

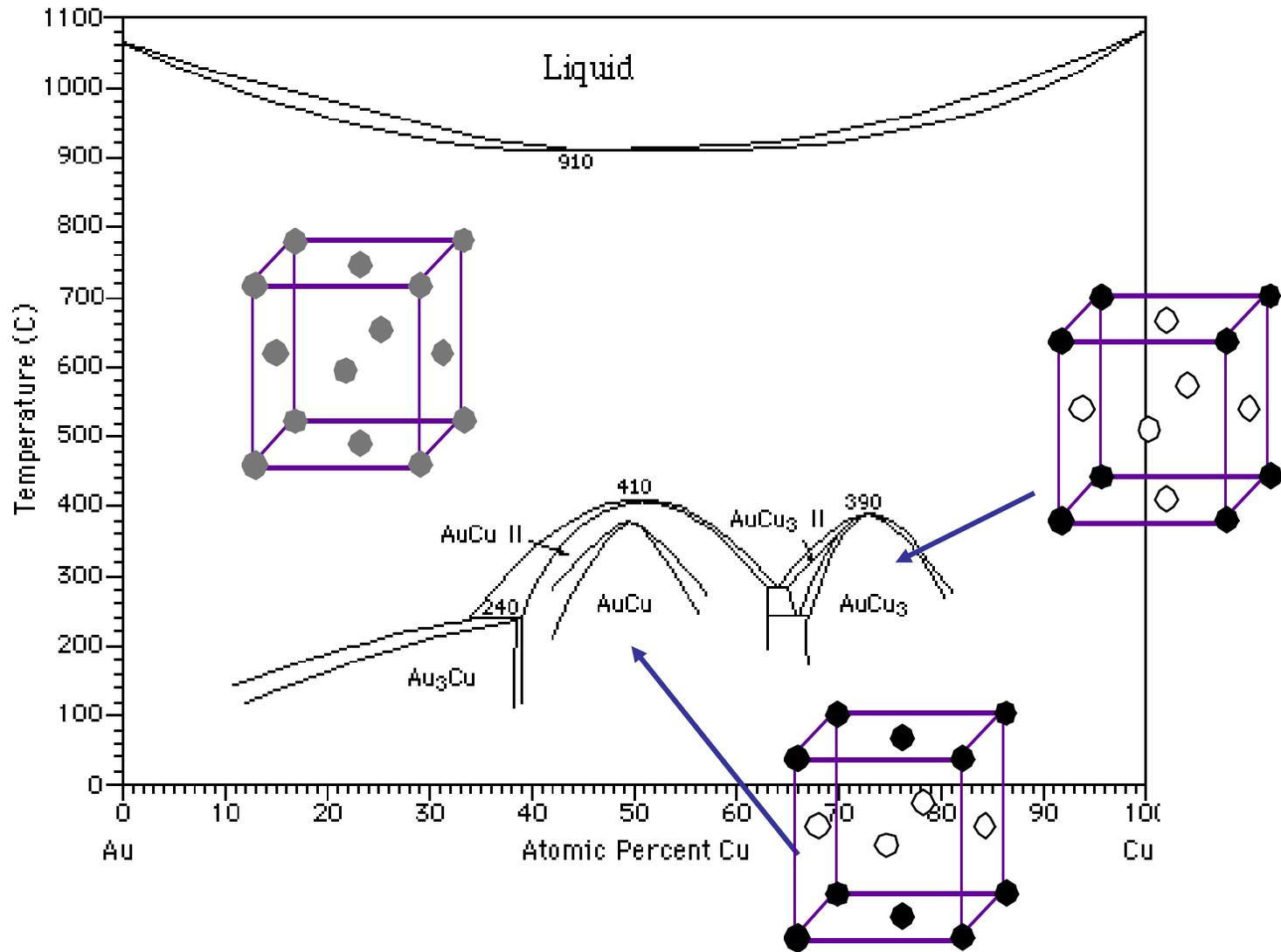
3.320: Lecture 22 (4/28/05)

Ab-Initio Thermodynamics and Structure Prediction: *Time Coarse-graining, Effective Hamiltonians and Cluster Expansions*

**Methods with multiple time scales:
*Coarse-grain fast one away***

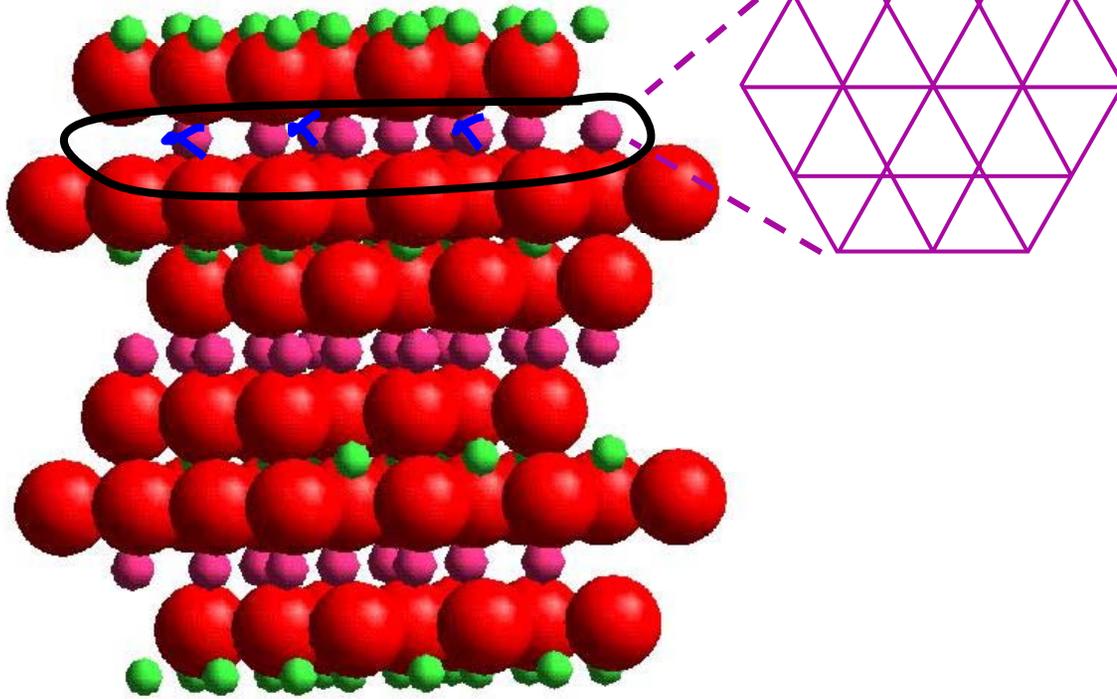
Model Hamiltonians: Example of Relevant Lattice Models

Cu-Au: Cu and Au on fcc sublattice



Configurational Disorder in Fixed Host

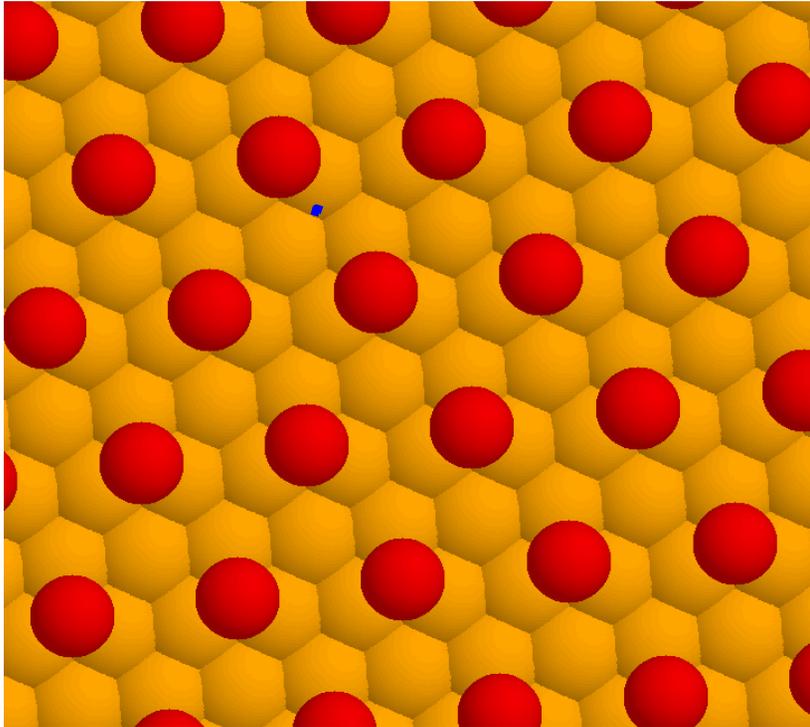
LiCoO_2 : Li and vacancies



Triangular lattice of
Li and vacancies

Surface Adsorption

e.g. O on Pt(111)



Possible “Hollow” sites form a triangular lattice

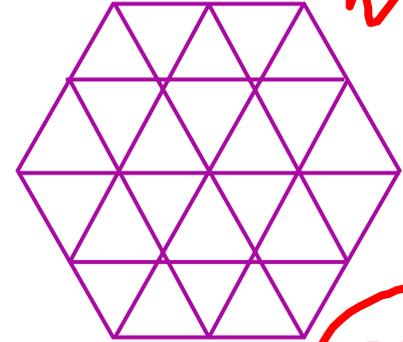
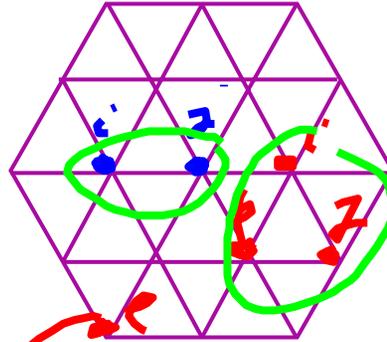
How to parameterize and equilibrate these models ?

A practical basis to expand $H(\{\sigma\})$ in

$$\{\sigma\} = \sigma_1, \sigma_2, \sigma_3, \dots, \sigma_N$$

Examples of cluster functions

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



$$\varphi_\alpha = \sigma_i \sigma_j$$

$$\varphi_\alpha = \sigma_i \sigma_j \sigma_k \dots \sigma_l$$

$$2^N$$

Basis is complete

Cluster function basis is orthogonal

suitable scalar product $\langle f(\{\sigma\}) | g(\{\sigma\}) \rangle = \frac{1}{2^N} \sum_{\{\sigma\}} f(\{\sigma\}) g(\{\sigma\})$

Note that for any basis function $\frac{1}{2^N} \sum_{\{\sigma\}} \varphi_\alpha = 0$

$\sigma_1 \sigma_2 \sigma_3 \dots$

orthogonality proof



$\langle \varphi_\alpha | \varphi_\beta \rangle = \frac{1}{2^N} \sum_{\{\sigma\}} \varphi_\alpha \varphi_\beta$

$\varphi_\alpha \varphi_\beta = \prod_{i \in \alpha \cap \beta} \sigma_i^2 \prod_{\substack{i \in \alpha \\ i \notin \beta}} \sigma_i \prod_{\substack{i \in \beta \\ i \notin \alpha}} \sigma_i = \delta_{\alpha\beta}$

(Handwritten notes: A red circle around the first term $\frac{1}{2^N} \sum_{\{\sigma\}}$ has an arrow pointing to the sum in the equation above. A blue arrow points from the intersection term $\prod_{i \in \alpha \cap \beta} \sigma_i^2$ to the text $\varphi_{\alpha+\beta}(\alpha \cap \beta)$. The final result $\delta_{\alpha\beta}$ is circled in red.)

Expand any function of configuration in cluster function basis: e.g. Energy

$$E(\{\sigma\}) = \sum_{\alpha} V_{\alpha} \varphi_{\alpha}$$

Coefficients V -> Effective Cluster Interactions

$$H(\{\sigma\}) = V_0 + V_1 \sum_i \sigma_i + \frac{1}{2} \sum_{i,j} V_{i,j} \sigma_i \sigma_j + \frac{1}{6} \sum_{i,j,k} V_{i,j,k} \sigma_i \sigma_j \sigma_k + \frac{1}{24} \sum_{i,j,k,l} V_{i,j,k,l} \sigma_i \sigma_j \sigma_k \sigma_l \dots$$

expanding the cluster functions into their spin products makes the expansion look like a generalized Ising model

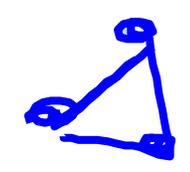
Now we are in a position to see what the formal definition of the interactions in the Ising-like model is

Definition of the Interactions

$+1 = A$
 $-1 = B$

$$\langle \varphi_\beta | E(\{\sigma\}) \rangle =$$

$$\sum_\alpha V_\alpha \langle \varphi_\alpha | \varphi_\beta \rangle = V_\beta$$

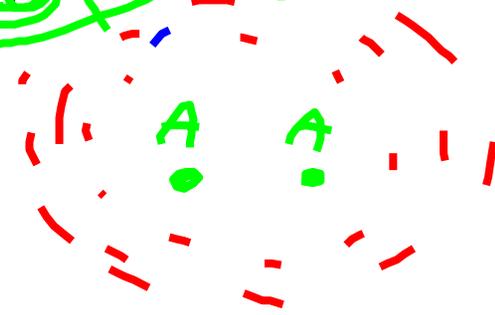


take scalar product with φ_β

$$V_\beta = \frac{1}{2^N} \sum_{\{\sigma\}} \varphi_\beta E(\{\sigma\}) = \frac{1}{2^{n_\beta}} \sum_{\substack{i=\pm 1 \\ i \in \beta}} \varphi_\beta \frac{1}{2^{N-n_\beta}} \sum_{\{\sigma\}} E(\{\sigma\})$$

Work out example for pair interaction

$$\varphi_\beta = (i, j)$$



$$V_{ij} = \frac{1}{4} \left[\langle E_{AA} \rangle + \langle E_{BB} \rangle - \langle E_{AB} \rangle - \langle E_{BA} \rangle \right]$$

Many direct and indirect methods have been developed for calculating the V_α

Practical Approach is to Determine them by fitting to the calculated energy of a large number of configurations.

