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),

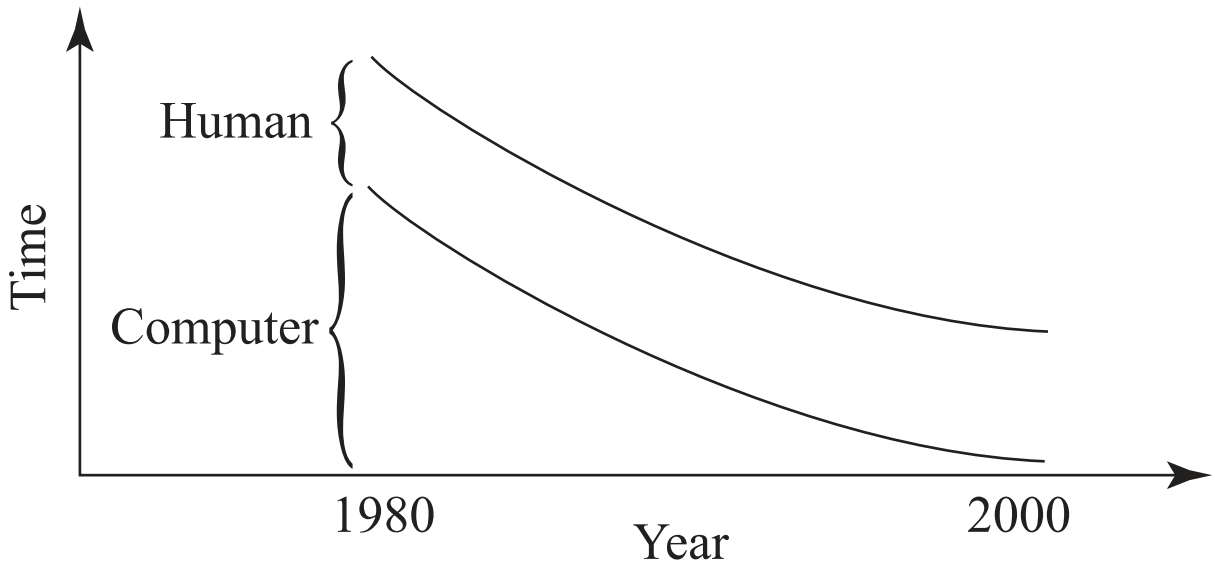
Ceder *et al.* (2000), Asta *et al.* (2001).)

First-principles Phase Diagram Calculation

Theory is well established:

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

But: the task is tedious in practice.

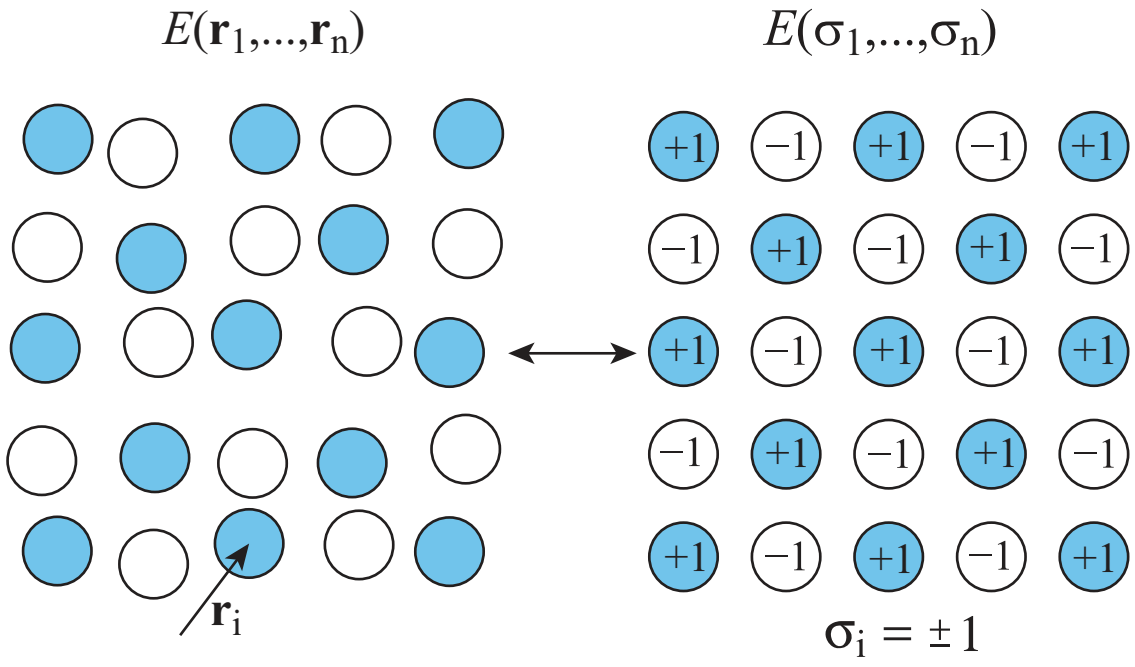


Our goal:

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

The cluster expansion

Alloy system ⟷ Lattice model

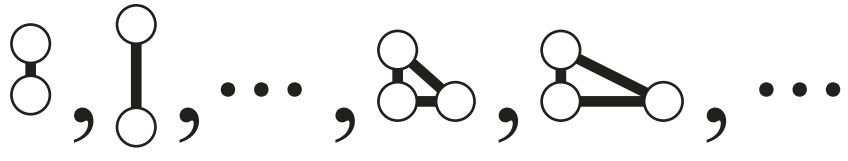


Parametrize configurational-dependence of the energy E with a polynomial in the occupation variables σ_i:

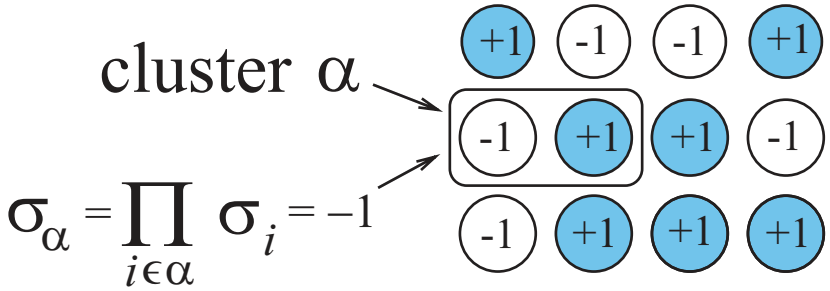
$$E(\sigma_1,\ldots,\sigma_n) = \sum_{\{i,j\}} J_{ij}\,\sigma_i\sigma_j + \sum_{\{i,j,k\}} J_{ijk}\,\sigma_i\sigma_j\sigma_k + \ldots$$

