Acquisition of Diffusion Data from Ab Initio

Comments on a "Good Usage" of the Pseudo-potential Method

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What Are We Talking About?

There is a suite of popular pseudo-potential codes available:

Abinit – www.abinit.org
Pseudo-potentials and plane-wave basis set

CAMPOS – www.fysik.dtu.dk/CAMP/CAMPOS_welcome.html
Pseudo-potentials and plane-wave basis set.

CASTEP – www.tcm.phys.cam.uk/castep
Pseudo-potentials and plane-wave basis set

FHI96MD – www.fhi-berlin.mpg.de/th/fhimd
Pseudo-potentials and plane-wave basis set,
with molecular dynamics capabilities based on the Car-Parrinello technique

PWSCF – www.pwscf.org
Pseudo-potentials and plane-wave basis set.
DFT codes include response function (phonon) features.

Quantum Expresso – www.democritos.it/scientific.php
Pseudo-potentials and LCAO basis set.
Open-source package for research in electronic structure, simulation, and optimization.

SIESTA – www.uam.es/depatamentos/ciencas/fismateriac/siesta
Pseudo-potentials and LCAO basis set

VASP – www.mpi.univie.ac.at/vasp
Pseudo-potentials and plane-wave basis set

What Are We Talking About?

The recommended standard potentials were used; **in a few cases we opted for harder potentials with semicore states treated as valence states**, Bi_d, Ga_d, Ge_d, Hf_pv, Li_sv, Mo_pv, Nb_pv, Pb_d, Sc_sv, Sn_d, Sr_sv, Ta_pv, Ti_sv, W_pv, Y_sv, and Zr_sv. For the lanthanides **we selected potentials with three f-like electrons treated as core states, Ce, Er, Gd, Ho, Lu, Nd, Pm, Pr, Sm, Tb, and Tm, or two f-like electrons treated as core states, Eu**.

DFT, VASP-PAW-GGA

D. Simonovic and M.H.F. Sluiter, “Impurity diffusion activation energies in Al from first principles”, Phys. Rev. **B79**, 054304 (2009).

For the first-principles calculations we use the Vienna *ab initio* simulation package VASP with projector augmented wave (PAW) potentials. **The potentials used for each of the elements Al, Mg, Si and Cu do not treat any semi-core states as valence**.

DFT, VASP-PAW-LDA/GGA

M. Mantina, Y. Wang, L.Q. Chen, Z.K. Liu, and C. Wolverton “First-principles impurity diffusion coefficients”, Acta Materialia **57**, 4102 (2009).

We used the Vienna *ab initio* Software Package (VASP)to perform DFT calculations with the generalized gradient approximation (GGA) as parametrized by Perdew, Burke, and Ernzerfhof (PBE) for the exchange-correlation functional. **Inadequate repulsion between Zn 3d and conduction-band levels in GGA calculations results in a significantly underestimated band gap**. We partially corrected this by using the GGA+U correction with a value of U–J =7. 5 eV **so that the valence-band and Zn 3d energy levels match experiments and self-interaction corrected calculations.** We used projector-augmented plane-wave (PAW) pseudopotentials **with valence configuration 3d 10, 4s 2 for Zn, 2s 2 2p 4 for O, and 4s 2 4p 3 for As, and a plane-wave energy cutoff of 600 eV.**

