ATAT - A software toolkit for modeling coupled configurational and vibrational disorder in alloy systems

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Materials Science and Engineering Department

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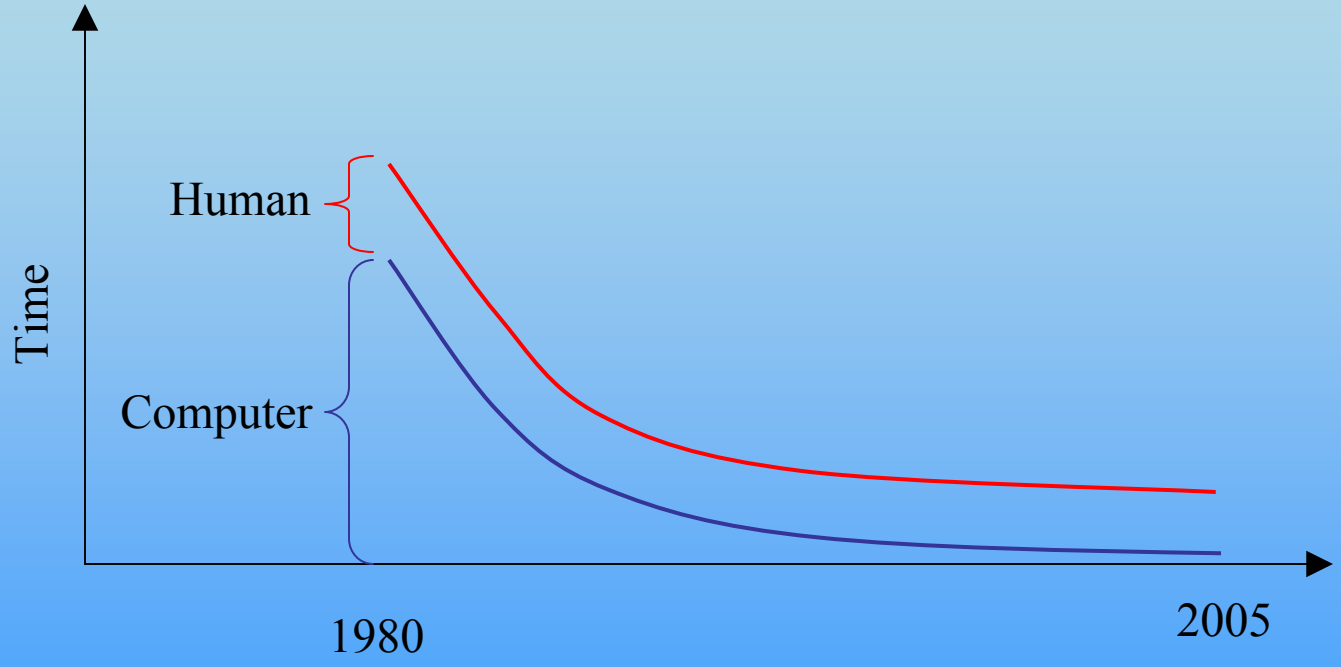
AFOSR-MEANS under grant no. F49620-01-1-0529

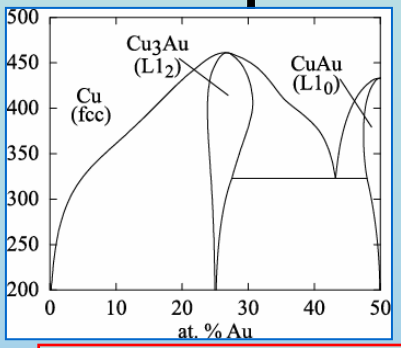
A matter of time...

Time needed to complete a given first-principles calculation



The procedure needs to be automated

First-principles Thermodynamic Calculations



Thermodynamic data

Lattice model &
Monte Carlo Simulations

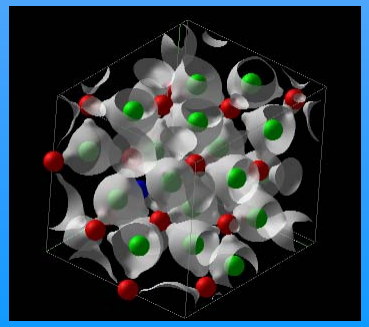
Alloy Automated
Theoretic Toolkit

Configurational disorder

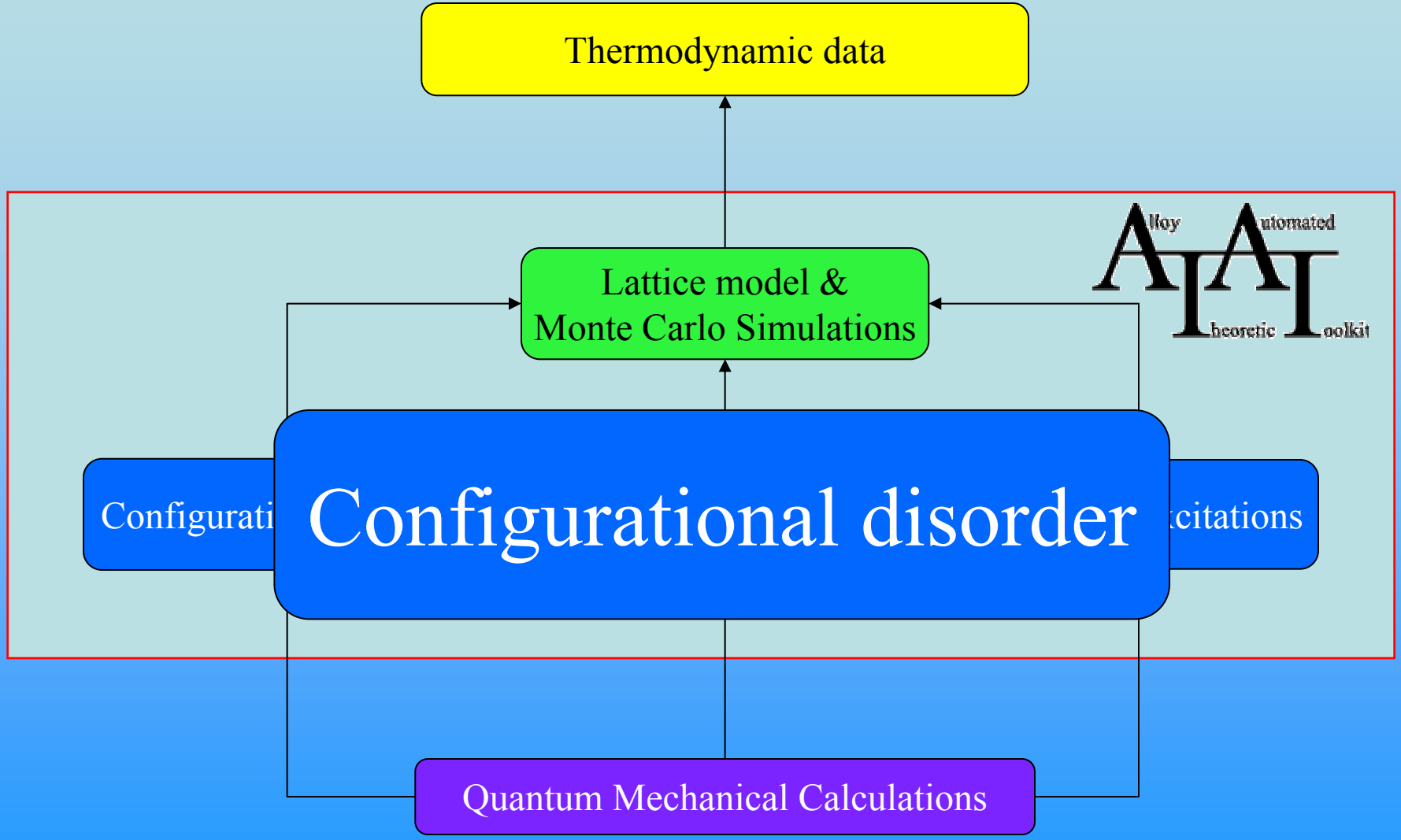
Lattice vibrations

Electronic excitations

Quantum Mechanical Calculations



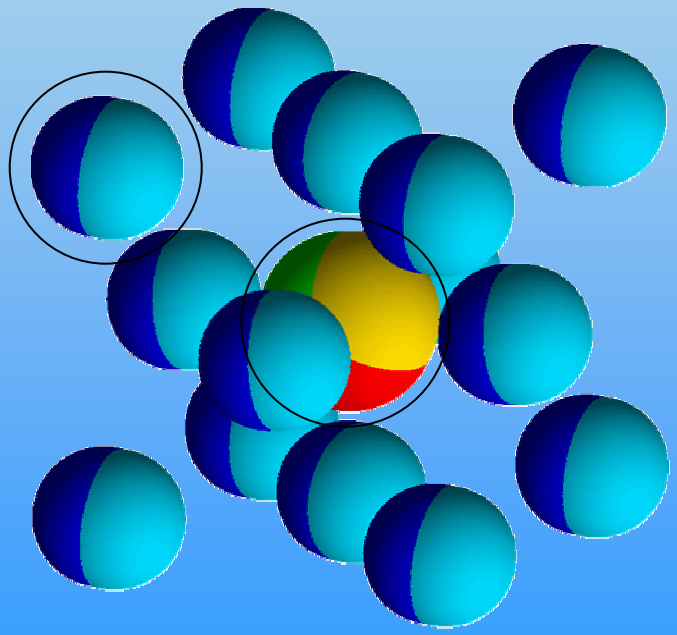
http://cms.northwestern.edu/atat


Thermodynamic data
Lattice model &
Monte Carlo Simulations
Configurati
Configurational disorder
citations
Quantum Mechanical Calculations

Coupled Sublattices Multicomponent Cluster Expansion

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

$\sigma_\alpha = \prod_i \Gamma(n_i, \alpha_i, \sigma_i)$ (# components)



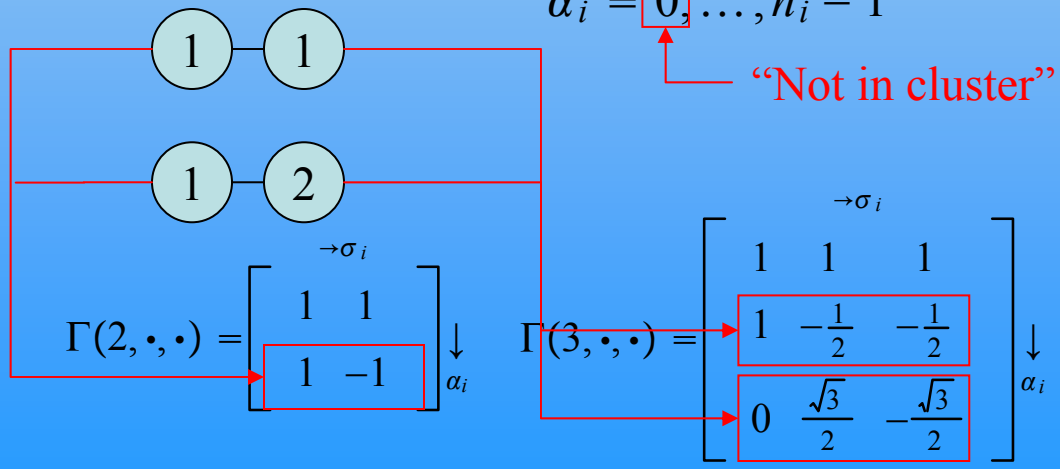
Example: binary fcc sublattice with ternary octahedral sites sublattice

