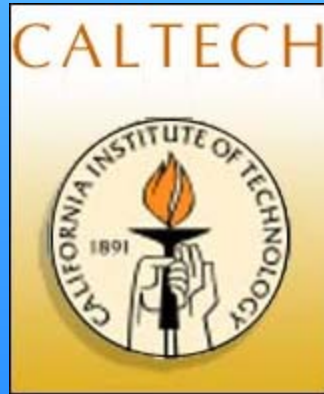


Ab initio thermodynamic modeling of multicomponent alloys

Axel van de Walle

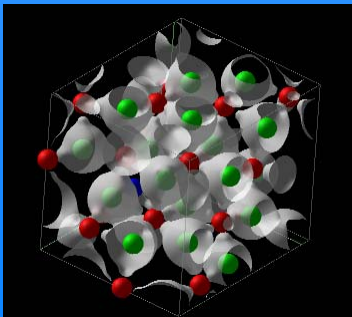
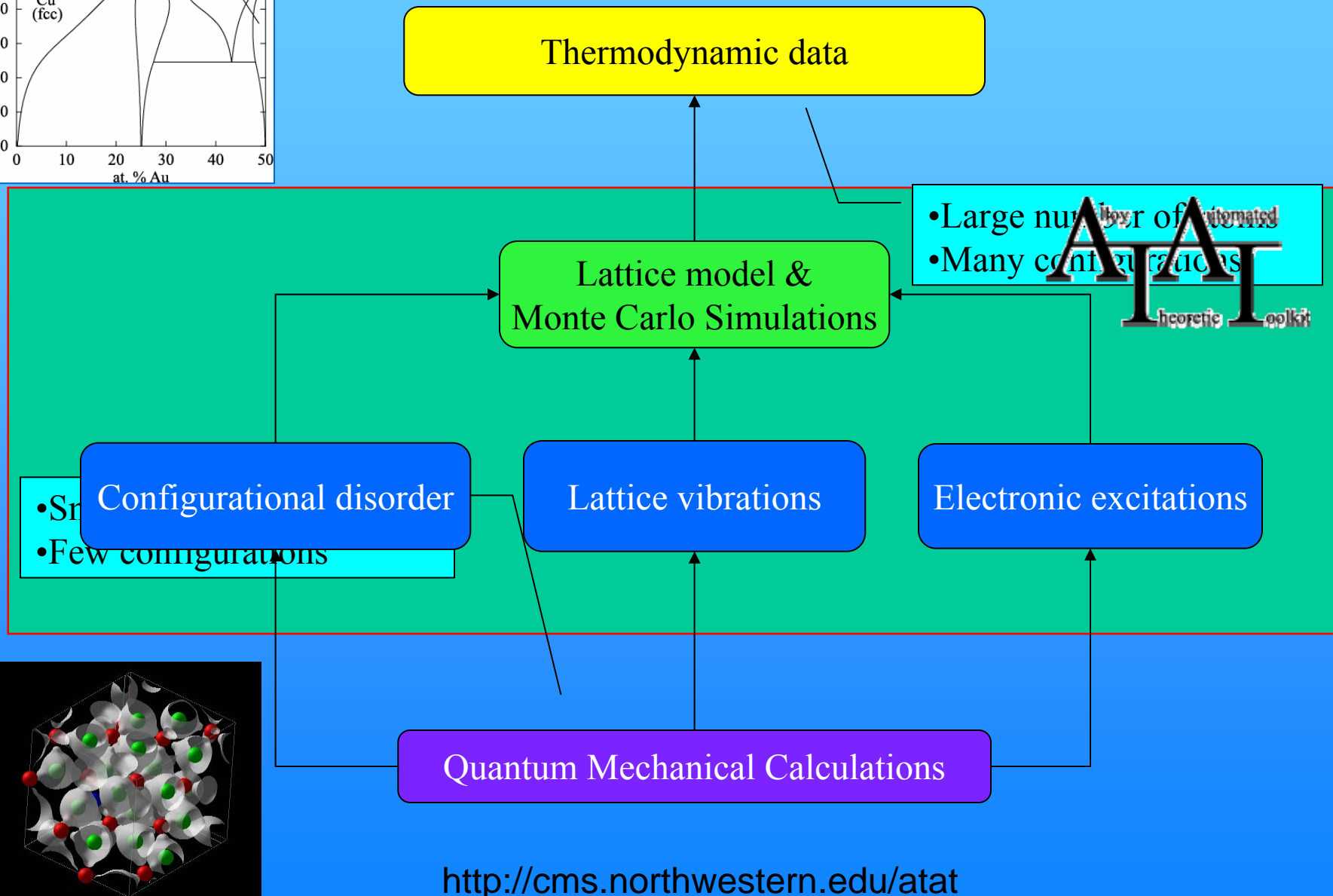
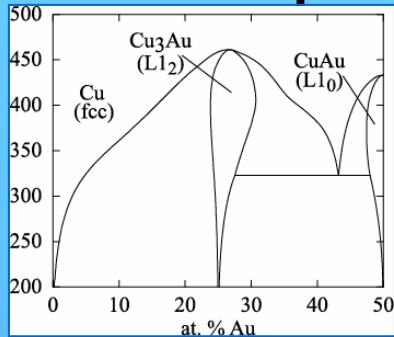
Computational Materials Science
Materials Science and Engineering



<http://www.its.caltech.edu/~avdw/>

This research was supported by the US National Science Foundation through TeraGrid resources provided by NCSA under grant DMR050013N, through the U.S. Department of Energy, National Energy Research Initiative Consortium (NERI-C), grant DE-FG07-07ID14893

First-principles Thermodynamic Calculations



Thermodynamic data

Lattice model &
Monte Carlo Simulations

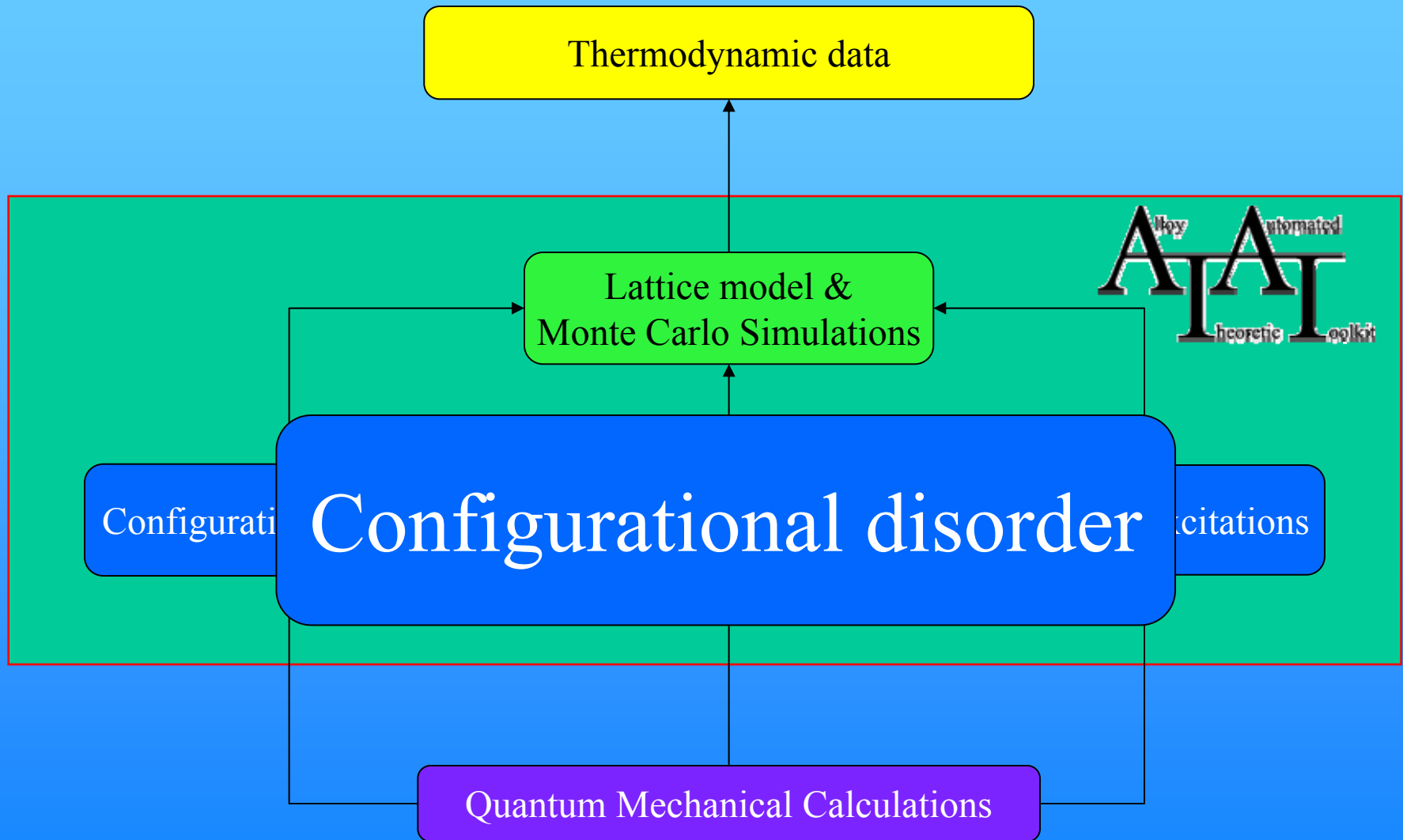
Alloy Automated
Theoretic Toolkit

Configurational

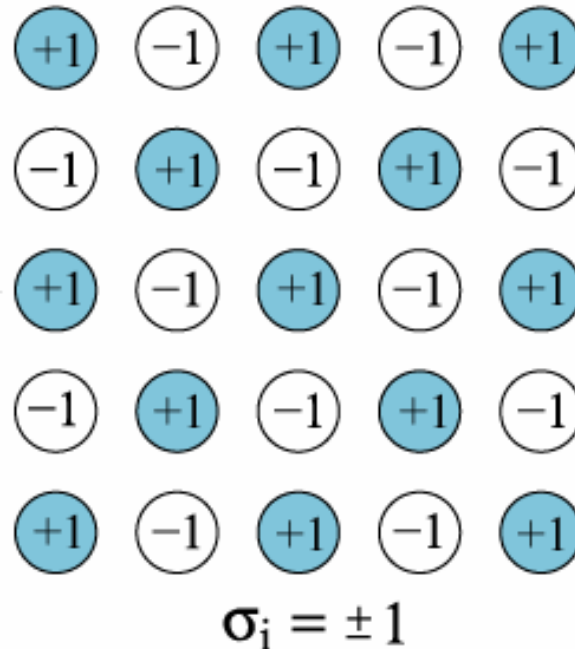
Configurational disorder

Excitations

Quantum Mechanical Calculations



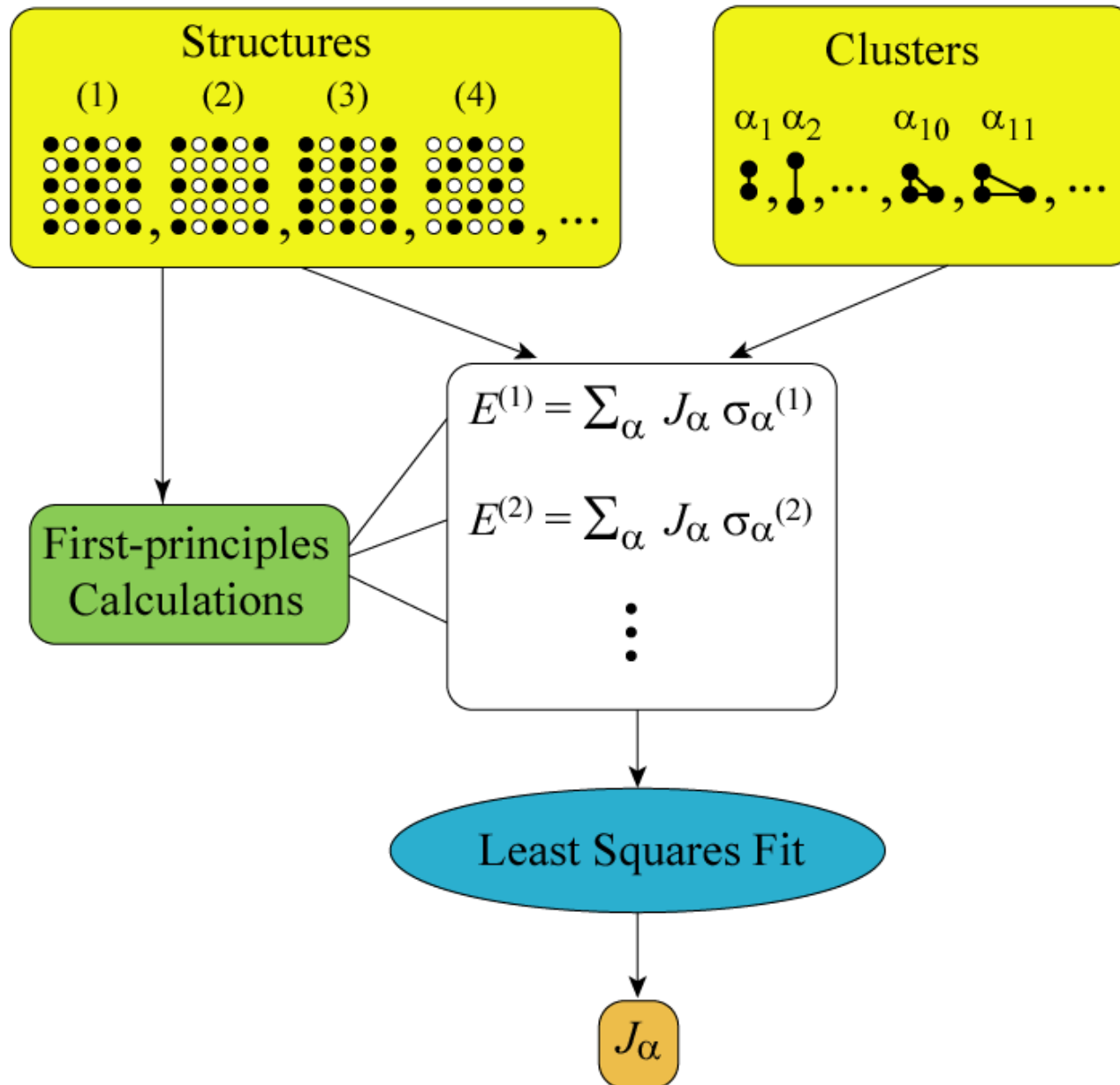
The Cluster Expansion Concept



$$\begin{aligned} E(\sigma_1, \dots, \sigma_n) &= \sum_{\{i,j\}} J_{ij} \sigma_i \sigma_j + \sum_{\{i,j,k\}} J_{ijk} \sigma_i \sigma_j \sigma_k + \dots \\ &= \sum_{\alpha} J_{\alpha} \Gamma_{\alpha}(\sigma) \quad \text{Sanchez, Ducastelle and Gratias (1984)} \end{aligned}$$

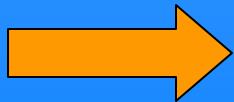
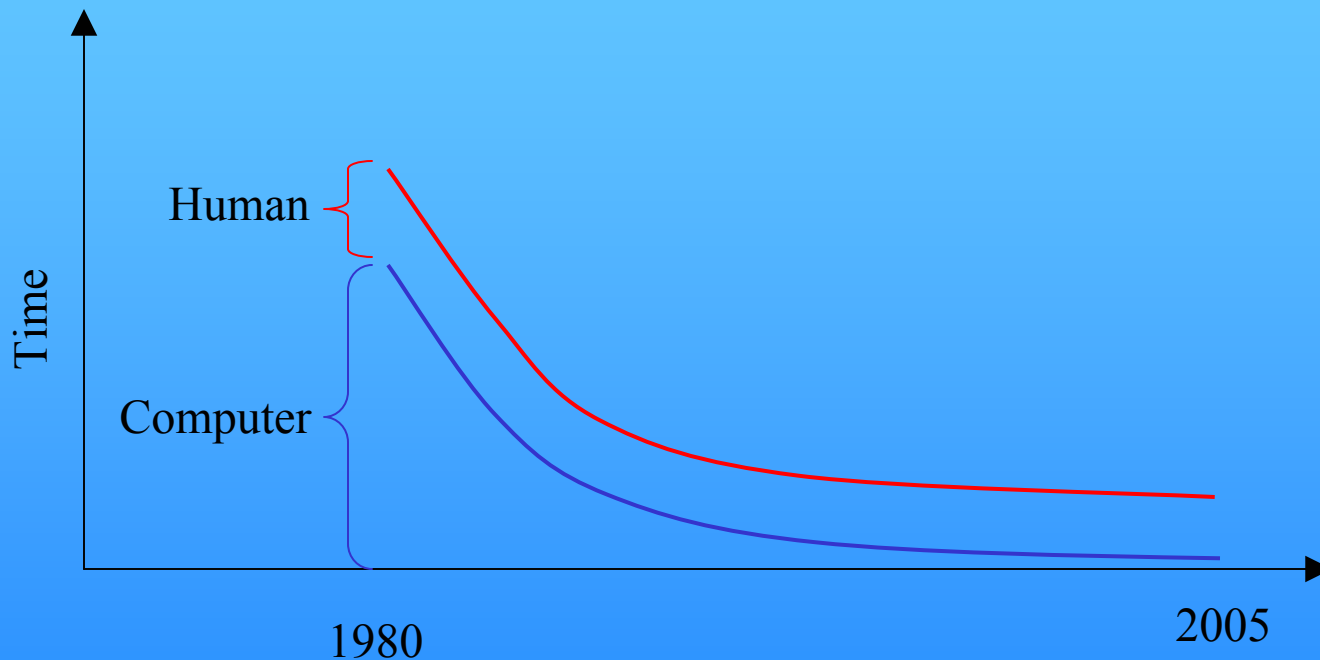
The $\Gamma_{\alpha}(\sigma)$ form a basis for the space of scalar functions of configuration.

Cluster expansion fit



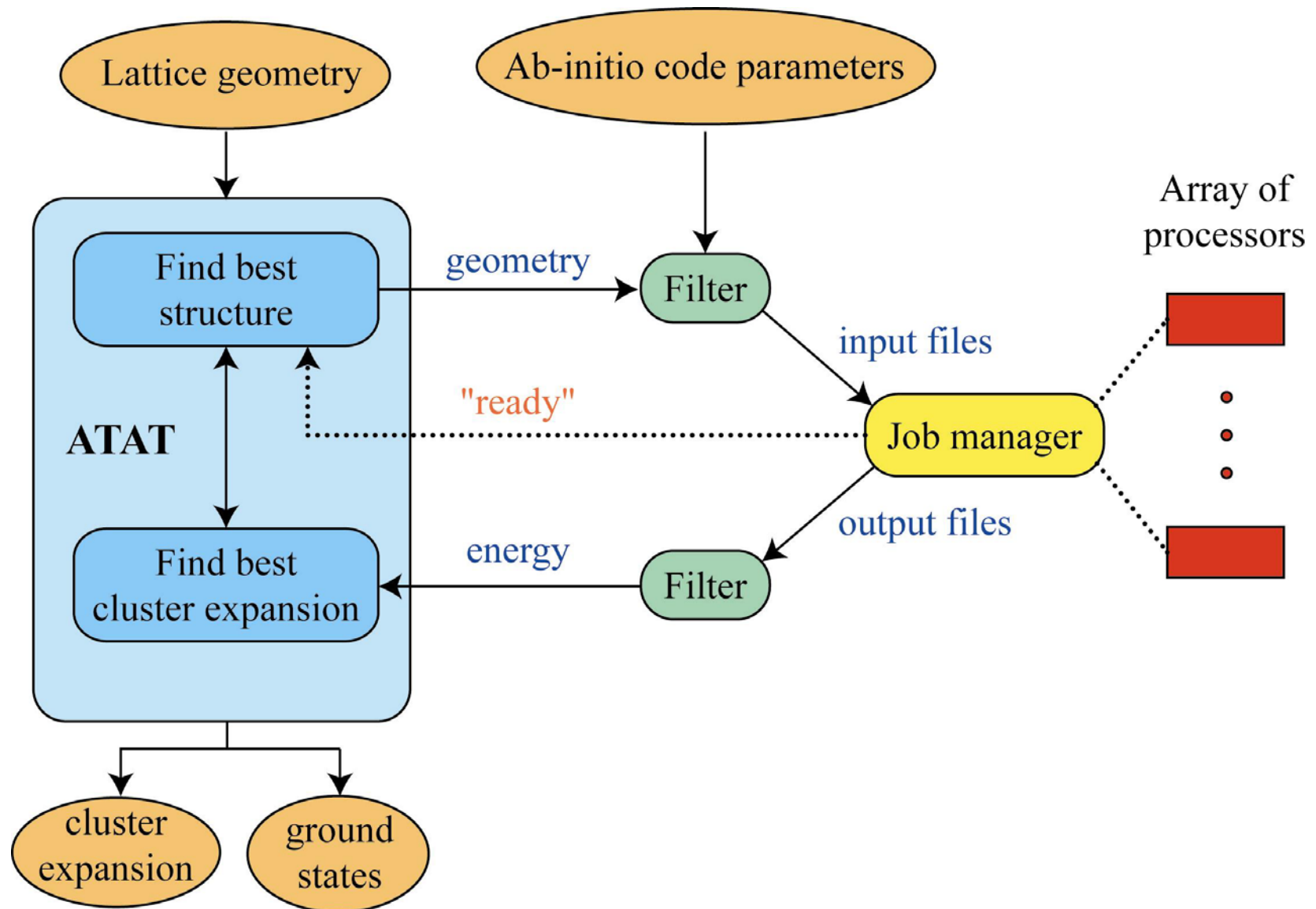
A matter of time...

Time needed to complete a given first-principles calculation



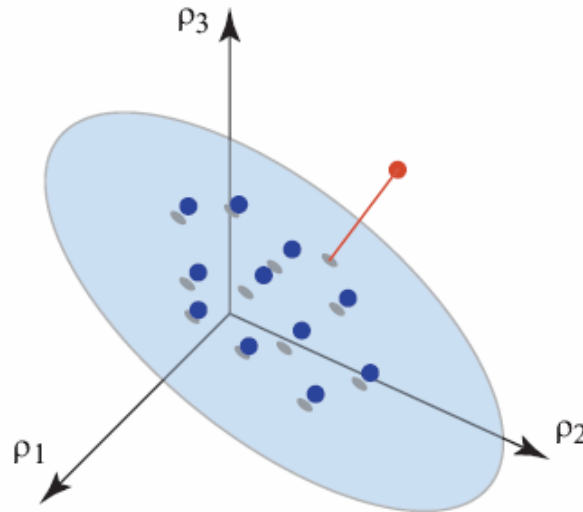
The procedure needs to be automated

Automated Cluster Expansion Construction



Structure selection

- Generate large database of structures (i.e. candidate compounds, atomic orderings or configurations).
- Calculate pair correlations functions
- Select structures that reveal the most information (most distinct correlations functions).