SO $H(\{\sigma\}) = V_0 + V_1 \sum_i \sigma_i + \frac{1}{2} \sum_{i,j} V_{i,j} \sigma_i \sigma_j + \frac{1}{6} \sum_{i,j,k} V_{i,j,k} \sigma_i \sigma_j \sigma_k + \frac{1}{24} \sum_{i,j,k,l} V_{i,j,k,l} \sigma_i \sigma_j \sigma_k \sigma_l \dots$?c

→

Truncate Hamiltonian Expansion



First Principles method

Calculate $H(\{\sigma\})$ for several configurations $\{\sigma\}$ (= structures)



Fit Hamiltonian Expansion to the direct First Principles calculations

Effective Cluster Interactions



Ising-like model

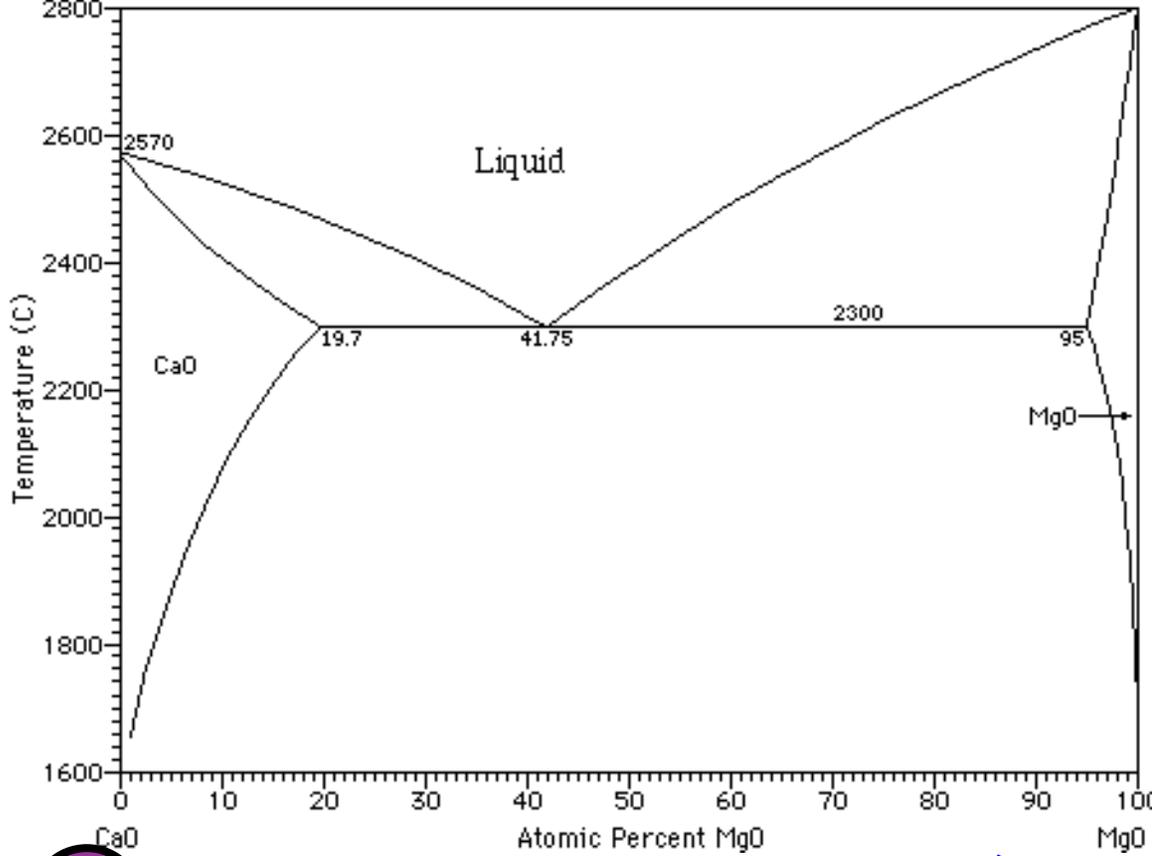
Monte Carlo simulation



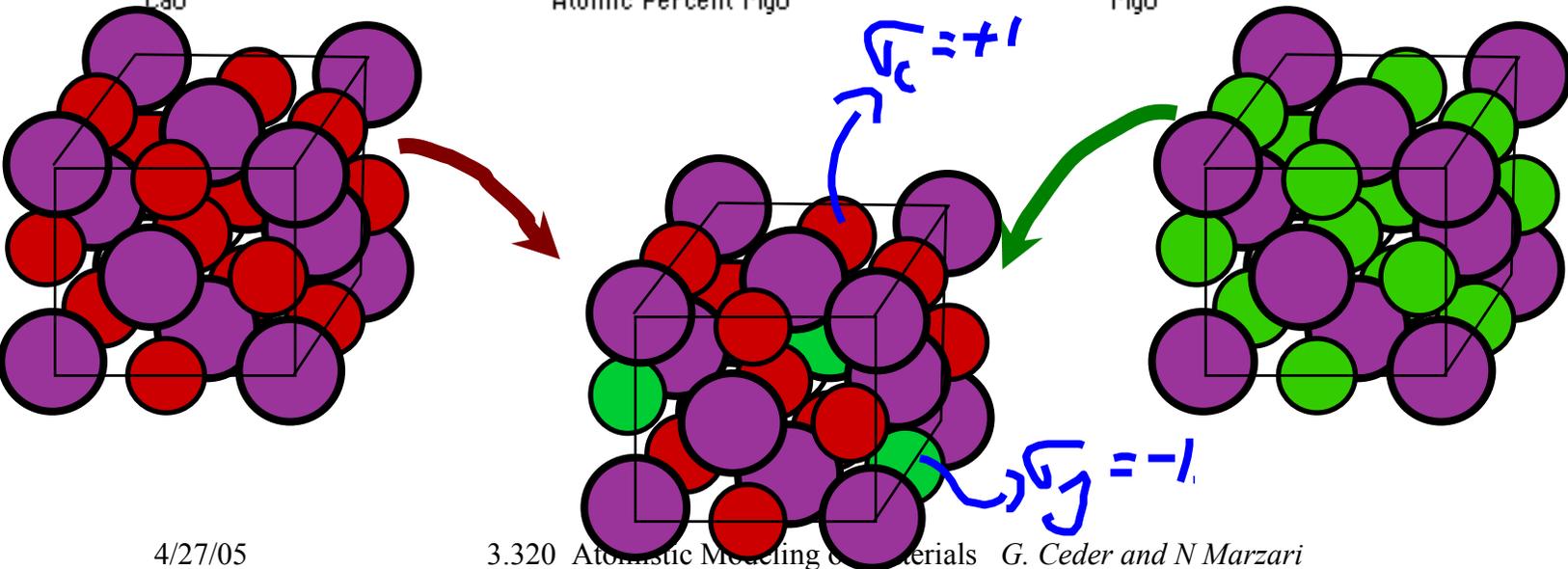
Phase diagram and thermodynamic quantities



CaO-MgO Phase Diagram

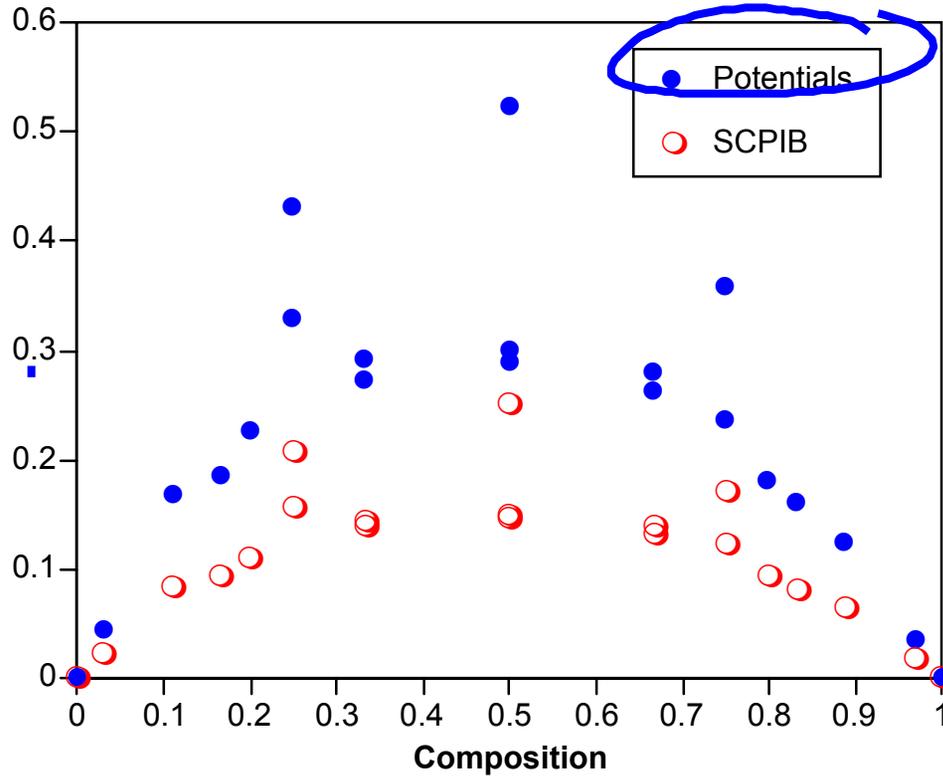


$$E(\{\sigma\}_{cation})$$



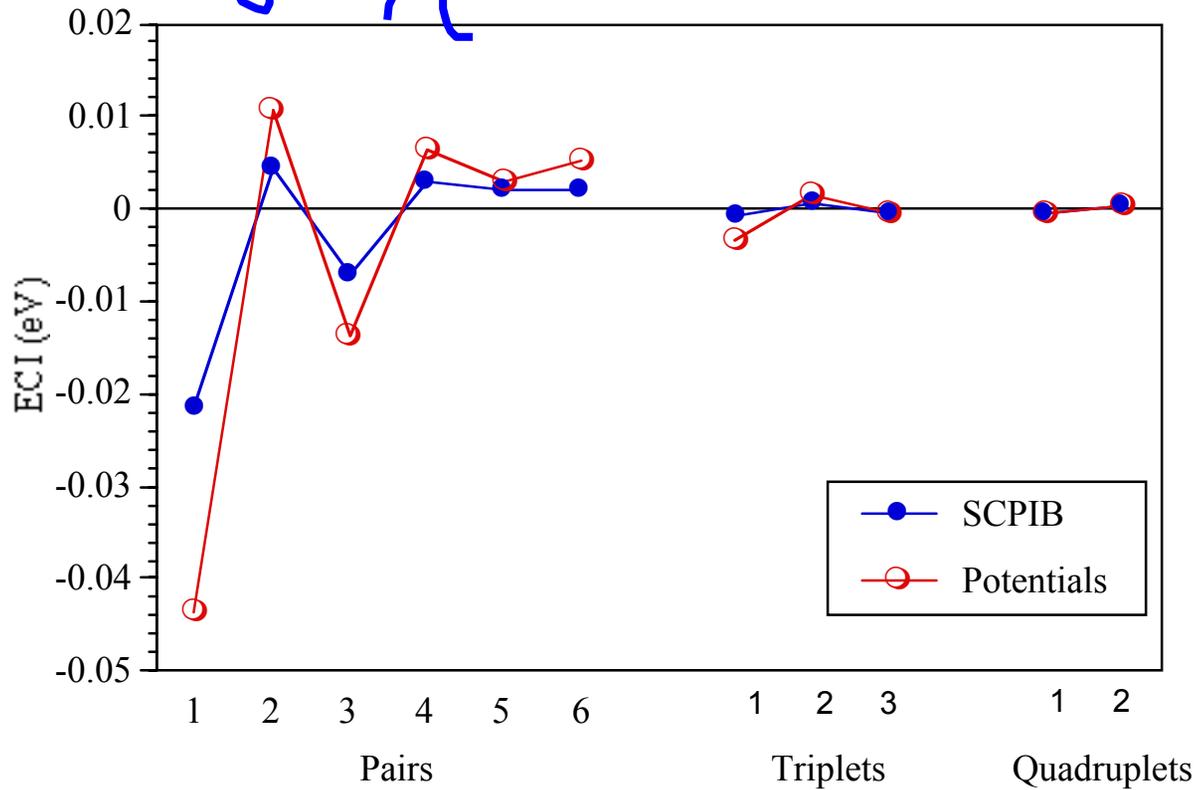
Calculated Mixing Energies as Input

E
eV/atom



Effective Cluster Interactions for CaO-MgO

$$V_{ij} = \frac{1}{4} \left[\langle E_{MgMg} \rangle + \langle E_{CaCa} \rangle - 2 \langle E_{CaMg} \rangle \right]$$