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

"Decorated" clusters: $\alpha = (\alpha_1, \ldots, \alpha_n)$

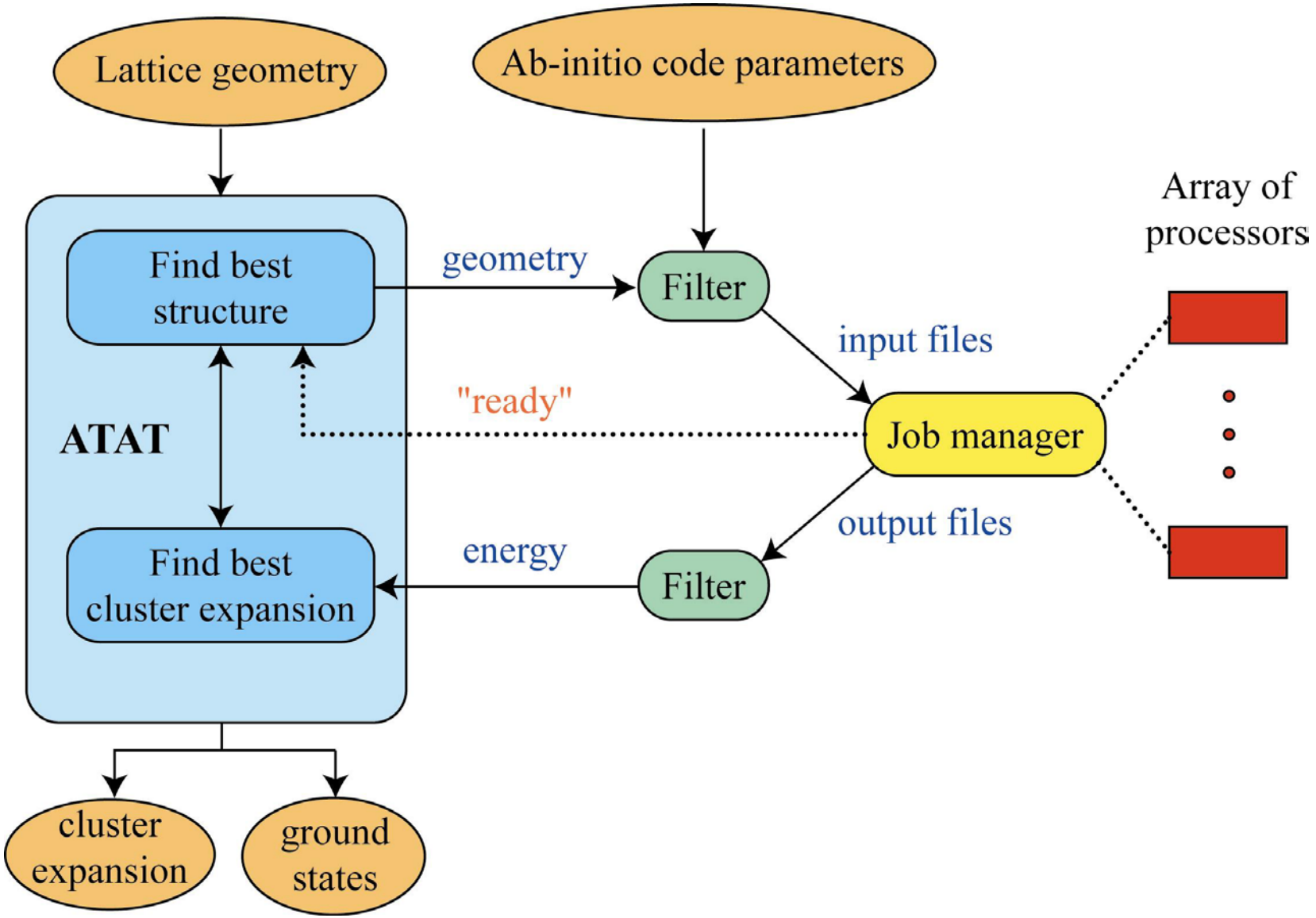
$\alpha_i = 0, \ldots, n_i - 1$

"Not in cluster"

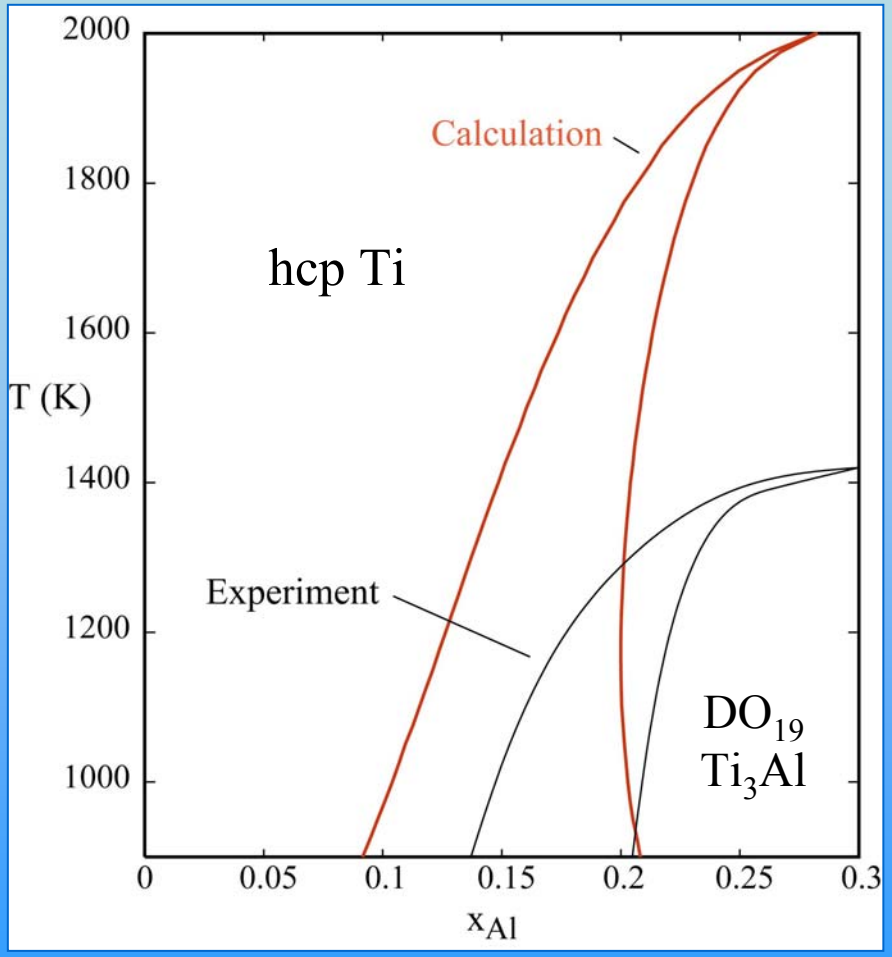


Sanchez, Ducastelle and Gratias (1984)
Tepesch, Garbulski and Ceder (1995)

Automated Cluster Expansion Construction



Temperature scale problem



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

Likely source of the discrepancy: Vibrational entropy.

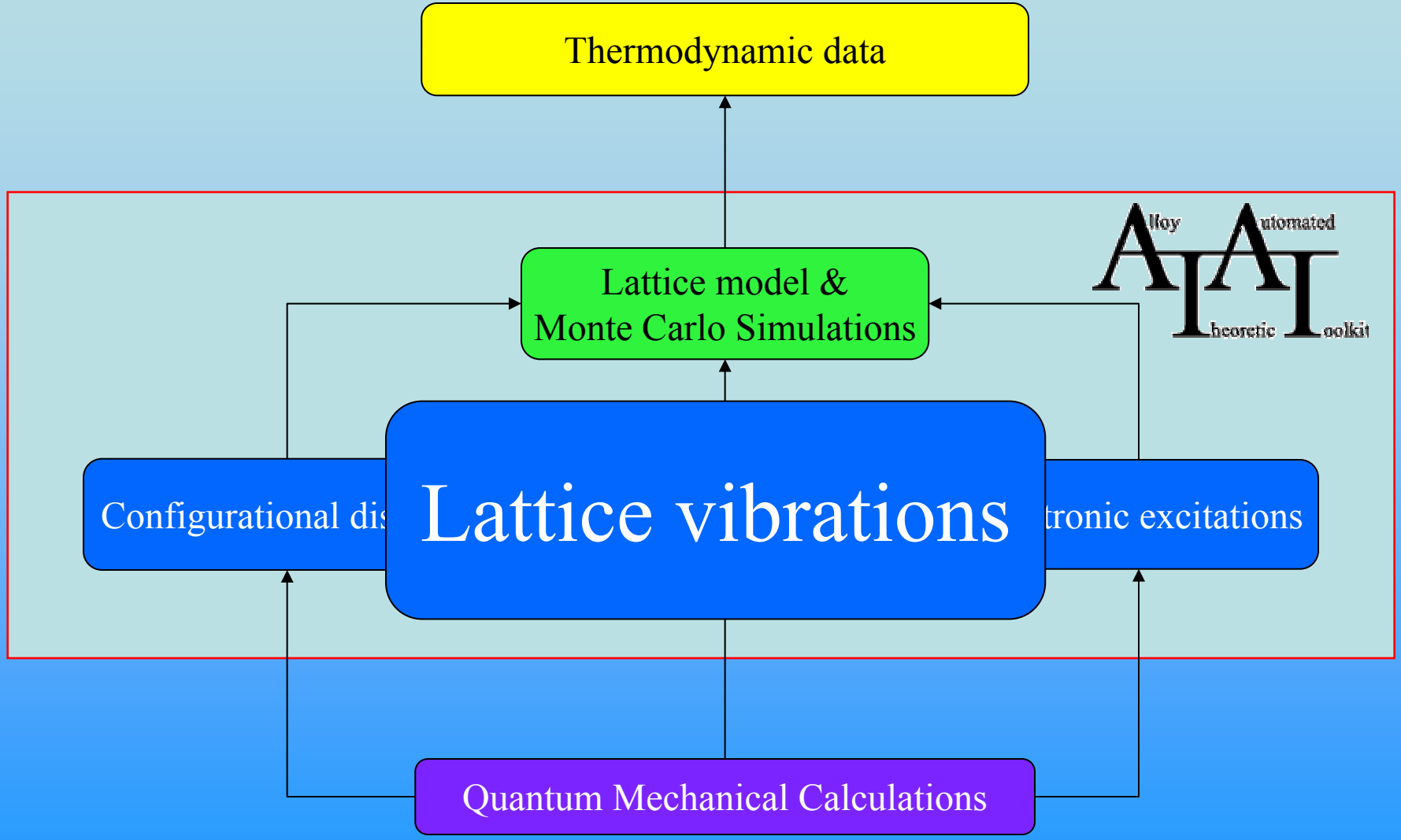
Fultz, Nagel, Antony, *et al.* (1993-1999)

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

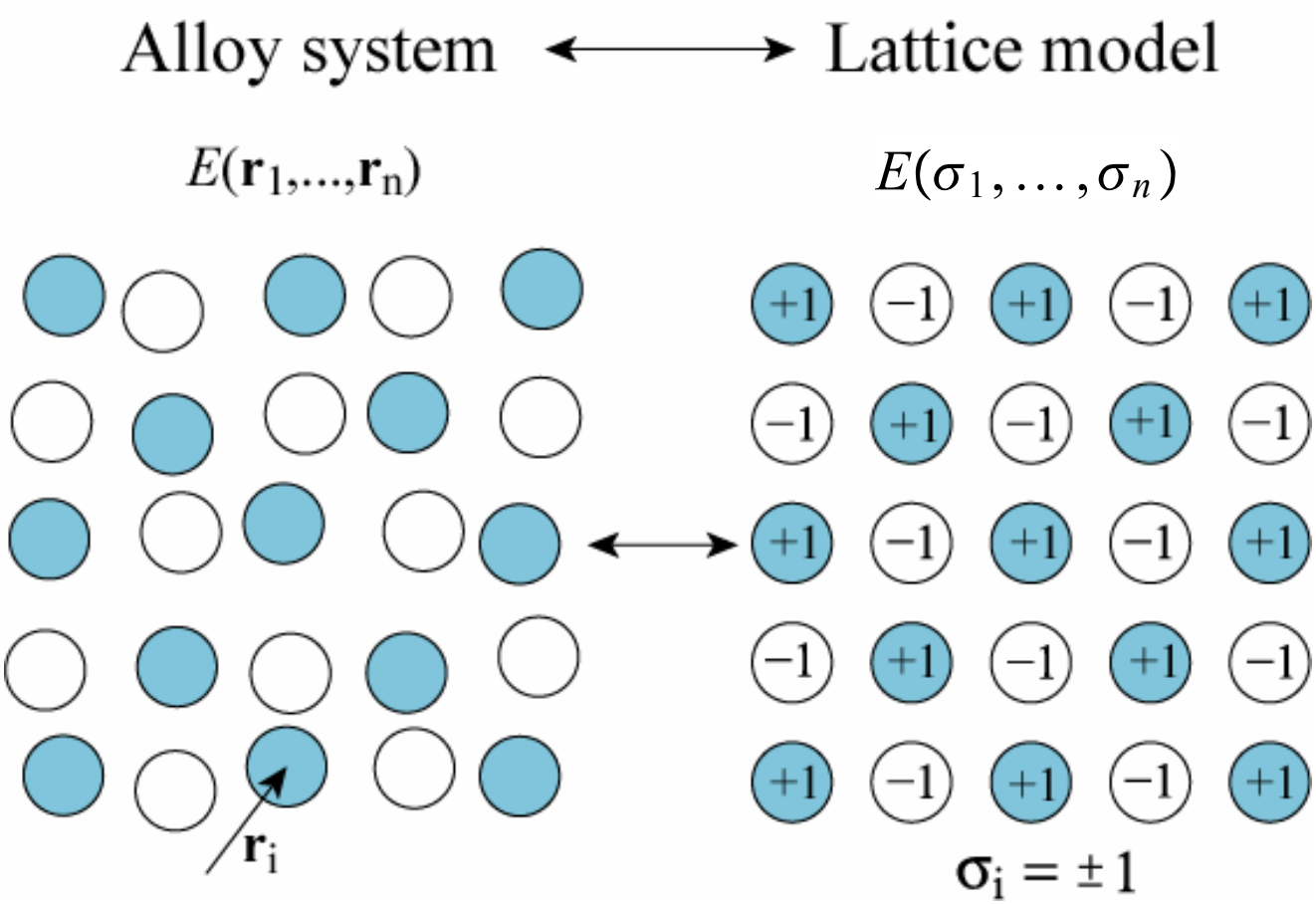
de Fontaine, Althoff, Morgan (1997-2000)

