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FROM AB-INITIO TO SEMI-EMPIRICAL POTENTIALS

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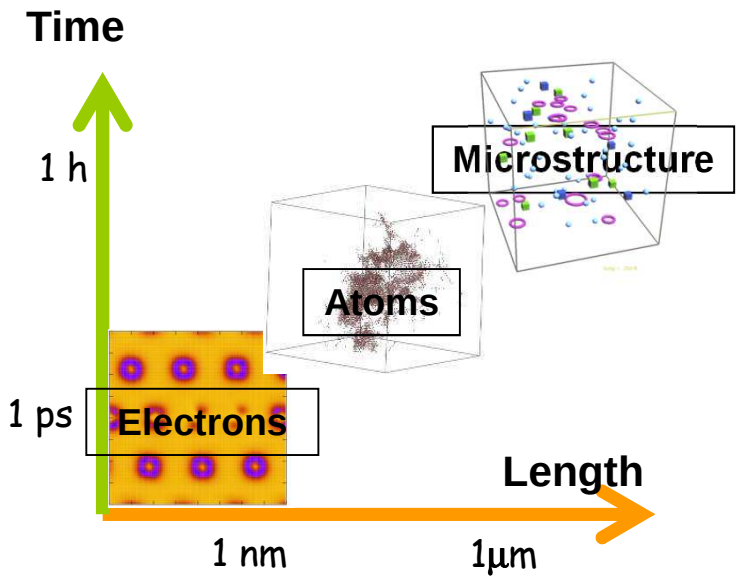
Introduction

Theory and
Multi-scale modelling

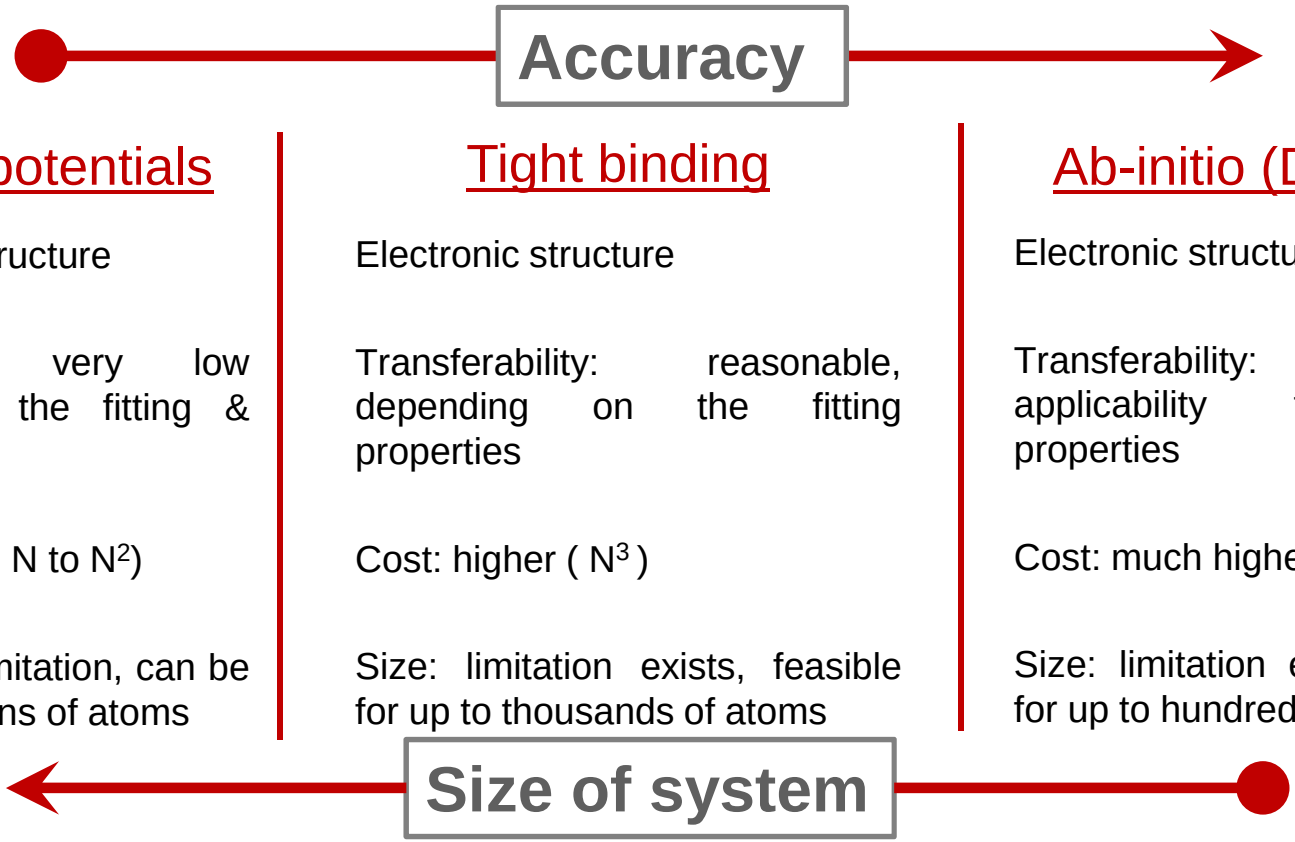


Advantage of semi-empirical methods : fast evaluation of the energy and forces.

Utility of semi-empirical methods: everywhere when the word “million” is associated with “atomistic”:

- Atomistic investigations for mechanical problems (millions of atoms)
- Finite temperature properties (millions of force evaluations) :
  - molecular dynamics investigations: protein folding, defects migrations, microstructural evolution, radiation damage etc
  - Thermodynamic properties
- Exploring exhaustively unknown energy landscape (millions of minima and saddle points).
- Gedankenexperiment: validation of models

Introduction



Introduction

- Towards semi-empirical potentials
  - DFT, TB, BOP, MEAM, EAM…
  - Istres 2015 potential « analytical BOP »
- Fitting an EAM potential metallic defects orientated
  - Database
  - Fitting
  - Limitations
- Forget EAM, BOP, MEAM? Machine learning ?
  - (Kernel) Ridge regression
  - Bayesian inference

- **Towards semi-empirical potentials**
  - **DFT, TB, BOP, MEAM, EAM…**
  - **Istres 2015 potential « analytical BOP »**
- **Fitting an EAM potential metallic defects orientated**
  - **Database**
  - **Fitting**
  - **Limitations**
- **Forget EAM, BOP, MEAM? Machine learning ?**
  - **(Kernel) Ridge regression**
  - **Bayesian inference**

DFT, TB, BOP, MEAM, EAM…

$$\mathcal{E}\left(\left\{\vec{R}_I\right\}\right) = E_e\left[\rho_e\right] + \frac{1}{2}\sum_{I\neq J}\frac{Z_I Z_J}{\left|\vec{R}_I - \vec{R}_J\right|}$$

Khon-Sham (1965) proposed a self-constent scheme:

$$\begin{aligned} E_e\left[\rho\right] &= T\left[\rho\right] + U\left[\rho\right] \\ U\left[\rho\right] &= \int v(\vec{r})\rho(\vec{r})d\vec{r} + E_{ee}\left[\rho\right] + E_{xc}\left[\rho\right] \end{aligned}$$

$$V_{KS}\left(\vec{r}\right) = v\left(\vec{r}\right) + \int \frac{\rho\left(\vec{r'}\right)}{\left|\vec{r} - \vec{r'}\right|}d\vec{r'} + \frac{\delta E_{xc}[\rho]}{\delta\rho}$$

$$\left[-\frac{\hbar^2}{2m}\boldsymbol{\Delta} + V_{KS}(\vec{r})\right]\phi_\alpha(\vec{r}) = \epsilon_\alpha\phi_\alpha(\vec{r})$$

$$T\left[\rho\right] = \sum_\alpha f_{FD}\left(\epsilon_F - \epsilon_\alpha\right)\epsilon_\alpha - \int V_{KS}(\vec{r})\rho(\vec{r})d\vec{r}$$

The Hohenberg-Kohn theorem: The Hohenberg-Kohn theorem states that:

1. the ground state energy E_e of the system of electrons in an external potential $v\left(\vec{r}\right)$:

$$v\left(\vec{r}\right) = \sum_I \frac{-Z_I}{\left|\vec{r} - \vec{R}_I\right|}\,; \qquad (1)$$

is a unique functional of the electron density $\rho(\vec{r})$,

$$E_e \equiv E_e\left[\rho\right]\,;$$

2. the functional $E\left[\rho\right]$ has its minimum value when $\rho(\vec{r})$ is the ground state electron density $\rho_e(\vec{r})$:

$$E_e\left[\rho\right] \geq E_e\left[\rho_e\right]\,; \qquad (2)$$

$$\begin{aligned} \mathcal{E}\left(\left\{\vec{R}_I\right\},\rho\right) &= \sum_\alpha f_{FD}\left(\epsilon_F - \epsilon_\alpha\right)\epsilon_\alpha + F\left[\left\{\vec{R}_I\right\},\rho\right], \\ F\left[\left\{\vec{R}_I\right\},\rho\right] &= E_{ee}[\rho] + E_{xc}[\rho] - \int V_{KS}(\vec{r})\rho(\vec{r})d\vec{r} + \frac{1}{2}\sum_{I\neq J}\frac{Z_I Z_J}{\left|\vec{R}_I - \vec{R}_J\right|}. \end{aligned}$$

DFT, TB, BOP, MEAM, EAM…

Mott and Jones, Slater, Friedel, Huckel (LCAO) in 60’

$$|n\rangle = \sum_{i\alpha} c^n_{i\alpha} |i\alpha\rangle$$

$$\underbrace{\underbrace{\underbrace{s}_{1}, \underbrace{p_x, p_y, p_z}_{3}}_{4 : \text{semi-conductors}}, \underbrace{d_{xy}, d_{yz}, d_{xz}, d_{x2-y^2}, d_{3z^2-r^2}}_{5 : \text{Transition Metals}}}_{9 : \text{Transition Metals}}$$

$$\mathbf{H} = -\frac{\hbar^2}{2m}\mathbf{\Delta} + \sum_I^{N_a} V_I$$

$$\mathbf{H}|n\rangle = \epsilon_n |n\rangle$$

$$\sum_{j\beta} H_{i\alpha,j\beta} c^n_{j\beta} = \epsilon_n c^n_{i\alpha} \qquad n_0 N_a \times n_0 N_a$$

Many TB models depending:

- Degree of « ab-initio »
- Orthogonal , non-orthogonal
- Parametrization of the hopping integrals

Order and Phase Stability in Alloys (Chapter 6)
F. Ducastelle, North Holland
Concenpts in Surface Physics (Chapter 5)
M.-C. Desjonquères, D. Spanjaard, Springer Verlag
Electronic Structure and the Properties of Solids
W. Harrisson, Dover
Electronic Structures of Materials
A.P. Sutton, Oxford University Press
Tight-Binding Modelling of Materials
Goringe et al. Rep. Prog. Phys, 1997
Linear Scalling Electronic Structure Methods
S. Goedecker, Review of Modern Physics, 1999

In site term

$$\langle i\alpha|\,\mathbf{H}\,|j\beta\rangle = \begin{cases} \epsilon^o_{i\alpha}\,\delta_{ij}\delta_{\alpha\beta} + < i\alpha| \sum_{K\neq i} V_K\,|j\beta>, & i = j \\ < i\alpha| \sum_{K\neq j} V_K\,|j\beta> = h_{i\alpha,j\beta} & i \neq j \end{cases}$$

