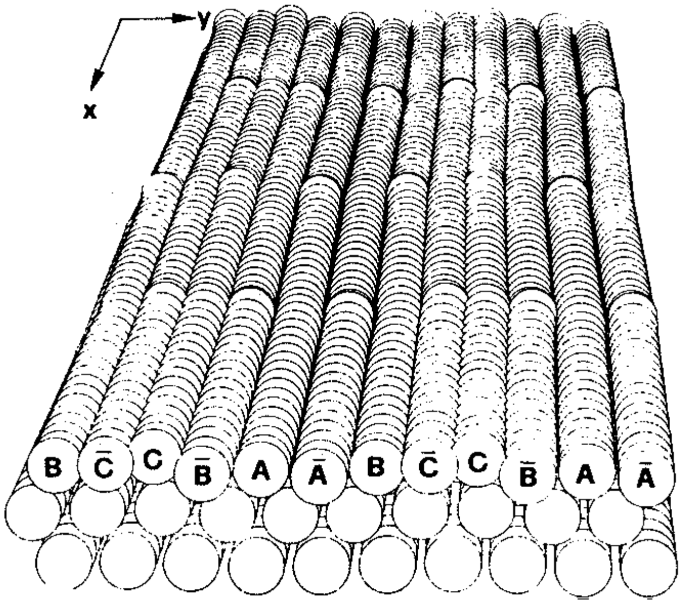
Phonon dispersion relation:

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). These potentials are often also called SMA or TB-based potentials [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:

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

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

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

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

  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 (yes, we did find this out he hard way).

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

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

where

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

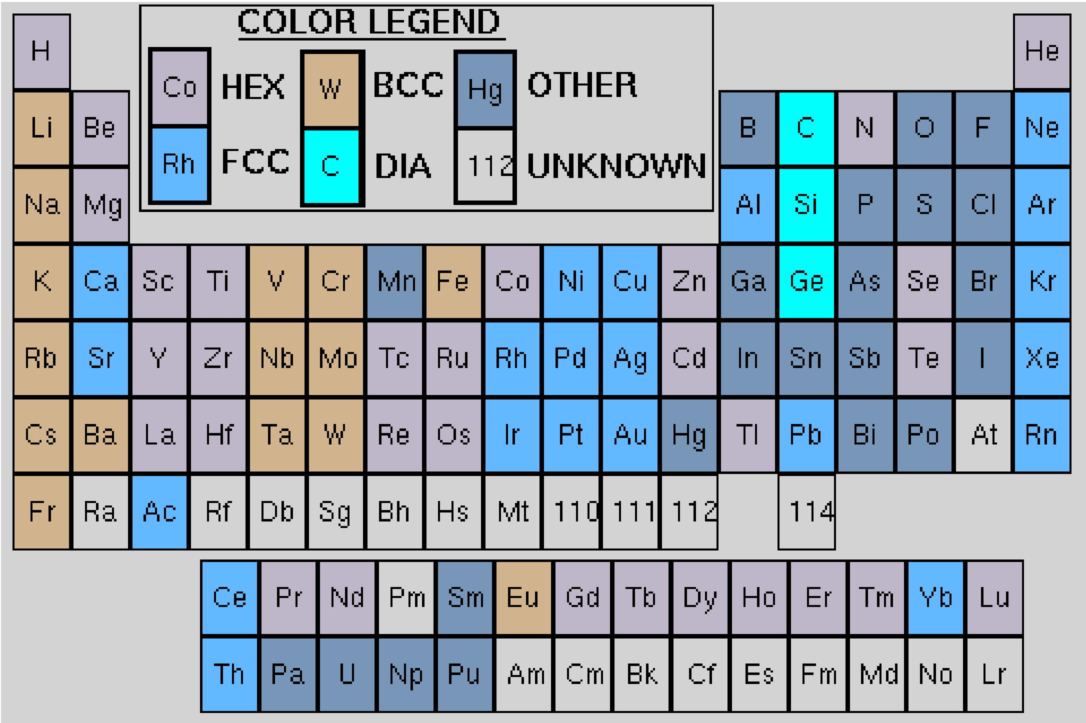
i.e. this is the same functional form as in EAM where the embedding function is simply $F(n_i) = -A\sqrt{n_i}$. The square root function can be motivated by the tight-binding model, as in the Rosato potentials.

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

Some EAM-like potentials

- Below I list some EAM potentials. So many exist by now that it is impossible to list all of them, so this is just a list of some common ones the lecturer has happened to run across. The point is not that you should learn these by heart, but can use this list as a starting point if you need to simulate a metal.

  Some of the notes below are really only understandable if you have good knowledge of condensed matter physics - but such issues will not be asked in the exam, so do no despair even if you do not understand everything.



FCC metals

- "**Original**" **EAM**-potentials [S. M. Foiles, Phys. Rev. B **32** (1985) 3409; *ibid.* 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.

- 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

  The Cu part of this potential seems to be very good for point defects [Nordlund and Averback, Phys. Rev. Lett. **80** (1998) 4201]:

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 $\pm$ 0.05 Ω [10]
H_v^f	1.27 eV^a	1.28 $\pm$ 0.05 eV [10]
S_v^f	2.3 $\pm$ 0.2 k	2.35 k [1]
H_v^m	0.77 eV^a	0.70 $\pm$ 0.02 eV [10]
$w_{0,v}$	510 $\pm$ 10 jumps/ps	
ΔV_{2v}	0.46 Ω	
H_{2v}^f	2.37 eV	
S_{2v}^f	5 $\pm$ 1 k	
H_{2v}^m	0.26 eV	
$w_{0,2v}$	10.0 $\pm$ 0.2 jumps/ps	
ΔV_i	2.0 Ω	1.55 $\pm$ 0.20 Ω [10]
H_i^f	3.2 eV	2.8 – 4.2 eV [10]
S_i^f	15 $\pm$ 2 k	
H_i^m	0.081 eV	0.117 eV [10]
$w_{0,i}$	7.6 $\pm$ 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 $\pm$ 1 [7]
T_{melt}	1295 $\pm$ 5	1356

^{a} Potential fitted to this property

- [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.

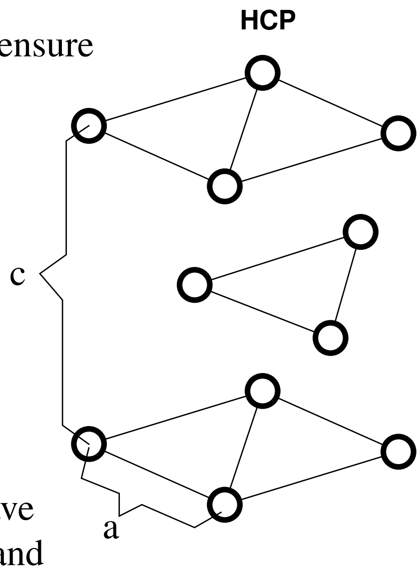
- [Ackland and Vitek, Phys. Rev. B **41** (1990) 10324]: EAM potentials for Cu, Ag, Au and alloys. Improvements in [Deng and Bacon, Phys. Rev. B **48** (1993) 10022].

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

$$C_{13} - C_{44} < 0 \quad \text{or} \quad 1/2\,(3\,C_{12} - C_{11}) < C_{13} - C_{44}\,.$$

  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.

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].

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].