John von Neumann Institute for Computing

Systematic Analysis and Extension of Embedded Atom Methods

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Introduction

- ✓ Embedded-atom method-type force fields (EAM) are among the most popular classical model potentials for pure metals and alloys

$$E_i = \frac{1}{2}\sum_{j \neq i} V(\vec{r}_{ij}) + F\left[\sum_{j \neq i} \rho(\vec{r}_{ij})\right]$$

- ✓ EAM composed of core repulsion V, embedding energy F and charge density ρ. V and F can be chosen to reproduce a given equation of state (EOS).

Introduction

- ✓ Some advantages:

  For exponential V and ρ, and $F \sim -\rho^{\alpha}$, $(0 < \alpha < 1)$,

  - Dissociation energy per atom E_0 scales as Z^{α}
  - Vacancy energies $\sim Z[Z^{\alpha} - (Z-1)^{\alpha}] \sim \alpha Z^{\alpha}$ - ...
  - Nearest neighbor distances $a_0 \sim \log(Z/Z_0)$

- ✓ Some challenges:

  - Charge distribution is rigid, no electrostatics
  - Directionality of bonding
  - FCC/HCP energy difference due to long range part

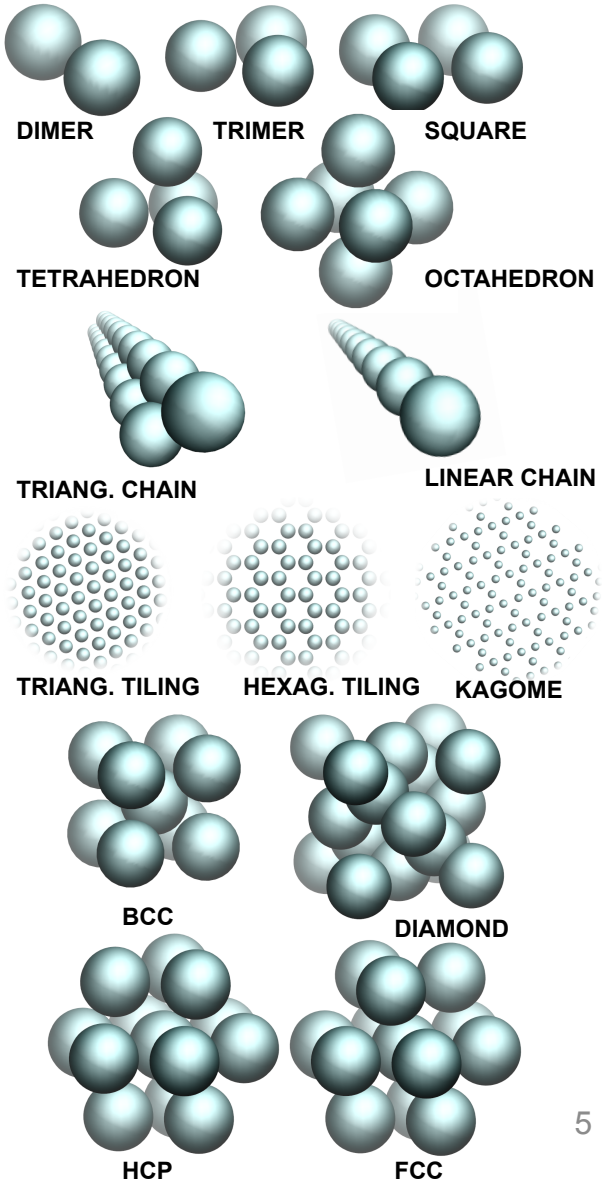
Motivation

- Transferability of EAM between different coordination environments?
- Ingredients yielding the highest transferability?
- How to overcome the limitations?
- How much complexity is really needed?

Methods

- ✓ Set of clusters, quasi-1D chains, layers and 3D lattices is constructed
- ✓ All systems are charge transfer free
- ✓ *Ab initio* copper taken as fictional reference material
- ✓ E_0, a_0 and $S = \left.\frac{\partial^2 E(a)}{\partial a^2}\right|_{a=a_0}$ from density functional theory (DFT) calculations
- ✓ Some systems metastable or purely hypothetical

- *Quantum Espresso DFT suite 5.0.3*
- *Hartwigsen-Goedecker-Hutter pseudopotential with semicore state in valence*
- *Perdew-Burke-Ernzerhof exchange-correlation functional*
- *16x16x16 k-point grid*
- *Planewave cut-off 200 Ry*