Calculated Phase Diagram

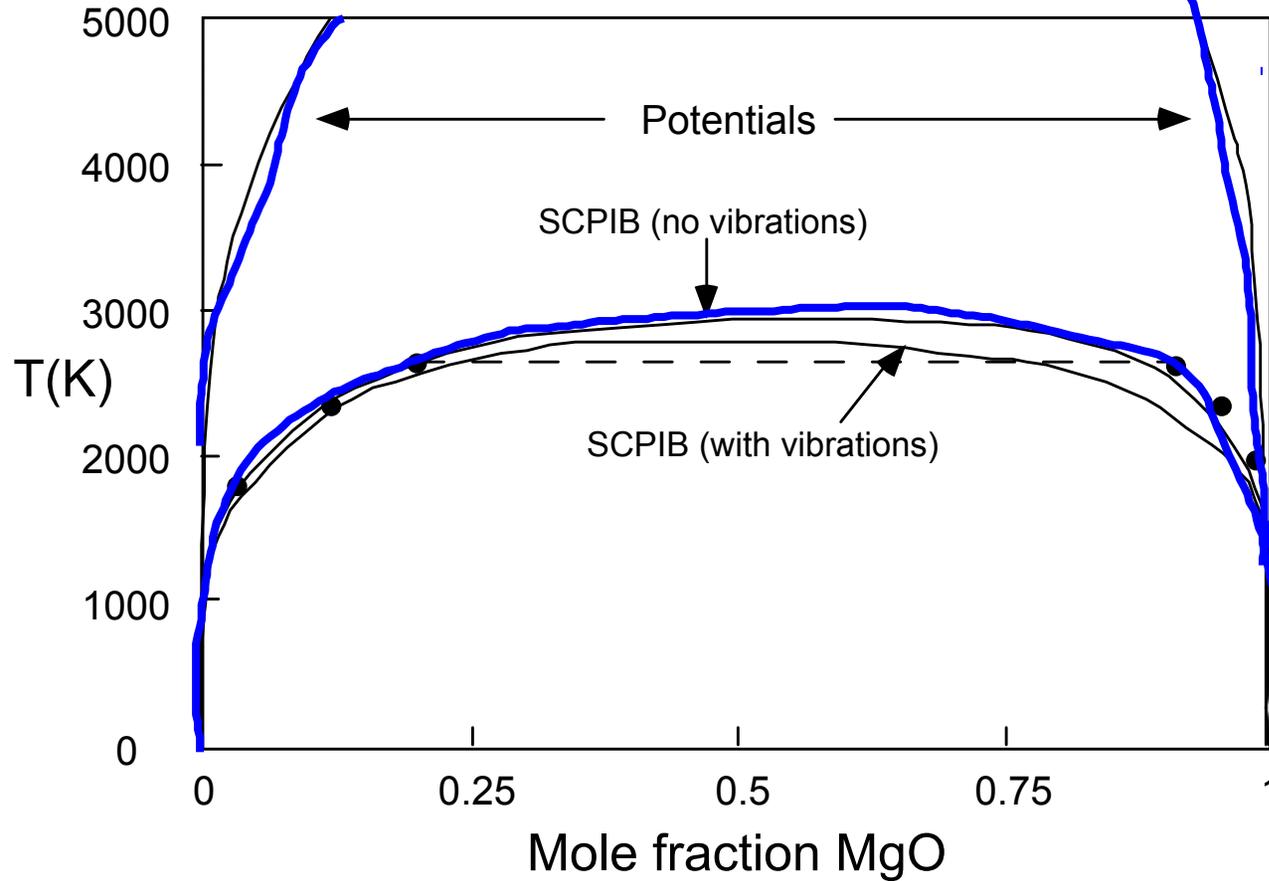
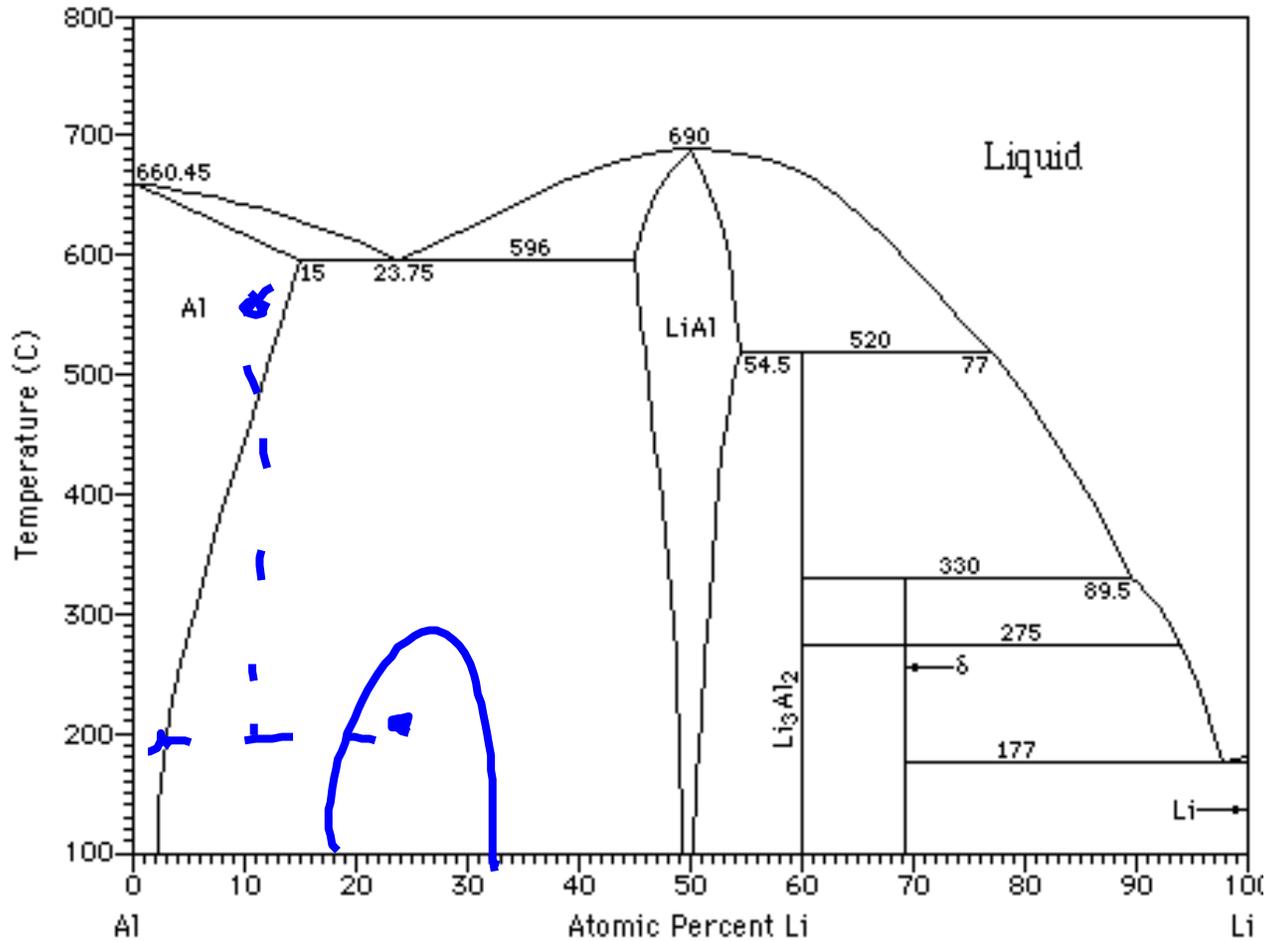


Figure after P. D. Tepeesch et al. *J. Am. Ceram. Soc.* **79** (1996): 2033-2040.

Calculating Metastable Phase in **Li-Al**



Calculated

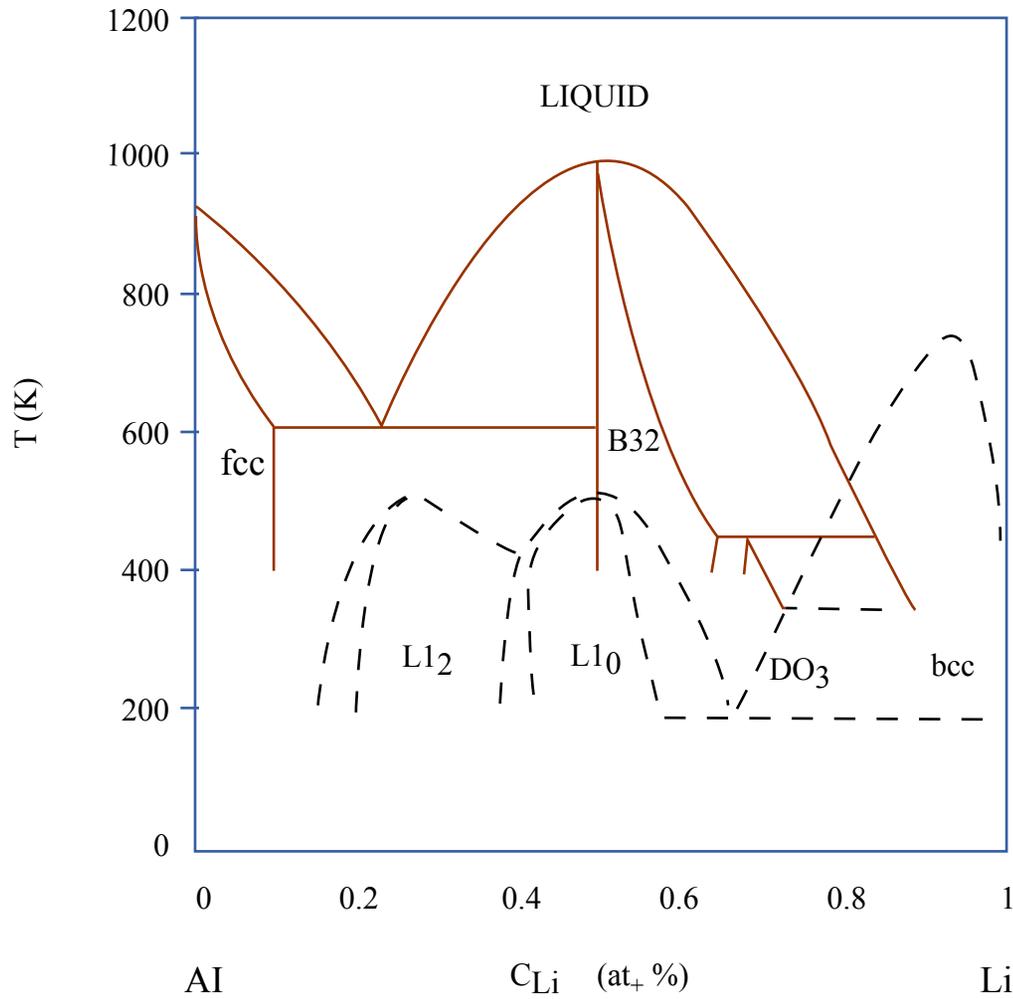


Figure by MIT OCW.

After M. Sluiter et al. *Phys. Rev. B* **42** (1990): 10460.