DFT, VASP-PAW-GGA+U

B. Puchala and D. Morgan, “Atomistic modeling of As diffusion in ZnO”, Phys. Rev. **B85**, 064106 (2012).

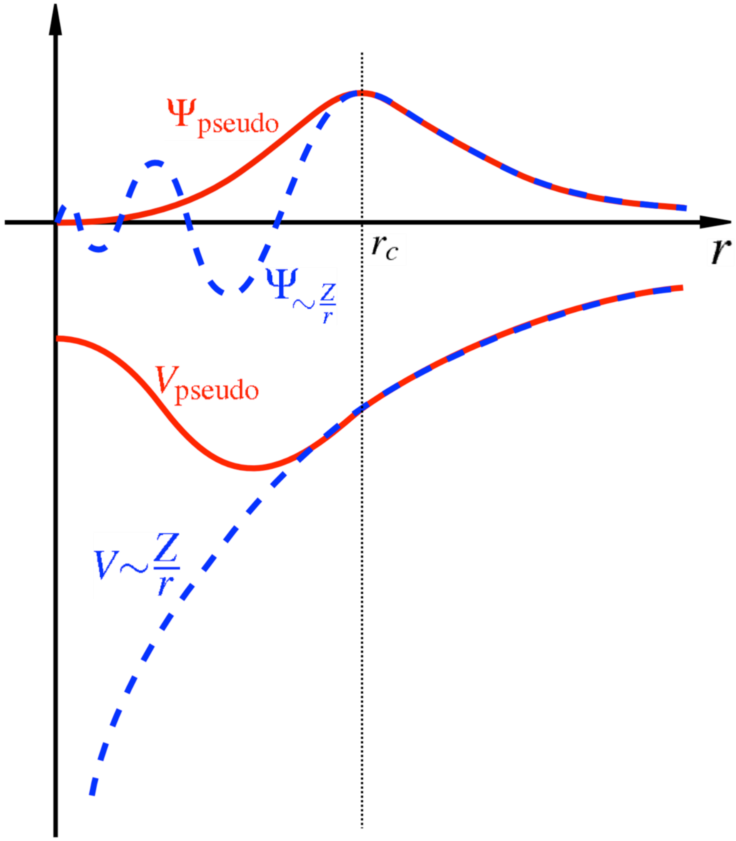
Why Pseudopotentials?

- ❖ Reduction of the basis set size.
- ❖ Reduction of the number of electrons.

Critical Approximations:

- ➢ One-electron picture
- ➢ No significant overlap between core and valence wavefunctions (frozen core)

The only role of the core electrons is to provide an effective external potential (or pseudopotential) in which the outer electrons move.



SPEED versus ACCURACY and TRANSFERABILITY

Results from a pseudo-potential-based code are as good as the pseudo-potentials are.

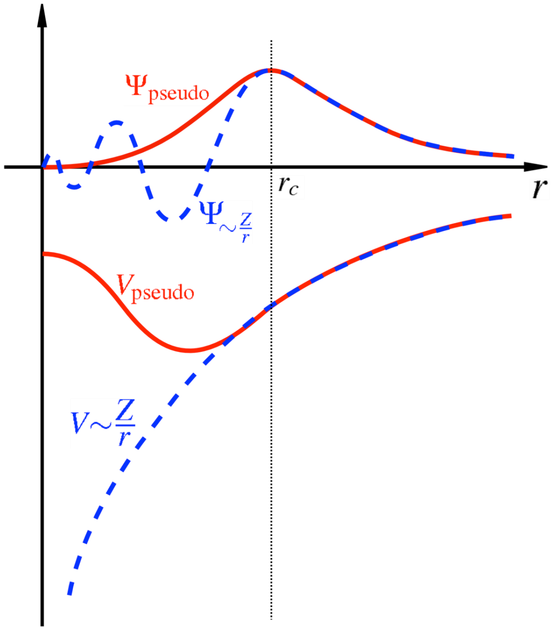
What Are We Talking About?

Norm-conserving pseudopotentials: outside r_c the norm of each pseudo-wavefunction is identical to its corresponding all-electron wavefunction.

Ultra-soft pseudopotentials: relax the norm-conserving constraint to reduce the basis set size (other related technique: PAW).

Critical Approximations (true for most DFT-based methods and codes):

- Exchange and correlation potential (LDA, LSDA, GGA, SIC, GWM, DMFT)
- Relativistic effects (scalar relativistic, fully relativistic, spin-orbit coupling)
- In most DFT-based codes, the zero-point motion contribution to the total energy is absent.



Why Construct a Pseudopotential?

- There is a handful of repositories with prefabbed pseudopotentials:
- Abinit's web site: http://www.abinit.org
- Rappe Group: http://lorax.chem.upenn.edu
- Vanderbilt's library of ultrasoft pseudopotentials:
  http://www.physics.rutgers.edu/~dhv/uspp/uspp-734.html

- But, it is very likely that you may want to make your own:
  - All elements may not be available
  - Pseudopotential may not give accurate results
  - Pseudopotential may be too expensive to use for your problem