Three center integrals neglected

DFT, TB, BOP, MEAM, EAM…

Key ingredient: accounts the « ability » of the electrons to « jump » from one site to other

$$\sum_{j\beta} H_{i\alpha,j\beta} c^n_{j\beta} = \epsilon_n c^n_{i\alpha}$$

$$h_{i\alpha,j\beta} = h_{i\alpha,j\beta}(\mathbf{r}_i - \mathbf{r}_j)$$

$$E = E_{band} + E_{rep} - E_{atoms} = \sum_{occ} \epsilon_n + \sum_{i\neq j} \phi(r_{ij}) - \sum_{i\alpha} N^a_{i\alpha} \epsilon^0_{i\alpha}$$

Density matrix or bond order

$$\rho_{i\alpha,j\beta} = \sum_{n\in occ} c^n_{i\alpha} c^n_{j\beta}$$

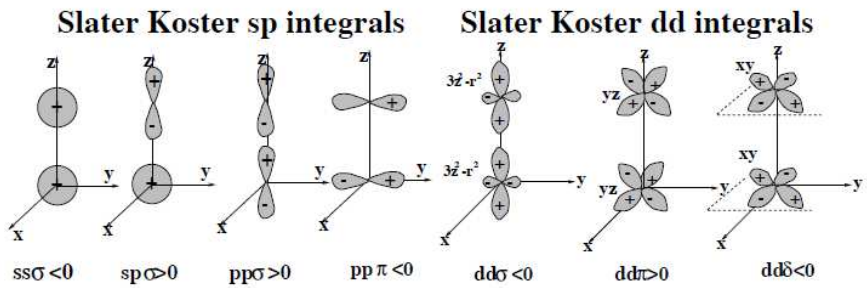
$$= \underbrace{\sum_{1\alpha\neq j\beta} \rho_{j\beta,i\alpha} h_{i\alpha,j\beta}}_{E_{bond}} + \sum_{i\neq j} \phi(r_{ij}) + \underbrace{\sum_{i\alpha} (2\rho_{i\alpha,i\alpha} - N^a_{i\alpha})\, \epsilon^0_{i\alpha}}_{E_{prom}}$$

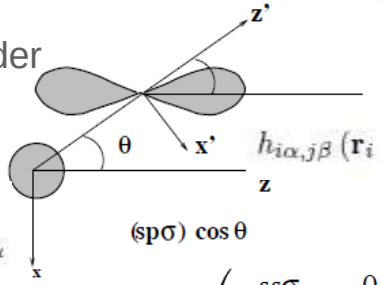
off-diagonal

Diagonal:

Used in self consistents TB models or TB-LCN

Which impose the local charge neutrality (LCN) condition





$$h_{i\alpha,j\beta}(\mathbf{r}_i - \mathbf{r}_j) = \mathbf{R}^{-1}(u_{ij}, v_{ij}, w_{ij})\, h_{\alpha,\beta}(\mathbf{z})\, \mathbf{R}(u_{ij}, v_{ij}, w_{ij})$$

$$\underbrace{\begin{pmatrix} ss\sigma & 0 & 0 & sp\sigma & 0 & 0 & 0 & 0 & sd\sigma \\ 0 & pp\pi & 0 & 0 & 0 & 0 & pd\pi & 0 & 0 \\ 0 & 0 & pp\pi & 0 & 0 & pd\pi & 0 & 0 & 0 \\ -sp\sigma & 0 & 0 & pp\sigma & 0 & 0 & 0 & 0 & pd\sigma \\ 0 & 0 & 0 & 0 & dd\delta & 0 & 0 & 0 & 0 \\ 0 & 0 & -pd\pi & 0 & 0 & dd\pi & 0 & 0 & 0 \\ 0 & -pd\pi & 0 & 0 & 0 & 0 & dd\pi & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & dd\delta & 0 \\ sd\sigma & 0 & 0 & -pd\sigma & 0 & 0 & 0 & 0 & dd\sigma \end{pmatrix}}_{h_{\alpha,\beta}(\mathbf{z})}$$

DFT, TB, BOP, MEAM, EAM…

Local density of states proposed by J. Friedel in 60’

$$n(E) = \sum_n \delta(E - \epsilon_n) = \sum_n \langle n| \delta(E - \mathbf{H}) |n\rangle$$

$$= \sum_{n,m,i\alpha} \langle n|i\alpha\rangle \langle i\alpha|m\rangle \langle m| \delta(E - \mathbf{H}) |n\rangle$$

$$= \sum_{i\alpha} \left[\sum_n |\langle i\alpha|n\rangle|^2 \delta(E - \epsilon_n) \right]$$

$$n_{i\alpha} = \sum |\langle i\alpha|n\rangle|^2 \delta(E - \epsilon_n) = \langle i\alpha|\delta(E - \mathbf{H})|i\alpha\rangle$$

$$E_{prom} = \sum_{i\alpha} \left(\int^{E_f} n_{i\alpha}(E) dE - N^a_{i\alpha} \right) \epsilon^0_{i\alpha}$$

$$E_{bond} = \sum_{i\alpha} \int^{E_f} (E - \epsilon^0_{i\alpha}) n_{i\alpha}(E) dE$$

If we have a way to have the local density of states the evaluation of the energy becomes order N

The proposed solution was done in 70s by the moments description of the function of local density of states.

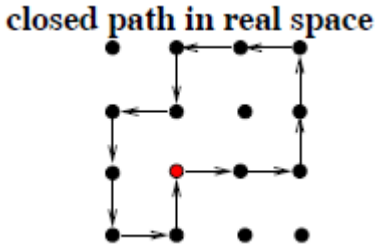
DFT, TB, BOP, MEAM, EAM…

$$\mu^{(n)} = \int_{X_m}^{X_M} (x - x_g)^n f(x) dx \qquad x_g = \int_{X_m}^{X_M} x f(x) dx$$

- $\mu^{(0)}$ gives the area under $f(x)$. This can be used as a normalization factor of the function $f(x)$;
- $\mu^{(1)}$ gives the "center of gravity" of $f(x)$
- $\mu^{(2)}$ gives the momentum of "inertia" of $f(x)$. Hence $\sqrt{\mu^{(2)}}$ is proportional to the width of the $f(x)$ in the root mean square sense;
- $\mu^{(3)}$ gives the asymmetry from 0, e.g. a large negative value of $\mu^{(3)}$ corresponds to a long tail of $f(x)$ in the region below $\mu^{(1)}$;
- $\mu^{(4)}$ measures the tendency for a gap in the middle of the band ...

$$\mu_{i\alpha}^{(p)} = \langle i\alpha|\mathbf{H}^p|i\alpha\rangle = \int E^p n_{i\alpha}(E)dE$$

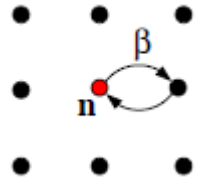
$$\mu_{i\alpha}^{(p)} = \sum_{j_1\beta_1,\ldots j_{p-1}\beta_{p-1}} H_{i\alpha,j_1\beta_1}H_{j_1\beta_1,j_2\beta_2}\ldots H_{j_{p-2}\beta_{p-2},j_{p-1}\beta_{p-1}}H_{j_{p-1}\beta_{p-1},i\alpha}$$



F. Ducastelle and F. Cyrot-Lackmann, J. Phys. Chem. Solids **31**, 1295 (1970)

Second moment approximation:

$$\mu_{i\alpha}^{(2)} = \sum_{j\beta} H_{i\alpha,j\beta}H_{j\beta,i\alpha} = \mathrm{Tr}\left\{[\mathrm{h}]^2\right\} = \mathrm{Tr}\left\{\left[\mathbf{R}^{-1}\mathbf{h}_{\alpha\beta}(r_{ij})\mathbf{R}\right]^2\right\} = \mathrm{Tr}\left\{[\mathbf{h}_{\alpha\beta}(r_{ij})]^2\right\}$$



$$\mu_i^{(2)} = Z_i \times C_h$$

$$E_{band} = \sum_i \int^{E_f} E n_i(E)\, dE \propto A\sum_i \sqrt{\mu_i^{(2)}} = A\sum_i \sqrt{\sum_j g(r_{ij})}$$

Tight binding second moment potentials

$$E = \sum_{i\neq j}\phi(r_{ij}) - \sum_i \sqrt{\rho_i}$$

M. W. Finnis, J. E. Sinclair, *Phil. Mag. A*. 50, 45–55 (1984)

A. P. Sutton, J. Chen, *Phil. Mag. Lett.* 61, 139 (1984).

Embedded-atom method potentials

$$E = \sum_{i\neq j}\phi(r_{ij}) + \sum_i F(\rho_i)$$

M. S. Daw & M.J. Baskes Phys. Rev. B 29, 6443 (1987).

DFT, TB, BOP, MEAM, EAM…

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Embedded-atom method potentials

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- Shielded Coulomb repulsion between the nuclei
- Embedding energy term describing the formation of collective bonds between the neighbouring atoms.

The EAM potentials are called also central force potentials for metals:

- Well suited and widely used for simple metals or noble metals with FCC or HCP structure
- Was also successfully applied for BCC metals with d-band only partially filled and consequently having angular character
- Other approaches for covalent systems should be developed … …

DFT, TB, BOP, MEAM, EAM…

$$\delta(x) = -\frac{1}{\pi}\lim_{\eta\to 0}\Im\left\{[x+i\eta]^{-1}\right\} \qquad n_{i\alpha} = \langle i\alpha|\delta(E-\mathbf{H})|i\alpha\rangle = -\frac{1}{\pi}\lim_{\eta\to 0}\Im\left\{\langle i\alpha|\,[E+i\eta-\mathbf{H}]^{-1}\,|i\alpha\rangle\right\}$$

$$\mathbf{G}(z) = [z-\mathbf{H}]^{-1} \qquad G_{i\alpha,j\beta}(z) = \langle i\alpha|\,[z-\mathbf{H}]^{-1}\,|j\beta\rangle \qquad n_{i\alpha} = -\frac{1}{\pi}\lim_{\eta\to 0}\Im\{G_{i\alpha,i\alpha}(E+i\eta)\}$$

$\lambda_1[\mathbf{T}_l]$

Is a very good approximation of

$\lambda_1[\mathbf{H}]$

$$\mathbf{T}_l = \begin{pmatrix} a_0 & b_1 & 0 & \cdots & 0 \\ b_1 & a_1 & b_2 & \cdots & 0 \\ 0 & b_2 & a_2 & \cdots & 0 \\ 0 & \ddots & \ddots & \cdots & 0 \\ 0 & & b_{l-2} & a_{l-2} & b_{l-1} \\ 0 & & 0 & b_{l-1} & a_{l-1} \end{pmatrix} \quad (\mathbf{u}_0, \mathbf{u}_1, \ldots, \mathbf{u}_{l-1})$$

$$\mathbf{H}\mathbf{u}_0 = a_0\mathbf{u}_0 + b_1\mathbf{u}_1$$

$$\mathbf{H}\mathbf{u}_1 = a_1\mathbf{u}_1 + b_1'\mathbf{u}_0 + b_2\mathbf{u}_2$$

$$\mathbf{u}_1\cdot(\mathbf{H}\mathbf{u}_0) = \mathbf{u}_0\cdot(\mathbf{H}\mathbf{u}_1)$$

$$\cdots$$

$$\mathbf{H}\mathbf{u}_k = a_k\mathbf{u}_k + b_k\mathbf{u}_{k-1} + b_{k+1}\mathbf{u}_{k+1}$$

$$\cdots$$

$$\mathbf{H}\mathbf{u}_{l-1} = a_{l-1}\mathbf{u}_{l-1} + b_{l-1}\mathbf{u}_{l-2}$$

$$\langle u_0|G|u_0\rangle = G_{00}(z) = \cfrac{1}{z-a_0-b_1^2\cfrac{1}{z-a_1-b_2^2\cfrac{1}{z-a_2-b_3^2\cfrac{1}{z-\cdots}}}}$$