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

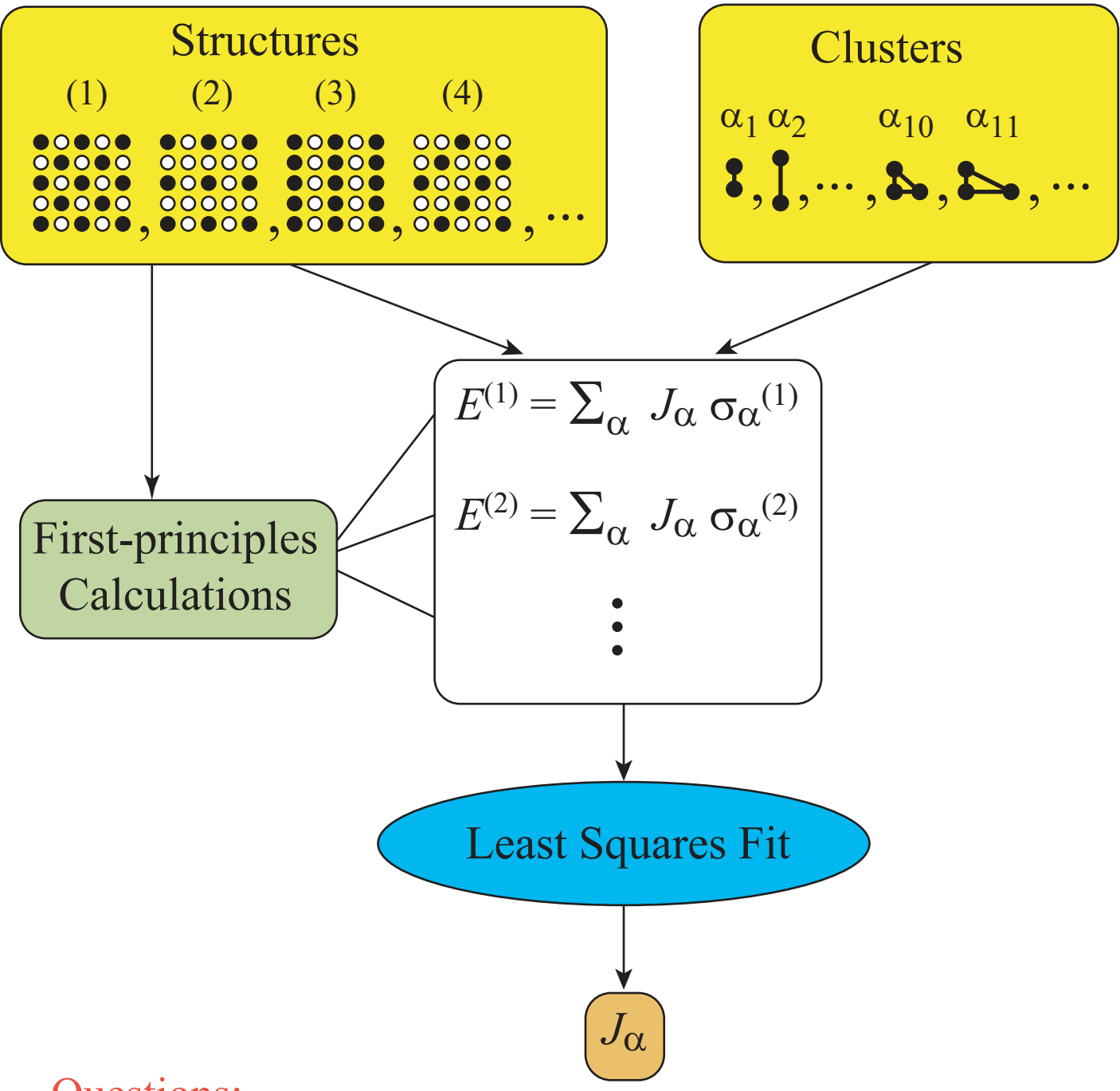
where

$\alpha =$ 

and



Cluster expansion fit

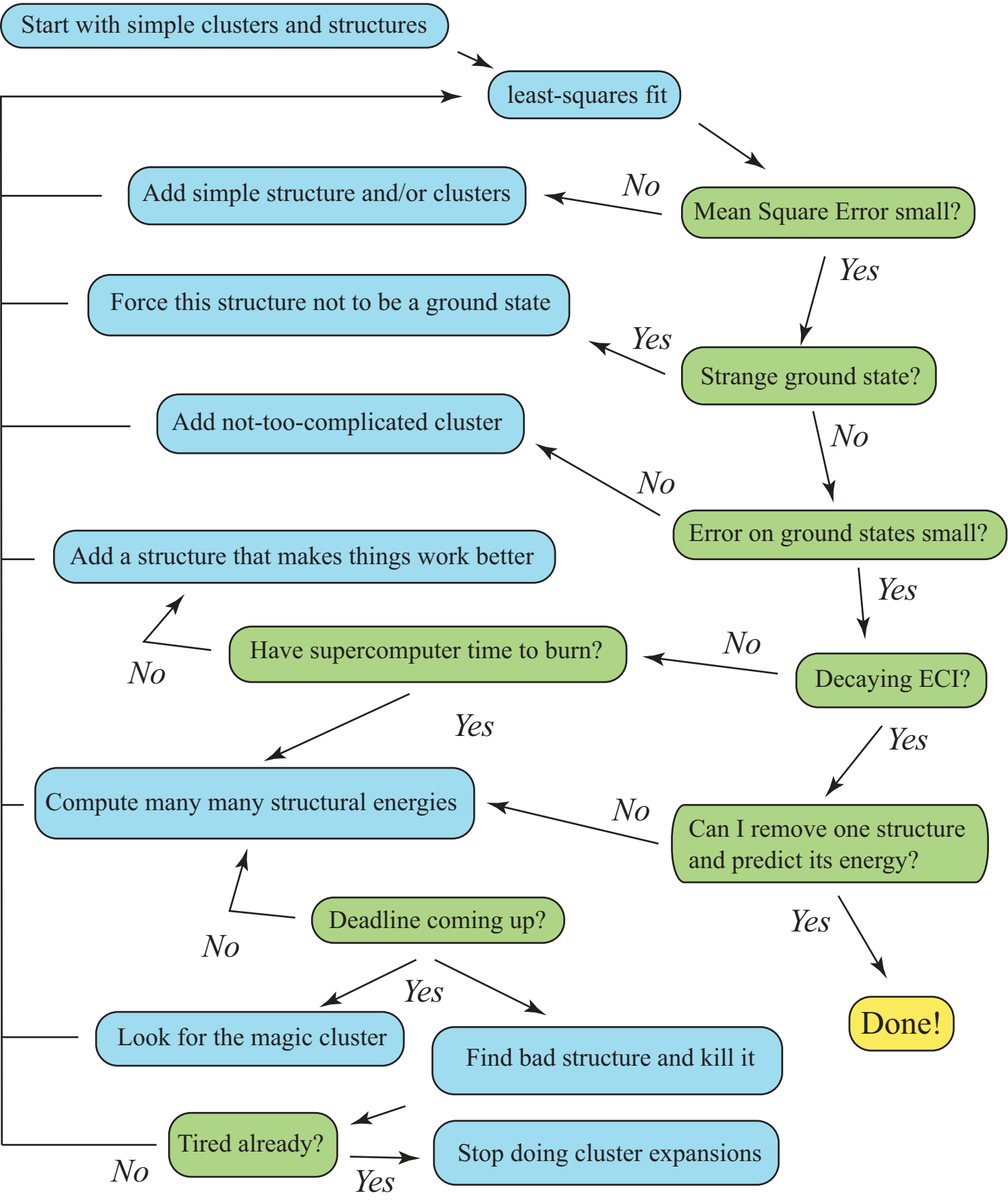


Questions:

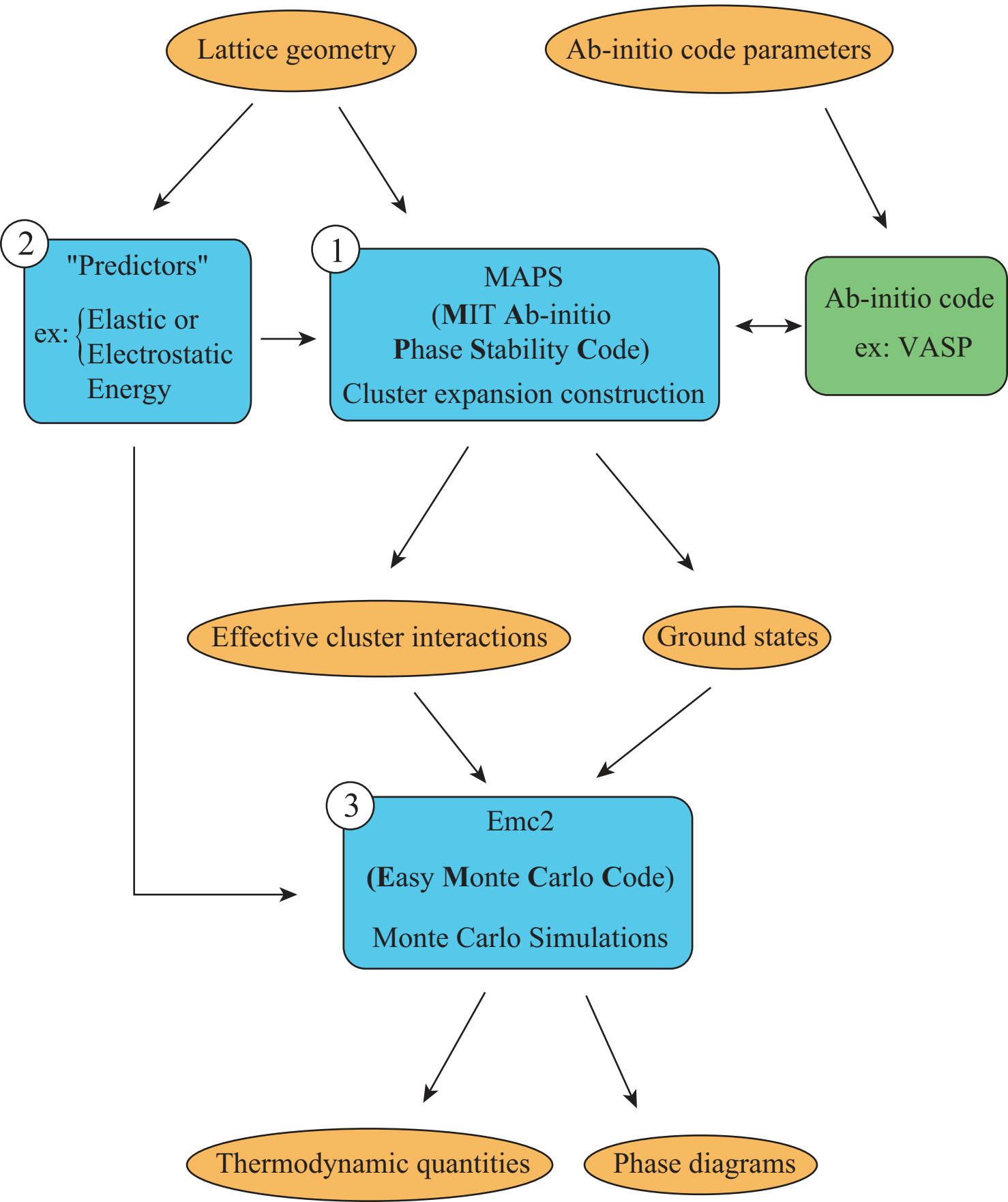
1) Which clusters α_1, α_2, ... to include?

2) Which structures (1), (2), ..., to include?

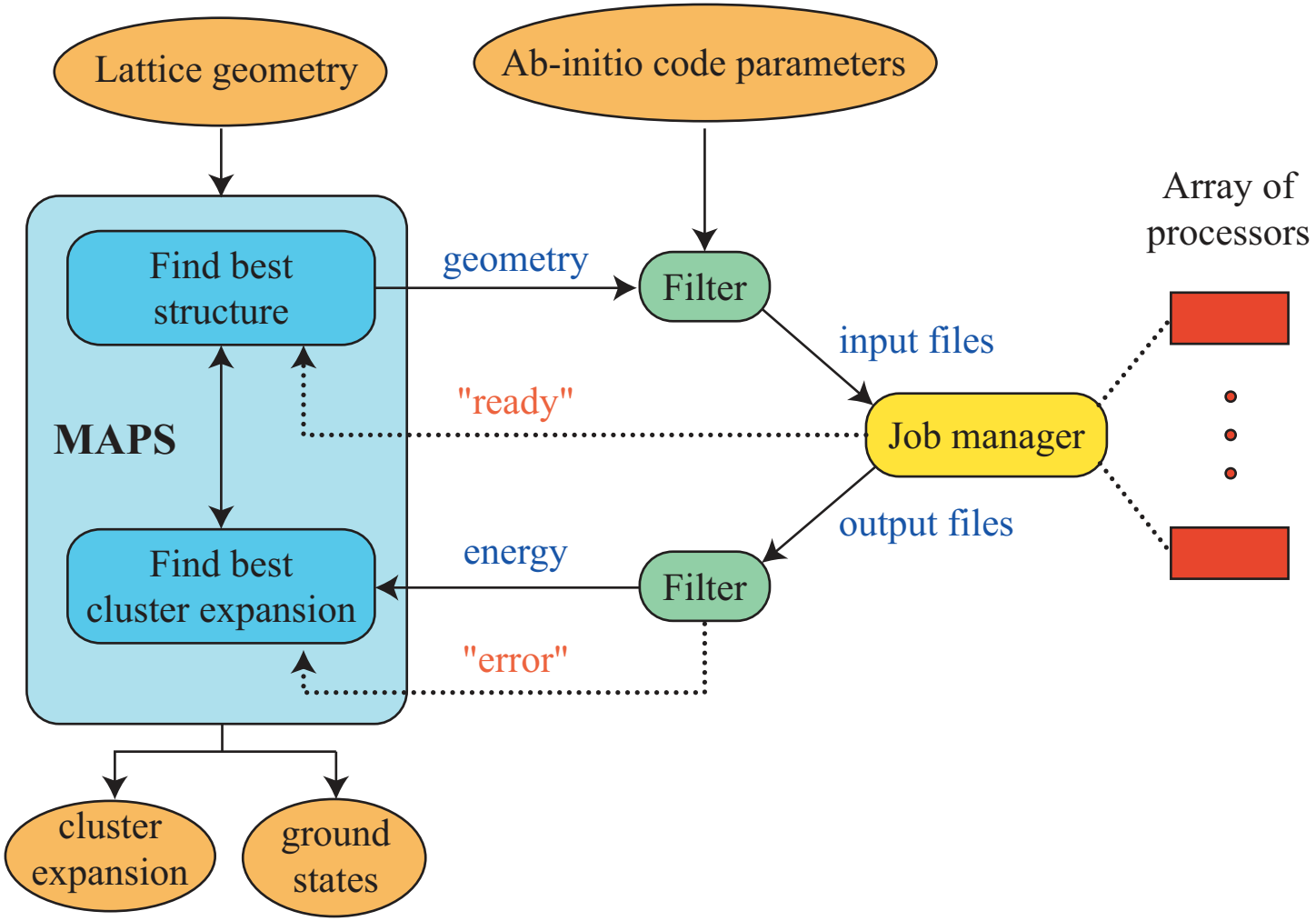
Cluster expansions construction: The Old Way