More Complicated Things: $\text{YBa}_2\text{Cu}_3\text{O}_z$

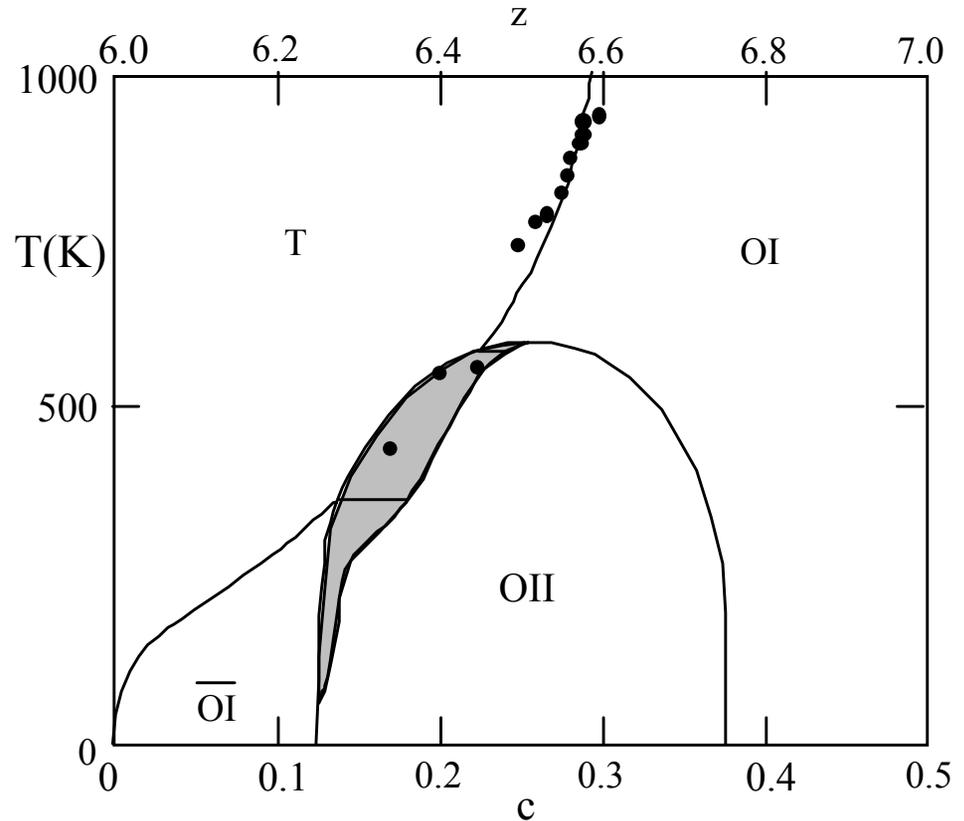
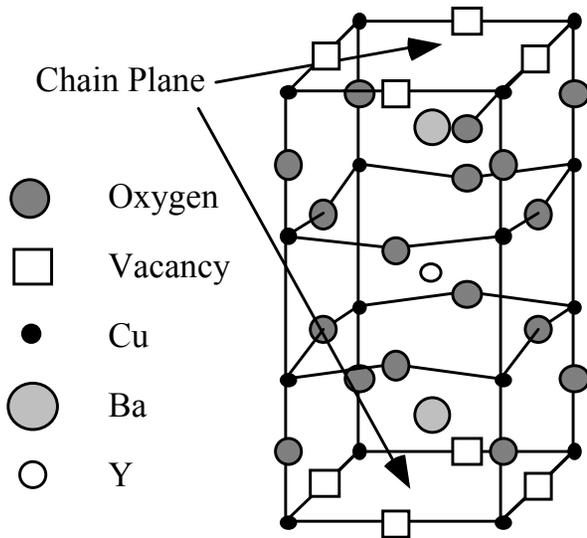
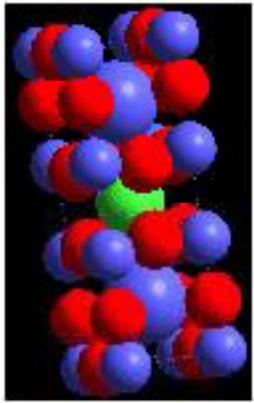
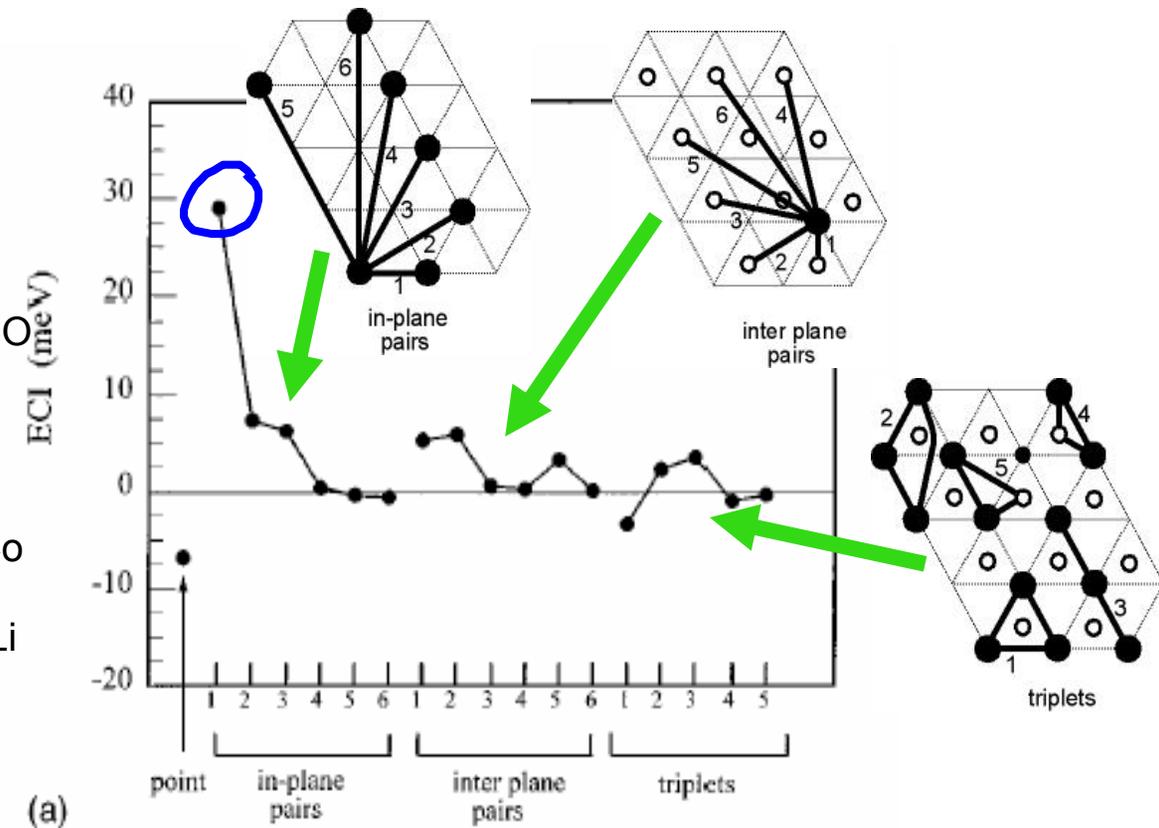
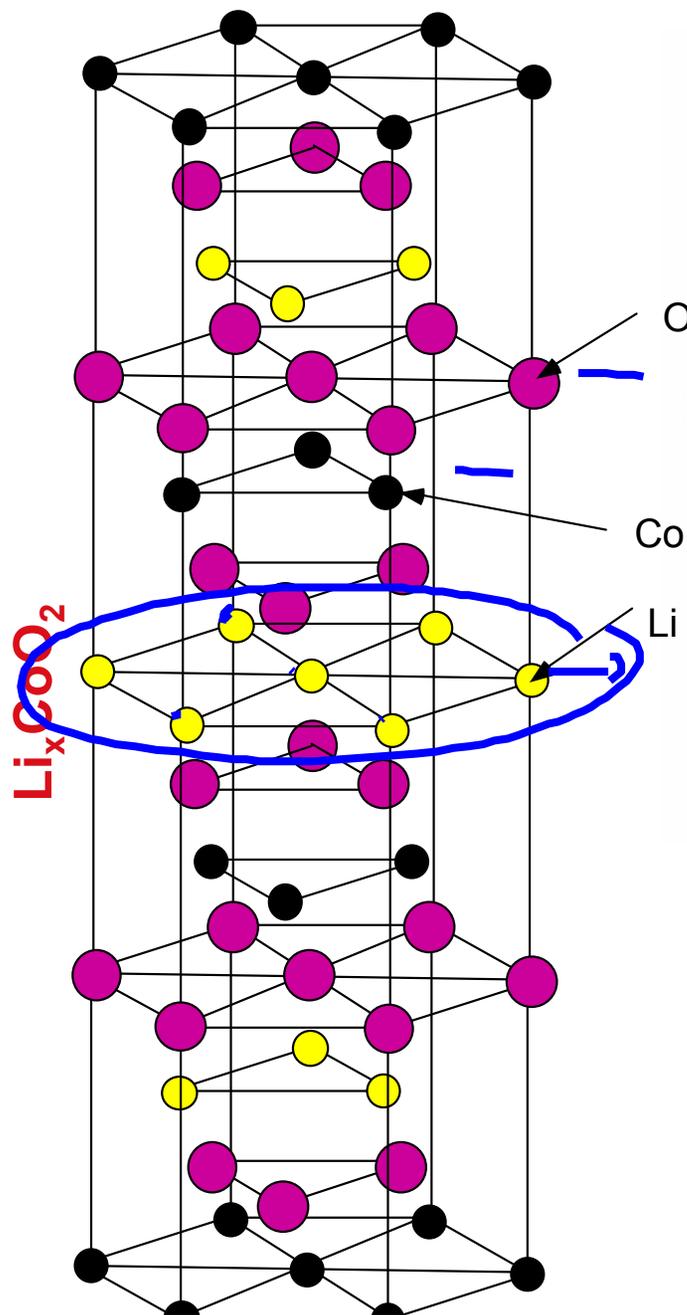


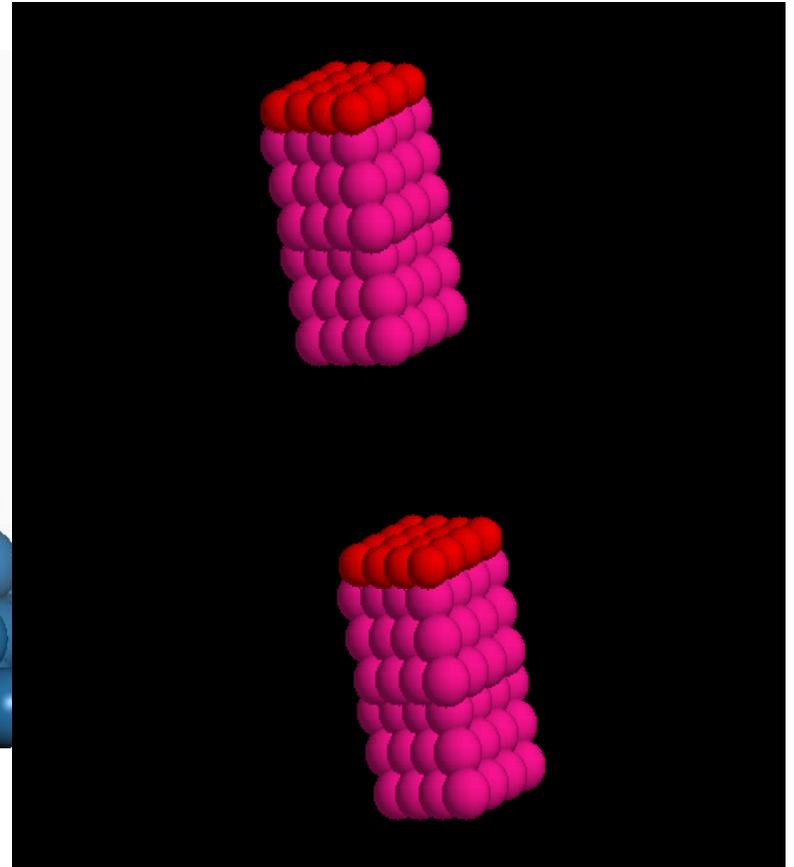
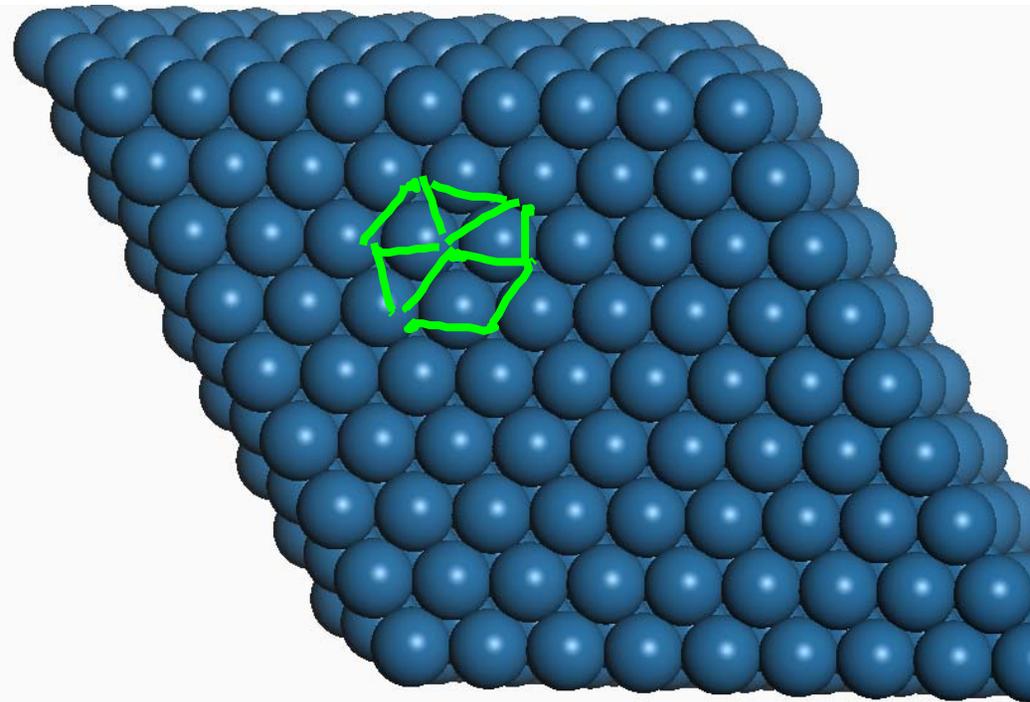
Figure after G. Ceder et al. *Phys. Rev. B* **41** (1990): 8698-8701.