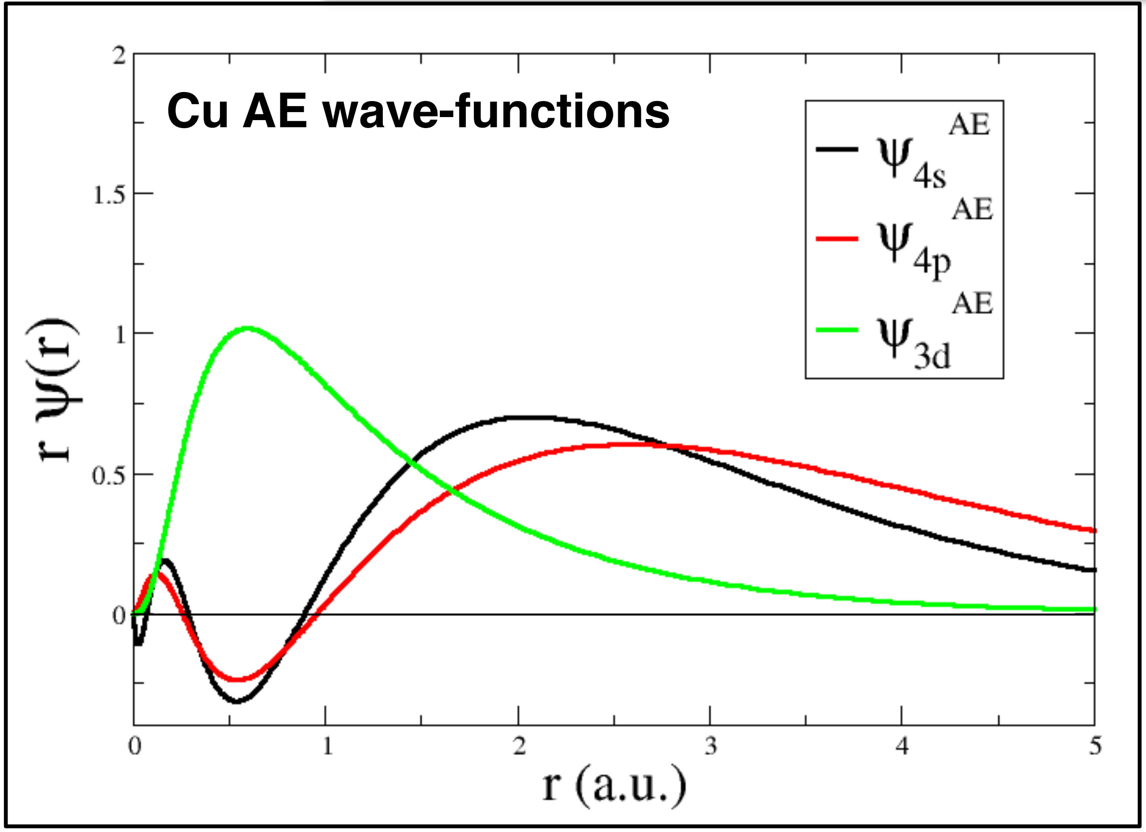
- Furthermore, having the ability to construct pseudopotentials can be an important research tool.

Pseudo-potential Construction: AE

$$\left\{\phi_l^{\mathrm{AE}}(r)\right\},\left\{\epsilon_l^{\mathrm{AE}}\right\}$$

- Get the all-electron eigenvalues and wavefunctions.

$$\left(-\frac{1}{2}\frac{d^2}{dr^2}+\frac{l(l+1)}{2r^2}-\frac{Z}{r}+V_{\mathrm{hxc}}[\rho(r)]\right)r\phi_l(r)=\epsilon_l r\phi_l(r)$$



Pseudo-potential Construction: PS

Select cut-off radii

$$\psi_l(r) = \begin{cases} \sum_i c_i \, j_l(q_i r) & r < r_c \\ \phi_l(r) & r \geq r_c \end{cases}$$

Construct pseudo-wavefunctions

$$V_l^{\text{ps}}(r) = \epsilon_l - \frac{l(l+1)}{2r^2} + \frac{1}{2r\psi_l(r)} \frac{d^2\left[r\psi_l(r)\right]}{dr^2} - V_{\text{hxc}}[\rho^{\text{val}}(r)]$$

