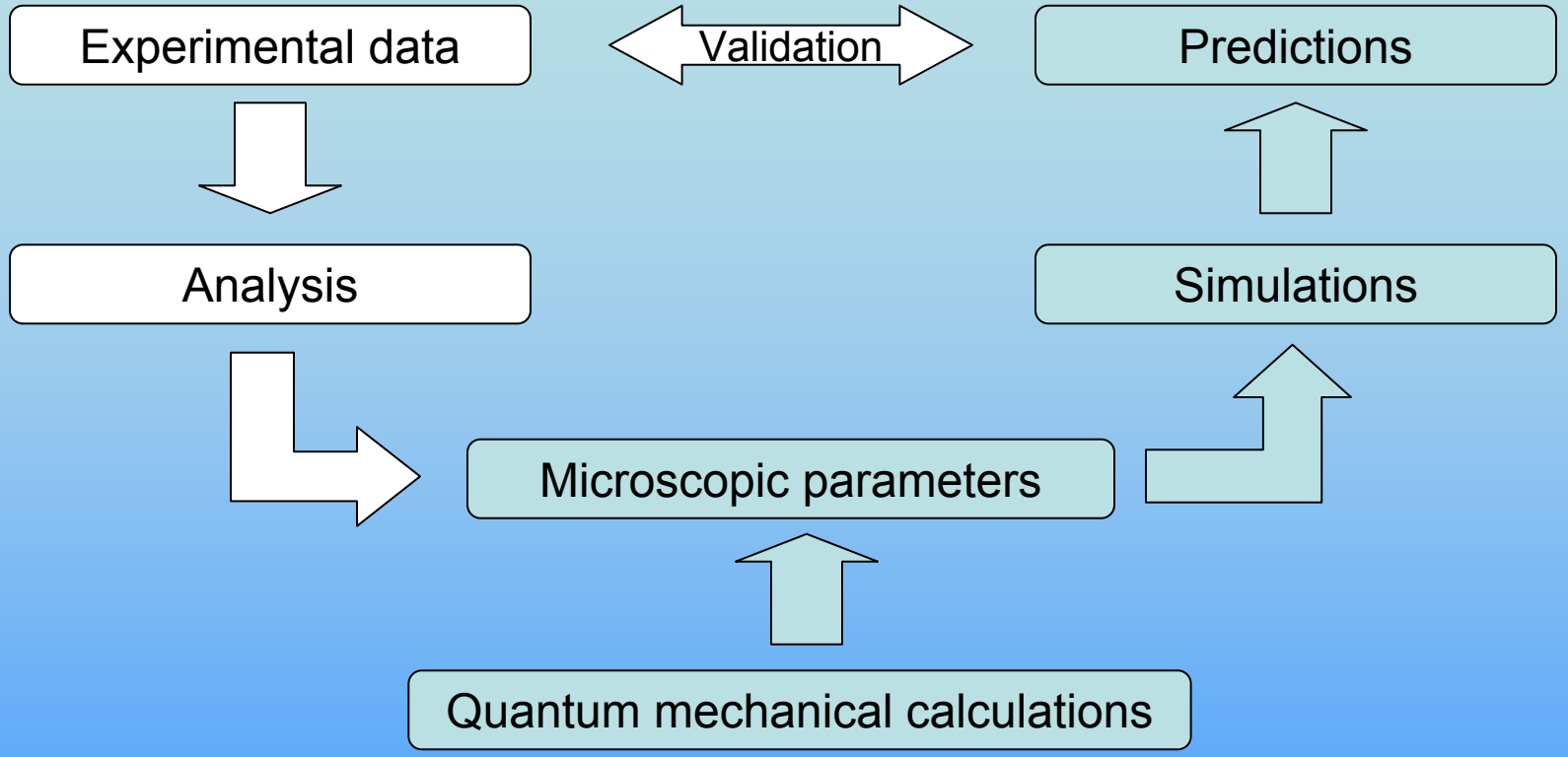
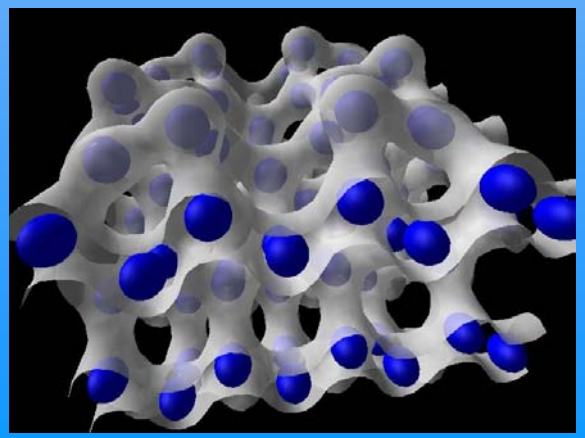
Traditional vs. *ab initio* modeling

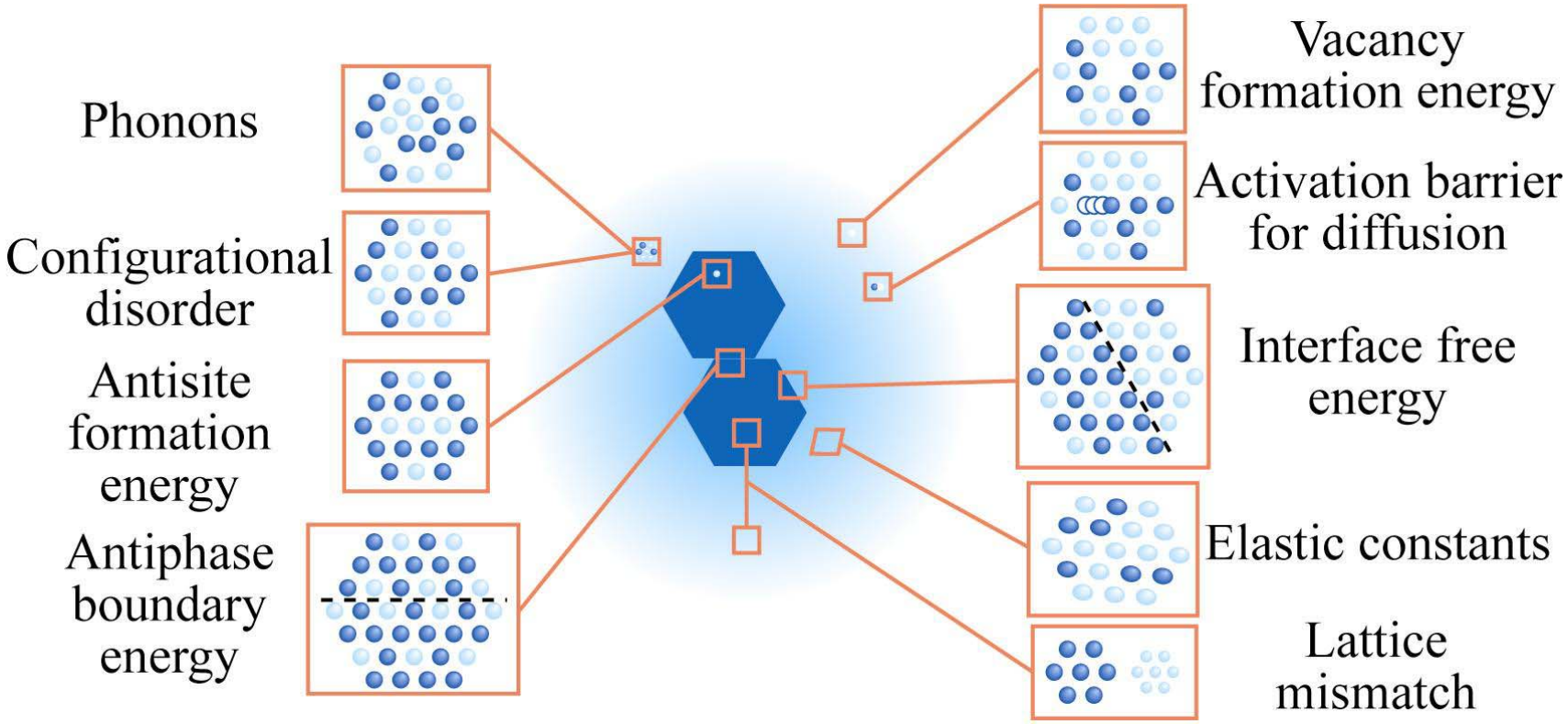




First-principles (or *ab initio*) calculations based on

Density Functional Theory (DFT).

Microscopic parameters governing materials properties

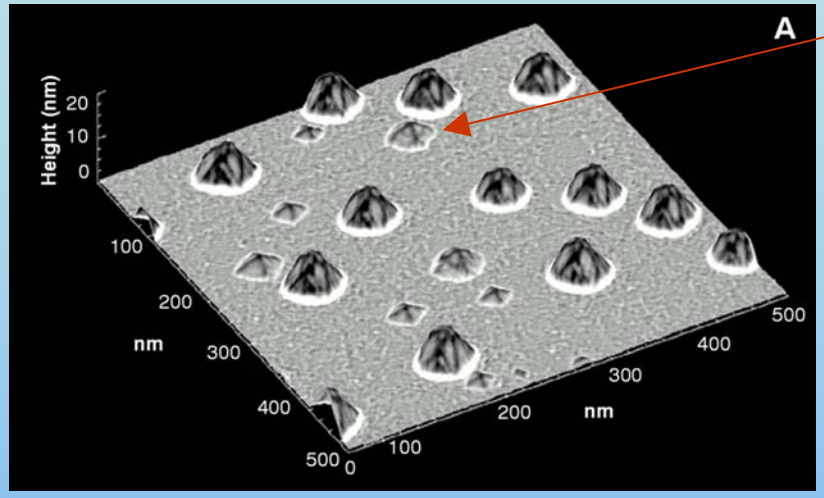


Example: nucleation and growth of precipitate

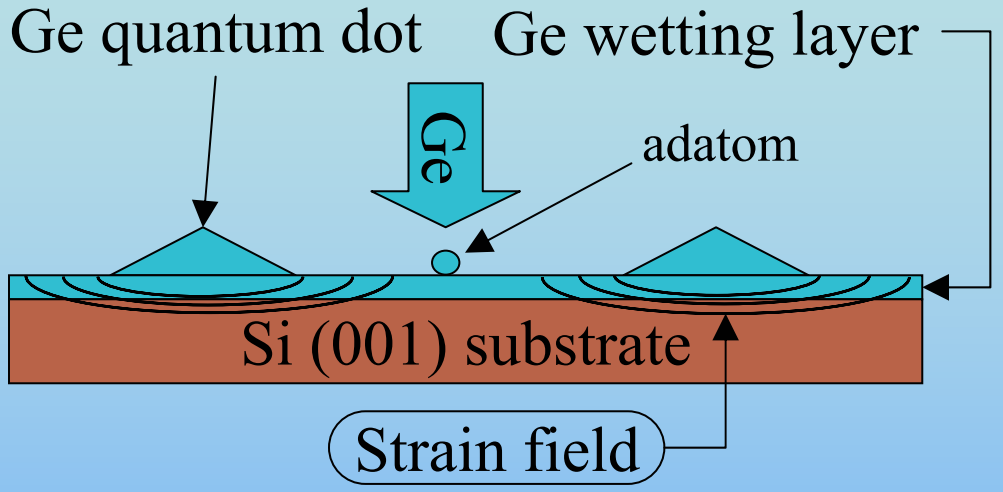
Outline

- Example of *ab initio* calculations
- Why *ab initio* Thermodynamics?
- Methods
- Applications

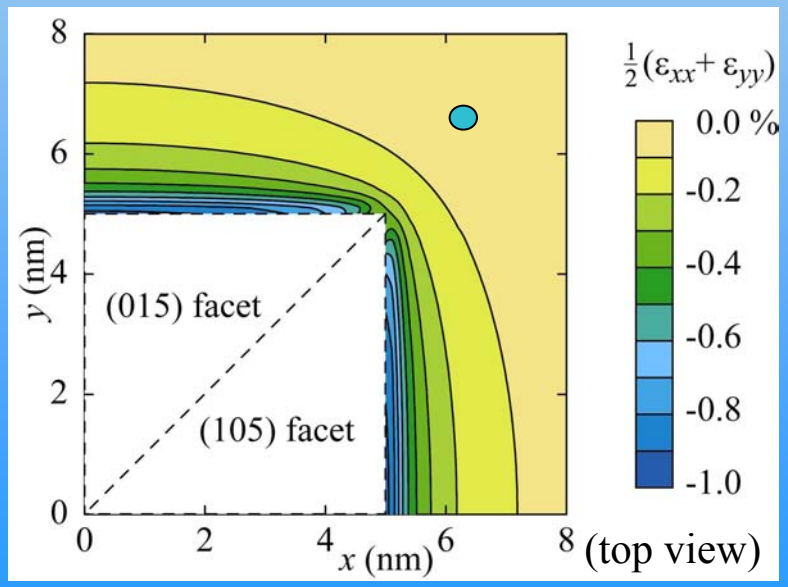
Self-Assembling Ge/Si(001) Quantum Dots



(Medeiros-Ribeiro, *et al.*, 1998)



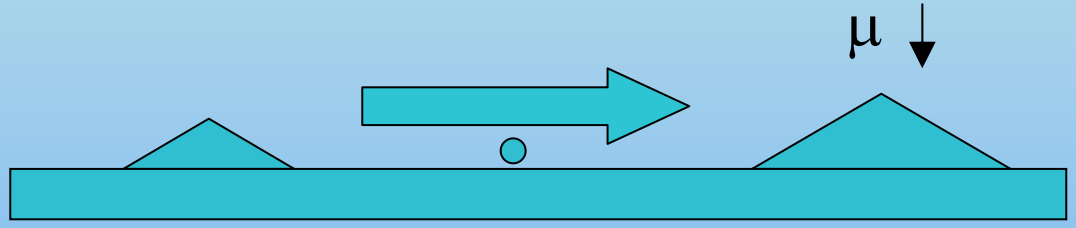
Goal: quantify the **strain-dependence** of the parameters governing **Ge adatom** diffusion



Related works: Roland and Gilmer (1992), Spjut and Faux (1994), Schroeder and Wolf (1997), Ratsch *et al.* (1997), Zoethout *et al.* (2000), Shu *et al.* (2001), Penev *et al.* (2001).

Unwanted Coarsening

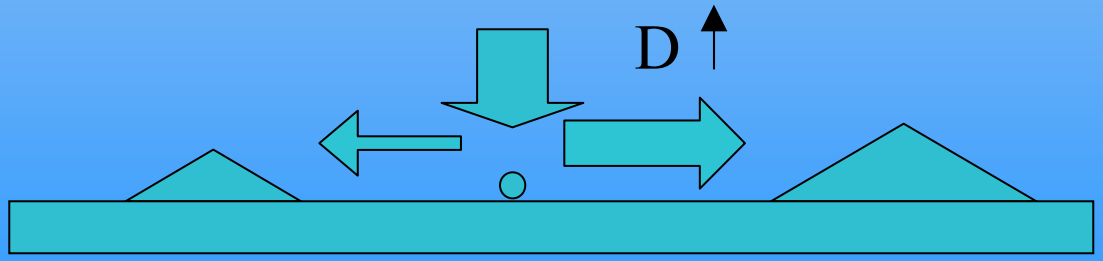
- Thermodynamic effect



Larger island:

Lower surface/volume (capillarity)

- Kinetic effect (?)

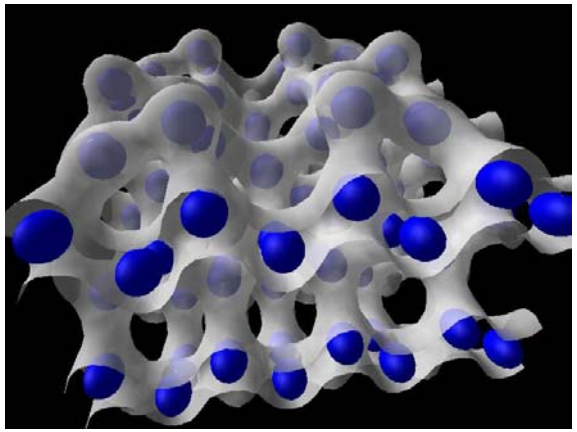


Near Larger island:

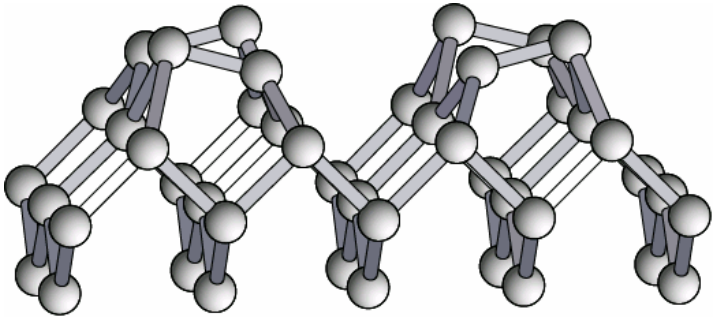
Higher adatom mobility

(Lower barrier for adatom attachement)
e.g. Koduvely and Zangwill (1999)

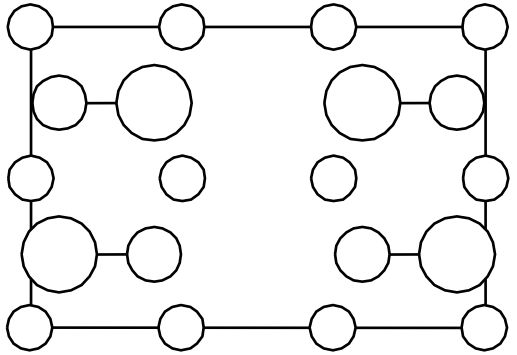
Ge (001) Surface c(4x2) Reconstruction



isoelectronic density plot



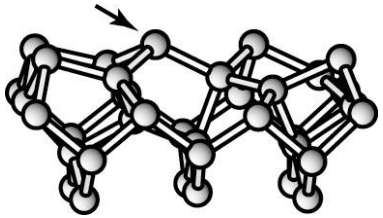
3D schematic

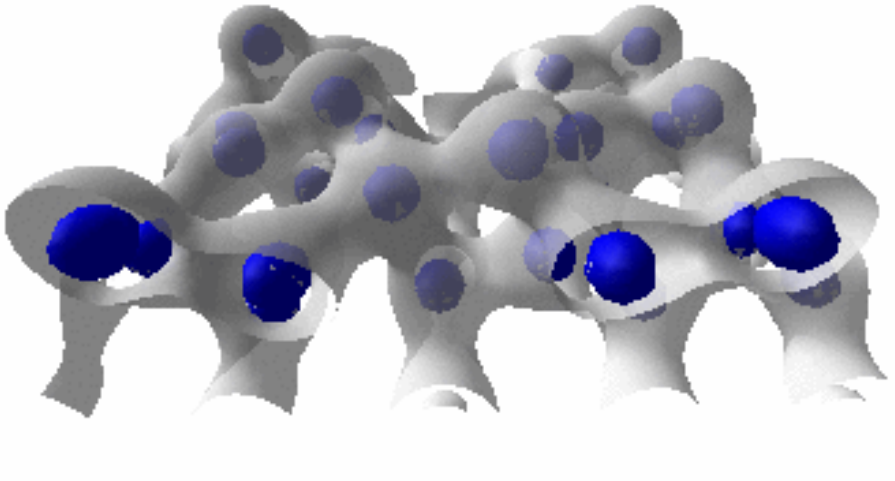


Schematic top view

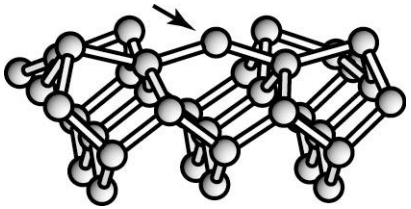
Ge Adatom Diffusion on Ge (001)

Binding site

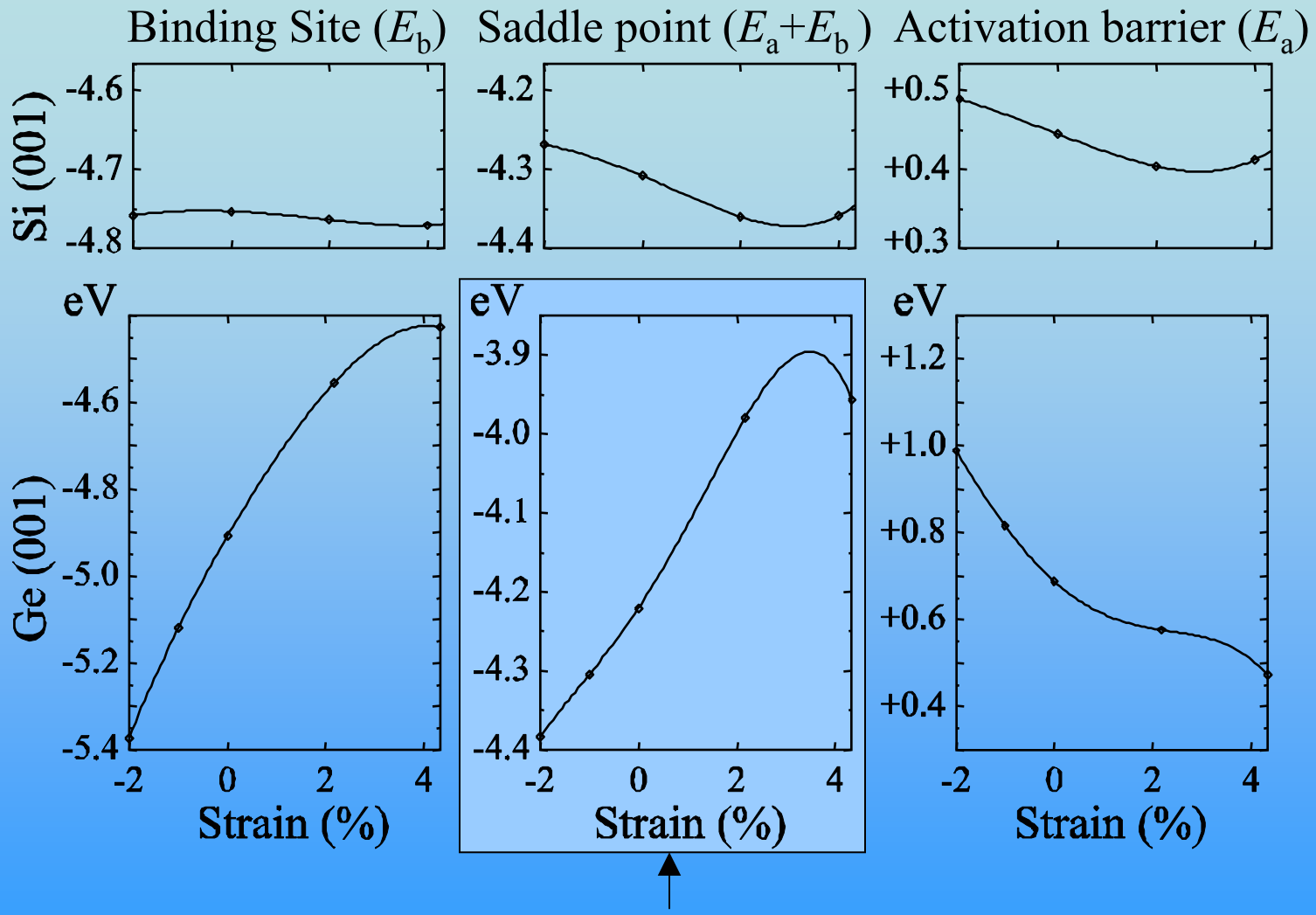




Saddle point



Strain dependence



Diffusion-driven kinetic coarsening

0 % strain = Si lattice param. 4 % strain = Ge lattice param.