$G_{i\alpha,i\alpha}(E+i\eta)$

Using Lanczos {a,b} can be deteremined.
The only required condition: you must know know how to apply the H on trial vector $|U_0\rangle$
{a,b} can be related to the all the moments of the LDOS $\left\{(a_i)_{i=0,p-2};(b)_{i=1,p-1}\right\} \Leftrightarrow \{\mu_i\}_{i=0,p}$

$$\mu_{i\alpha}^{(0)} = 1,$$

$$\mu_{i\alpha}^{(1)} = a_0,$$

$$\mu_{i\alpha}^{(2)} = a_0^2 + b_1^2,$$

$$\mu_{i\alpha}^{(3)} = a_0^3 + 2a_0b_1^2 + a_1b_1^2,$$

$$\mu_{i\alpha}^{(4)} = a_0^4 + 3a_0^2b_1^2 + 2a_0a_1b_1^2 + a_1^2b_1^2 + b_1^2b_2^2 + b_1^4.$$

DFT, TB, BOP, MEAM, EAM…

{a,b} can be related to the all the moments of the LDOS

$$\left\{(a_i)_{i=0,p-2};(b)_{i=1,p-1}\right\} \Leftrightarrow \{\mu_i\}_{i=0,p}$$

Bond Order Potential (BOP): is simplified TB model:

- Using Ducastelle-Cyrot Lackmann theorem in order to reconstruct DOS from moments
- Lanczos algorithm from the Green function in order to estimates the moments

$$\Theta_{i\alpha,j\beta} = 2\rho_{i\alpha,j\beta} = -\frac{2}{\pi}\lim_{\eta\to 0}\Im\left\{\int^{E_f} G_{i\alpha,j\beta}(E+i\eta)dE\right\}$$

$$= \sum_{1\alpha\neq j\beta}\rho_{j\beta,i\alpha}h_{i\alpha,j\beta}+\sum_{i\neq j}\phi(r_{ij})+\sum_{i\alpha}\left(2\rho_{i\alpha,i\alpha}-N^a_{i\alpha}\right)\epsilon^0_{i\alpha}$$

$$E = \frac{1}{2}\sum f_{\rm cut}(r_{ij})\left[f_{\rm R}(r_{ij}) + b_{ij}f_{\rm A}(r_{ij})\right]$$

$$f_{\rm R}(r_{ij}) = A_{ij}\exp(-\lambda_{ij}r_{ij})$$

$$f_{\rm A}(r_{ij}) = -B_{ij}\exp(-\mu_{ij}r_{ij})$$

$$f_{\rm cut}(r_{ij}) = \begin{cases} 1 & \text{if } r_{ij} < R_{ij} \\ \frac{1}{2}+\frac{1}{2}\cos\left(\pi\frac{r_{ij}-R_{ij}}{S_{ij}-R_{ij}}\right) & \text{if } R_{ij} < r_{ij} < S_{ij} \\ 0 & \text{if } r_{ij} > S_{ij} \end{cases}$$

$$b_{ij} = \chi_{ij}(1+\beta_i^{n_i}\zeta_{ij}^{n_i})^{1/2n_i}$$

$$\zeta_{ij} = \sum_{k\neq i,j} f_{\rm cut}(r_{ik})\omega_{ik}g(\theta_{ijk})$$

$$g(\theta_{ijk}) = 1+\frac{c_i^2}{d_i^2}-\frac{c_i^2}{d_i^2+(h_i-\cos\theta_{ijk})^2}.$$

D. G. Pettifor, *Phys. Rev. Lett.* 63, 2480–2483 (1989).

A. P. Horsfield, A. M. Bratkovsky, M. Fearn, D. G. Pettifor, M. Aoki, Phys. Rev. B. 53, 12694–12712 (1996).

BOP potentials have been developed in the last 20 years:

- Many parametrization have been transition metals including Fe, W or Mo
- are appropriate for covalent systems
- Exist also in the version of « analytical BOP »
- The main problem is the evaluation of the force.

From BOP to new formalism: Istres 2015

Tight binding Hamiltonian with one orbital per atom

$$H = \sum_{i,j} t_{ij} |i\rangle\langle j|$$

$t_{ii} = 0$ (no restriction, just redefinition of the energy or Fermi level)

$t_{ij} = t_{ji}$

$|u_0\rangle = |i\rangle$

$$\langle i|G(z)|i\rangle = G_{i,i}(z) = \cfrac{1}{z - a_0 - b_1^2 \cfrac{1}{z - a_1 - b_2^2 \cfrac{1}{z - a_2 - b_3^2 \cfrac{1}{z - \dots}}}}$$

$$a_0 = \langle i|H|i\rangle = t_{ii} = 0$$

$$|u_1'\rangle = H|u_0\rangle - a_0|u_0\rangle = \sum_j t_{ij}|j\rangle$$

$$b_1^2 = \langle u_1'|u_1'\rangle = \sum_j (t_{ij})^2$$

$$|u_1\rangle = \frac{1}{b_1}|u_1'\rangle = \frac{\sum_j t_{ij}|j\rangle}{\sqrt{\sum_j (t_{ij})^2}}$$

$$a_1 = \langle u_1|H|u_1\rangle = \frac{\sum_{k,j,k\neq j\neq i\neq k} t_{ik}t_{kj}t_{ji}}{\sum_j (t_{ij})^2}$$

$$|u_2\rangle = H|u_1\rangle - a_1|u_1\rangle$$

$$b_2^2 = \langle u_2'|u_2'\rangle$$

$$|u_2\rangle = \frac{1}{b_2}|u_2'\rangle$$

$$a_2 = \langle u_2|H|u_2\rangle$$

We stop HERE by taking B2=0

$$\mathbf{H}\mathbf{u}_0 = a_0\mathbf{u}_0 + b_1\mathbf{u}_1$$

$$\mathbf{H}\mathbf{u}_1 = a_1\mathbf{u}_1 + b_1'\mathbf{u}_0 + b_2\mathbf{u}_2$$

$$\mathbf{u}_1 \cdot (\mathbf{H}\mathbf{u}_0) = \mathbf{u}_0 \cdot (\mathbf{H}\mathbf{u}_1)$$

$$\dots$$

$$\mathbf{H}\mathbf{u}_k = a_k\mathbf{u}_k + b_k\mathbf{u}_{k-1} + b_{k+1}\mathbf{u}_{k+1}$$

$$\dots$$

$$\mathbf{H}\mathbf{u}_{l-1} = a_{l-1}\mathbf{u}_{l-1} + b_{l-1}\mathbf{u}_{l-2}$$

From BOP to new formalism: Istres 2015

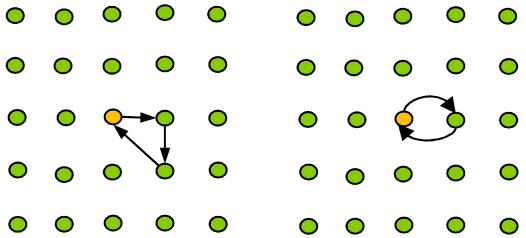
$$G_{i,i}(z) = \frac{1}{z - a_0 - b_1^2 \frac{1}{z - a_1}}$$

$$a_0 = \langle i | H | i \rangle = t_{ii} = 0$$

$$b_1^2 = \langle u_1' | u_1' \rangle = \sum_j (t_{ij})^2 = \rho_{0,i}$$

$$a_1 = \langle u_1 | H | u_1 \rangle = \frac{\sum_{k,j,k \neq j \neq i \neq k} t_{ik} t_{kj} t_{ji}}{\sum_j (t_{ij})^2} = \frac{\rho_{1,i}}{\rho_{0,i}}$$

$$\rho_{1,i} = \sum_{j,k} t_{ij} t_{jk} t_{ki} \qquad \rho_{0,i} = \sum_j t_{ij} t_{ji}$$



We cut the Green function by taking B2=0

$$U = \sum_i \int n_i(E) dE \qquad n_i(E) = -\frac{1}{\pi} \lim_{\eta \to 0} \mathrm{Im} \{ \langle i | G(E + i\eta) | i \rangle \}$$

$$z^- = \frac{1}{2\rho_{0,i}} \left(\rho_{1,i} - \sqrt{4\rho_{0,i}^3 - \rho_{1,i}^2} \right) \qquad z^+ = \frac{1}{2\rho_{0,i}} \left(\rho_{1,i} + \sqrt{4\rho_{0,i}^3 - \rho_{1,i}^2} \right)$$

$$U = \sum_i \frac{1}{2\sum_j t_{ij} t_{ji}} \left[\sum_{j,k} t_{ij} t_{jk} t_{ki} - \sqrt{\left(4 \left(\sum_j t_{ij} t_{ji} \right)^3 + \left(\sum_{j,k} t_{ij} t_{jk} t_{ki} \right)^2 \right)} \right]$$

If we consider that embedded term is much higher that the angular term $\rho_{0,i} \gg \rho_{1,i}$

$$U = \sum_i \frac{1}{2\rho_{0,i}} \left(\rho_{1,i} - \sqrt{4\rho_{0,i}^3 - \rho_{1,i}^2} \right) \simeq \sum_i \left(-\sqrt{\rho_{0,i}} + \frac{\rho_{1,i}}{2\rho_{0,i}} + \frac{\rho^3_{1,i}}{8\rho^{5/3}_{0,i}} + \ldots \right)$$

DFT, TB, BOP, MEAM, EAM…

$$U = \sum_i \left(-\sqrt{\rho_{0,i}} + \frac{\rho_{1,i}}{2\rho_{0,i}} + \frac{\rho^3_{1,i}}{8\rho^{5/3}_{0,i}} + \ldots \right)$$

Istres 2015 analytical BOP:

$$E^{BOP}_{Istres\,2015} = \sum_{i \neq j} \phi_{ij} + \sum_i \left(-\sqrt{\rho_{0,i}} + \frac{\rho_{1,i}}{2\rho_{0,i}} + \frac{\rho^3_{1,i}}{8\rho^{5/3}_{0,i}} \right)$$

MEAM potential for silicon

$$\rho_i = \sum_{j \neq i} \rho(r_{ij}) + \sum_{j \neq i,\, k \neq i} \rho(r_{ij})\rho(r_{ik})g(\cos\theta_{jik})$$

$$g(\cos\theta_{jik}) = 1 - 3\cos^2\theta_{jik}$$

M. I. Baskes, Phys. Rev. Lett., 59, 2666 (1987).

Modified embedded-atom method (MEAM) potentials for cubic materials and impurities

$$\bar{\rho}_i = \rho_i^{(0)} \left\{ 1 + \tfrac{1}{2} \sum_{l=1}^{3} t_i^{(l)} (\rho_i^{(l)} / \rho_i^{(0)})^2 + \cdots \right\}$$

M. I. Baskes, , Phys. Rev. B, 46, (1992).

$$(\rho_i^{(1)})^2 = \sum_\alpha \left[\sum_{j\,(\neq i)} x_{ij}^\alpha \rho_j^{a(1)}(R_{ij}) \right]^2,$$

$$(\rho_i^{(2)})^2 = \sum_{\alpha,\beta} \left[\sum_{j\,(\neq i)} x_{ij}^\alpha x_{ij}^\beta \rho_j^{a(2)}(R_{ij}) \right]^2 - \frac{1}{3} \left[\sum_{j\,(\neq i)} \rho_j^{a(2)}(R_{ij}) \right]^2,$$

$$(\rho_i^{(3)})^2 = \sum_{\alpha,\beta,\gamma} \left[\sum_{j\,(\neq i)} x_{ij}^\alpha x_{ij}^\beta x_{ij}^\gamma \rho_j^{a(3)}(R_{ij}) \right]^2,$$