Alloy Theoretic Automated Toolkit



Cluster expansion construction module (MAPS)



Alloy theory "Engine"	Ab-initio code Interface	Processes Interface	Hardware

Cross-Validation

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

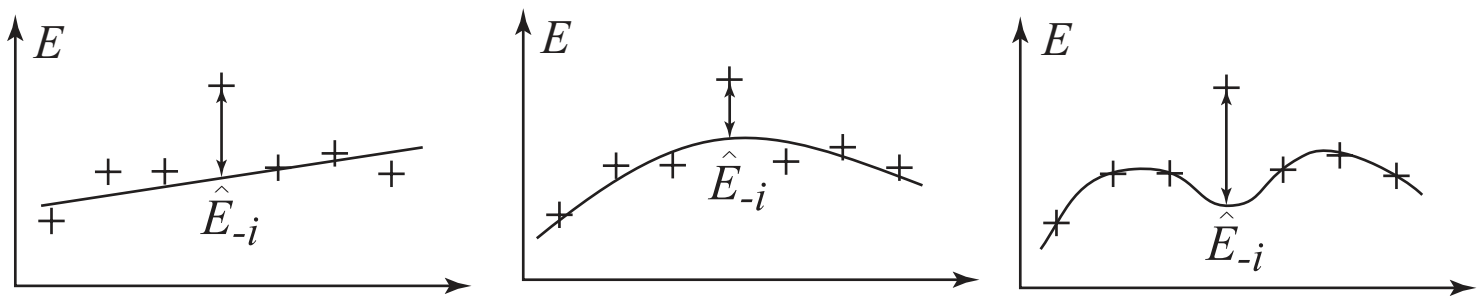
True energy of structure i

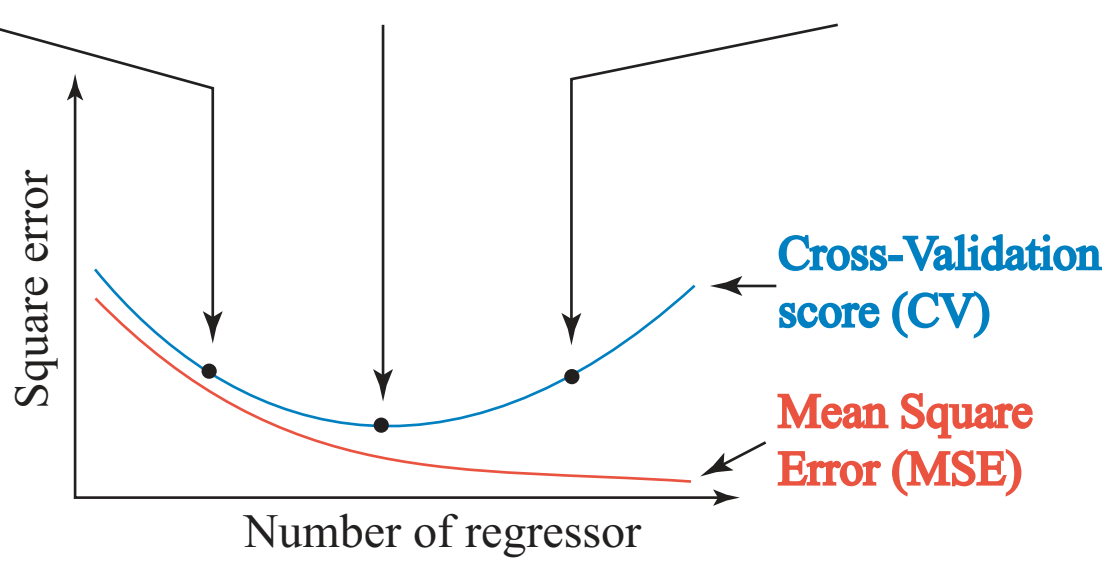
Energy of structure i predicted from a fit to structures 1, 2, ... , i–1, ,i+1, ... , n

i removed

"Leave-one-out estimator"

Example for polynomial fit





CV prevents under- or over- fitting

Cluster Hierarchy

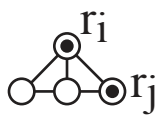
Rules:

1) Include cluster only if all its subclusters are also included.

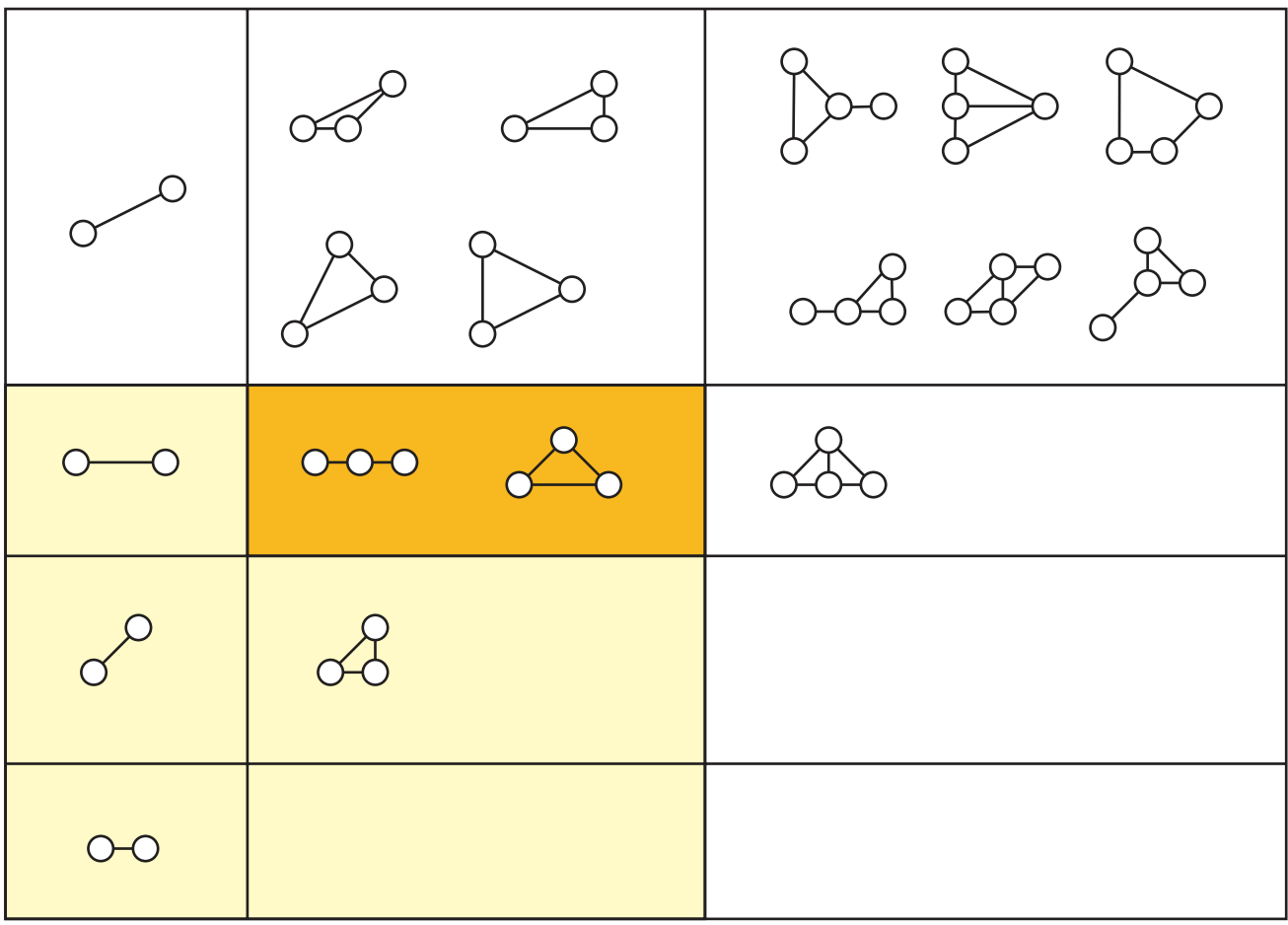
2) Include cluster only if all *smaller* clusters are also included.