A. van de Walle and G. Ceder, J. Phase Equilibria **23**, 348 (2002)

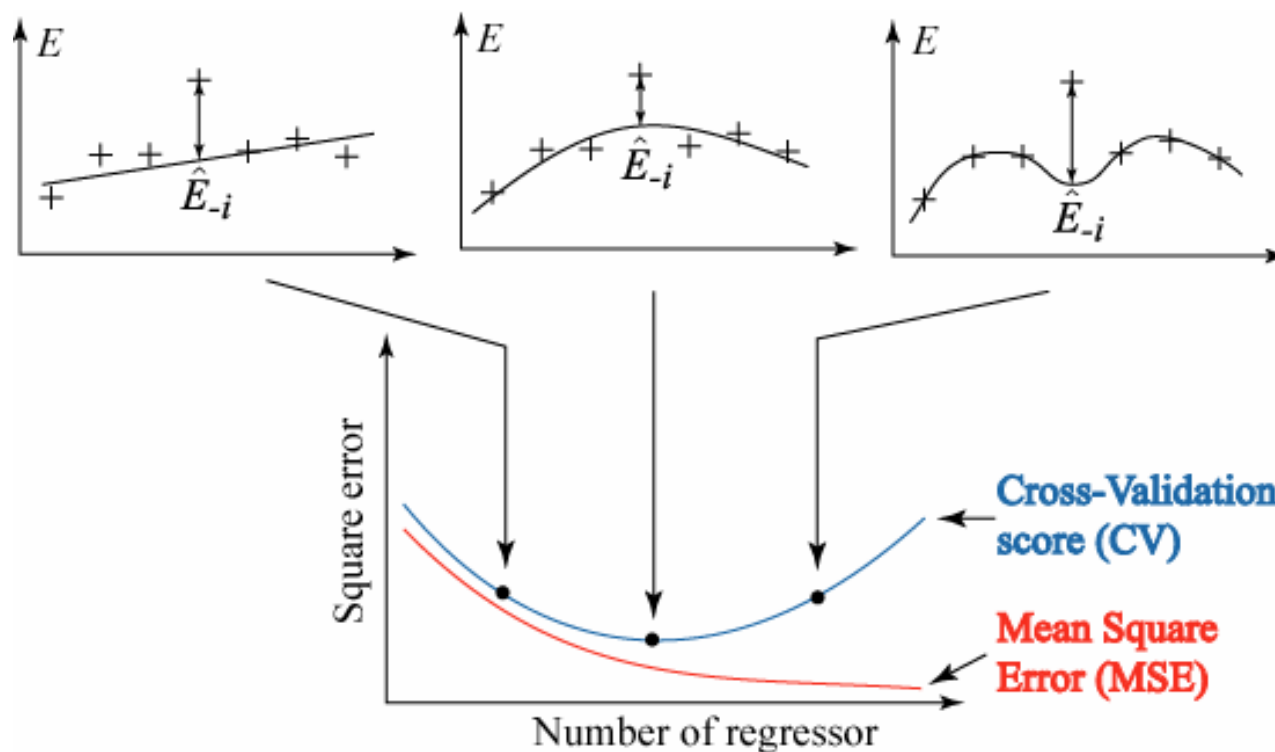
Cross-validation

True energy of structure i

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

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 of polynomial fit:

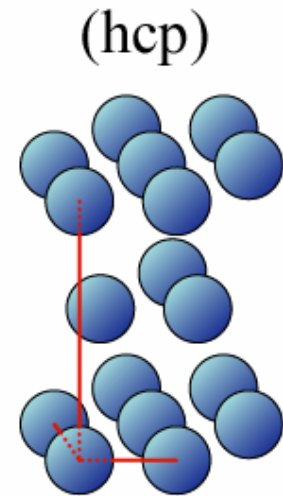


A. van de Walle and G. Ceder, J. Phase Equilibria **23**, 348 (2002)

Application to Ti-Al Alloys

Simple lattice input file

	a	b	c	α	β	γ
Coordinate system	2.94	2.94	4.8	90	90	120
Unit cell	1	0	0			
	0	1	0			
	0	0	1			
Atoms	0.666667	0.333333	0.500000	Al,Ti		
	0.000000	0.000000	0.000000	Al,Ti		