Methods

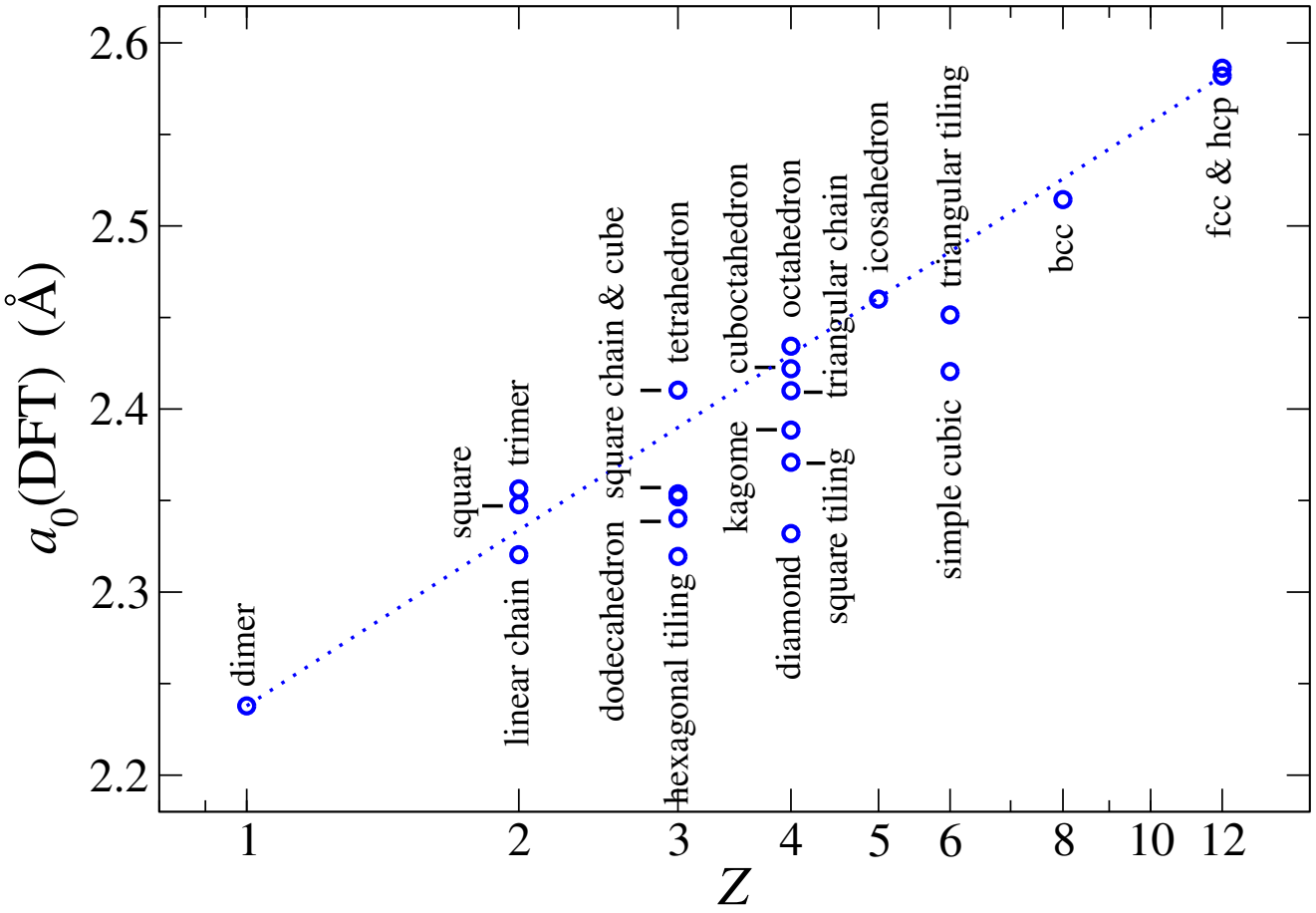
- ✓ Gupta potential[1] is chosen as reference model:

$$V(r) = V_0 \exp(-r/\sigma_R), \quad \rho(r) = \exp(-r/\sigma_Q), \quad F[\bar{\rho}] = -A\bar{\rho}^{1/2}$$

- ✓ Charge density, core repulsion and embedding function are varied one at a time
- ✓ Parameters fitted by optimizing a fitness function $\chi^2(E_0, a_0, S)$