Zunger, Ozolins, Wolverton (1998-2001)

Many other examples…


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

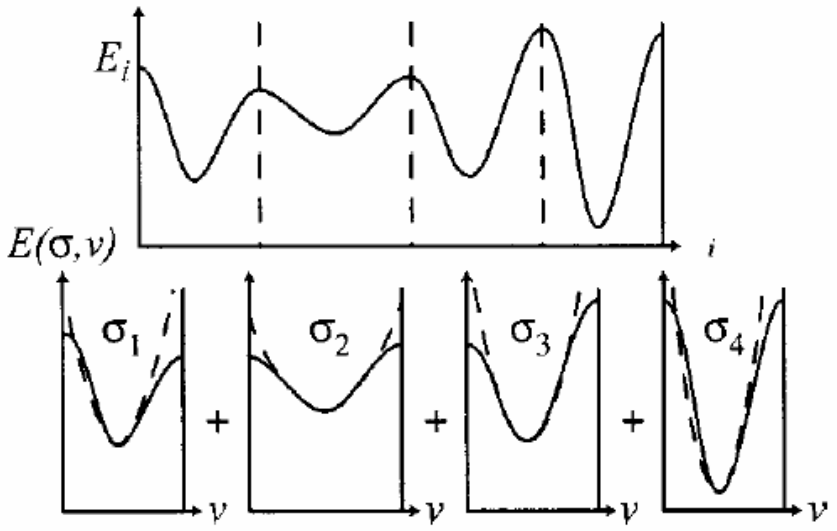
The Cluster Expansion Formalism with Coarse-Graining



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

Coarse-Graining of the Free Energy

Graphically:



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

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

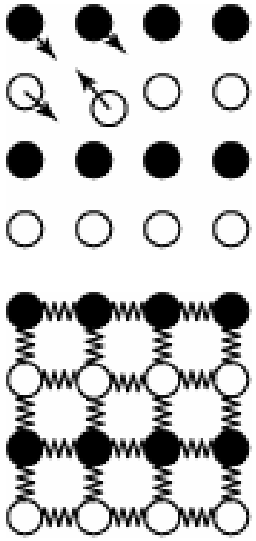
where

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

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

First-principles lattice dynamics

First-principles data

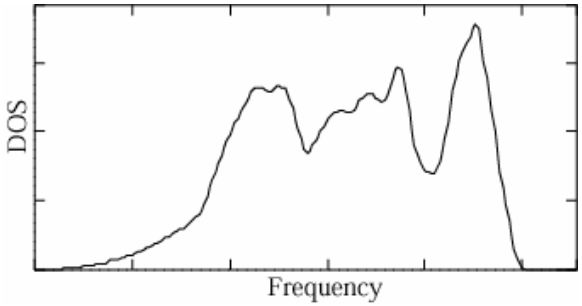


Computationally intensive!

Must be done for many configurations!

Least-squares fit to Spring model

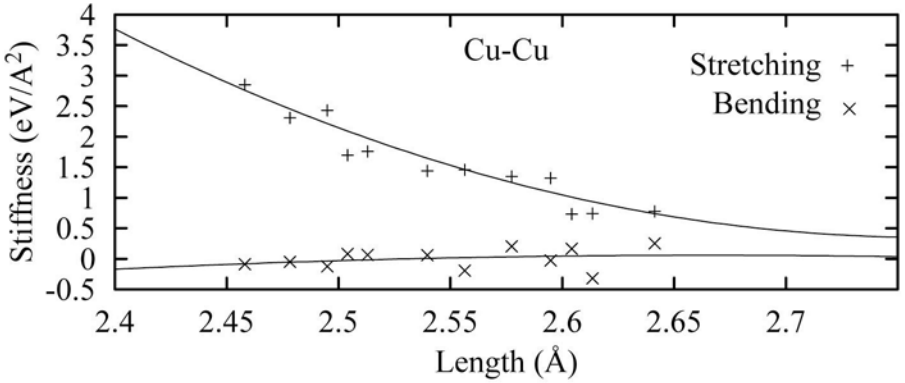
Phonon density of states

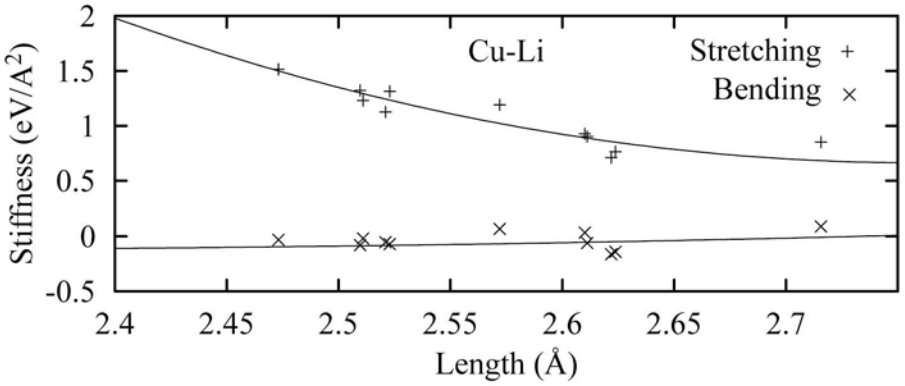


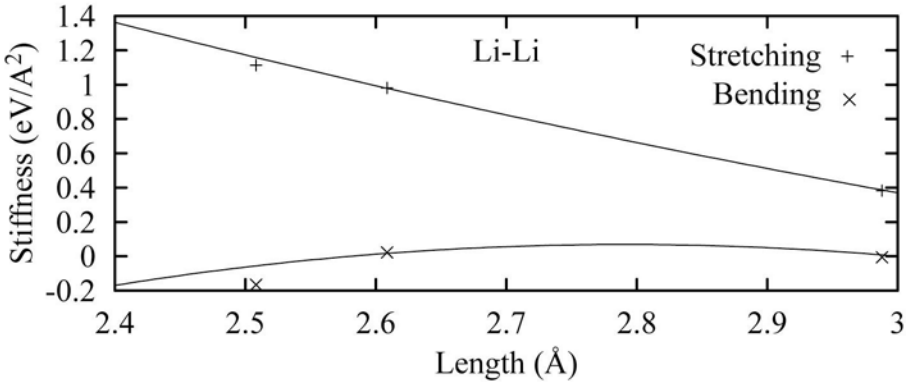
Thermodynamic Properties

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

Transferable Force Constants

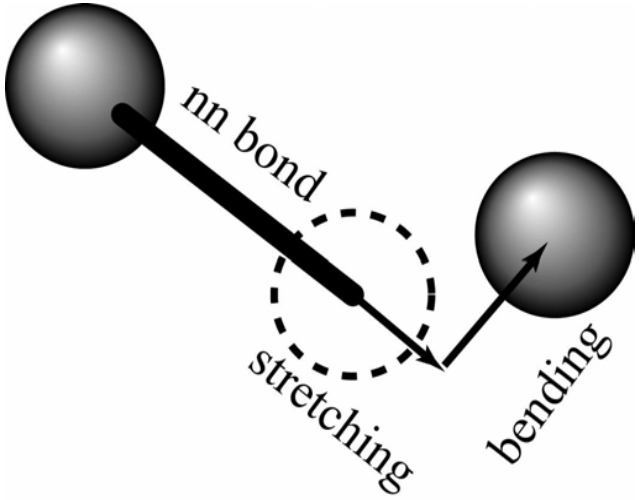






Chemical bond type and bond length:

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

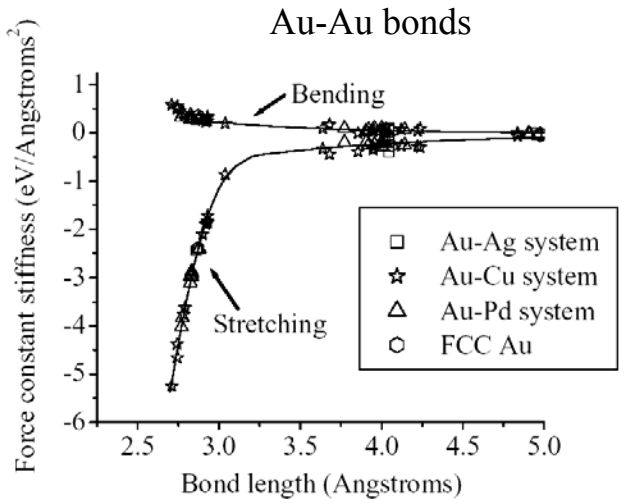


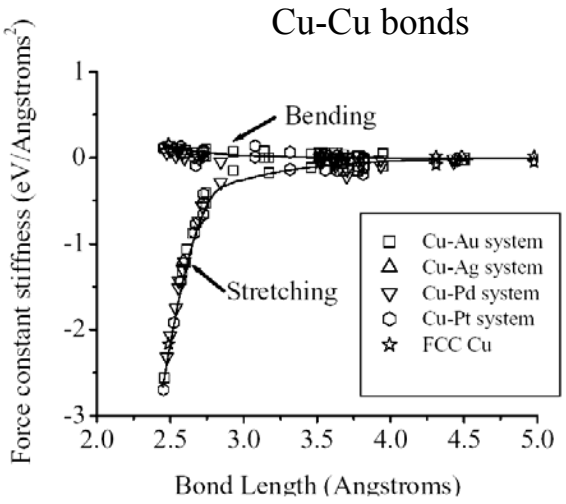
Relationship holds across different structures on the same lattice (here fcc is shown).

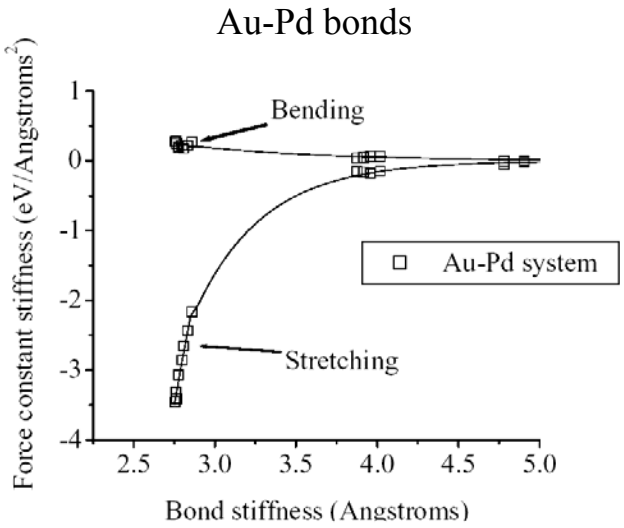
van de Walle and Ceder (2000,2002)

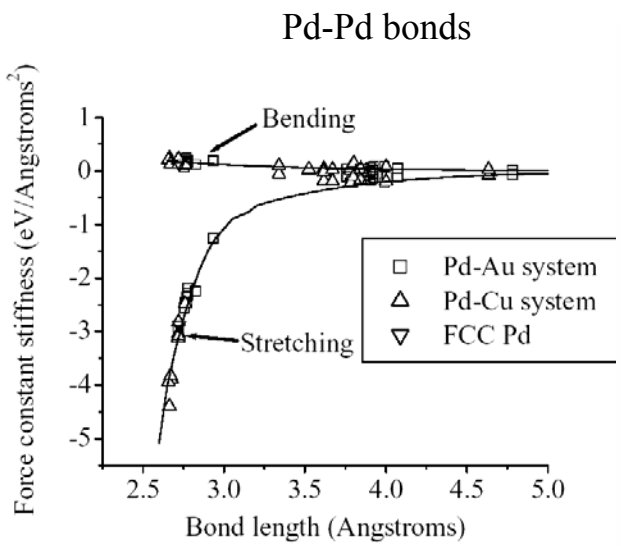
Further tests...