Simple ab initio code input file

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

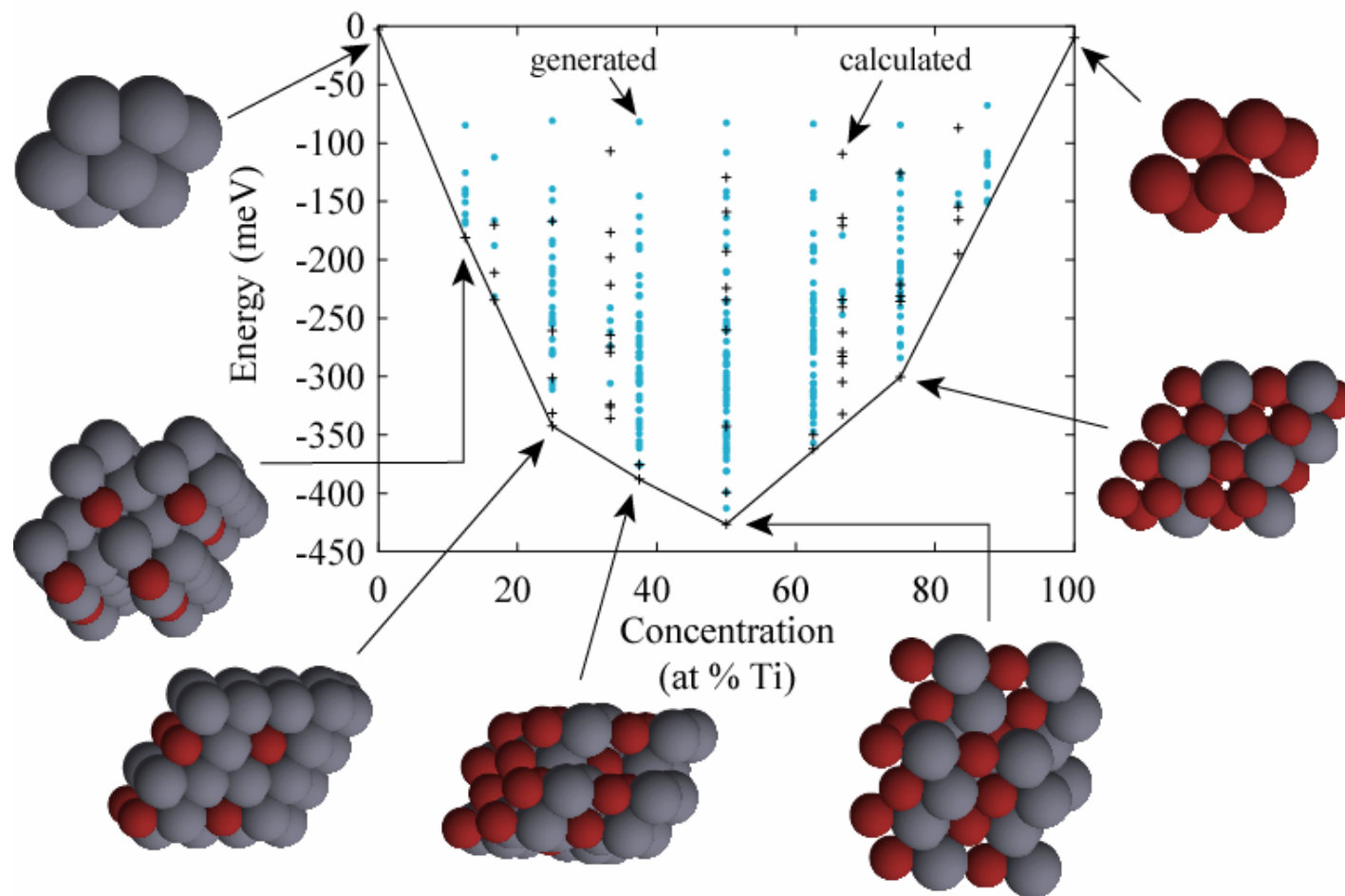
KPPRA = 1000
DOSTATIC
```

} Standard VASP tokens

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

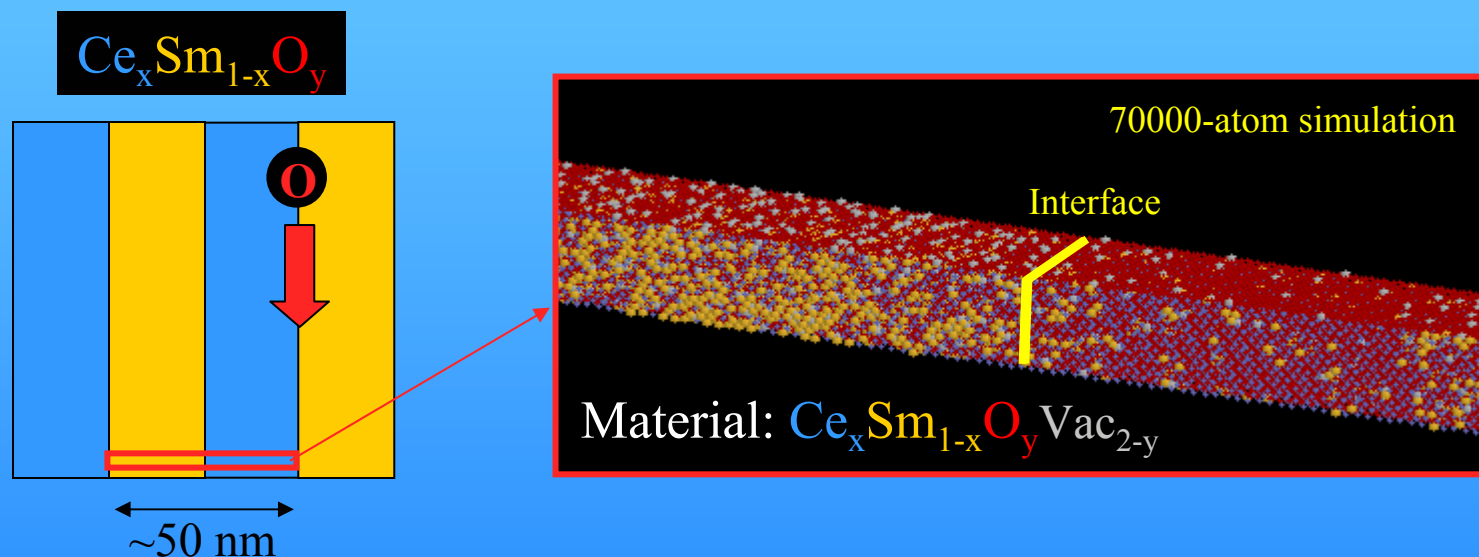
do static run

Ground States Search



Application Example

- (Sm/Ce)O₂ Superlattices have been shown to exhibit enhanced Oxygen conductivity*.



- Goal: study interface thermodynamics to help understand origin of enhanced conductivity.

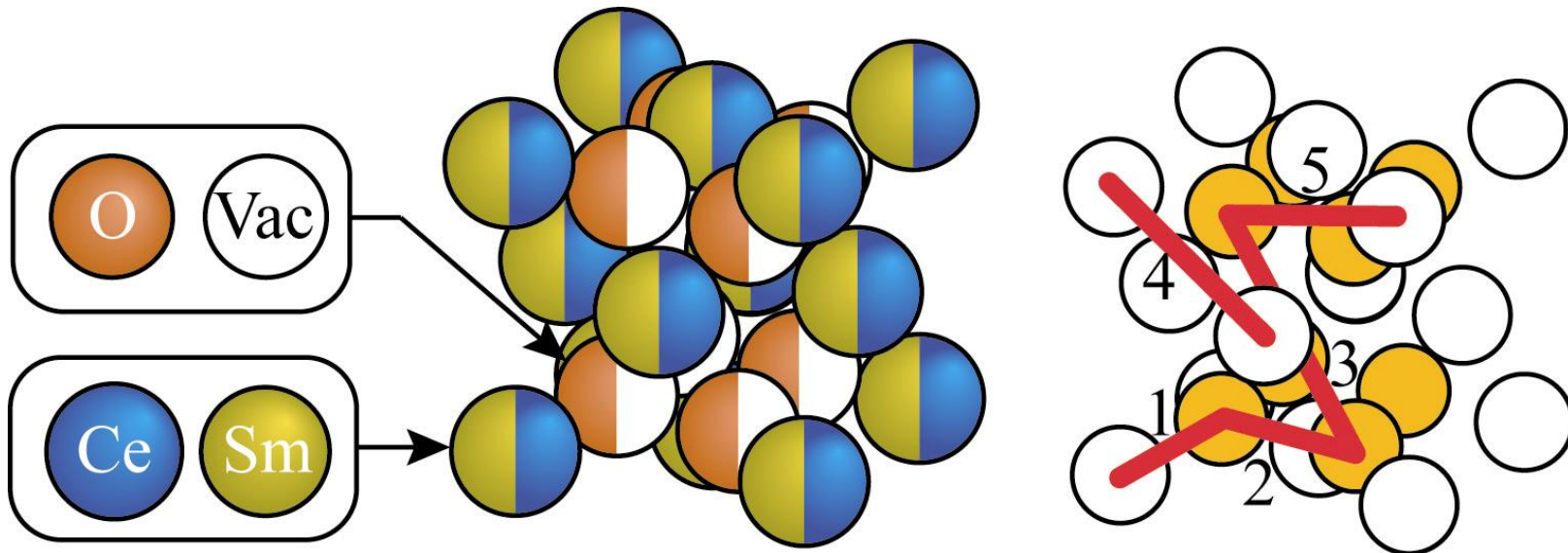
*I. Kosackia, T. Christopher, M. Rouleau, P. F. Becher, J. Bentley, D. H. Lowndes, Solid State Ionics 176, 1319 (2005) and I. Kosacki, C.M. Rouleau, P.F. Becher and D.H. Lowndes, in press.

Coupled Sublattices Multicomponent Cluster Expansion

Tepesch, Garbulski and Ceder (1995) Sanchez, Ducastelle and Gratias (1984)

Same basic form: $E(\sigma_1, \dots, \sigma_n) = \sum_{\alpha} J_{\alpha} \sigma_{\alpha}$

Occupation variables: $\sigma_i = 0, \dots, n_i - 1$



Completeness

Can any function of configuration be represented as $\sum_{\alpha} J_{\alpha} \sigma_{\alpha}$?


(Sublattices with different # of components not covered by Sanchez et al.'s proof.)

Need to show: $\langle \sigma_{\alpha}, \sigma_{\beta} \rangle \equiv \sum_{\sigma} \sigma_{\alpha} \sigma_{\beta} = \delta_{\alpha\beta}$

$$\begin{aligned} \sum_{\sigma} \sigma_{\alpha} \sigma_{\beta} &= \sum_{\sigma} \prod_i \Gamma(n_i, \alpha_i, \sigma_i) \Gamma(n_i, \beta_i, \sigma_i) \\ &= \prod_i \left(\underbrace{\sum_{\sigma_i} \Gamma(n_i, \alpha_i, \sigma_i) \Gamma(n_i, \beta_i, \sigma_i)}_{\delta_{\alpha_i \beta_i}} \right) = \delta_{\alpha\beta} \end{aligned}$$

By orthogonality between rows of Γ matrices.

Cluster functions form an orthonormal basis
As many cluster functions as configurations

}  Complete basis

Combinational Explosion?

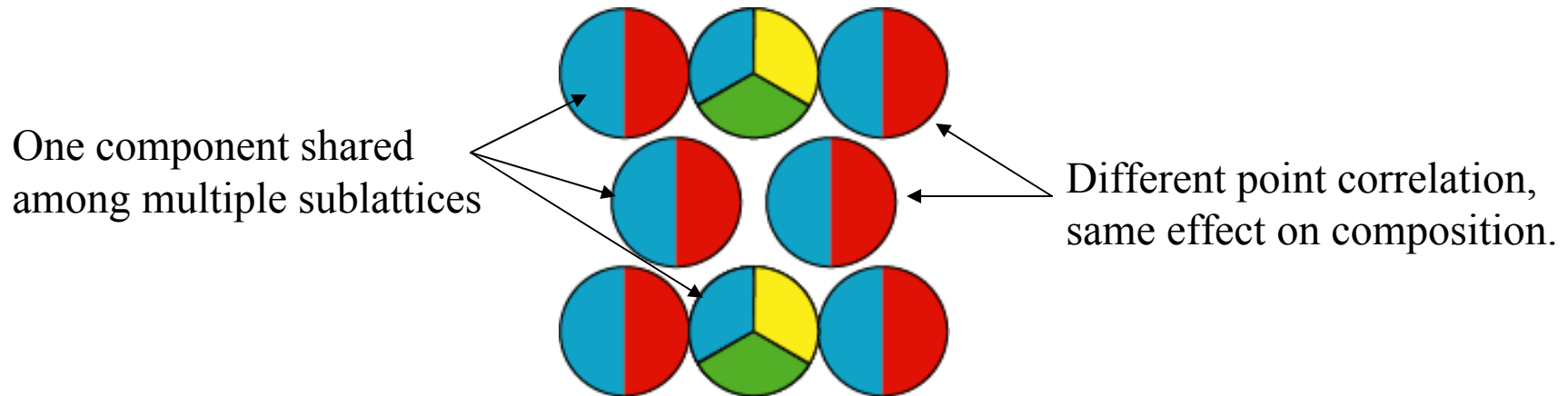
The number of distinct clusters increases much more rapidly with interaction range in a multicomponent system than in a binary system.

However, the number of distinct configurations **also** increase much more rapidly with unit cell size in a multicomponent system than in a binary system.

In a multicomponent system, one has access to a large pool of small-cell superstructures to fit the cluster expansion.