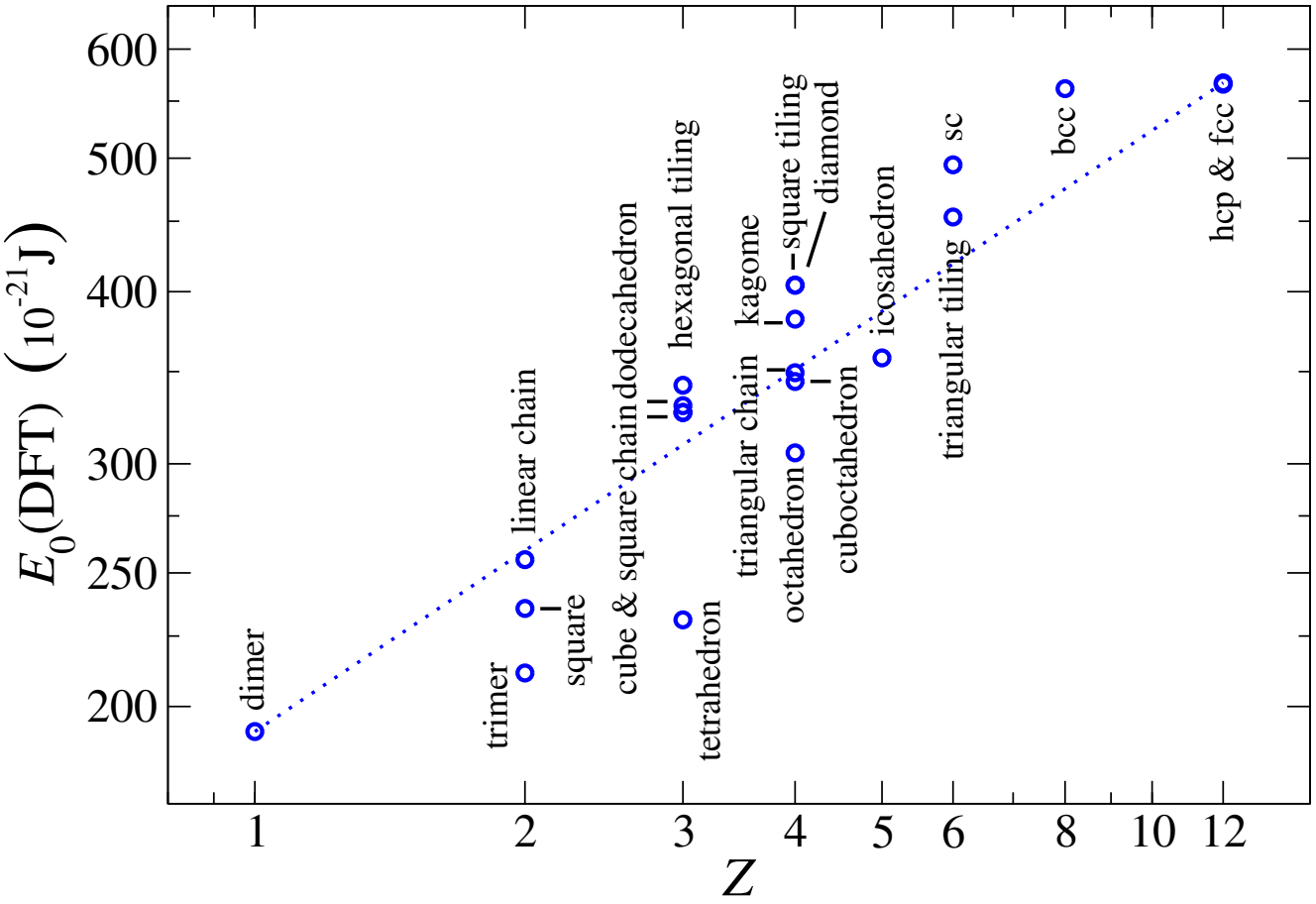
- [1] *R. P. Gupta, Phys. Rev. B, **23**, 6265, (1981)*