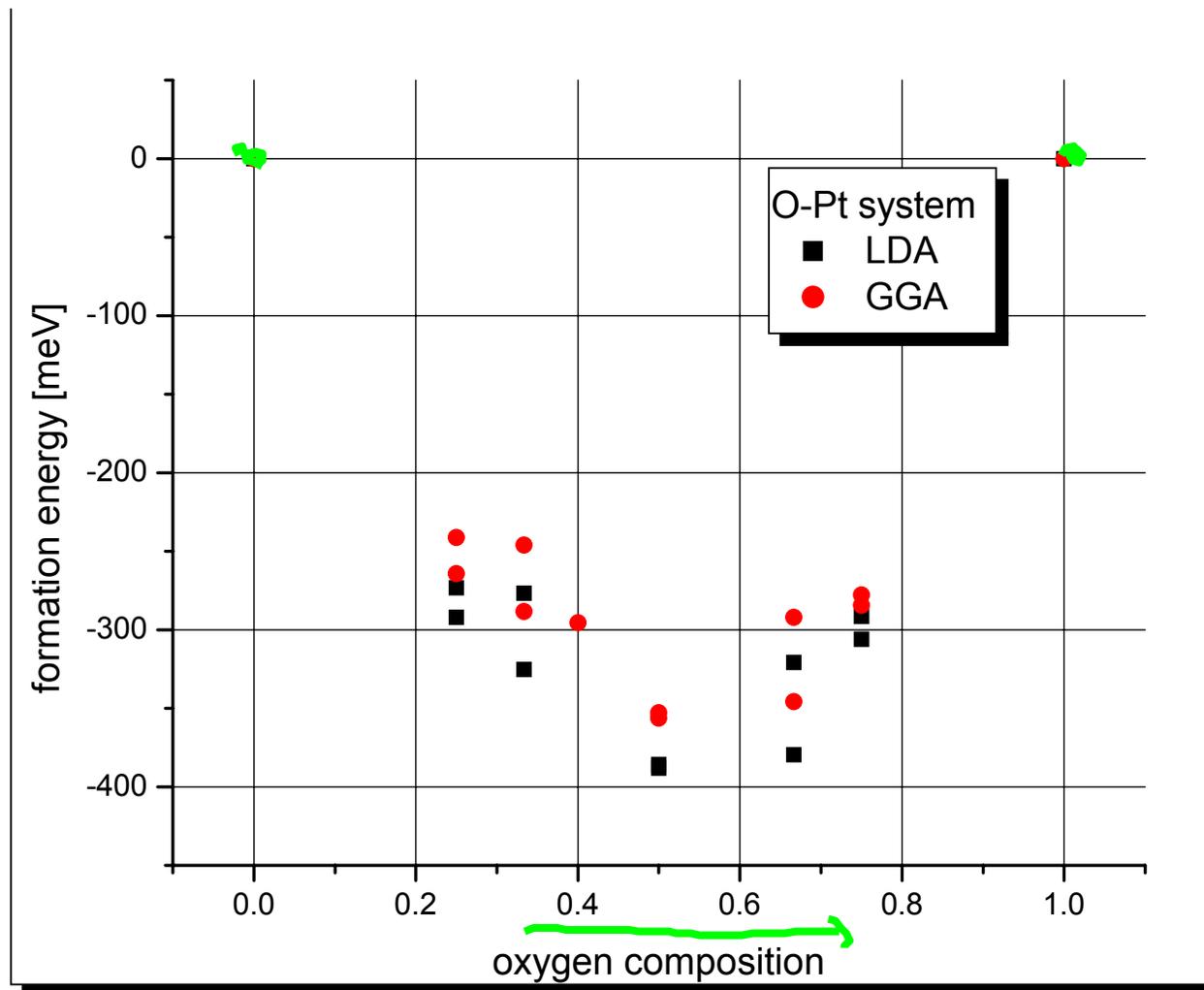
After A. Van der Ven et al. *Phys. Rev. B* **58**, (1998) 2975-2987.

Surface adsorption: On on Pt(111) (similar to your lab assignment)

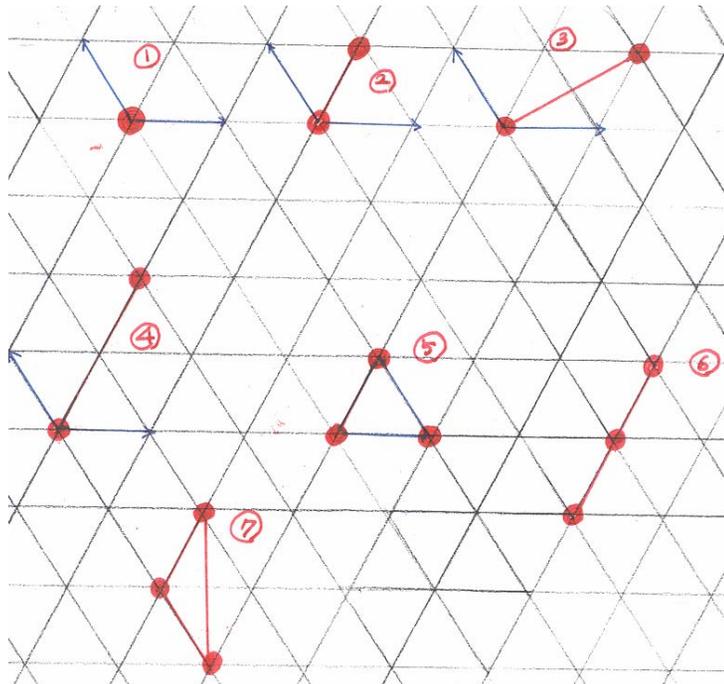
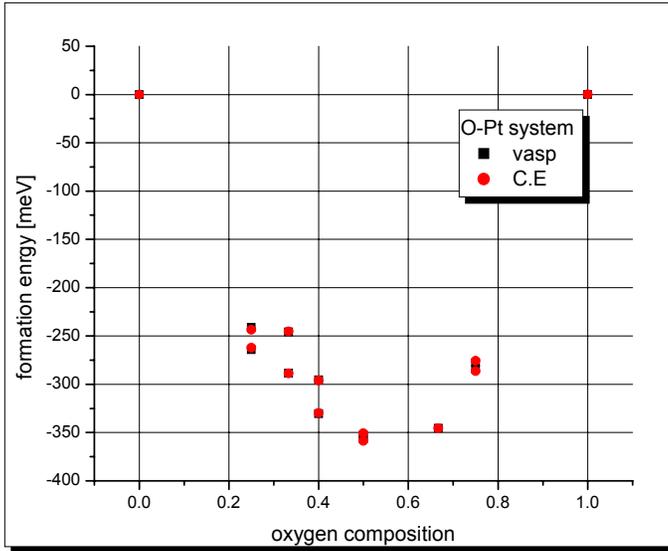
LDA/GGA calculations on slab geometry



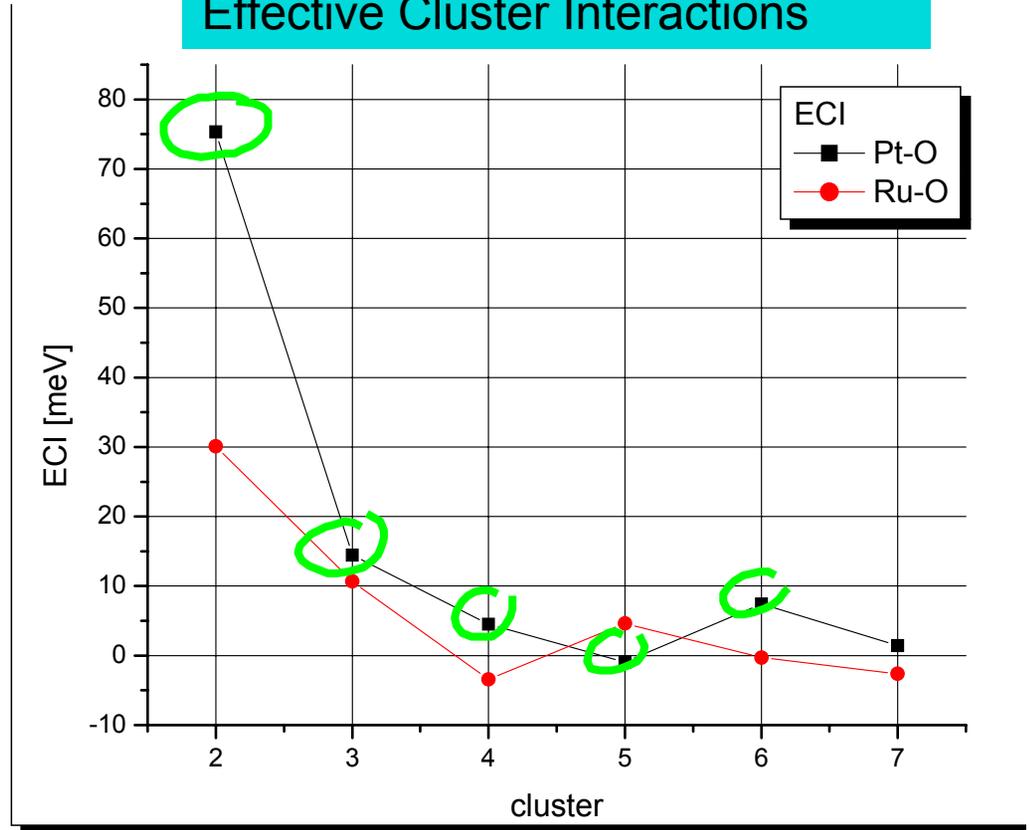
Adsorption energies for various O arrangements



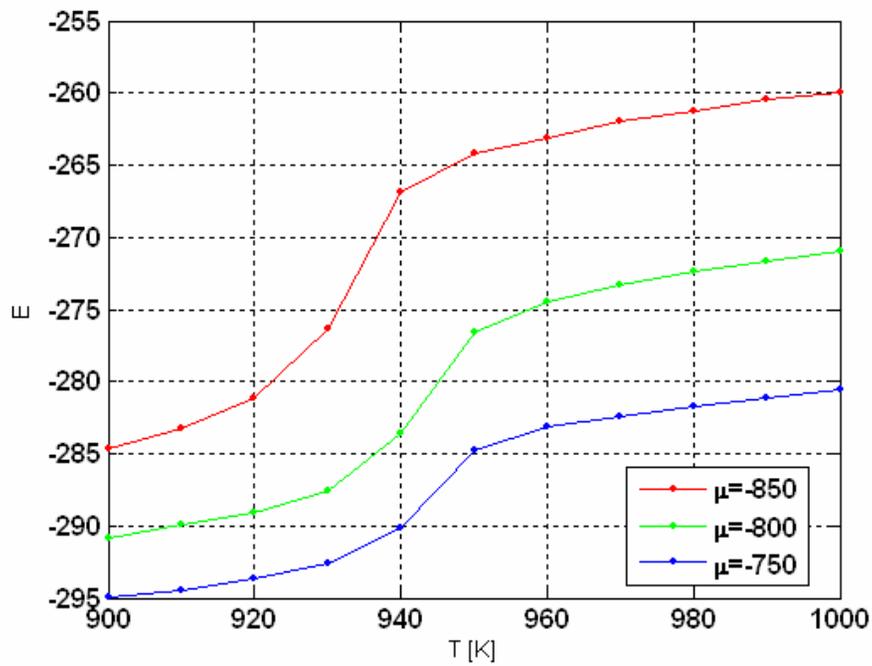
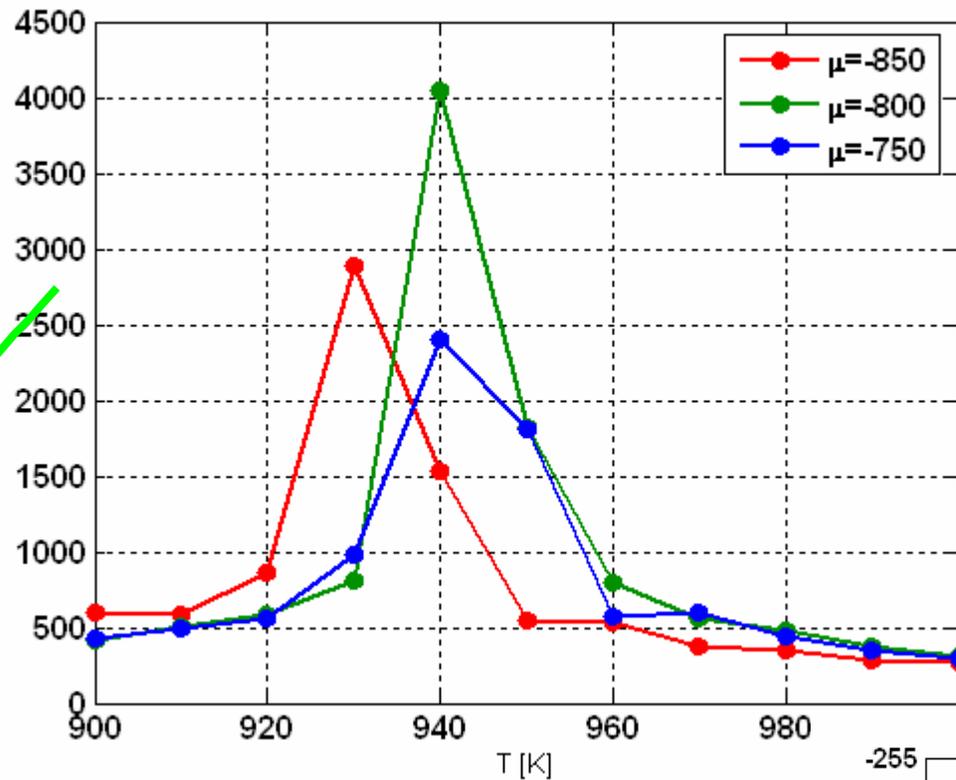
Cluster Expansion