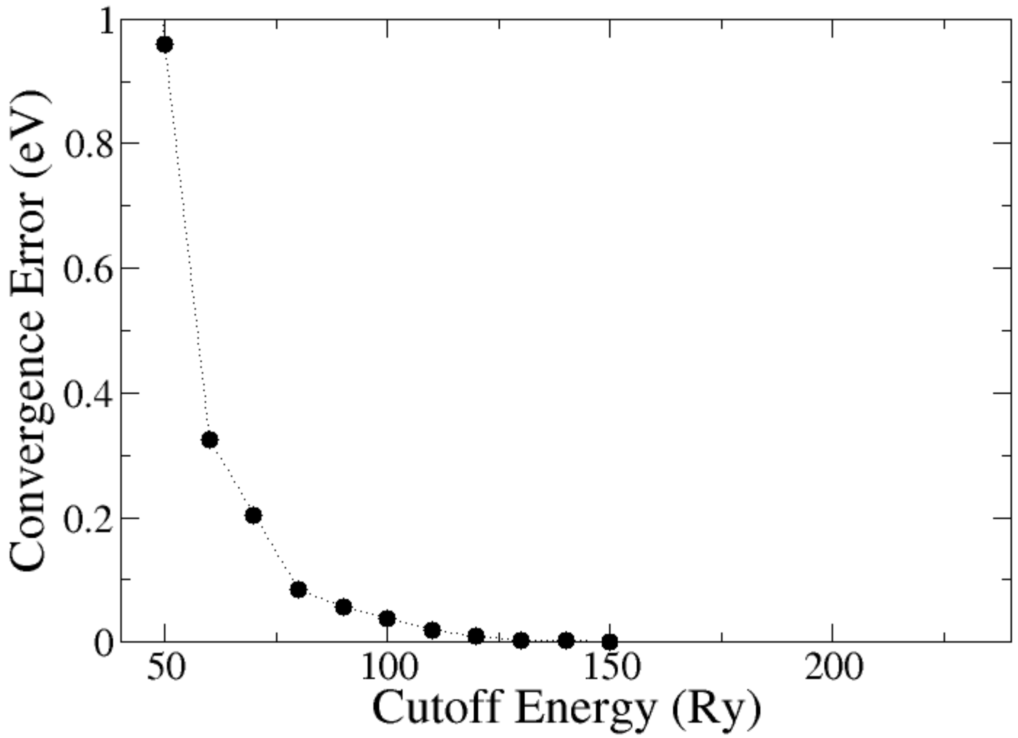
Invert the KS equation to find the semi-local pseudo-potential: $V_l^{\text{ps}}(r)$

$$\left(-\frac{1}{2}\frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} + V_l^{\text{ps}} + V_{\text{hxc}}[\rho(r)] \right) r\psi_l(r) = \epsilon_l r\psi_l(r)$$

Solve the KS equations using semi-local pseudo-potential

Pseudo-potential Convergence

Error in Total Energy vs. PSP Cut-off energy (E_{cut})



- Cut-off energy is a measure of the size of the plane-wave basis
- Want to minimize Ecut
- Larger E_{cut} → longer run time

Optimized method delivers highly efficient pseudo-potentials

Atomic Criteria

- First step of construction is to design pseudo-wavefunctions
- Choose reference configuration and cutoff radii (**r_c**)

5 rules for a “good” pseudo-potential

1. $$\{\epsilon_l^{\mathrm{AE}}\}_{\mathrm{ref}} = \{\epsilon_l^{\mathrm{PS}}\}_{\mathrm{ref}}$$

2. $$\psi_{l,\mathrm{ref}}^{\mathrm{AE}} = \psi_{l,\mathrm{ref}}^{\mathrm{PS}} \qquad r \geq r_c$$

3. $$N_{l,\mathrm{ref}}^{\mathrm{AE}} = N_{l,\mathrm{ref}}^{\mathrm{PS}}$$

4. $$D_l^{\mathrm{AE}}(\epsilon, r_c) = D_l^{\mathrm{PS}}(\epsilon, r_c)$$

5. $$\frac{\partial}{\partial\epsilon} D_l^{\mathrm{AE}}(\epsilon, r_c) = \frac{\partial}{\partial\epsilon} D_l^{\mathrm{PS}}(\epsilon, r_c)$$

True for all norm conserving pseudo-potentials

D. R. Hamann, M. Schlüter, and C. Chiang, PRL **43**, 1494 (1979)

Norm conservation guarantees

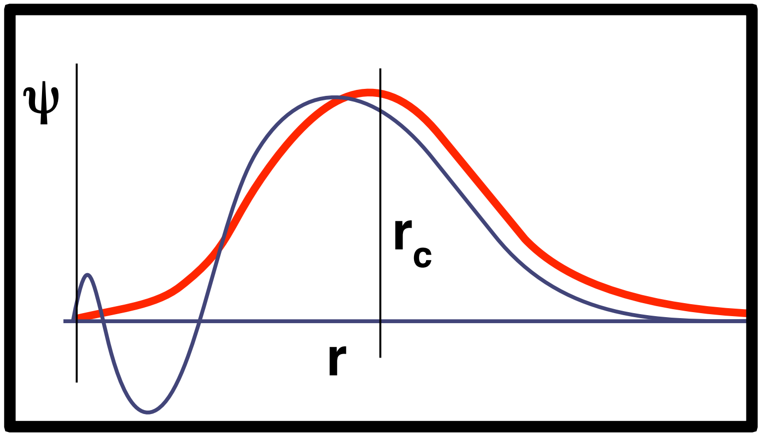
But how good???