Ab initio nearest neighbor distances



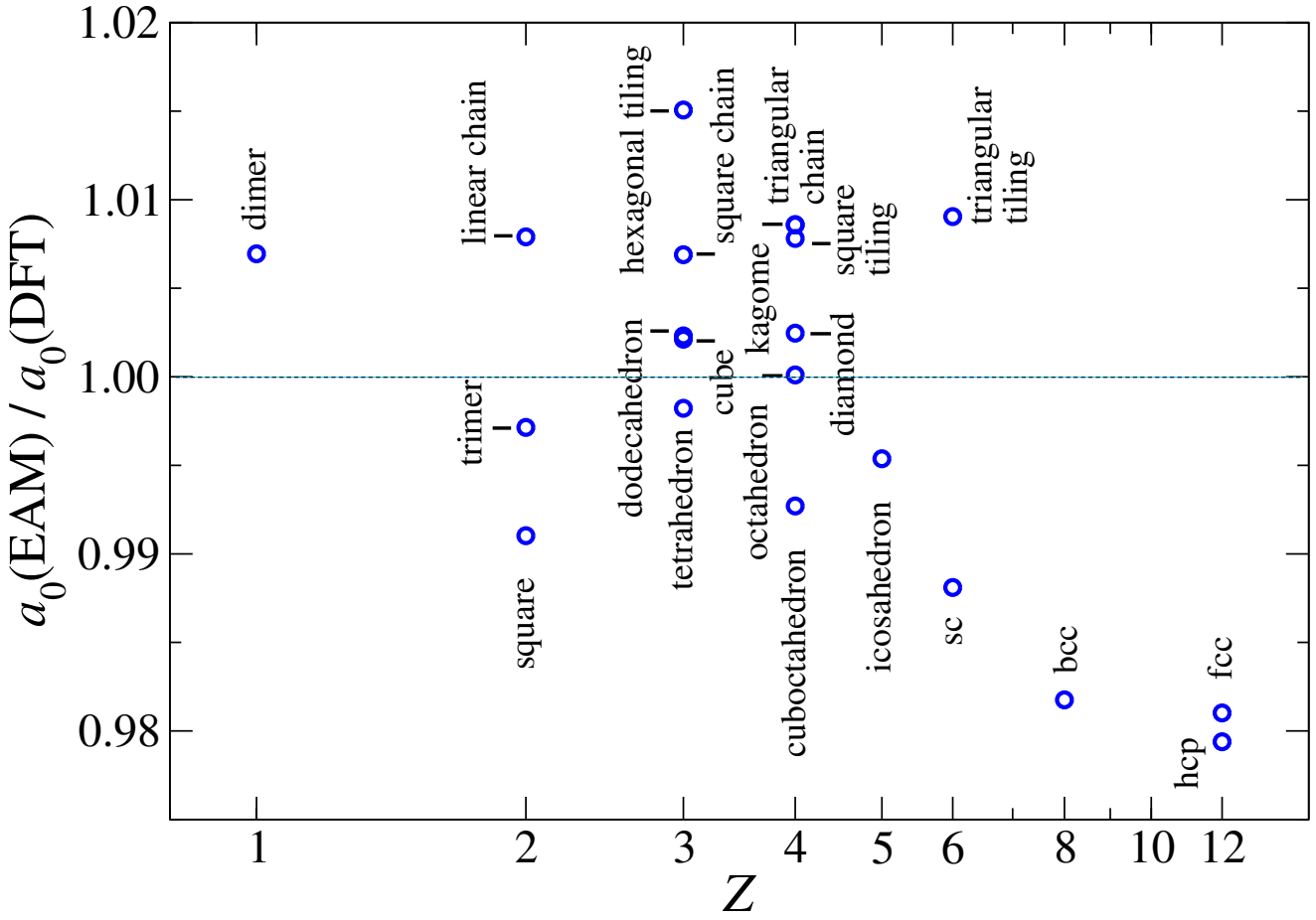
✓ Trend is roughly logarithmic

Ab initio dissociation energies



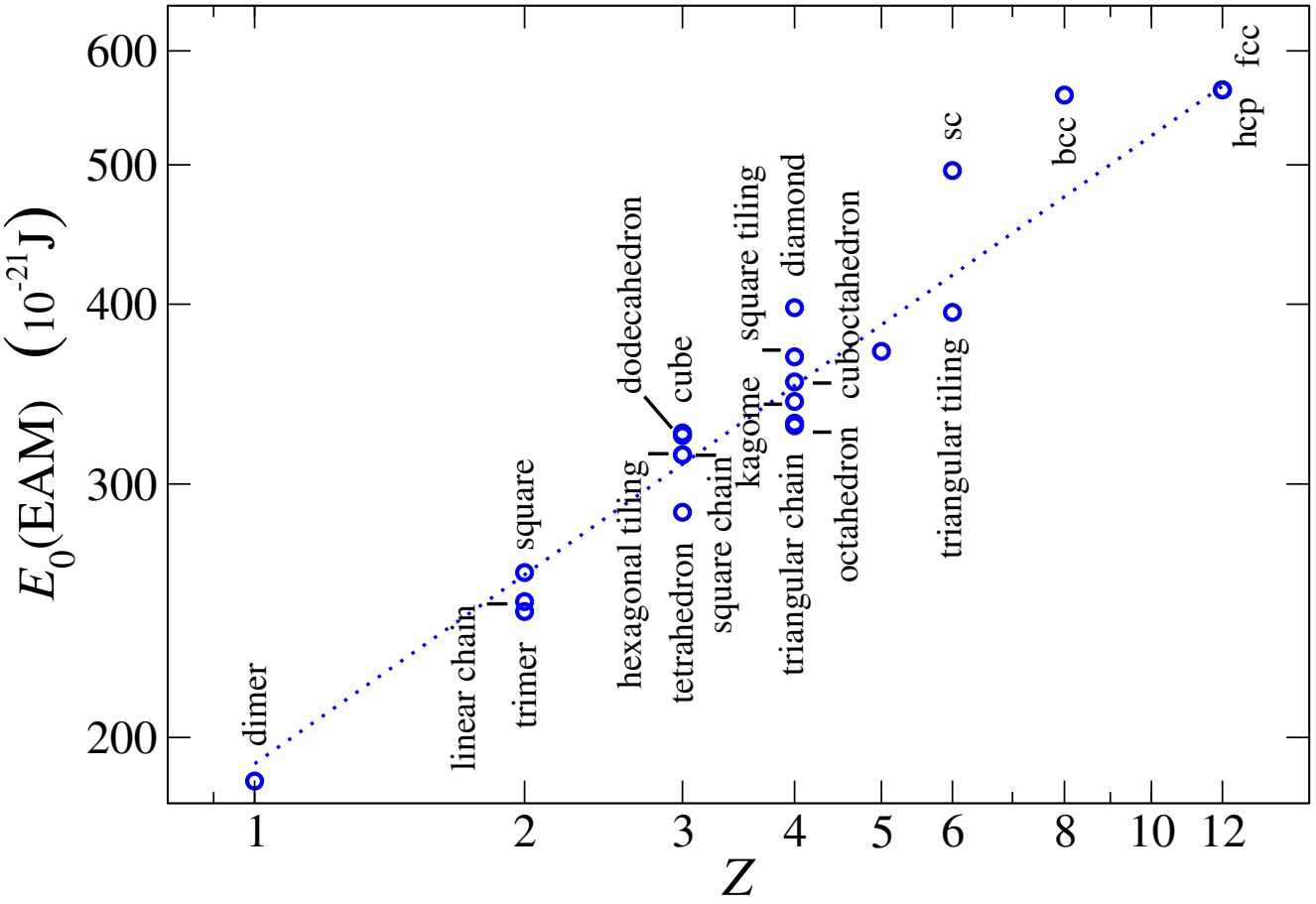
✓ Line corresponds to exponent ~ 0.405

Gupta nearest neighbor distances



- ✓ Bulk underestimated, low dimensions overestimated

Gupta dissociation energies



✓ The scatter is relatively narrow

Core Repulsions

$$E_i = \frac{1}{2}\sum_{j\neq i} V(\vec{r}_{ij}) + F\left[\sum_{j\neq i}\rho(\vec{r}_{ij})\right]$$

$V(r)$	Exponential (Gupta)	Gaussian	Screened Coulomb	Rose-Vinét	Birch-Murnaghan
χ	0.67	0.69	0.67	0.84	0.81

$\chi^2 = 1$ when $\Delta a/a_{DFT} \sim 1\%$, $\Delta E/E_{DFT} \sim 5\%$ and $\Delta S/S_{DFT} \sim 15\%$.