Magnitude of the effect

Reference	System adatom/subst.	dE_b/de (eV/%)	dE_a/de (eV/%)
Roland *et al.* (1992)	Si/Si(001)		-0.023
Ratsch *et al.* (1997)	Ag/Ag(111)	-0.028	0.007
Zoethout *et al.* (2000)	Si_2/Si(001)		0.038
Penev *et al.* (2001)	In/GaAs(001)	-0.050	-0.020
Shu *et al.* (2001)	Si/Si(001)		-0.050
Present	Ge/Si(001)	0.002	-0.022
Present	Ge/Ge(001)/Si	0.212	-0.128

The “Virtual” Laboratory

Advantages

- Absolute control over “experimental’’ conditions
- Unlimited “characterization’’ capabilities
- Ability to perform thought experiments
- Automation of repetitive tasks
- “Materials by design”

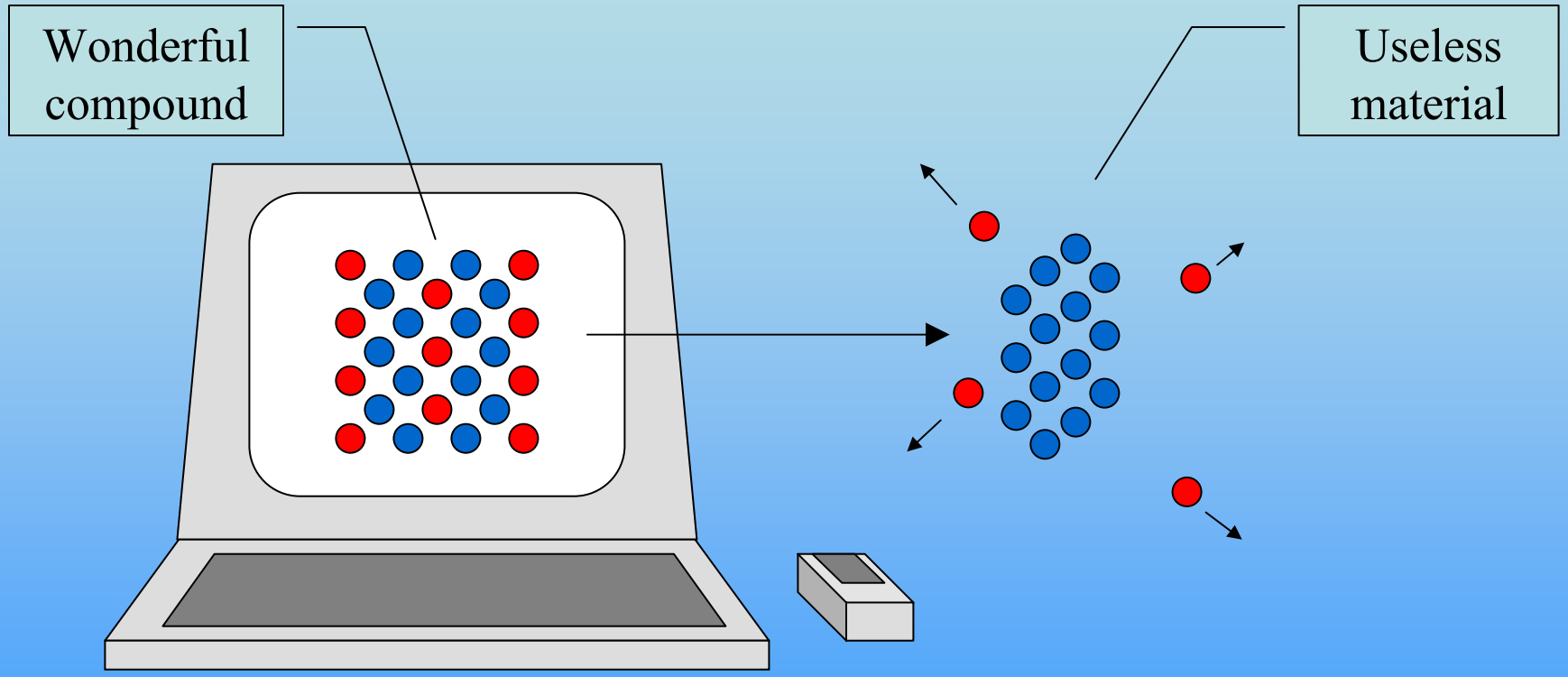
Weaknesses

- Limited by computational resources
- Cannot predict effects not included in simulation

Outline

- Example of *ab initio* calculations
- Why *ab initio* Thermodynamics?
- Methods
- Applications

From a virtual to a real material...



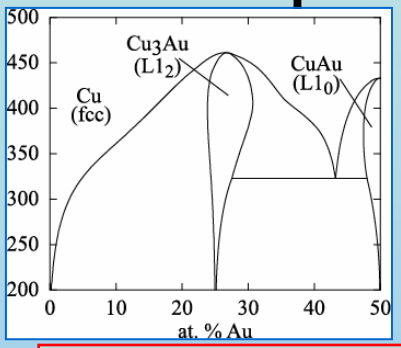
We need a way to predict phase stability:

First-principles phase diagram calculations

Outline

- Example of *ab initio* calculations
- Why *ab initio* Thermodynamics?
- Methods
- Applications

First-principles Thermodynamic Calculations



•Large number of atoms
•Many configurations

Thermodynamic data

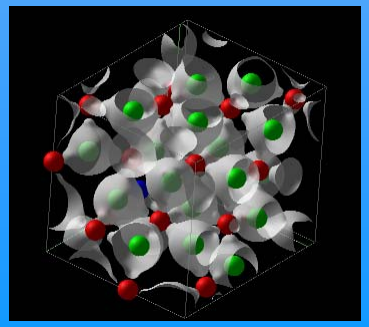
Lattice model &
Monte Carlo Simulations

Alloy Automated Theoretic Toolkit

Configurational disorder

Lattice vibrations

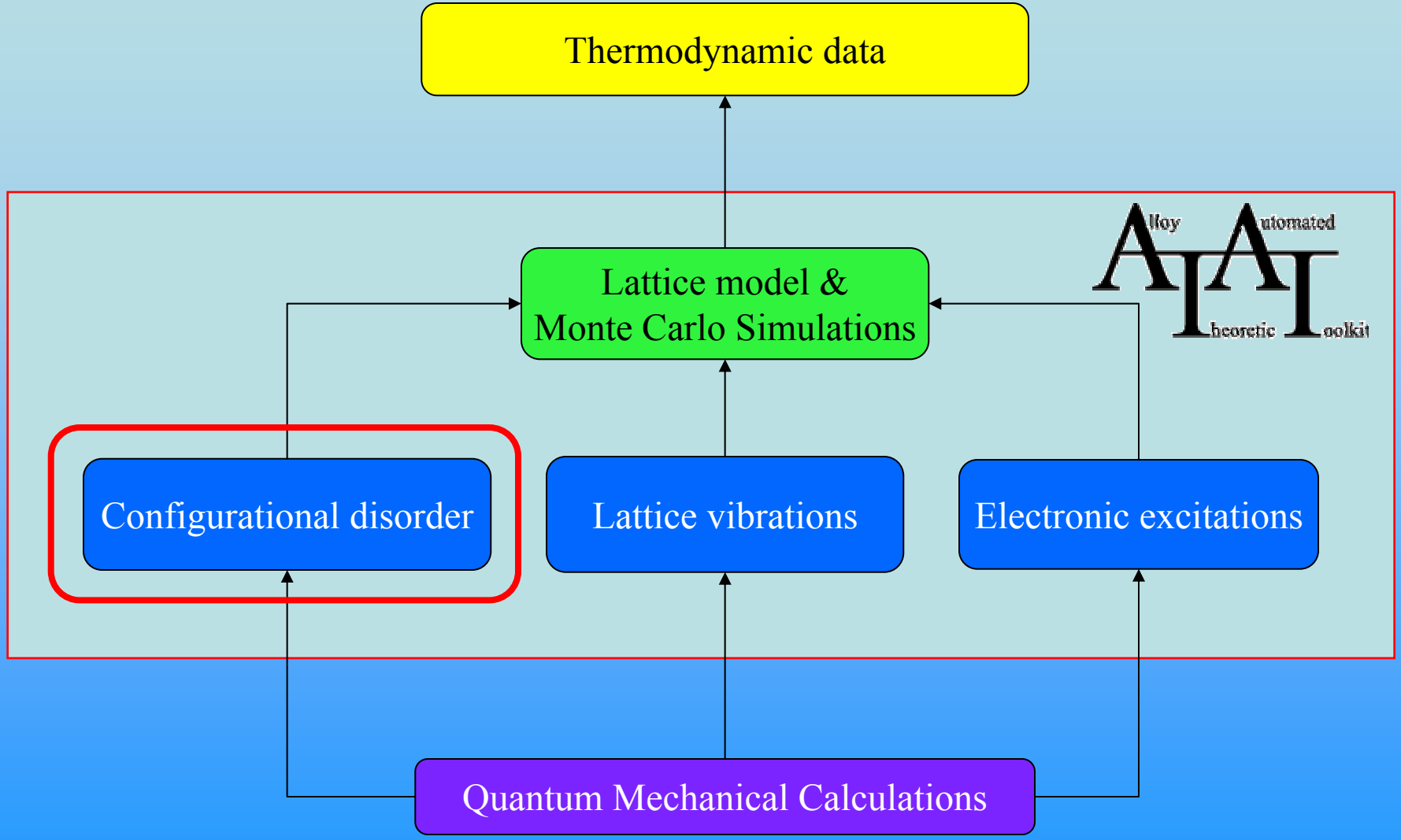
Electronic excitations



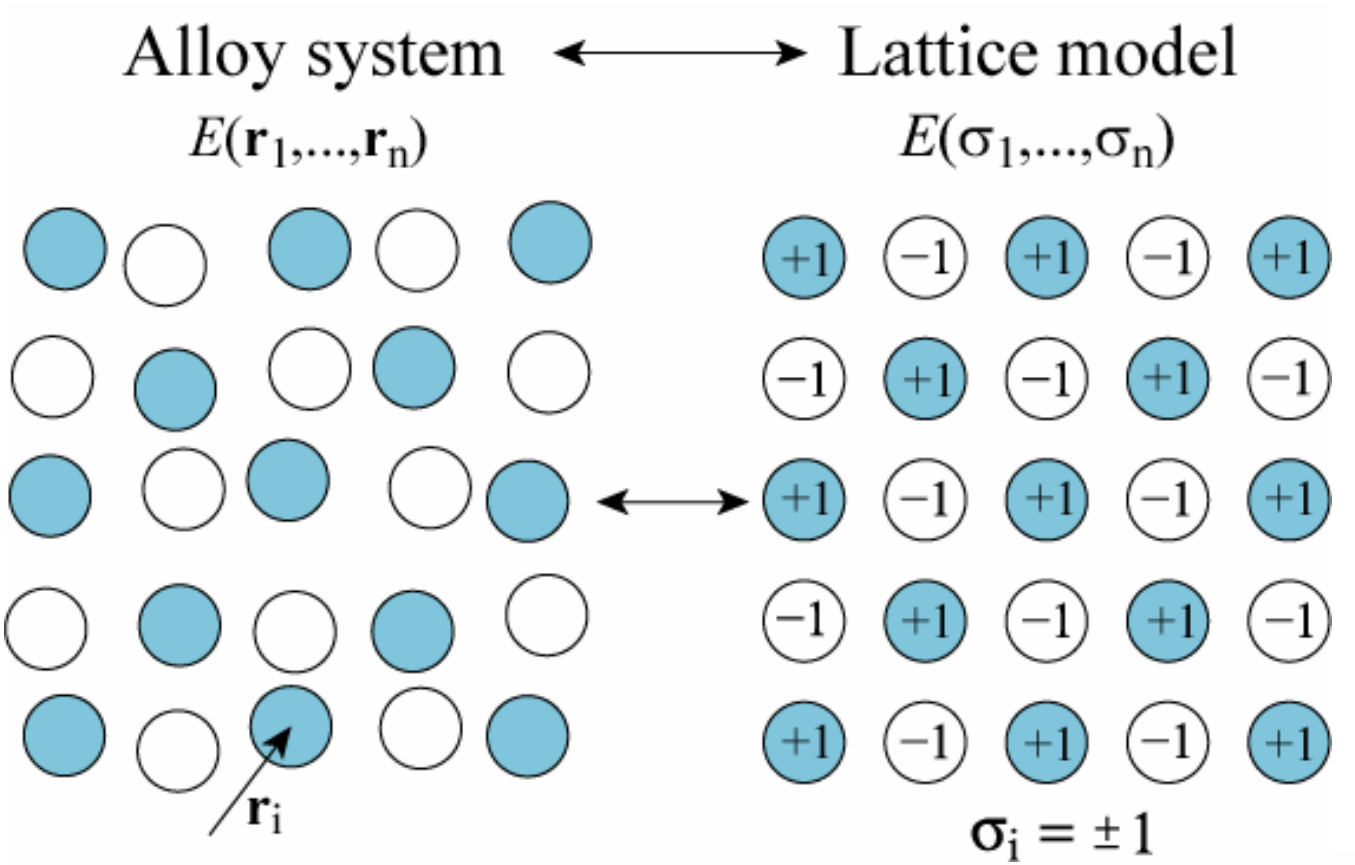
Quantum Mechanical Calculations

•Small number of atoms
•Few configurations

http://cms.northwestern.edu/atat


Thermodynamic data
Lattice model &
Monte Carlo Simulations
Alloy Automated
Theoretic Toolkit
Configurational disorder
Lattice vibrations
Electronic excitations
Quantum Mechanical Calculations

The Cluster Expansion Formalism



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

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

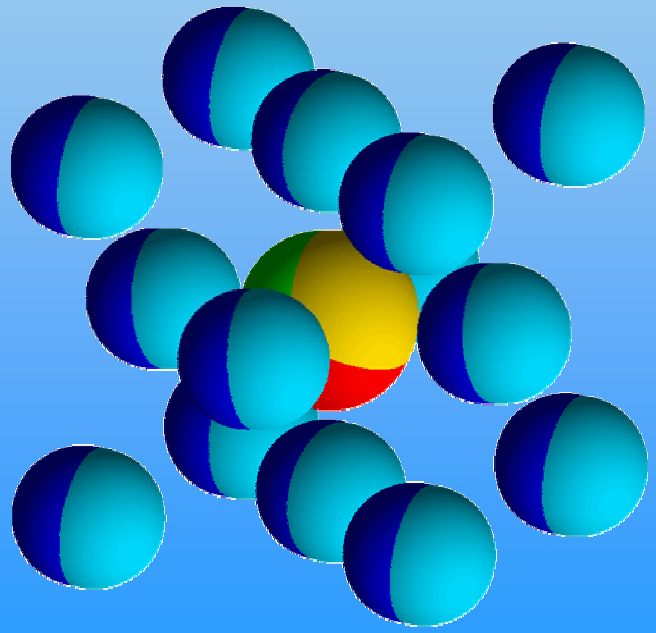
Sanchez, Ducastelle and Gratias (1984)

Coupled Sublattices Multicomponent Cluster Expansion

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

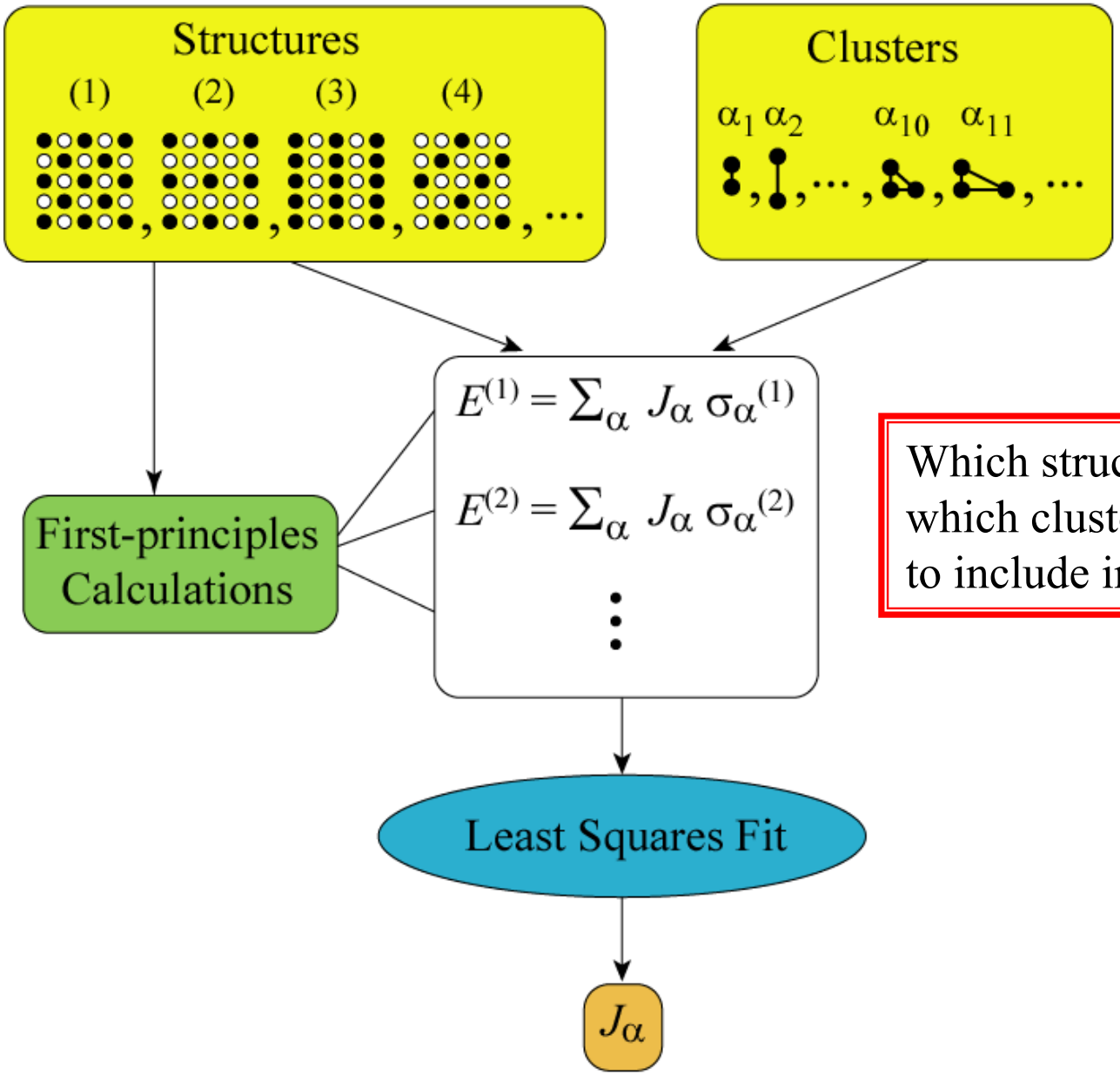
Same basic form: $E(\sigma_1, \ldots, \sigma_n) = \sum_\alpha J_\alpha \sigma_\alpha$

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



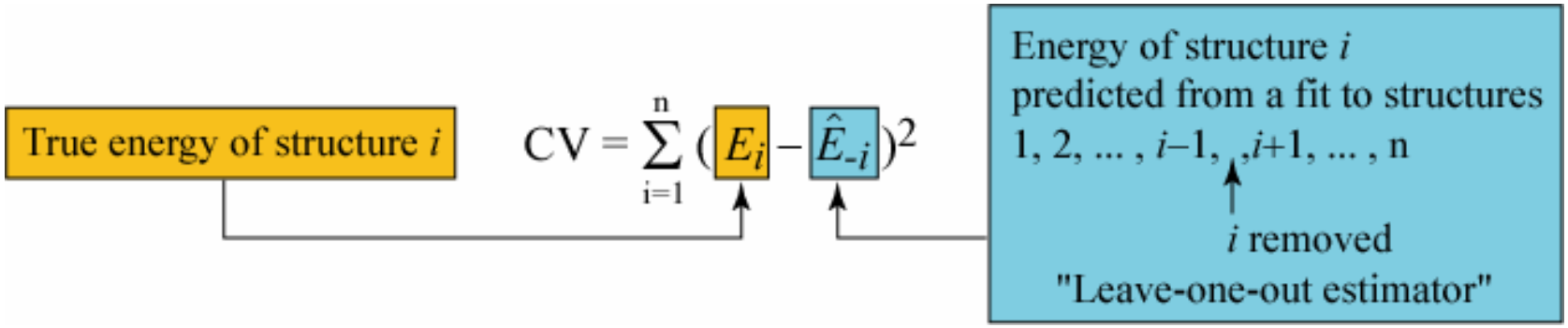
Example: binary fcc sublattice with ternary octahedral sites sublattice