Computational cost of DFT calculations does not increase too much in multicomponent systems.

Compositions vs point correlations



Full vector of compositions: x ← To output

Vector of independent compositions: r ← For ground state search

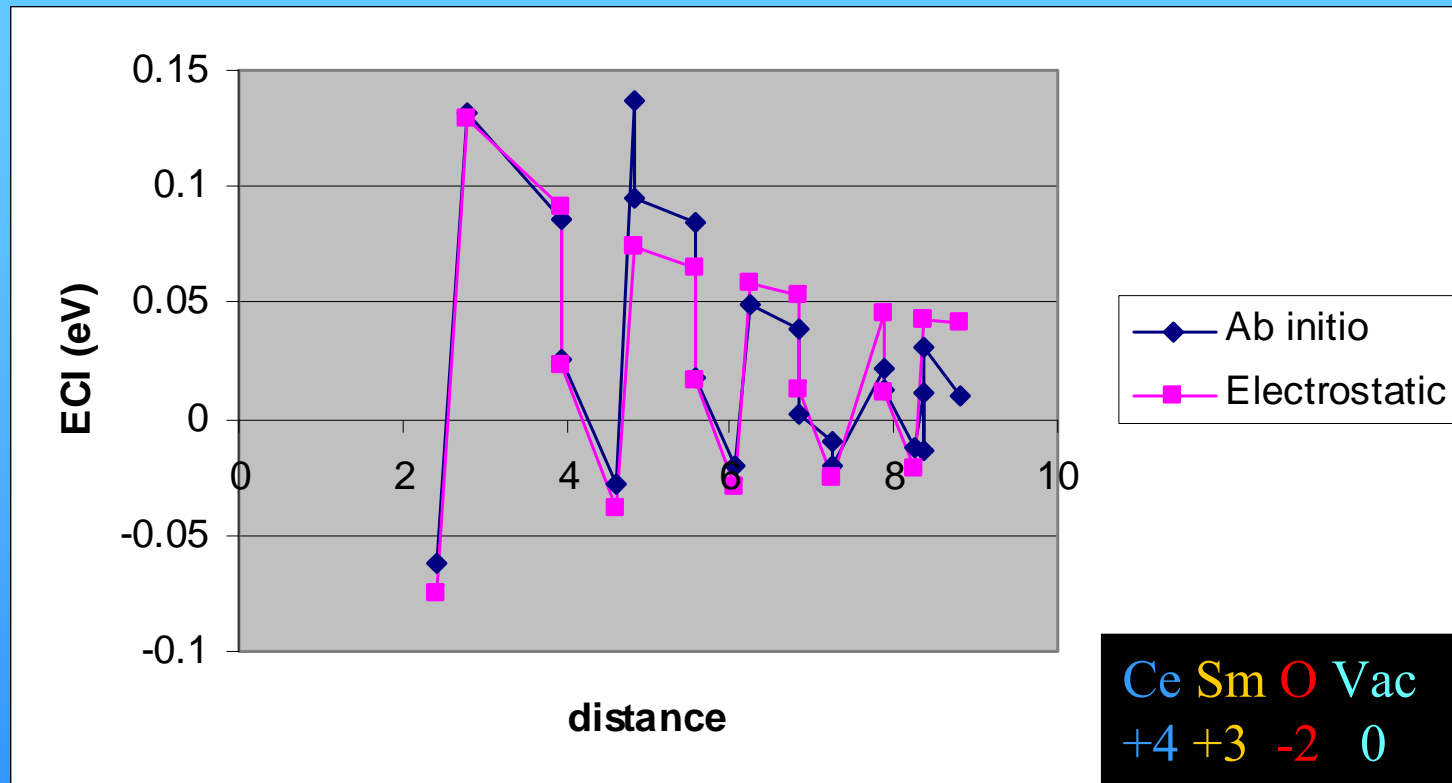
Vector of point correlations: γ ← For cluster expansion

$$r = M_{r\gamma} \gamma$$

$$x = M_{x\gamma} \gamma + c_\gamma$$

$$\mu_x^T x = \mu_x^T M_{x\gamma} \gamma + \mu_x^T c_\gamma = \underbrace{(\mu_x^T M_{x\gamma})^T}_{J_{\{i\}}} \gamma + \underbrace{\mu_x^T c_\gamma}_{J_\emptyset}$$

Effective Cluster Interactions



➔ **Model interactions as:**

Electrostatic contribution
(calculated analytically)

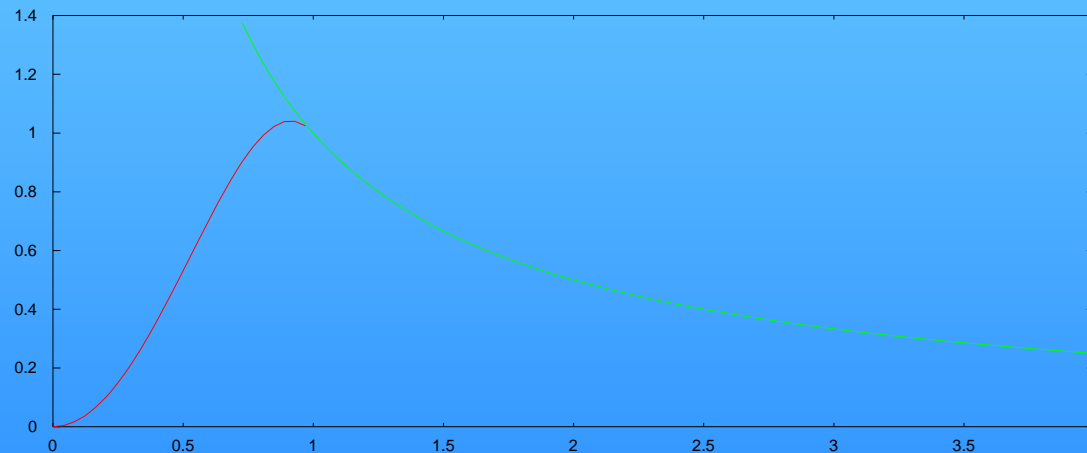
+

Chemical & elastic contribution
(fitted from *ab initio* data)

(effective ϵ fitted to *ab initio* data)

Efficient handling of long-range electrostatic interactions in MC

- Electrostatic energy calculated entirely in reciprocal space
 - Trick: Smooth cutoff as $r \rightarrow 0$ in real space, since short distance never sampled in lattice model.

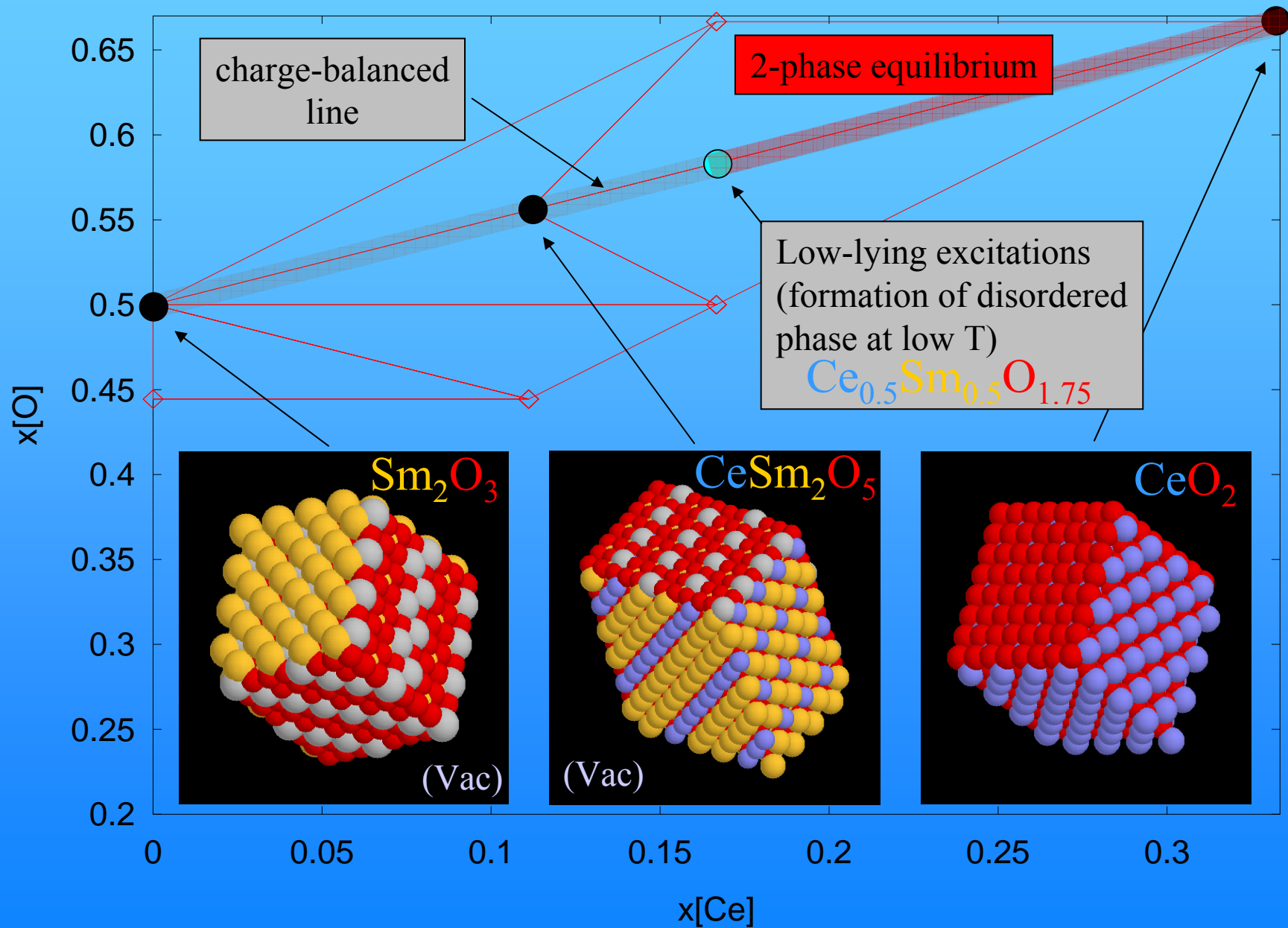


Smoothness \Rightarrow fast decay of Fourier transform

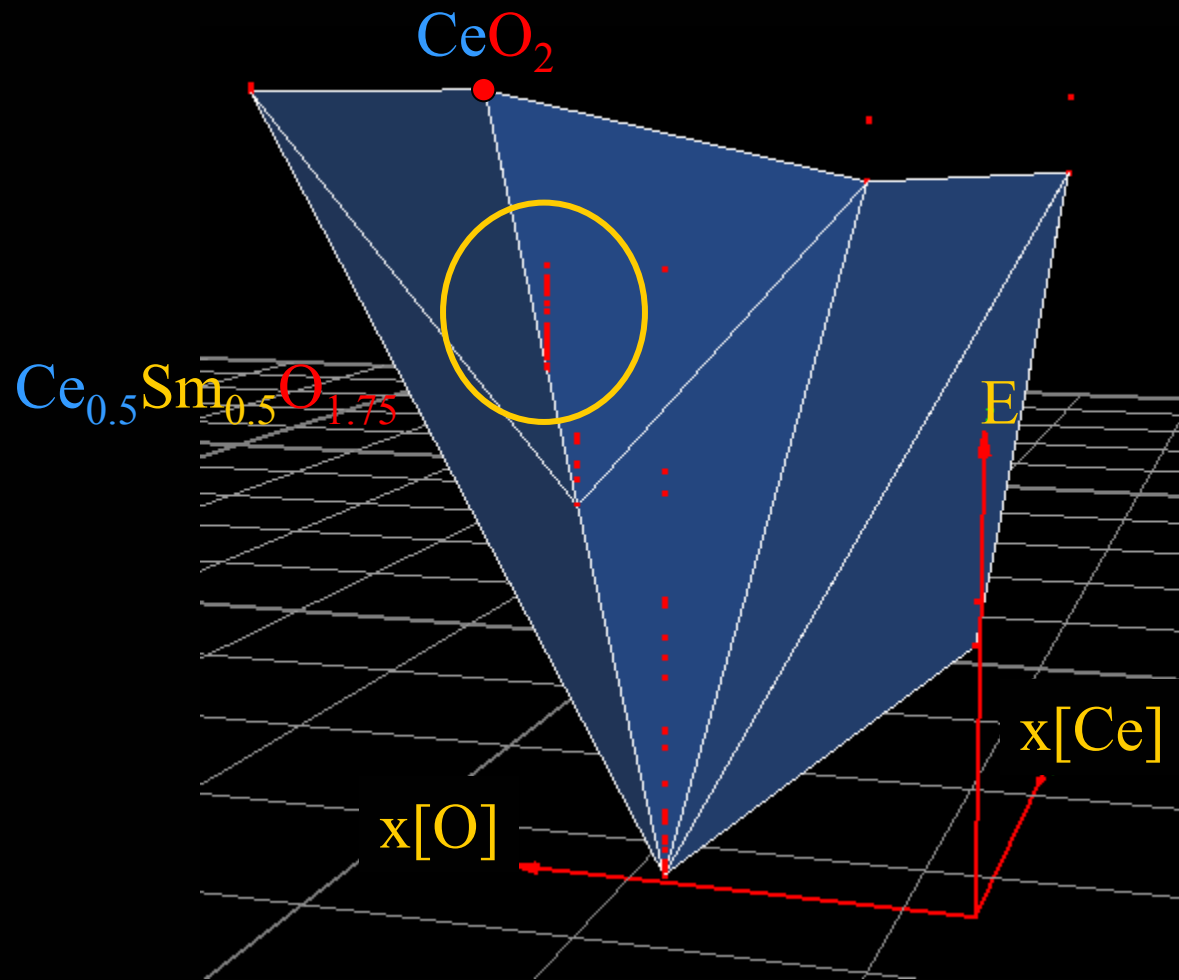
- Use efficient mixed-basis method* to update energy at each MC step.

*Lu Z W, Laks D B, Wei S-H and Zunger A 1994 *Phys. Rev. B* **50** 6642

Compound search



Convex hull construction



Thermodynamic data

Lattice model &
Monte Carlo Simulations

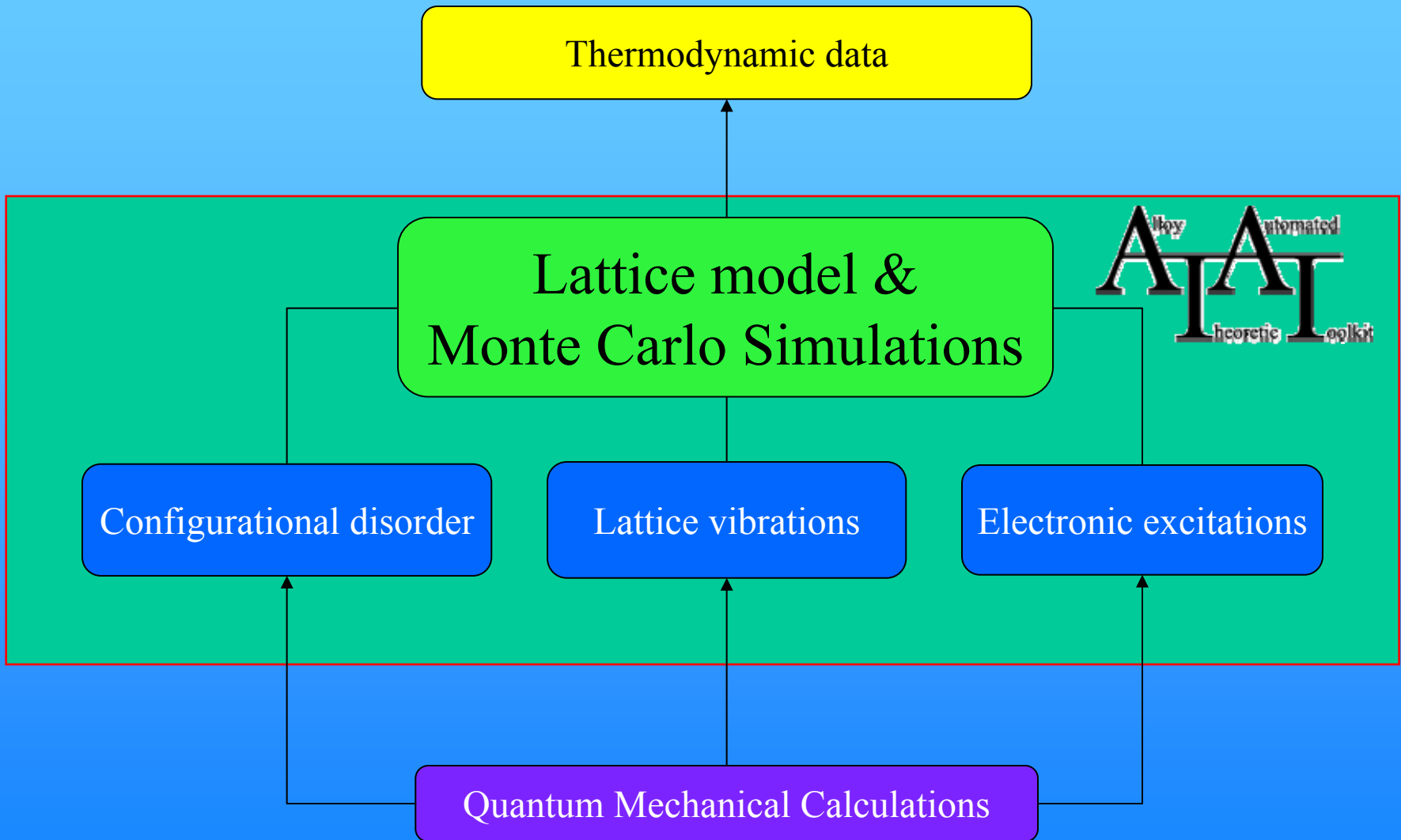
Alloy Automated
Theoretic Toolkit

Configurational disorder

Lattice vibrations

Electronic excitations

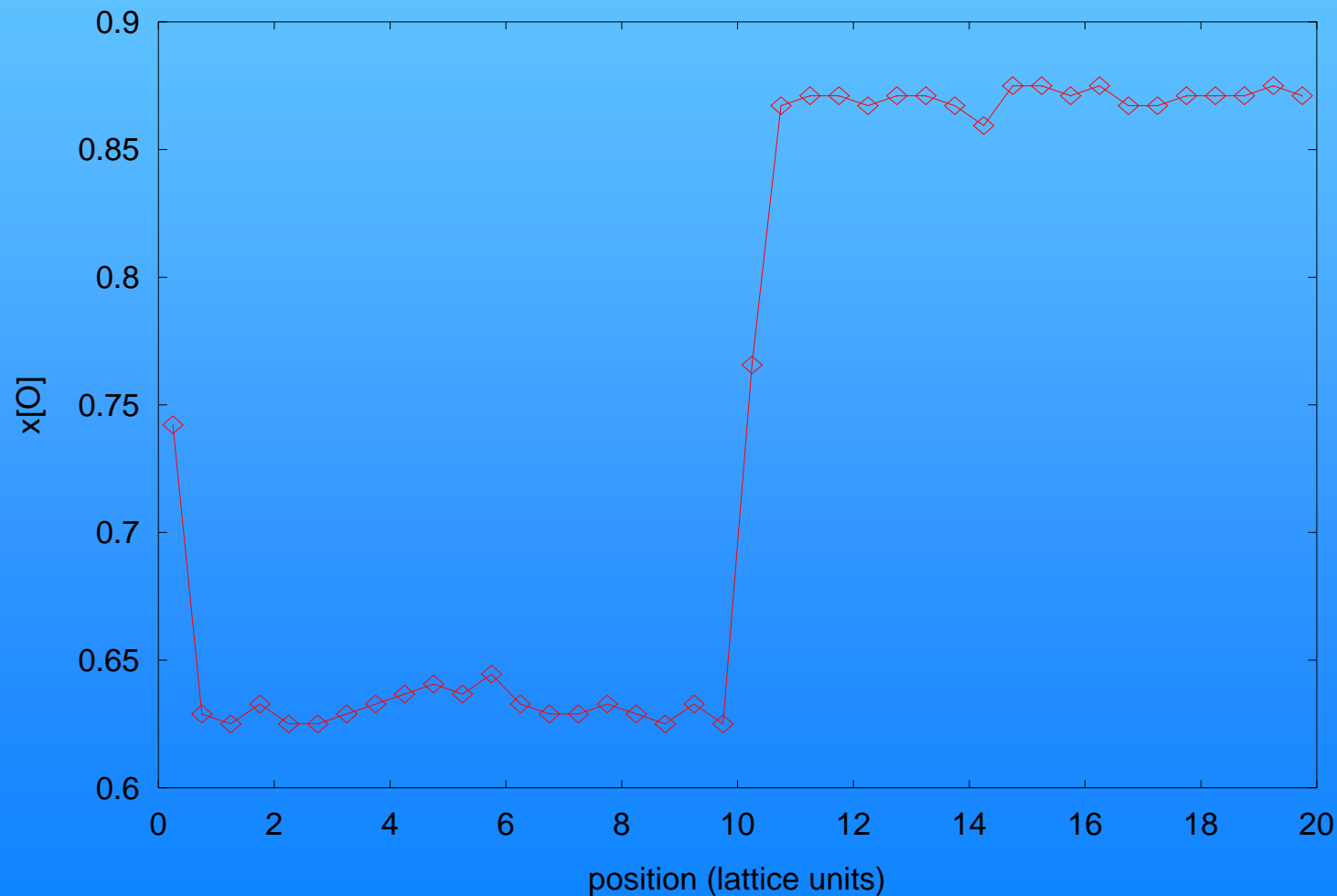
Quantum Mechanical Calculations



Hybrid Canonical/Grandcanonical Monte Carlo

- To stabilize interface, two options:
 - keep some species completely fixed (cations)
 - keep composition of at least one specie fixed (Here the cation composition).
- For oxygen, two alternatives:
 - Oxygen is free to exchange with environment. (constant O chemical potential)
 - System remains “charge-balanced”.

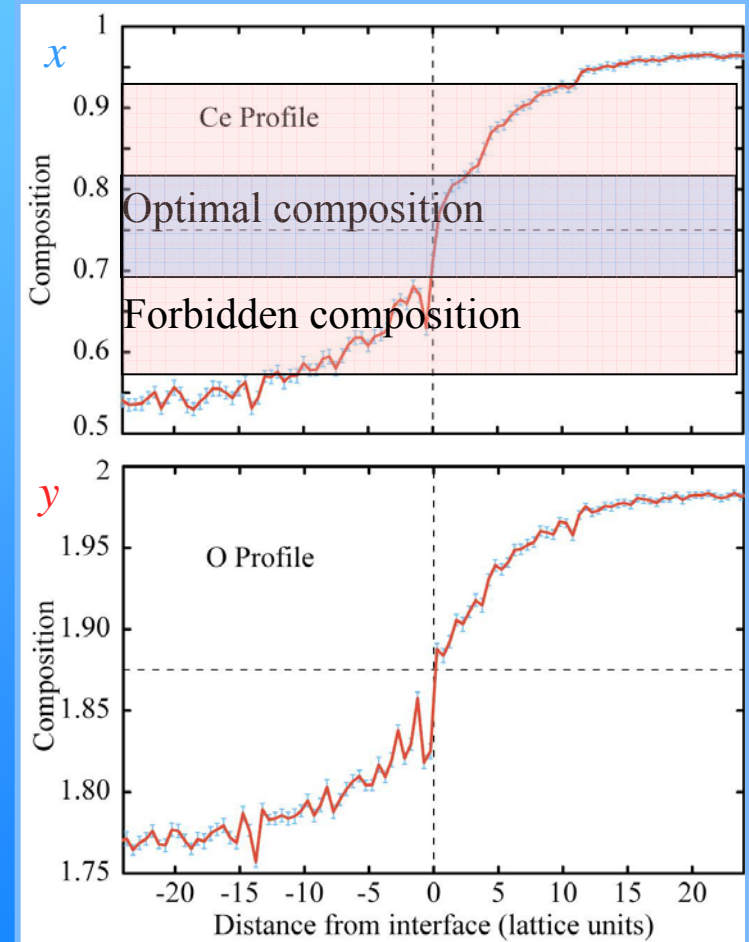
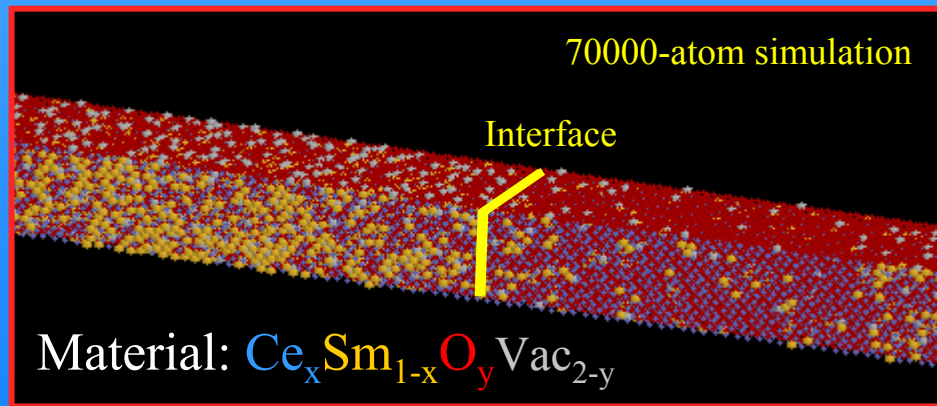
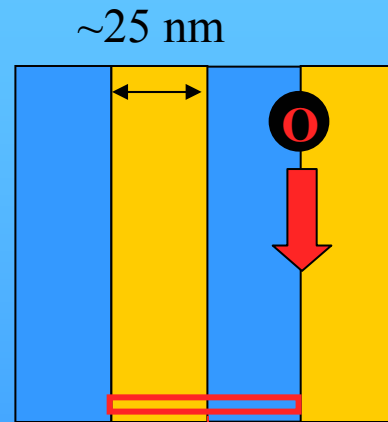