Embedding Functions

$$E_i = \frac{1}{2}\sum_{j \neq i} V(\vec{r}_{ij}) + F\left[\sum_{j \neq i} \rho(\vec{r}_{ij})\right]$$

$F(\bar{\rho})$	Square root (Gupta)	ρ log ρ	Taylor polynomial $O(\rho^4)$	Rose-Vinét	Birch-Murnaghan
χ	0.67	0.92	1.17	0.75	0.57

$\chi^2 = 1$ when $\Delta a/a_{DFT} \sim 1\%$, $\Delta E/E_{DFT} \sim 5\%$ and $\Delta S/S_{DFT} \sim 15\%$.

Charge Densities

$$E_i = \frac{1}{2}\sum_{j \neq i} V(\vec{r}_{ij}) + F\left[\sum_{j \neq i} \rho(\vec{r}_{ij})\right]$$

$\rho(r)$	Exponential (Gupta)	Gaussian	Double Gamma	Finnis-Sinclair
χ	0.67	0.78	0.89	0.65

$\chi^2 = 1$ when $\Delta a/a_{DFT} \sim 1\%$, $\Delta E/E_{DFT} \sim 5\%$ and $\Delta S/S_{DFT} \sim 15\%$.

Charge Densities

$$E_i = \frac{1}{2}\sum_{j\neq i} V(\vec{r}_{ij}) + F\left[\sum_{j\neq i} \rho(\vec{r}_{ij})\right]$$

$\rho(r)$	Exponential (Gupta)	Gaussian	Double Gamma	Finnis-Sinclair	Orig. MEAM
χ	0.67	0.78	0.89	0.65	0.64

$\chi^2 = 1$ when $\Delta a/a_{DFT} \sim 1\%$, $\Delta E/E_{DFT} \sim 5\%$ and $\Delta S/S_{DFT} \sim 15\%$.

Charge Density Gradient Corrections

- ✓ Stott and Zaremba[1] proposed gradient corrections already in 1980
- ✓ Modified Embedded-Atom Method[2] charge density can also be cast in a similar form
- ✓ We denote

$$\rho_{\alpha_1,\ldots,\alpha_n} = \sigma_Q^n \frac{\partial^n \rho(r)}{\partial\alpha_1 \cdots \partial\alpha_n}$$

where each $\alpha_i \in \{x, y, z\}$

- [1] *M. J. Stott and E. Zaremba, Phys. Rev. B,* ***22****, 1564, (1980)*
- [2] *M. I. Baskes, J. S. Nelson and A. F. Wright, Phys. Rev. B,* ***40****, 6085, (1989)*

Charge Density Gradient Expansions of Energy Functional

- ✓ Energy functional can be expanded in terms of rotation- and reflection symmetric combinations of $\bar{\rho}_{\alpha_1,\ldots,\alpha_N}$,