Note: α *smaller* than β iff

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

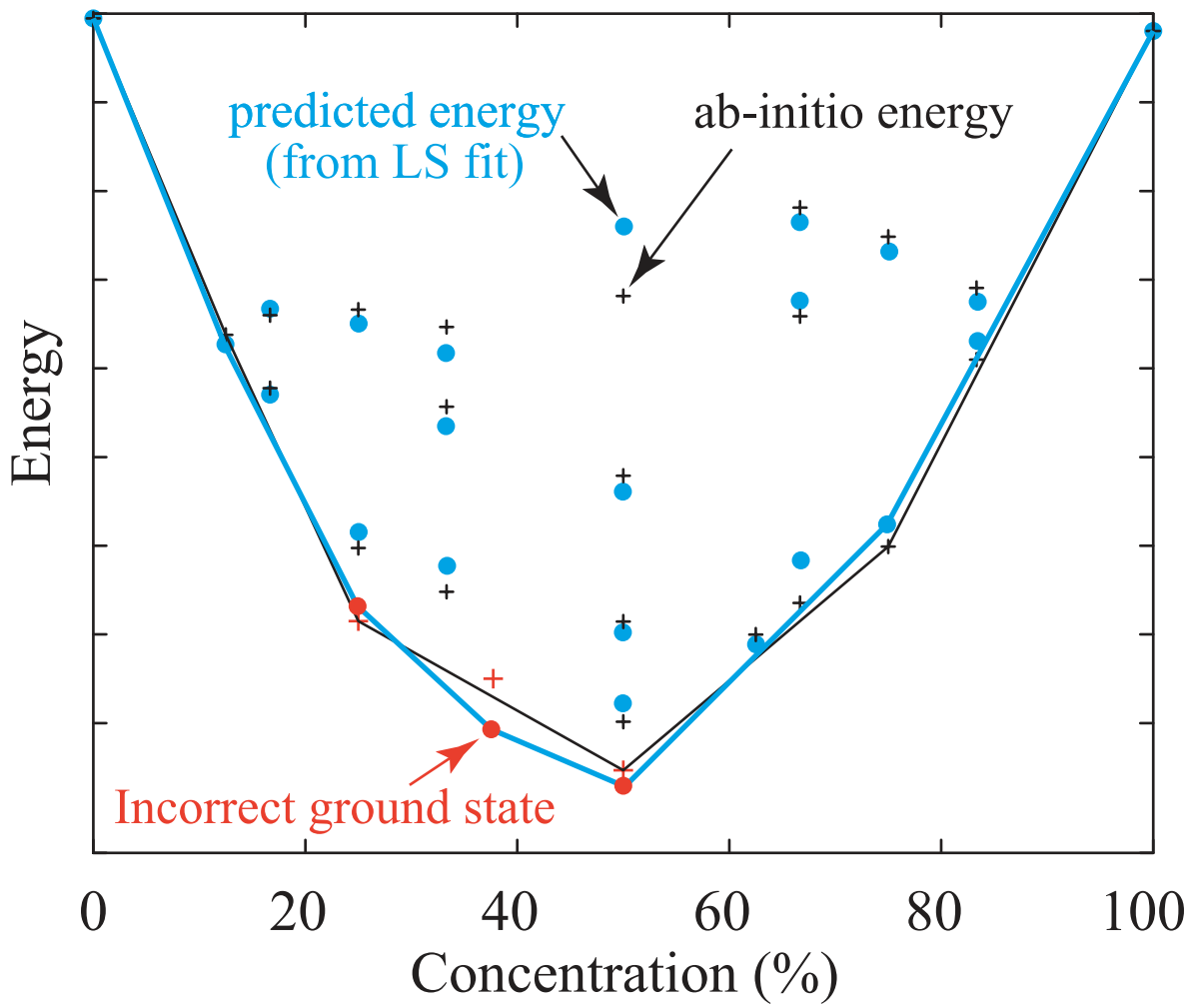


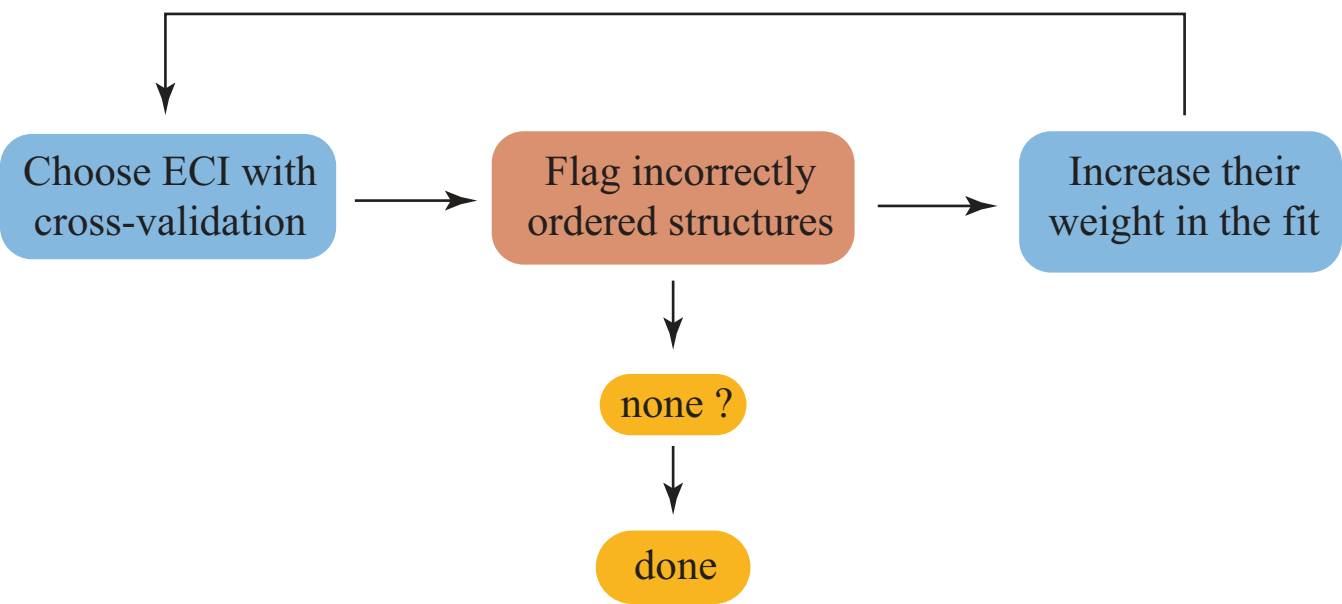
Example: square lattice 



Include these clusters only if those clusters included.

Ensuring ground state accuracy

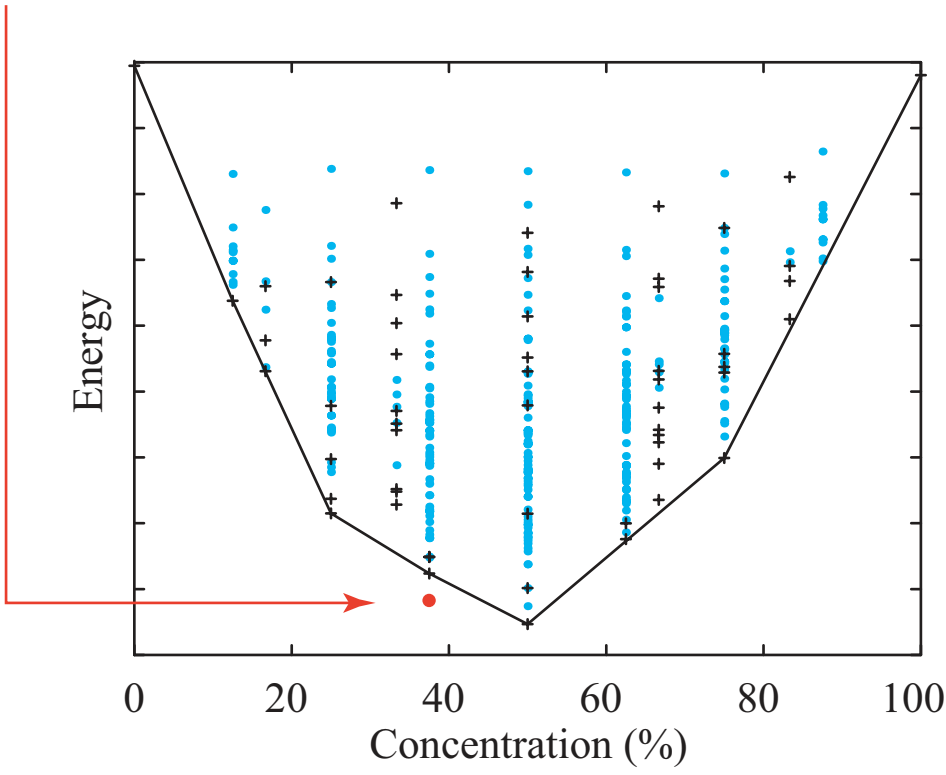




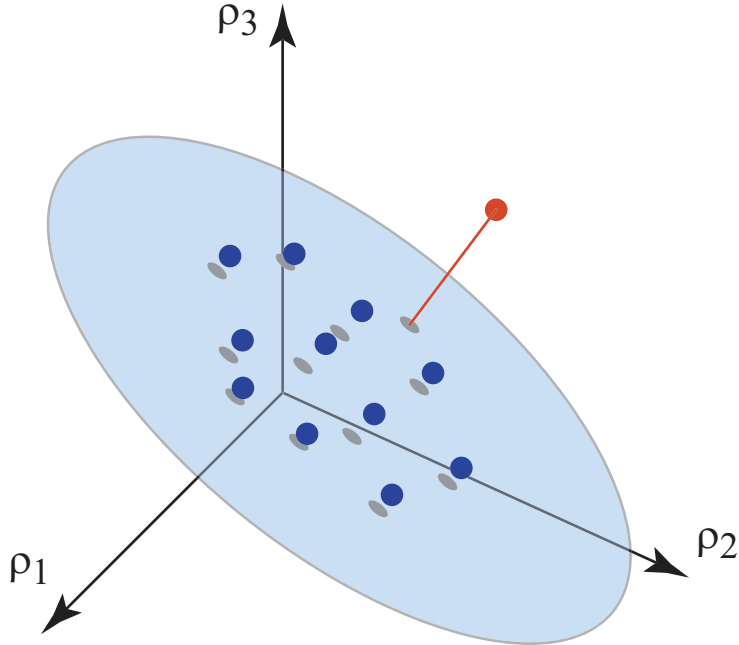
Structure generation

Criteria:

1) look for predicted ground states



2) Minimize variance
(look for noncoplanar structure in correlation space)



Input Files

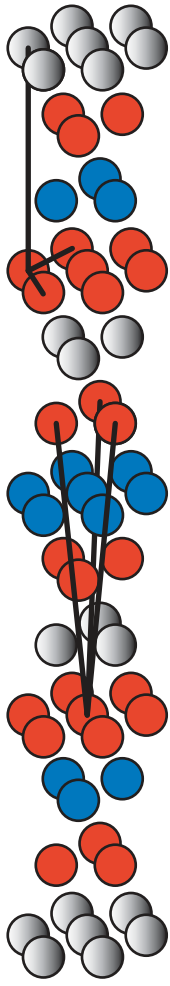
1) Lattice geometry

```
 a   b    c          α   β   γ
 3   3   7.35        90  90  120

 1   2   1.33
-2  -1   1.33
 1  -1   1.33

 0   0   1.0000   O
 2   1   0.6666   Co
 1   2   0.3333   O
 0   0   0.0000   Li,Vac
```