O composition profile across interface within the frozen cation approximation



Equilibrium Composition profile



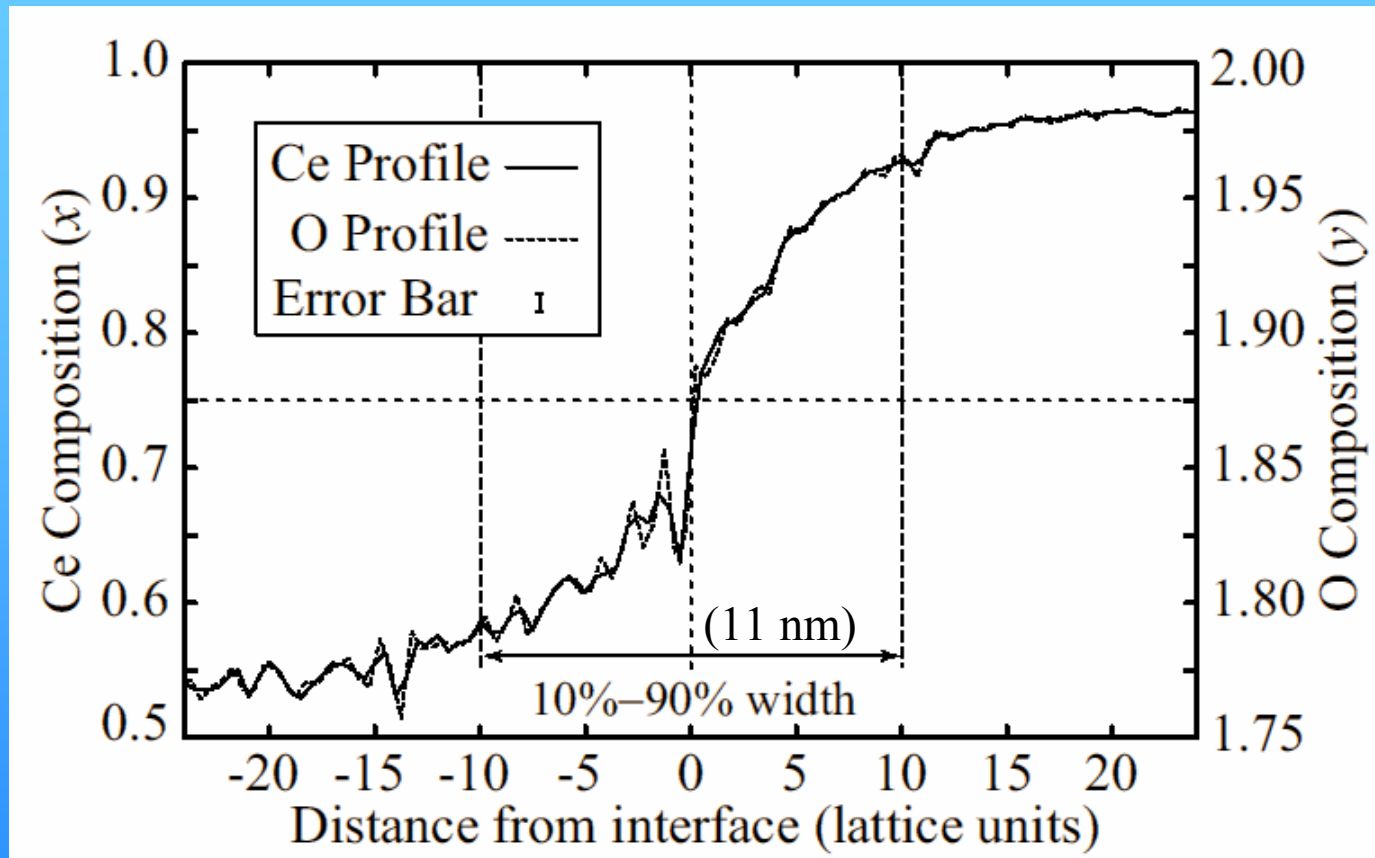
Superlattices



van de Walle & Ellis, Phys. Rev. Lett. **98**, 266101 (2007)

Space Charge effect?

No:

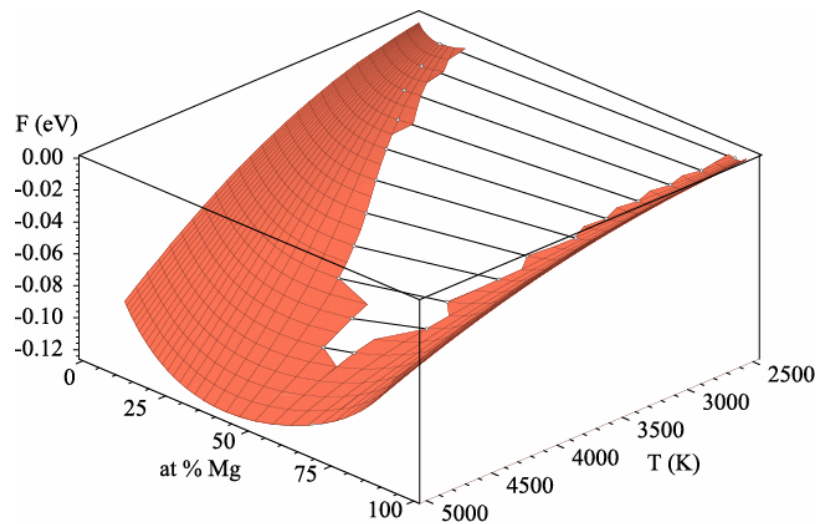


Origin of oscillations:

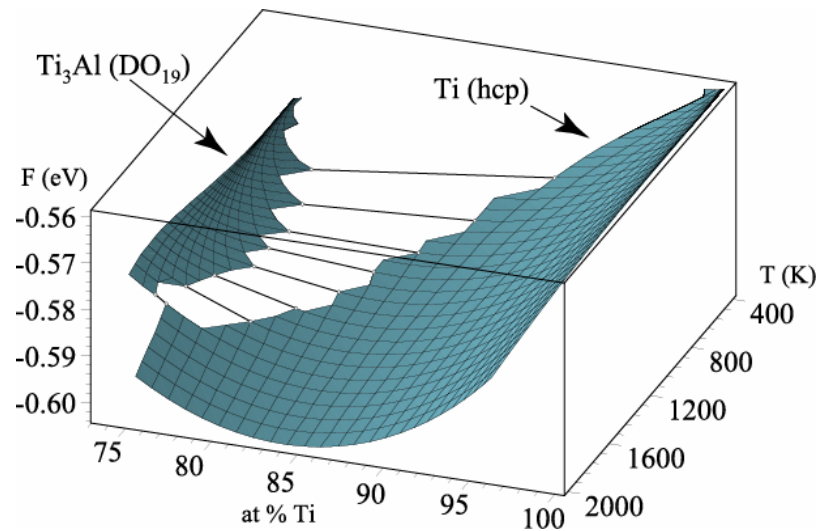
Crystalline analogue of density oscillation
found in other systems dominated by electrostatics,
e.g. liquid alkali metals or plasmas surfaces.

(Goodisman & Rosinberg, (1983), Iwamatsu & Lai (1992).)

Calculated free energies

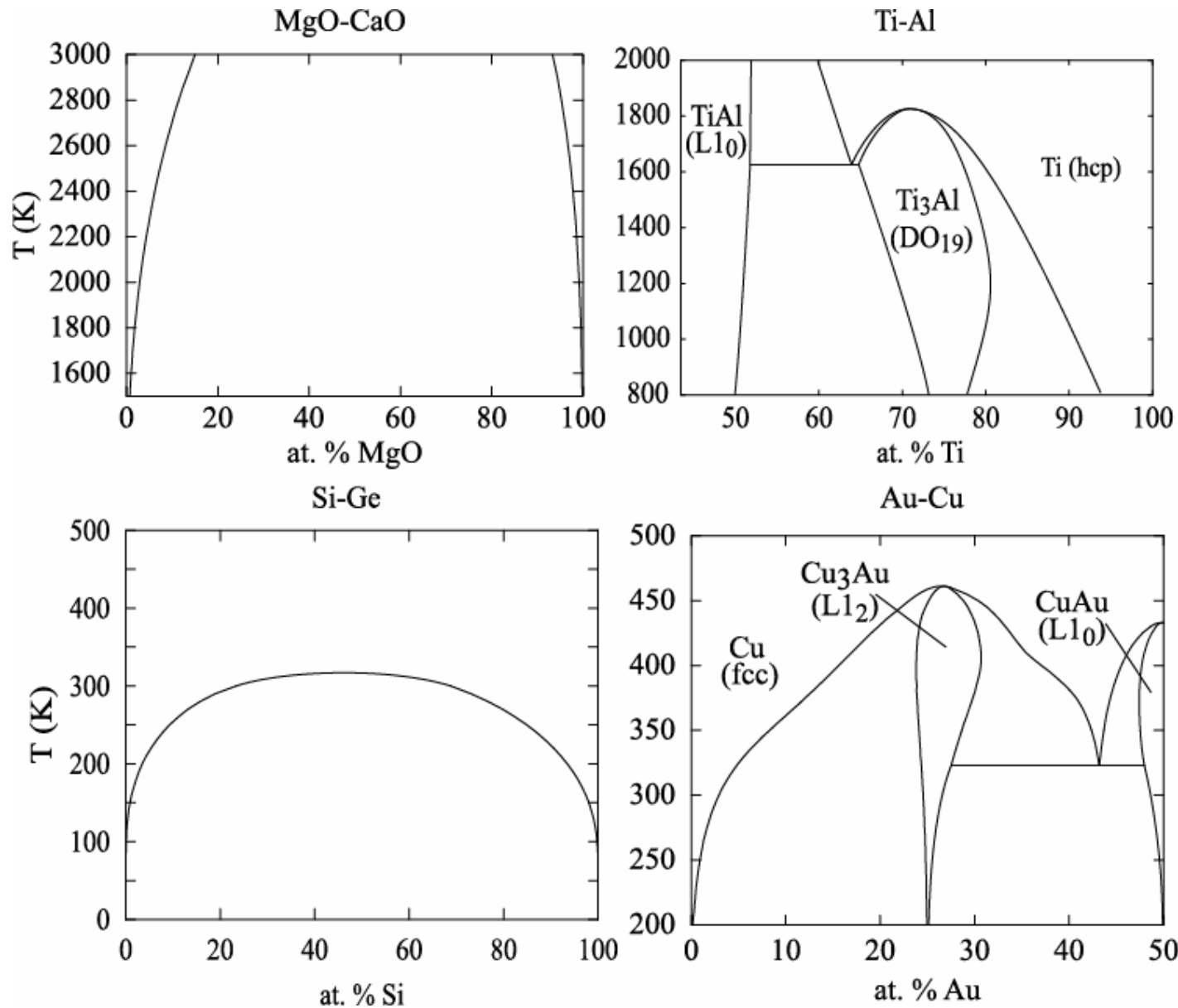


Cao-MgO system

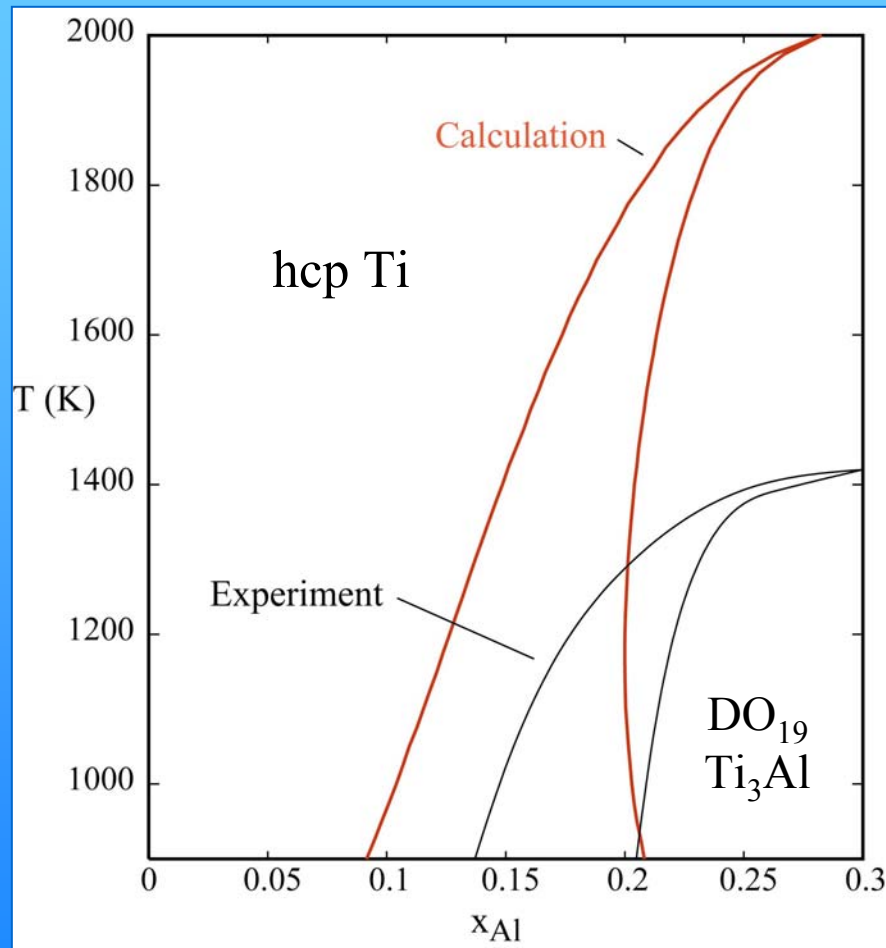


Ti-Al system

Calculated phase diagrams



Temperature scale problem



Van de Walle, Asta and Ceder (2002),
Murray (1987) (exp.)

Likely source of the discrepancy:
Vibrational entropy.

Fultz, Nagel, Antony, *et al.* (1993-1999)
Ceder, Garbulsky, van de Walle (1994-2002)
de Fontaine, Althoff, Morgan (1997-2000)
Zunger, Ozolins, Wolverton (1998-2001)

Many other examples...

Thermodynamic data

Lattice model &
Monte Carlo Simulations

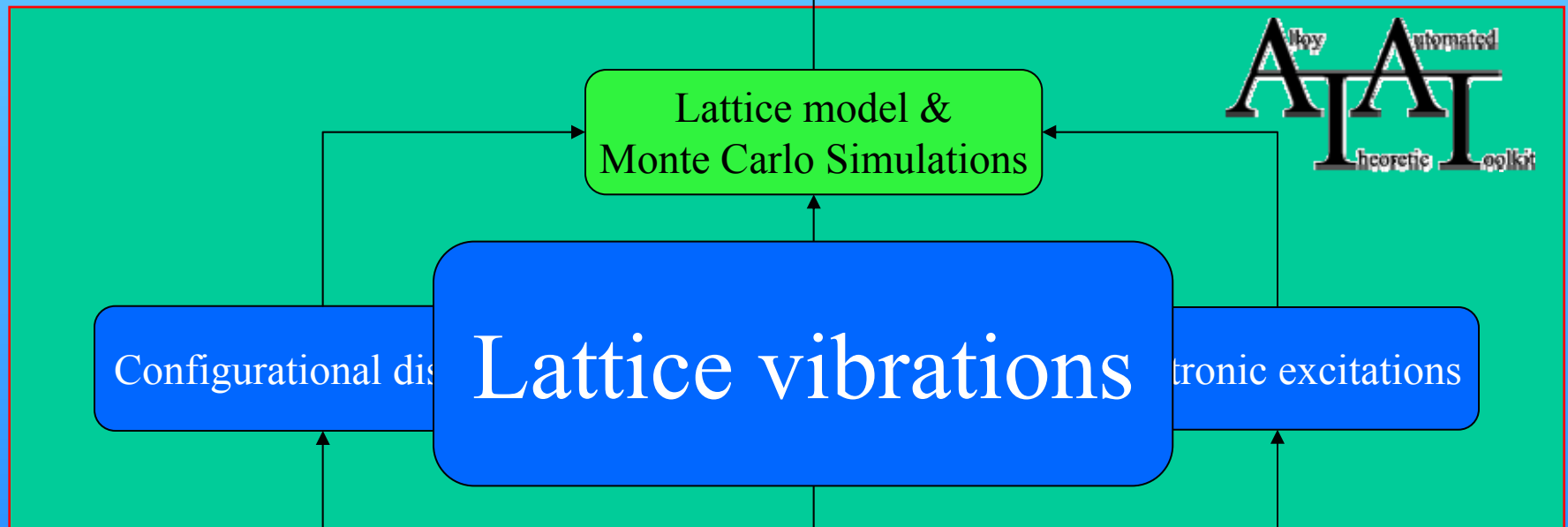
Alloy Automated
Theoretic Toolkit

Configurational dis

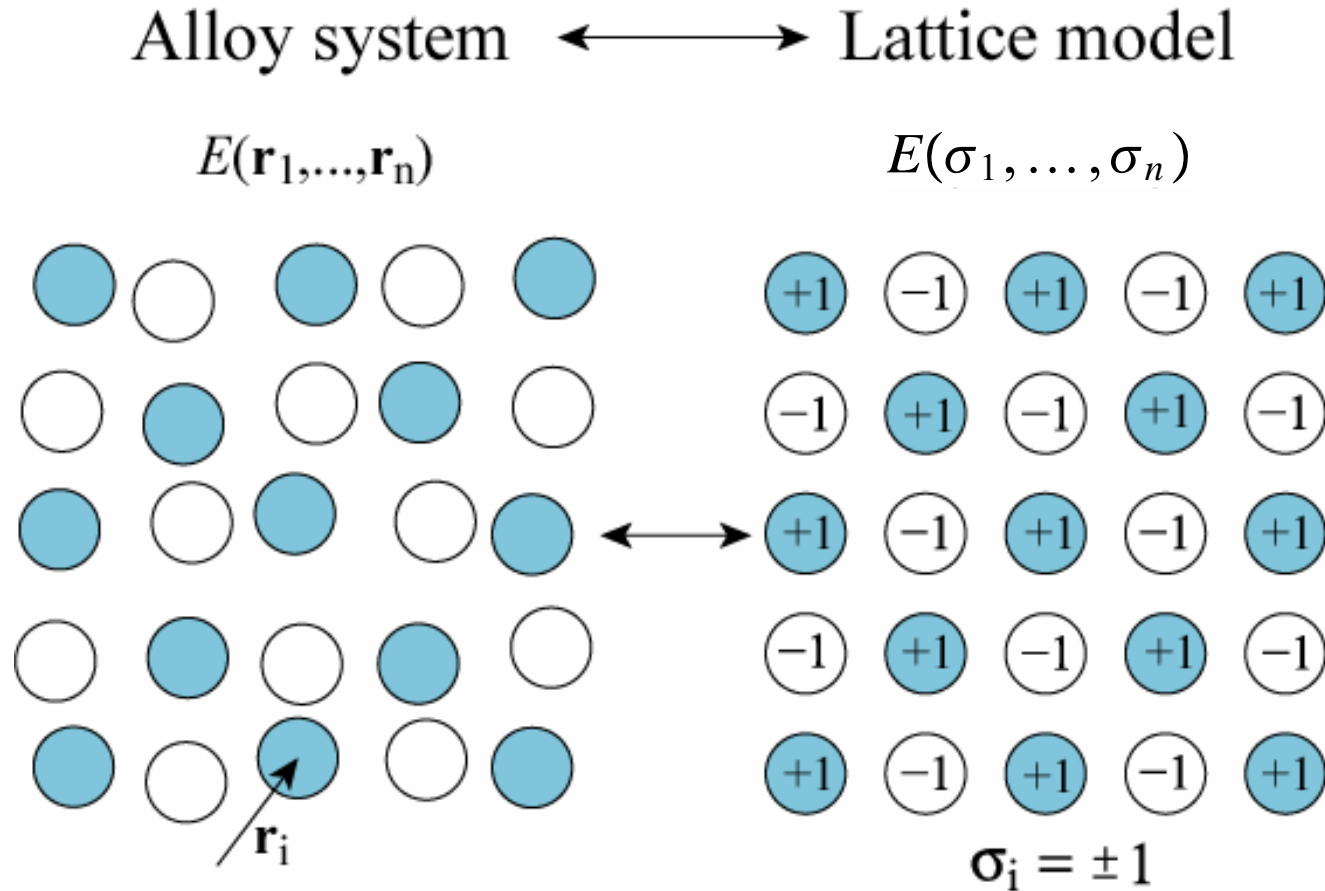
Lattice vibrations

Electronic excitations

Quantum Mechanical Calculations



The Cluster Expansion Formalism

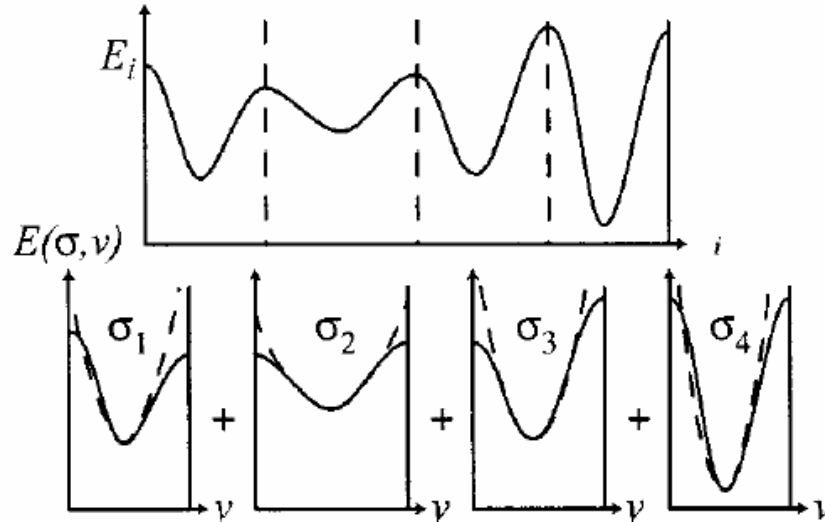


$$F(\sigma_1, \dots, \sigma_n) = \sum_{\alpha} J_{\alpha} \boxed{(T)} \sigma_{\alpha}$$

$\prod_{i \in \alpha} \sigma_i$

Coarse-Graining of the Free Energy

Graphically:



Formally: (Ceder (1993), Garbulski and Ceder (1994-1996))

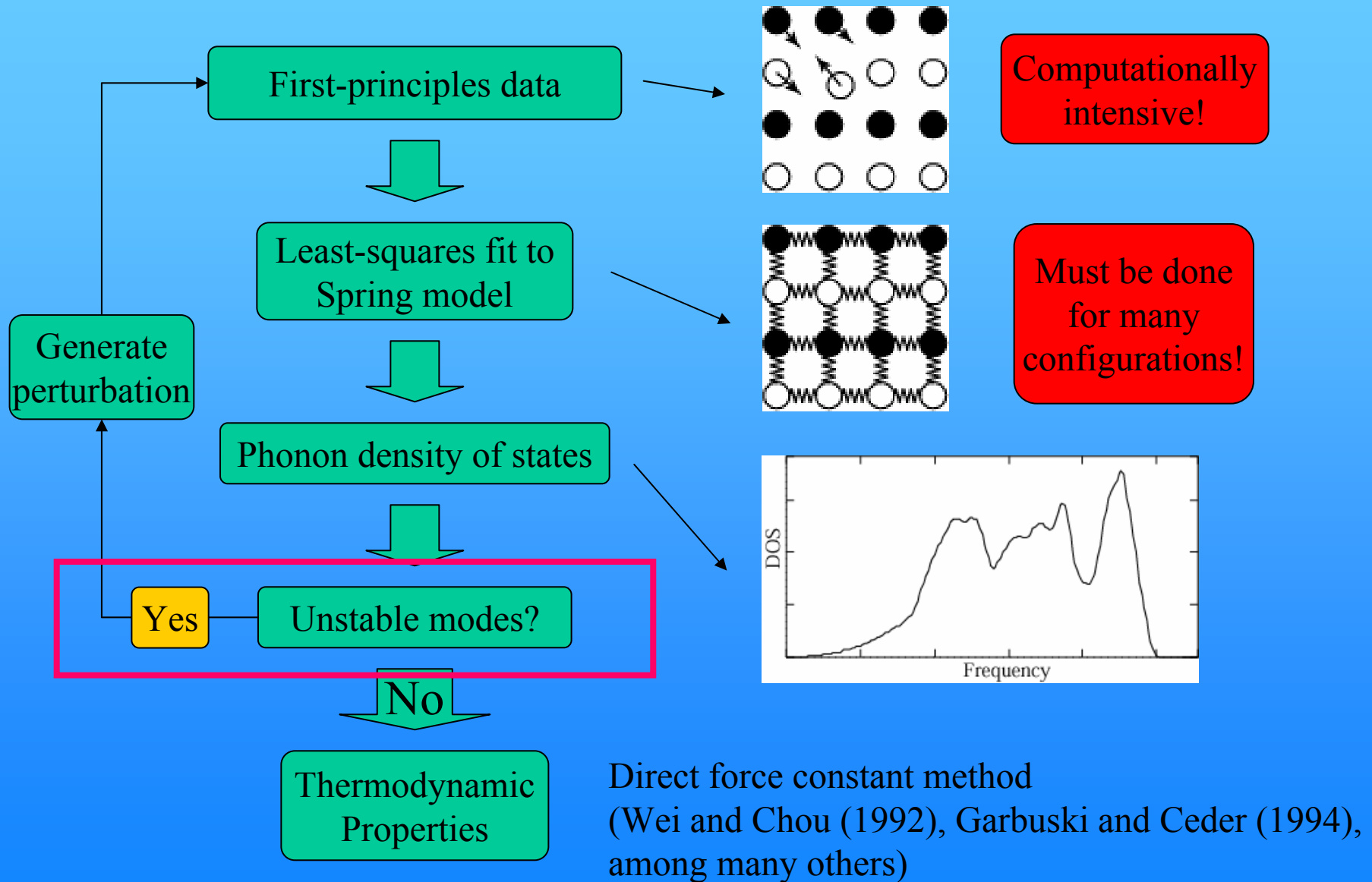
$$\begin{aligned}
 F &= -\beta^{-1} \ln \left(\sum_i e^{-\beta E_i} \right) = -\beta^{-1} \ln \left(\sum_{\sigma} \sum_{i \in \sigma} e^{-\beta E_i} \right) \\
 &= -\beta^{-1} \ln \left(\sum_{\sigma} e^{-\beta F(\sigma)} \right)
 \end{aligned}$$

where

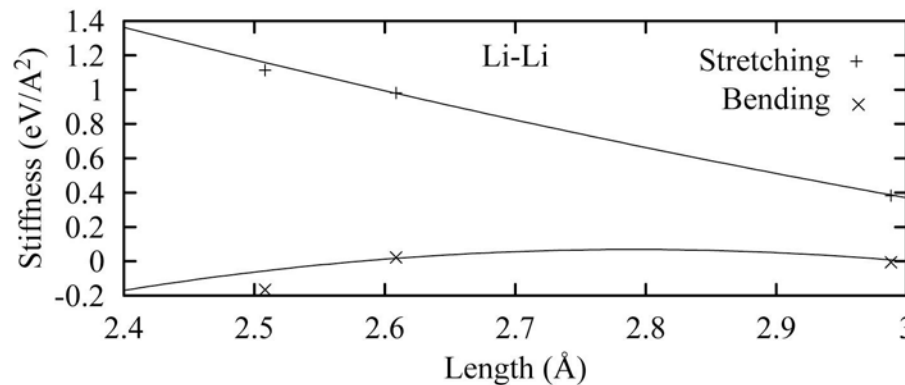
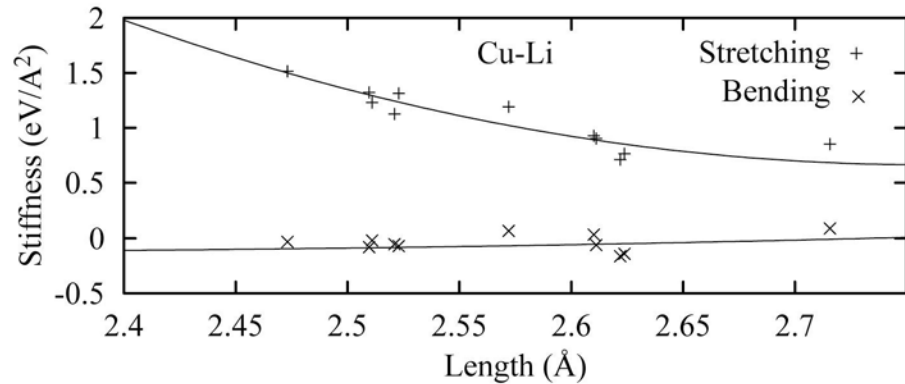
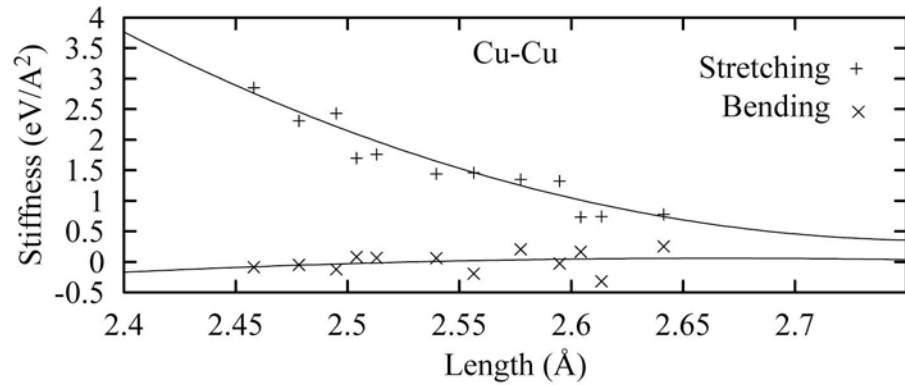
$$F(\sigma) = -\beta^{-1} \ln \left(\sum_{i \in \sigma} e^{-\beta E_i} \right)$$

$$\beta = (k_B T)^{-1}$$

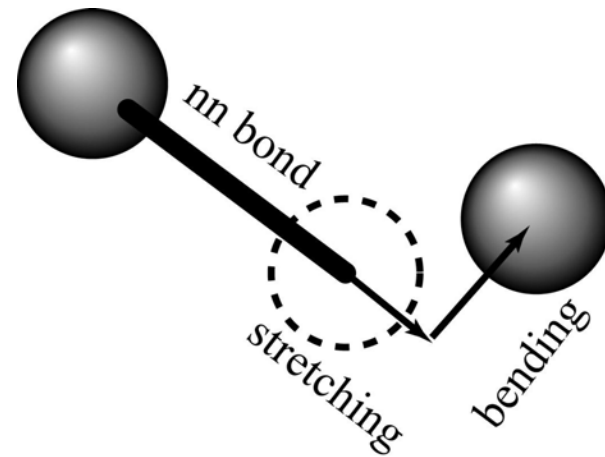
First-principles lattice dynamics



Length-Dependent Transferable Force Constants (LDTFC)