where it has been denoted

$$\bar{\rho}(\vec{r}) = \sum_j \rho(|\vec{r}_j - \vec{r}|)$$

Table 1: All invariants of ranks 2 and 4

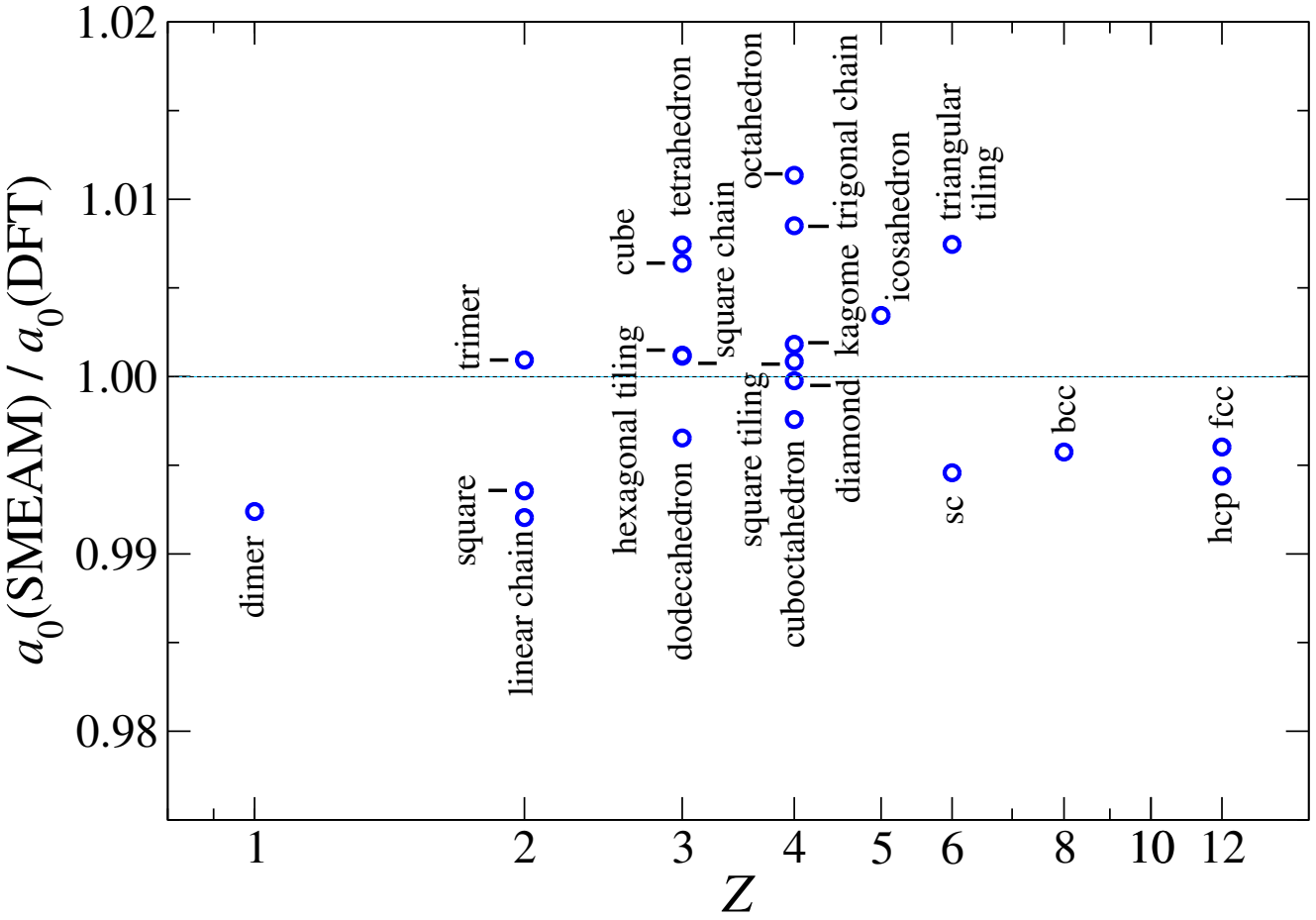
$\bar{\rho}_{\alpha_1}\bar{\rho}_{\alpha_1} \equiv SG$	$(SG)^2 \equiv SG2$
$\bar{\rho}_{\alpha_1\alpha_1} \equiv H$	$H^2 \equiv H2$
	SGH
	$\bar{\rho}_{\alpha_1}\bar{\rho}_{\alpha_1\alpha_2\alpha_2} \equiv GT$
	$\bar{\rho}_{\alpha_1\alpha_2}\bar{\rho}_{\alpha_1\alpha_2} \equiv H2'$
	$\bar{\rho}_{\alpha_1\alpha_1\alpha_2\alpha_2} \equiv F$
	$\bar{\rho}_{\alpha_1}\bar{\rho}_{\alpha_2}\bar{\rho}_{\alpha_1\alpha_2} \equiv SGH'$