Pseudo-wavefunctions are nodeless and satisfy (at least) the above criteria

$$\mathrm{N}_l = \int_{r_c}^{\infty} r^2 \psi_l^2(r) dr$$ tail norm

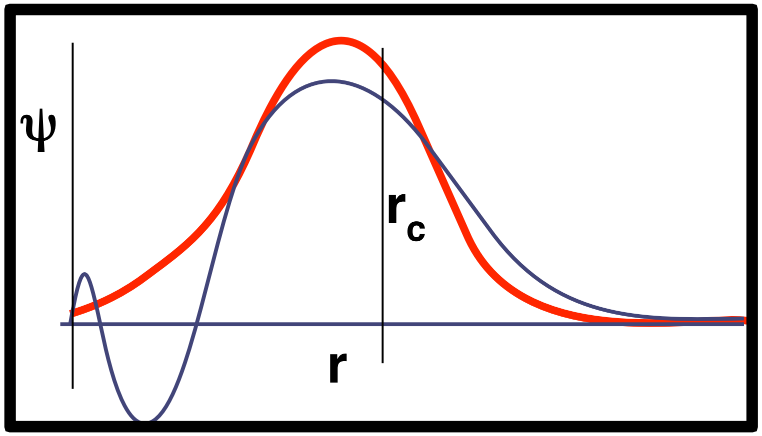
$$D_l(\epsilon, r) = r \frac{d}{dr} \ln \psi_l(\epsilon, r)$$ log. derivative

Eigenvalues and Tail Norm



$$\epsilon^{\mathrm{ae}} = \epsilon^{\mathrm{ps}}$$

$$\mathrm{N}^{\mathrm{ae}} \neq \mathrm{N}^{\mathrm{ps}}$$



$$\epsilon^{\mathrm{ae}} \neq \epsilon^{\mathrm{ps}}$$

$$\mathrm{N}^{\mathrm{ae}} = \mathrm{N}^{\mathrm{ps}}$$

Must enforce conservation of both!

What is a Good Pseudo-potential?

- For a pseudo-potential to be useful, it must be both accurate and efficient

accuracy - reproduction of all-electron atomic properties

efficiency - cost of using the pseudo-potential in solid-state calculations

- Need a self-contained program to construct and test the accuracy and efficiency of pseudo-potentials

Open-source Pseudopotential Interface and Unification Module

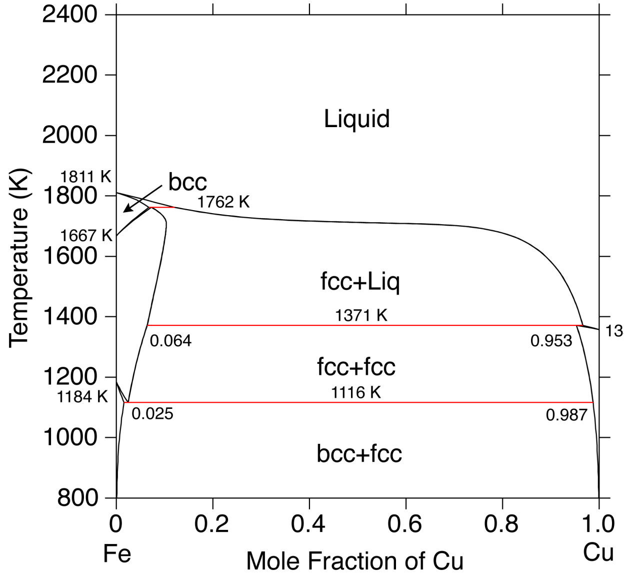
(J. Bennett & A.M. Rappe)