- Towards semi-empirical potentials
  - DFT, TB, BOP, MEAM, EAM…
  - Istres 2015 potential « analytical BOP »
- Fitting an EAM potential metallic defects orientated
  - Database
  - Fitting
  - Limitations
- Forget EAM, BOP, MEAM? Machine learning ?
  - (Kernel) Ridge regression
  - Bayesian inference

$$E = \sum_{i \neq j} \phi(r_{ij}) + \sum_i F(\rho_i) \qquad \phi(r) = \sum_{i=1}^{n_\phi} w_i^\phi \left(r - w_i^{\delta,\phi}\right)^3 H\left(r - w_i^{\delta,\phi}\right) \qquad 2x\ n_\phi$$

$$\rho(r) = \sum_{i=1}^{n_\rho} w_i^\rho \left(r - w_i^{\delta,\rho}\right)^3 H\left(r - w_i^{\delta,\rho}\right) \qquad 2x\ n_\rho$$

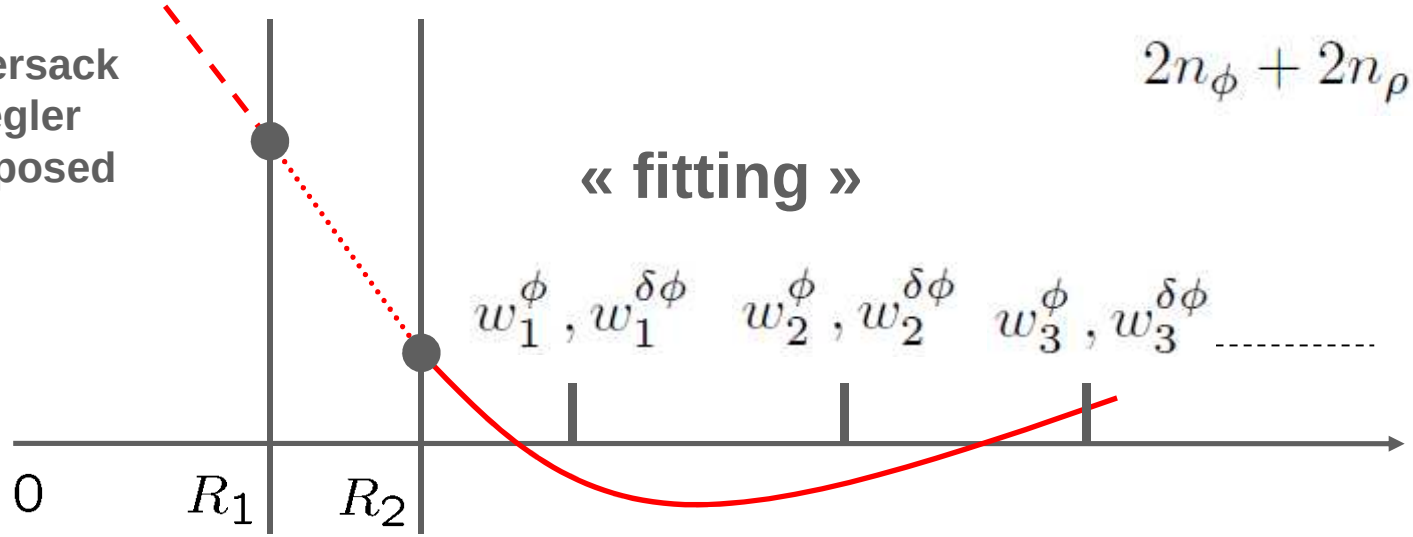
$$F(x) = -\sqrt{x} + w_F x^2$$

$$\mathbf{w} = \left(w_1^\phi, w_2^\phi \ldots w_{n_\phi}^\phi, w_1^{\phi\delta}, w_2^{\phi\delta} \ldots w_{n_\phi}^{\phi\delta}, w_1^\rho, w_2^\rho \ldots w_{n_\rho}^\rho, w_1^{\rho\delta}, w_2^{\rho\delta} \ldots w_{n_\rho}^{\rho\delta}, w_F\right)$$

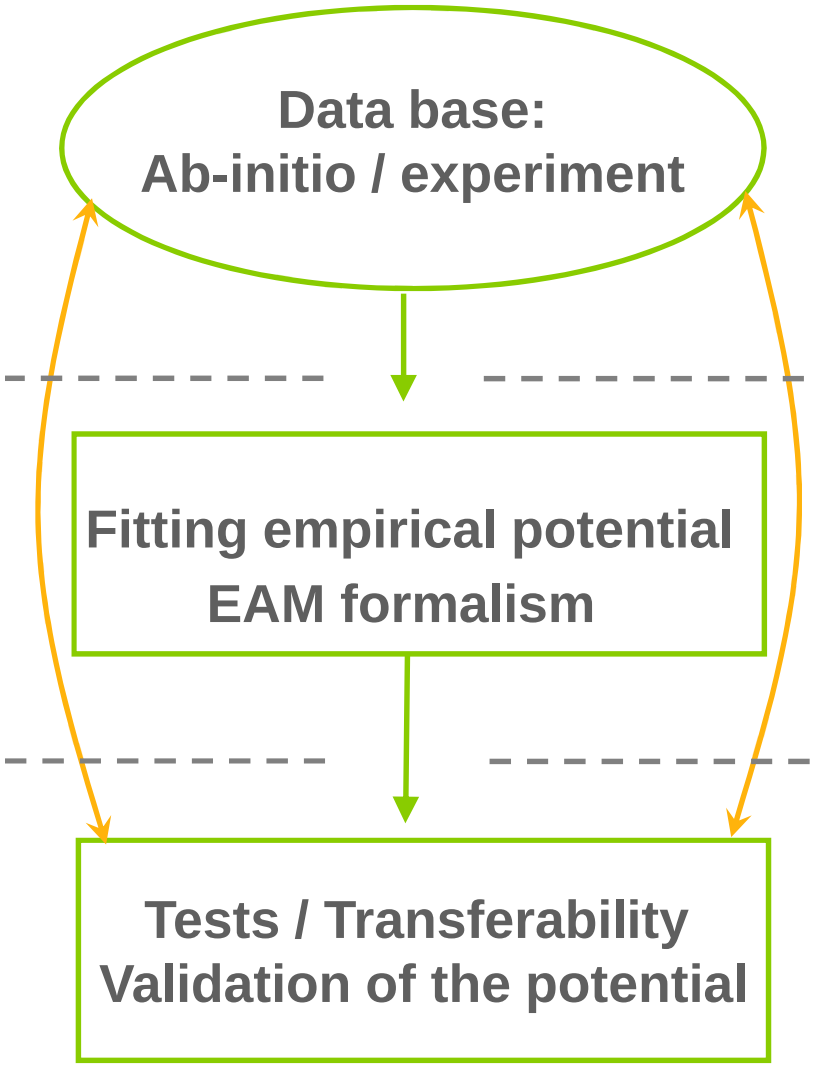
Biersack Ziegler imposed

$$2n_\phi + 2n_\rho + 1$$

« fitting »



Our approach: EAM potential fitted on ab-initio data



1. Bulk properties
   - elastic constants,
   - A0 lattice parameter
   - Cohesive energy BCC, FCC
2. Other properties …
   - Surface energies
   - Defects properties
   - Phonons
   - ….

$$J(\mathbf{w}) = \frac{1}{2}\sum_{obs}\sum_{i} a_i^{obs}\left[F_i(\mathbf{w}) - Y_i^{obs}\right]^2$$

$$\frac{1}{2}\sum_i a_i^E\left[E_i^{EAM}(\mathbf{w}) - E_i^{DFT}\right]^2$$

$$+\frac{1}{2}\sum_{xx} a_{xx}^C\left[C_{xx}^{EAM}(\mathbf{w}) - C_{xx}^{EXP}\right]^2$$

$$\ldots$$

EAM potentials fitted on experimental data

The empirical potentials which are fitted only on the bulk properties are not very reliable when used for point defects such as interstitials and vacancies.

An example: One of the best potential for iron developed by G. Ackland in 97 and which fit very well the perfect bulk properties as:

- FCC, BCC, lattice parameters
- elastic constants,
- phonons spectrum

. G. J. Ackland et al. *Phil. Mag. A*, **75**, (1997) 713

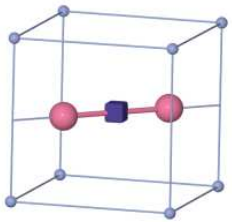
- **Johnson (1965)**
- **Johnson and Oh (1989)**
- **Harrison *et al.* (1989)**
- **Haftel *et al.* (1990)**
- **Calder and Bacon (1993)**
- **Simonelli *et al.* (1993)**
- **Ackland *et al.* (1997)**
- **Ludwig *et al.* (1998)**

$$E = \sum_{i \neq j} \phi(r_{ij}) + \sum_{i} \sqrt{\rho_i}$$

+

fitted only on the bulk properties

Fails for description of mono interstitial in iron:



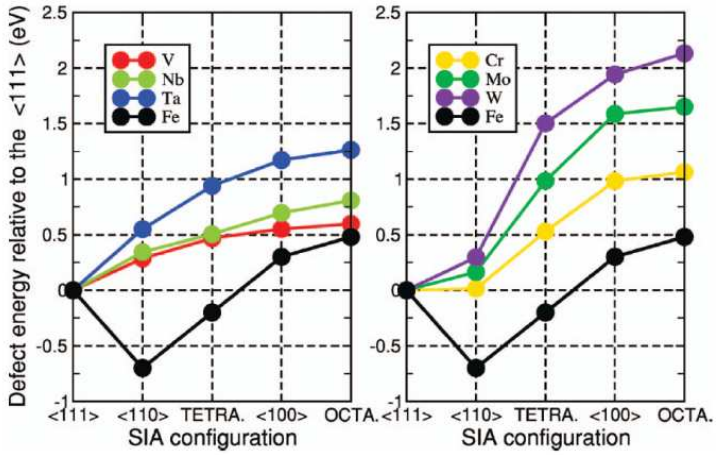
<110> dumbbell
Huang scattering

Migration:

- E_m=0.3 eV
- $E_m(I_2)$=0.4 eV

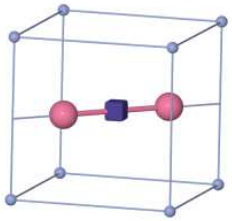
(resistivity recovery)

WHY?



D. Nguyen-Manh, A. P. Horsfield, et S. L. Dudarev. *PRB* 73, 020101 (2006).
C. Domain, C. S. Becquart, Phys. Rev. B 65, 024103 (2001)
C.-C. Fu, F. Willaime, and P. Ordejon, Phys. Rev. Lett. 92, 175503 (2004).