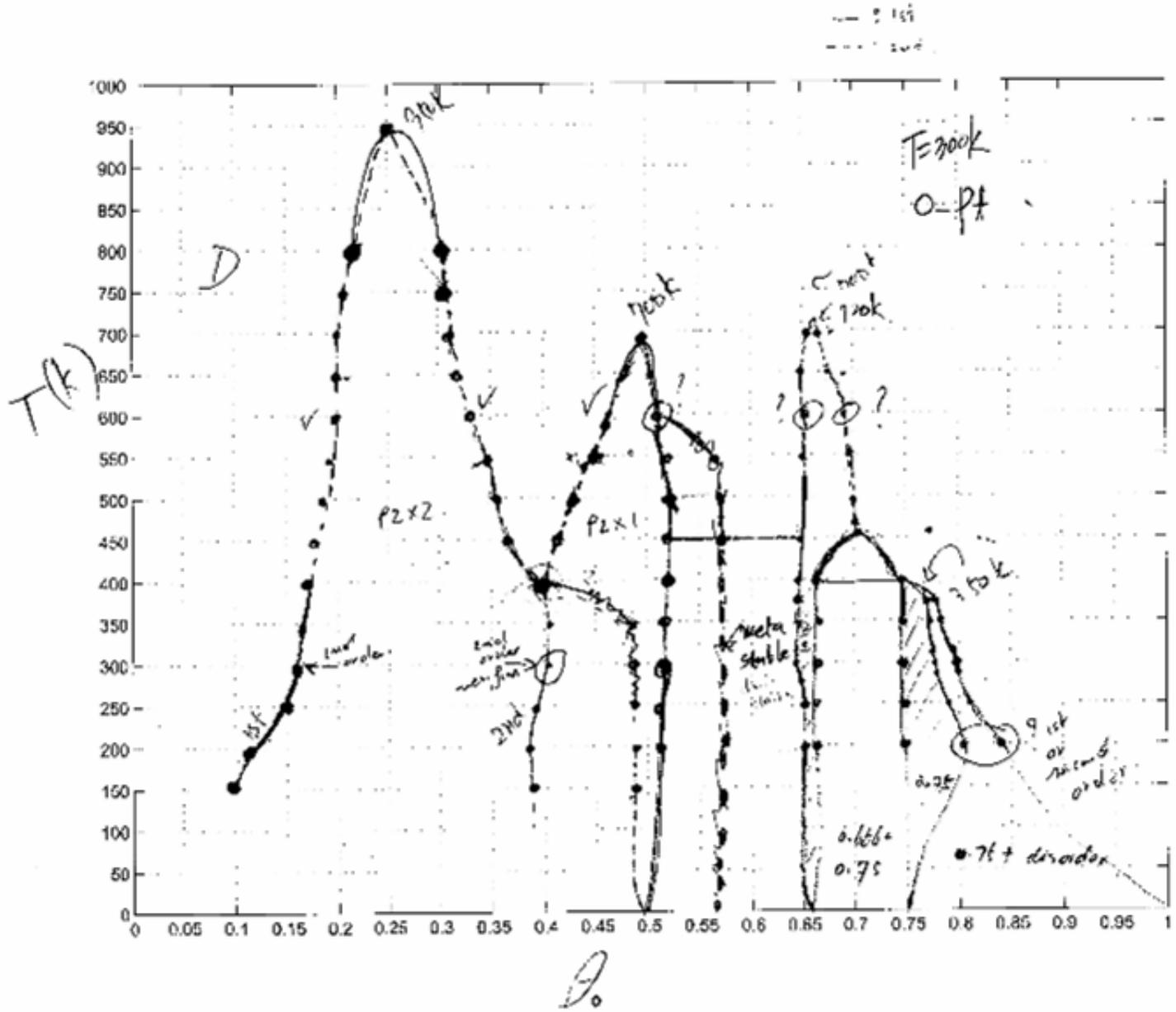
Effective Cluster Interactions

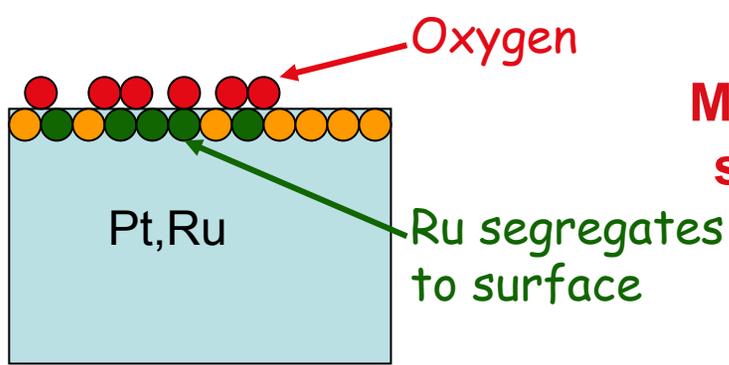


Monte Carlo Simulation

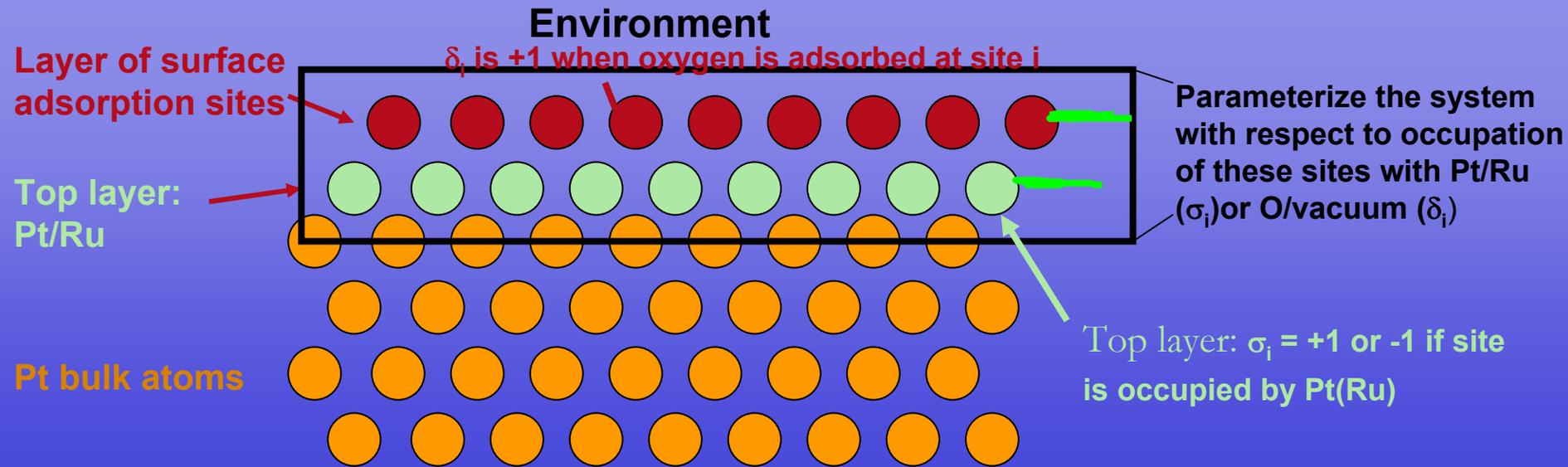


Phase Diagram





More complicated: Combined segregation and Adsorption



Technique used: Coupled Cluster Expansion (P.D. Tapesch, G.D. Garbulsky and G. Ceder, A Model for the Configurational Thermodynamics in Ionic Systems, *Phys. Rev. Lett.*, **74**:2272-75 (1995))

$$E(\sigma_1, \sigma_2, \dots, \sigma_N, \delta_1, \delta_2, \dots, \delta_N) =$$

$$V_0 + \sum_i V_i \sigma_i + \sum_i V_i \delta_i + \sum_{i,j} V_{i,j} \sigma_i \sigma_j + \sum_{i,j} V_{i,j} \sigma_i \delta_j + \sum_{i,j} V_{i,j} \delta_i \delta_j + \dots$$

Oxidation drags Ru to the surface

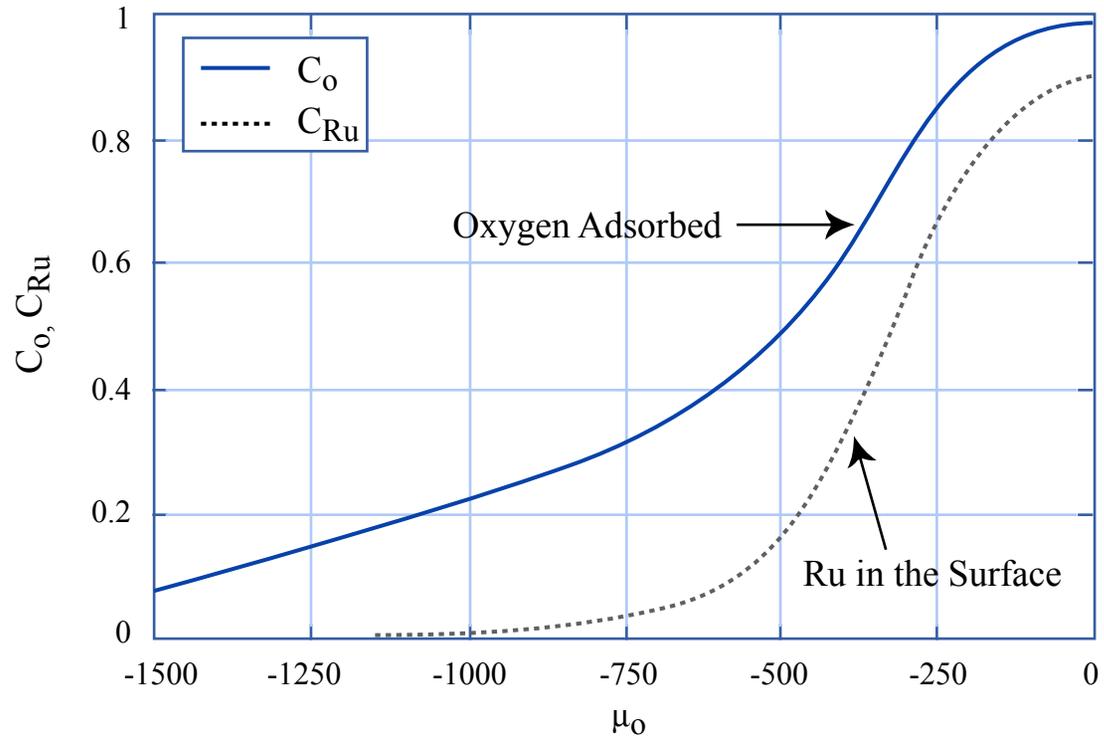


Figure by MIT OCW.