Cluster expansion fit

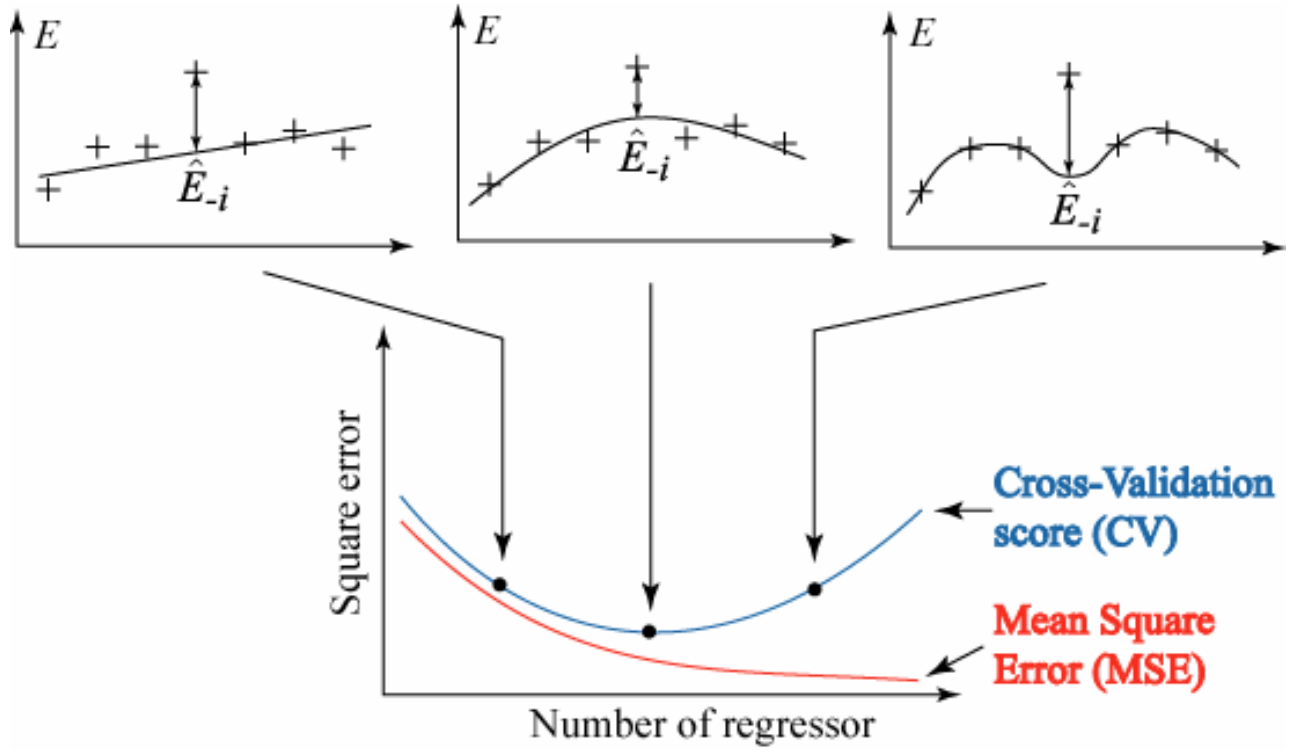


Which structures and which clusters to include in the fit?

Cross-validation

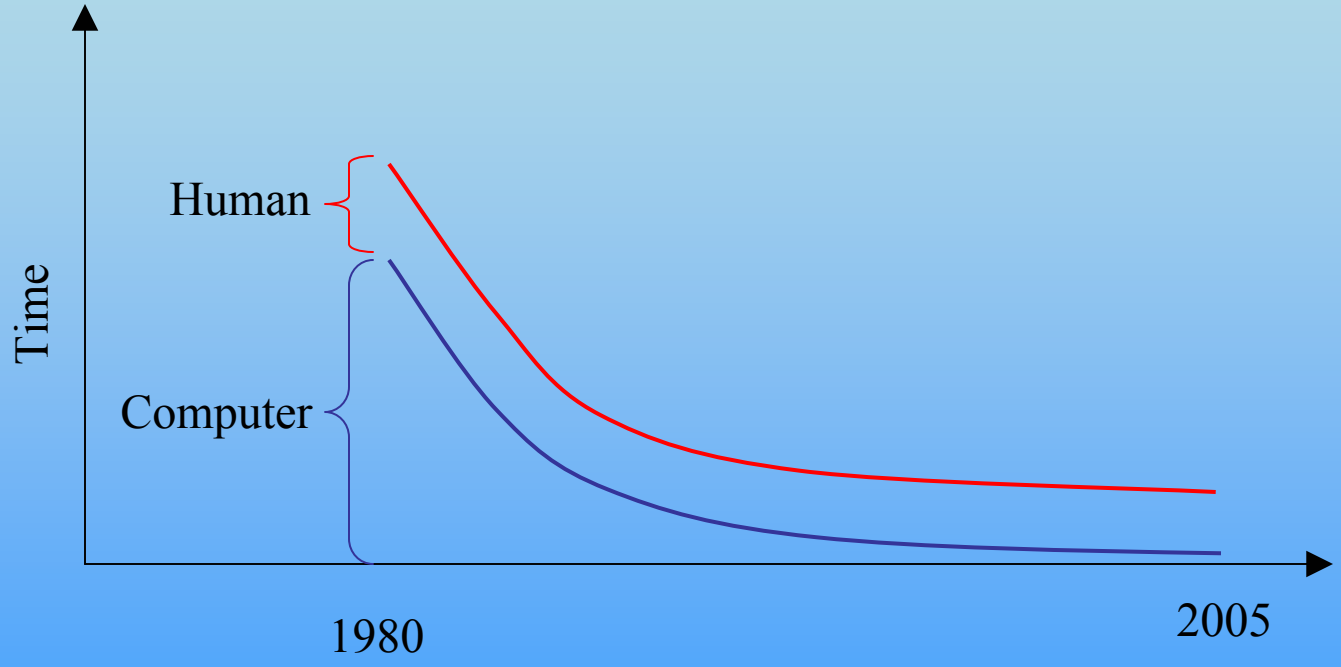


Example of polynomial fit:



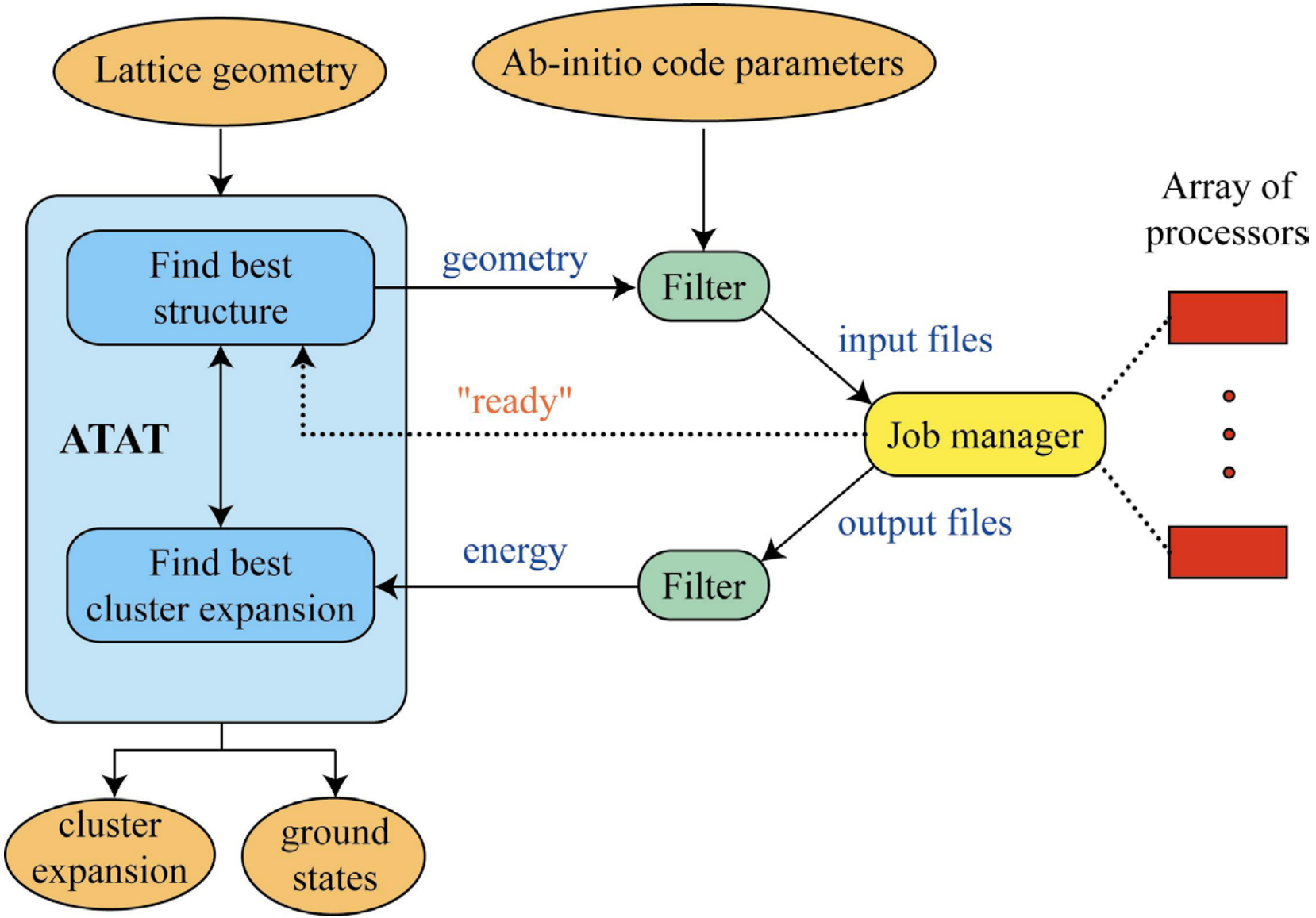
A matter of time...

Time needed to complete a given first-principles calculation



The procedure needs to be automated

Automated Cluster Expansion Construction

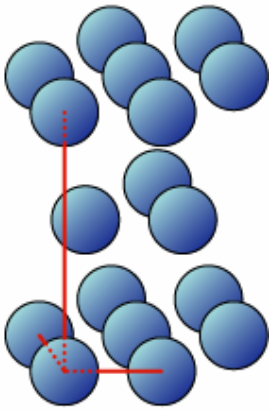


Application to Ti-Al Alloys

Simple lattice input file

```
                a       b       c       α   β   γ
Coordinate system
                2.94    2.94    4.8     90  90  120

                1  0  0
Unit cell       0  1  0
                0  0  1

                0.666667 0.333333 0.500000 Al,Ti
Atoms           0.000000 0.000000 0.000000 Al,Ti
```

(hcp)



Simple ab initio code input file

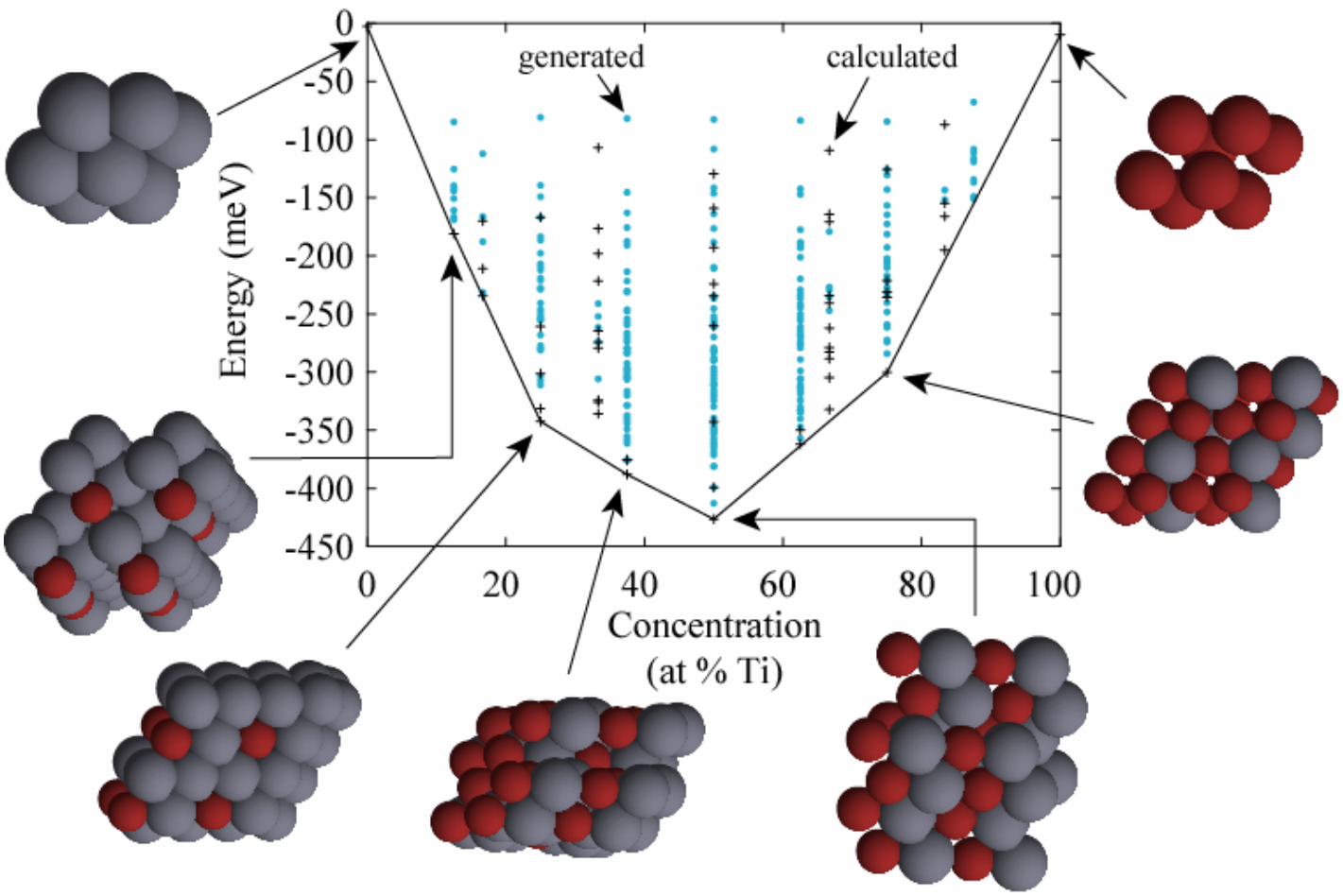
```
[INCAR]
PREC = high
ISMEAR = -1
SIGMA = 0.1
NSW=41
IBRION = 2
ISIF = 3

KPPRA = 1000
DOSTATIC
```

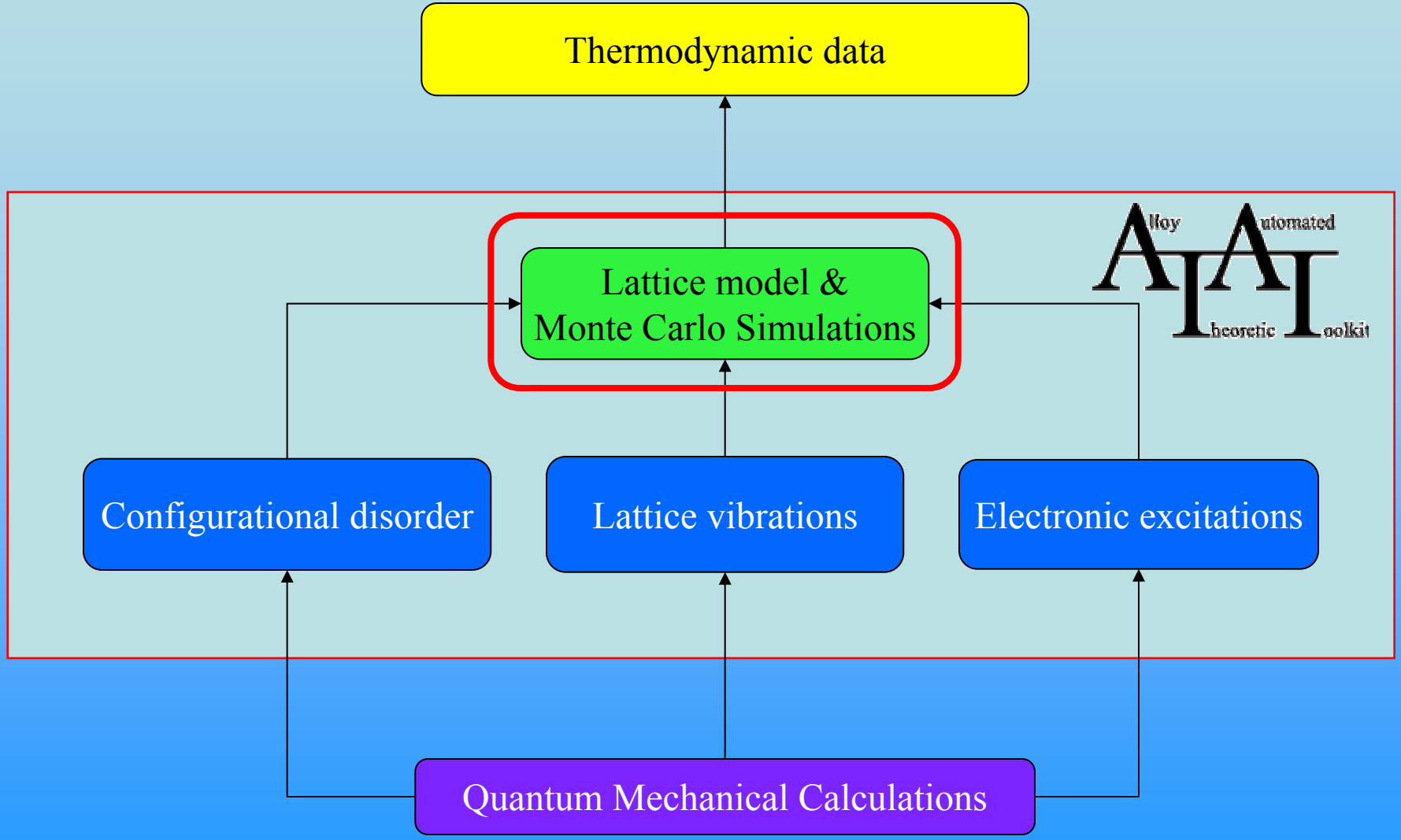
} Standard VASP tokens

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

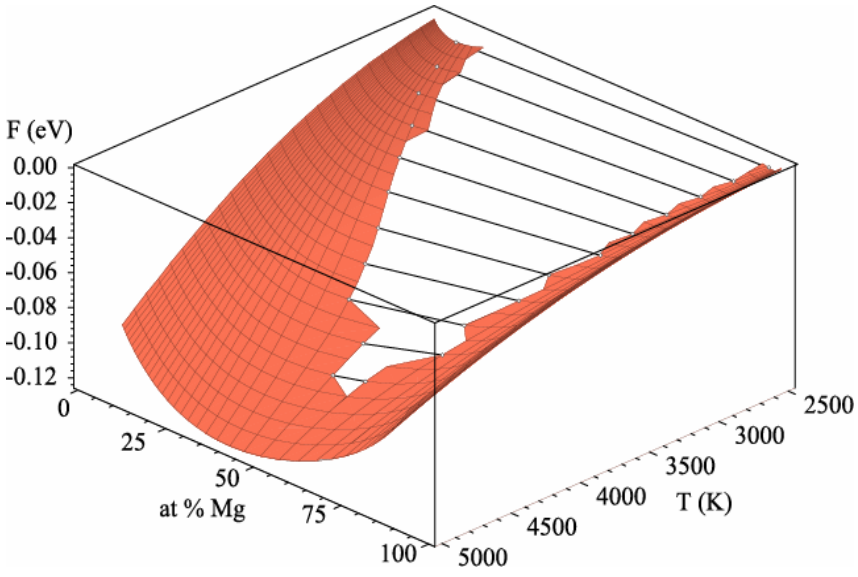
do static run

Ground States Search

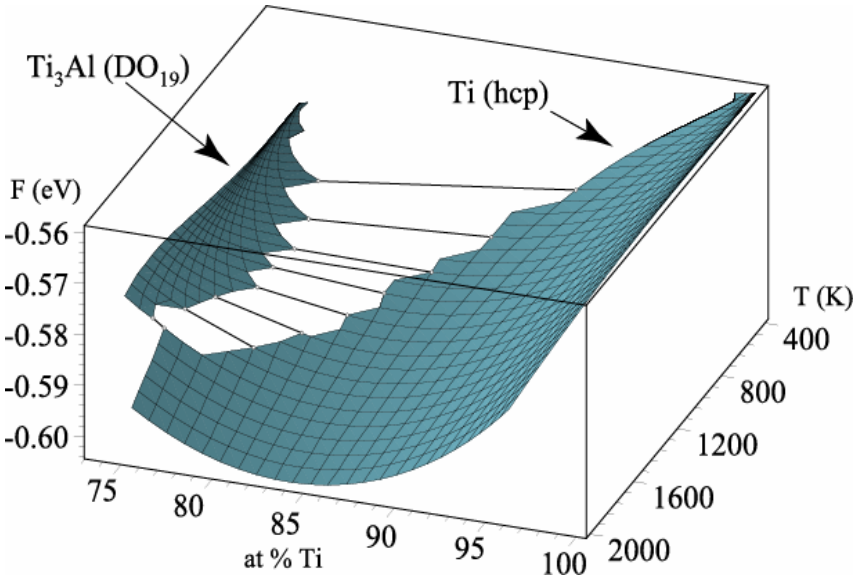



Thermodynamic data
Lattice model &
Monte Carlo Simulations
Alloy Automated
Theoretic Toolkit
Configurational disorder
Lattice vibrations
Electronic excitations
Quantum Mechanical Calculations