Chemical bond type and bond length:
Good predictor of nearest-neighbor force constants (stretching and bending terms)

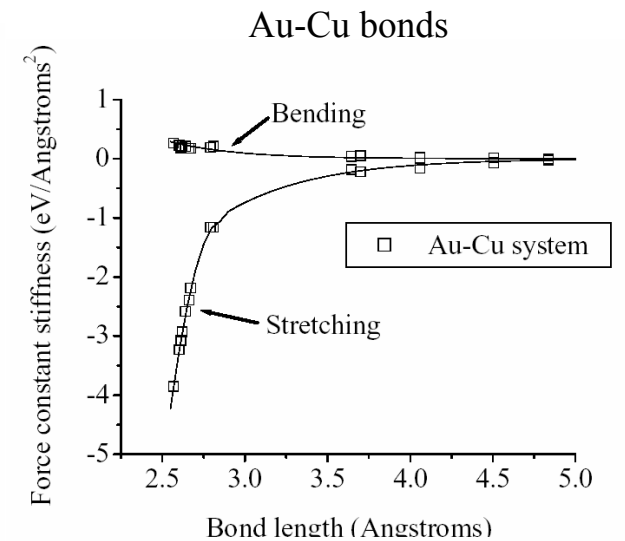
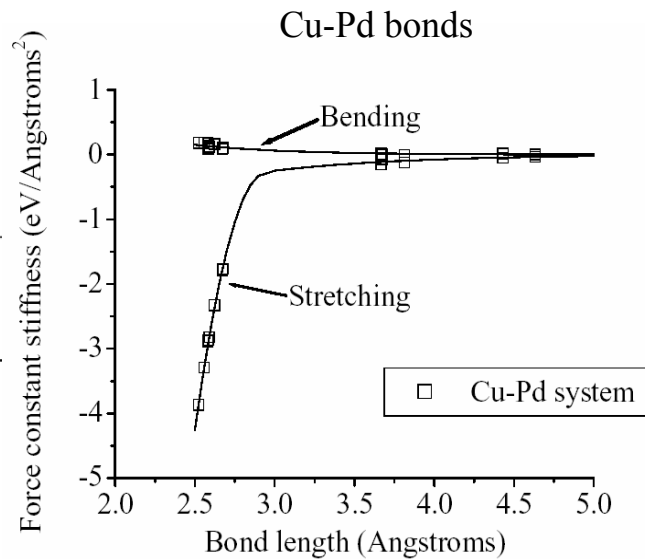
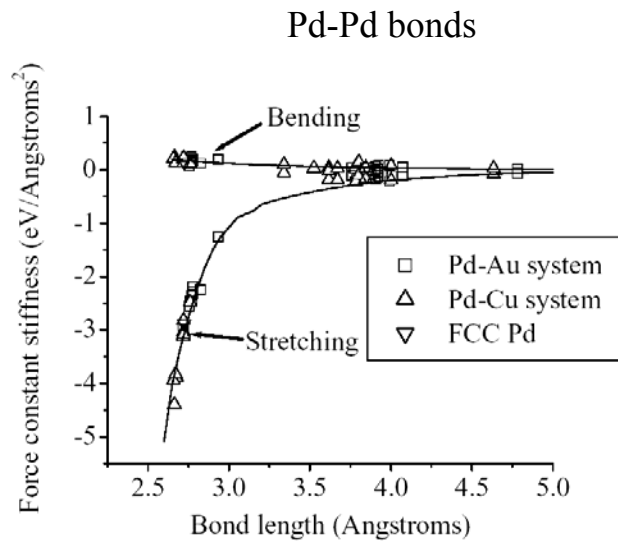
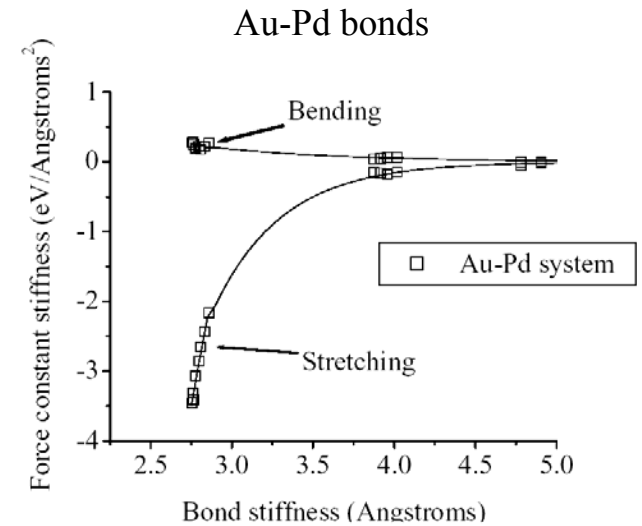
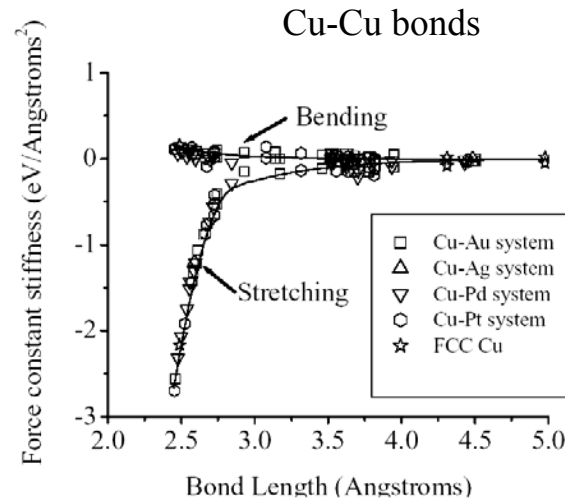
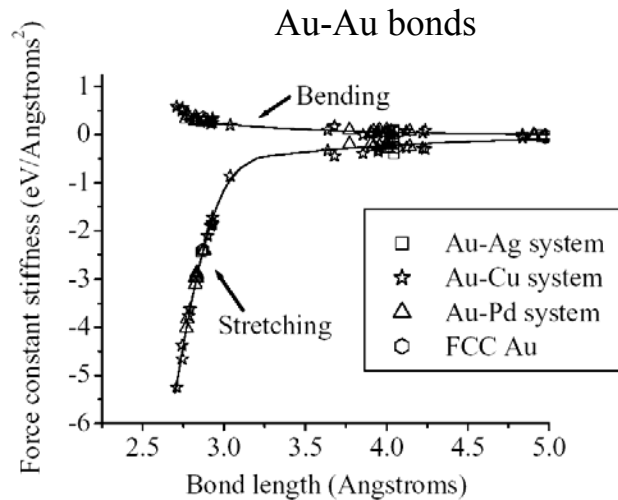


Relationship holds across different structures on the same lattice (here fcc is shown).

van de Walle and Ceder (2000,2002)

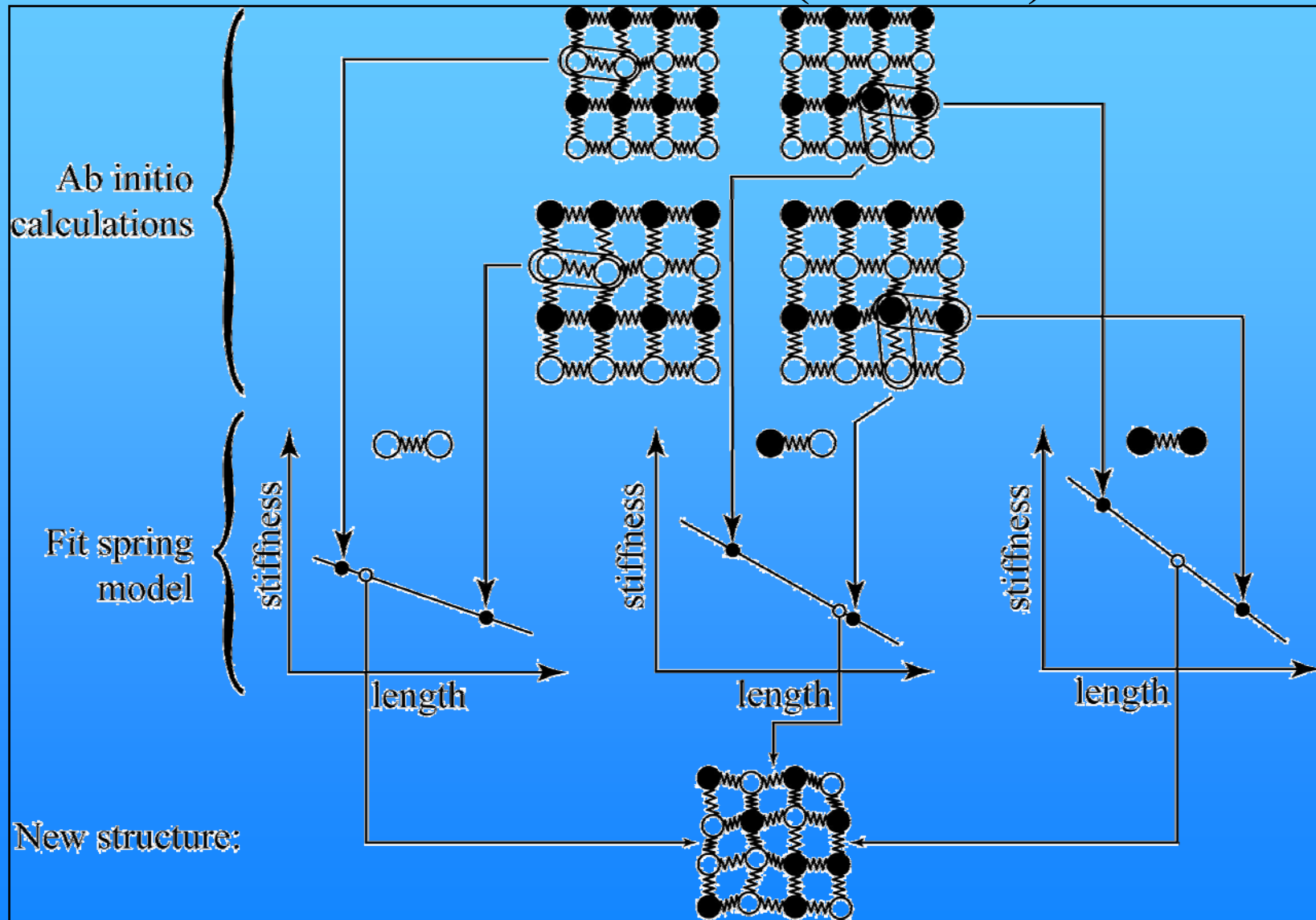
Further tests...

Wu, Ceder, van de Walle (2002)

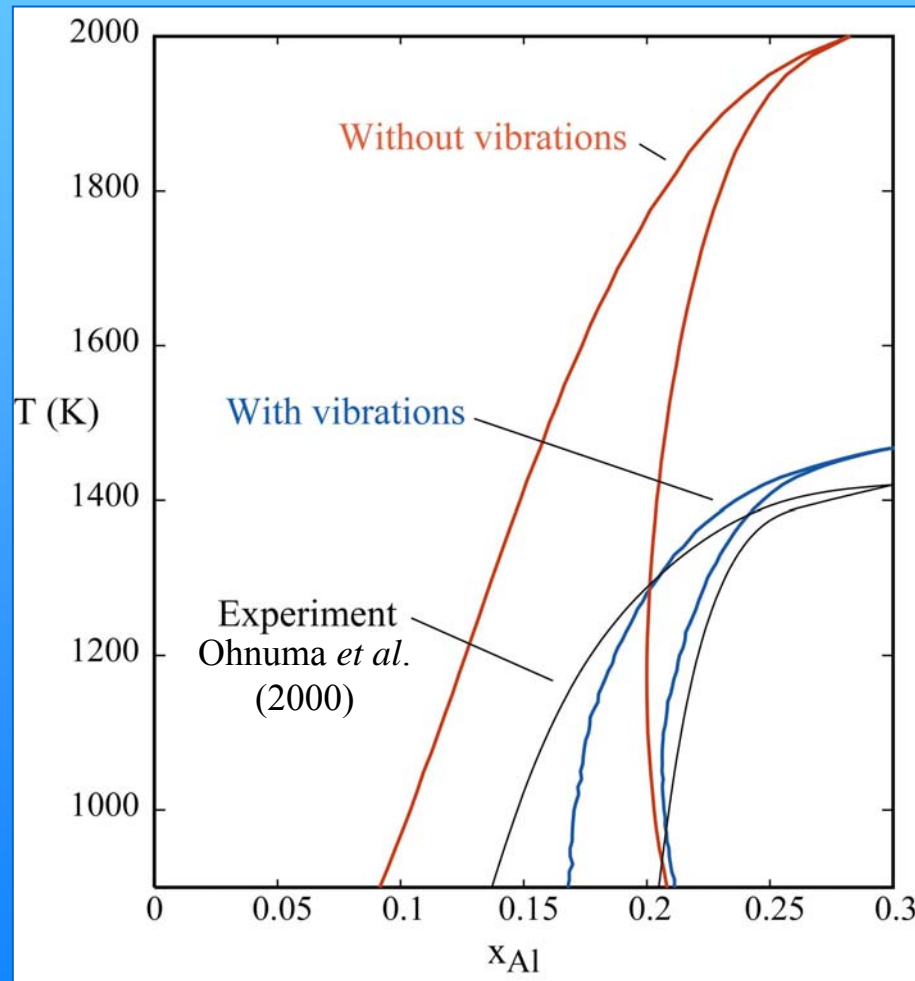


Accuracy $\sim 0.03 k_B$

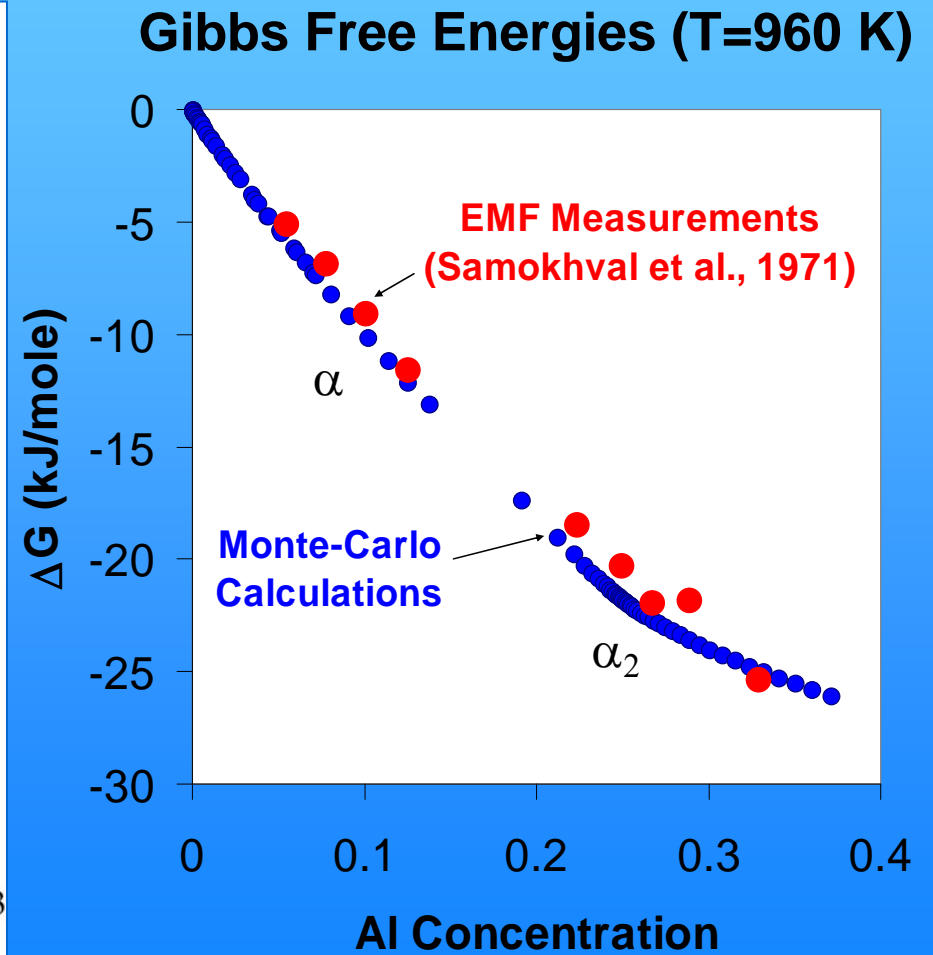
Length-Dependent Transferable Force Constants (LDTFC)



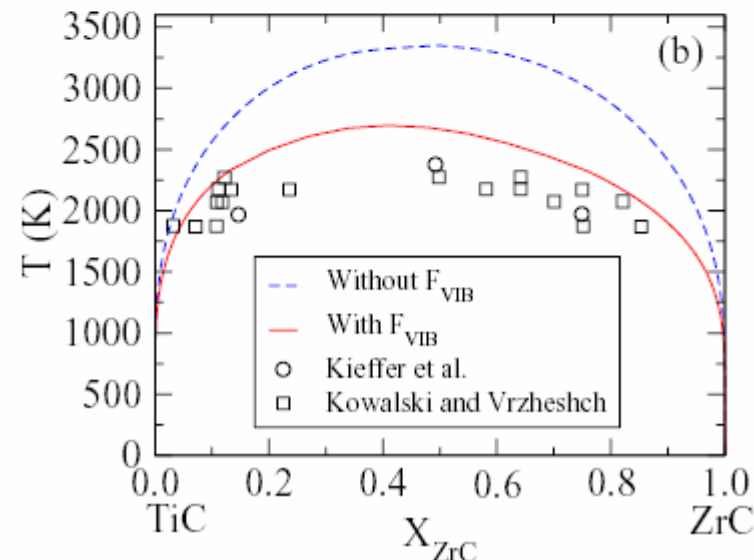
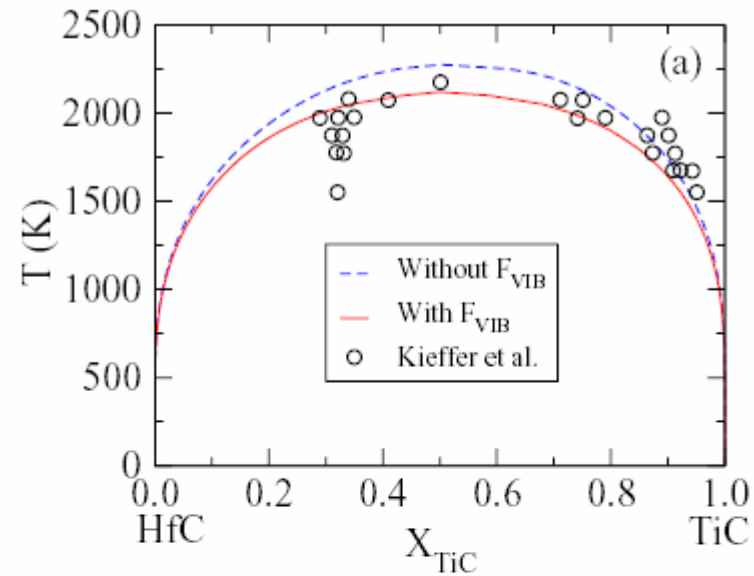
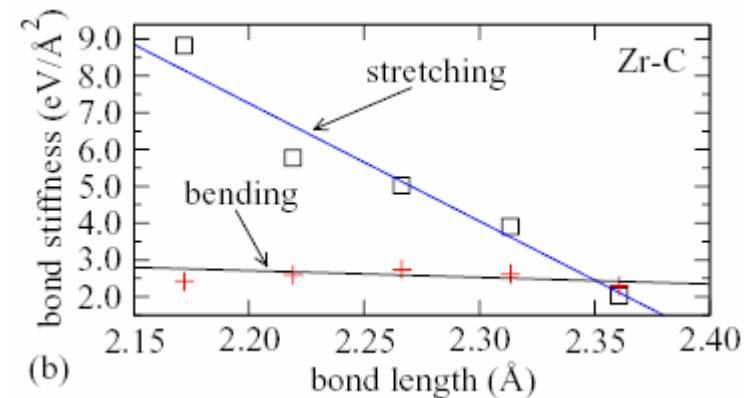
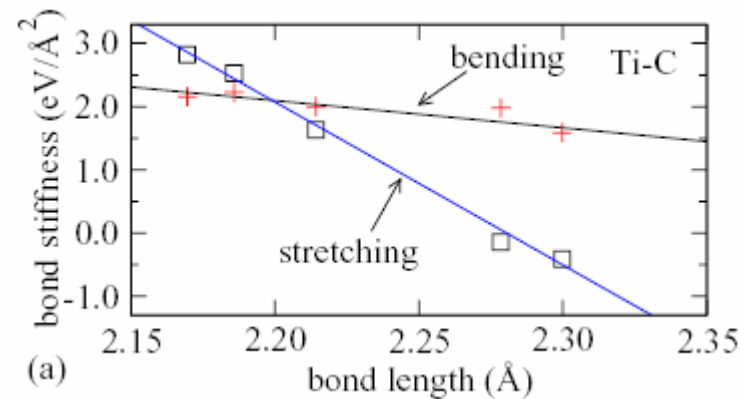
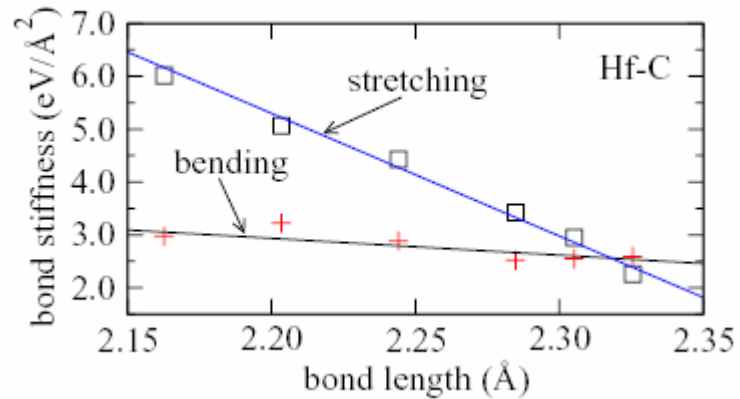
Calculated Ti-Al Phase Diagram & Thermodynamic Properties



van de Walle, Ghosh, Asta (2007)

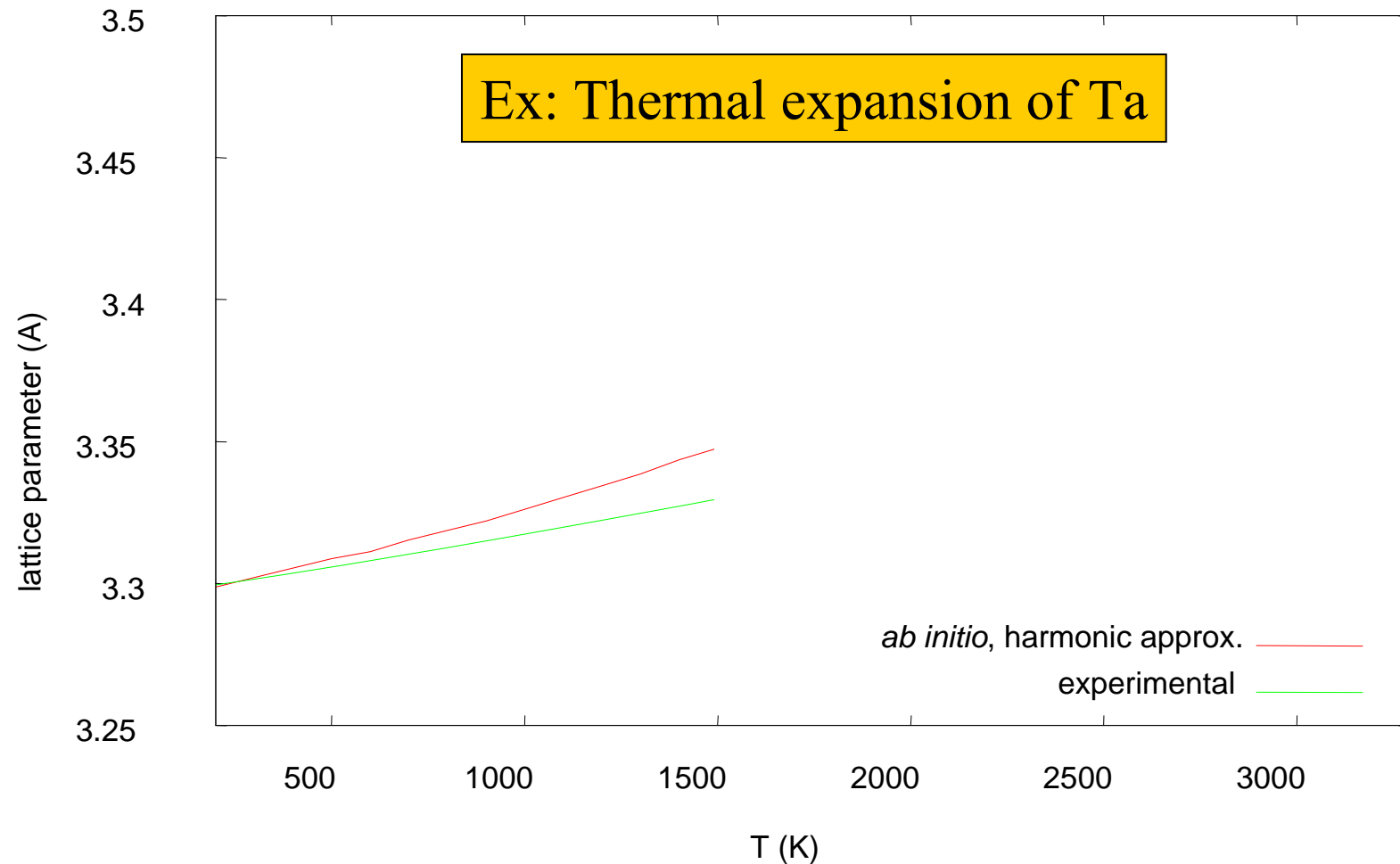


HfC-TiC and TiC-ZrC Phase diagrams

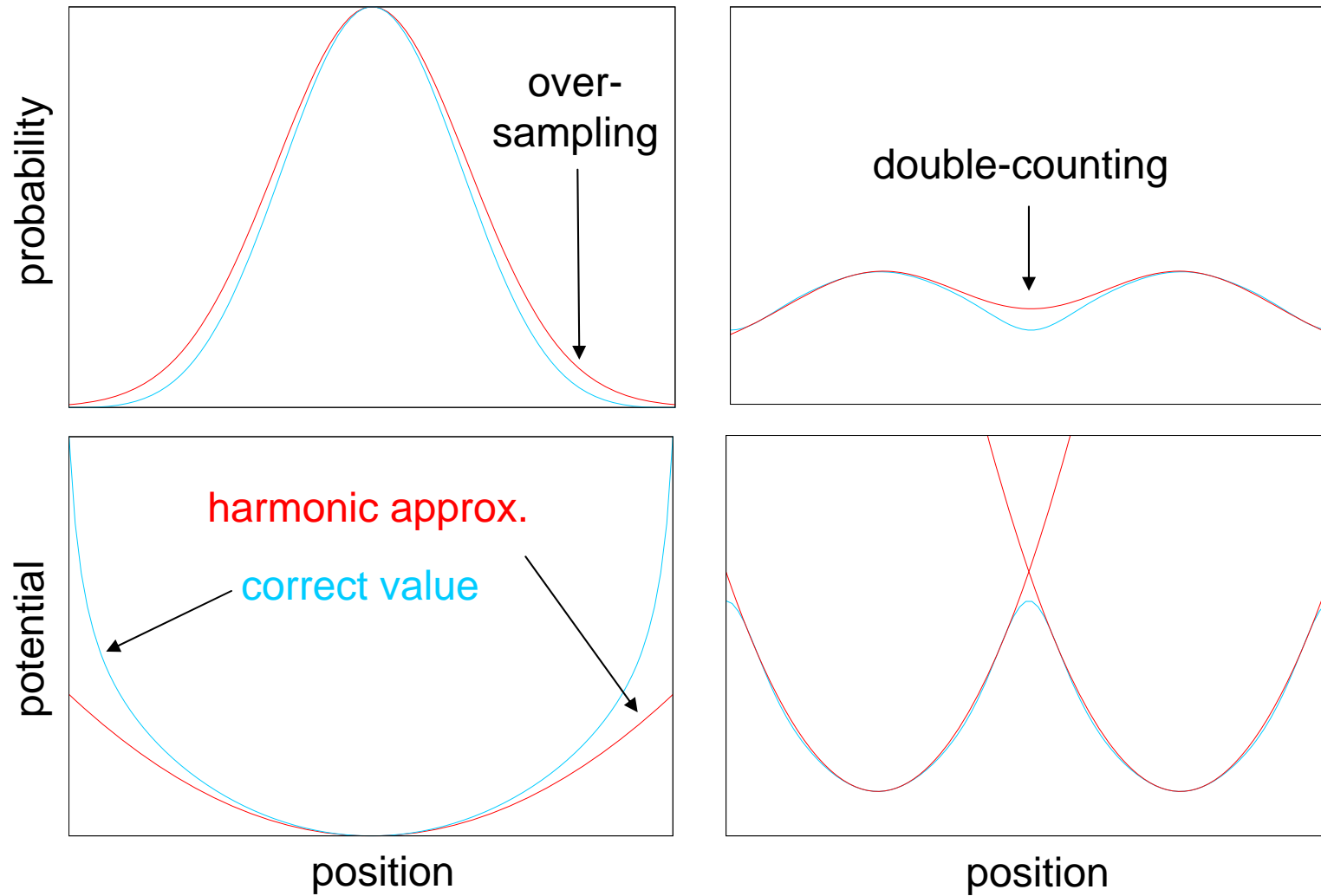


Adjaoud, Steinle-Neumann, Burton and A. van de Walle (2009)

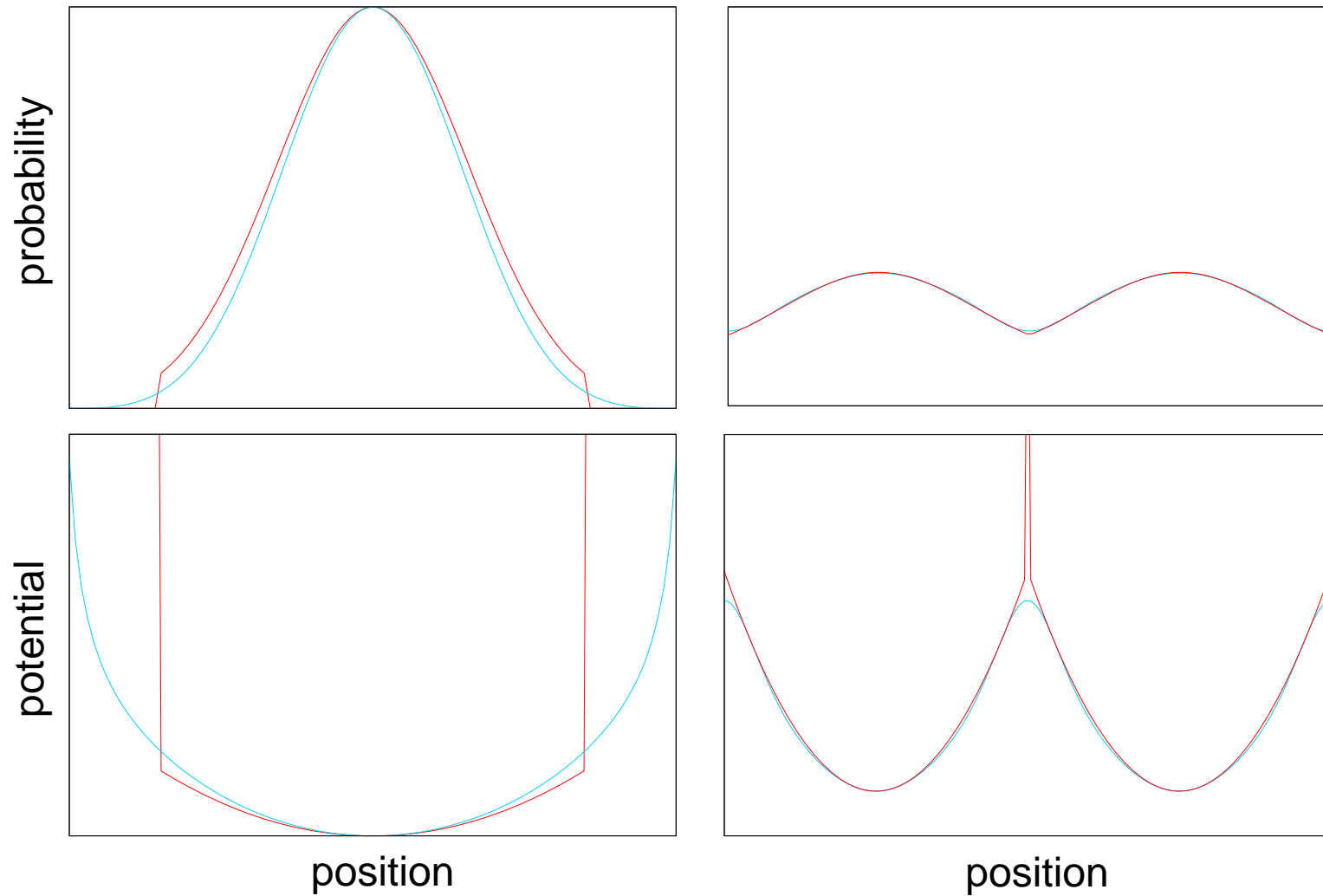
Weaknesses of the quasiharmonic approx.



Weaknesses of the harmonic approx.

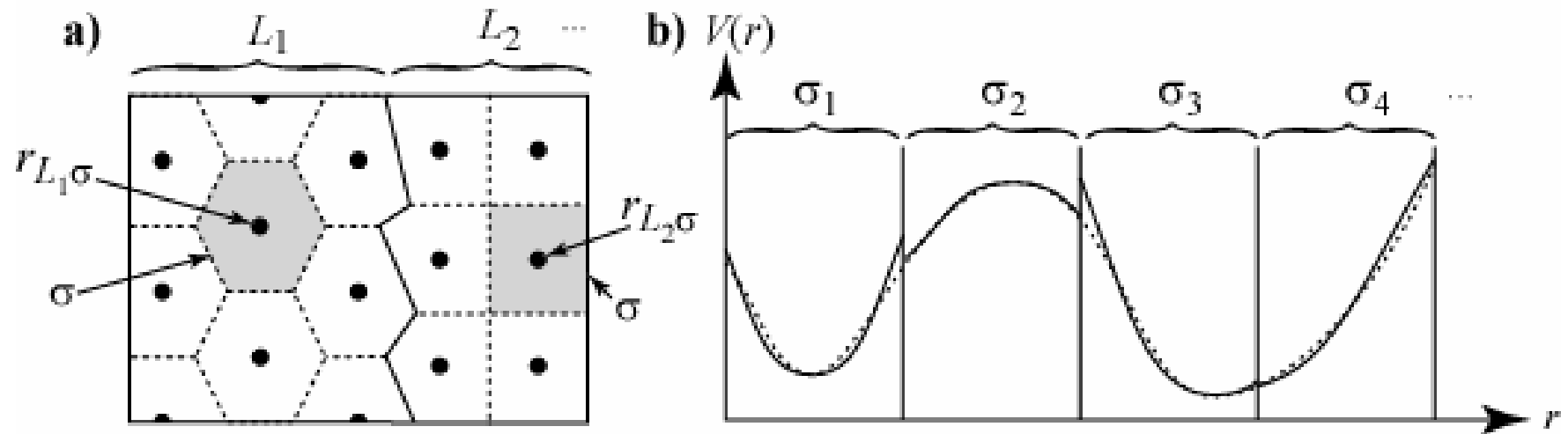


Boxed-harmonic approximation



A. van de Walle & G. Ceder, *Rev. Mod. Phys.* **74** 11 (2002)

Fully ab initio treatment using Voronoi Tessellation



Derivation of the Boxed-QH approx.

Classical partition function for 1 mode (out of 3N):

$$\frac{1}{h} \int_{-\infty}^{\infty} \exp\left(-\frac{p^2}{2kT}\right) dp \int_{-L}^L \exp\left(-\frac{(2\pi\nu)^2 q^2}{2kT}\right) dq = \frac{kT}{h|\nu|} \left| \text{erf}\left(\frac{2\pi\nu L}{\sqrt{2kT}}\right) \right|$$

Classical result

where

k : Boltzman's constant h : Planck's constant

T : Temperature ν : phonon frequency (real or imaginary)

L : cutoff q, p : "position" and "momentum"

"Boxed" correction

Requiring entropy of solid to be less than entropy of an idea gas gives upper bound and an order of magnitude for L :

$$L \leq \frac{1}{2} (\Omega e)^{1/3} \sqrt{m}$$

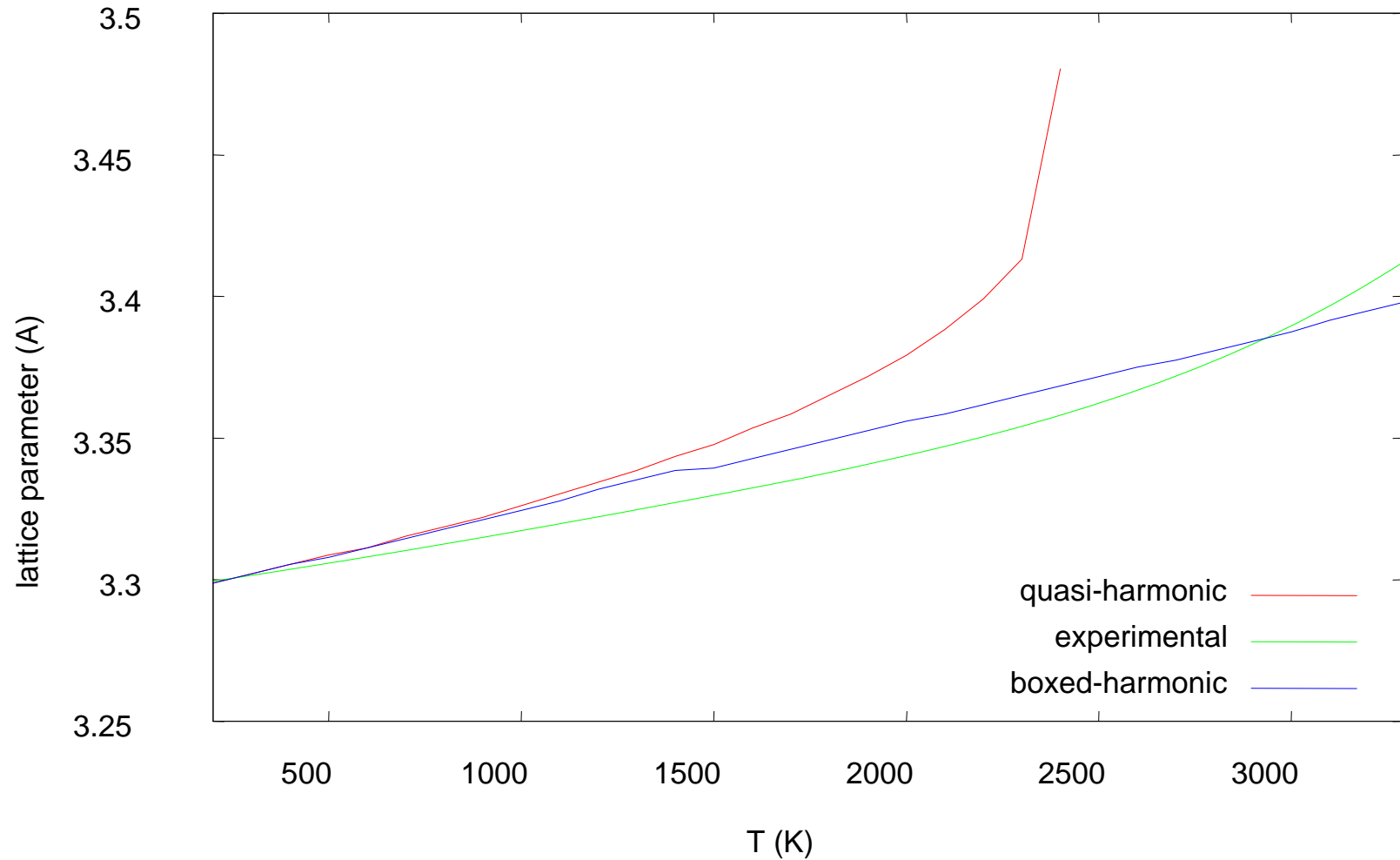
