

Automating first-principles phase diagram calculations

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Previous successes of first-principles thermodynamic calculations

Composition-temperature phase diagrams

Thermodynamic properties of stable and metastable phases,

Short-range order in solid solutions,

Thermodynamic properties of planar defects

Morphology of precipitate microstructures

(Ducastelle (1991), Fontaine (1994), Zunger (1994,1997),

Ozolins *et al.* (1998), Wolverton *et al.* (2000),

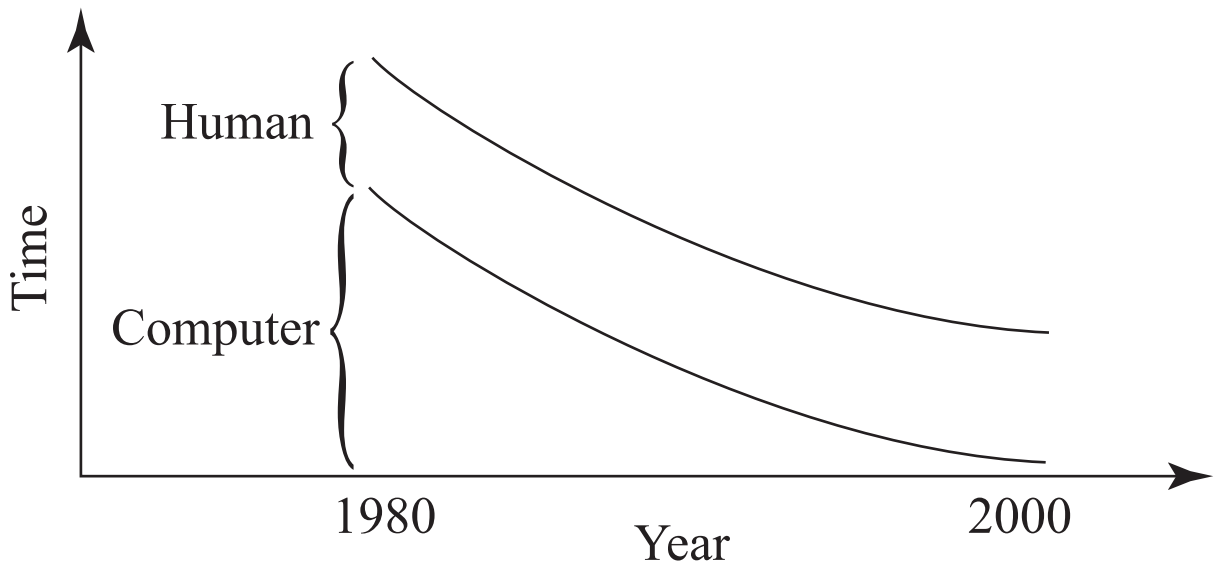
Ceder *et al.* (2000), Asta *et al.* (2001).)

First-principles Phase Diagram Calculation

Theory is well established:

(Ducastelle (1991), Fontaine (1994), Zunger (1994))

But: the task is tedious in practice.

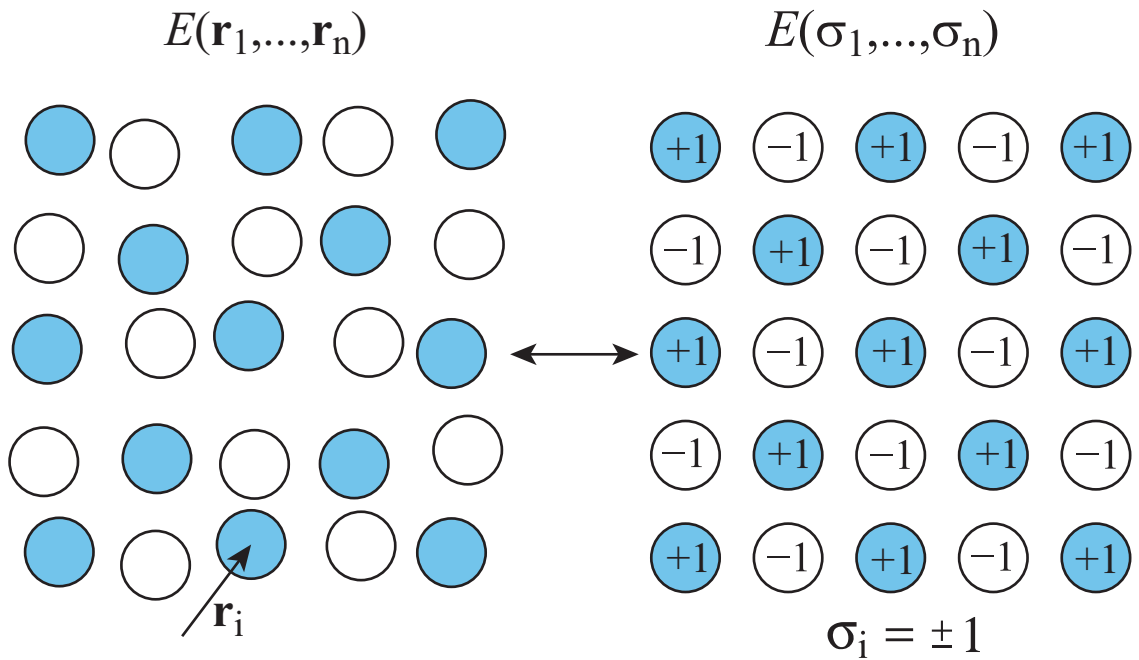


Our goal:

Automate the process in order to make this tool available to a wider community

The cluster expansion

Alloy system \longleftrightarrow Lattice model

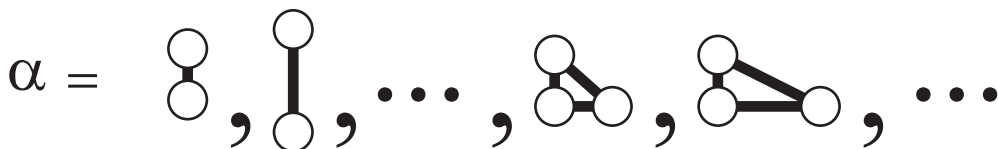


Parametrize configurational-dependence of the energy E with a polynomial in the occupation variables σ_i :

$$E(\sigma_1, \dots, \sigma_n) = \sum_{\{i,j\}} J_{ij} \sigma_i \sigma_j + \sum_{\{i,j,k\}} J_{ijk} \sigma_i \sigma_j \sigma_k + \dots$$