Monte Carlo output: Free energies

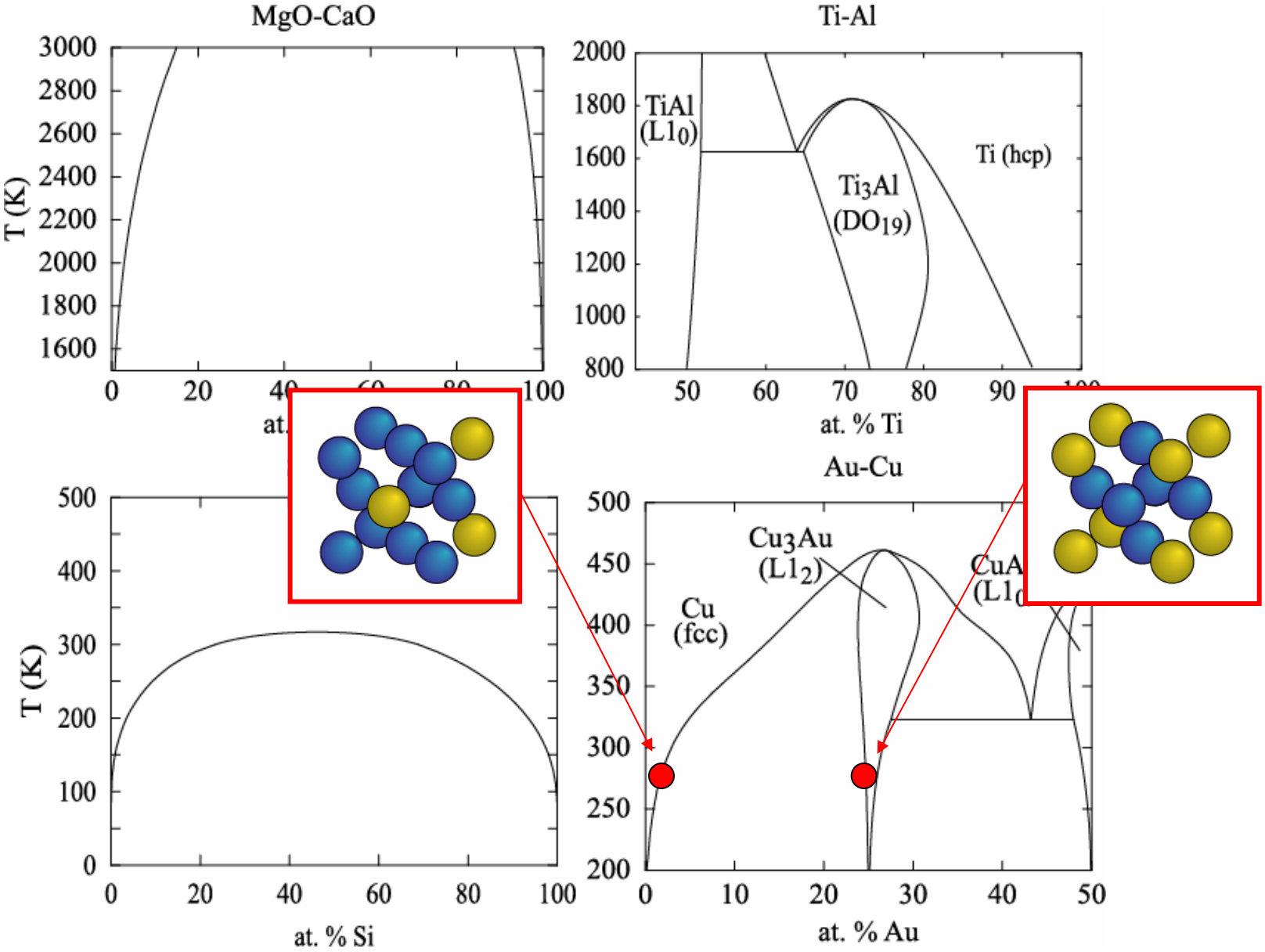


Cao-MgO system

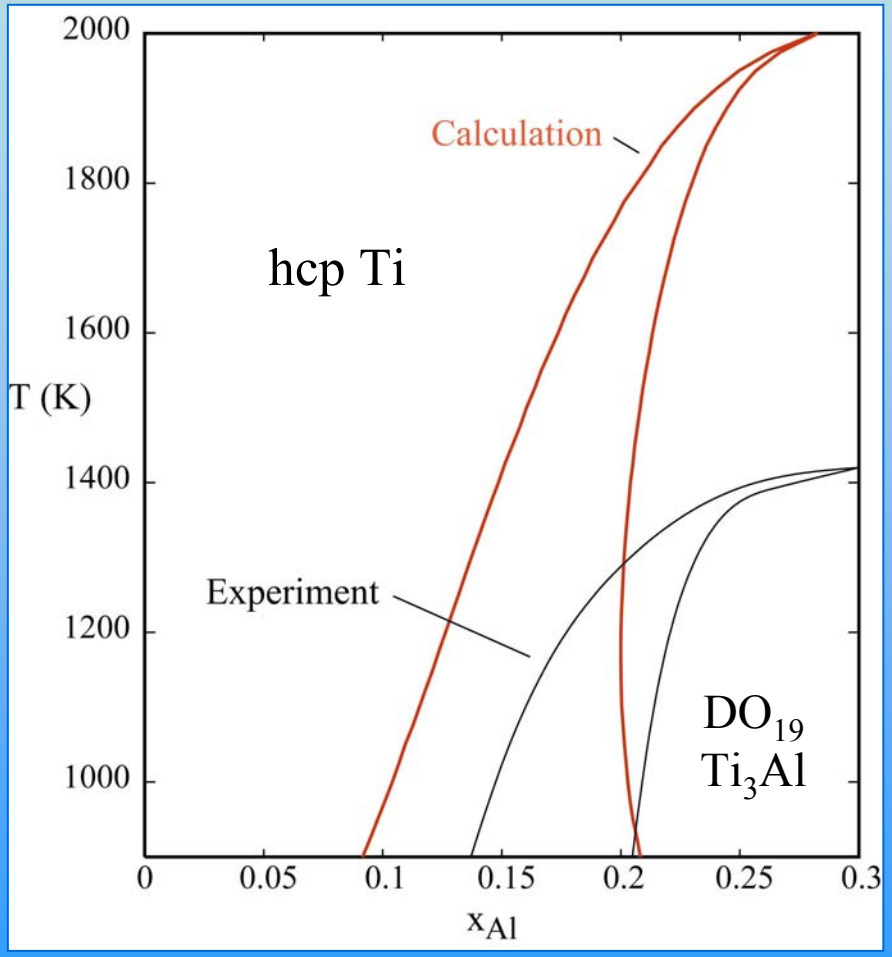


Ti-Al system

Calculated phase diagram



Temperature scale problem



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

Likely source of the discrepancy: Vibrational entropy.

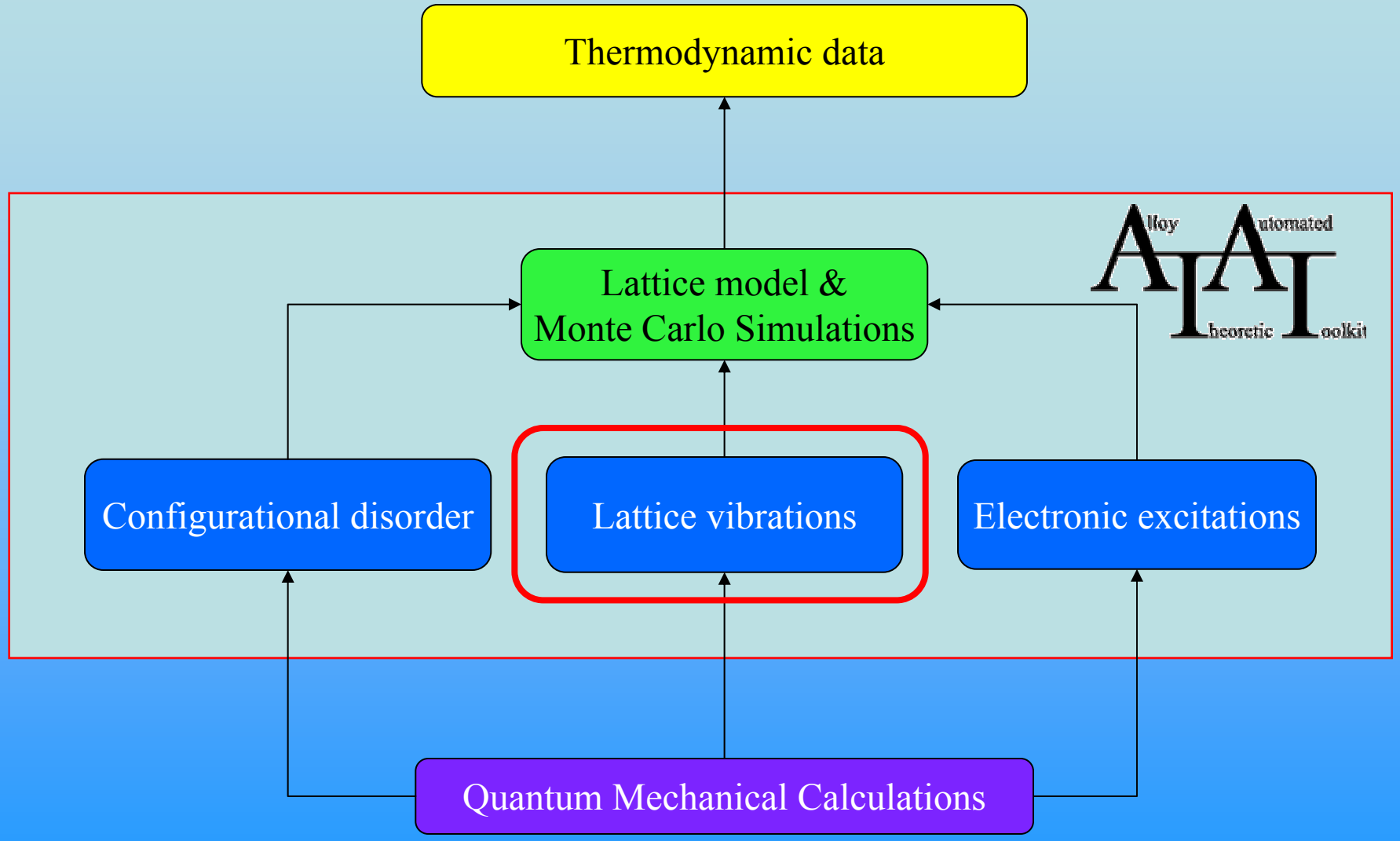
Fultz, Nagel, Antony, *et al.* (1993-1999)

Ceder, Garbulsky, van de Walle (1994-2002)

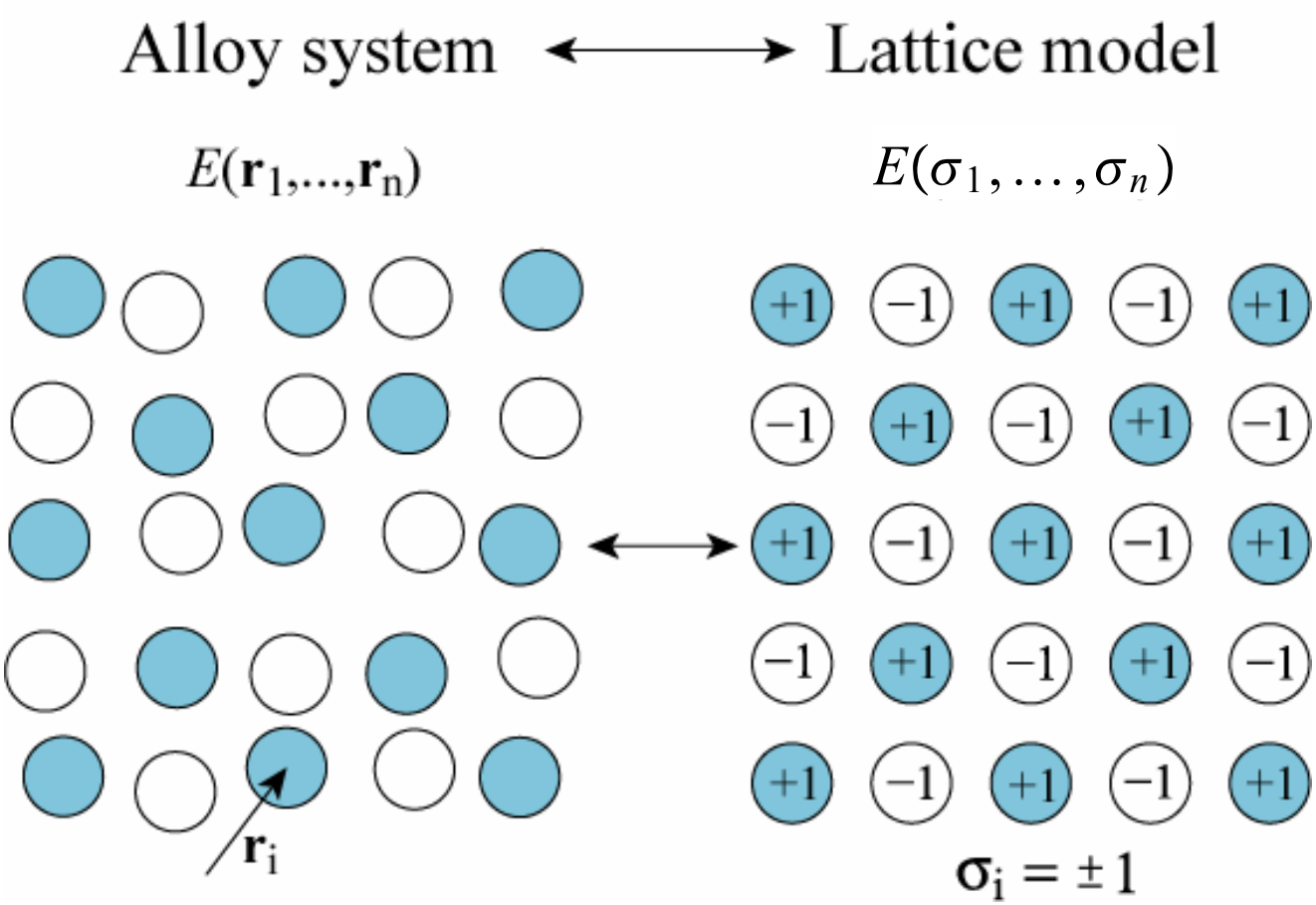
de Fontaine, Althoff, Morgan (1997-2000)

Zunger, Ozolins, Wolverton (1998-2001)

Many other examples…


Thermodynamic data
Lattice model &
Monte Carlo Simulations
Alloy Automated
Theoretic Toolkit
Configurational disorder
Lattice vibrations
Electronic excitations
Quantum Mechanical Calculations

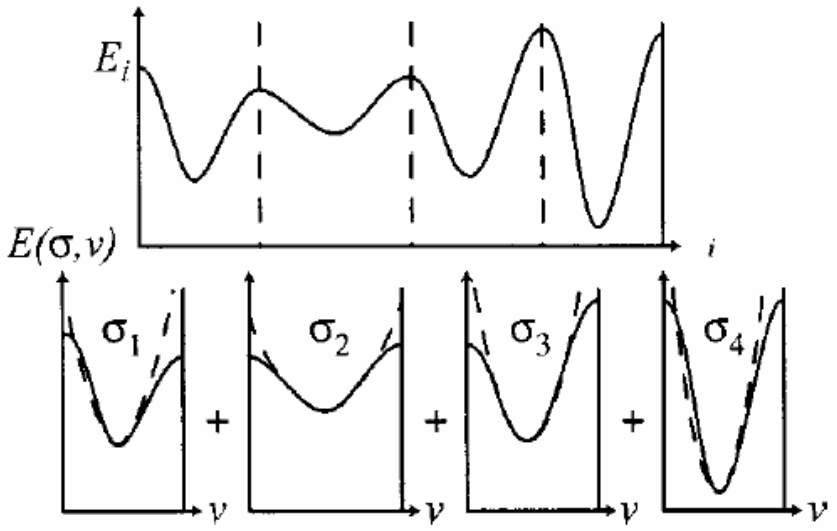
The Cluster Expansion Formalism



$$F(\sigma_1,\ldots,\sigma_n) = \sum_\alpha J_\alpha(T)\sigma_\alpha$$

Coarse-Graining of the Free Energy

Graphically:



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

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

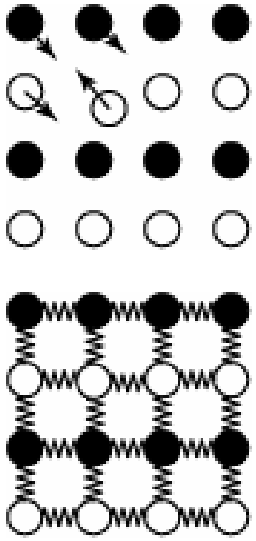
where

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

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

First-principles lattice dynamics

First-principles data

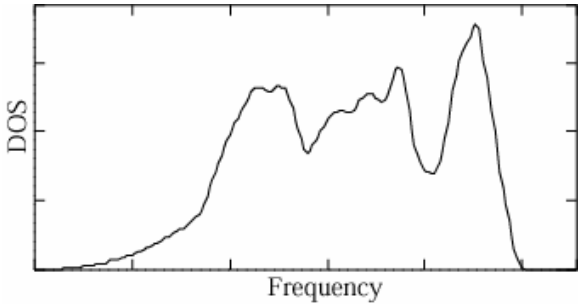


Computationally intensive!

Must be done for many configurations!

Least-squares fit to Spring model

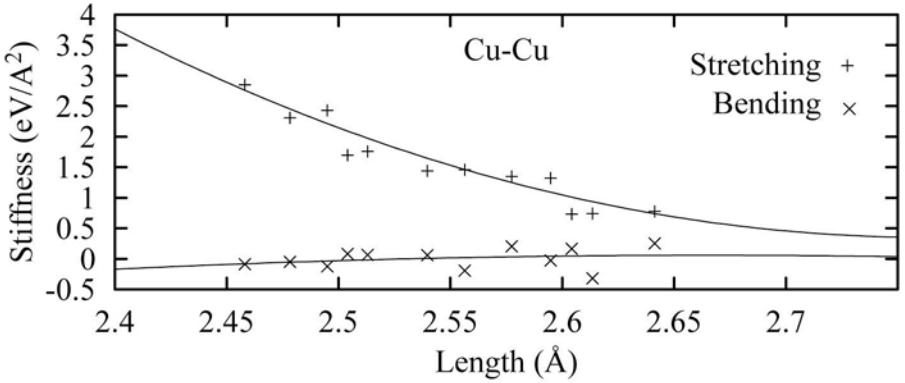
Phonon density of states

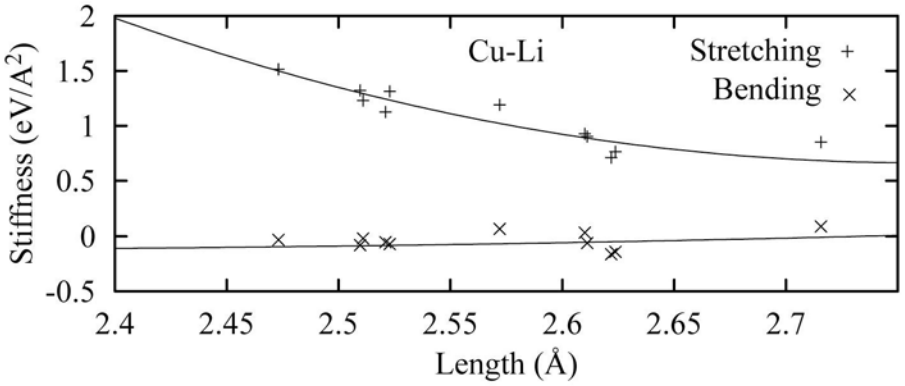


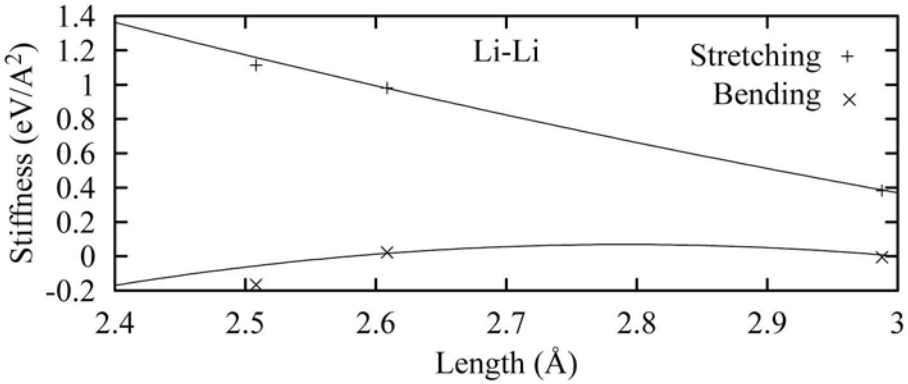
Thermodynamic Properties

Direct force constant method
(Wei and Chou (1992), Garbuski and Ceder (1994), among many others)

Transferable Force Constants

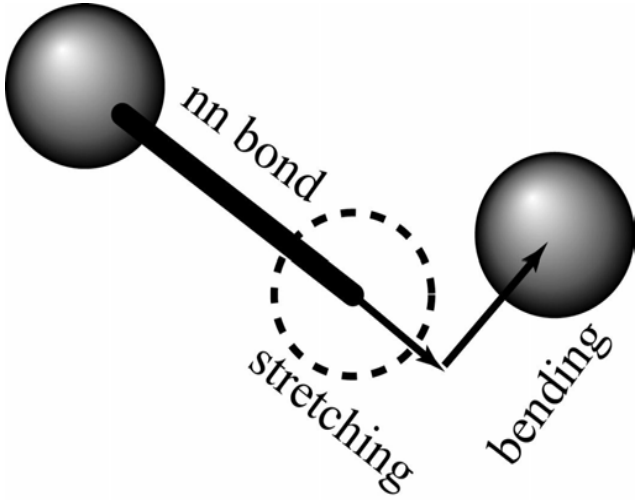






Chemical bond type and bond length:

Good predictor of nearest-neighbor force constants (stretching and bending terms)

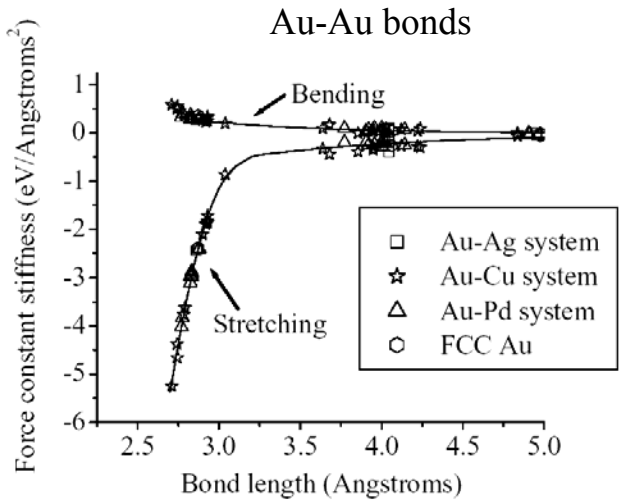


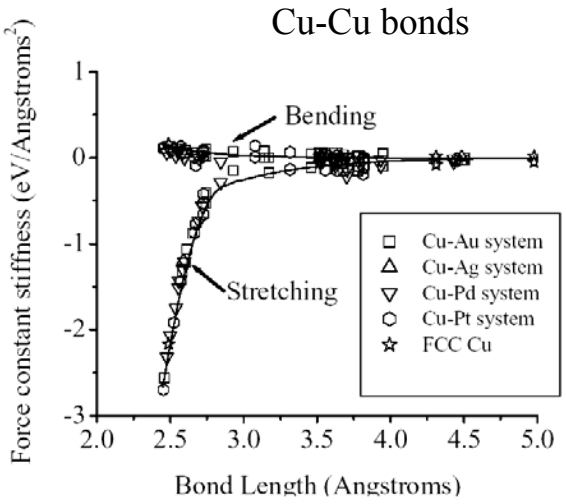
Relationship holds across different structures on the same lattice (here fcc is shown).