EAM potential fitted on experimental and ab-initio data



d_{SIA}=2.1 A
a_{1NN}=2.44 A
a_{2NN}=2.87 A

They add to standard bulk properties:

- FCC, BCC, lattice parameters
- elastic constants,
- Unrelaxed vacancy
- Some mono self interstitials configurations
- Surface energies

.

$$F(x) = -\sqrt{x} + w_F x^2$$

M. I. Mendelev, D. J. Srolovitz, G. J. Ackland, D. Y. Sun, M. Asta, *Phil. Mag.*, **83** (2003) 3977/

G. J. Ackland, M. I. Mendelev, D. J. Srolovitz, S. Han, A. V. Barashev, *J. Phys.: Condens. Matter*, 16 (2004) 2629

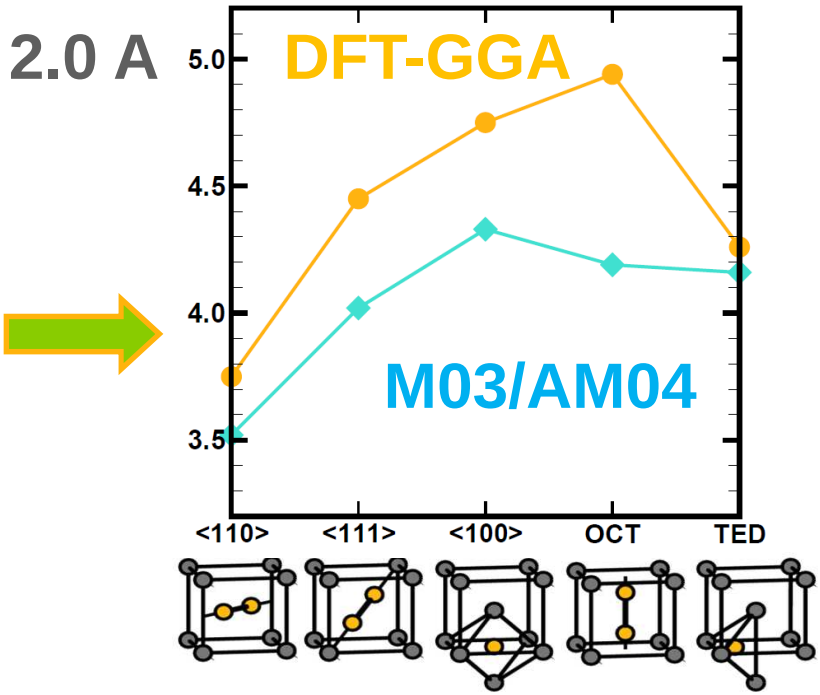
+

F. Ercolessi and J. B. Adams *Europhys. Lett.*, **26** (1994) 583

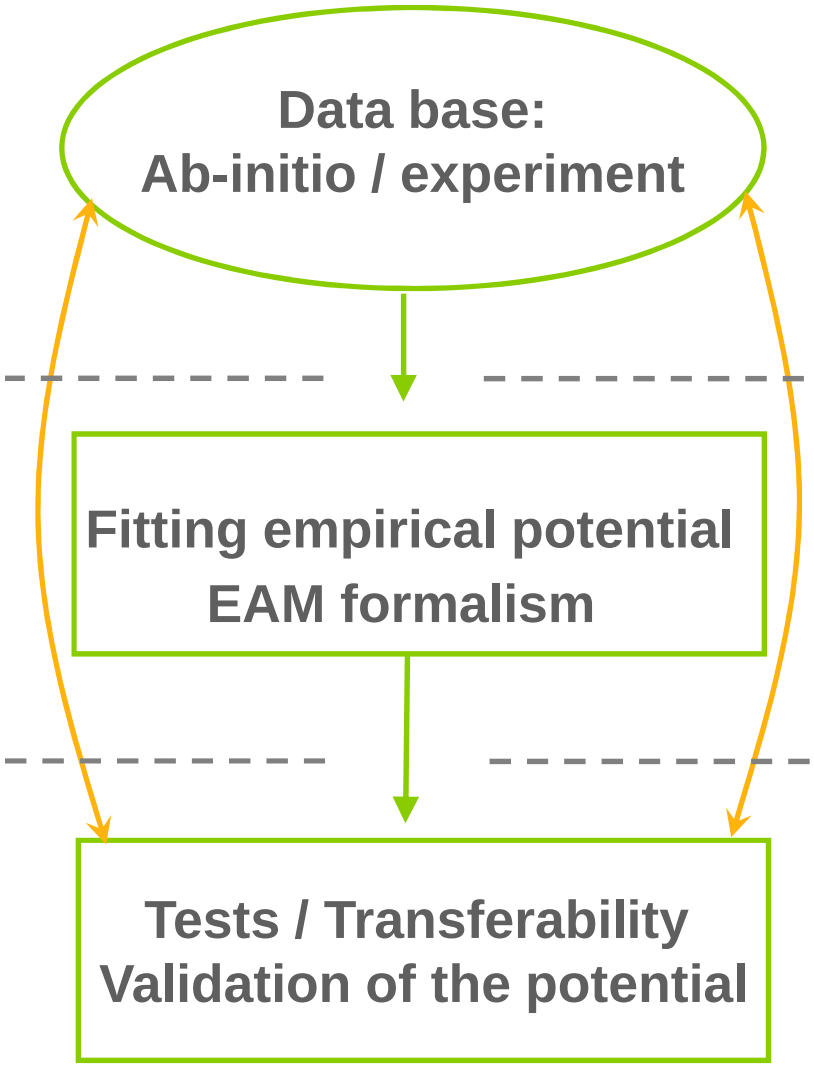
Force matching method on “liquid” iron configuration

.

d > 2.0 A



Our approach: EAM potential fitted on ab-initio data



1. Bulk properties
   - elastic constants, a0
   - Cohesive energy BCC, FCC
2. Ab-initio database (Typical unit cell with 128 atoms)
   - mono-interstitial (5 configuration)
   - di-,tri-interstials
   - relaxed vacancy
   - 400 Fe liquid configurations (around 100 atoms for each configuration)

$$J(\mathbf{w}) = \frac{1}{2}\sum_{obs}\sum_{i} a_i^{obs}\left[F_i(\mathbf{w}) - Y_i^{obs}\right]^2$$

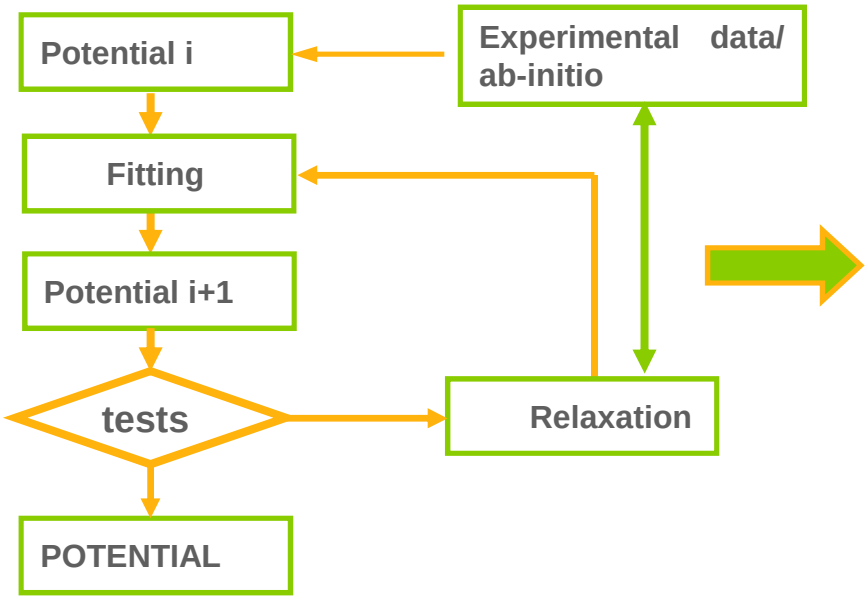
$$\frac{1}{2}\sum_i a_i^E\left[E_i^{EAM}(\mathbf{w}) - E_i^{DFT}\right]^2$$

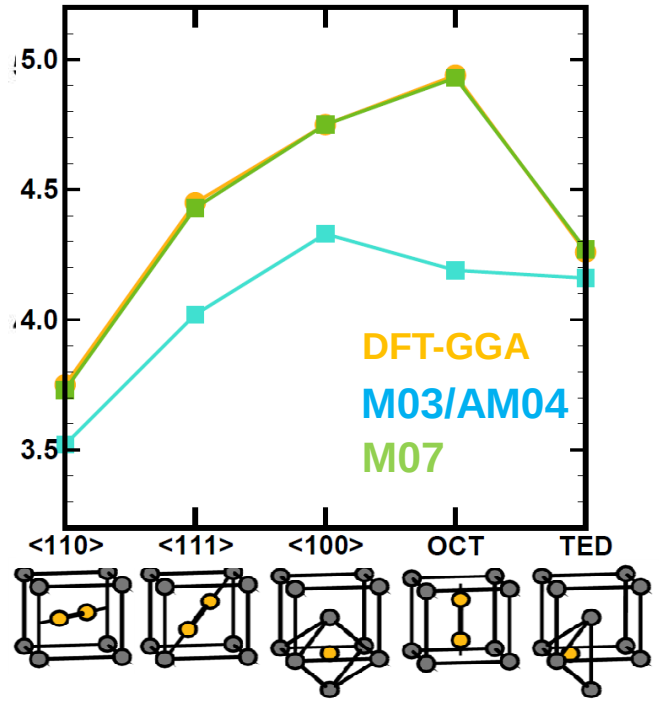
$$+\frac{1}{2}\sum_{xx} a_{xx}^C\left[C_{xx}^{EAM}(\mathbf{w}) - C_{xx}^{EXP}\right]^2$$

$$+\frac{1}{2}\sum_i\sum_{I\alpha} a_i^f\left[f_{i,I\alpha}^{EAM}(\mathbf{w}) - f_{i,I\alpha}^{DFT}\right]^2$$

F. Ercolessi and J. B. Adams, « Interatomic Potentials from First-Principles Calculations: The Force-Matching Method », *Europhys. Lett.*, **26** (1994) 583