$$= \sum_{\alpha} J_{\alpha} \sigma_{\alpha}$$

where

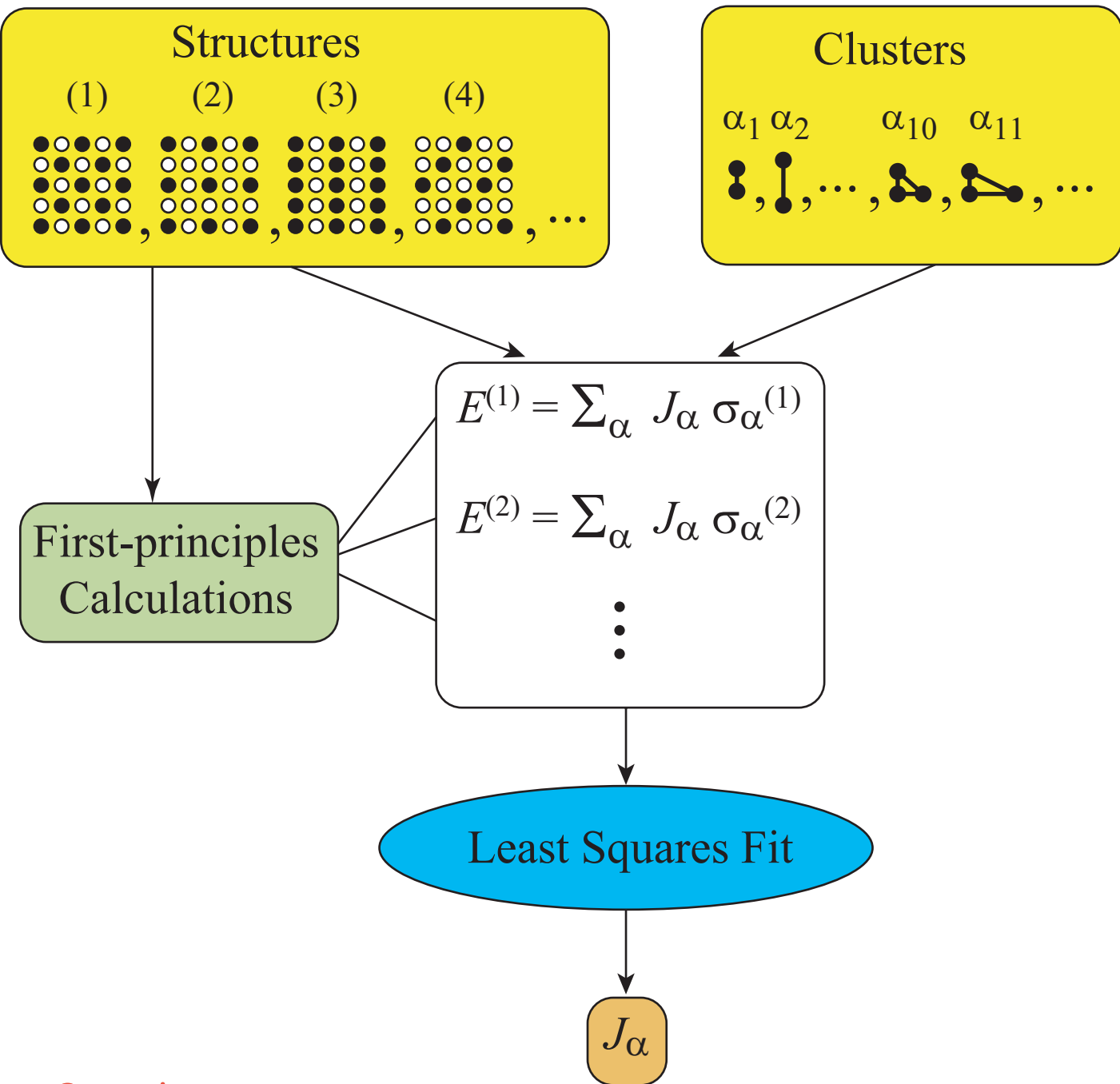


and

cluster α

$$\sigma_{\alpha} = \prod_{i \in \alpha} \sigma_i = -1$$

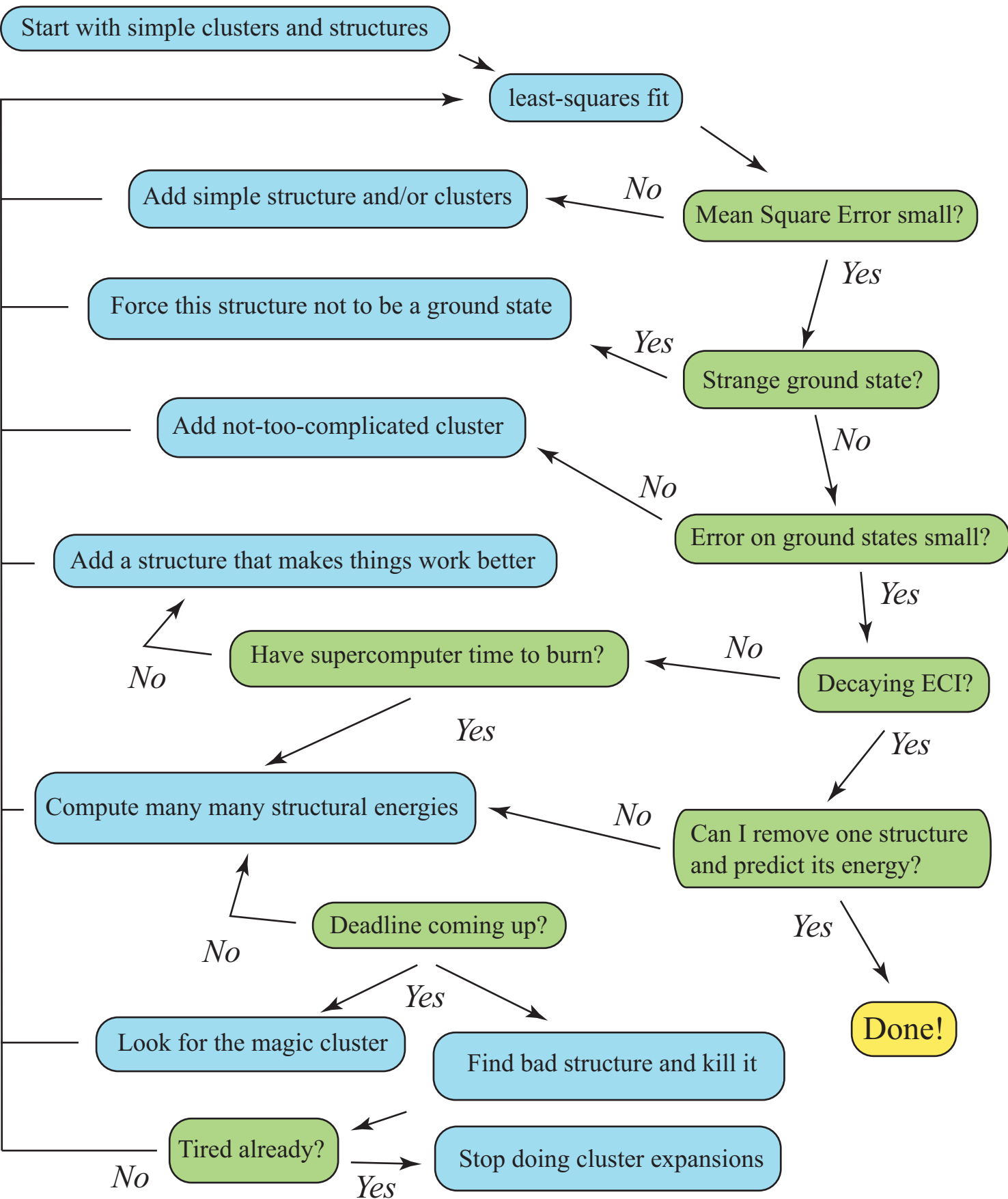
Cluster expansion fit



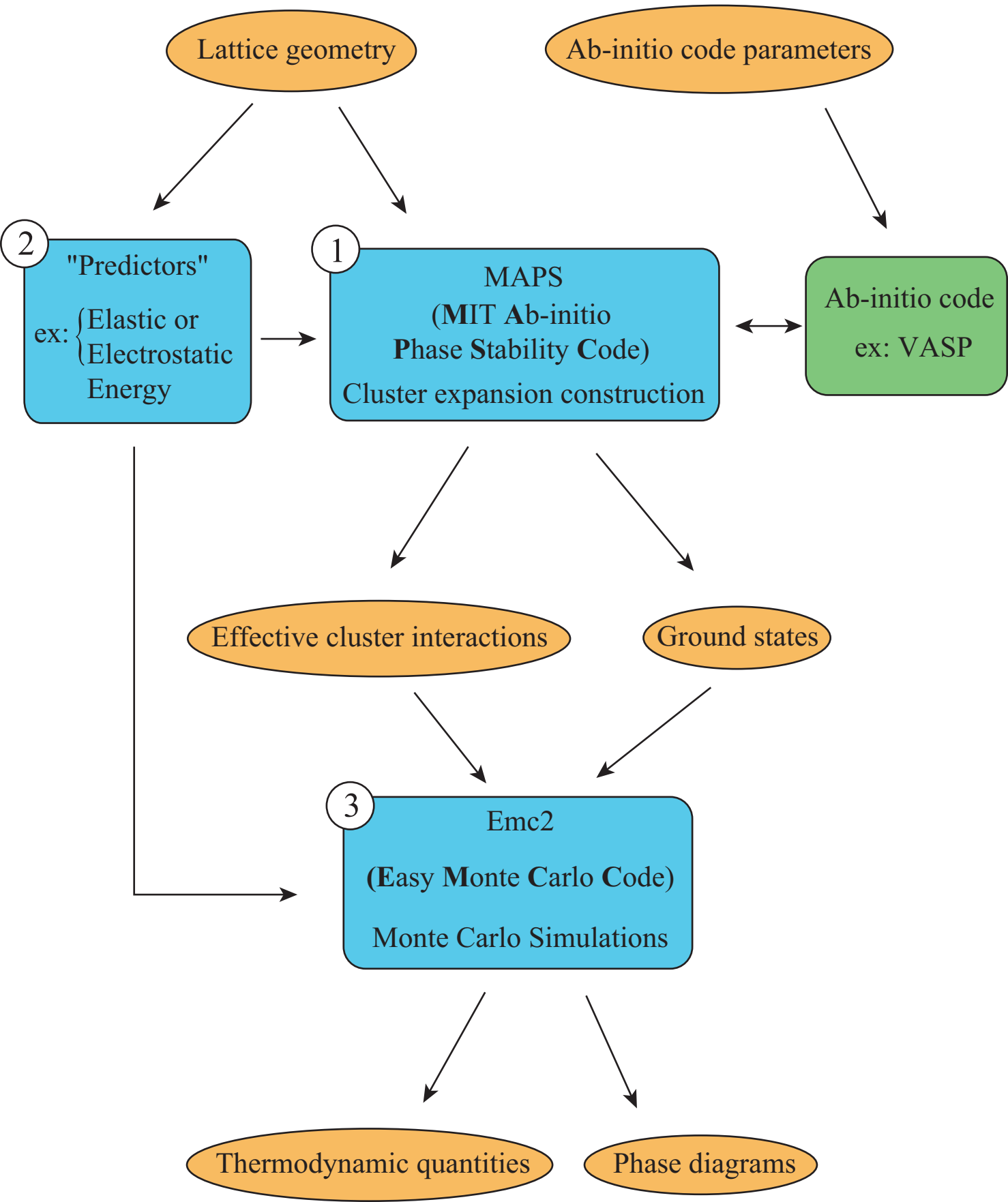
Questions:

- 1) Which clusters $\alpha_1, \alpha_2, \dots$ to include?
- 2) Which structures (1), (2), \dots , to include?

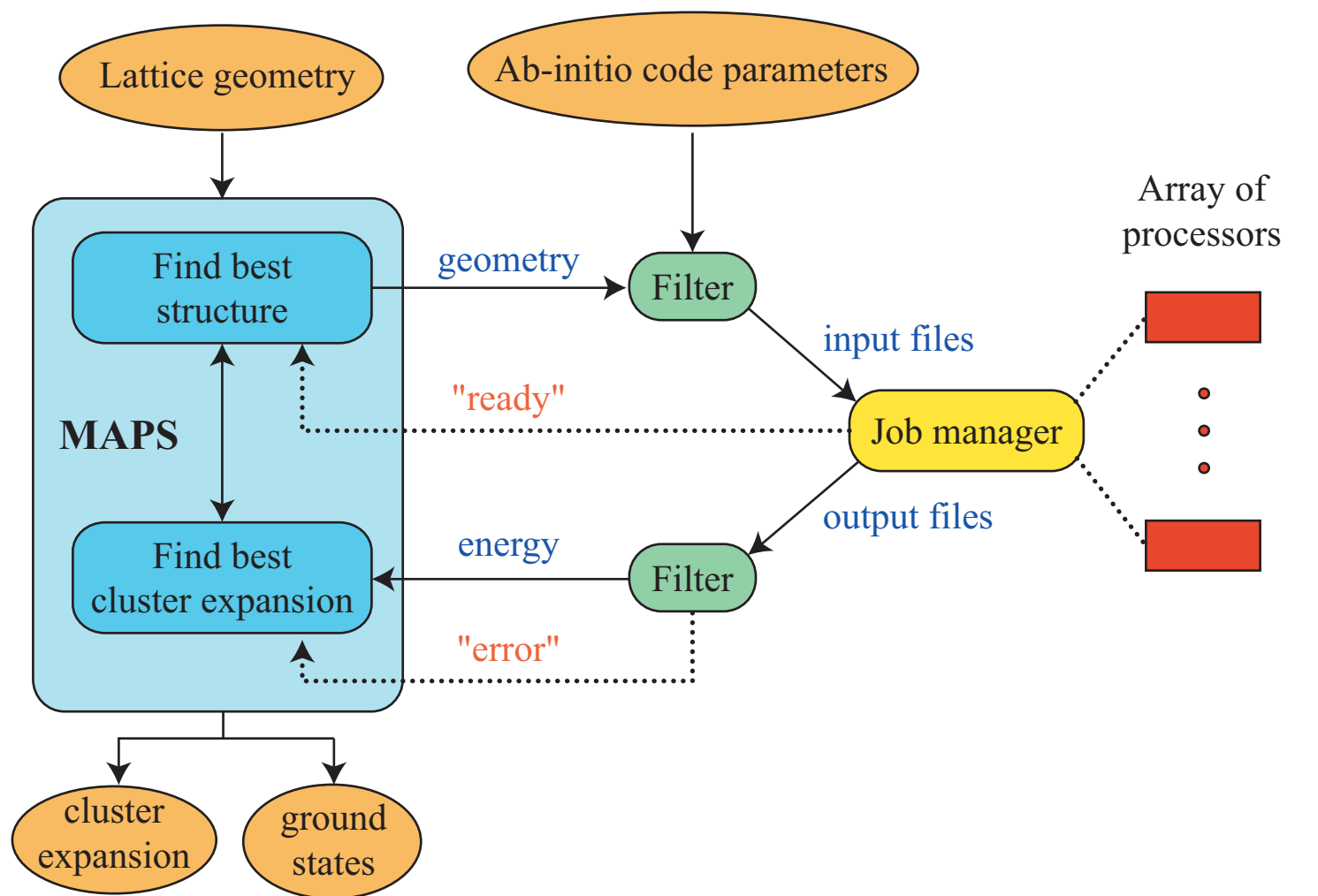
Cluster expansions construction: The Old Way