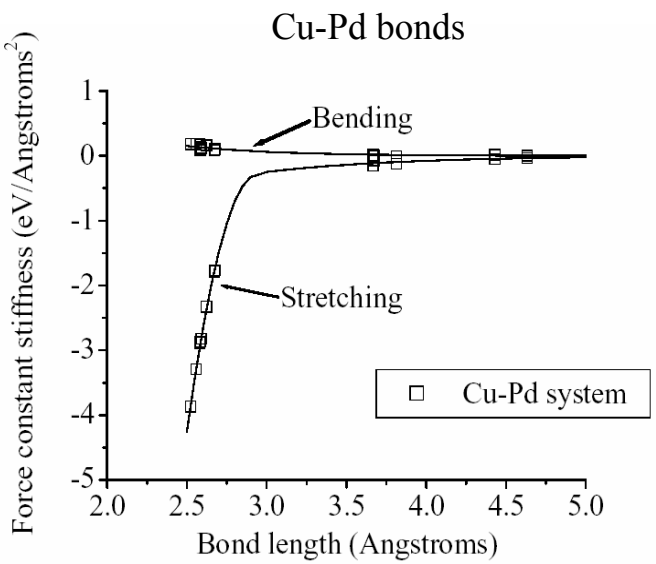
Wu, Ceder, van de Walle (2002)

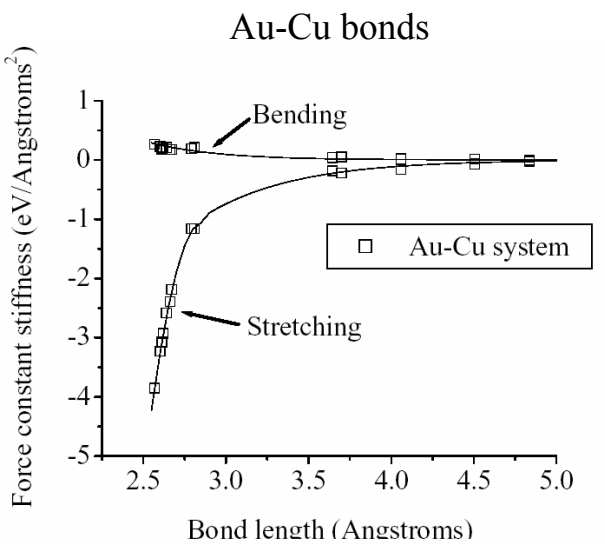






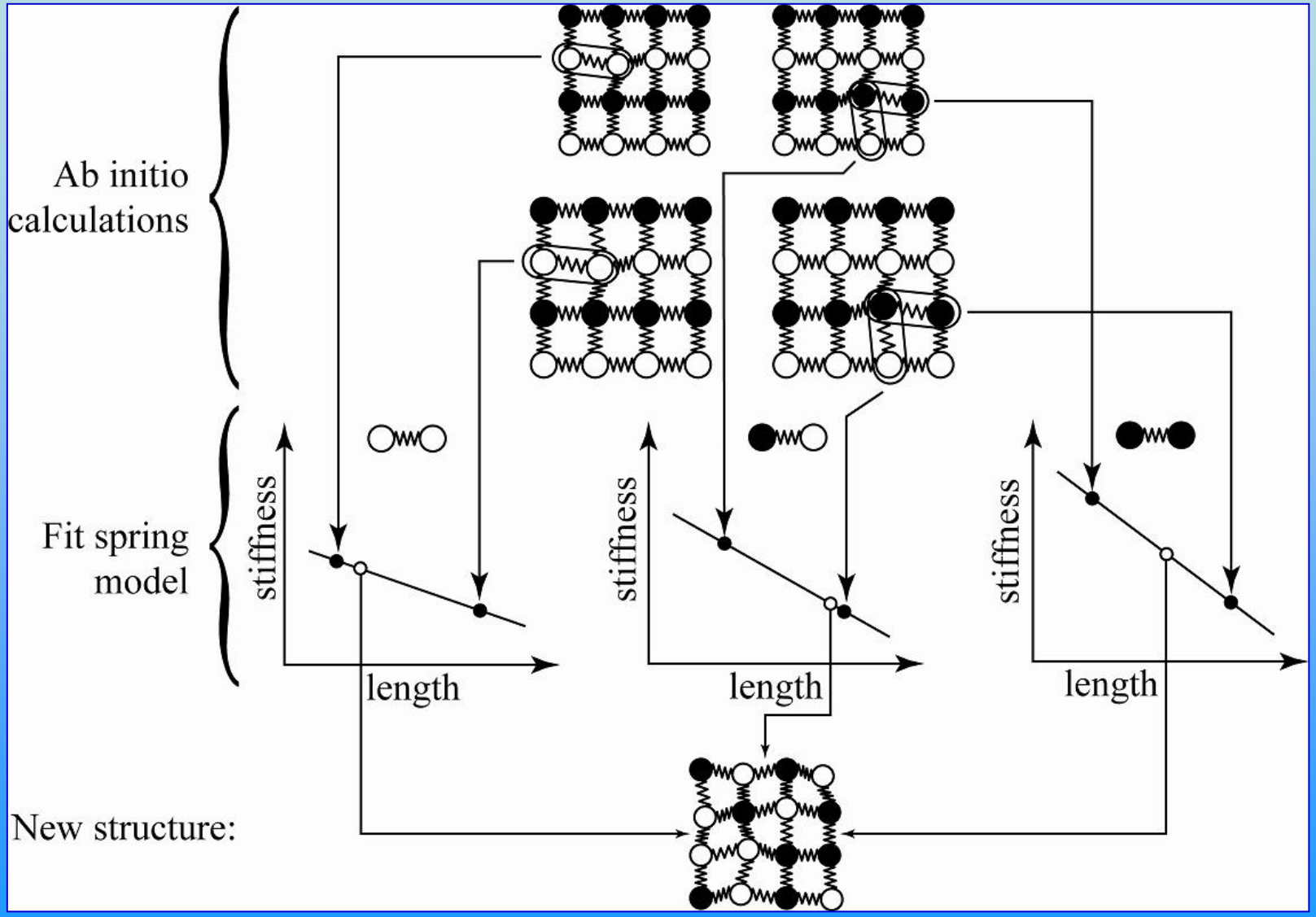






Accuracy ~ 0.03 k_B

Length-Dependent Transferable Force Constants (LDTFC)



van de Walle and Ceder (2000,2002)

Quasi-harmonic model

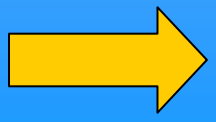
$$F(T,V) = E(V) + F_H(T,V)$$

Energy of a relaxed motionless lattice with externally imposed volume V

Vibrational free energy of a harmonic solid at temp. *T* with externally imposed volume *V*

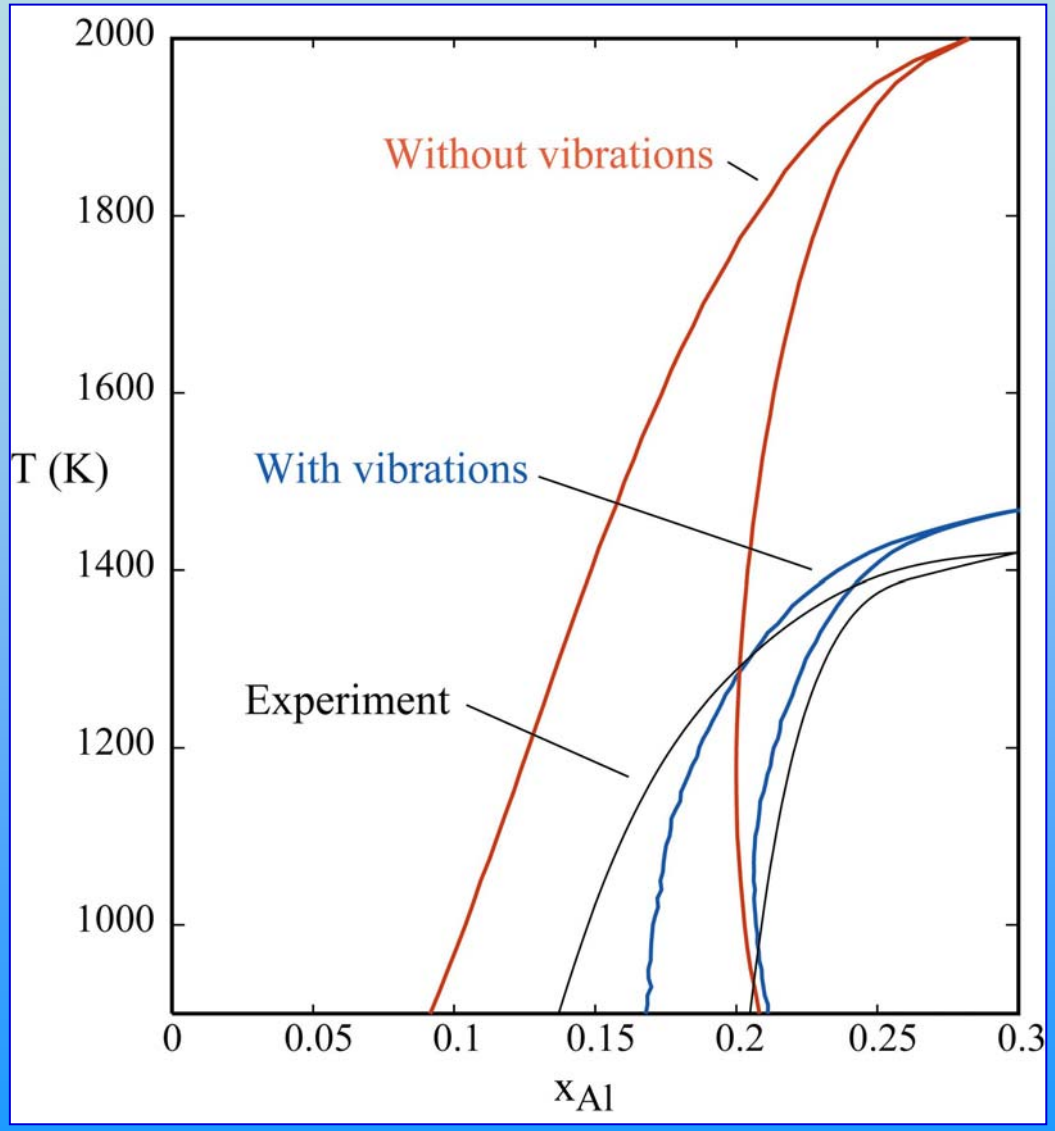
Thermal expansion: $V^*(T) = \arg\min_V F(T,V)$