More oxidation strength



Oxidation drags Ru to the surface

Low oxidation

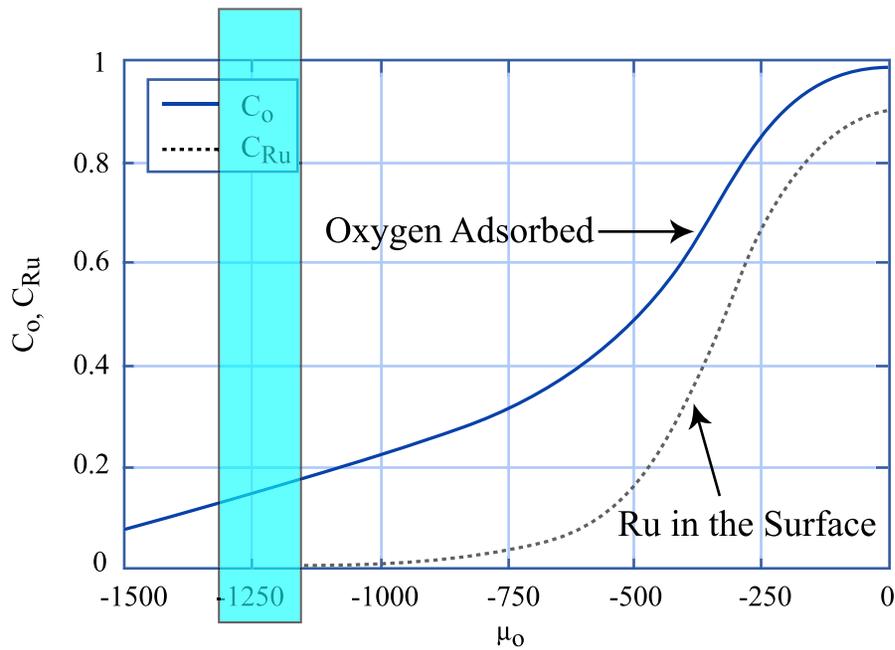
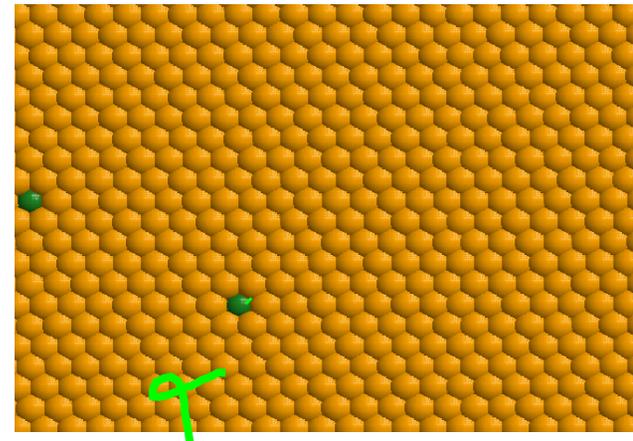
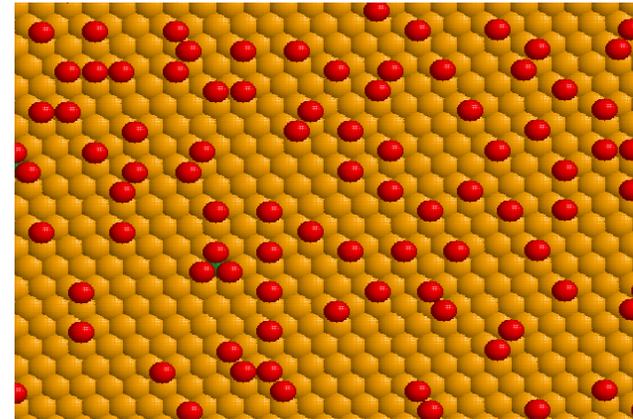


Figure by MIT OCW.



More oxidation strength



Oxidation drags Ru to the surface

Medium oxidation

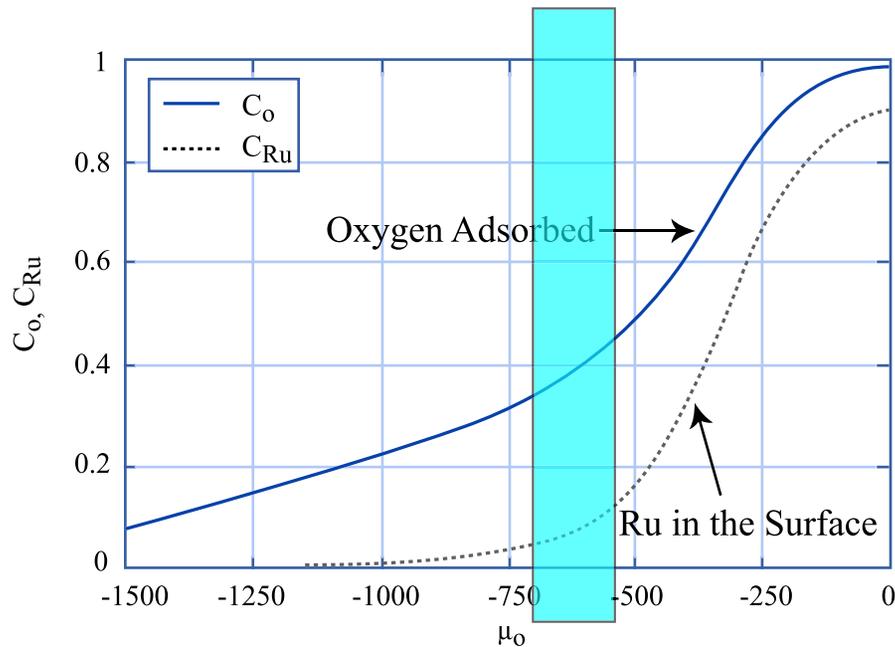
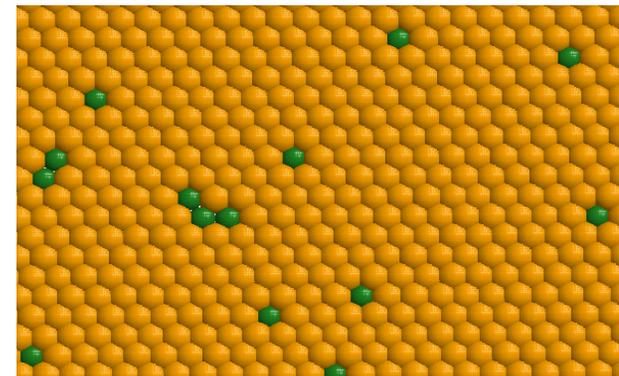
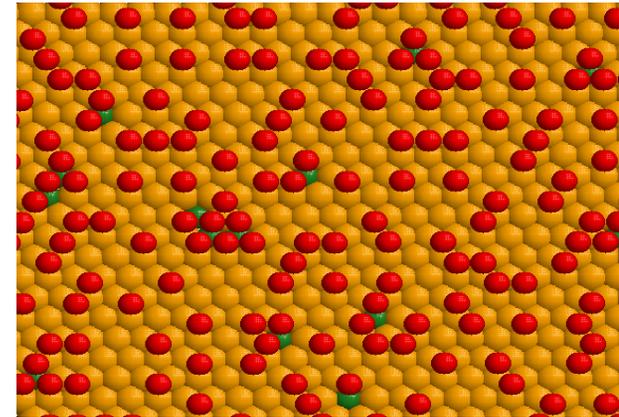


Figure by MIT OCW.



More oxidation strength



Oxidation drags Ru to the surface

High oxidation

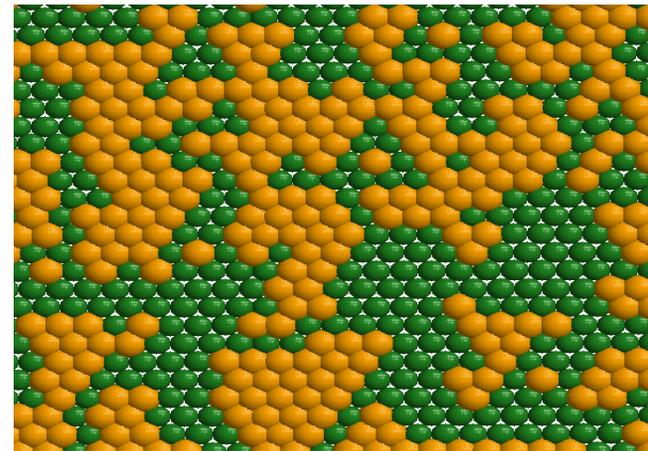
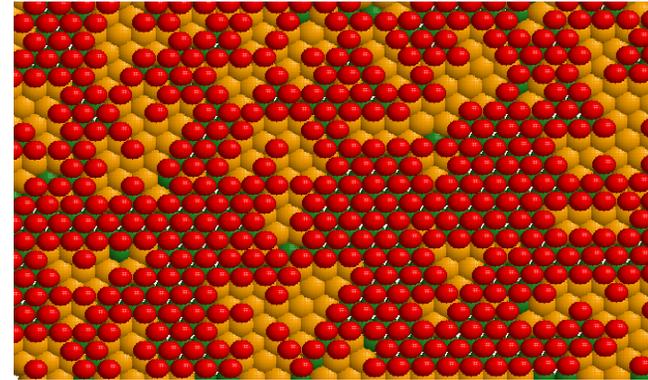
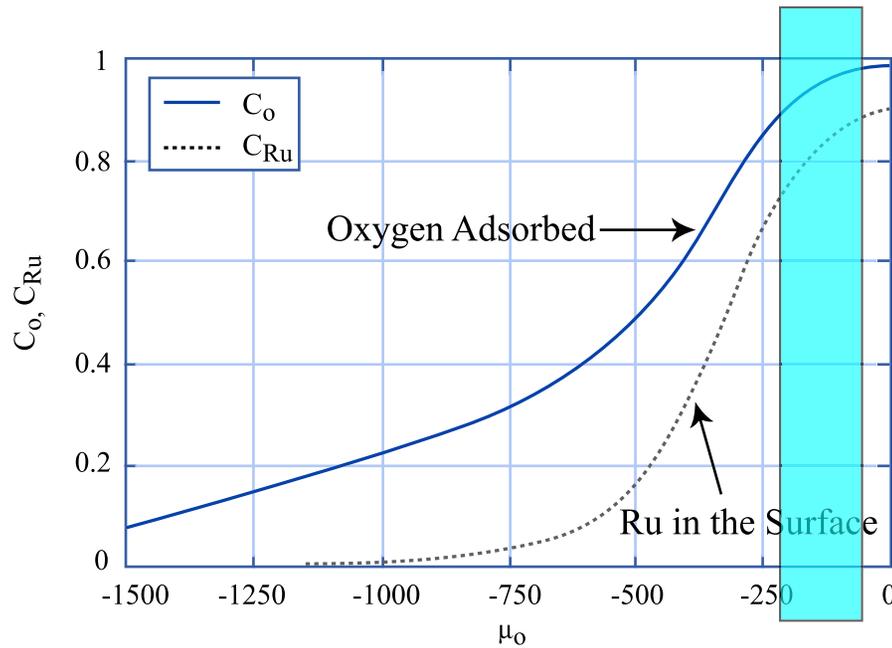
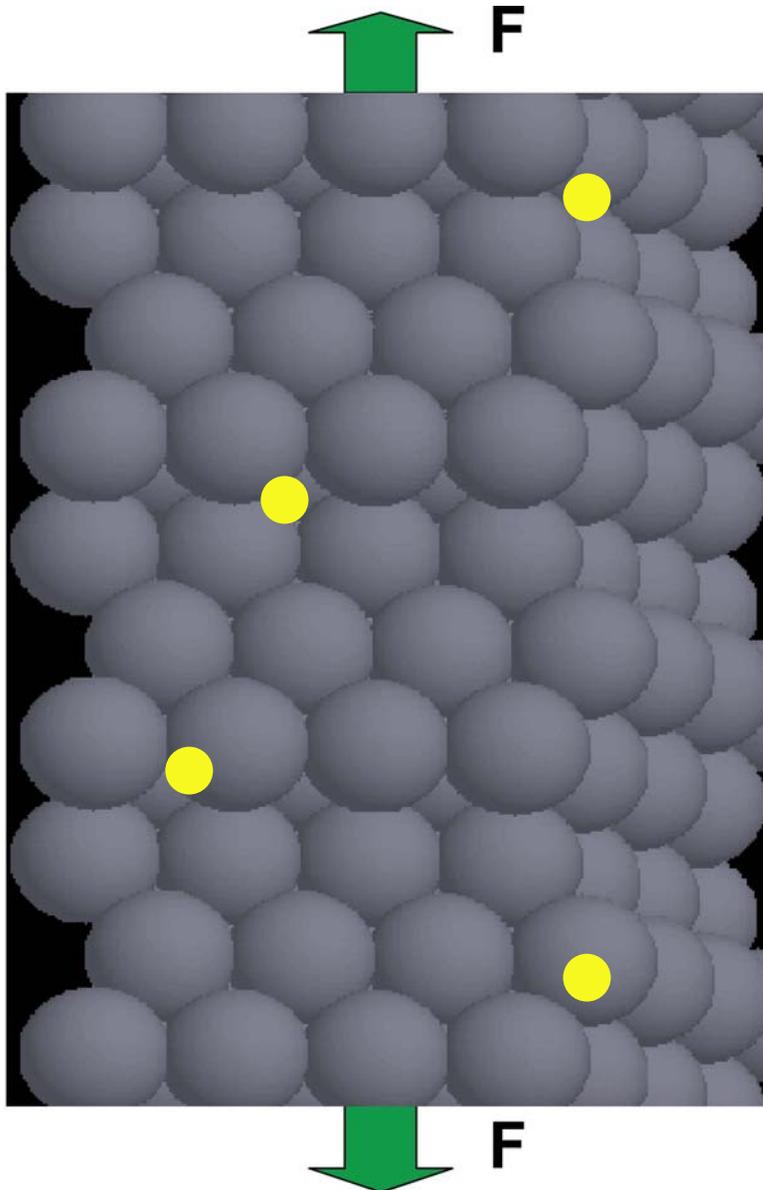


Figure by MIT OCW.