Alloy Theoretic Automated Toolkit



Cluster expansion construction module (MAPS)



Alloy theory
"Engine"

Ab-initio code
Interface

Processes
Interface

Hardware

Cross-Validation

$$CV = \sum_{i=1}^n (E_i - \hat{E}_{-i})^2$$

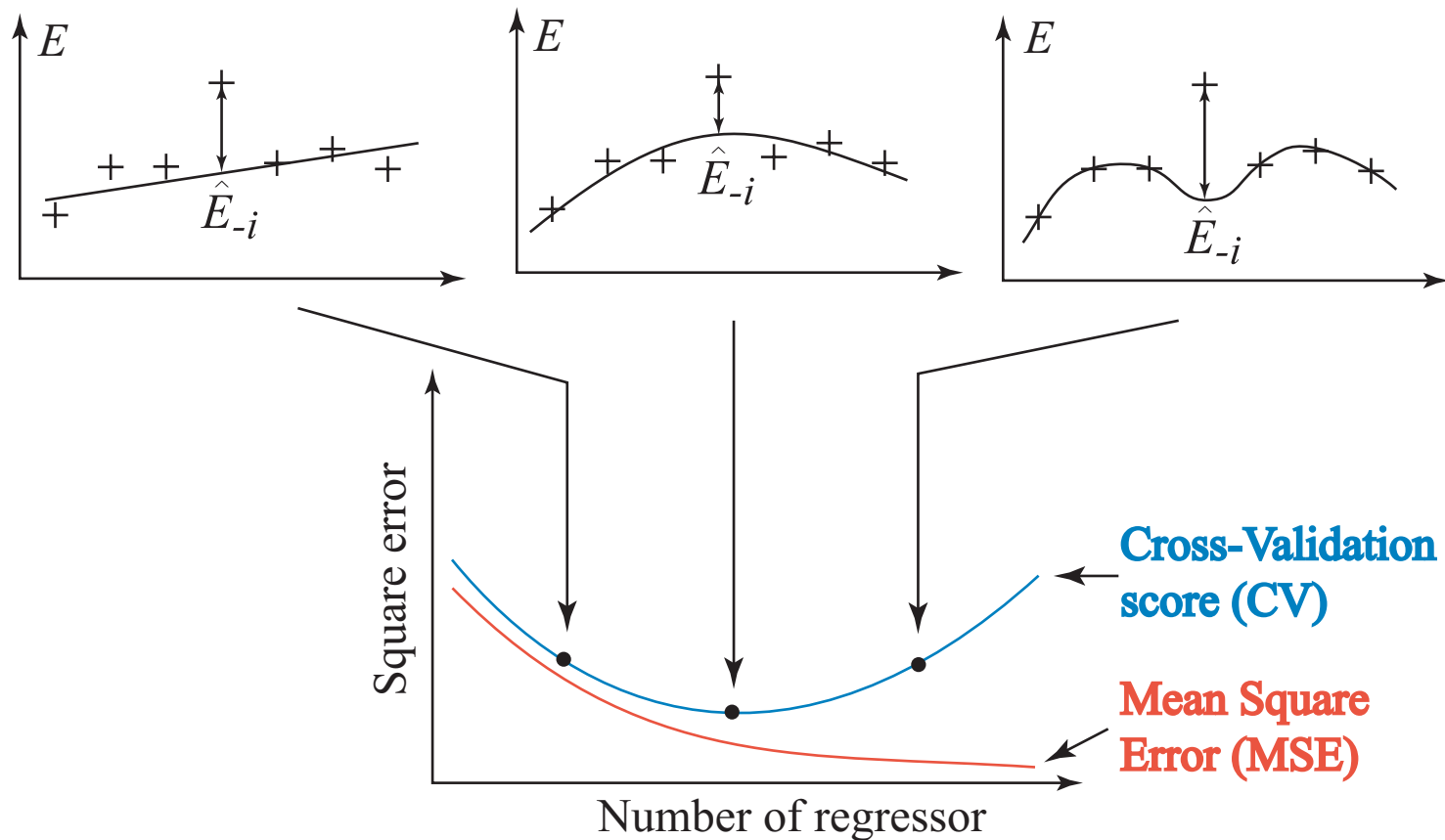
True energy of structure i

Energy of structure i
predicted from a fit to structures
 $1, 2, \dots, i-1, i+1, \dots, n$

i removed

"Leave-one-out estimator"

Example for polynomial fit



CV prevents under- or over- fitting

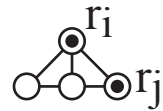
Cluster Hierarchy

Rules:

- 1) Include cluster only if all its subclusters are also included.
- 2) Include cluster only if all *smaller* clusters are also included.

Note: α *smaller* than β iff

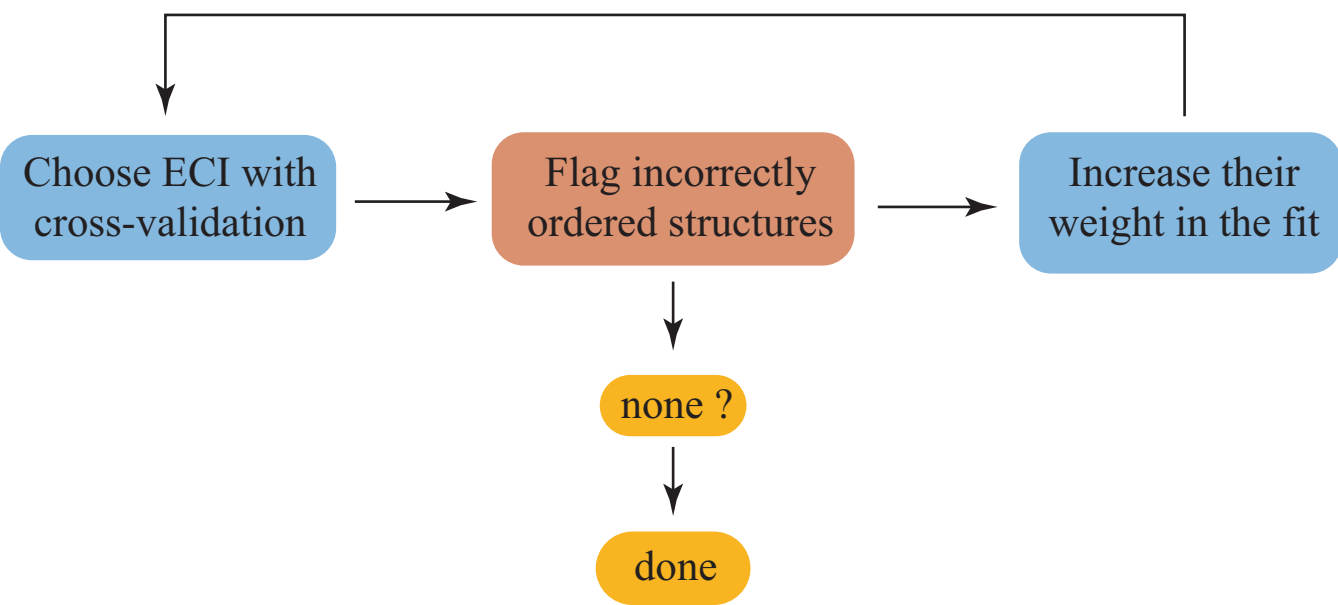
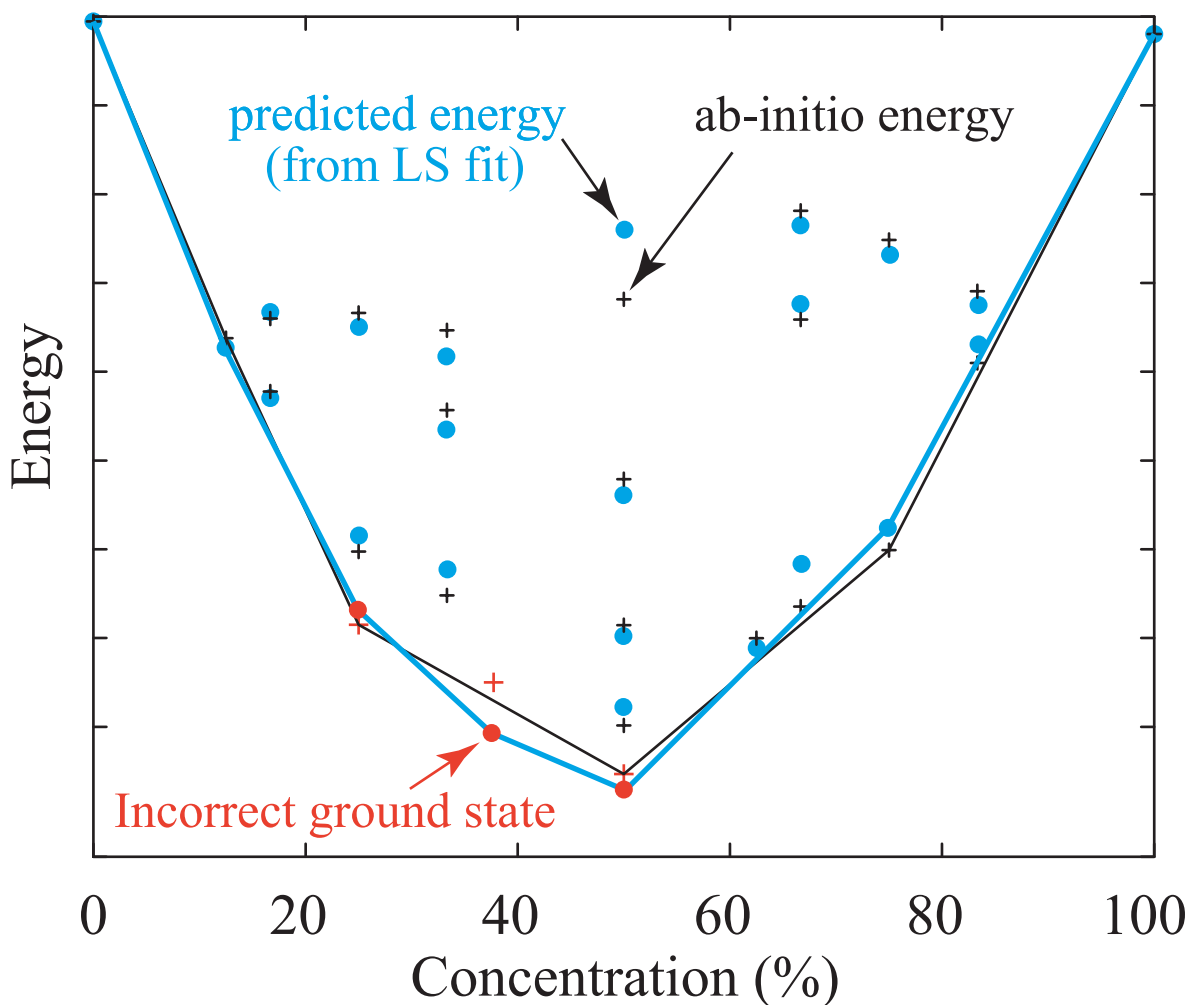
$$\max_{i,j \in \alpha} \|r_i - r_j\| \leq \max_{i,j \in \beta} \|r_i - r_j\|$$



Example: square lattice $\begin{matrix} \circ & \circ \\ \circ & \circ \end{matrix}$

Include these clusters only if those clusters included.