"True" free energy: $F(T) = F(T,V^*(T))$



Ideal for use with length-dependent transferable force constants

Calculated Ti-Al Phase Diagram



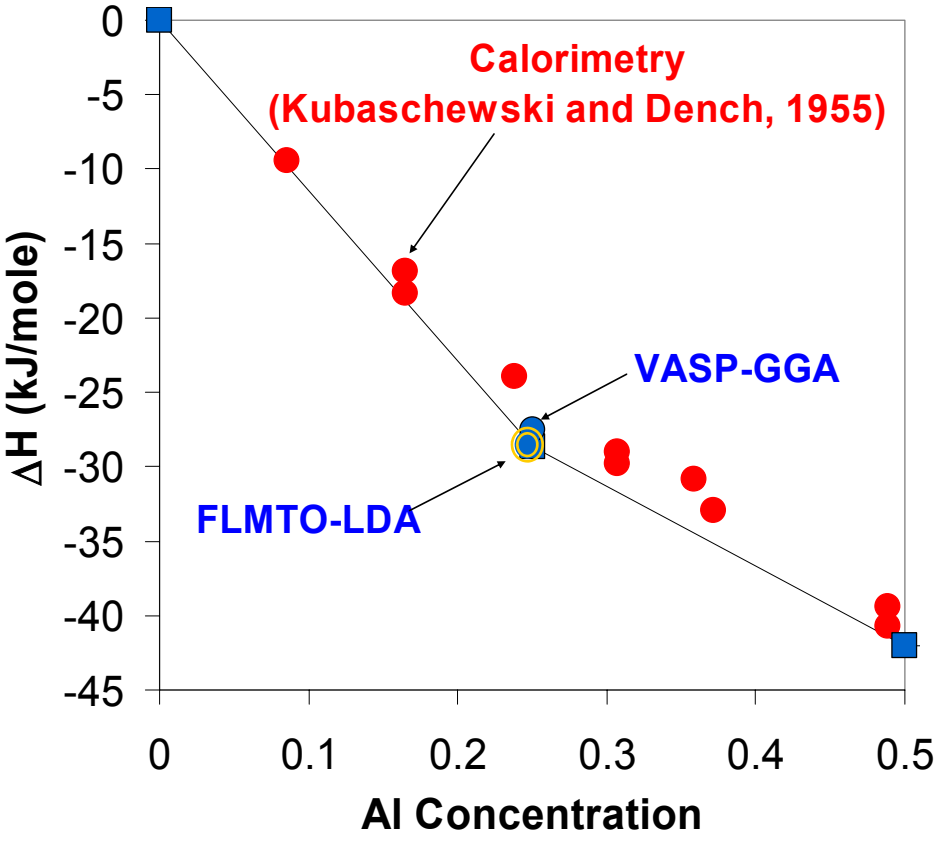
Assessed Phase Diagram:
I. Ohnuma *et al*., Acta Mater. **48**, 3113 (2000)

1st-Principles Calculations:
van de Walle and Asta

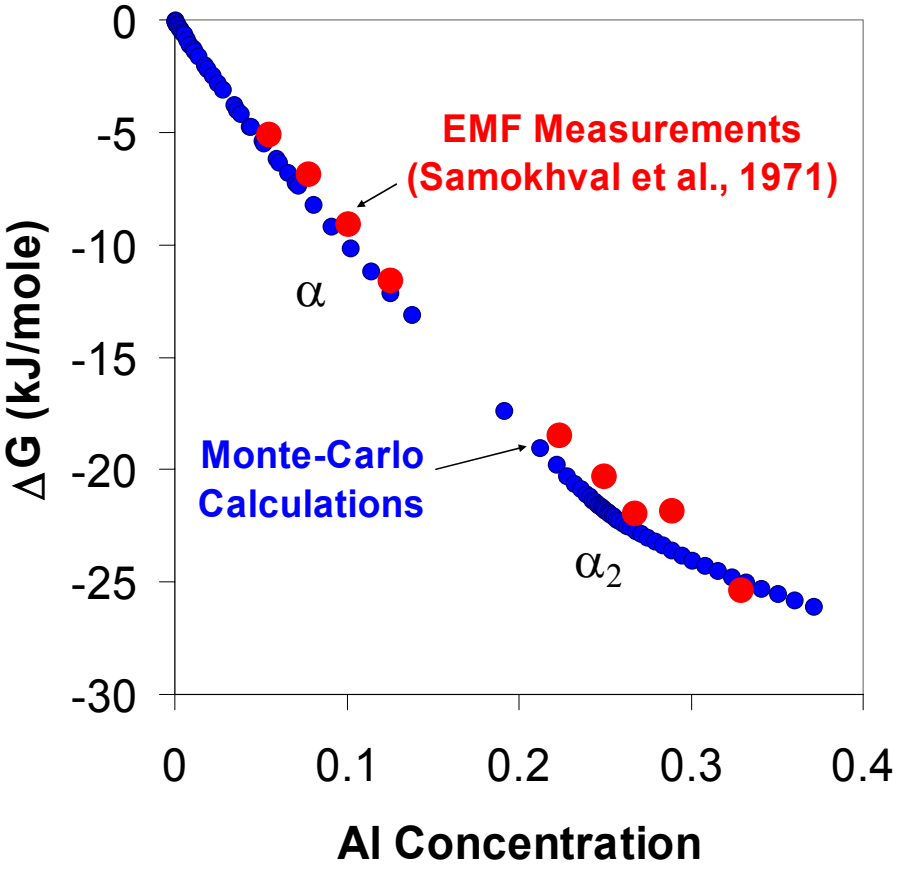
Ti-Al Thermodynamic Properties

1st-Principles Calculations vs. Measurements

Heats of Formation



Gibbs Free Energies (T=960 K)

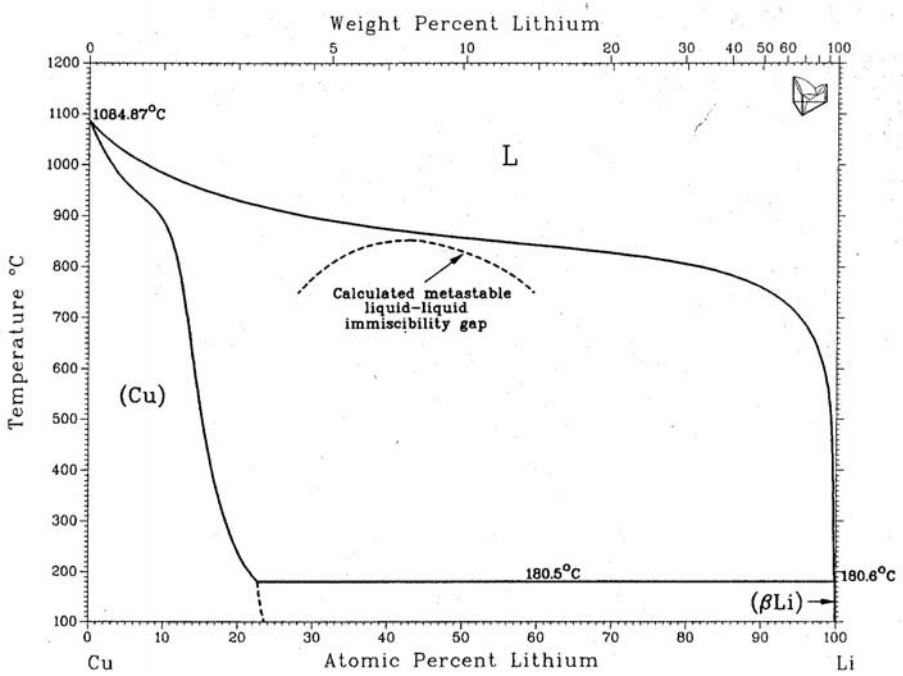


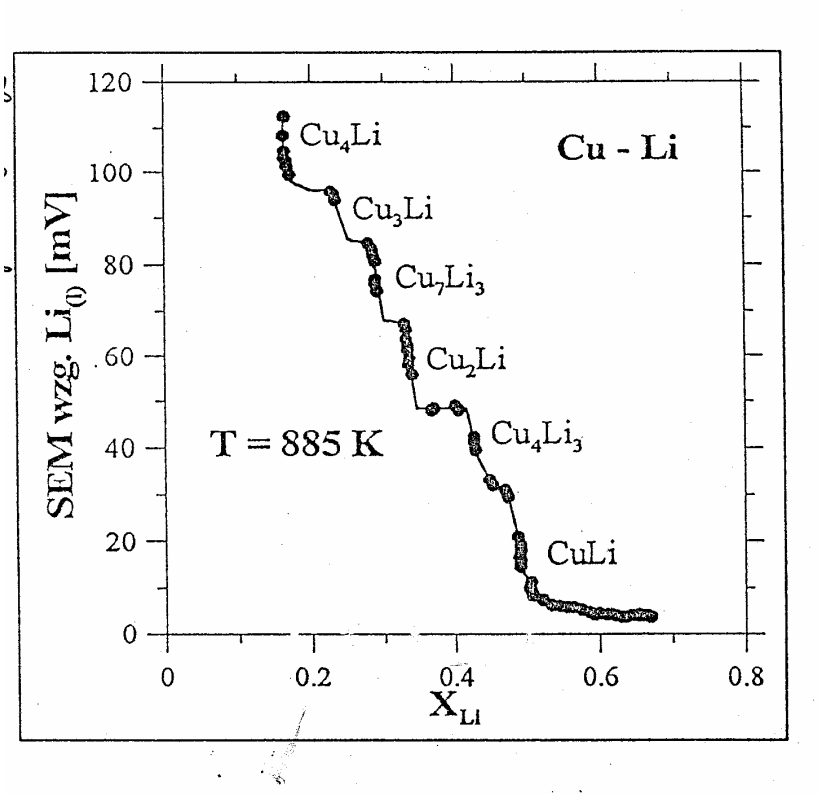
Ordering in the Cu-Li system?

Widely used assessments

do not include ordered phases

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





Evidence from EMF measurements

Ordered Cu_4Li phase also suggested by

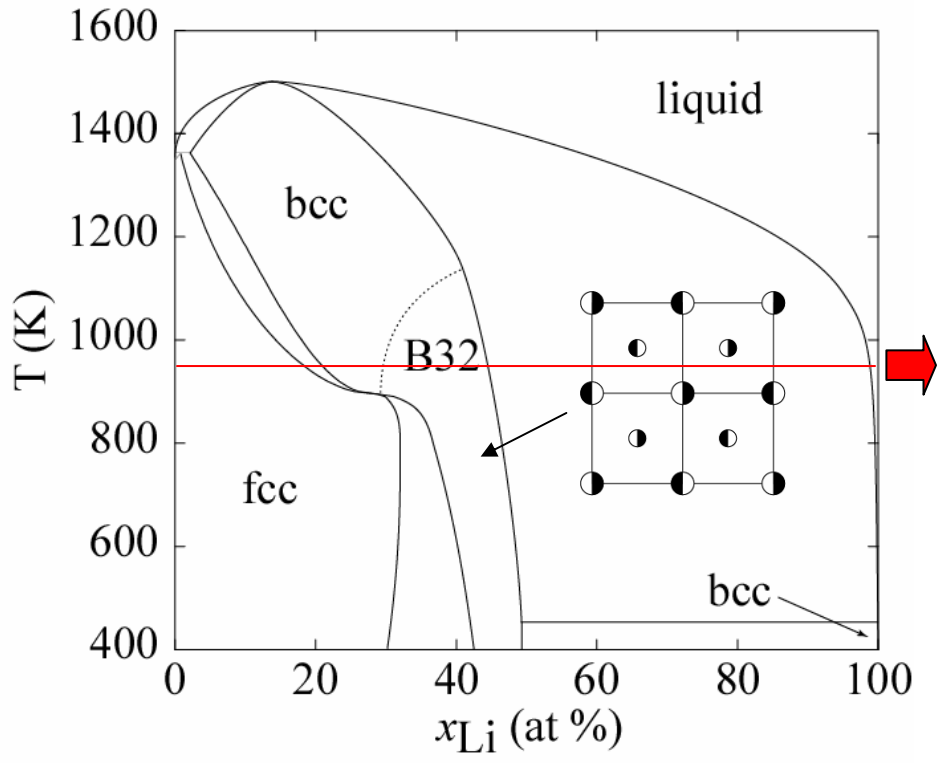
Borgsttedt & Gumiński (1996),

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

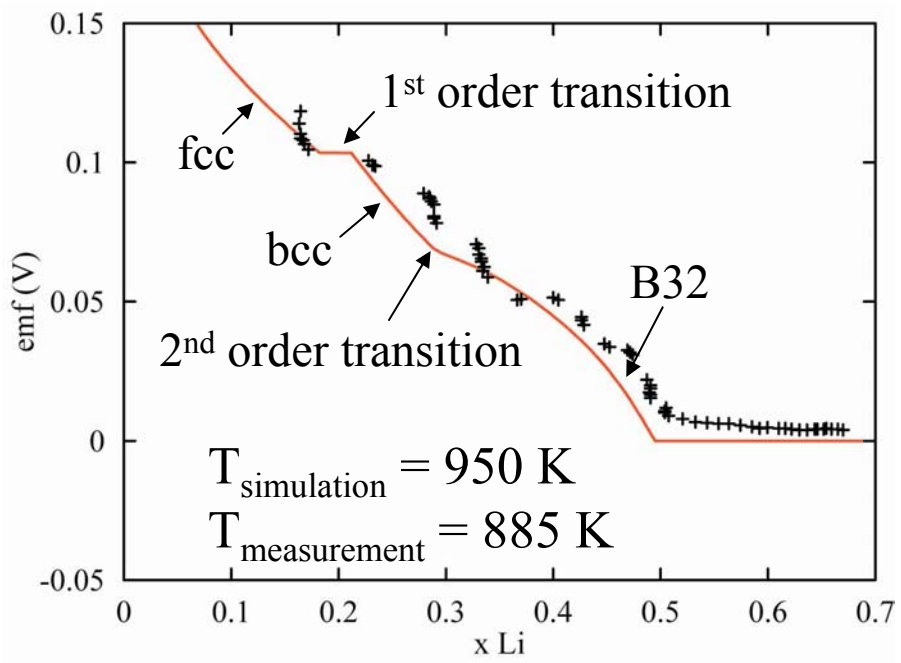
Old & Trawena (1981).