Fitting procedure



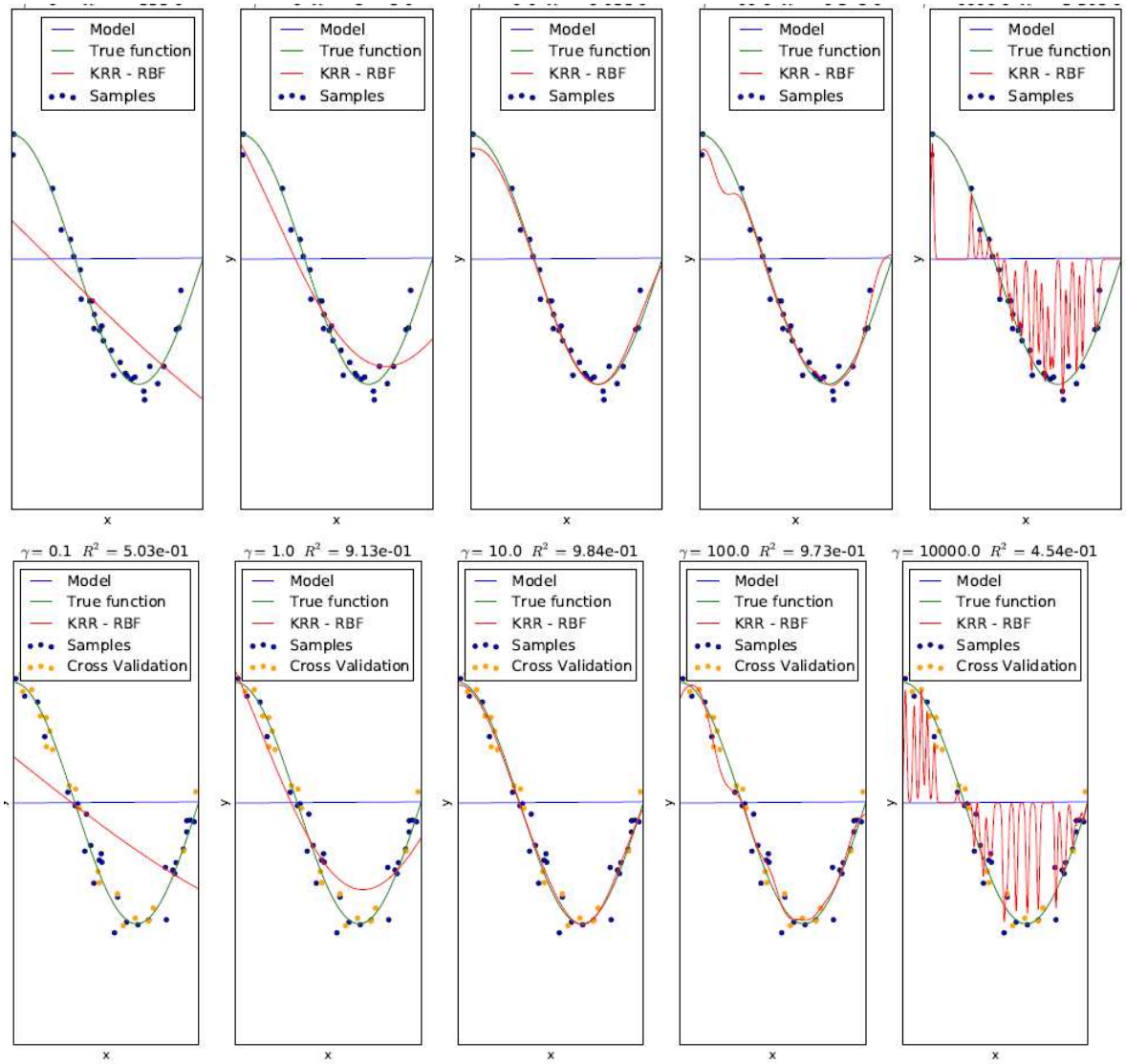


On-the-fly fitting:

a) Out off equilibrium configurations are not relaxed
b) Equilibrium configurations are relaxed with the previous version of the potential. The ab initio positions are used only in the first cycle. Then only the energies are kept fixed.

Fitting procedure is based on adjoint method in order to estimates the derivatives of the objective function

Avoid overfitting



Try to devide the database into two classes:

- Sample data
- Validation data

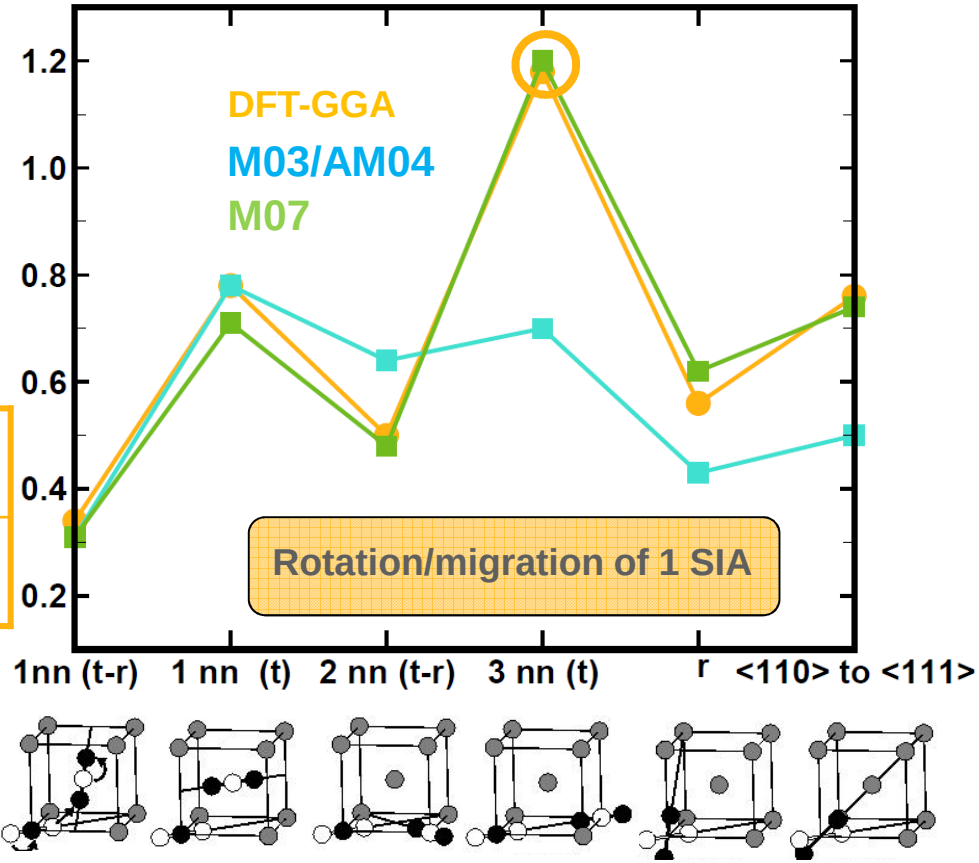
Systematic way to validate parmeters:

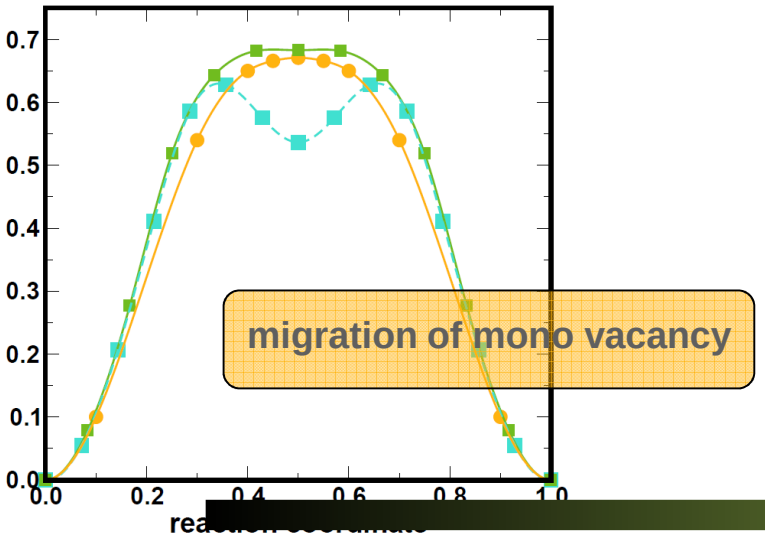
- use the k-fold cross validation

EAM potential fitted on ab-initio data

With this new Fe potentials we are able to be in good agreement over many ab-intio data which are not included in the fit:

Exp	DFT-GGA	Mendelev	M07
2.35±0.20 eV	2.1-2.2 eV	1.84 eV	2.12 eV





*Malerba et al. JNM 406, 19 (2010) with one typo corrected in:
MCM et al, PRL 108, 025501 (2012)

Adjoint method

$$J(\mathbf{w}) = \frac{1}{2}\sum_{obs}\sum_{i} a_i^{obs}\left[F_i(\mathbf{w}) - Y_i^{obs}\right]^2$$

$$J(\mathbf{w}) = \frac{1}{2}\langle \mathbf{F}(w) - \mathbf{Y}^{obs}, \mathbf{F}(w) - \mathbf{Y}^{obs}\rangle$$

F is supposed to be sufficintly regular in w0:
Tangent-linear model

$$\delta\mathbf{F} = \mathbf{A}(\mathbf{w_0})\,\delta\mathbf{w}$$

$$J(\mathbf{w}) = J(\mathbf{w_0}) + \langle \nabla_{\mathbf{w}} J(\mathbf{w_0}), \mathbf{w} - \mathbf{w_0}\rangle$$

$$\delta J = \langle \nabla_{\mathbf{w}} J(\mathbf{w_0}), \delta\mathbf{w}\rangle$$

$$J(\mathbf{w}) = \frac{1}{2}\langle \mathbf{A}(\mathbf{w_0})\,\delta\mathbf{w} - \mathbf{Y}^{obs}, \mathbf{A}(\mathbf{w_0})\,\delta\mathbf{w} - \mathbf{Y}^{obs}\rangle$$

$$\delta J = \langle \left[\mathbf{F}(\mathbf{w}) - \mathbf{Y}^{obs}\right], \mathbf{A}(\mathbf{w_0})\,\delta\mathbf{w}\rangle$$

$$\nabla_{\mathbf{w}} J(\mathbf{w_0}) = \mathbf{A}^{\star}(\mathbf{w_0})\left[\mathbf{F}(\mathbf{w}) - \mathbf{Y}^{obs}\right]$$

$$\langle u, Av\rangle = \langle A^{\star}u, v\rangle$$

Many advantages of the adjoint model over the direct finite diferences

Adjoint: relates gradients, the role is inversed between input and output
Tangent: relates perturbations, takes perturbations of the input to determine those of the output

$$\delta J = \langle \mathbf{A}^{\star}(\mathbf{w_0})\left[\mathbf{F}(\mathbf{w}) - \mathbf{Y}^{obs}\right], \delta\mathbf{w}\rangle$$

Adjoint model

Efficiency (in « J evaluation » units) :

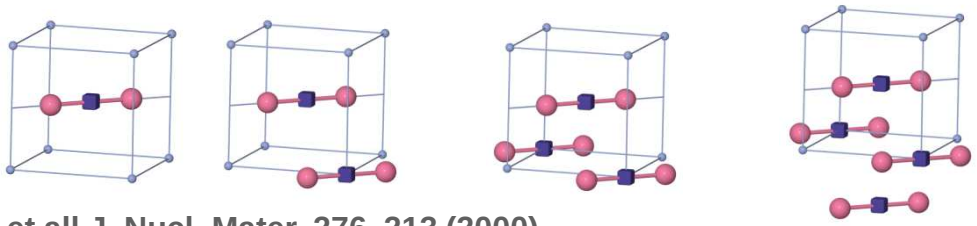
- Adjoint: 2-5 evaluations
- Tangent: n + 1 evaluations in finite differences

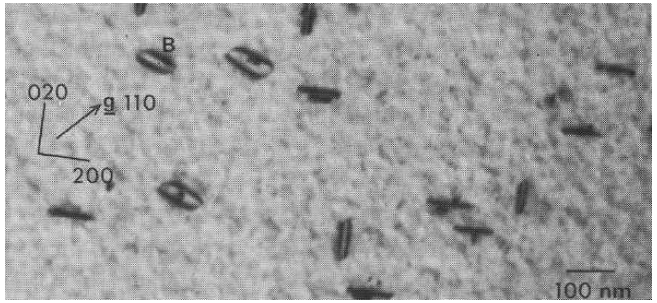
Stability:

- Adjoint: very stable
-Tangent: unstable
- Adjoint: it can be demonstrated that is the optimal approach: the error is minimized

EAM potential fitted on ab-initio data

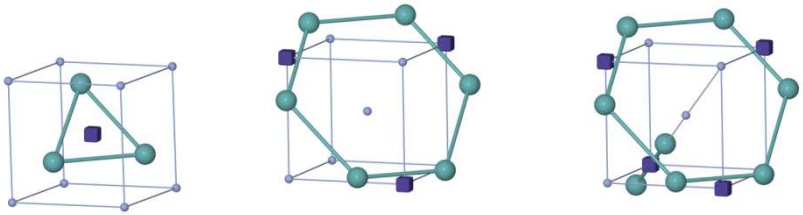
n=1 2 3 4 100-10 000 # SIAs in cluster



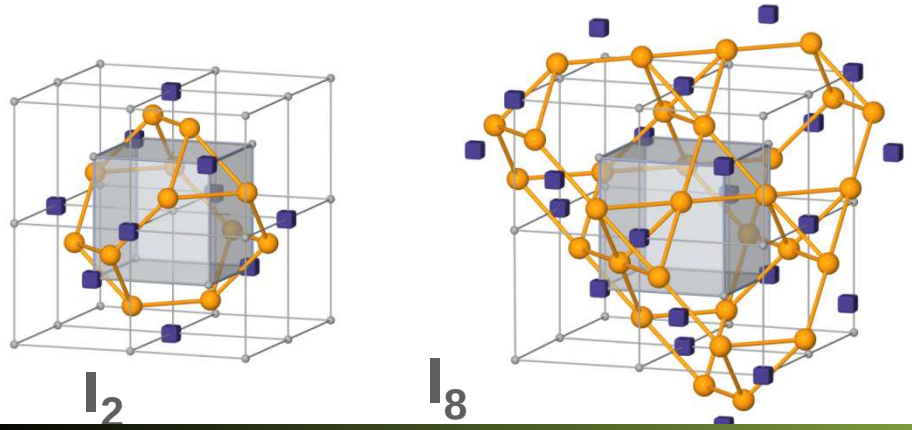


F. Gao et all J. Nucl. Mater. 276, 213 (2000).
C. Domain, C. S. Becquart, Phys. Rev. B 65, 024103 (2001)
C.-C. Fu, F. Willaime, and P. Ordejon, Phys. Rev. Lett. 92, 175503 (2004).