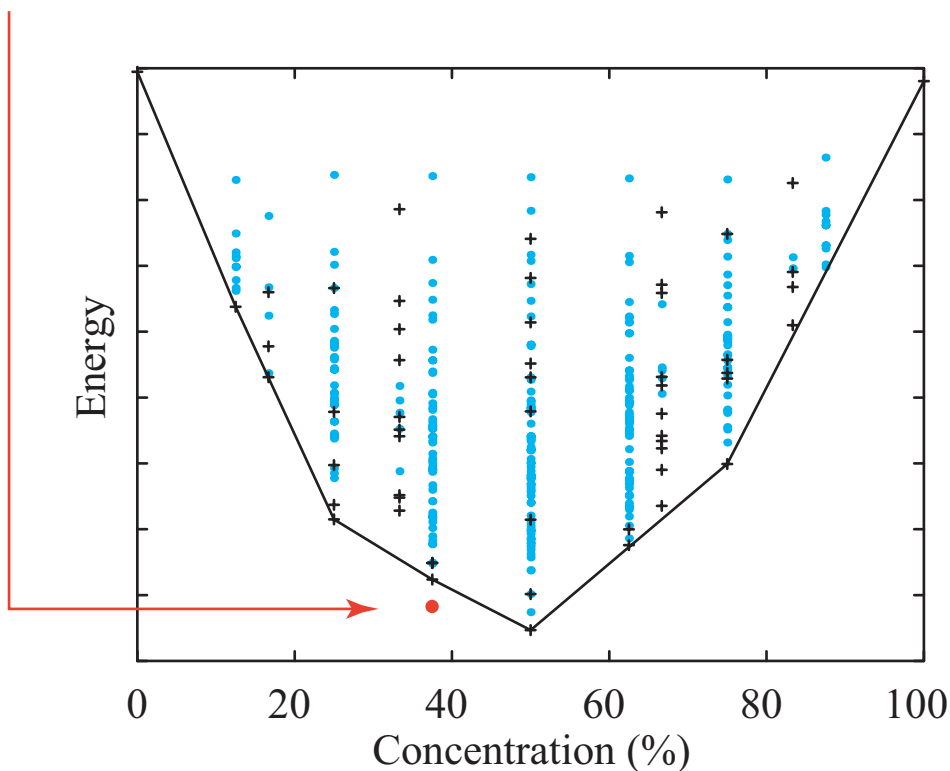
Ensuring ground state accuracy



Structure generation

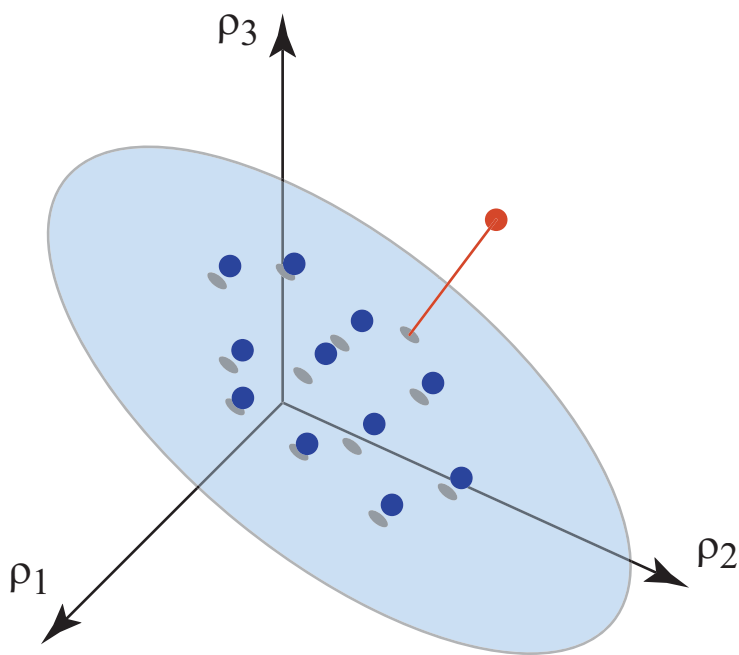
Criteria:

1) look for **predicted ground states**



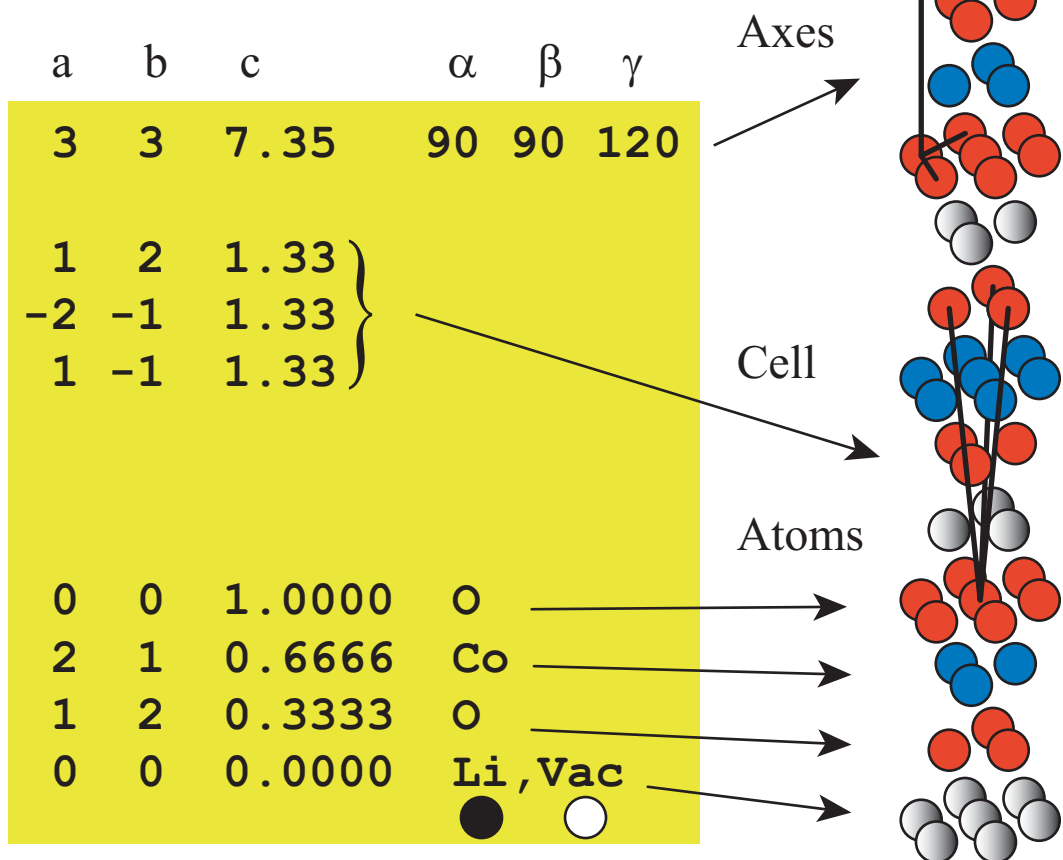
2) Minimize variance

(look for **noncoplanar** structure in correlation space)



Input Files

1) Lattice geometry



2) First-principles code parameters

```
[INCAR]
PREC = high
ISMEAR = -1
SIGMA = 0.1
NSW=41
IBRION = 2
ISIF = 3

KPPRA = 1000
DOSTATIC
```