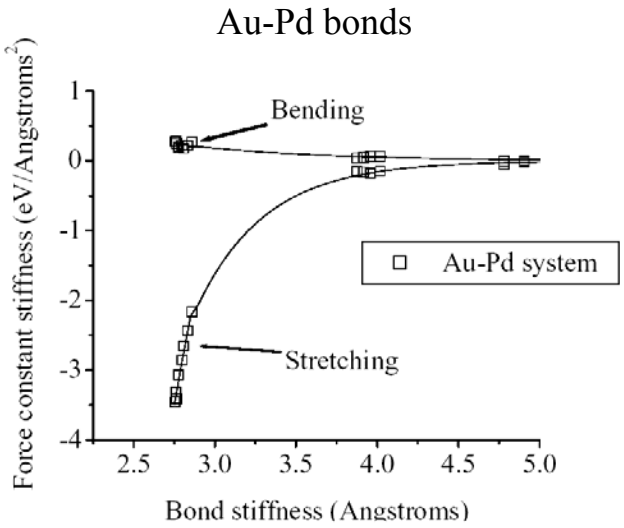
van de Walle and Ceder (2000,2002)

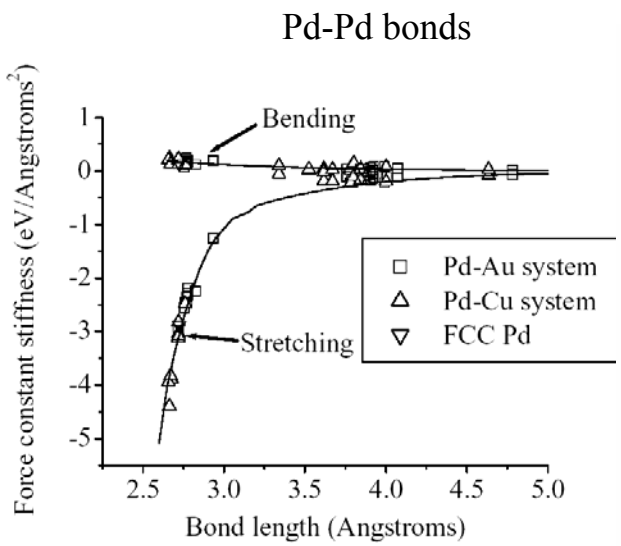
Further tests...

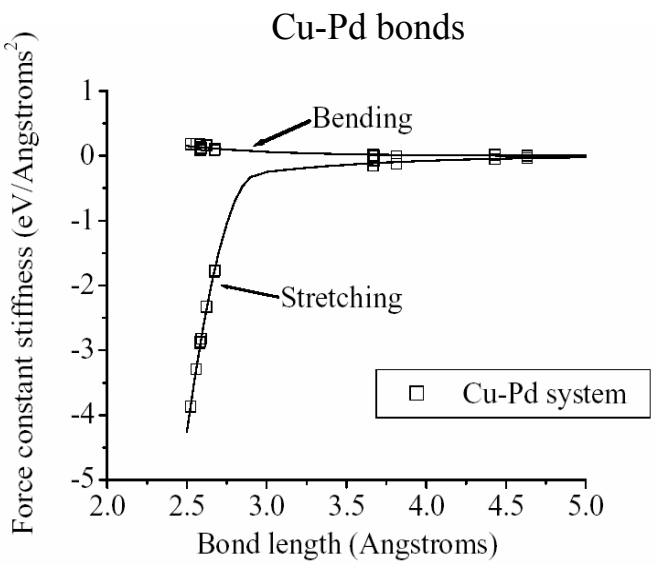
Wu, Ceder, van de Walle (2002)

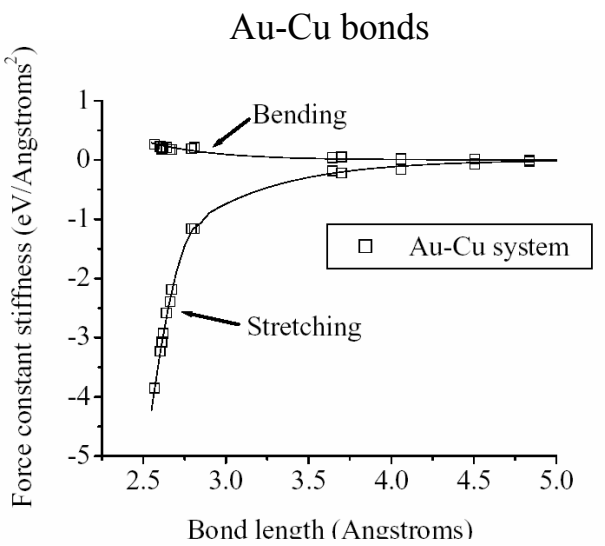






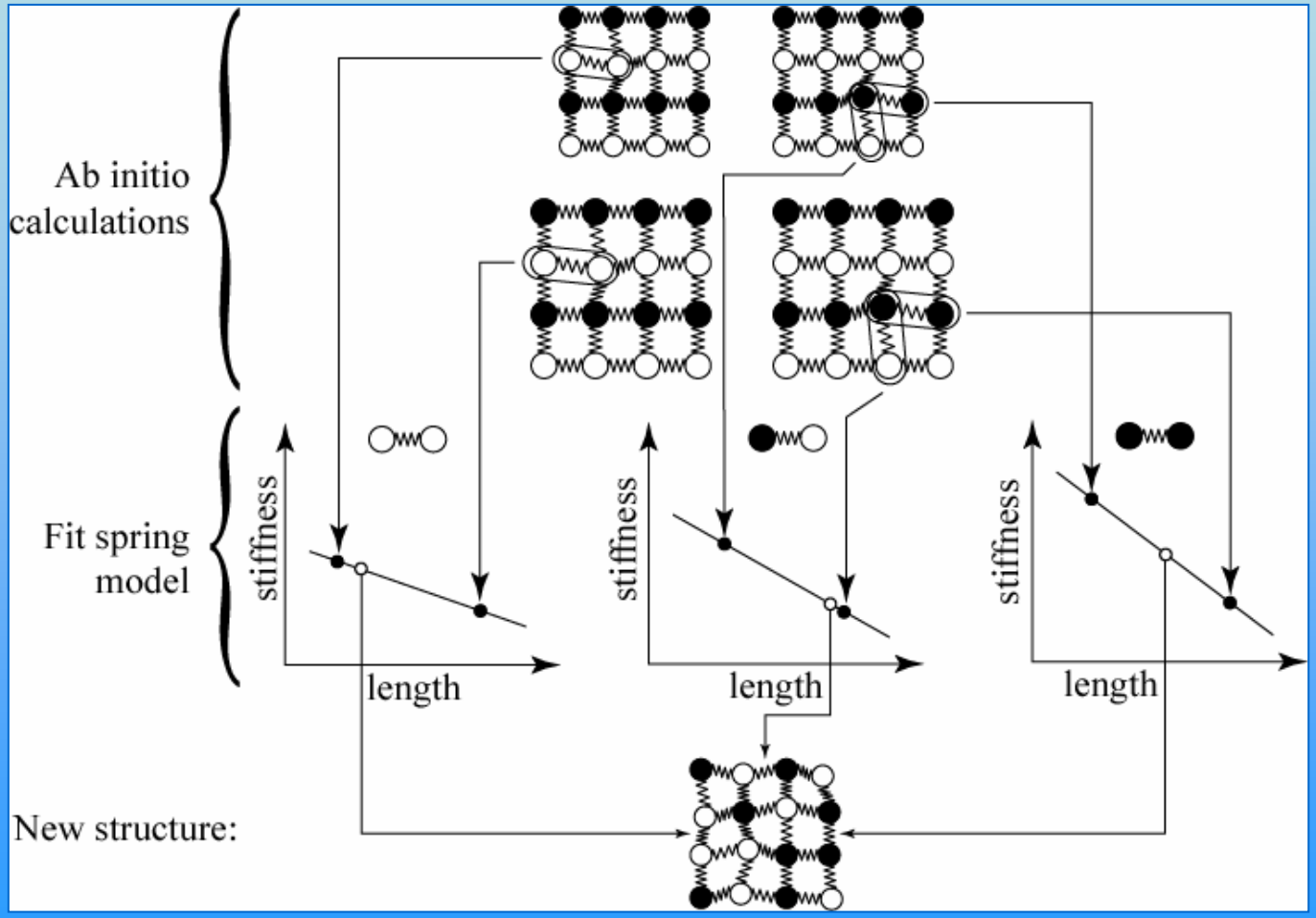






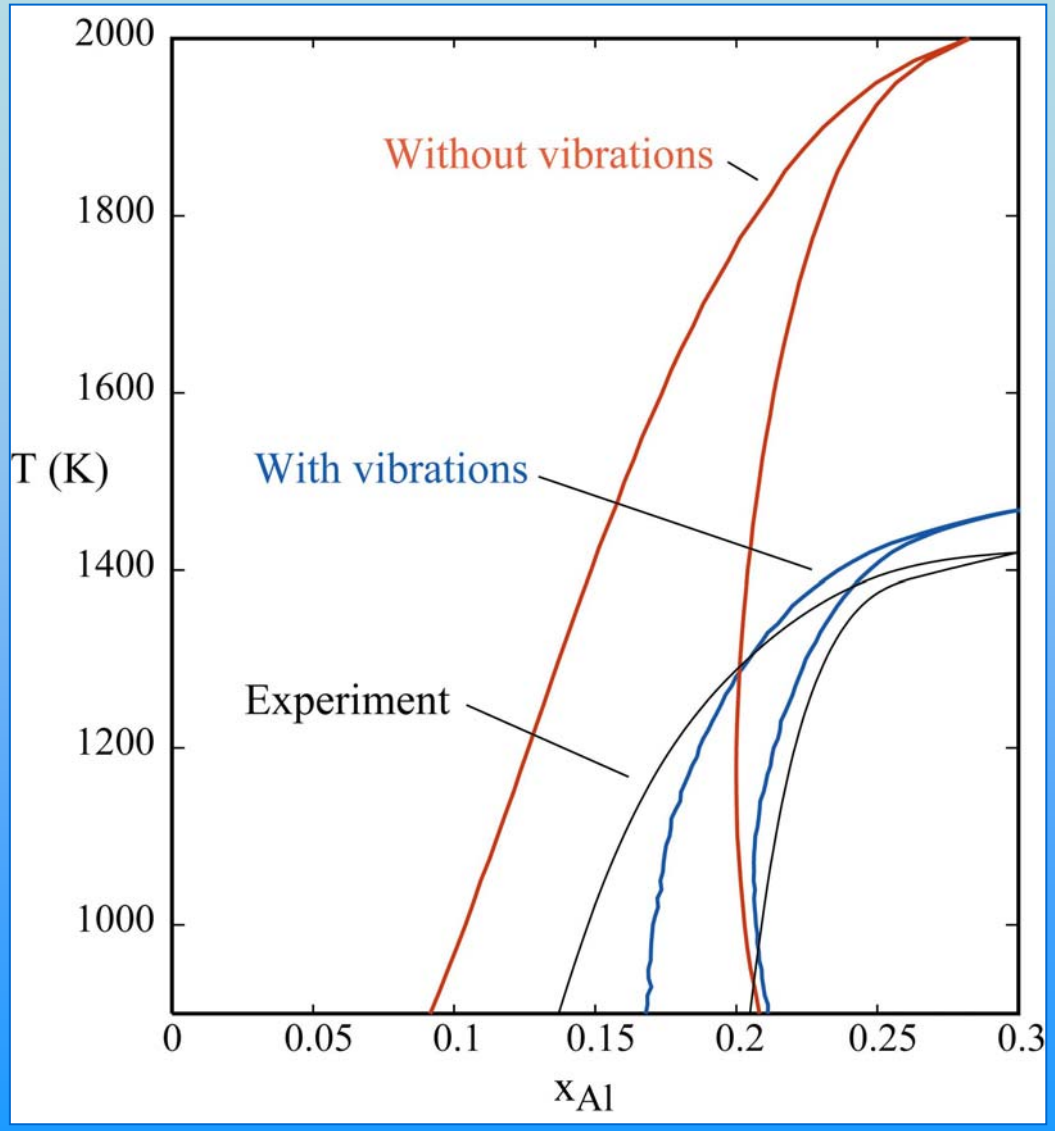
Accuracy ~ 0.03 k_B

Length-Dependent Transferable Force Constants (LDTFC)



van de Walle and Ceder (2000,2002)

Calculated Ti-Al Phase Diagram



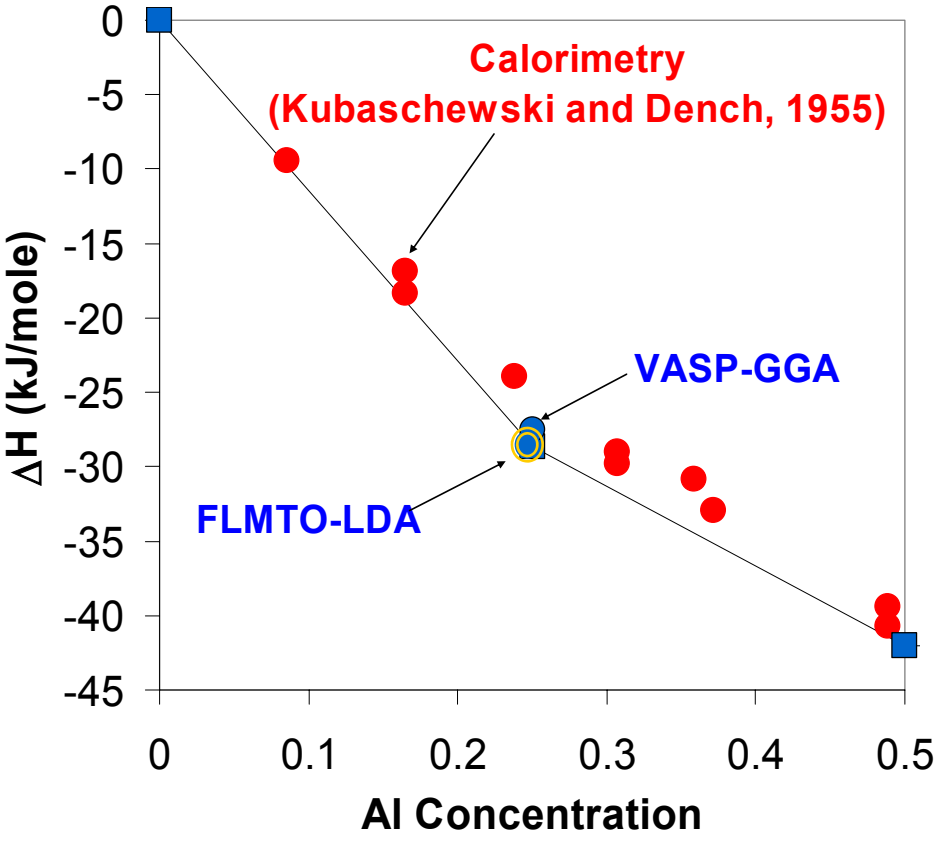
Assessed Phase Diagram:
I. Ohnuma *et al*., Acta Mater. **48**, 3113 (2000)

1st-Principles Calculations:
van de Walle and Asta

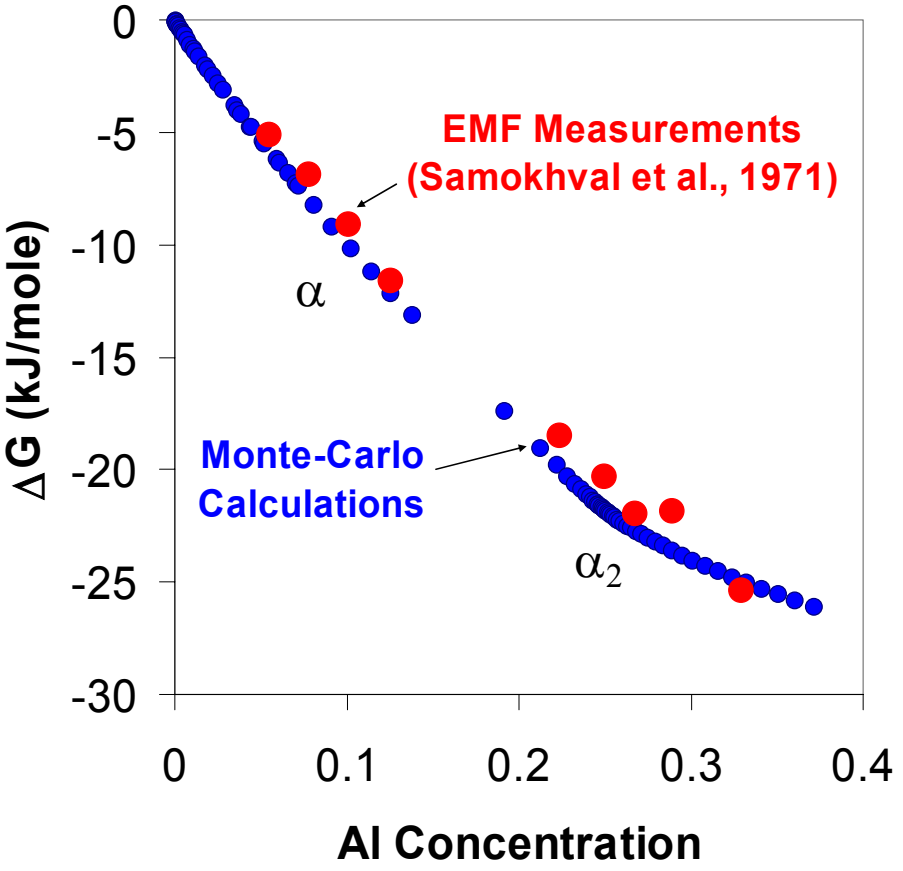
Ti-Al Thermodynamic Properties

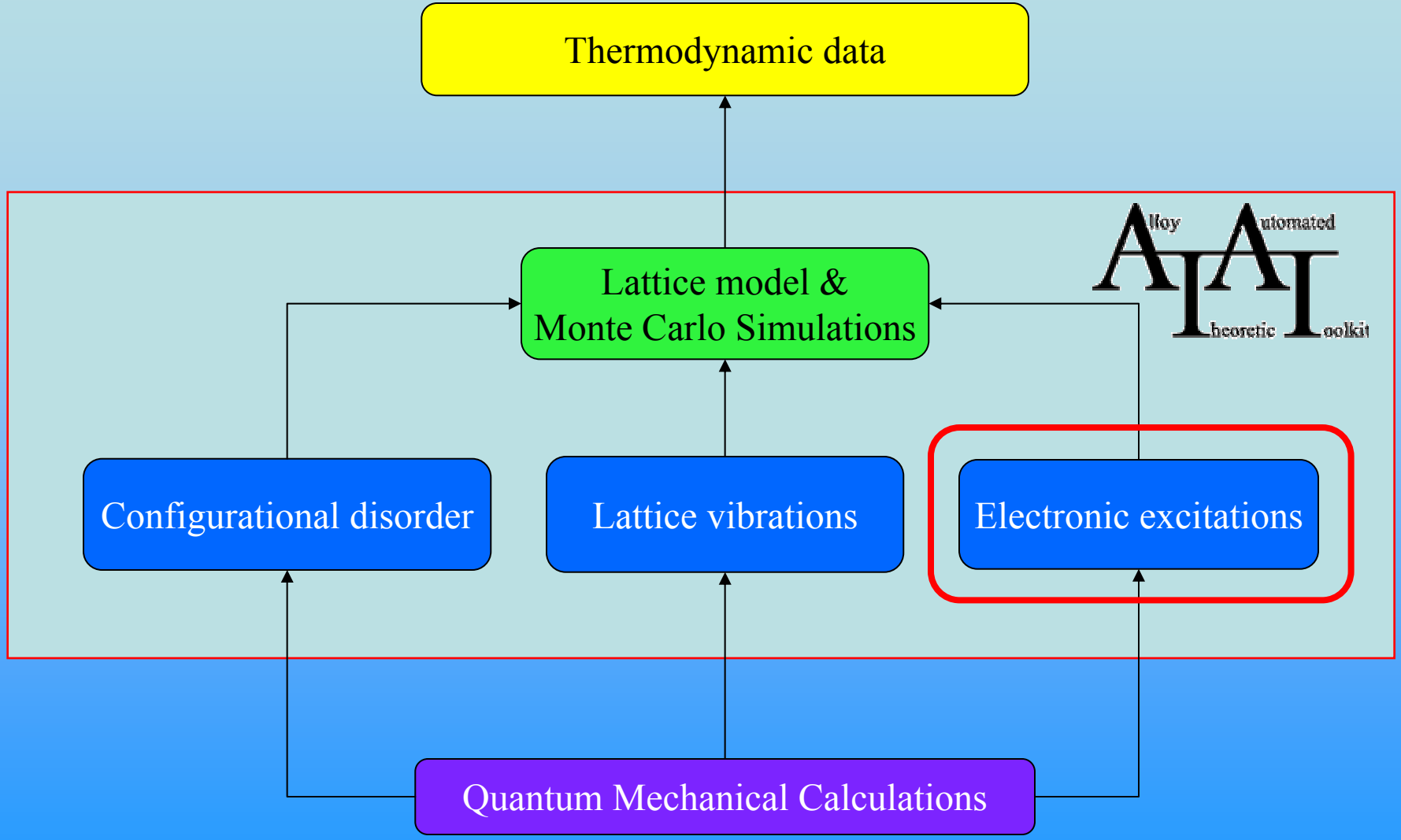
1st-Principles Calculations vs. Measurements