http://opium.sourceforge.net/index.html

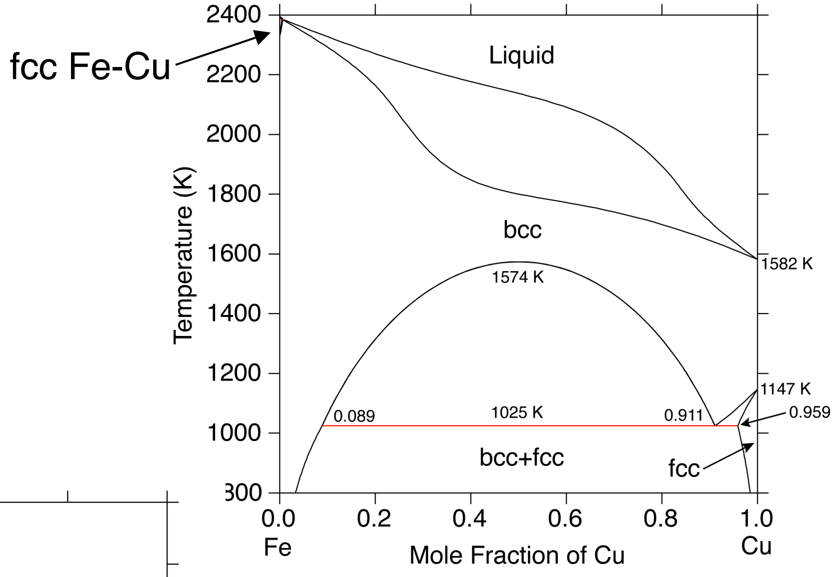
What about 2nd-principles approaches to Alloy property simulations? EAM Phase Diagrams

The case of Fe-Cu alloys

Experimental Phase Diagram



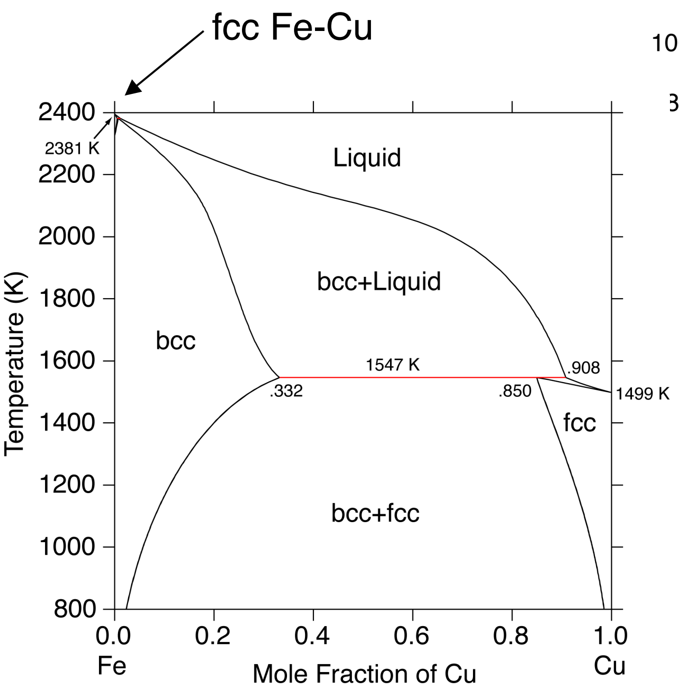
EAM Phase Diagram with Ackland' s Potentials



E. M. Lopasso, M. Caro, A. Caro, and P. E. A. Turchi, "The phase diagram of Fe-Cu as predicted by an empirical potential", Phys. Rev. B **68**, 214205-1 to 9 (2003)

A. Caro, P. E. A. Turchi, M. Caro, and E. M. Lopasso, "Thermodynamics of an Empirical Potential Description of Fe-Cu Alloys", J. of Nucl. Mater. **336**, 233-242 (2005).

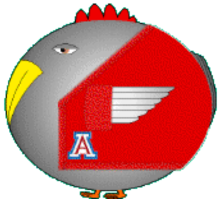
A. Caro, M. Caro, E. M. Lopasso, P. E. A. Turchi, and D. Farkas, "Thermodynamics of Fe-Cu Alloys as Described by Classic Potential", J. of Nucl. Mater. **349**, 317-326 (2006).



EAM Phase Diagram with Ludwig-Farkas Potentials

Conclusions

- Yes, there are plenty of “good” user friendly pseudopotential-based codes out there



- The question is: are the potentials for a given set of elements designed to tackle a problem never looked at before?
  - Pseudo-potentials must be checked out within a new atomic configuration space (the same way EAM potentials should) to make sure that accuracy is preserved

- There will always be a trade off between speed and accuracy (and therefore transferability)