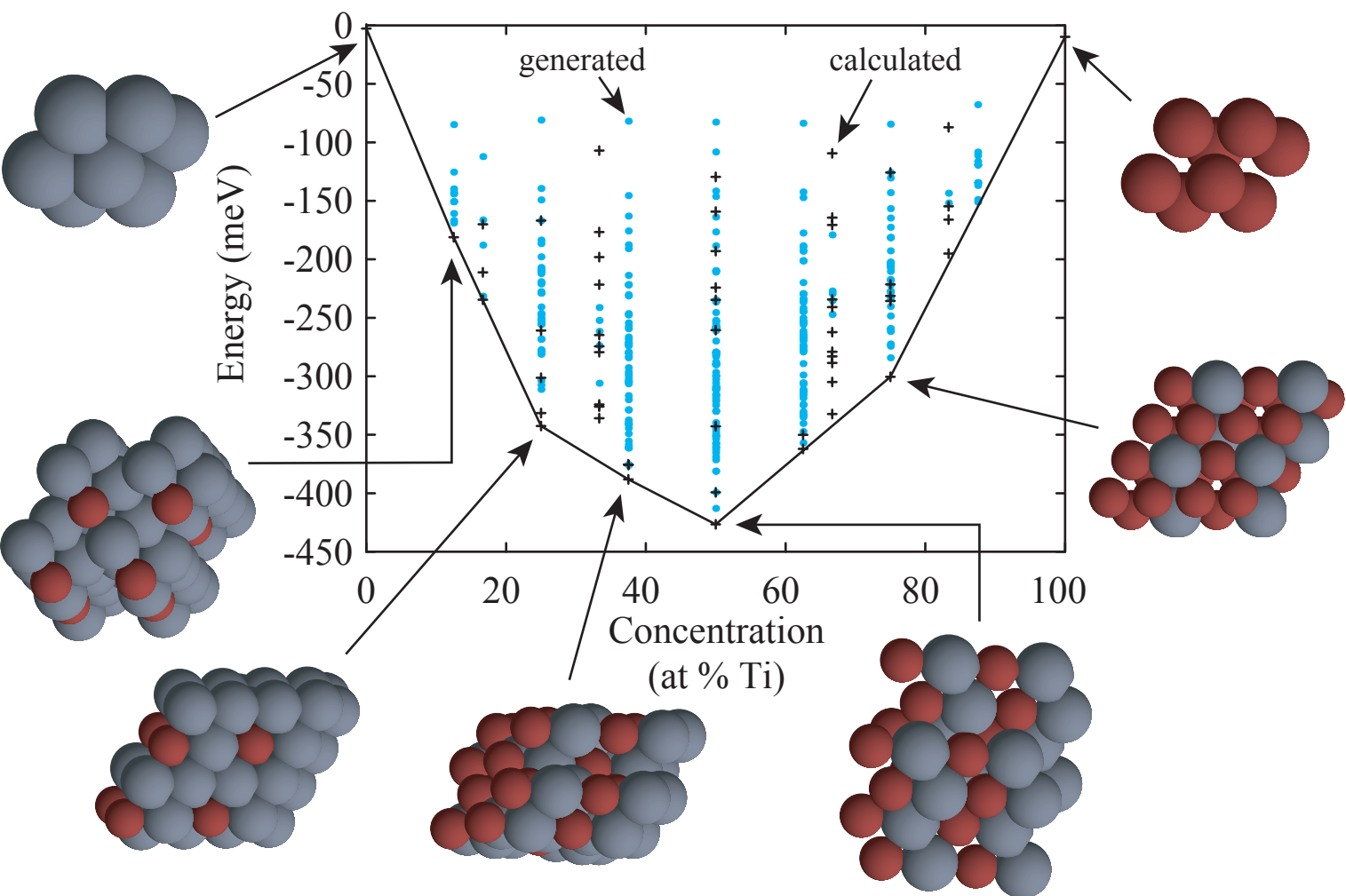
} Standard VASP tokens

{ *k*-point density
{ **(k point per reciprocal atom)**

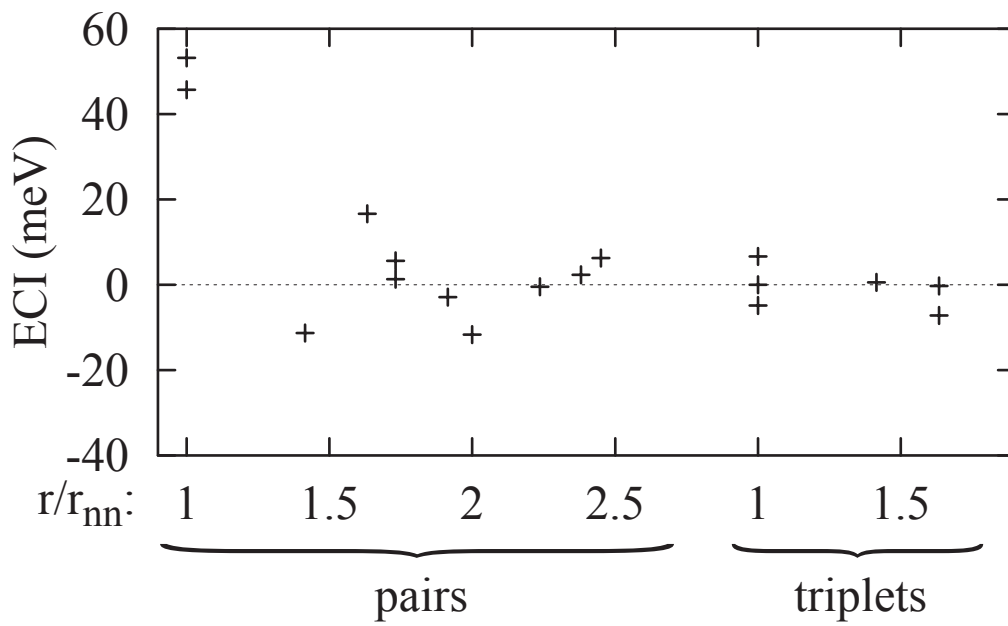
do static run

Example output (hcp Ti-Al system)

1) Formation Energies and Ground States



2) Effective Cluster Interactions



Energy Predictors

Presence of long range interactions:

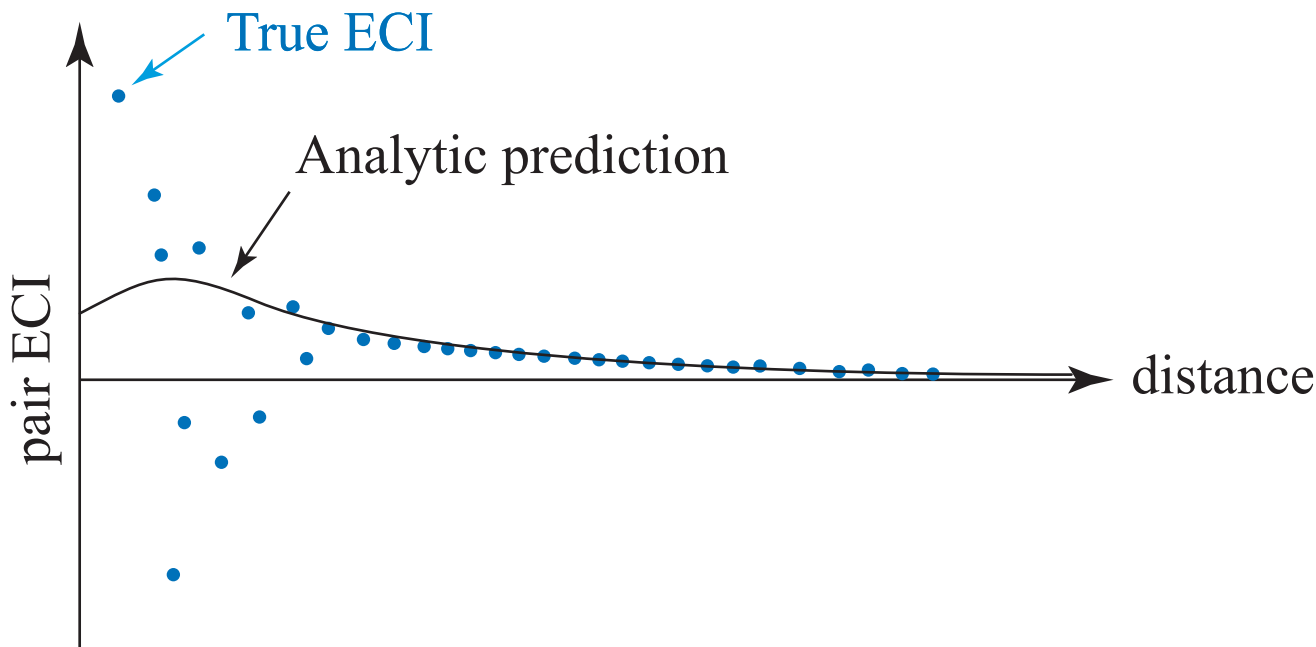
Elastic interactions

Electrostatic interactions

Hard to fit so many ECI...

Solution:

1) Look for analytic solution for long-range ECI behavior:



2) Subtract out long-range analytic contribution

3) Fit short-range contribution to *ab initio* calculations

Energy predictors **easy to add** to MAPS:

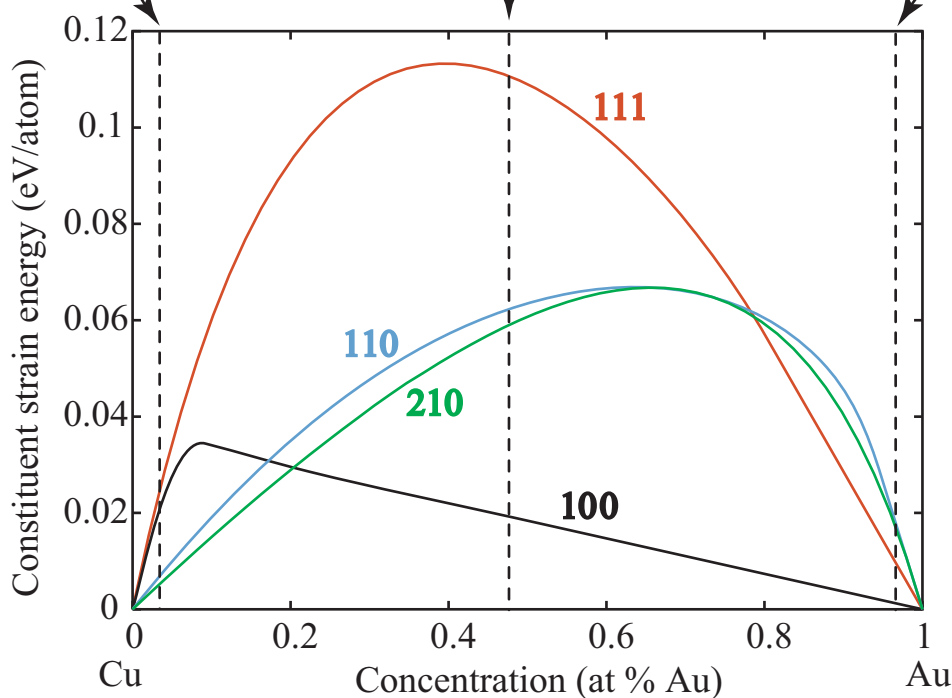
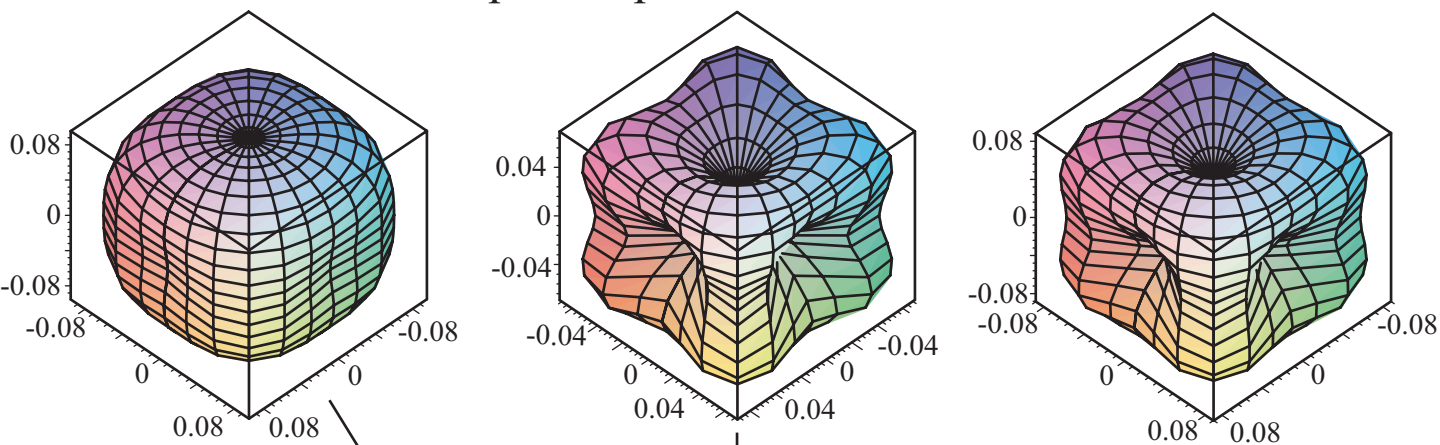
No change needed in the code,
just **link** with user-specified routines

Constituent strain formalism implementation

(Laks, Ferreira, Froyen, and Zunger, 1992)

Output:

Angular-dependence of the
 k -space expansion coefficients



Concentration-dependence of the
constituent strain energy

Input:

100
110
111
210

Superlattice
Directions

+

ab-initio
code
parameters

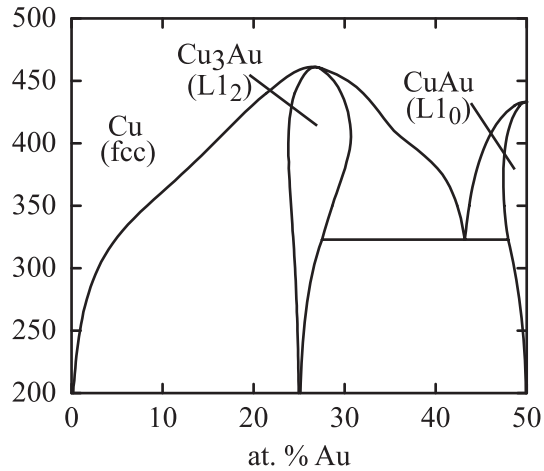
Monte Carlo Simulations

From cluster expansions:

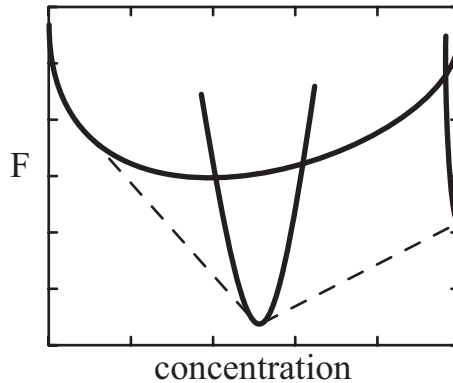
$$E = \sum_{\alpha} J_{\alpha} \sigma_{\alpha}$$

to thermodynamic quantities:

Phase diagrams:



Free energies:



Tasks to perform:

How to determine when target accuracy reached?