Axes

Cell

Atoms



2) First-principles code parameters

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

KPPRA = 1000
DOSTATIC
```

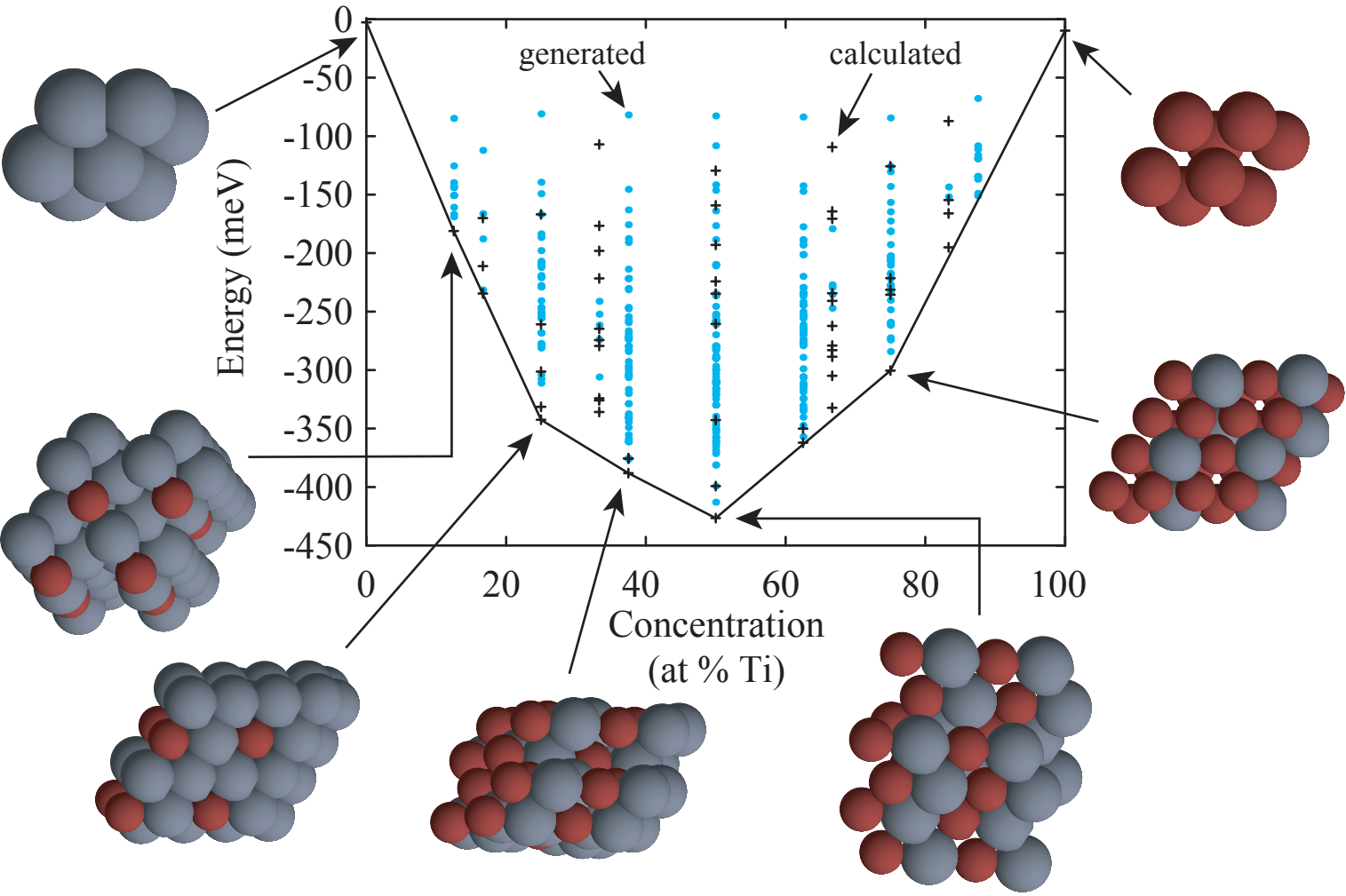
Standard VASP tokens

k-point density
(**k** point **p**er **r**eciprocal **a**tom)

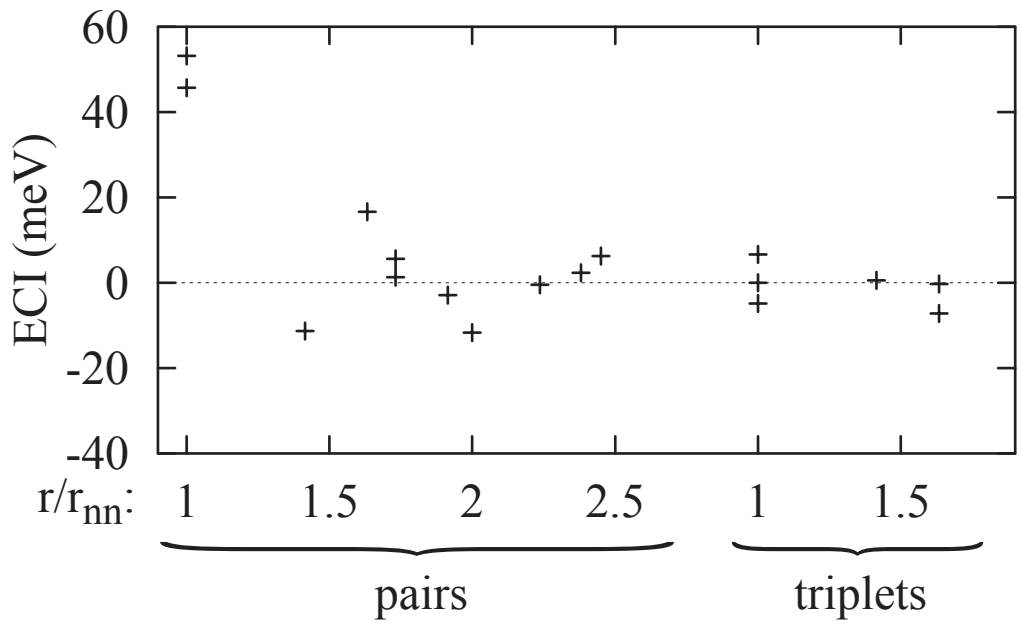
do static run

Example output (hcp Ti-Al system)

1) Formation Energies and Ground States



2) Effective Cluster Interactions



Energy Predictors

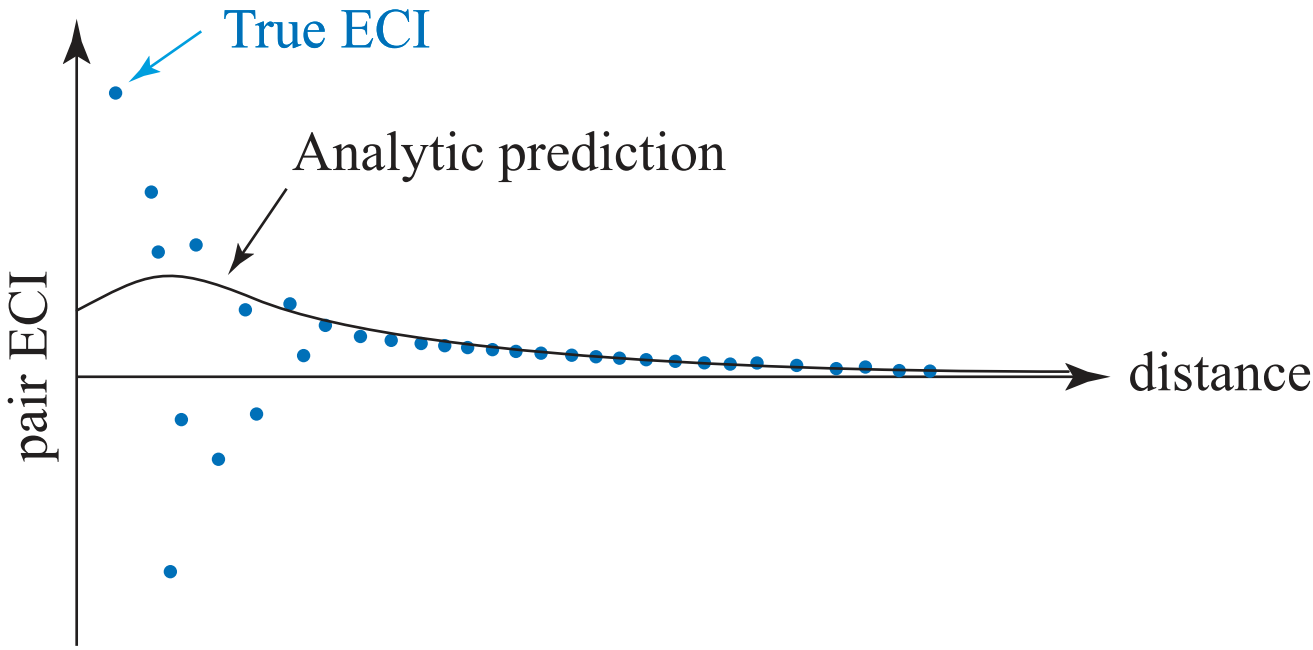
Presence of long range interactions:

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:

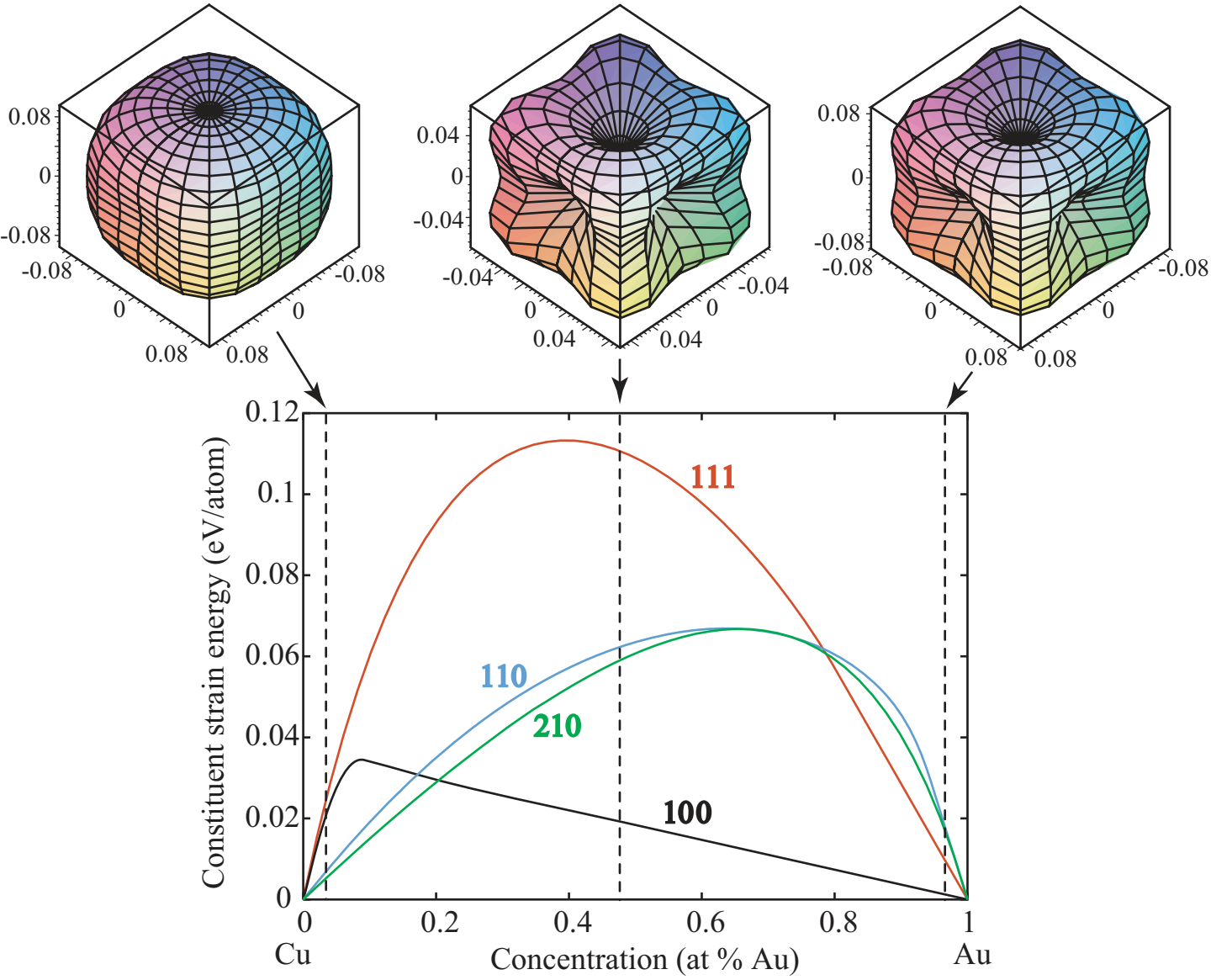
No change needed in the code,
just link with user-specified routines

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

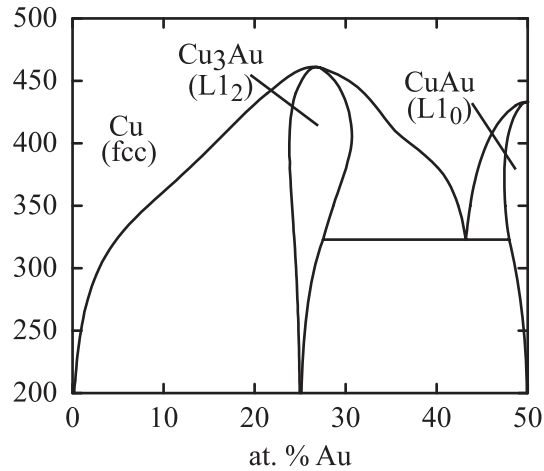
Monte Carlo Simulations