D.A Terentyev et al. Phys. Rev. Lett. 100, 145503 (2008)



M.-C. Marinica, F. Willaime J-P Crocombette, Phys. Rev. Lett. (2012)

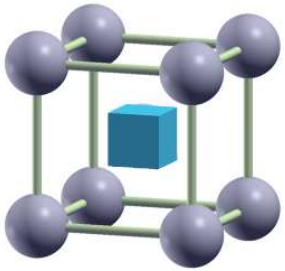


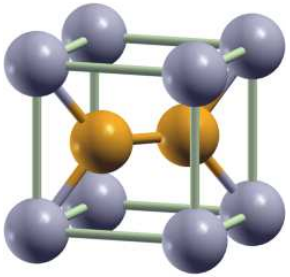
I_2 I_8

Nano-cristals

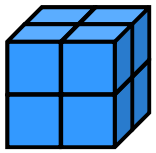
MORPHOLOGY OF DEFECT CLUSTERS IN METALS UNDER IRRADIATION

n=1 — 10 — 100-10 000 # defects in cluster



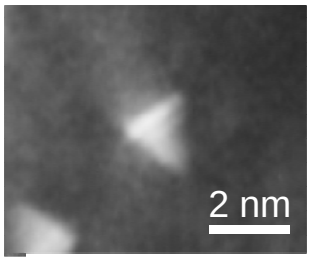


3D



voids

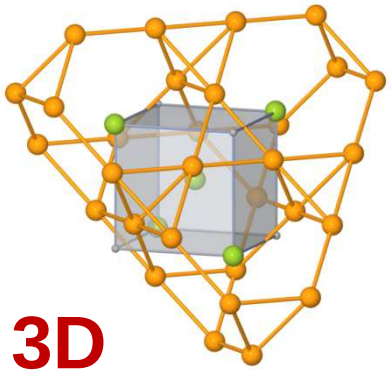
3D



SFT

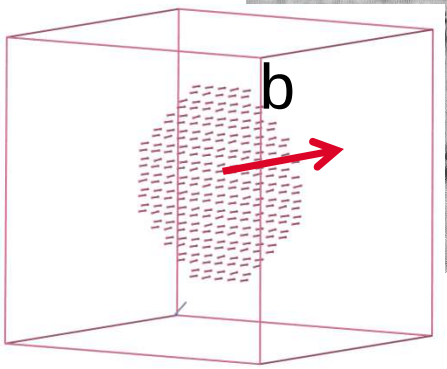
2D

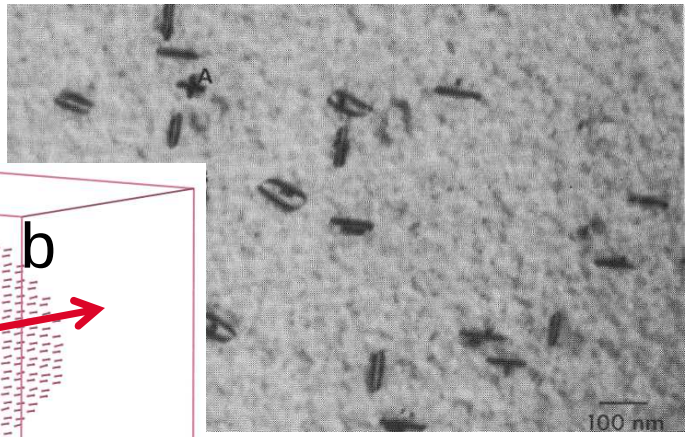
loops



3D

Prediction from atomistic simulations

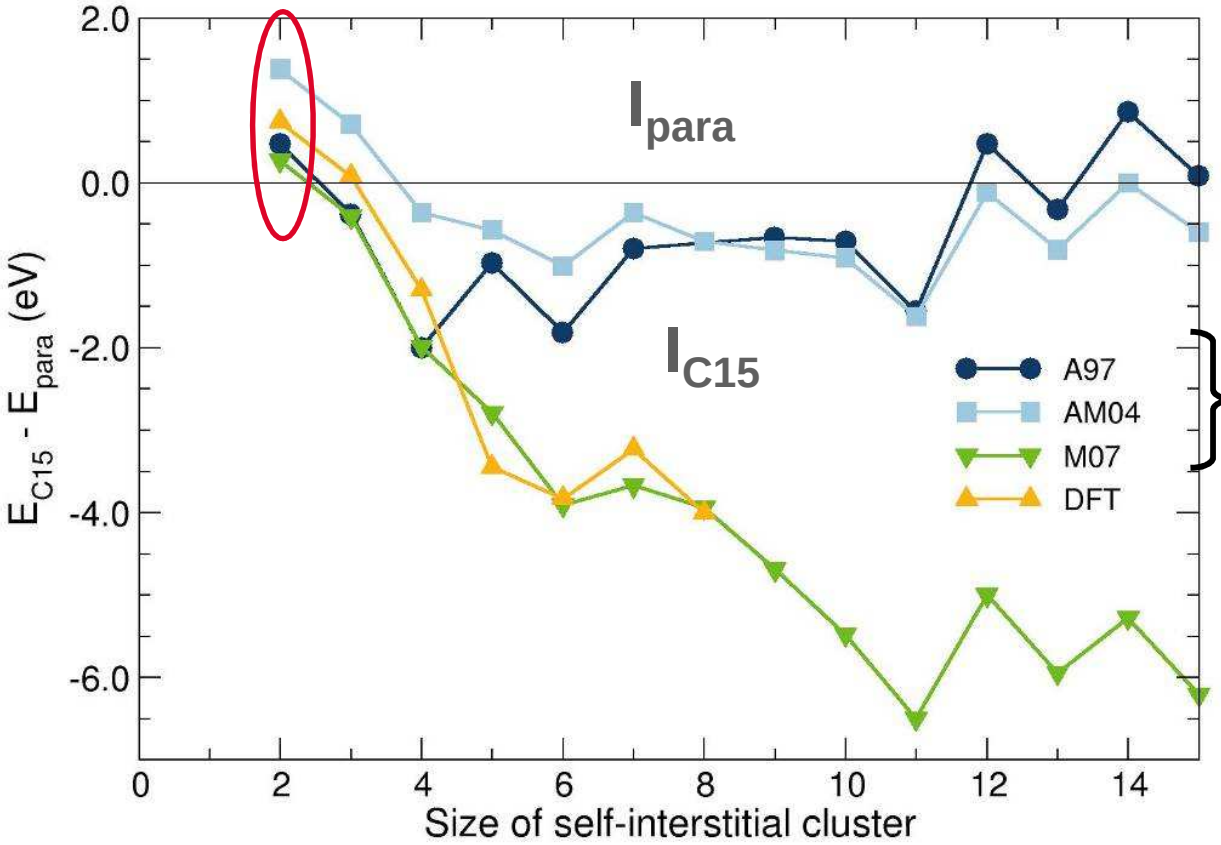




2D

STABILITY OF C15 INTERSTITIAL CLUSTERS IN FE

Stability of C15 clusters against loops

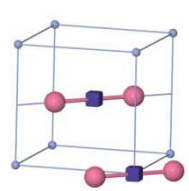
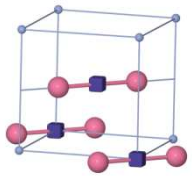
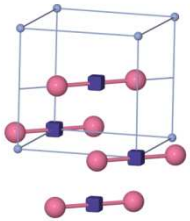


M07: improved by including in the fit a large data base of DFT defect properties (no C15 clusters)

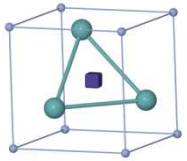
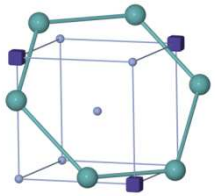
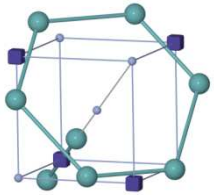
EAM potentials

DFT calculations: PWSCF code, 250 atoms, tested against pseudopotential (USPP and PAW), semicore states, LDA/GGA, cell size

EAM potential fitted on ab-initio data

1. **Self-trapped configurations (I4)**
2. **Stabilized at high temperature**

D.A Terentyev, T.P.C Klaver, P. Olsson, M.-C. Marinica, F. Willaime, C. Domain, L. Malerba, Phys. Rev. Lett. 100, 145503 (2008)

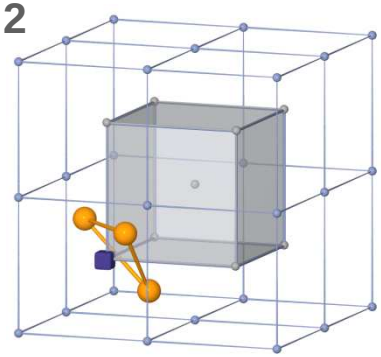
+ 0.31 AM04

- 0.11 DFT

+ 0.02 M07

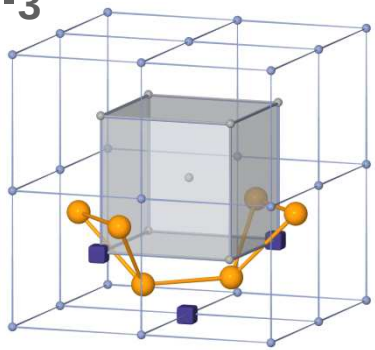
C15 clusters: a combination of ring and triangle configuration