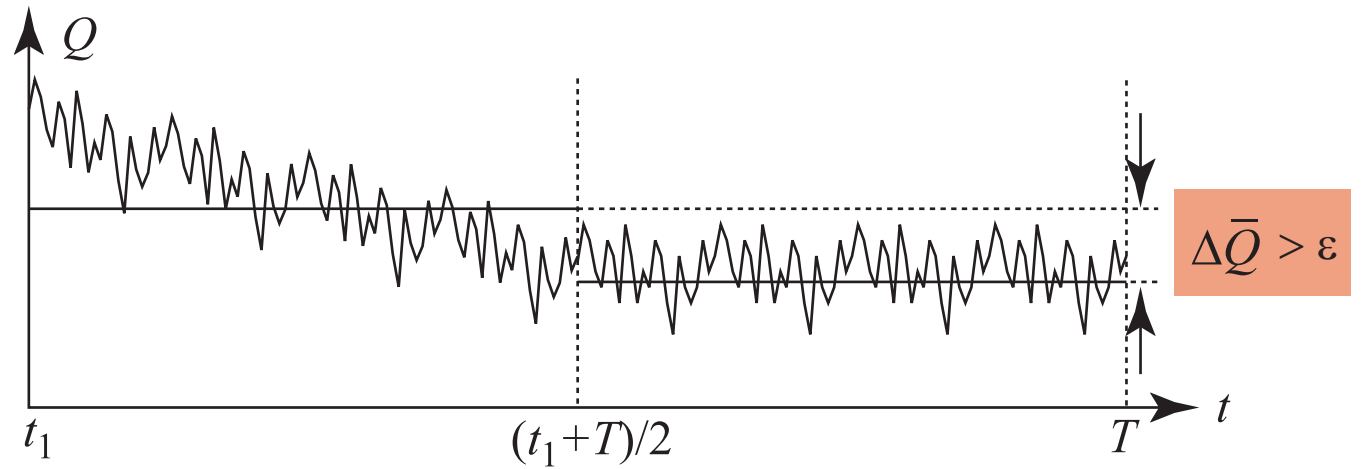
How to detect phase transitions?

How to efficiently calculate phase boundaries?

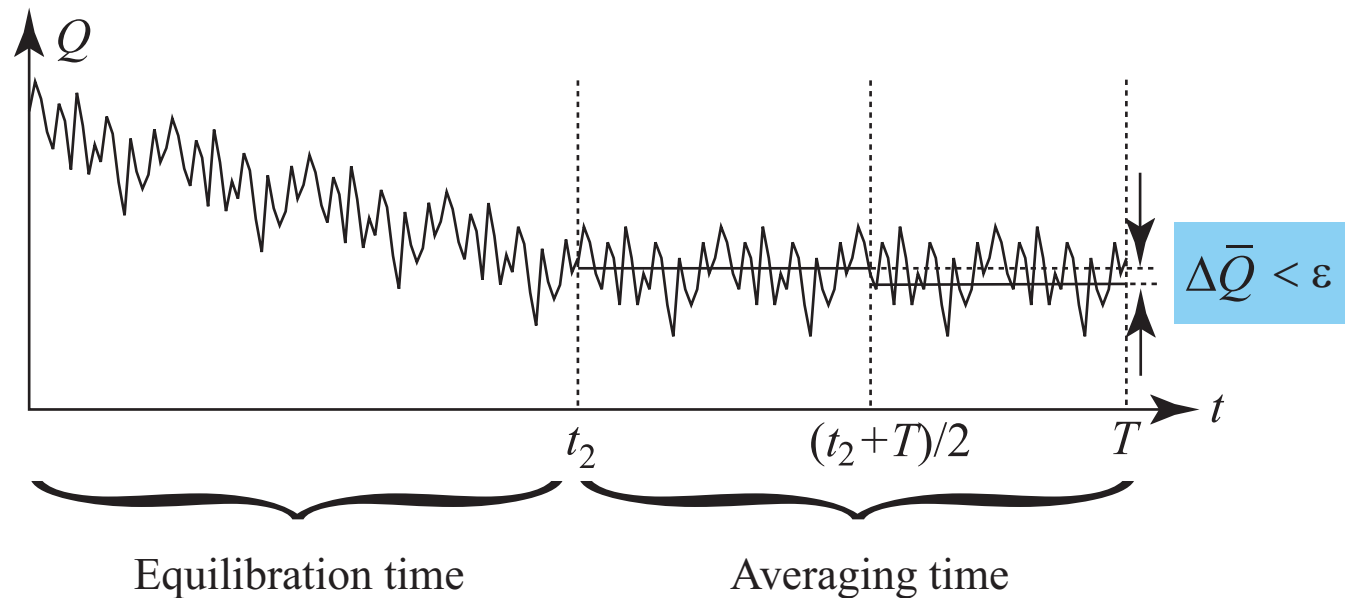
Equilibration and Averaging times

Given tolerance: ε $\frac{\downarrow}{\uparrow}$ on some thermodynamic quantity $Q = (\mathbf{E}, \mathbf{x}, \mathbf{SRO})$

Equilibrium not reached at t_1



Equilibrium reached at t_2



Choose averaging time such that

$$\sigma_{\bar{Q}} < \varepsilon$$

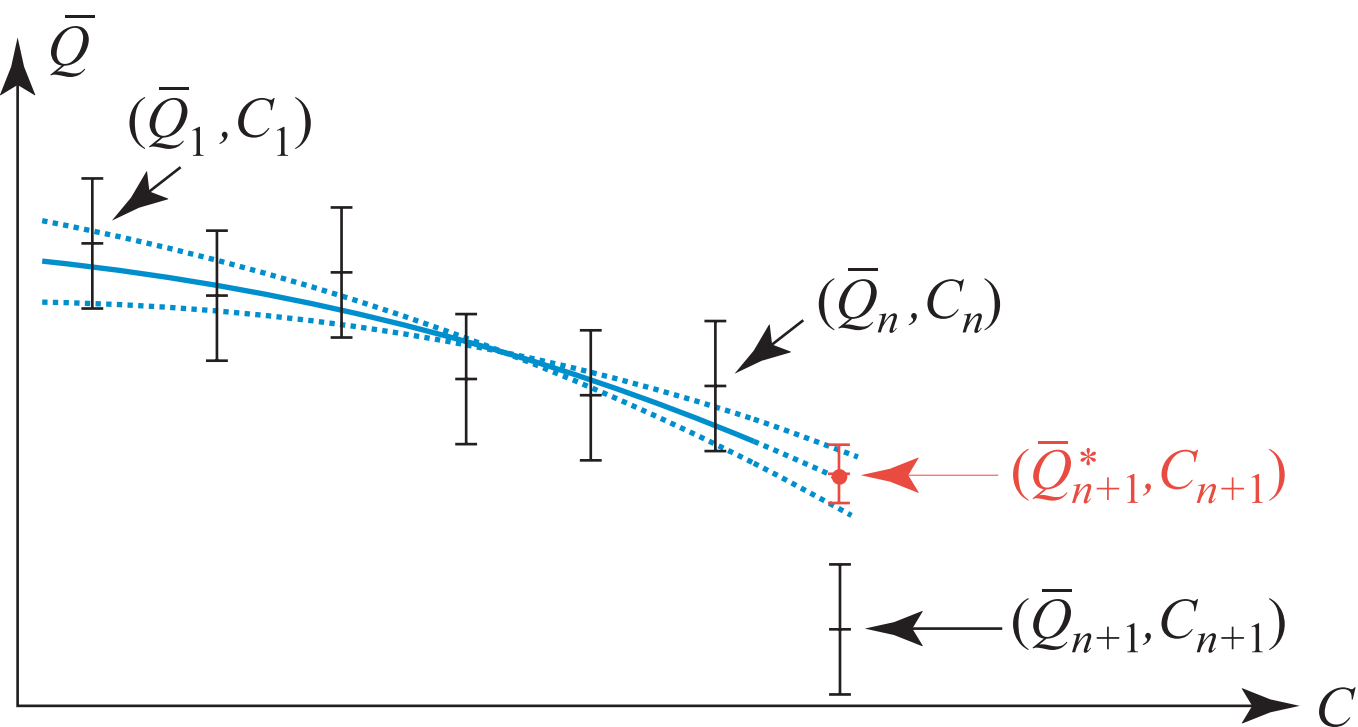
Detecting phase transitions

Goal: find discontinuity in $Q(C)$

Thermodynamic
quantity
 (E, x, SRO)

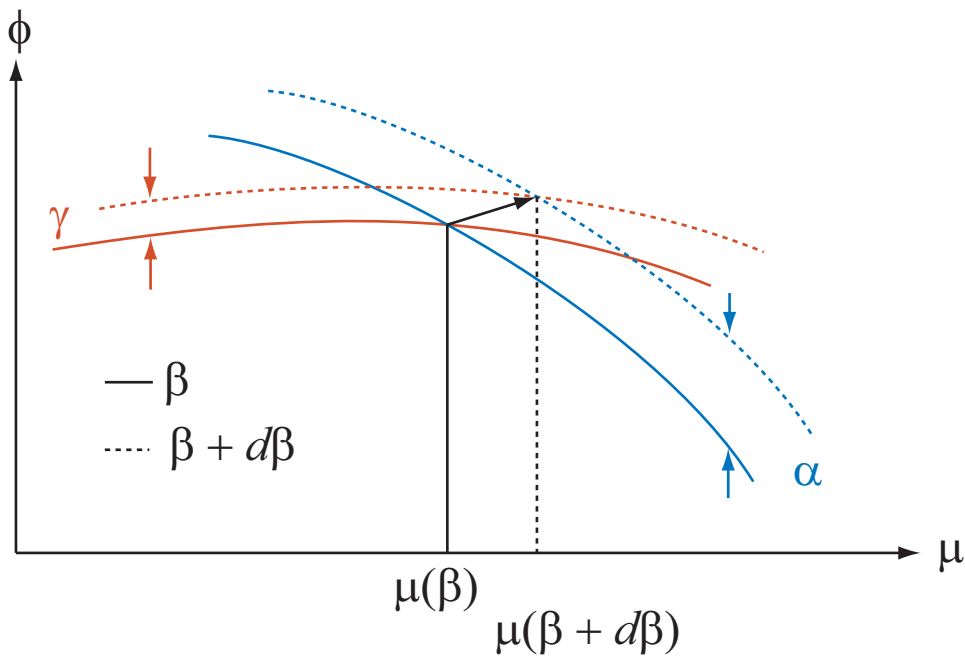
Control
variable
 (μ, T)