SMEAM method

- ✓ Not all invariants are of equal importance
- ✓ We find promising results with $\chi \sim 0.33$ when the prefactor of the Gupta embedding function is replaced with a linear combination of invariants SG, H2' and SG^3:

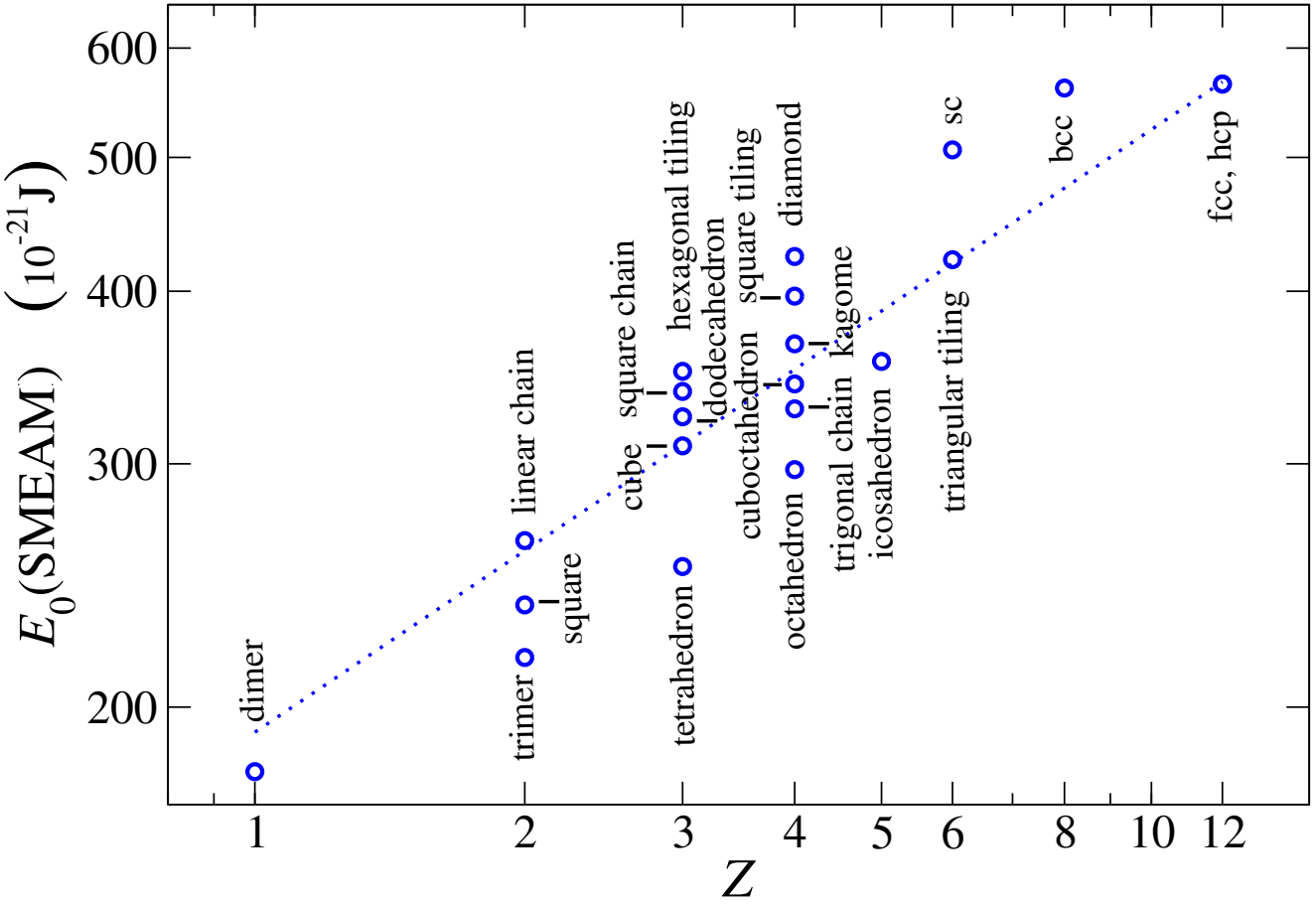
$$F_{SMEAM} = -A\sqrt{\bar{\rho}}\left(1 + c_{SG}\frac{\bar{\rho}_\alpha^2}{\bar{\rho}^2} + c_{H2'}\frac{\bar{\rho}_{\alpha\beta}^2}{\bar{\rho}^2} + c_{SG^3}\frac{\bar{\rho}_\alpha^2}{\bar{\rho}^2}\frac{\bar{\rho}_\beta^2}{\bar{\rho}^2}\frac{\bar{\rho}_\gamma^2}{\bar{\rho}^2}\right)$$