From cluster expansions:

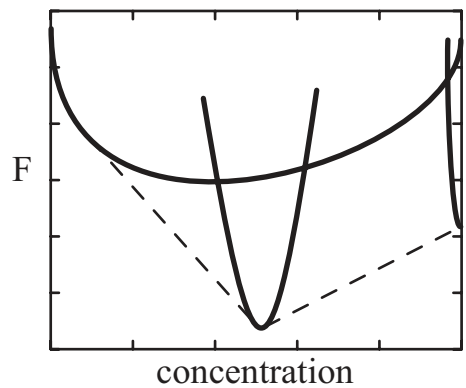
$$E = \sum_{\alpha} J_{\alpha}\, \sigma_{\alpha}$$

to thermodynamic quantities:

Phase diagrams:



Free energies:



Tasks to perform:

How to determine when target accuracy reached?

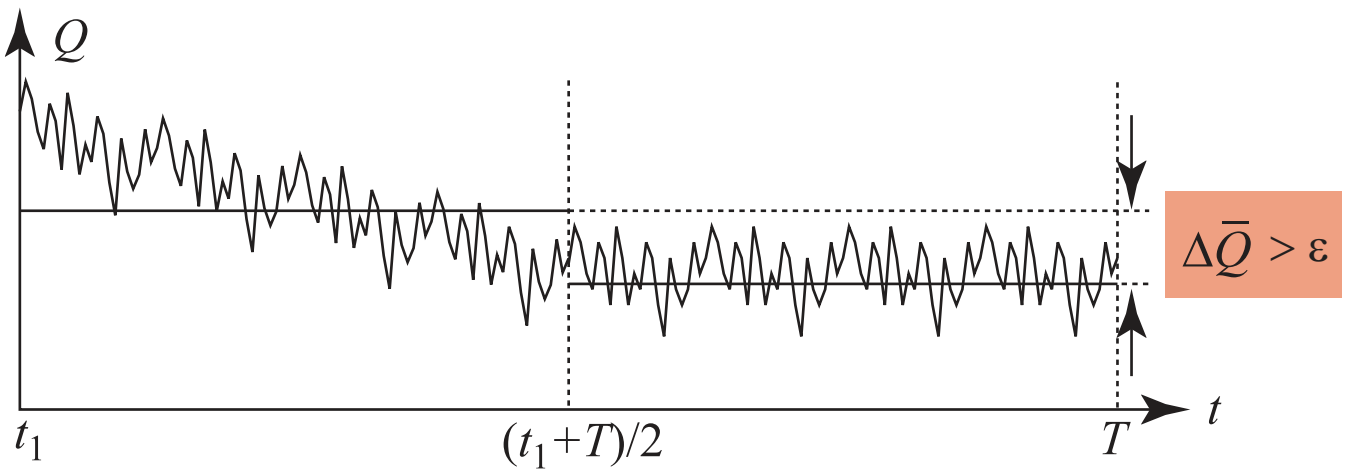
How to detect phase transitions?

How to efficiently calculate phase boundaries?

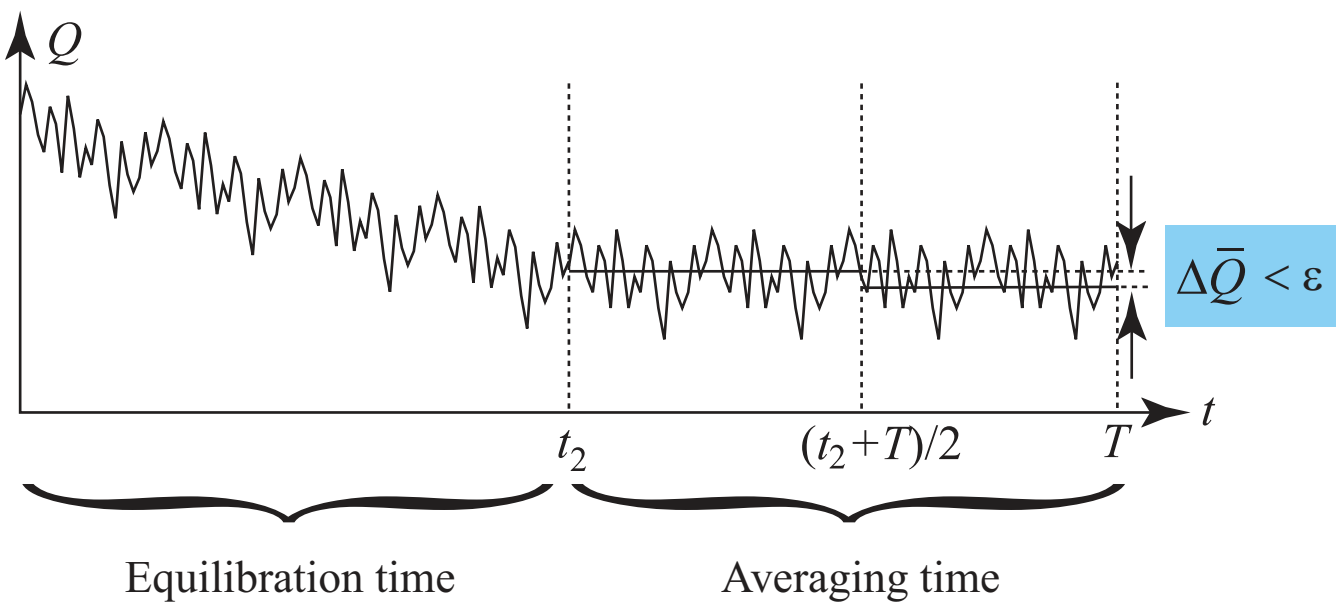
Equilibration and Averaging times

Given tolerance: ε on some thermodynamic quantity Q = **(*E*, *x*, SRO)**

Equilibrium not reached at t_1



Equilibrium reached at t_2



Equilibration time

Averaging time

Choose averaging time such that $\sigma_{\bar{Q}} < \varepsilon$

Detecting phase transitions

Goal: find discontinuity in $Q(C)$

Thermodynamic quantity **(E, x, SRO)**