Calculated Thermodynamic data for Cu-Li system

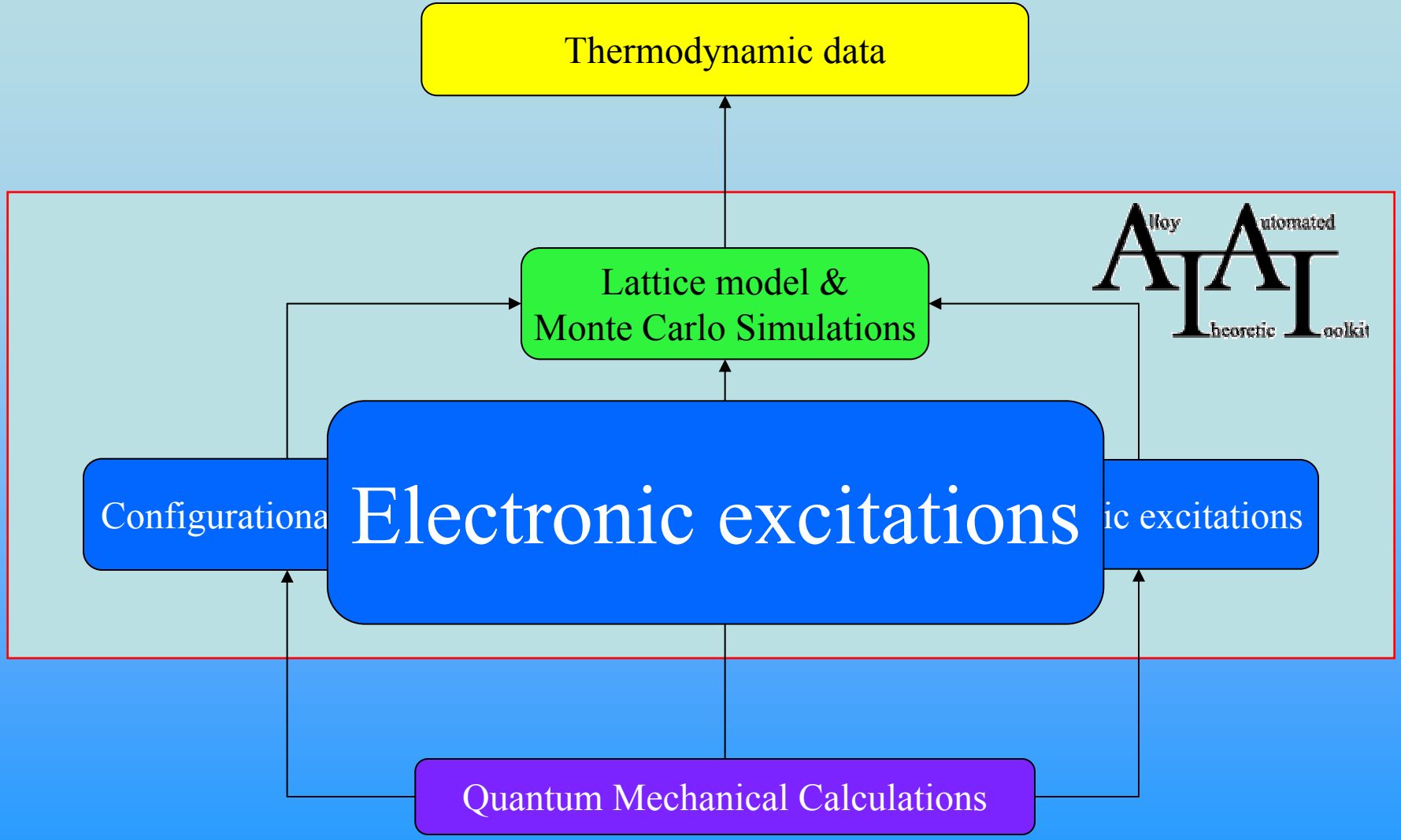
Phase diagram



Electromotive Force (EMF)



2 adjustable parameters:
$T_{simulation}$ + chemical potential of Li (liq)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Configurationa
Electronic excitations
ic excitations
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Theoretic Toolkit

Electronic Excitations

Finite-temperature DFT

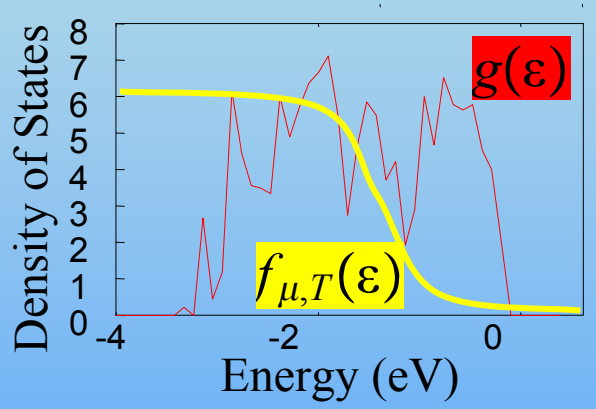
T-independent DOS and charge density

Advantage: Get F_{elec} "for free"

Electronic DOS

Fermi-Dirac Distribution

Electronic Free energy



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

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

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

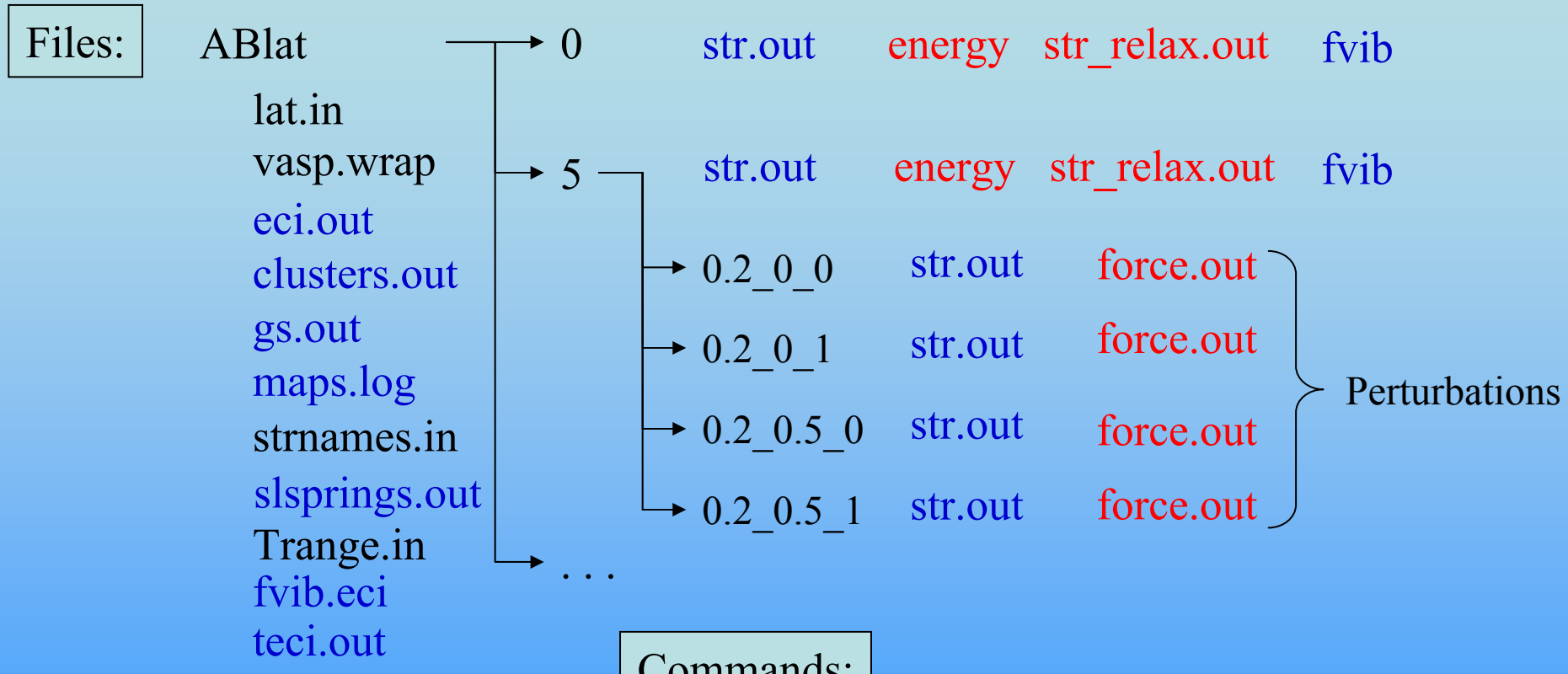
Cluster expansion:

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

Using ATAT

- Overview of the input/output files
- Syntax of the files
- Sample output

File structure



Commands:

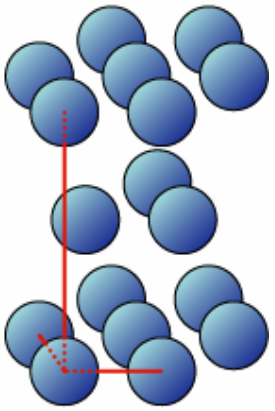
maps -d	fitsvsl -f
run *ab initio* code	foreachfile str.out svsl -d
fitsvsl -d	clusterexpand fvib
run *ab initio* code	mkteci fvib.eci

Example of input files

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

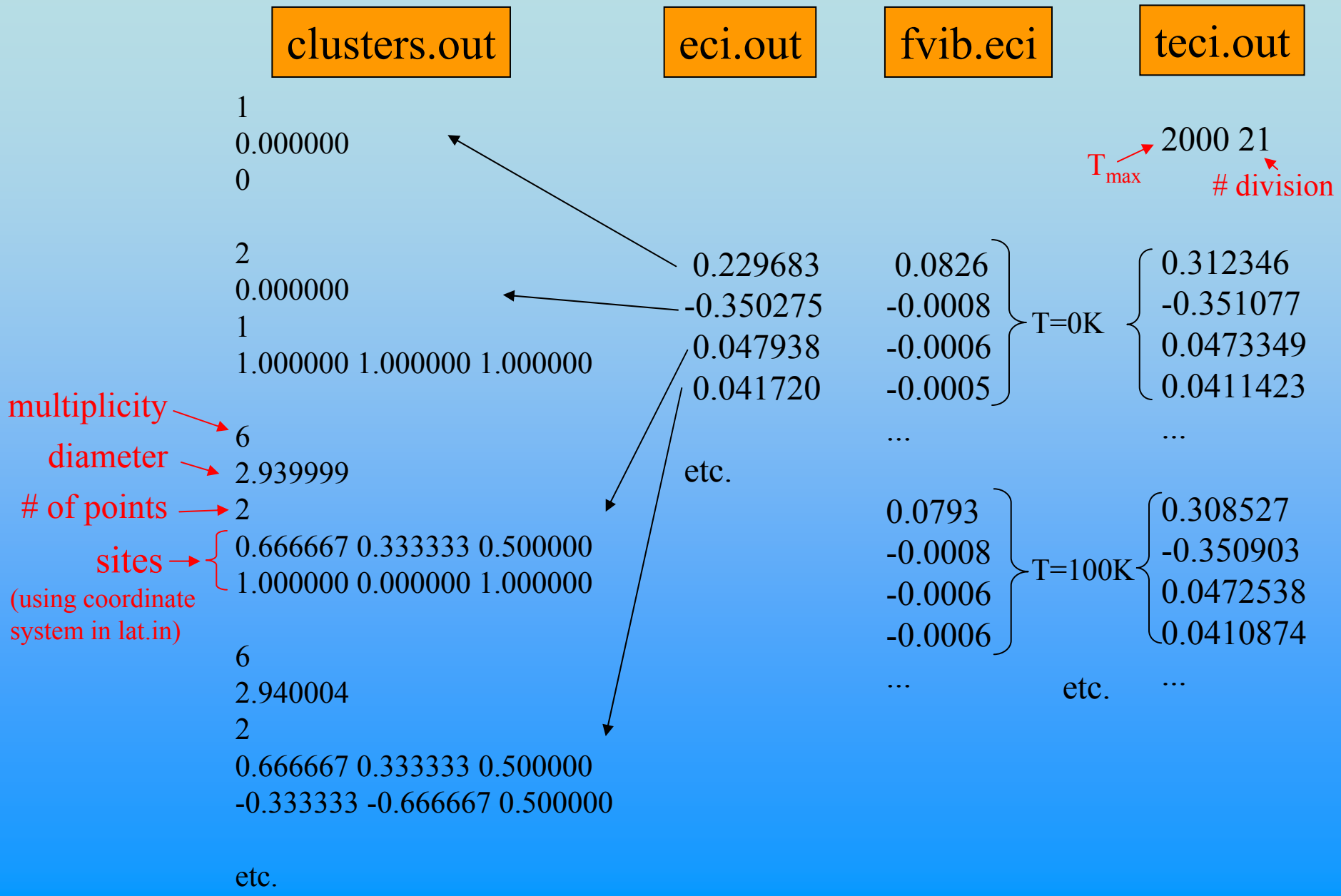
```
[INCAR]
PREC = high
ISMEAR = -1
SIGMA = 0.1
NSW=41
IBRION = 2
ISIF = 3

KPPRA = 1000
DOSTATIC
```