- 1) Fit polynomial through (Q_i, \bar{C}_i)
- 2) Use cross-validation to find optimal order of polynomial
- 3) Extrapolate \bar{Q}_{n+1}^* using fitted polynomial
- 4) Perform statistical test of equality between \bar{Q}_{n+1}^* and \bar{Q}_{n+1}
(Accounting for noise in MC averages)



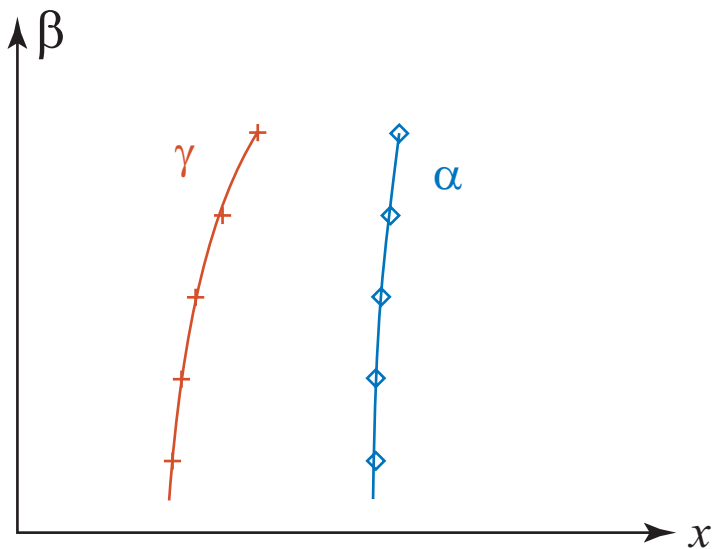
Phase boundary tracing

Principle: $\left\{ \begin{array}{l} \text{as temperature } \beta \text{ changes,} \\ \text{need to update } \mu \text{ to preserve } \phi^\gamma = \phi^\alpha \end{array} \right.$



$$\frac{d\mu}{d\beta} = \frac{E^\gamma - E^\alpha}{\beta(x^\gamma - x^\alpha)} - \frac{\mu}{\beta}$$

$\mu(\beta)$ is known \rightarrow find $x^\gamma(\mu(\beta))$ and $x^\alpha(\mu(\beta))$



Input parameters (Monte Carlo Code)

Phase
Boundaries
Determination

-dx=1e-3

-er=35

-gs1=3

-gs2=4

-dT=20

-k=8.617e-5

Thermodynamic
Integration

-dx=1e-3

-er=35

-gs=3

-mu0=3.5

-mu1=4.5

-dmu=0.05

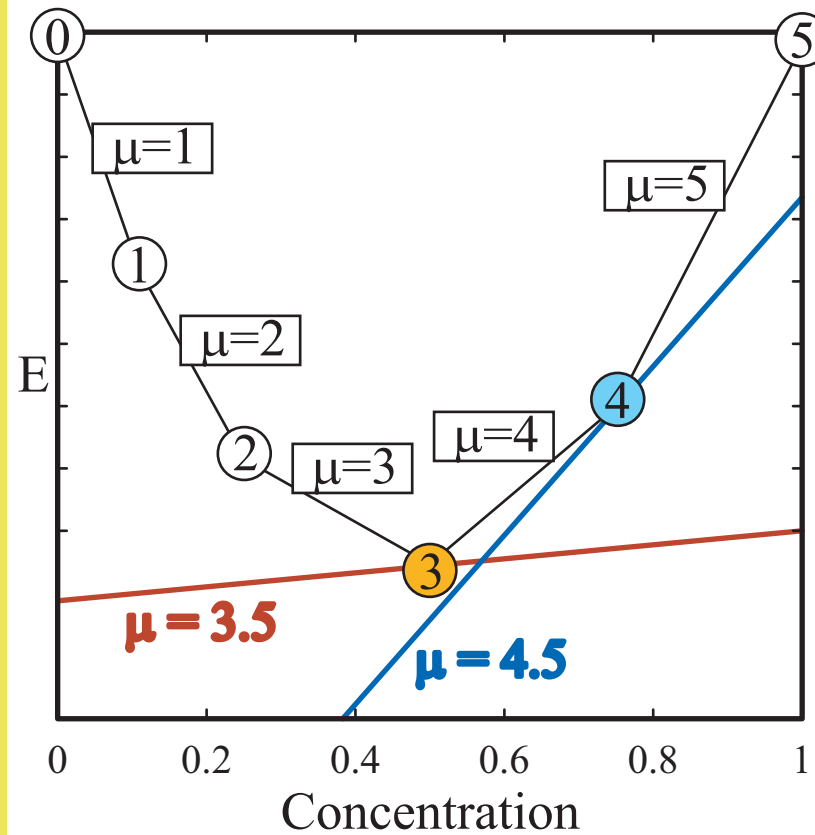
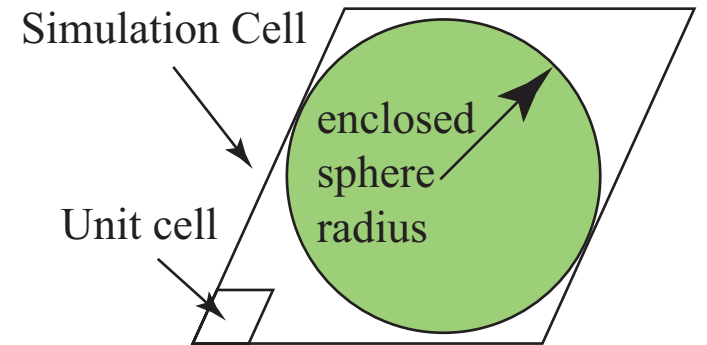
-T0=100