where Ω : atomic volume m : atomic mass $e = \exp(1)$

Treat L as an adjustable parameter (can be fitted to ab initio MD).

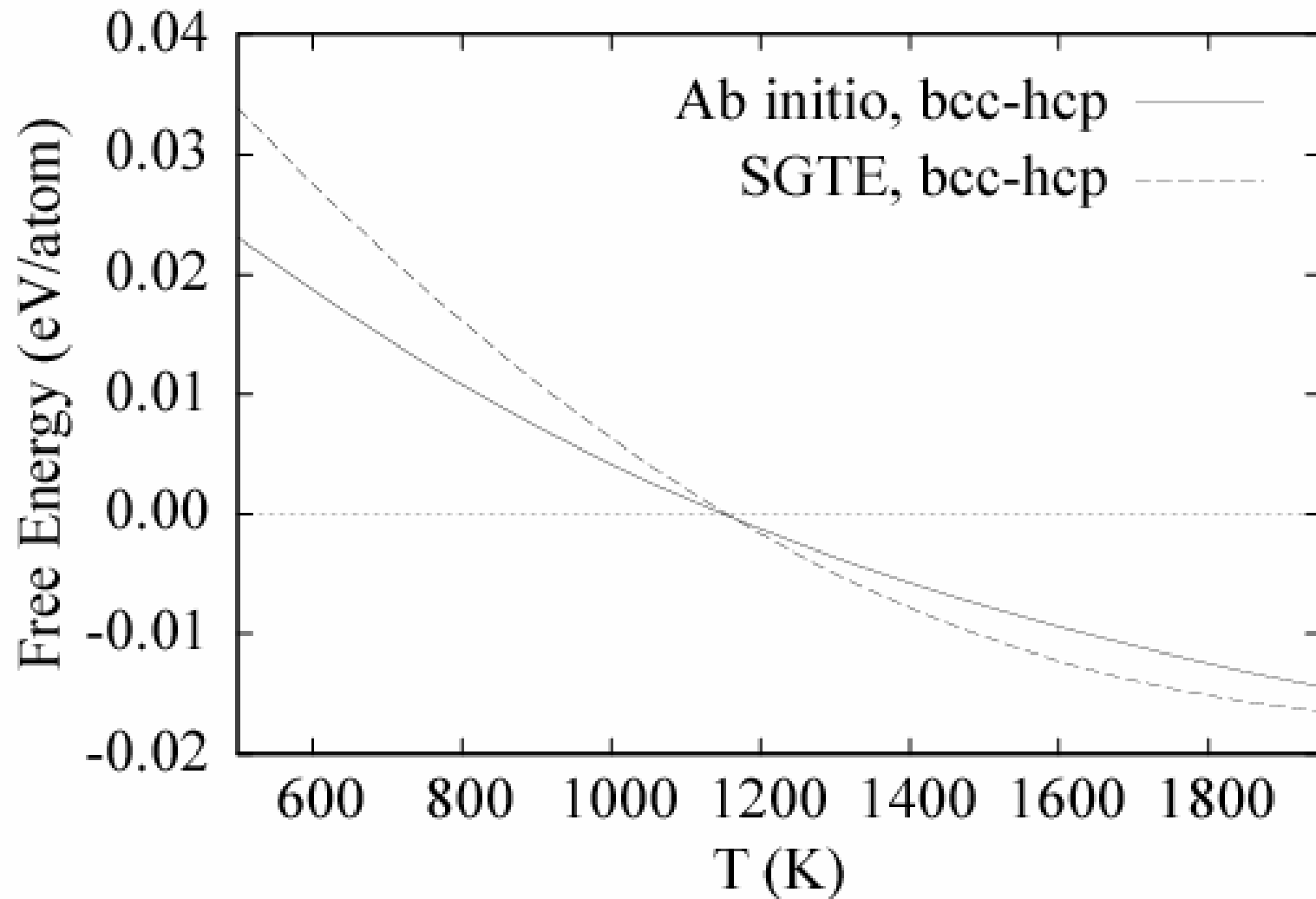
Fully quantum-mechanical expression of free energy:

$$F = \frac{E}{N} + \frac{kT}{N} \sum_m \left(\ln\left(2 \sinh\left(\frac{h|\nu_m|}{2kT}\right)\right) - \ln\left|\text{erf}\left(\frac{2\pi\nu_m L}{\sqrt{2kT}}\right)\right| \right)$$

Thermal expansion of Ta



Free energy difference between bcc and hcp Ti



Thermodynamic data

Lattice model &
Monte Carlo Simulations

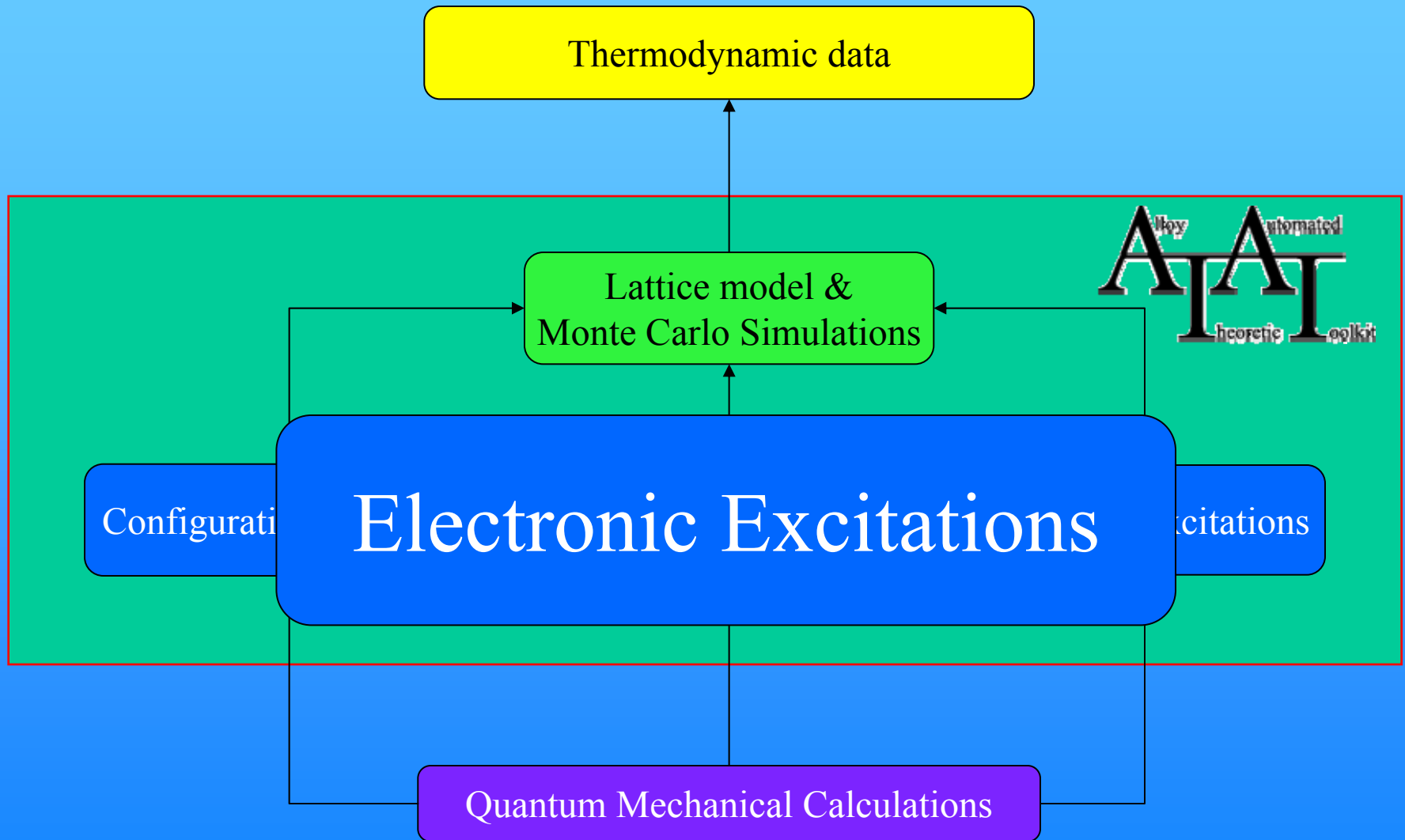
Automated
Theoretic Toolkit

Configurati

Electronic Excitations

citations

Quantum Mechanical Calculations



Electronic Excitations

Finite-temperature DFT

T-independent DOS and charge density

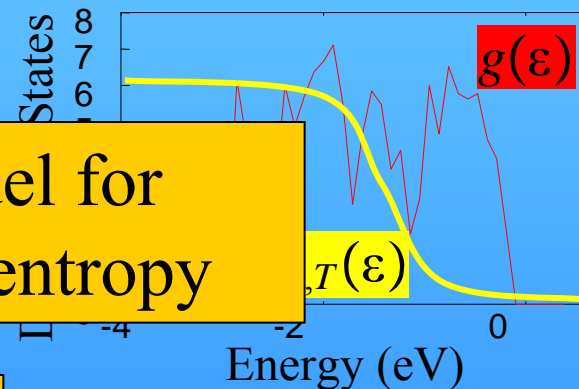
Advantage: Get F_{elec} “for free”

Electronic DOS

Fermi-Dirac Distr

Electronic Free e

Any model for
electronic entropy



$$F_{\text{elec}}(T) = E_{\text{elec}}(T) - E_{\text{elec}}(0) - TS_{\text{elec}}(T)$$

$$E_{\text{elec}}(T) = \int f_{\mu,T}(\epsilon) \epsilon g(\epsilon) d\epsilon$$

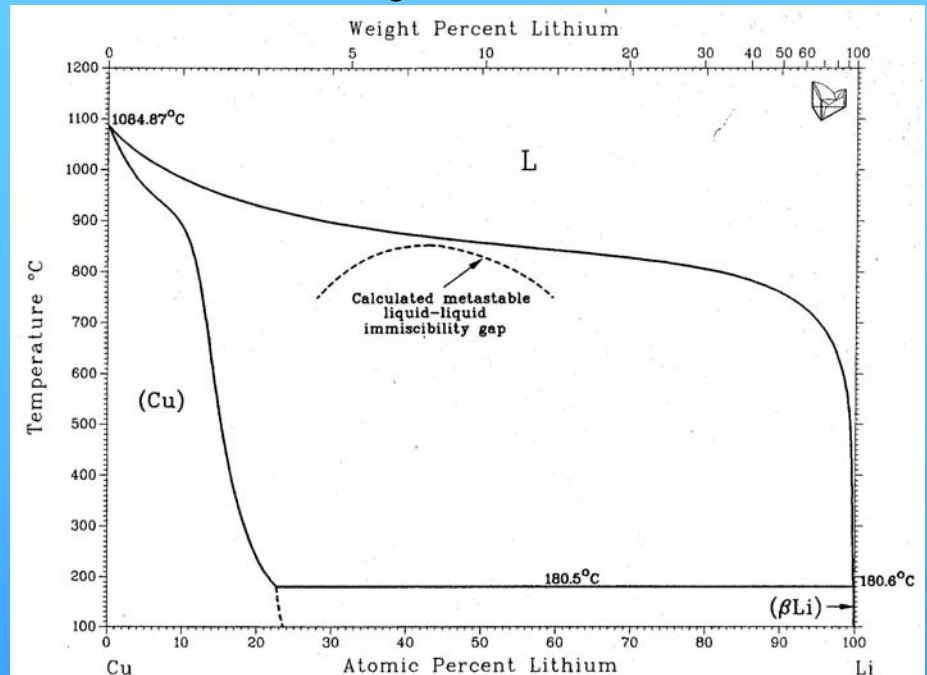
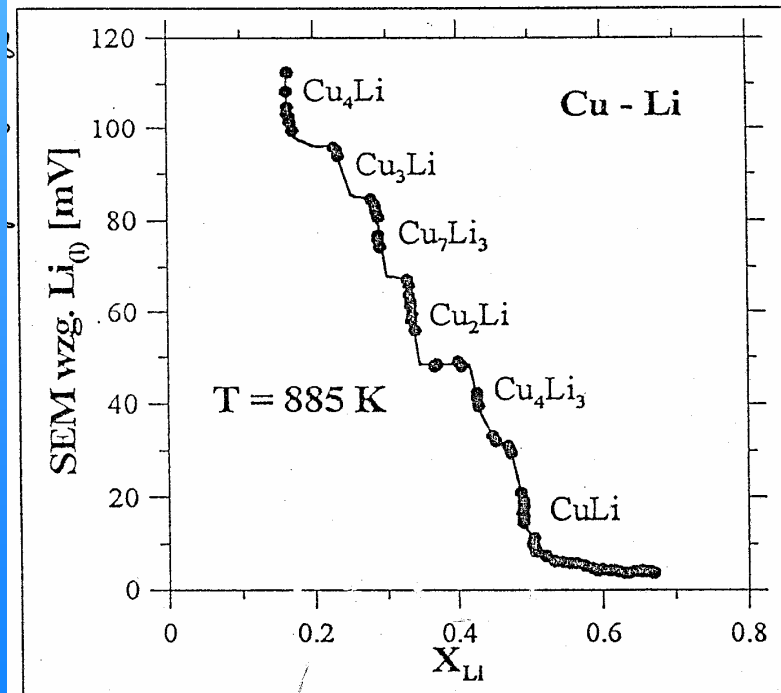
$$S_{\text{elec}}(T) = -k_B \int (f_{\mu,T}(\epsilon) \ln f_{\mu,T}(\epsilon) + (1 - f_{\mu,T}(\epsilon)) \ln(1 - f_{\mu,T}(\epsilon))) g(\epsilon) d\epsilon$$

Cluster expansion:

$$F(\sigma_1, \dots, \sigma_n) = \sum_{\alpha} J_{\alpha}(T) \sigma_{\alpha}$$

Ordering in the Cu-Li system?

Widely used assessments
do not include ordered phases
(Pelton (1986), Saunders (1998)).

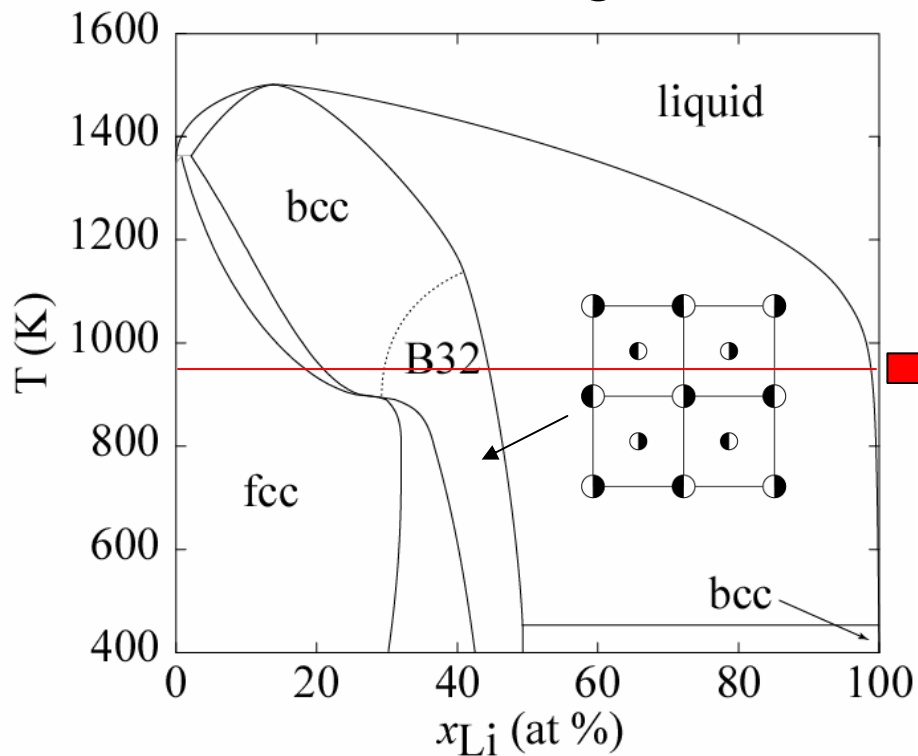


Evidence from EMF measurements

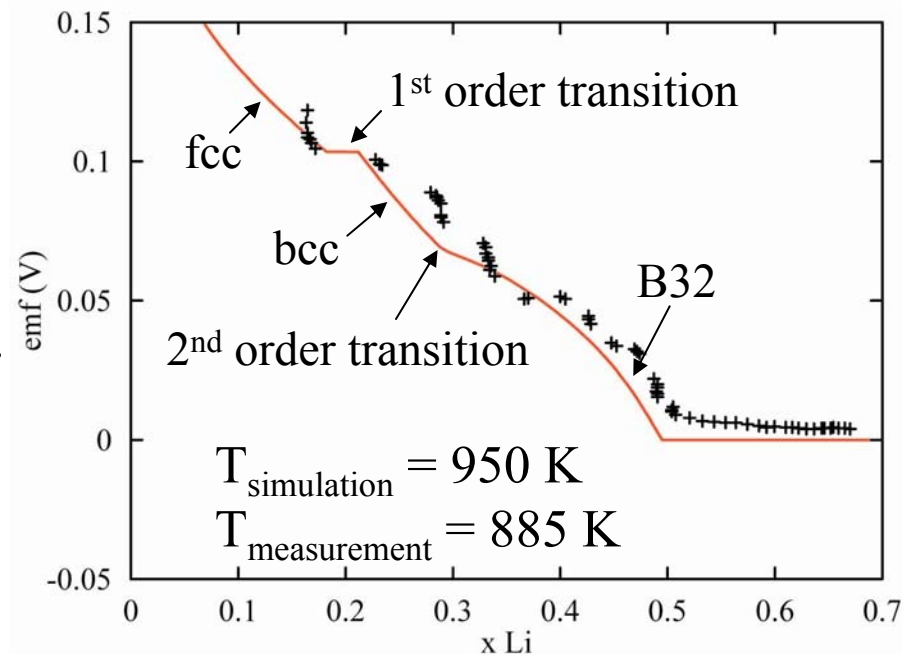
Ordered Cu_4Li phase also suggested by
Borgsttedt & Gumiński (1996),
Krauss, Mendelson, Gruen, *et al.* (1986),
Old & Trawena (1981).

Calculated Thermodynamic data for Cu-Li system

Phase diagram



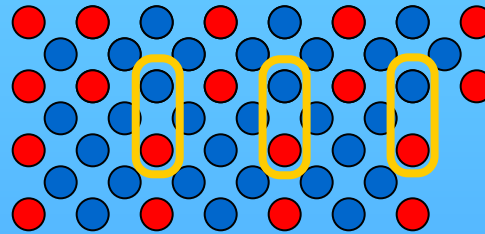
Electromotive Force (EMF)



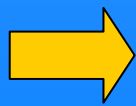
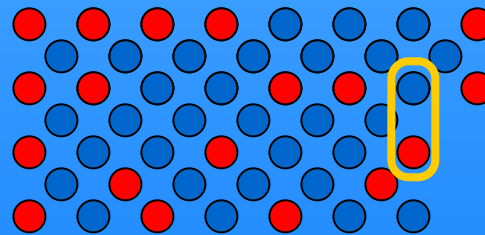
2 adjustable parameters:

$T_{\text{simulation}}$ + chemical potential of Li (liq)

Antiphase Boundary

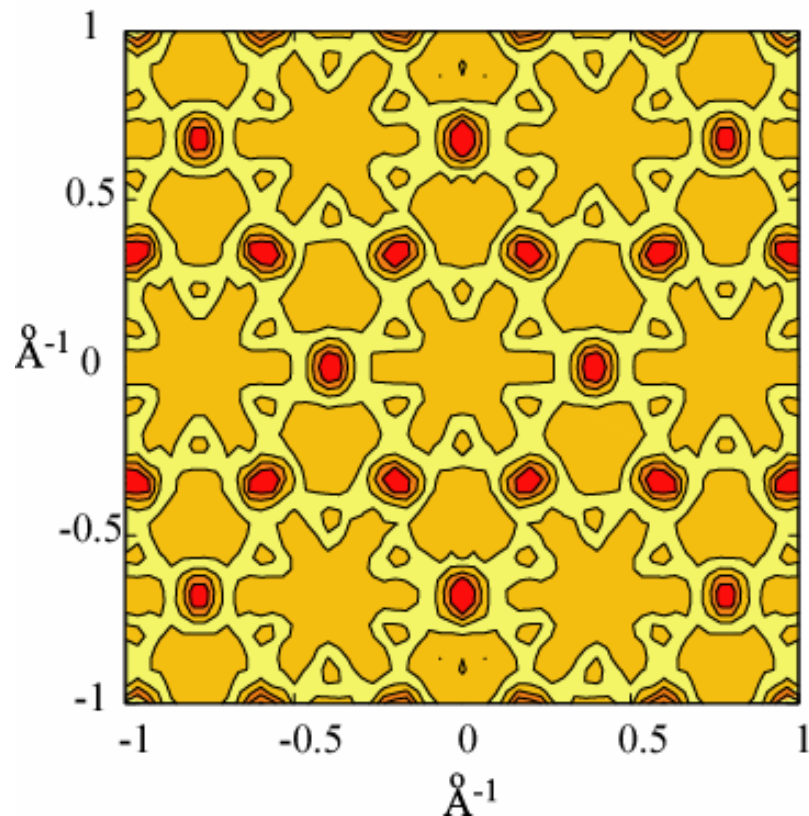


Diffuse Antiphase Boundary

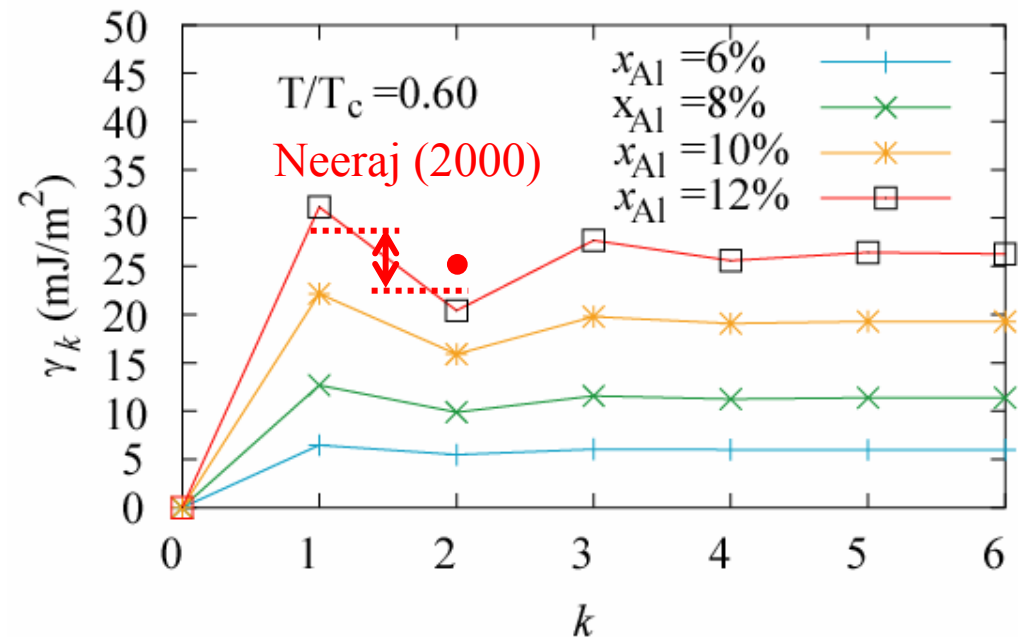