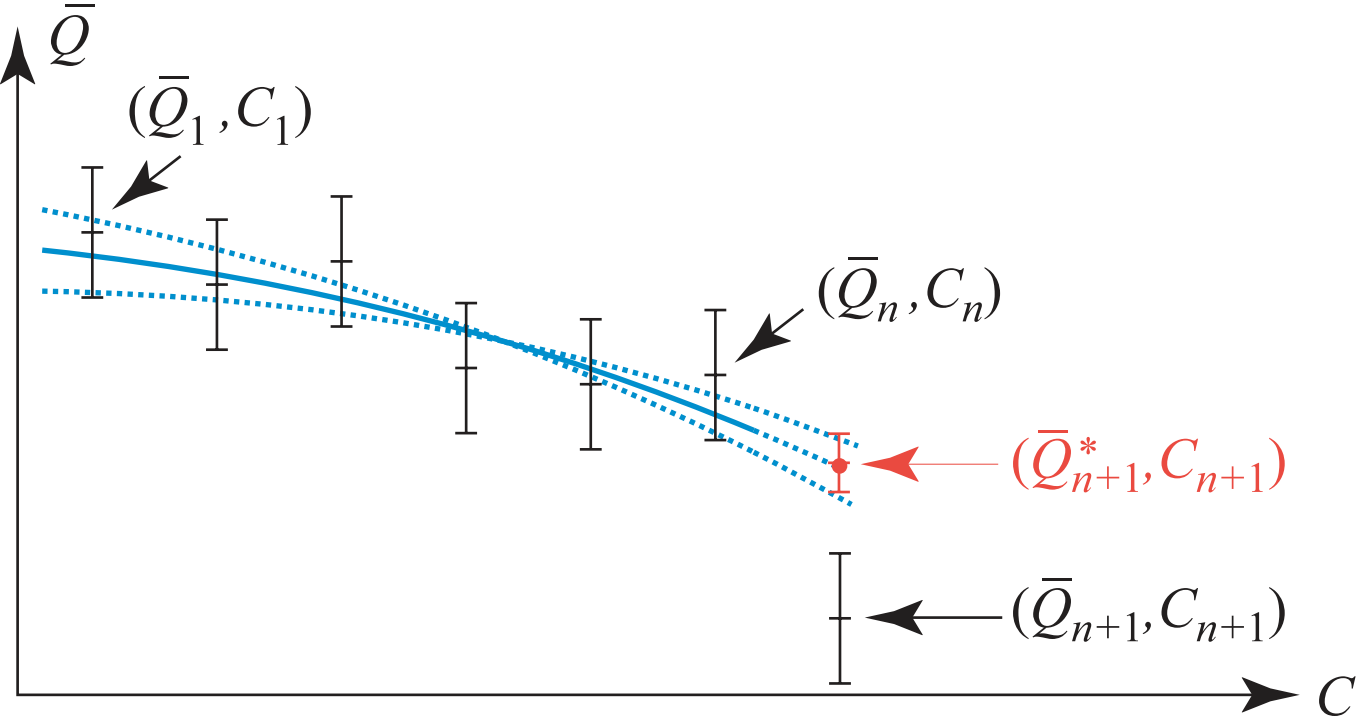
Control variable **(μ, T)**

1) Fit polynomial through $(\bar{Q}_i, \bar{C}_i)$

2) Use cross-validation to find optimal order of polynomial

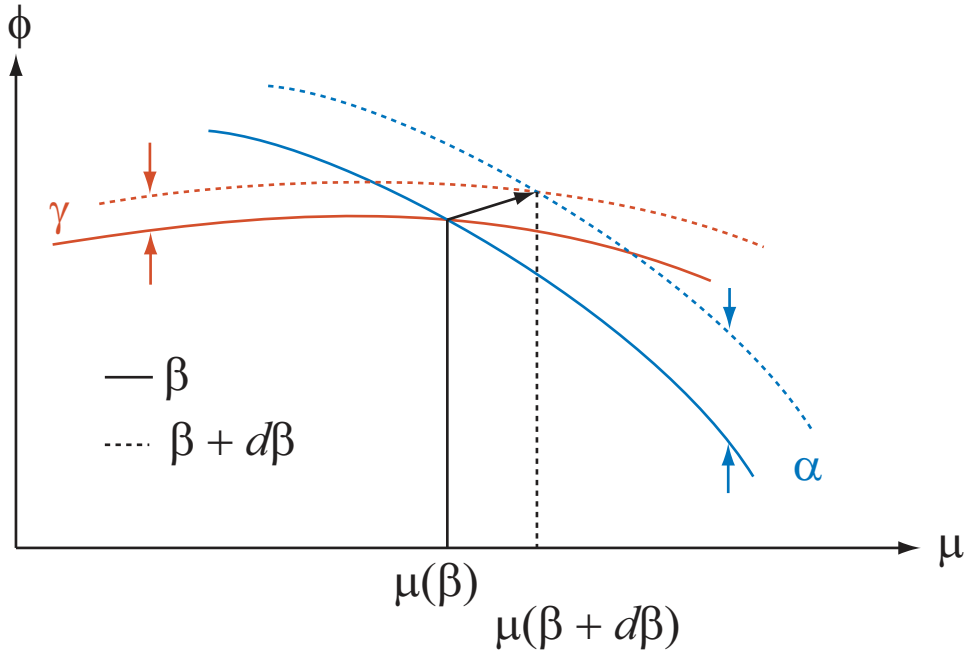
3) Extrapolate $\bar{Q}^*_{n+1}$ using fitted polynomial

4) Perform statistical test of equality between $\bar{Q}^*_{n+1}$ and $\bar{Q}_{n+1}$
(Accounting for noise in MC averages)



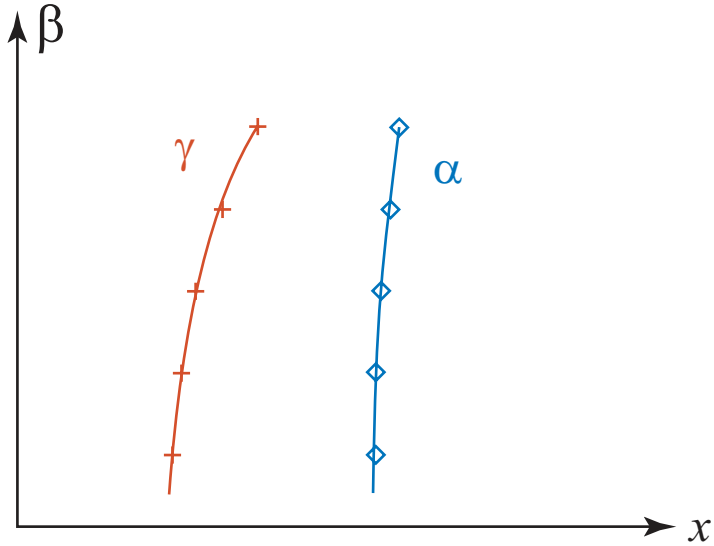
Phase boundary tracing

Principle: { as temperature β changes,
need to update μ to preserve $\phi^\gamma = \phi^\alpha$



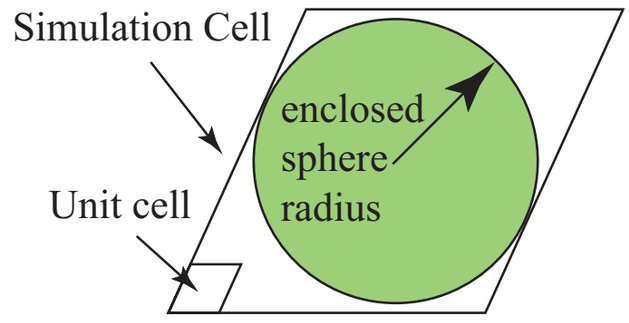
$$\frac{d\mu}{d\beta} = \frac{E^\gamma - E^\alpha}{\beta(x^\gamma - x^\alpha)} - \frac{\mu}{\beta}$$

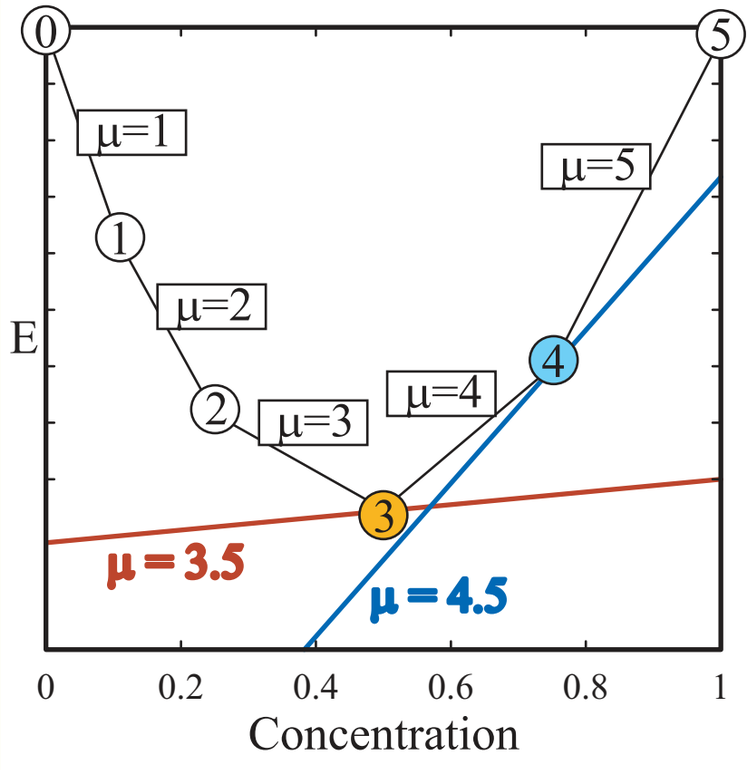
μ(β) is known → find $x^\gamma(\mu(\beta))$ and $x^\alpha(\mu(\beta))$