SMEAM nearest neighbor distances



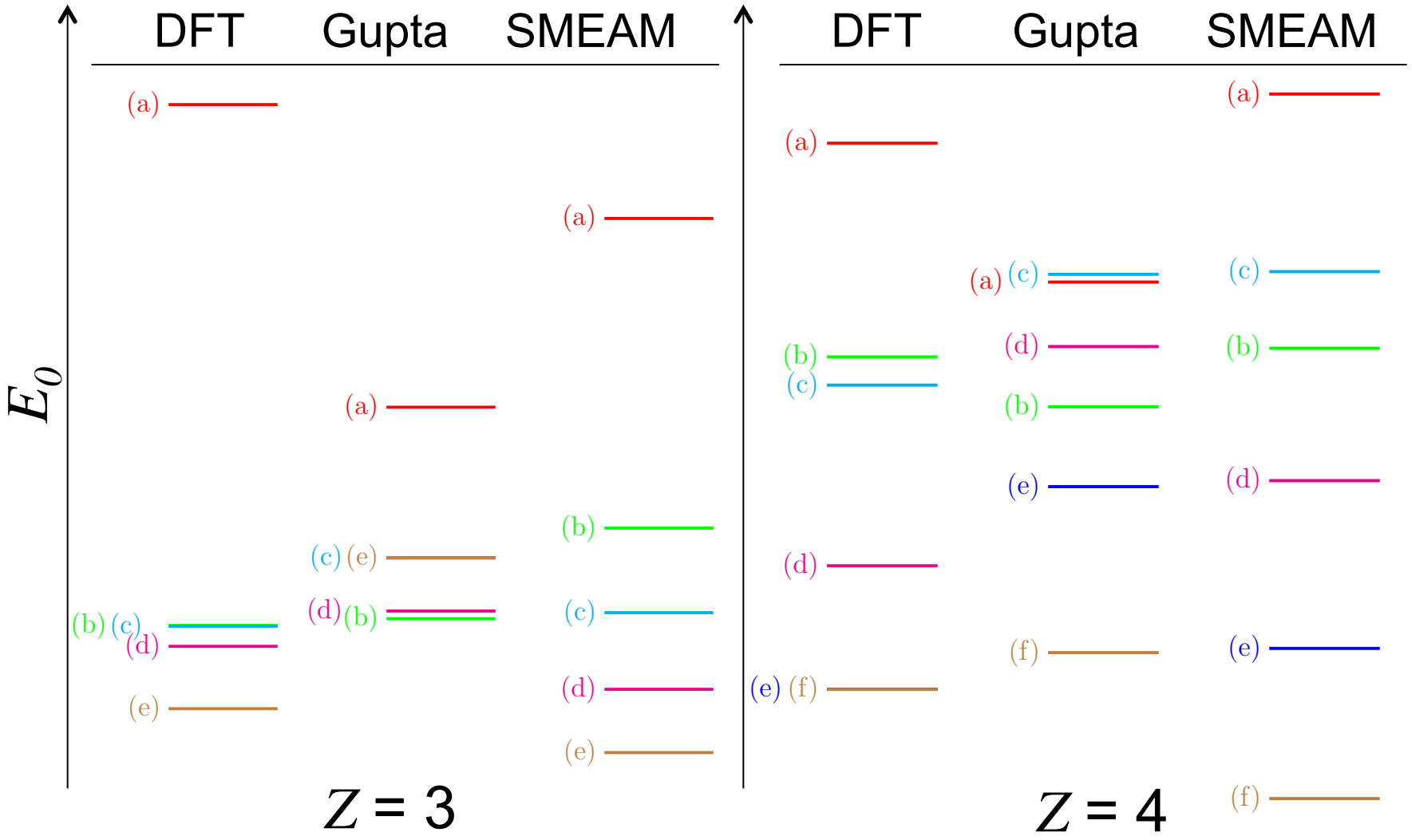
✓ Nearly all within 1% from reference

SMEAM dissociation energies

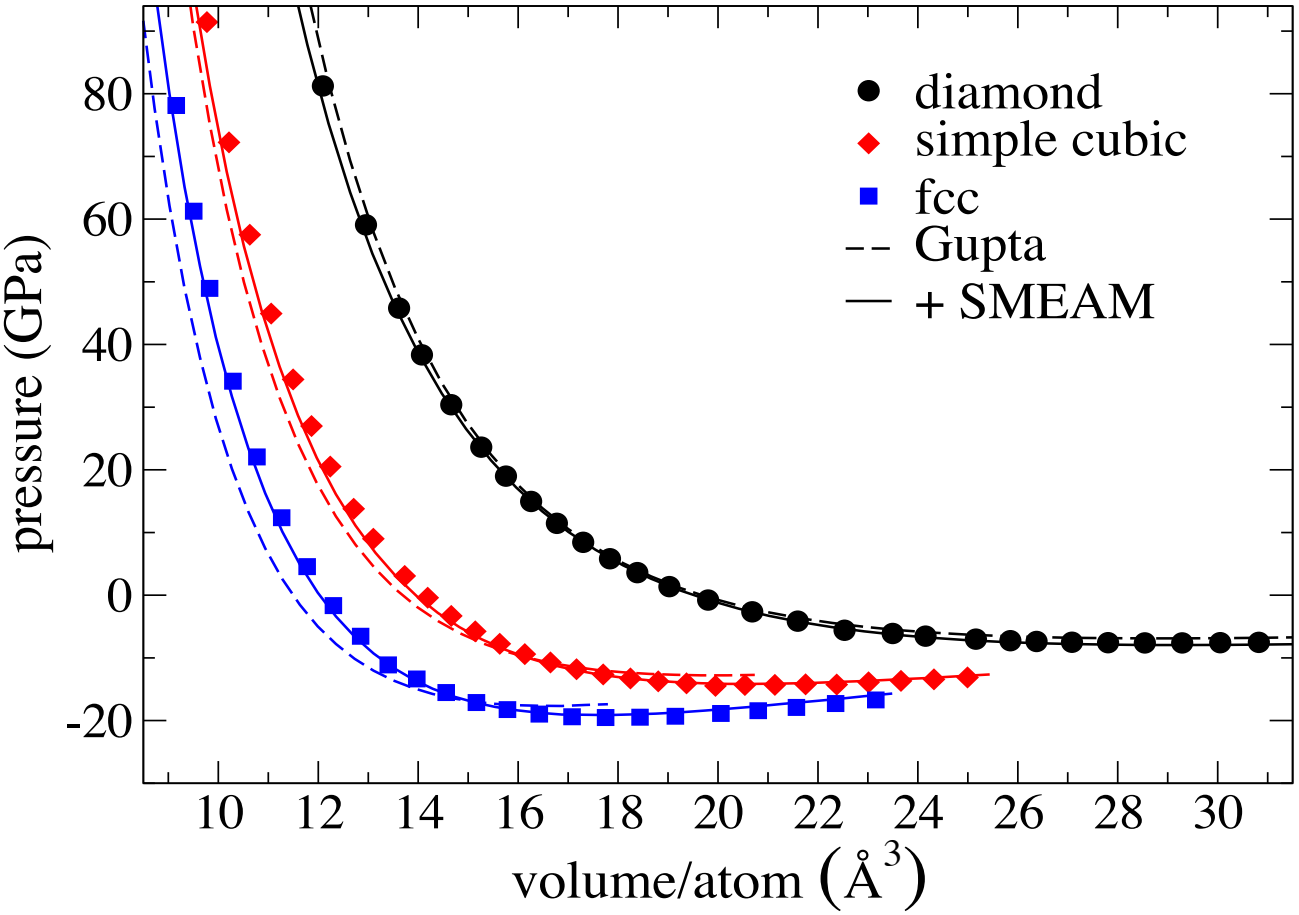


✓ Resemblance to *ab initio* is improved

Further results



Further results



✓ EOS for DC, SC and FCC reproduced up to and beyond 100 GPa

Further results

	C_{11}(fcc)	C_{12}(fcc)	C_{44}(fcc)	γ(111)	γ(100)	γ(110)	E_v
DFT	164	128	80	1.36	1.44	1.66	0.205
Gupta	164	115	81	1.45	1.64	1.53	0.215
SMEAM	160	122	67	1.45	1.62	1.74	0.184

	C_{11}(sc)	C_{12}(sc)	C_{44}(sc)	C_{11}(dc)	C_{12}(dc)	C_{44}(dc)
DFT	136	80	-13	85	36	93
Gupta	275	2.7	-24	34	57	42
SMEAM	263	15	-20	42	58	59

- *C_{ij} in units of GPa, surface energies in J/m^2, vacancy energies in 10^{-18} J.*

Conclusions

- Most forms of EAM components can be fitted to yield a similar level of transferability between geometries with $1 \leq Z \leq 12$.
- Birch-Murnaghan EOS, Finnis-Sinclair and Gupta are slightly above average.
- Transferability can be improved with charge density gradient dependent terms.