Creation of a plane with easy dislocation motion:
Work softening

Short-range order and diffuse antiphase boundary energy calculations

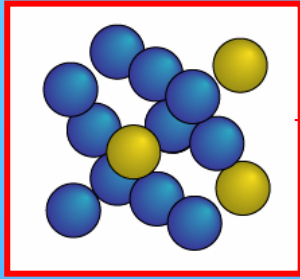


Calculated diffuse X-ray scattering
in Ti-Al hcp solid-solution

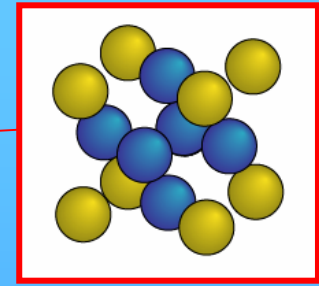
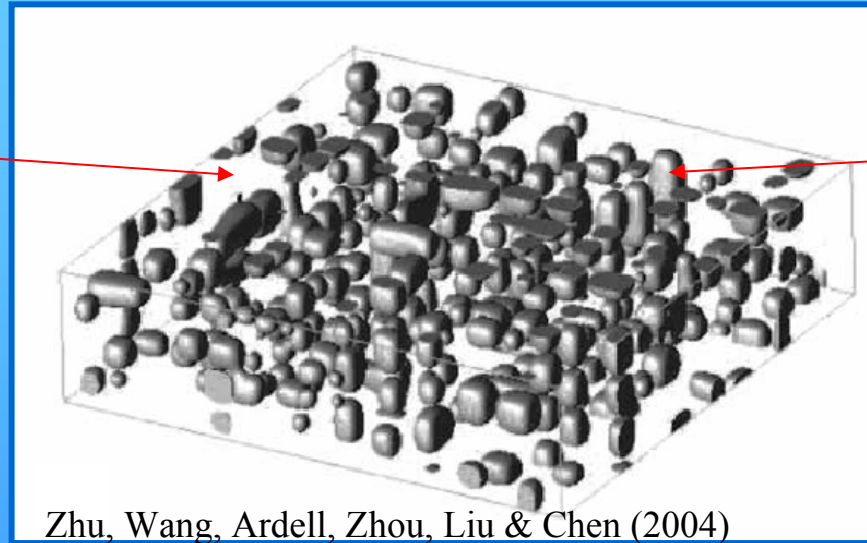


Energy cost of creating a diffuse anti-phase boundary in a Ti-Al hcp short-range ordered alloy by sliding k dislocations

Phase Field Modeling of System



Ni-rich fcc
solid solution



L1₂ Ni₃Al

Free energy:

$$F = \int_V \left[f(c, \phi_i) + \frac{\varepsilon^2}{2} \sum_i (\nabla \phi_i)^2 \right] dV$$

Thermodynamic term

phase fields

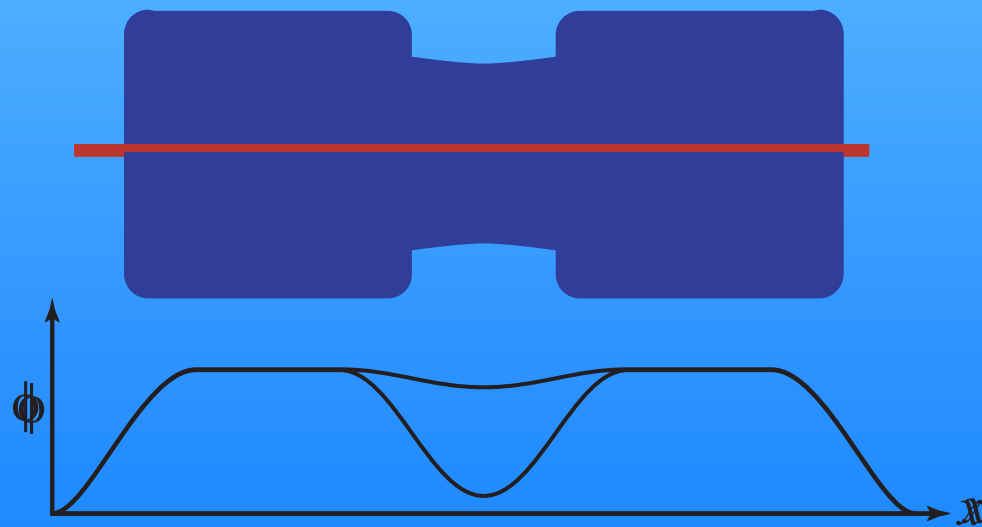
“gradient energy” term

Input parameters needed: Bulk thermodynamic data, Kinetic coefficients,
Interfacial free energy,
Interface width

Interface Width & Coalescence

In phase field modeling:

- ♦ Interface width usually a *numerical parameter*.
- ♦ Can get correct behavior with a larger-than-physical width **except** if modeling of coalescence required.



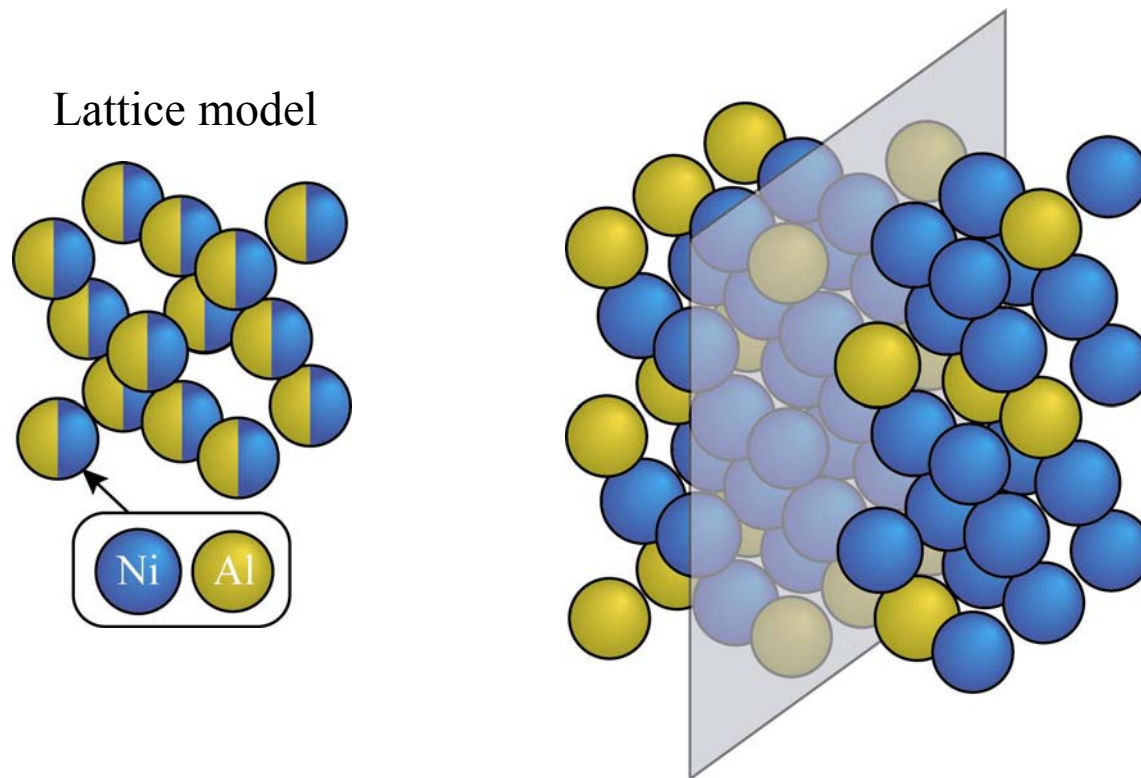
Wider Interface



Increased coalescence

$\text{Ni}_3\text{Al}/\text{Ni}$ (001)

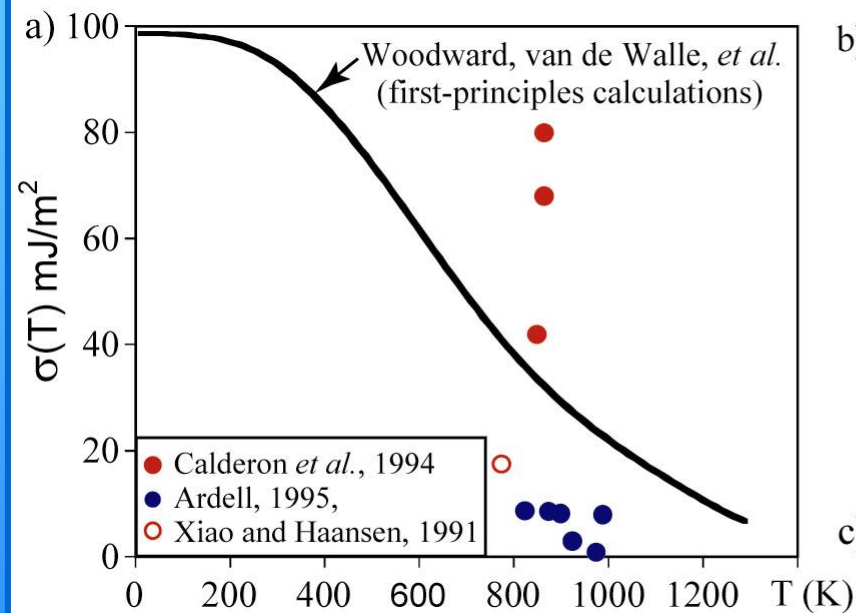
Diffuse Coherent Interface



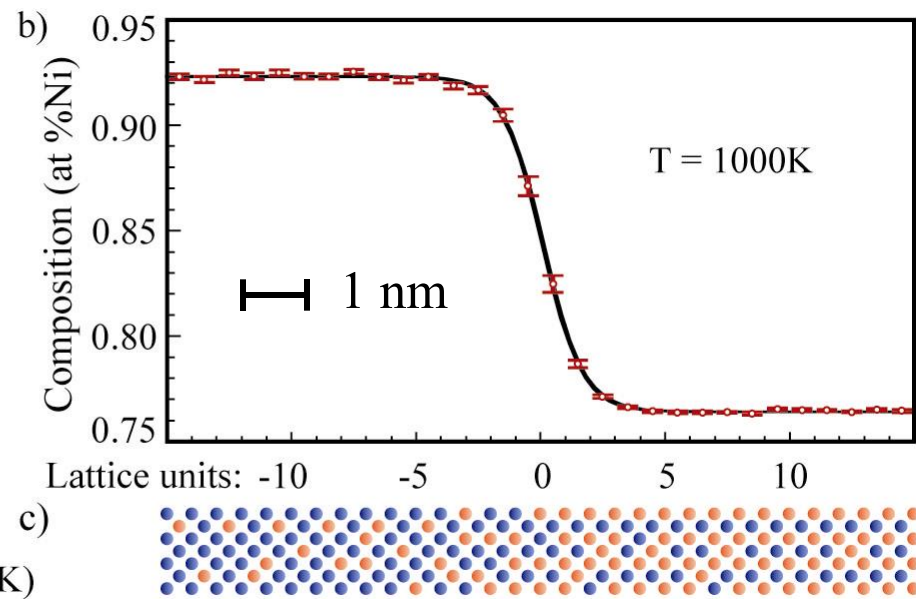
Interfacial Thermodynamics

$\text{Ni}_3\text{Al}/\text{Ni}$ (001) diffuse coherent interface

Interfacial free energy

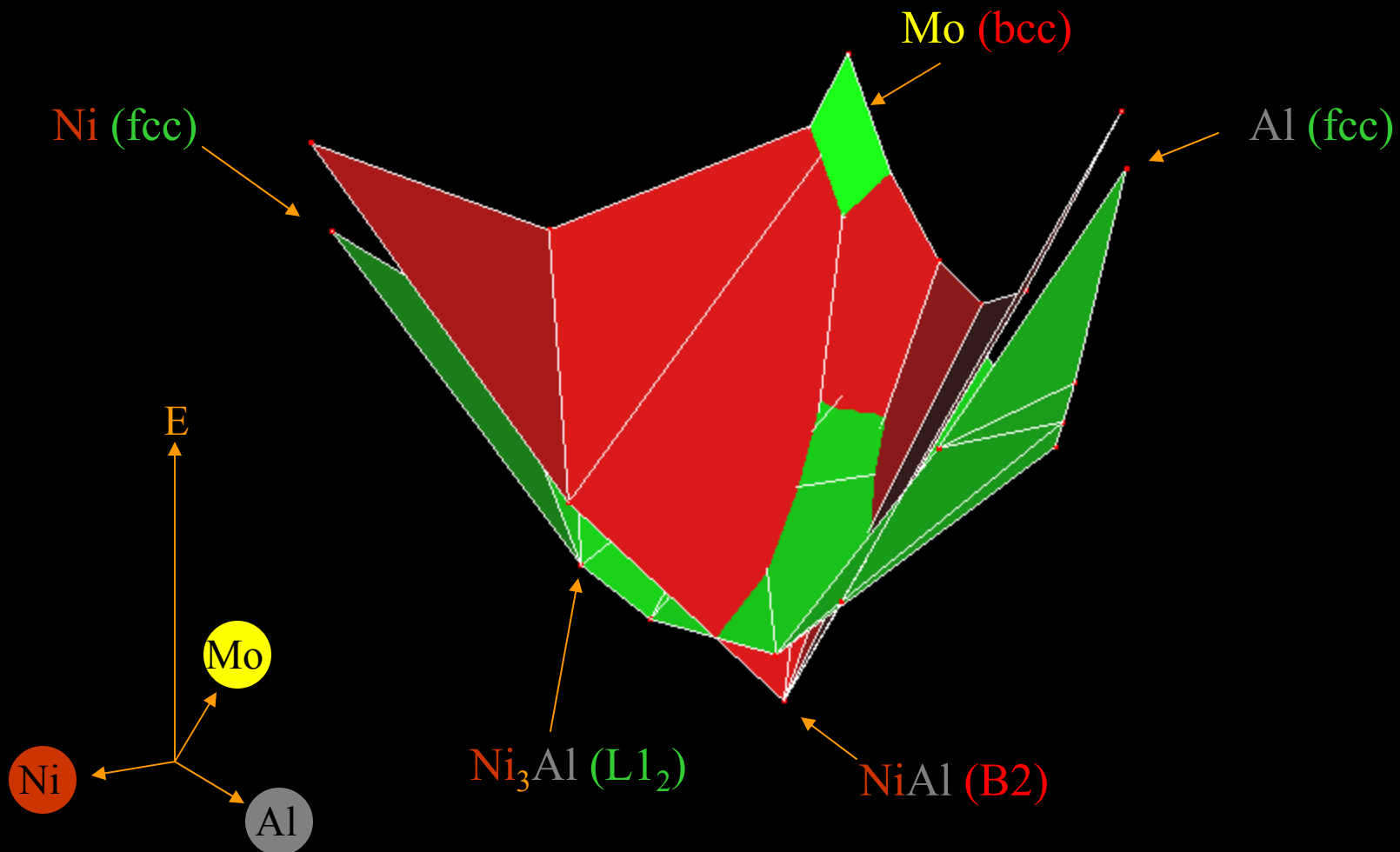


Interface width



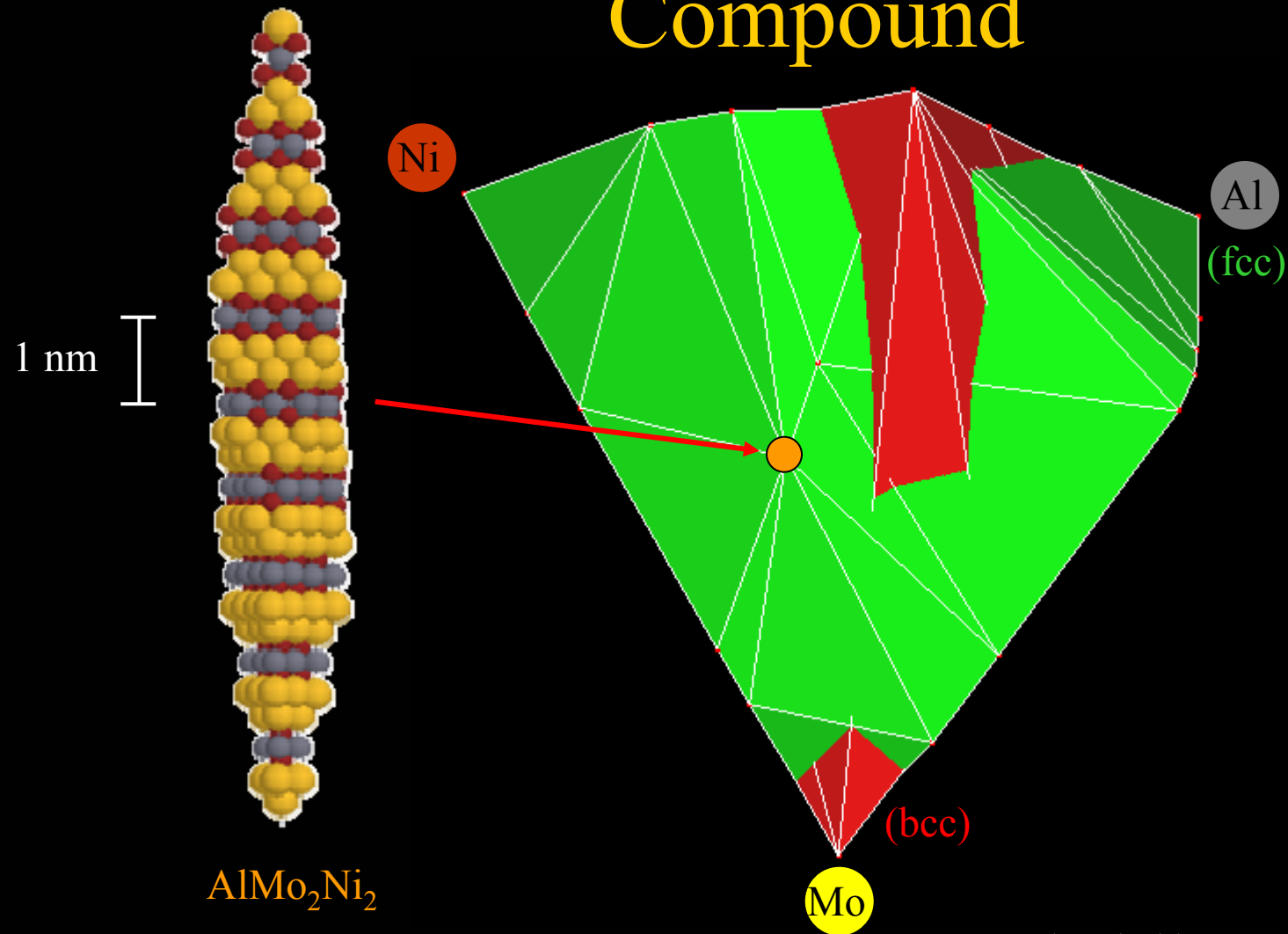
Important input for mesoscale phase field simulations:
provides the “gradient energy” term

Search for new compounds in the Al-Mo-Ni system



plotted with *MEDIT*, INRIA-Rocquencourt.

Predicted Nano-Structured Compound



plotted with *MEDIT*, INRIA-Rocquencourt.

Key aspects of *ab initio* alloy thermodynamics calculations

- Multicomponent multisublattice cluster expansion
- Efficient handling of electrostatic interactions (in ionic systems)
- Hybrid canonical-grandcanonical lattice-gas Monte-Carlo simulations
- Efficient construction of phase diagrams via stochastic sampling
- Importance of coupling between configurational and vibrational excitations
- Efficient *ab initio* modeling of lattice vibrations, including **anharmonicity**