I_2



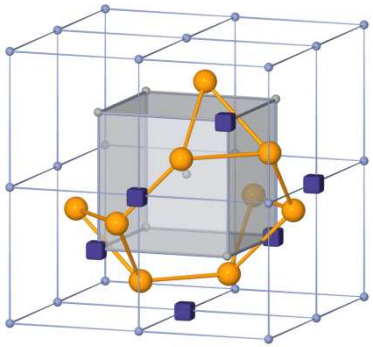
3i - 1v

I_3



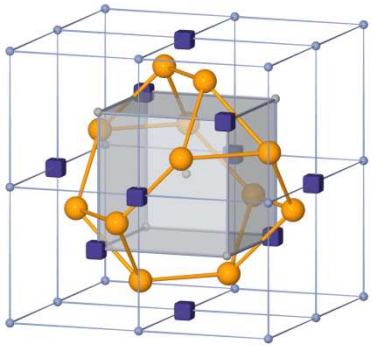
6i - 3v

I_3



9i - 6v

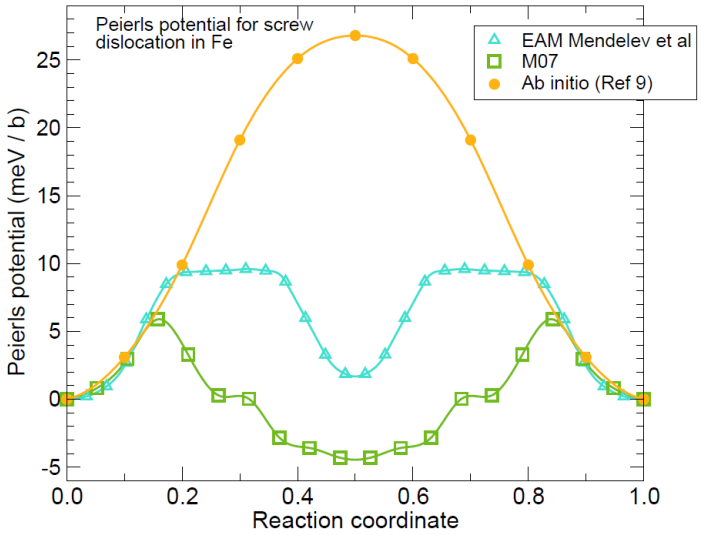
I_2



12i - 10v

4 triangles
4 rings

Fe EAM potentials: screw dislocation



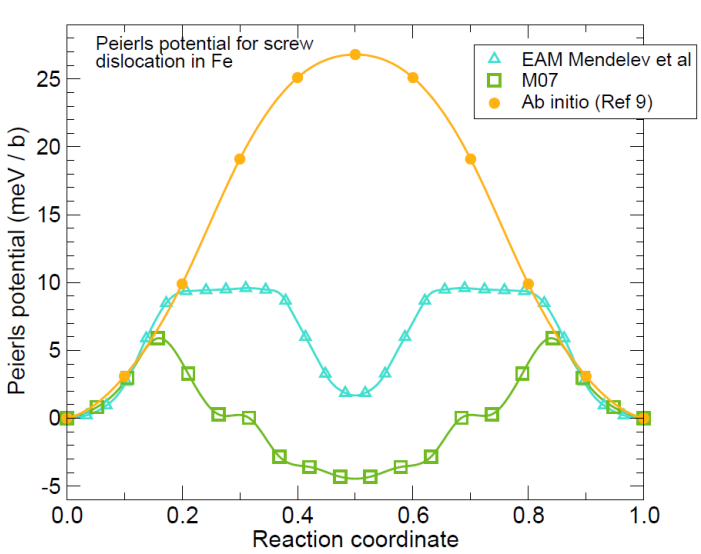
Refitting by changing the weights in objective function in order to have more equilibrated potential

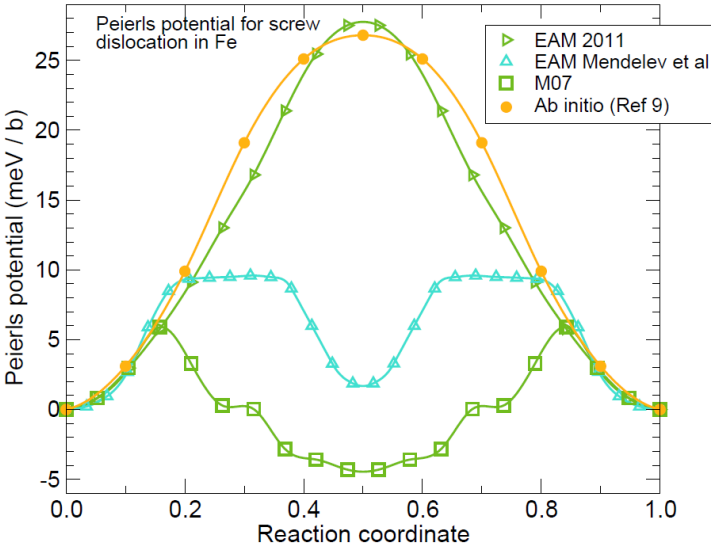
$$J(\mathbf{w}) = \frac{1}{2}\sum_{obs}\sum_{i} a_i^{obs}\left[F_i(\mathbf{w}) - Y_i^{obs}\right]^2$$

L. Proville, D. Rodney, and M.-C. Marinica, Nature Materials, **11** (2012) 845

	SIA		VAC		Surfaces		Phonons		Screw d	
	1,2	N>2	1,2	N>2					P	Gp
Fe-Mendelev 2003	+/-	+/-	+/-	+/-	+	+/-	+	-	-	+
Fe-Marinica 2007	+	+	+	+	+	+	+	+	-	-
Fe-Ackland-Mendelev 2004	+/-	+/-	+/-	+/-	+	+/-	+	+	-	-

Fe EAM potentials: screw dislocation



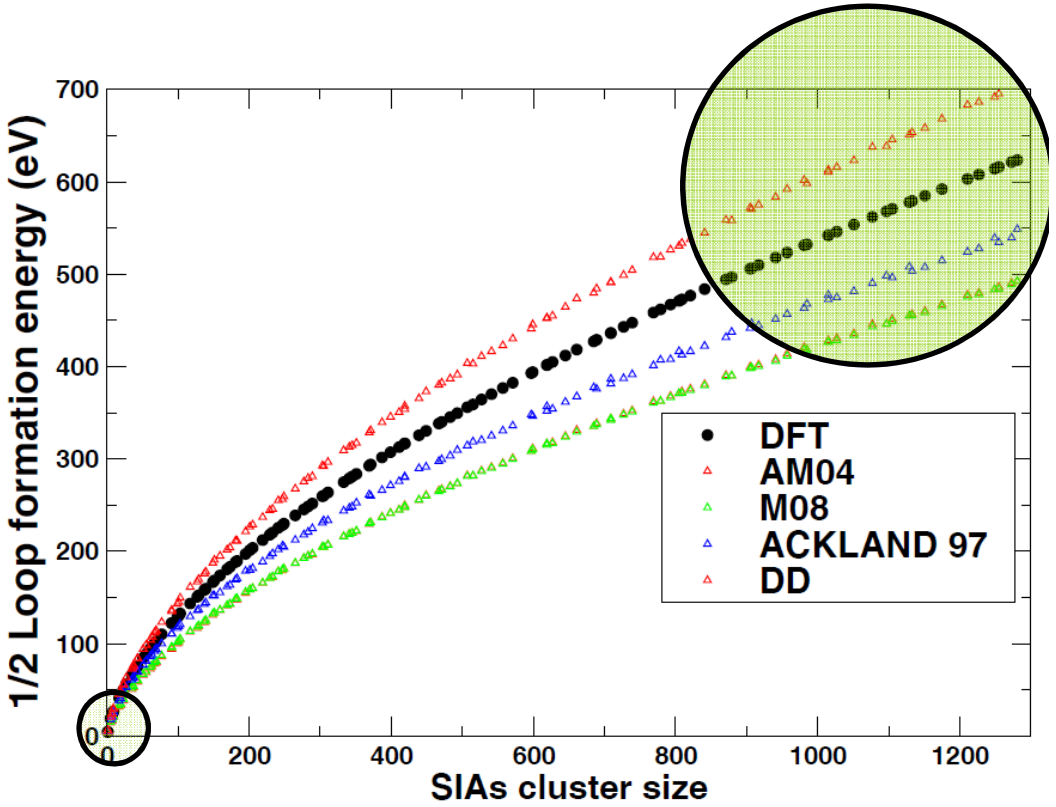


	SIA		VAC		Surfaces		Phonons		Screw d	
	1,2	N>2	1,2	N>2					P	Gp
Fe-Mendelev 2003	+/-	+/-	+/-	+/-	+	+/-	+	-	-	+
Fe-Marinica 2007	+	+	+	+	+	+	+	+	-	-
Fe-Ackland-Mendelev 2004	+/-	+/-	+/-	+/-	+	+/-	+	+	-	-
Fe-Proville 2012	-	-	+	+	+	+/-	+/-	+/-	+	+

FORMATION ENERGY OF DISLOCATION LOOPS IN IRON

Extrapolation to millions of atoms:

- Limitations
- Problem to link with continuum theories as the elasticity



Rebecca's thesis topic. Ask Rebecca for more …

EAM Potentials: Discussion & Summary

	SIA		VAC		Surfaces		Phonons		Screw d	
	1,2	N>2	1,2	N>2	γ	γ_{GSF}	$p=0$	$p\neq 0$	P	Gp
Fe-Mendelev 2003	+/-	+/-	+/-	+/-	+	+/-	+	-	-	+
Fe-Marinica 2007	+	+	+	+	+	+	+	+	-	-
Fe-Ackland-Mendelev 2004	+/-	+/-	+/-	+/-	+	+/-	+	+	-	-
Fe-Gordon Mendelev 2011	+	+	+/-	+/-	+	+/-	+	+	-	+
Fe-Proville 2012	-	-	+/-	+/-	+	+/-	+/-	+/-	+	+
W-EAM4-Marinica 2013	+	+/-	+/-	+	+/-	+	+	+/-	+	-
W-EAM2-Marinica 2013	+/-	-	+/-	+/-	+/-	+/-	+	+	+/-	+

Trying to play with the weights in the database ….

$$J(\mathbf{w}) = \frac{1}{2}\sum_{obs}\sum_{i} a_i^{obs}\left[F_i(\mathbf{w}) - Y_i^{obs}\right]^2$$

EAM Potentials: Discussion & Summary

	SIA		VAC		Surfaces		Phonons		Screw d	
	1,2	N>2	1,2	N>2	γ	γ_{GSF}	$p=0$	$p\neq 0$	P	Gp
Fe-Mendelev 2003	+/-	+/-	+/-	+/-	+	+/-	+	-	-	+
Fe-Marinica 2007	+	+	+	+	+	+	+	+	-	-
Fe-Ackland-Mendelev 2004	+/-	+/-	+/-	+/-	+	+/-	+	+	-	-
Fe-Gordon Mendelev 2011	+	+	+/-	+/-	+	+/-	+	+	-	+
Fe-Proville 2012	-	-	+/-	+/-	+	+/-	+/-	+/-	+	+
Fe-Alexander 2014	+/-	+/-	+/-	+/-	+	+/-	+	+	+/-	+
W-EAM4-Marinica 2013	+	+/-	+/-	+	+/-	+	+	+/-	+	-
W-EAM2-Marinica 2013	+/-	-	+/-	+/-	+/-	+/-	+	+	+/-	+
W-EAM3-Marinica 2013	+/-	+	+/-	+/-	+/-	+/-	+	+	+/-	+

Probably we try to ask too much. A good approach is to:

- **design potentials adapted for a well defined problem.**
- **Use the potentials as imaginary experiment in order to understand the physics**

- Towards semi-empirical potentials
  - DFT, TB, BOP, MEAM, EAM…
  - Istres 2015 potential « analytical BOP »
- Fitting an EAM potential metallic defects orientated
  - Database
  - Fitting
  - Limitations
- Forget EAM, BOP, MEAM? Machine learning ?
  - (Kernel) Ridge regression
  - Bayesian inference