-T1=1000

-dT=20

-k=8.617e-5

$\sigma_{\bar{x}}$ Target precision

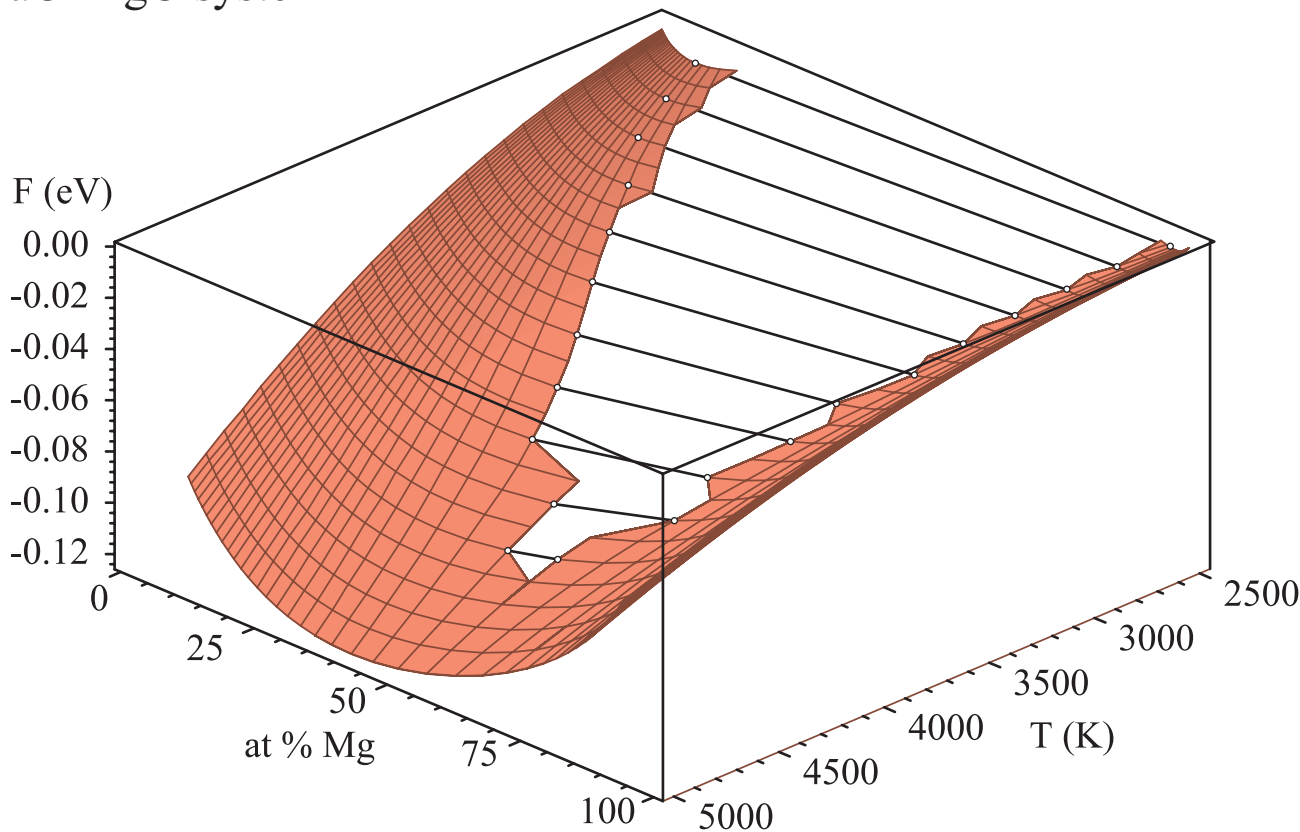


Temperature range

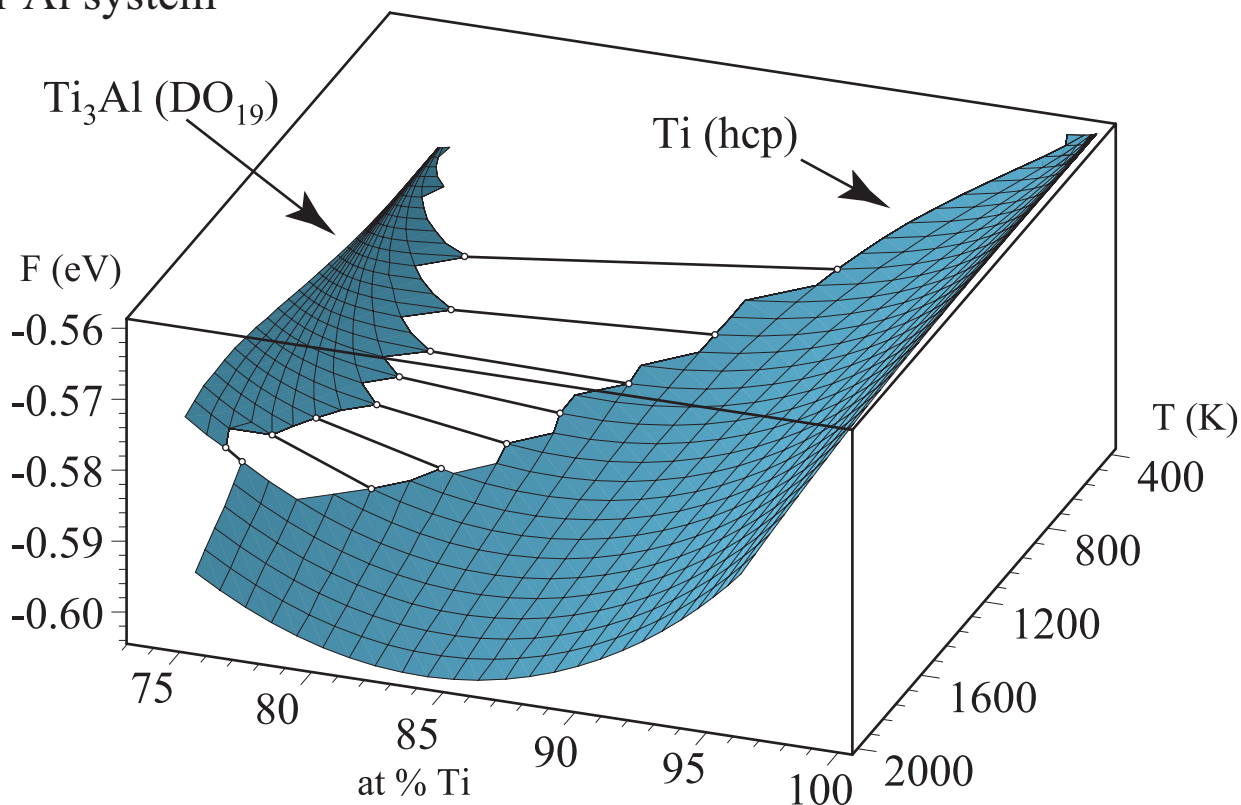
Boltzman's k_B

Emc2 output: Free energy surfaces

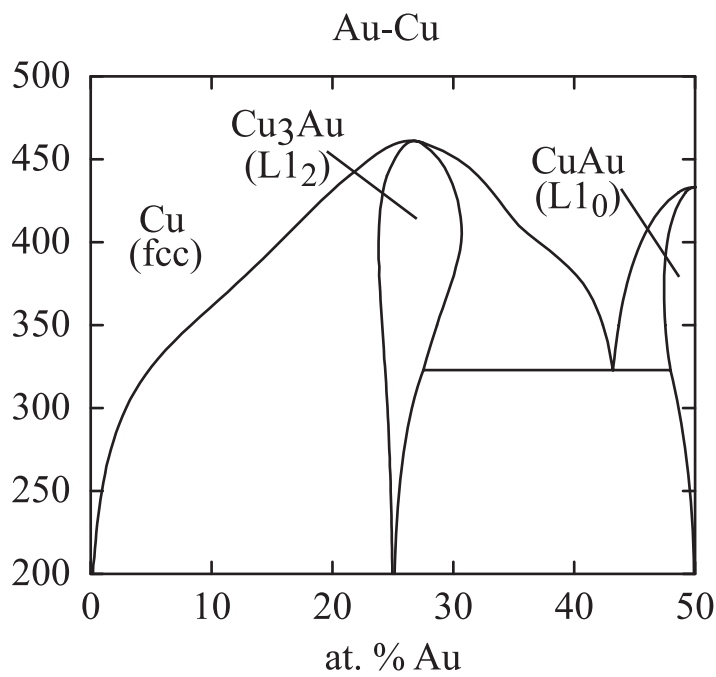
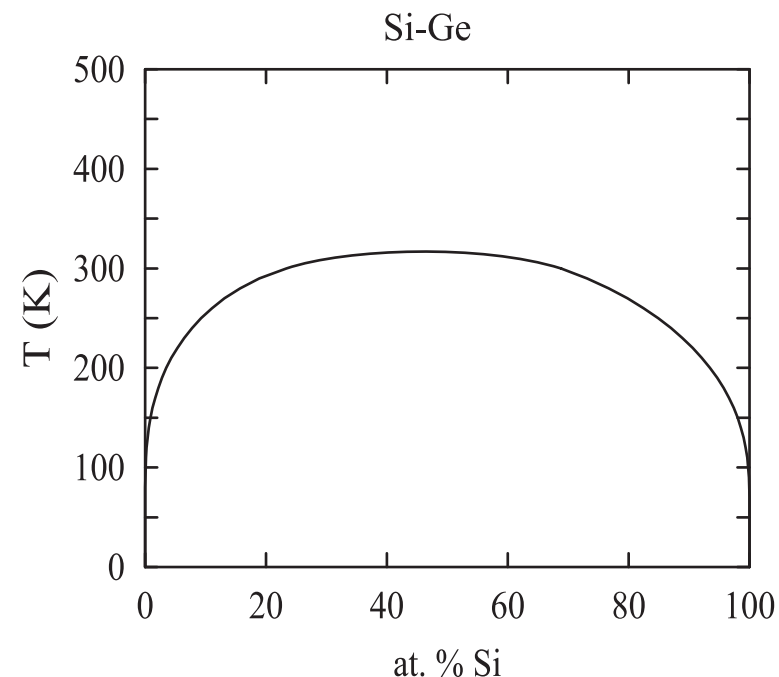
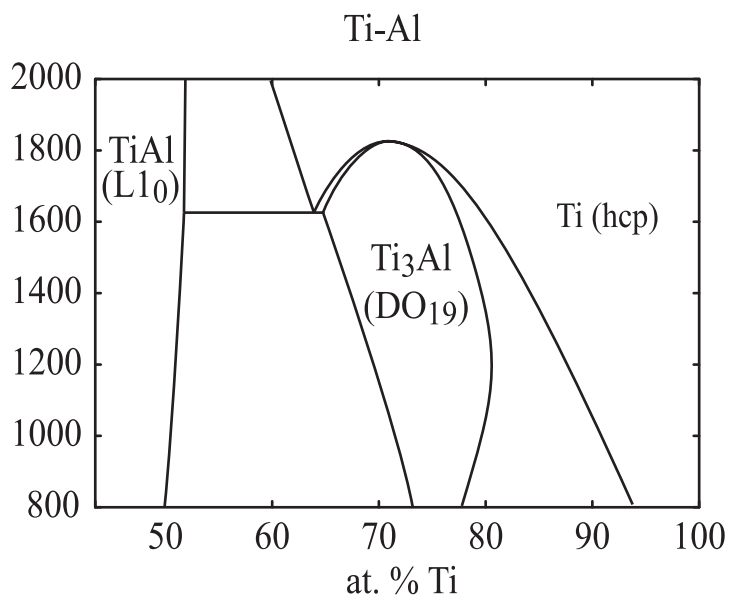
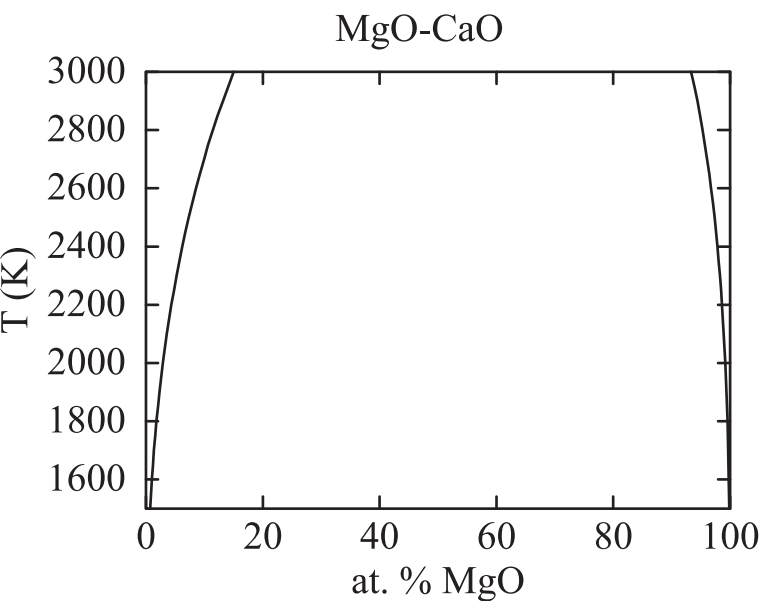
CaO-MgO system



Ti-Al system

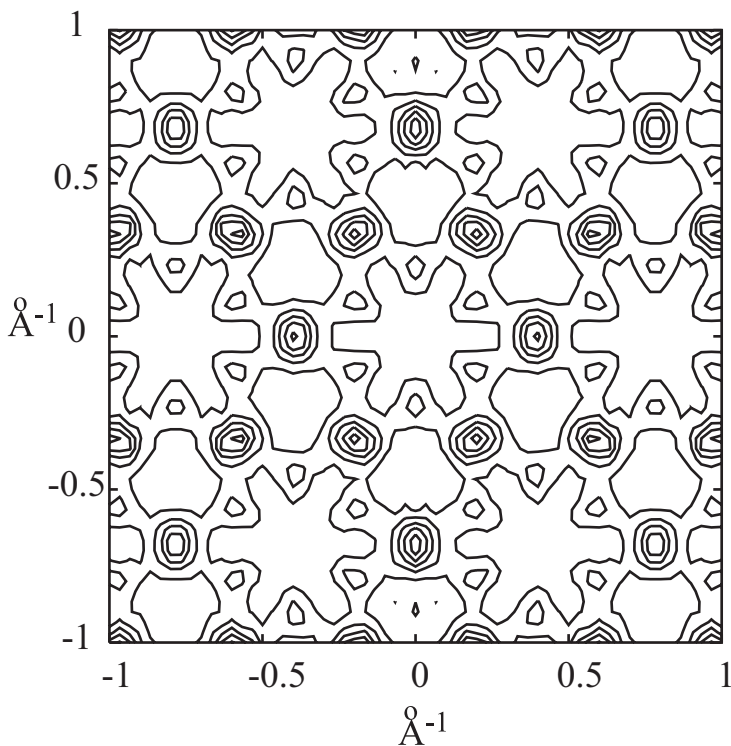


Emc2 output: Phase diagrams



Short-range order calculations

Calculated diffuse X-ray scattering in Ti-Al hcp solid-solution



Energy cost of creating a diffuse anti-phase boundary in a Ti-Al short-range ordered alloy by sliding k dislocations