Heats of Formation



Gibbs Free Energies (T=960 K)




Thermodynamic data
Lattice model &
Monte Carlo Simulations
Alloy Automated
Theoretic Toolkit
Configurational disorder
Lattice vibrations
Electronic excitations
Quantum Mechanical Calculations

Electronic Excitations

Finite-temperature DFT

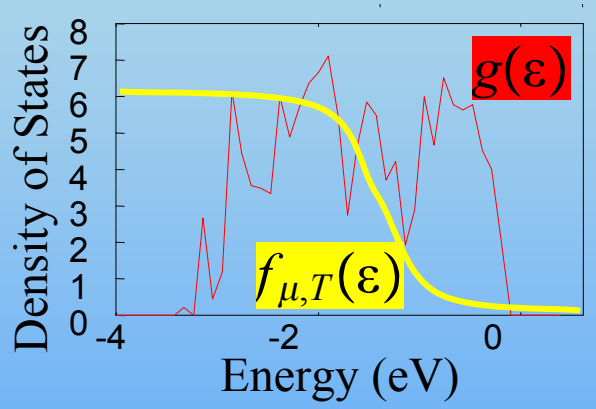
T-independent DOS and charge density

Advantage: Get F_{elec} "for free"

Electronic DOS

Fermi-Dirac Distribution

Electronic Free energy



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

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

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

Cluster expansion: $F(\sigma_1,\ldots,\sigma_n) = \sum_\alpha J_\alpha(T)\sigma_\alpha$

Or: any other model of electronic entropy

Outline

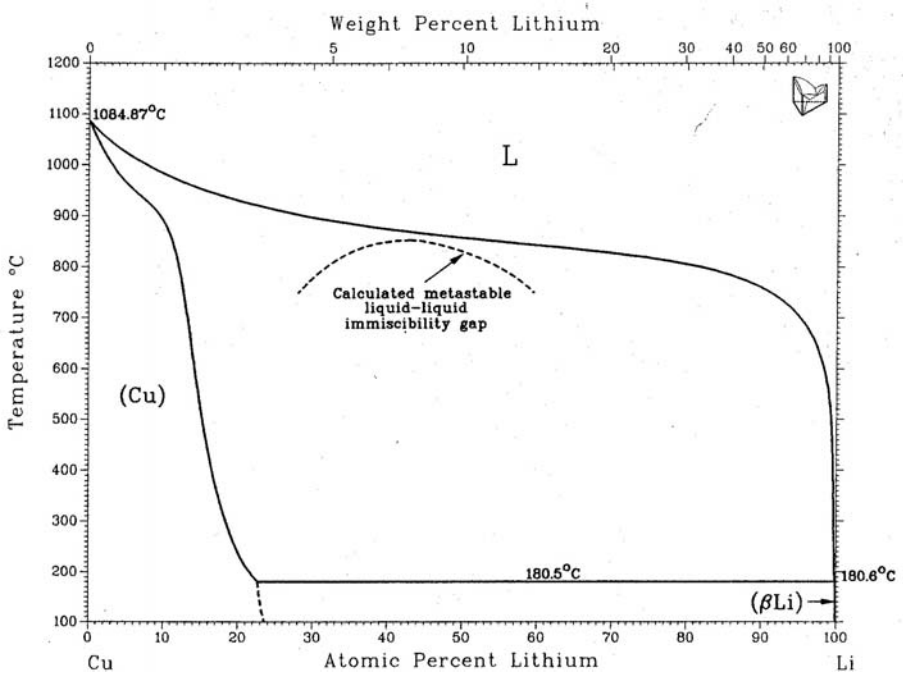
- Example of *ab initio* calculations
- Why *ab initio* Thermodynamics?
- Methods
- Applications

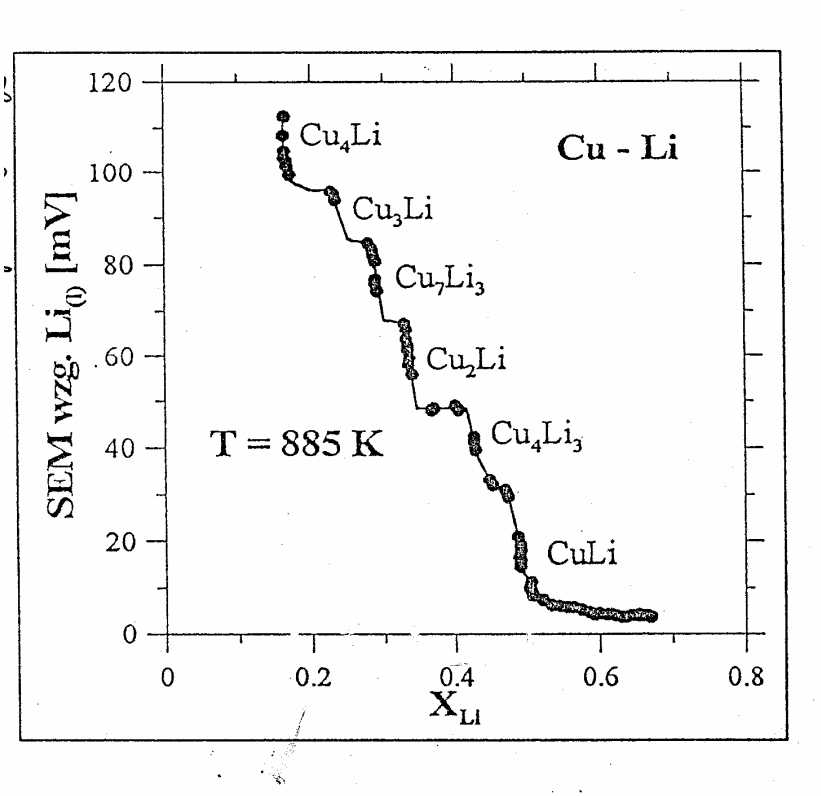
Ordering in the Cu-Li system?

Widely used assessments

do not include ordered phases

(Pelton (1986), Saunders (1998)).





Evidence from EMF measurements

Ordered Cu_4Li phase also suggested by

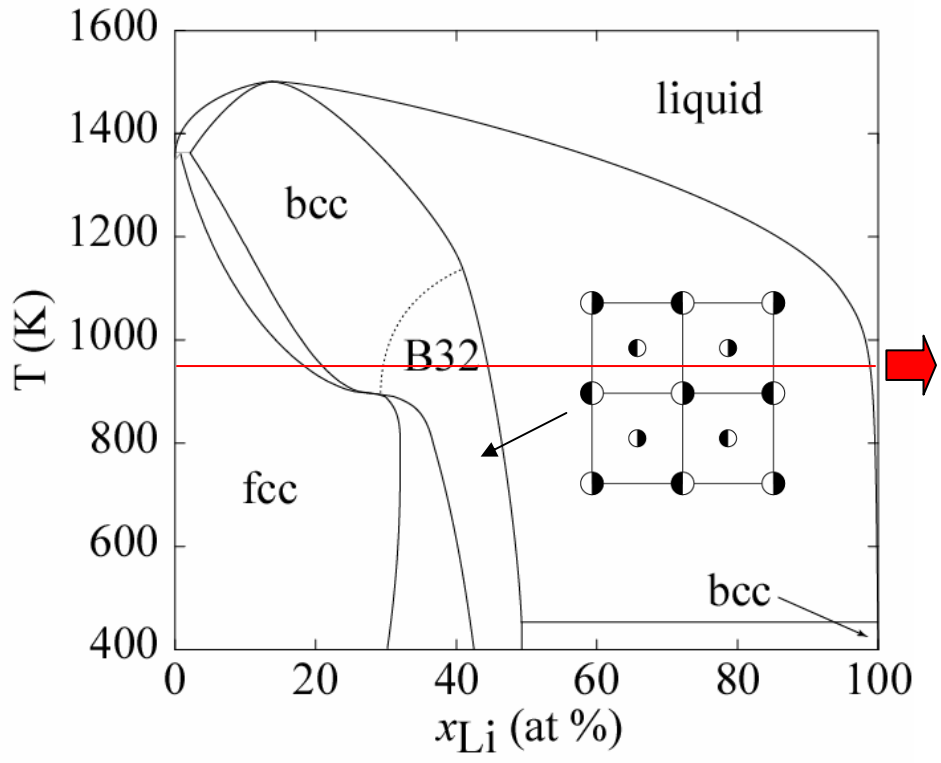
Borgsttedt & Gumiński (1996),

Krauss, Mendelson, Gruen, *et al.* (1986),

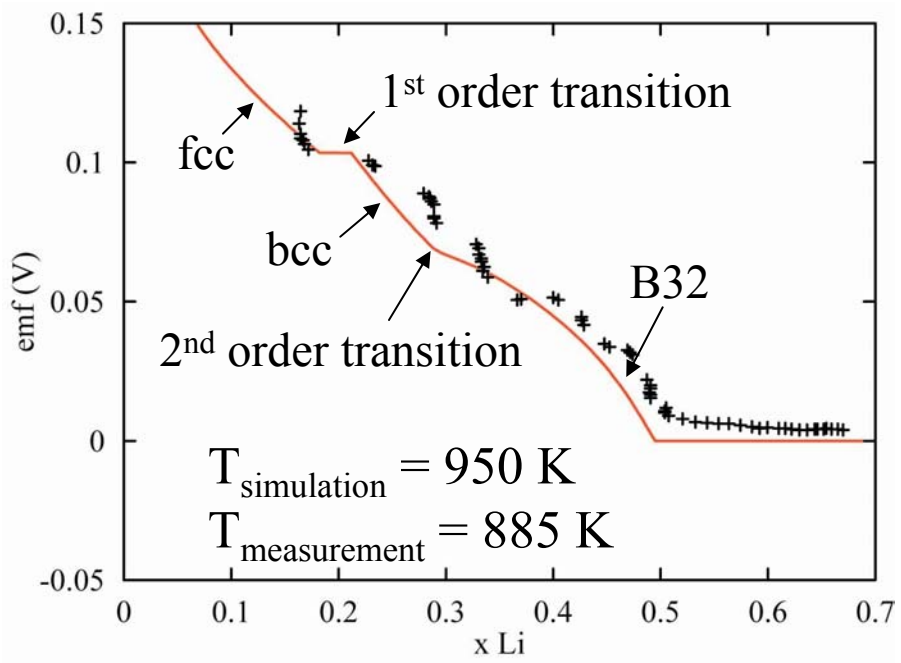
Old & Trawena (1981).

Calculated Thermodynamic data for Cu-Li system

Phase diagram

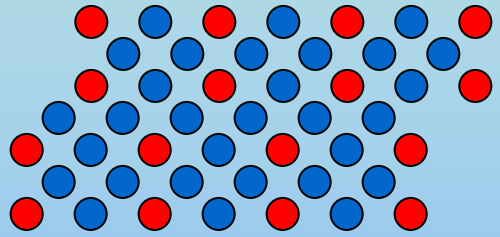


Electromotive Force (EMF)

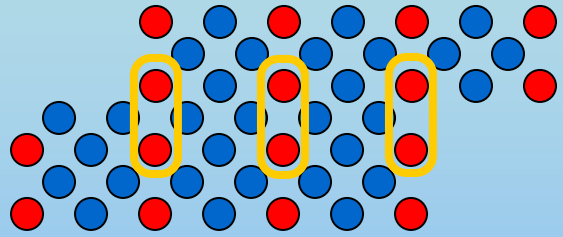


2 adjustable parameters:
$T_{simulation}$ + chemical potential of Li (liq)

Antiphase Boundary

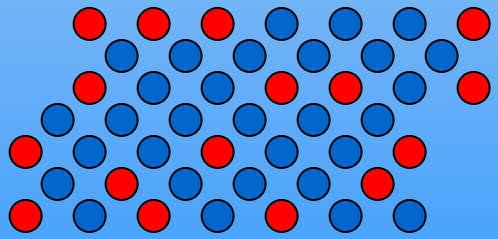


after passage of 1 dislocation

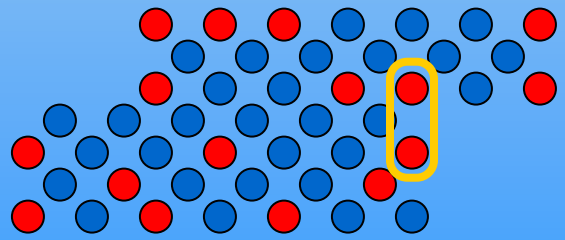


after passage of 2 dislocations

Diffuse Antiphase Boundary



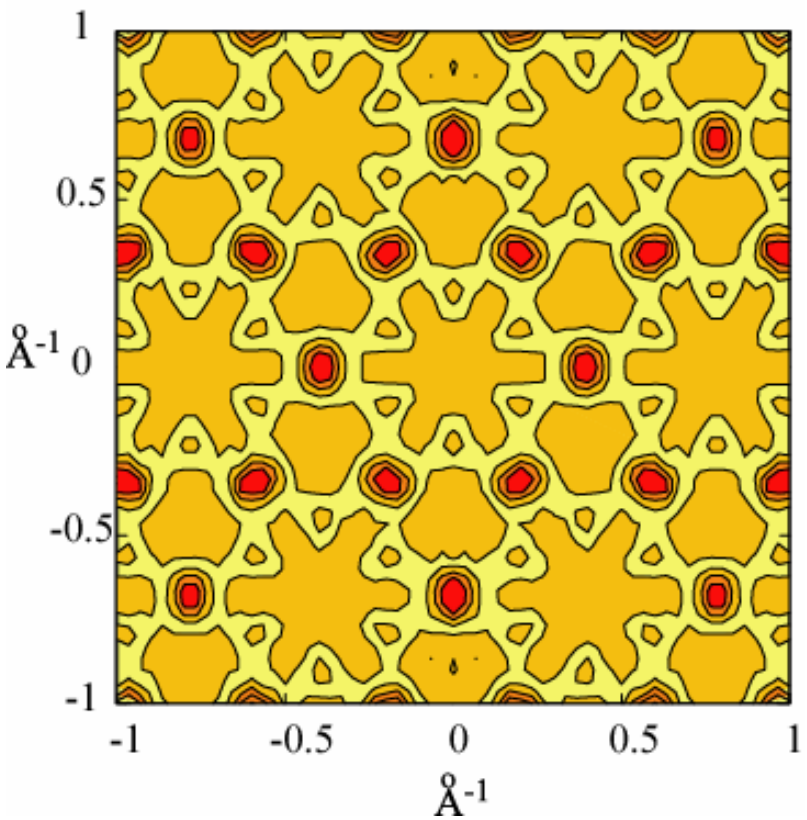
after passage of 1 dislocation



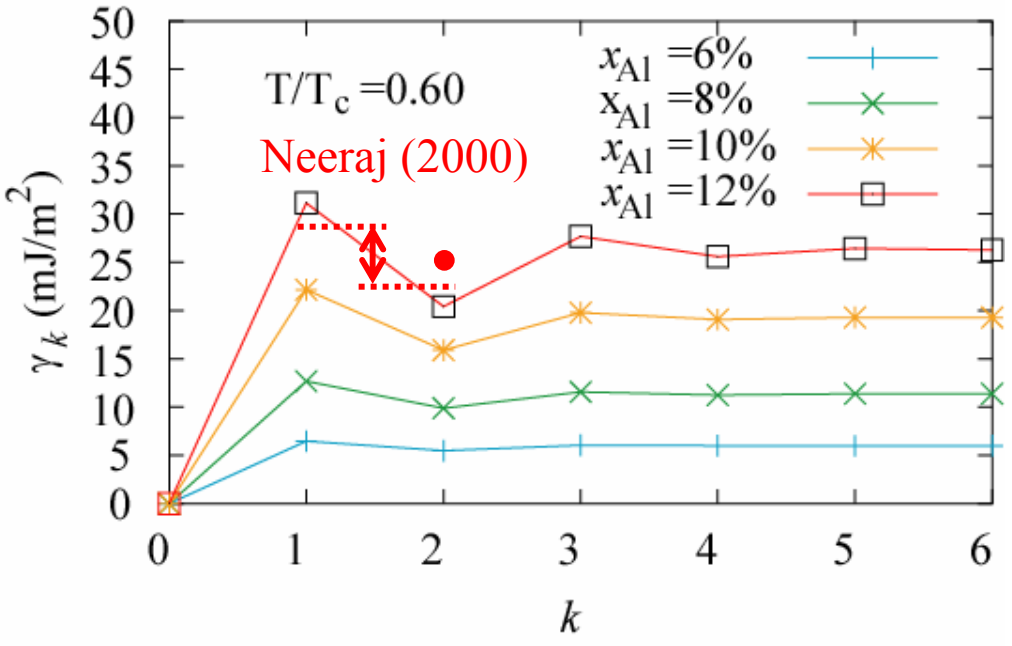
after passage of 2 dislocations

Creation of a plane with easy dislocation motion:
Work softening

Short-range order and diffuse antiphase boundary energy calculations

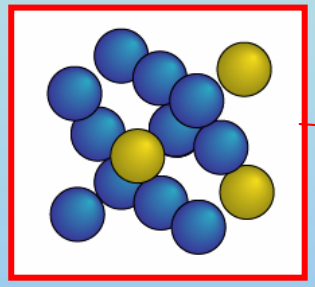


Calculated diffuse X-ray scattering in Ti-Al hcp solid-solution

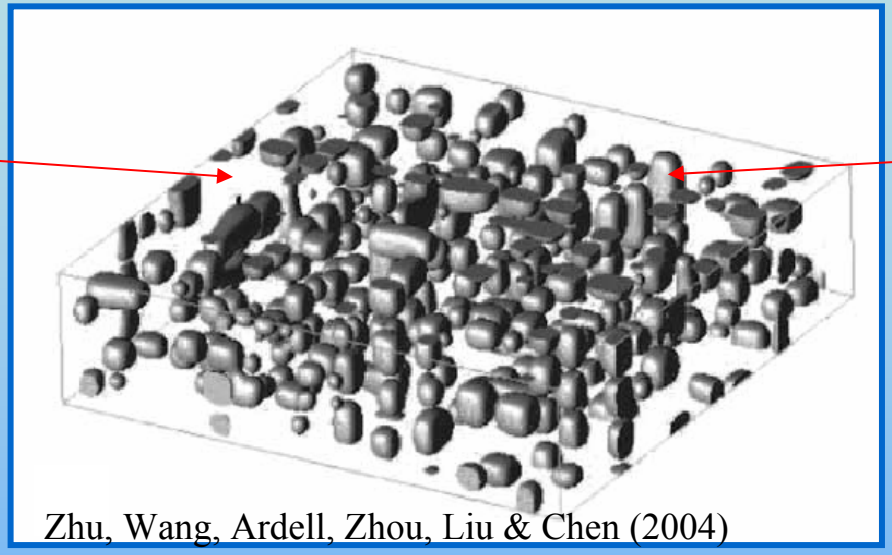


Energy cost of creating a diffuse anti-phase boundary in a Ti-Al hcp short-range ordered alloy by sliding *k* dislocations

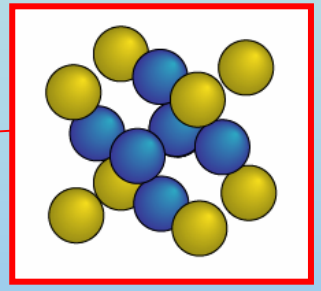
Phase Field Modeling of Ni Al System



Ni-rich fcc
solid solution



Zhu, Wang, Ardell, Zhou, Liu & Chen (2004)



$L1_2$ Ni_3Al

Free energy:

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

Thermodynamic term

phase fields

"gradient energy" term

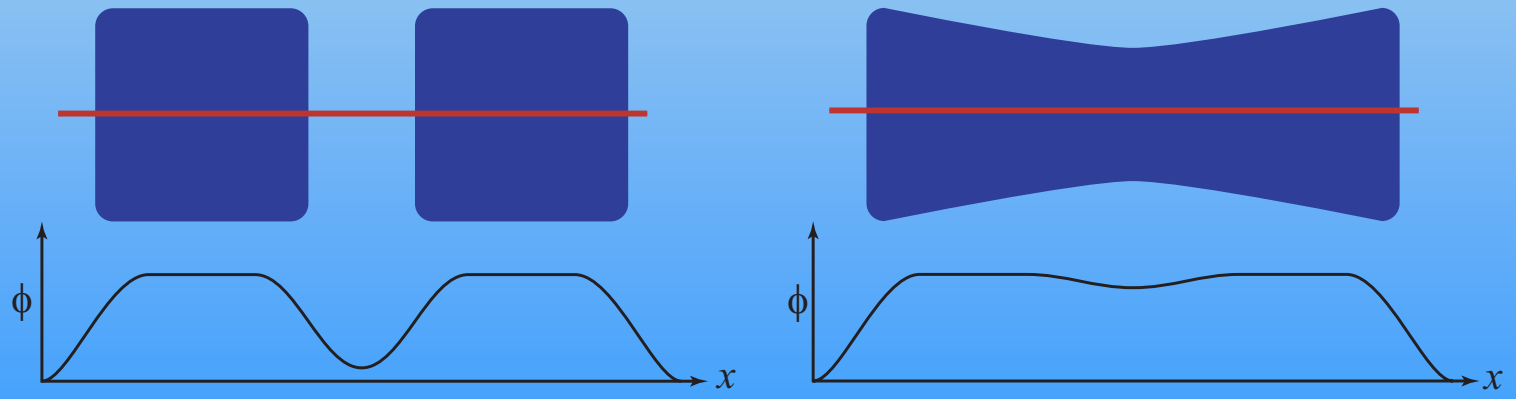
Input parameters needed: Bulk thermodynamic data, Kinetic coefficients,
Interfacial free energy,
Interface width

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.