} Standard VASP tokens

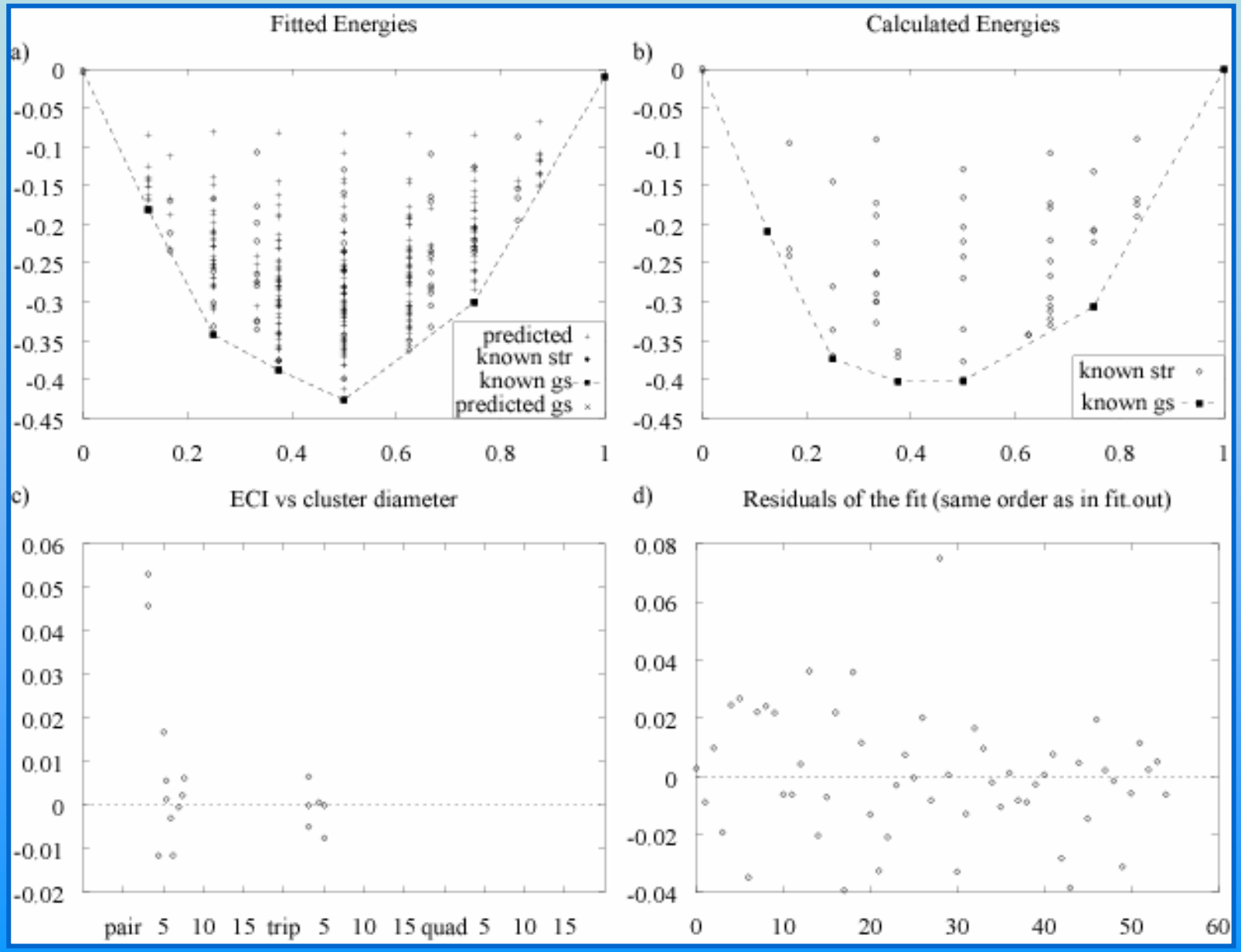
} *k*-point density (**k** point **p**er **r**eciprocal **a**tom)

do static run

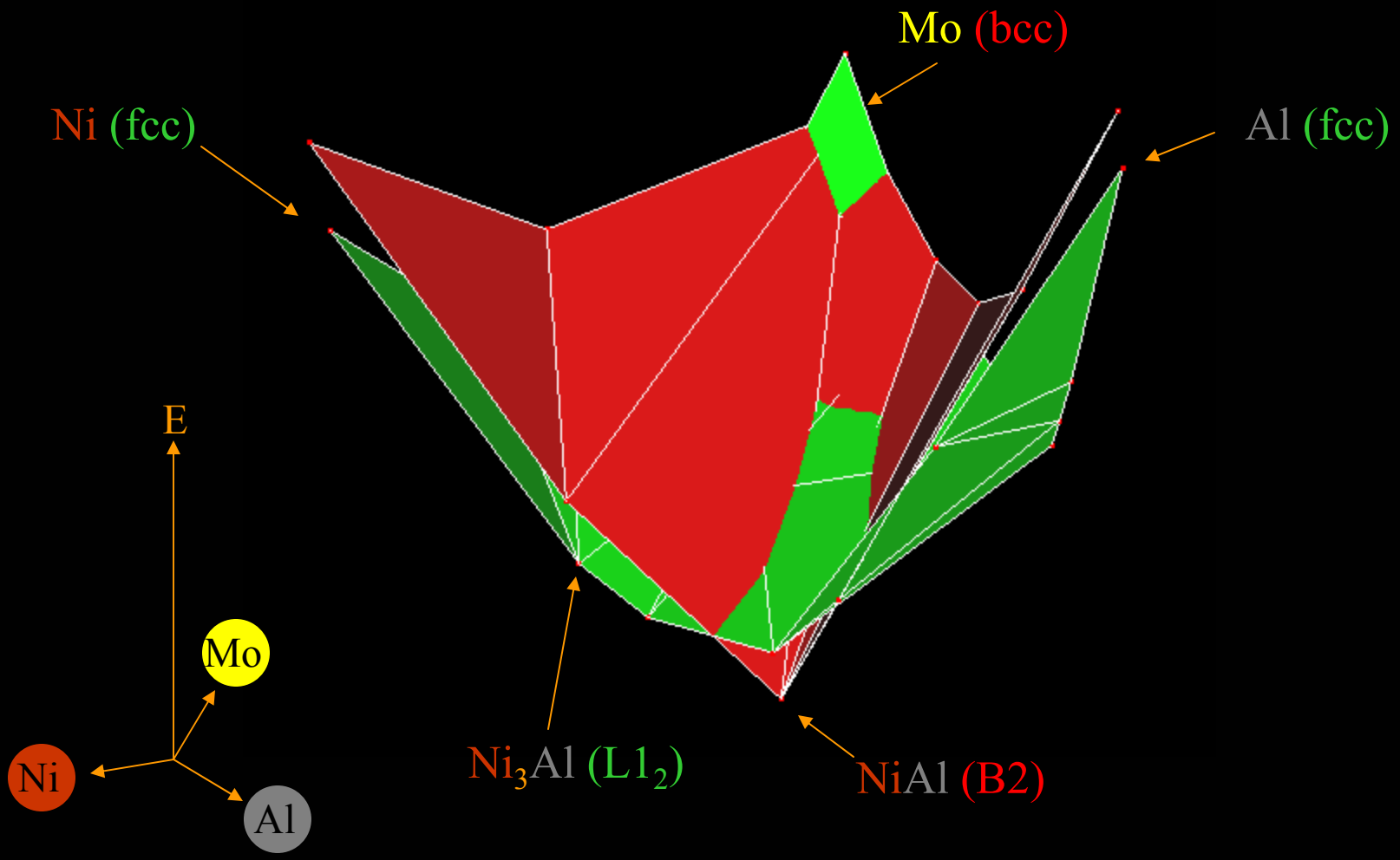
Clusters and ECI files



maps graphical output

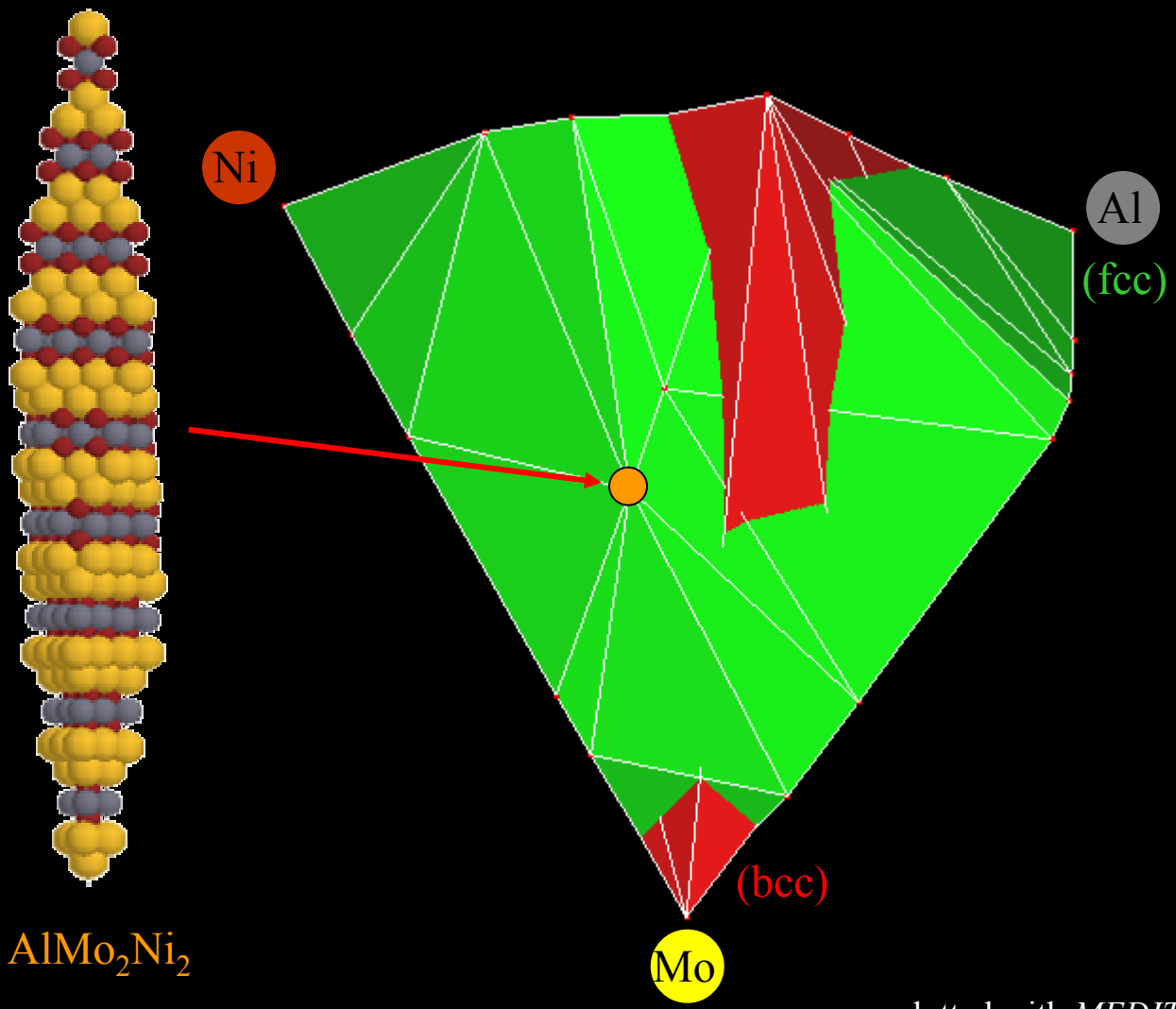


Search for new compounds in the Al-Mo-Ni system



plotted with *MEDIT,* INRIA-Rocquencourt.