Input parameters
(Monte Carlo Code)

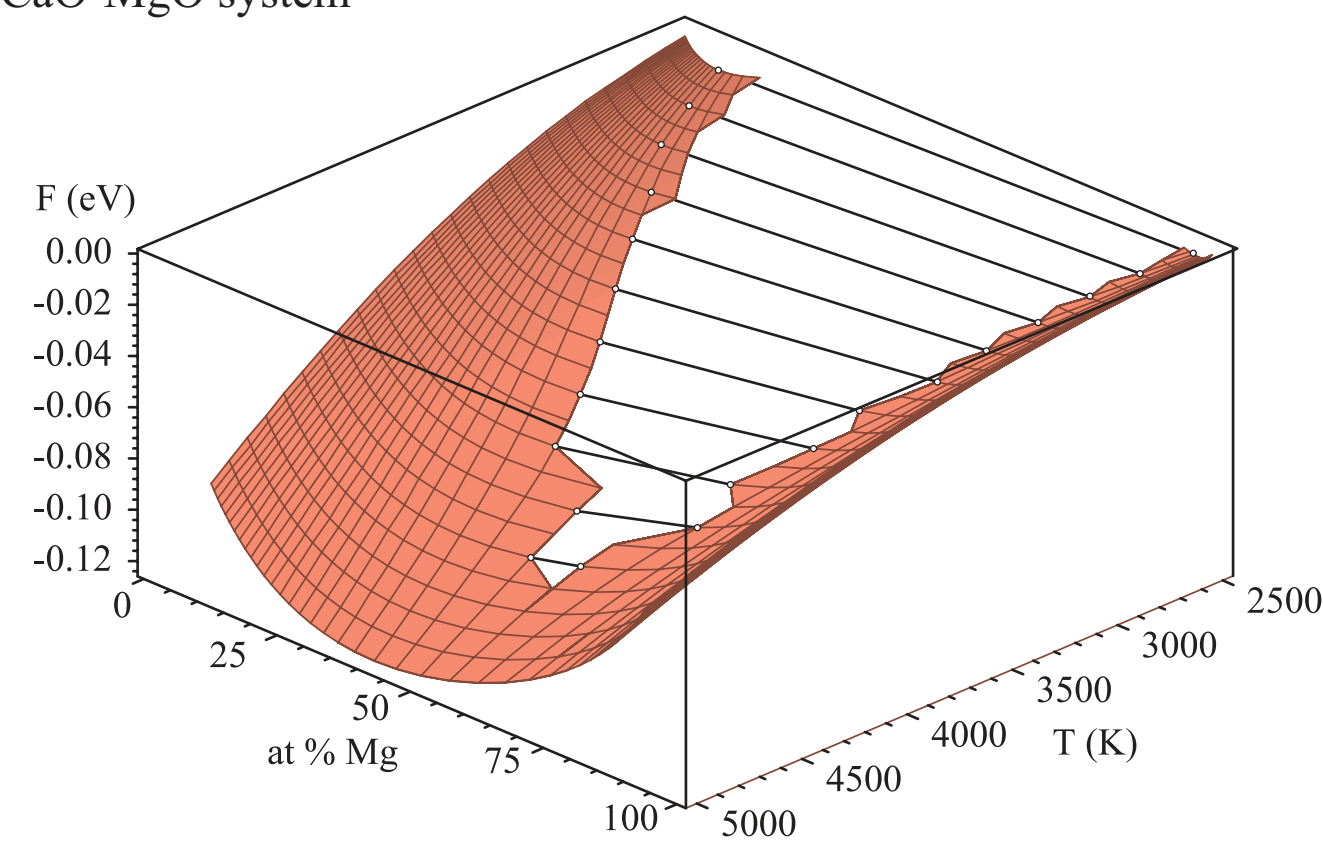
Phase Boundaries Determination	Thermodynamic Integration	
`-dx=1e-3`	`-dx=1e-3`	← $\sigma_{\bar{x}}$ Target precision
`-er=35`	`-er=35`	
`-gs1=3`	`-gs=3`	
`-gs2=4`	`-mu0=3.5`	
	`-mu1=4.5`	
	`-dmu=0.05`	
`-dT=20`	`-T0=100`	Temperature range
	`-T1=1000`	
	`-dT=20`	
`-k=8.617e-5`	`-k=8.617e-5`	← Boltzman's k_B



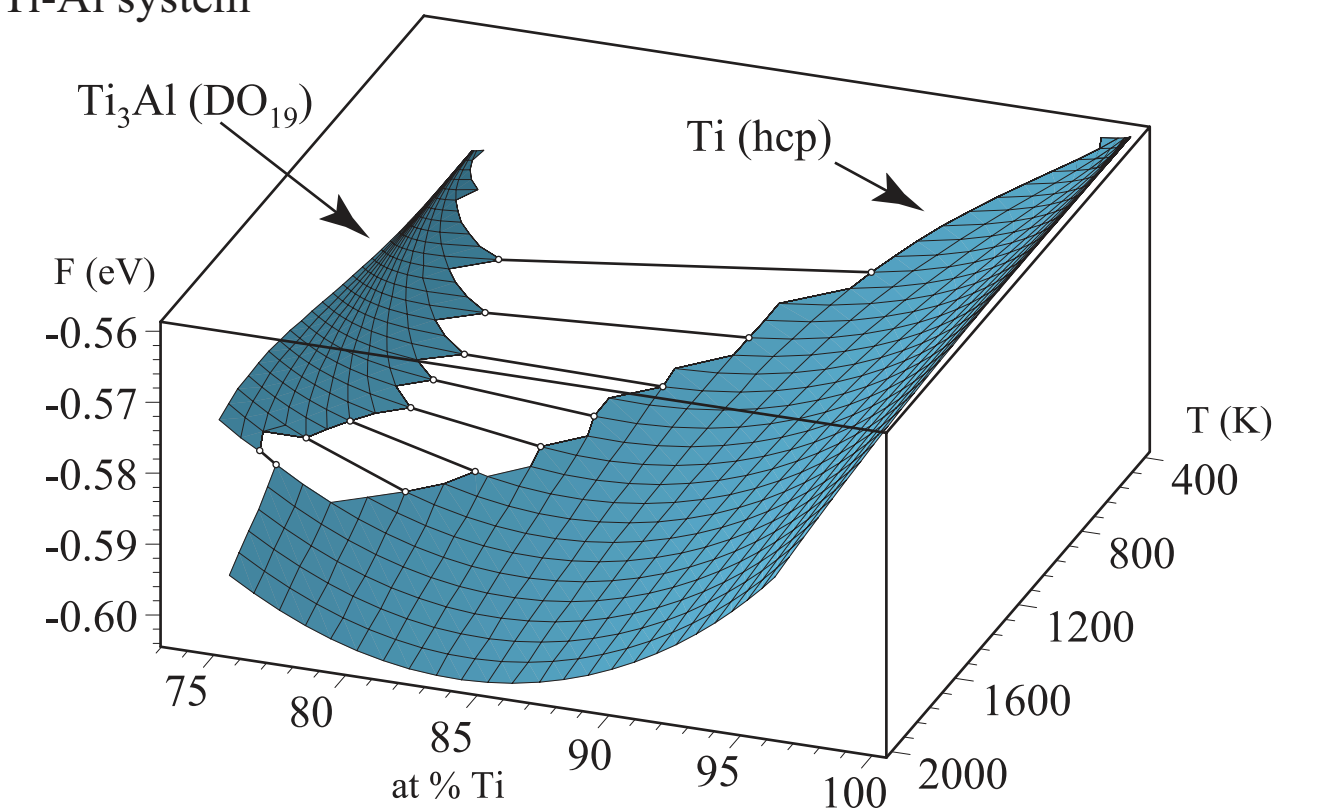


Emc2 output:
Free energy surfaces

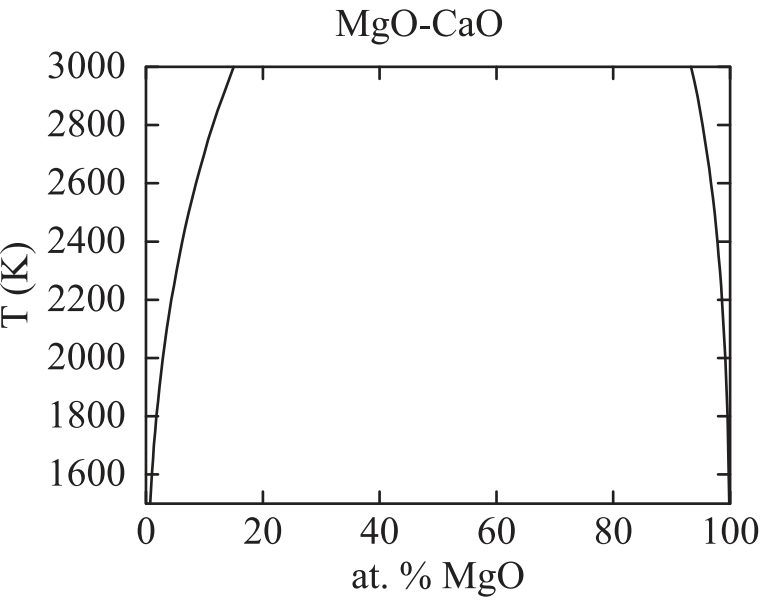
CaO-MgO system

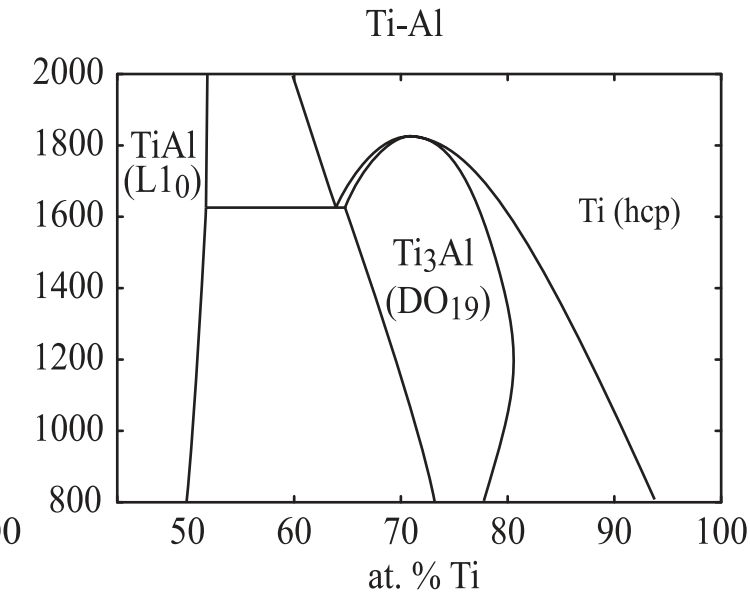


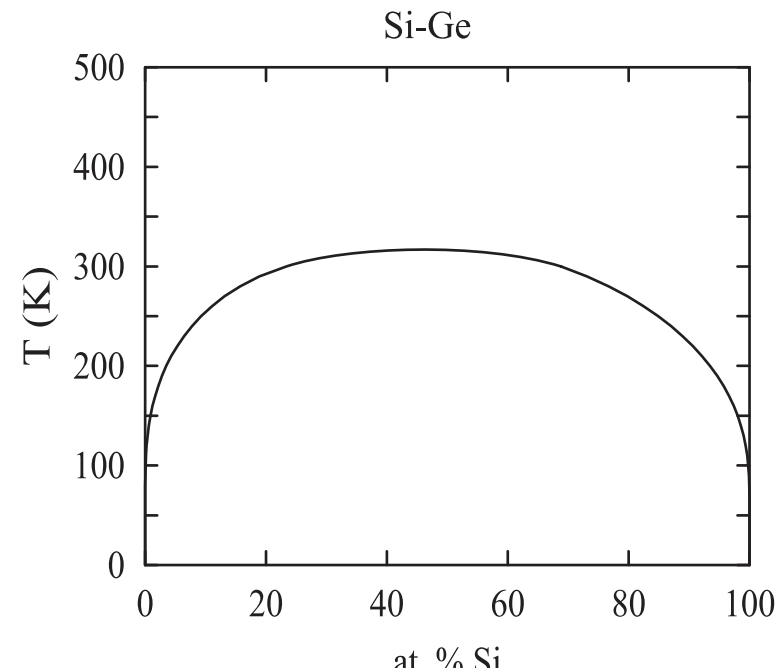
Ti-Al system

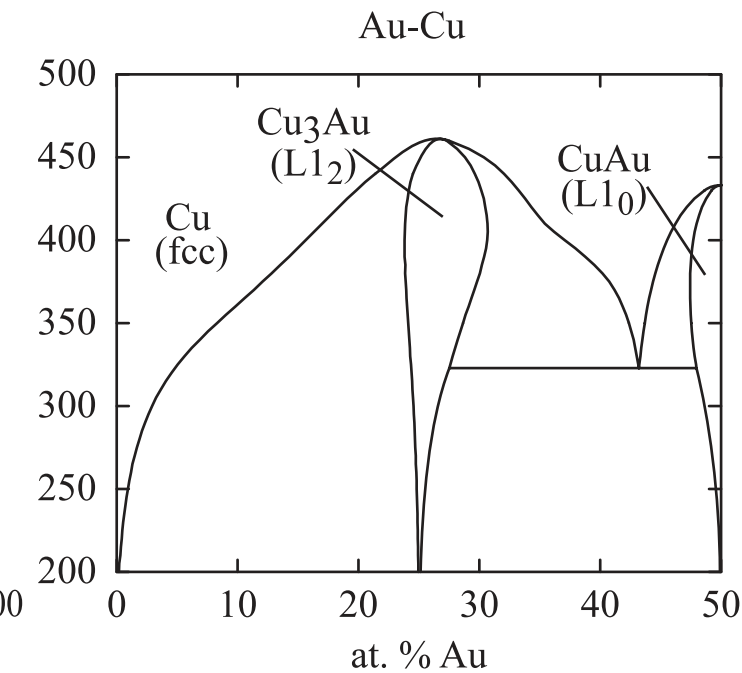


Emc2 ouput:
Phase diagrams



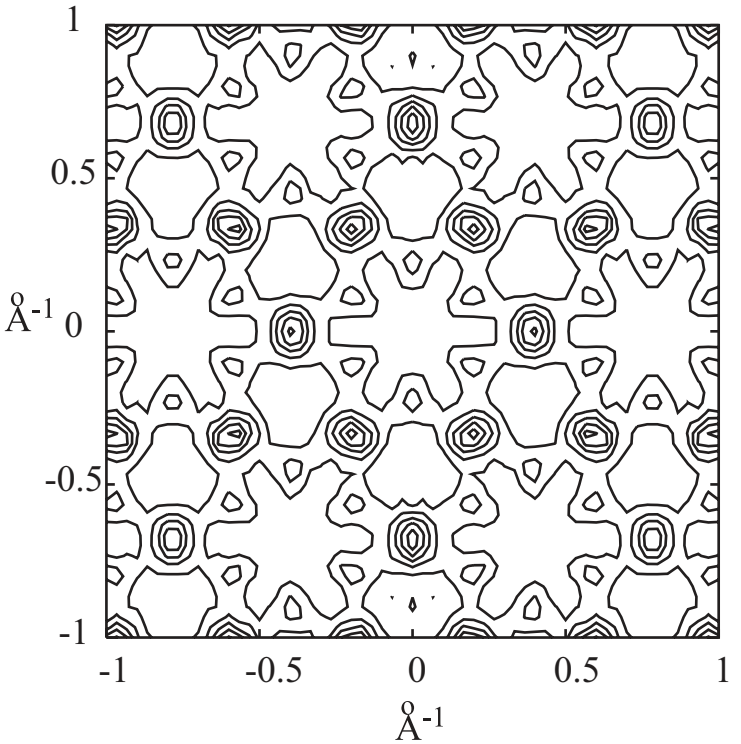






Short-range order calculations

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