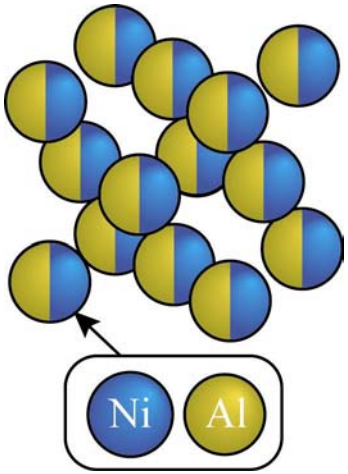


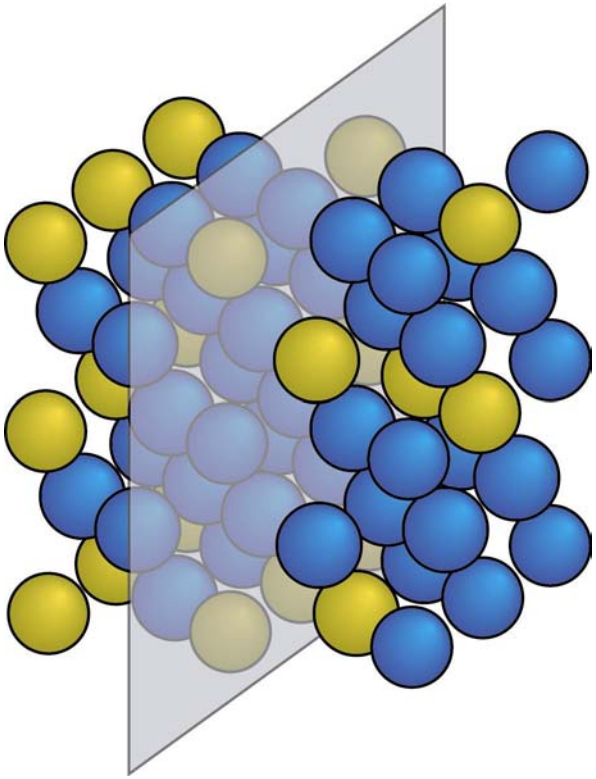
Wider Interface → Increased coalescence

Ni_3Al/Ni (001)

Diffuse Coherent Interface

Lattice model



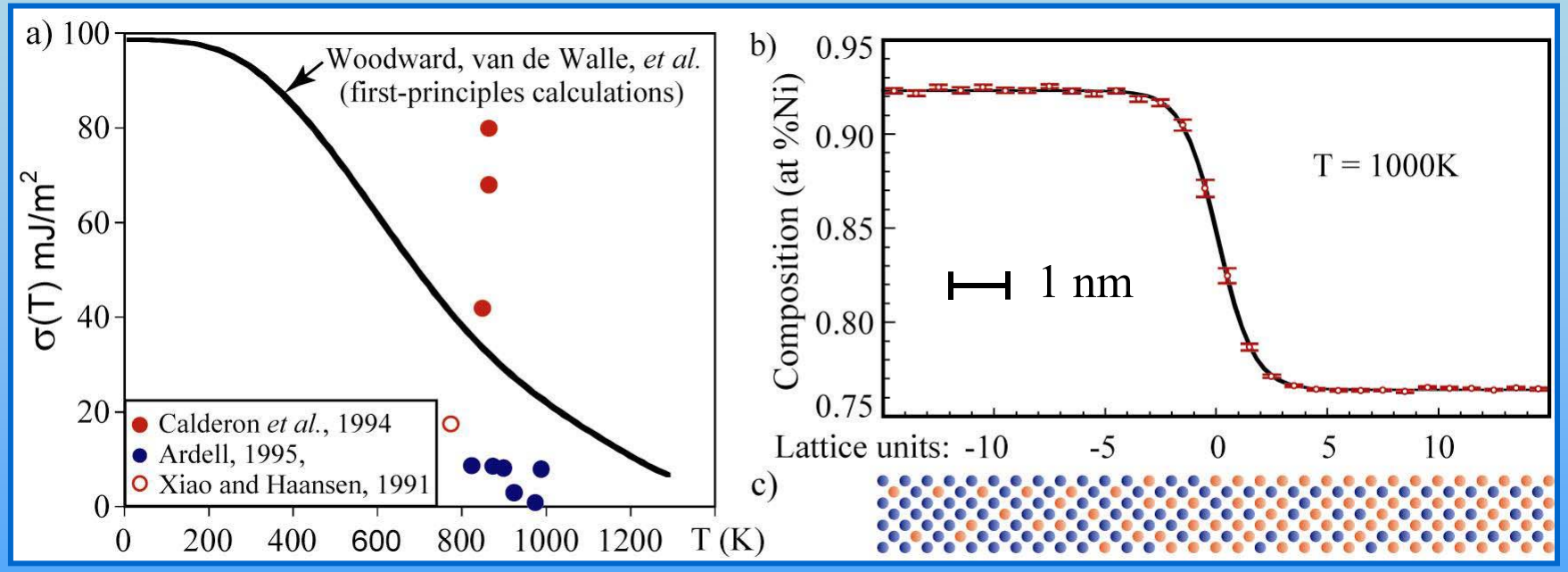


Interfacial Thermodynamics

Ni_3Al/Ni (001) diffuse coherent interface

Interfacial free energy

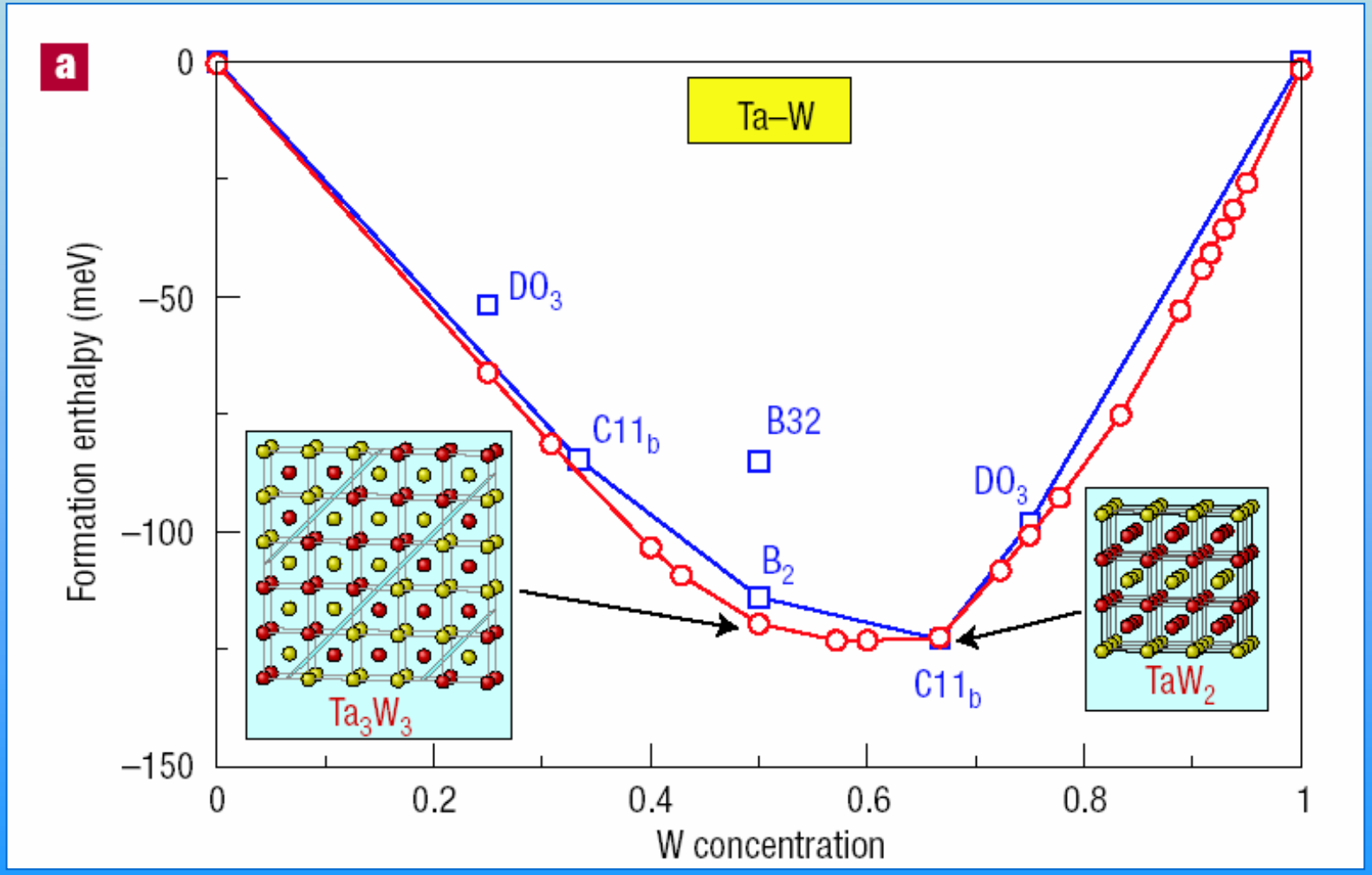
Interface width



Important input for mesoscale phase field simulations:

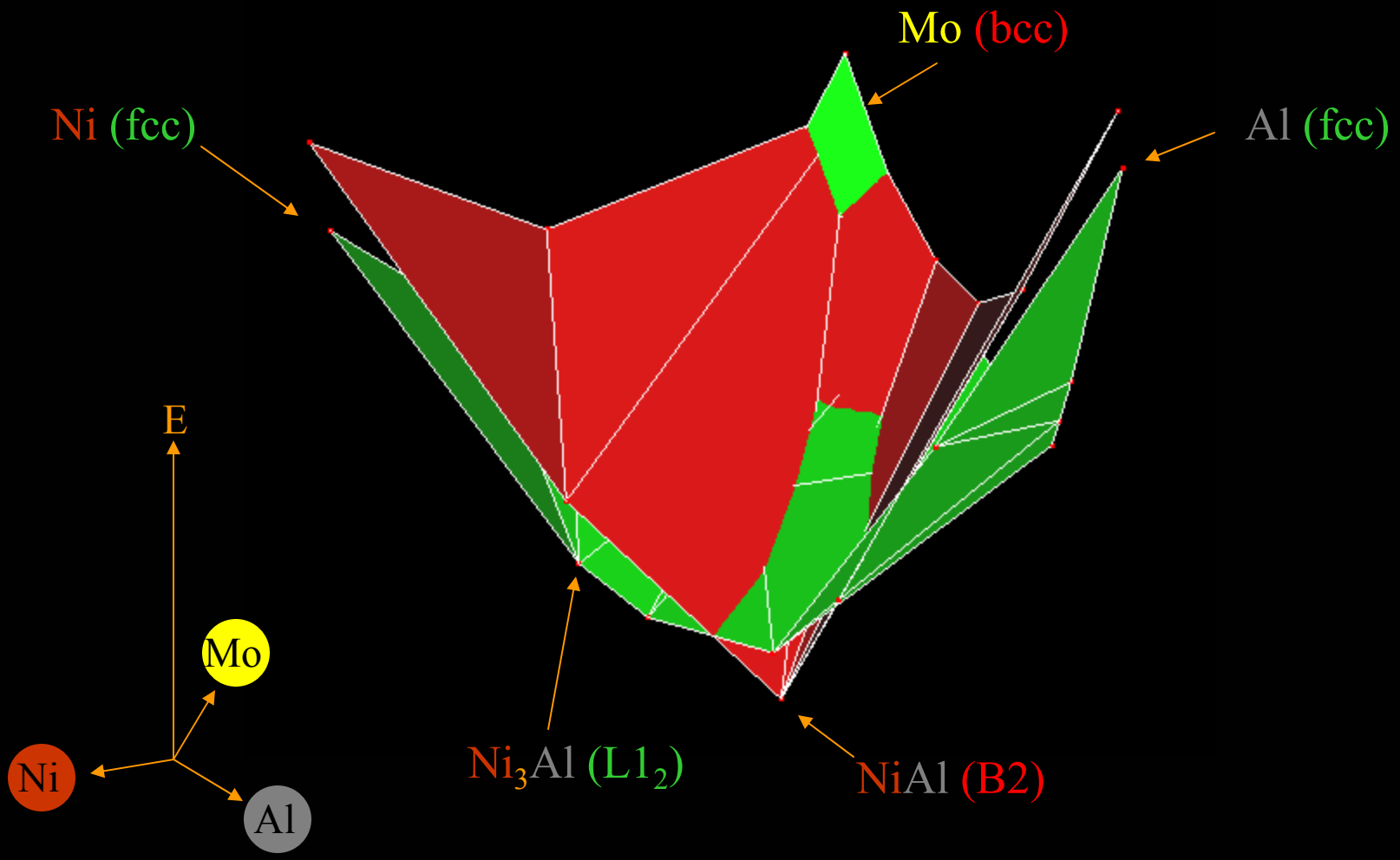
provides the “gradient energy” term

Search for new compounds



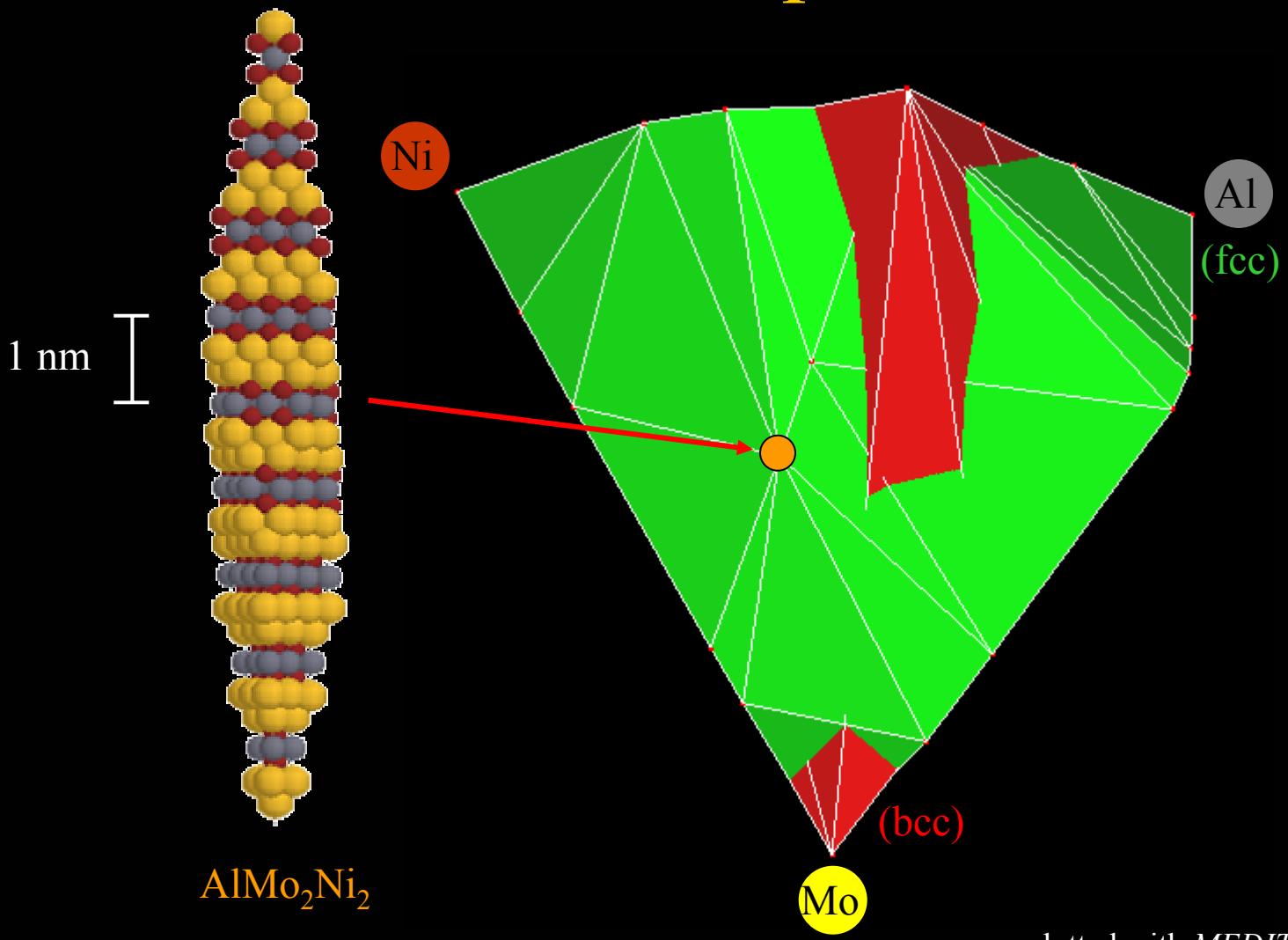
Hart, Blum, Walorski & Zunger, *Nat. Mat.* **4**, 391 (2005)

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



plotted with *MEDIT,* INRIA-Rocquencourt.

Predicted Nano-Structured Compound



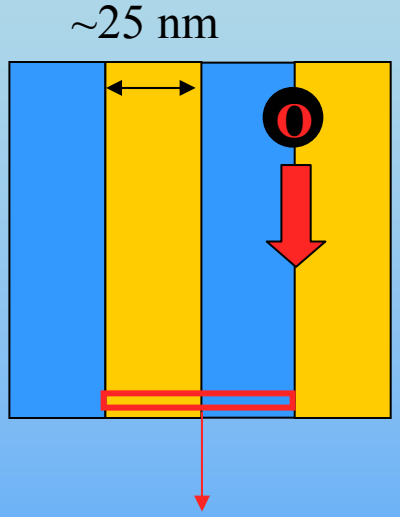
plotted with *MEDIT,* INRIA-Rocquencourt.