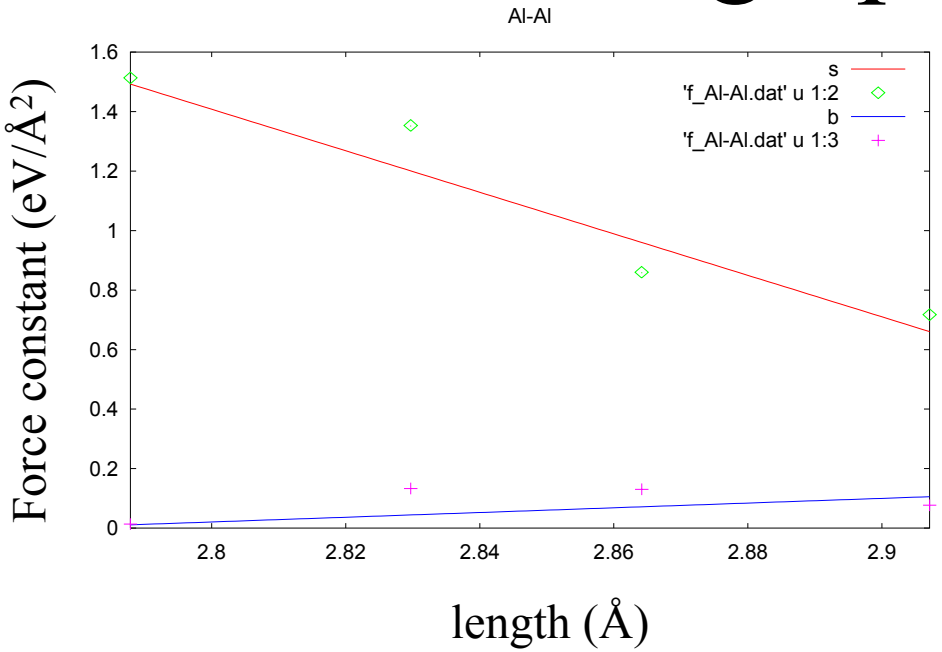
Predicted Compound

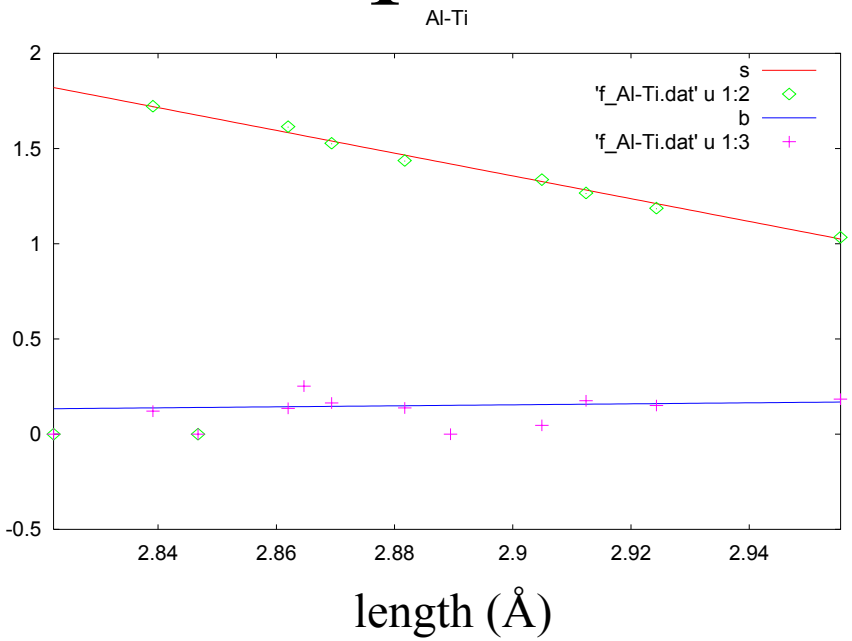


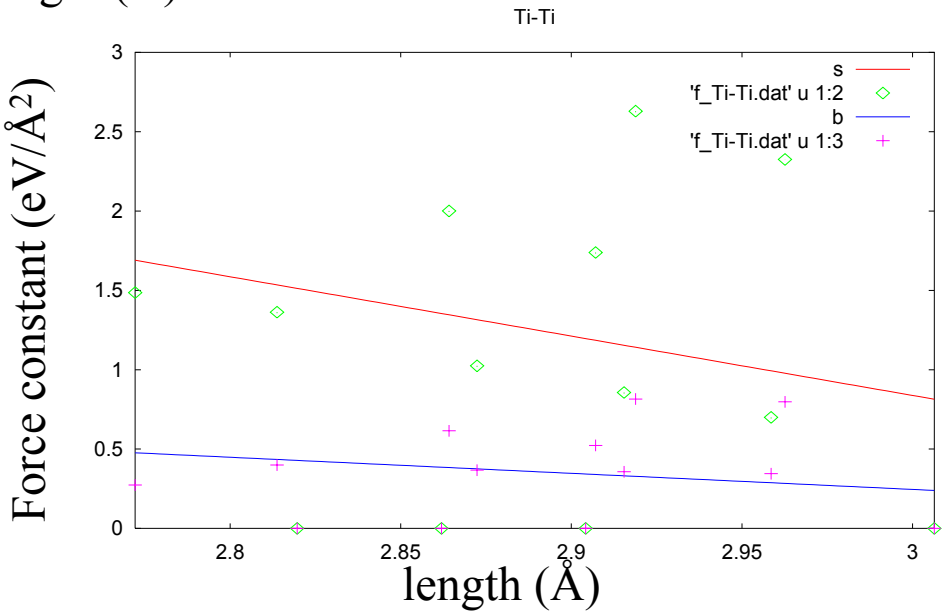
$AlMo_2Ni_2$

plotted with *MEDIT,* INRIA-Rocquencourt.

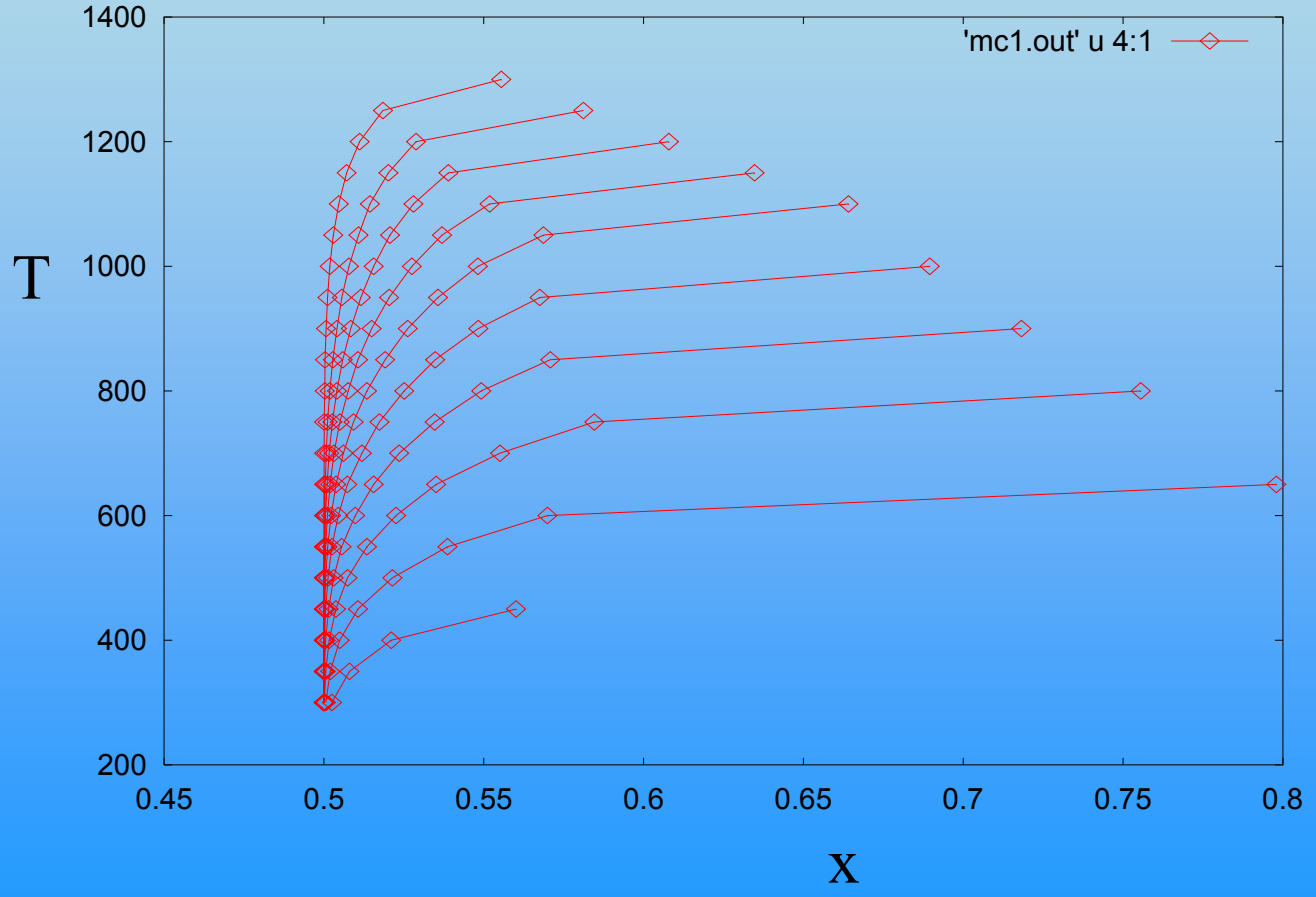
fitsvsl graphical output







emc2 graphical output



Other outputs:

1) T: Temperature
2) mu: chemical potential
3) E-mu*x: Average energy
4) x: Average Concentration
5) phi: grand canonical potential
6) E2: heat capacity
7) x2: susceptibility
8) E_lte-mu*x_lte: from LTE
9) x_lte
10) phi_lte
11) E_mf-mu*x_mf: from MF
12) x_mf
13) phi_mf
14) E_hte-mu*x_hte: from HTE
15) x_hte
16) phi_hte
17) lro: Long Range Order parameter
18-) corr: correlations

Miscellanea (I)

ATAT Utilites

- maps : Cluster expansion builder
- mmaps : Multicomponent version of maps
- emc2 : General purpose Monte Carlo code
- phb : Phase-transition-tracing Monte Carlo code
- checkrelax : Excessive relaxation detector
- corrdump : Cluster generator/correlation calculator
- clusterexpand : Manual cluster expansion generator
- genstr : Super structure generator
- gensqs : Special Quasirandom Structure generator
- pdef : Point defect supercells generator
- csfit : Constituent strain calculator
- cellcvrt : General crystal structure file format conversion utility
- lsfit : Least-squares fitting code
- fitfc : Phonon calculation with direct force method
- fitsvsl : Length-Dependent Transferable Force Constants generator
- svsl : Phonon calculations using LDTFC
- felec : Electronic free energy calculator

Miscellanea (II)

ATAT Utilites

runstruct_vasp : Interface with vasp
runstruct_abinit : Interface with abinit
runstruct_pwscf : Interface with pwscf
} *ab initio*

runstruct_gulp : Interface with gulp ← empirical potential

pollmach : A job dispatcher for computer clusters
foreachfile : A "loop over directories" utility
str2xyz : File conversion utility for viewing with rasmol

makelat : Database of crystal structures

getvalue, (just)after, (just)before, (just)between sspp : Text extractors

memc2 : Multicomponent version of emc2 (in development)

Getting Help

- Run command without any argument to get usage help
- Use –h option to get detailed help
- http://cms.northwestern.edu/atat/manual/manual.html

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- Web site: http://cms.northwestern.edu/atat
- This afternoon's tutorial: http://cms.northwestern.edu/atat/tutorial