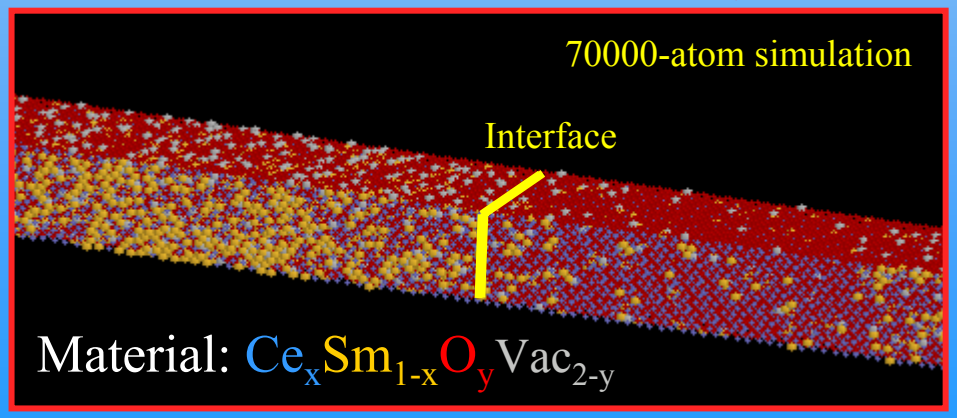
Nanostructured Electrolyte

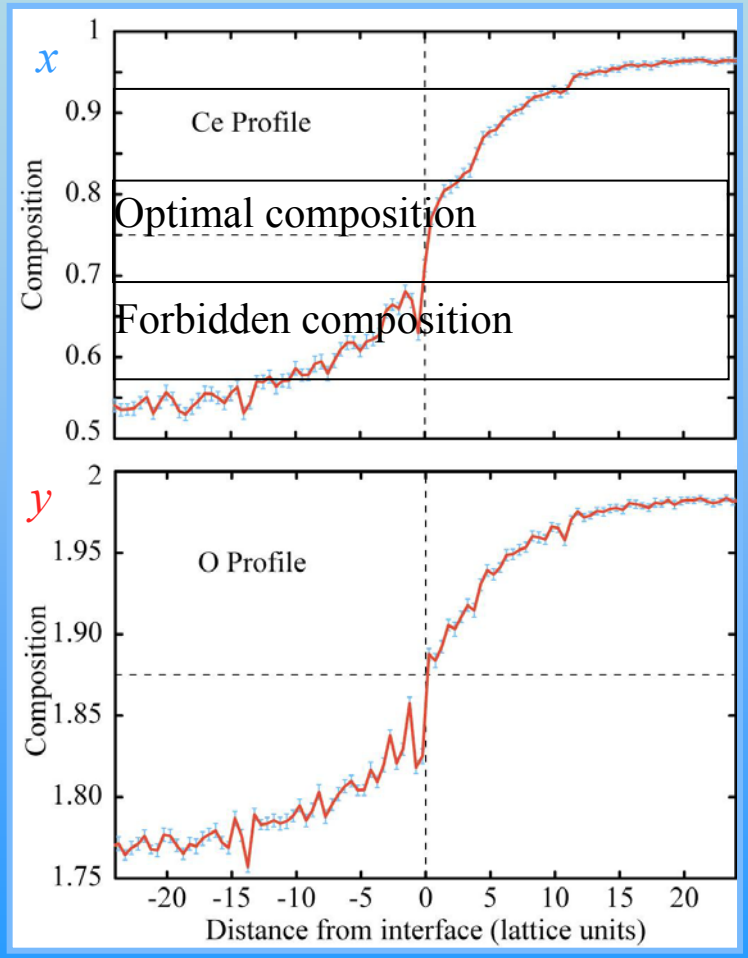
(for fuel cell applications)

$Ce_xSm_{1-x}O_y$

Superlattices

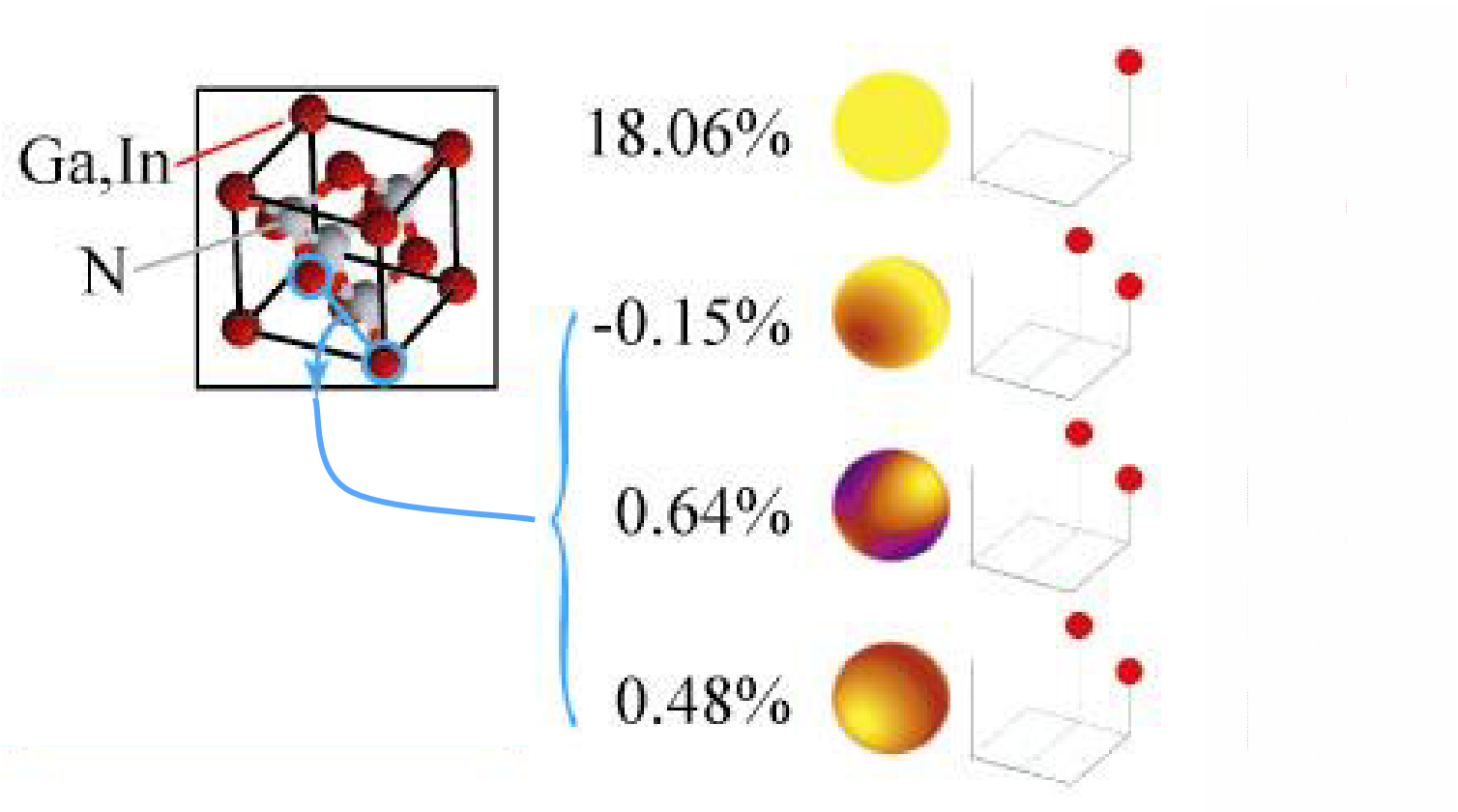






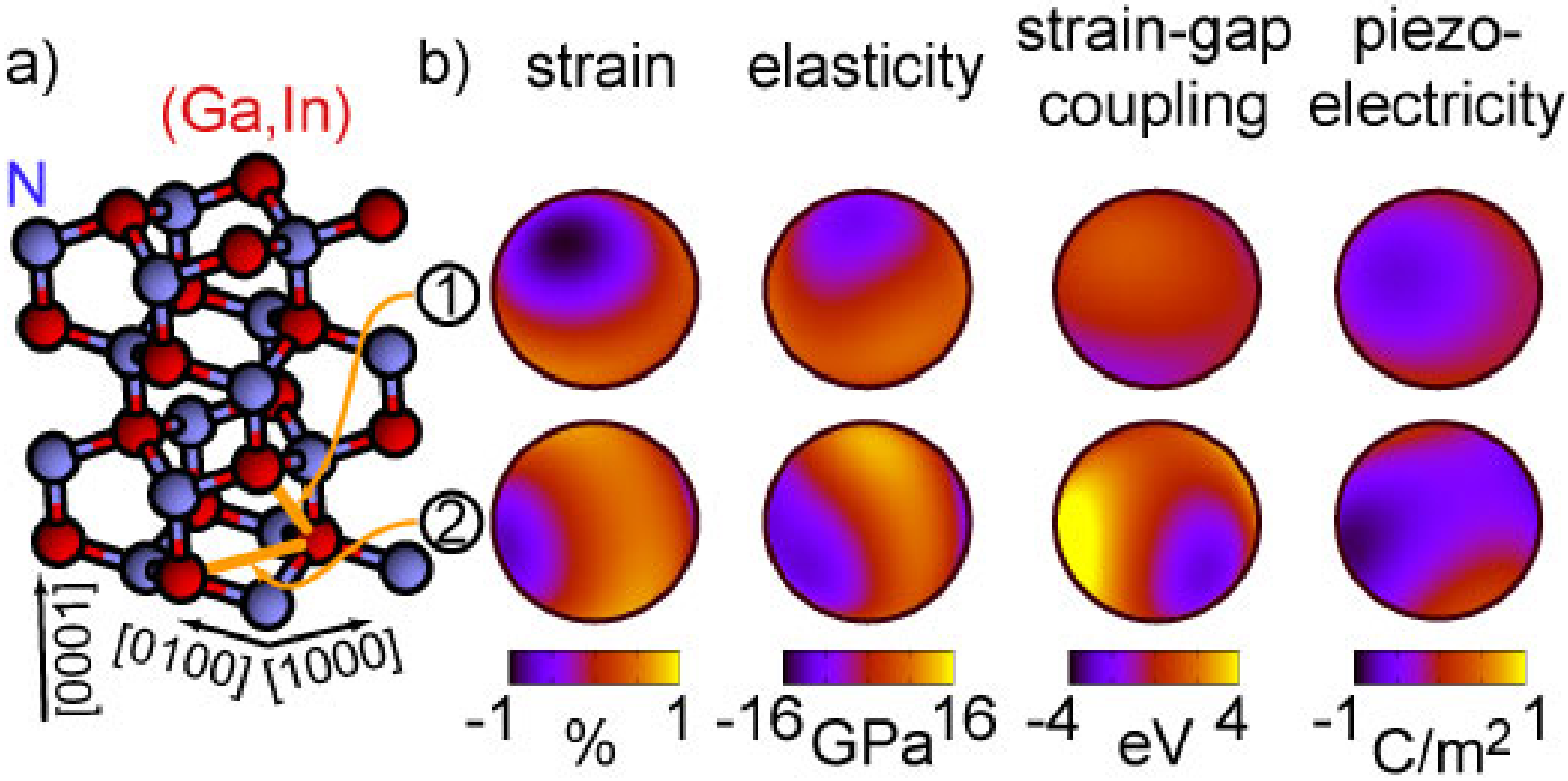
van de Walle & Ellis, Phys. Rev. Lett. **98**, 266101 (2007)

First-principles determination of Structure-Property Relationships



Example: Configuration-strain coupling

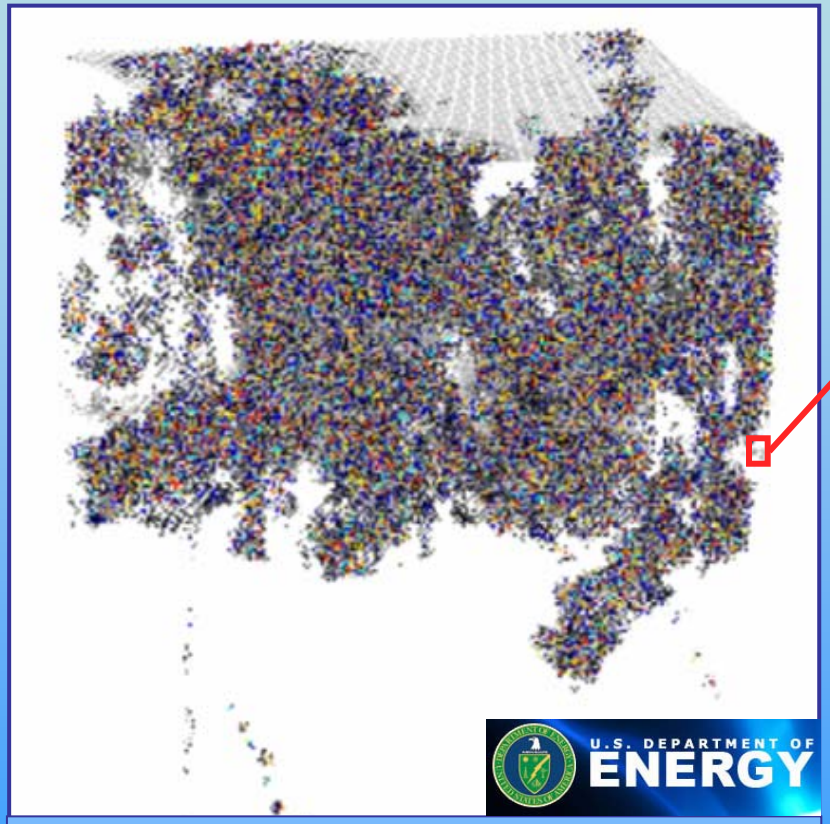
More Structure-Property Relationship!

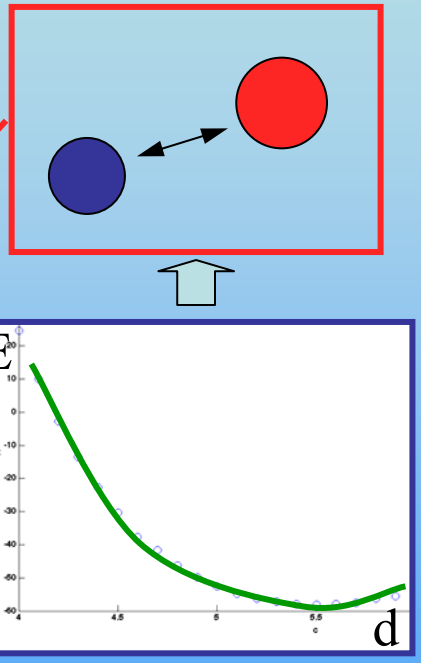


⇨ Useful input for design and optimization of optoelectronic devices

TeraGrid

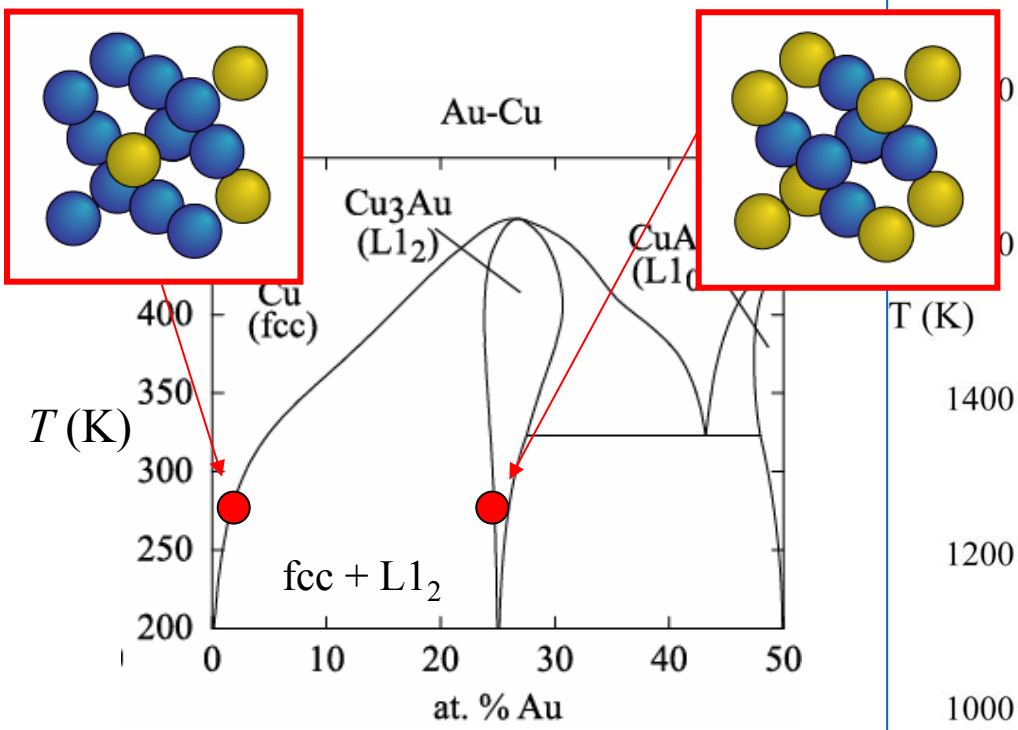
Interatomic Potential Construction from Quantum-Mechanics





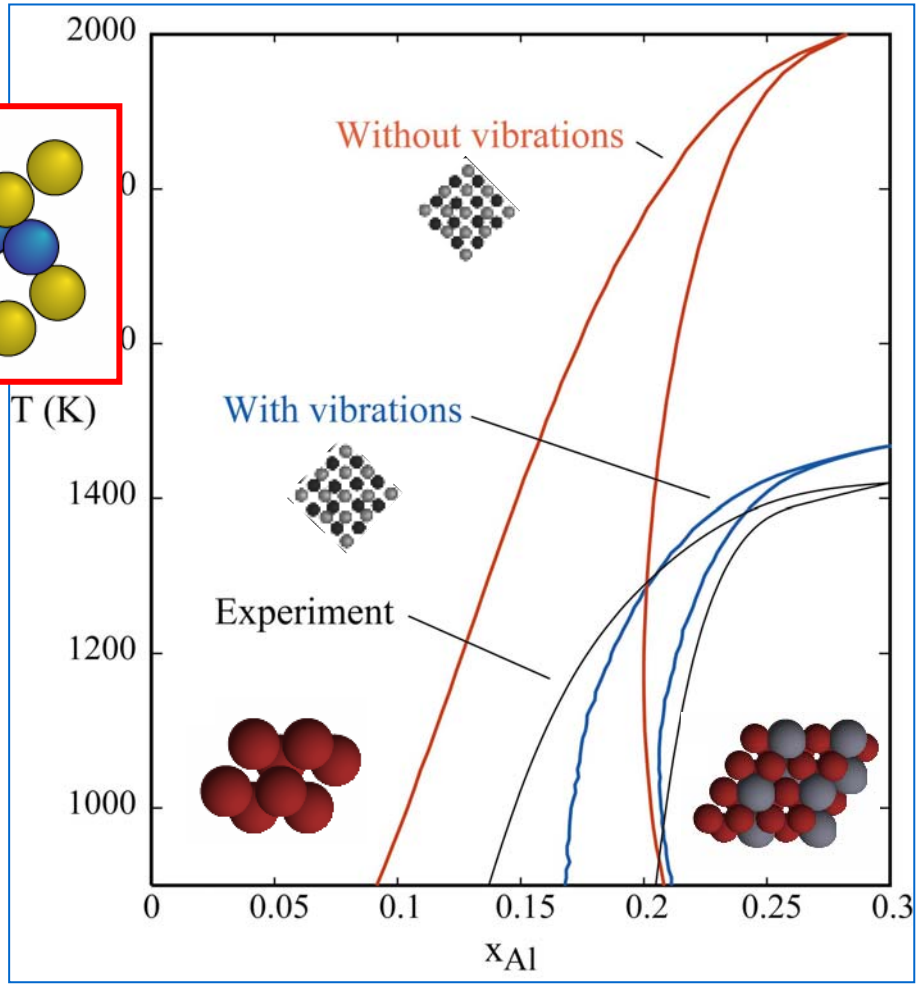
Radiation damage in nuclear fuel for advanced burner Reactors: modeling and experimental validation (PI: N. Jensen, UC Davis; Student: P. Tiwary)

Calculated phase diagrams

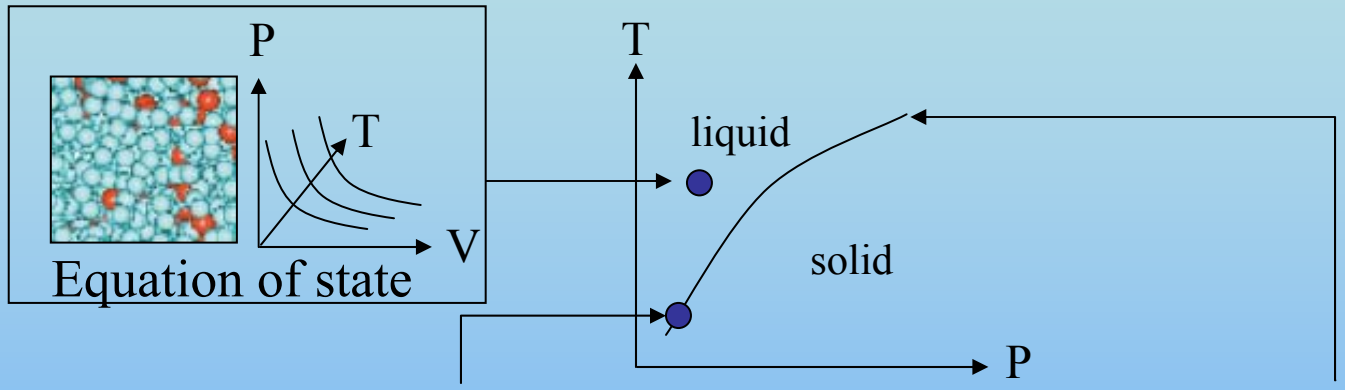


Alloy Automated Theoretic Toolkit

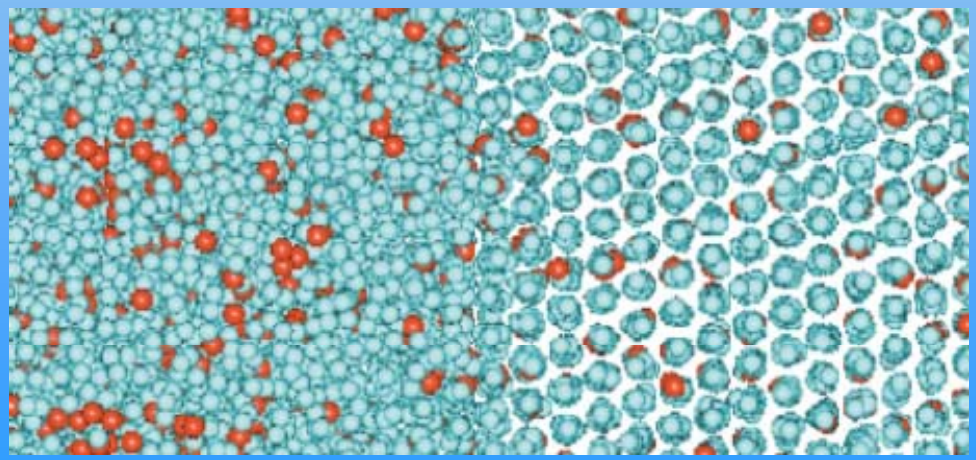
Ti-Al



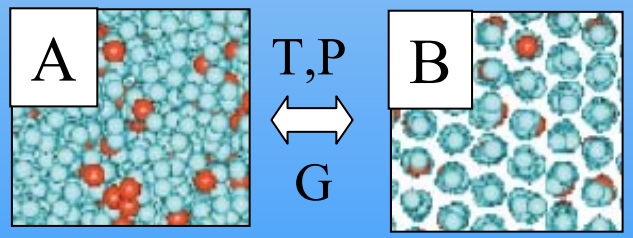
Locating Phase Transitions and Equation of State (EOS) Calculations



Phase coexistence method



Free Energy Equalization



Boundary tracing:

$$\frac{dP}{dT} = \frac{1}{T}\frac{H^B - H^A}{V_B - V_A}$$

Ramalingam, Asta, van de Walle & Hoyt, *Interface Sci.,* 10: 149, 2002

PSAAP Center for the Predictive Modeling and Simulation of High Energy Density Dynamic Response of Materials (PI: M. Ortiz, Caltech).