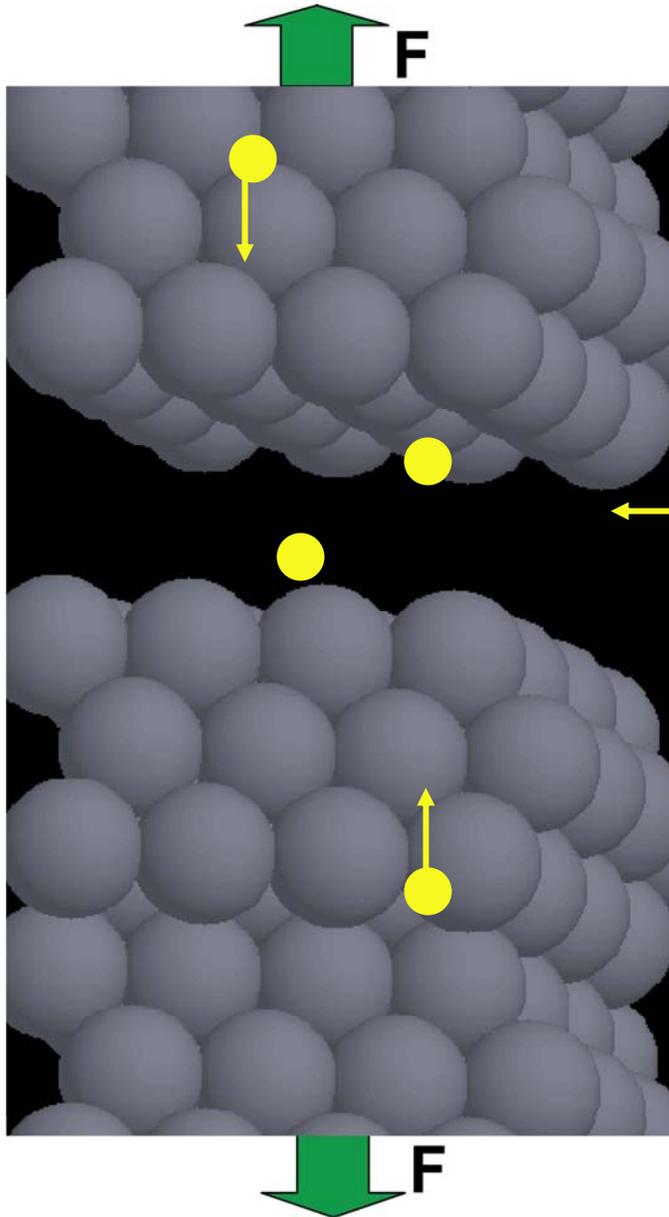
More oxidation strength



Equilibration of Structure and Chemistry also key in other problems: Hydrogen Modified Al Fracture



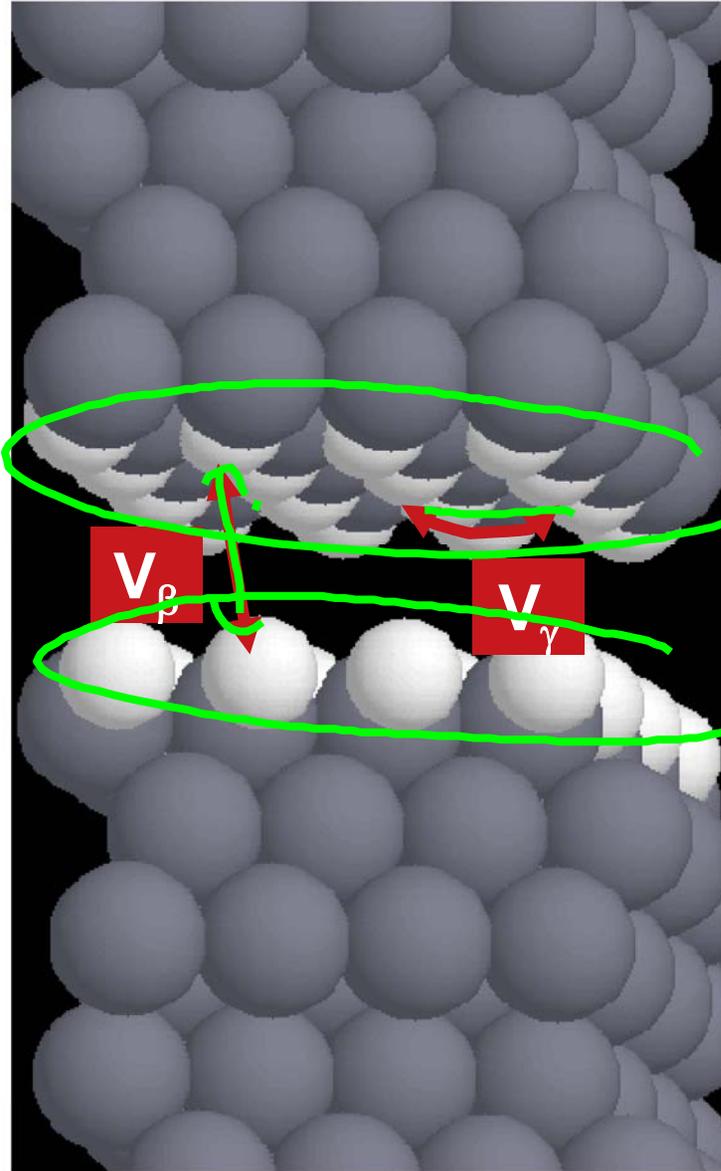
For slow separation impurities can flow in



Free energy of separation (and force displacement relation) depend on amount and arrangement of impurity

Need to equilibrate both amount and arrangement of H on Al(111) for each separation

Lattice model for H on separating Al(111) surfaces



- H in tetrahedral sites
- Lattice model of tetrahedral sites on (111)
- Interaction in-plane and between surfaces

Procedure

Calculate energy of different H configurations on surface at different plane separations.

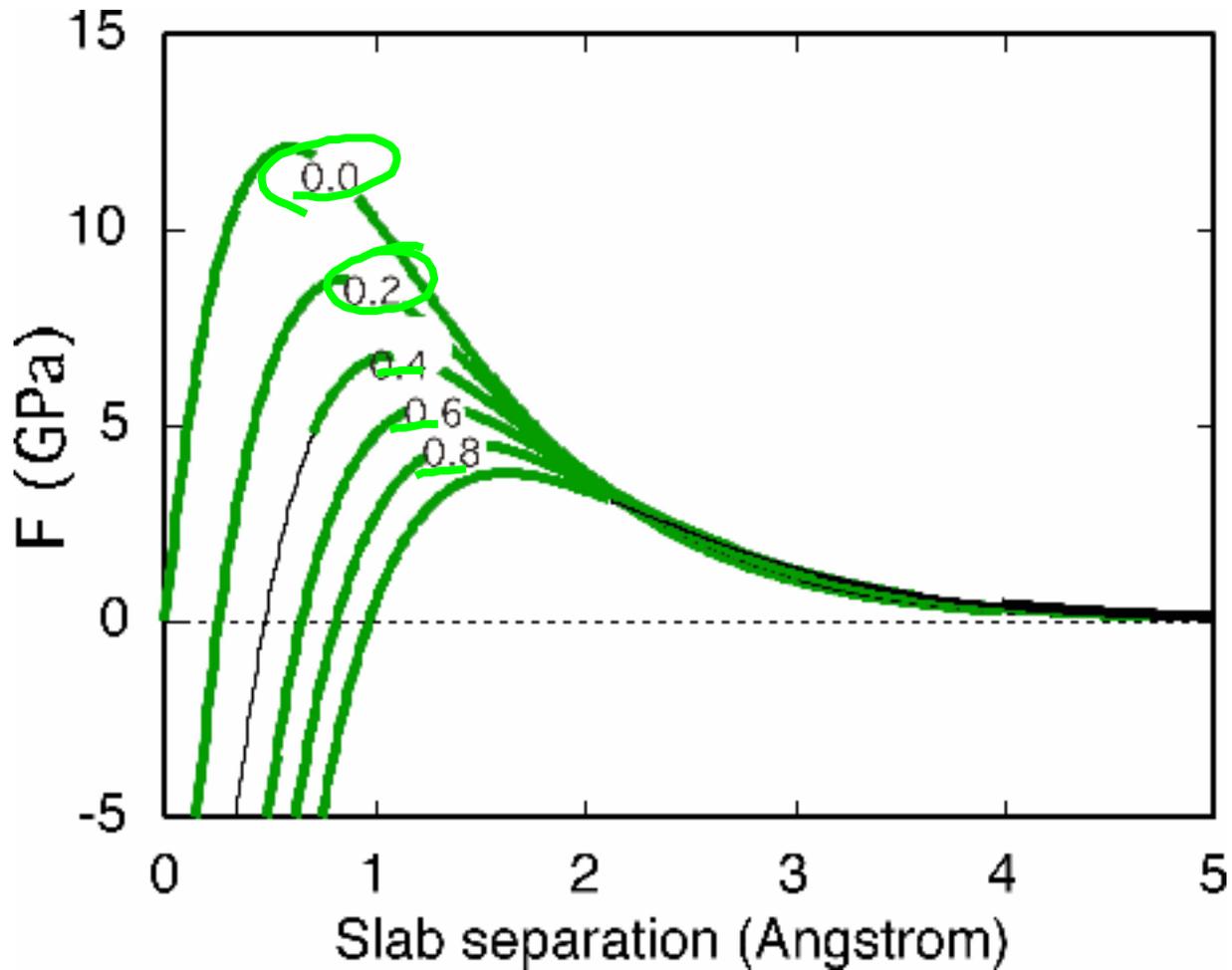
Cluster expand H configuration energy at each plane separation

Monte Carlo simulation at each plane separation

Take derivatives of free energy (to get force)

Construct grand potentials and construct equilibrium “trajectory”

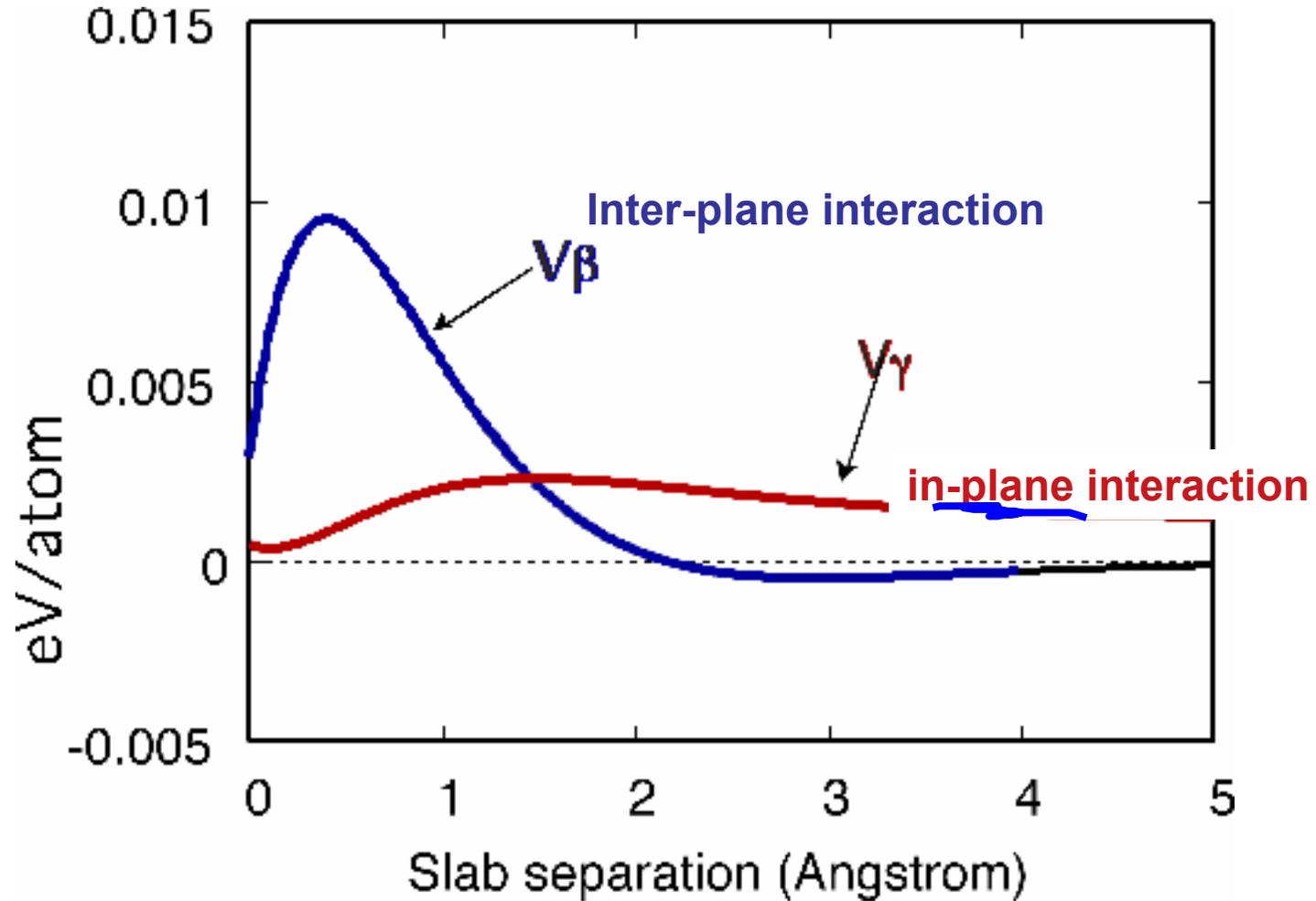
Calculate Energy versus separation for various H concentrations and configurations



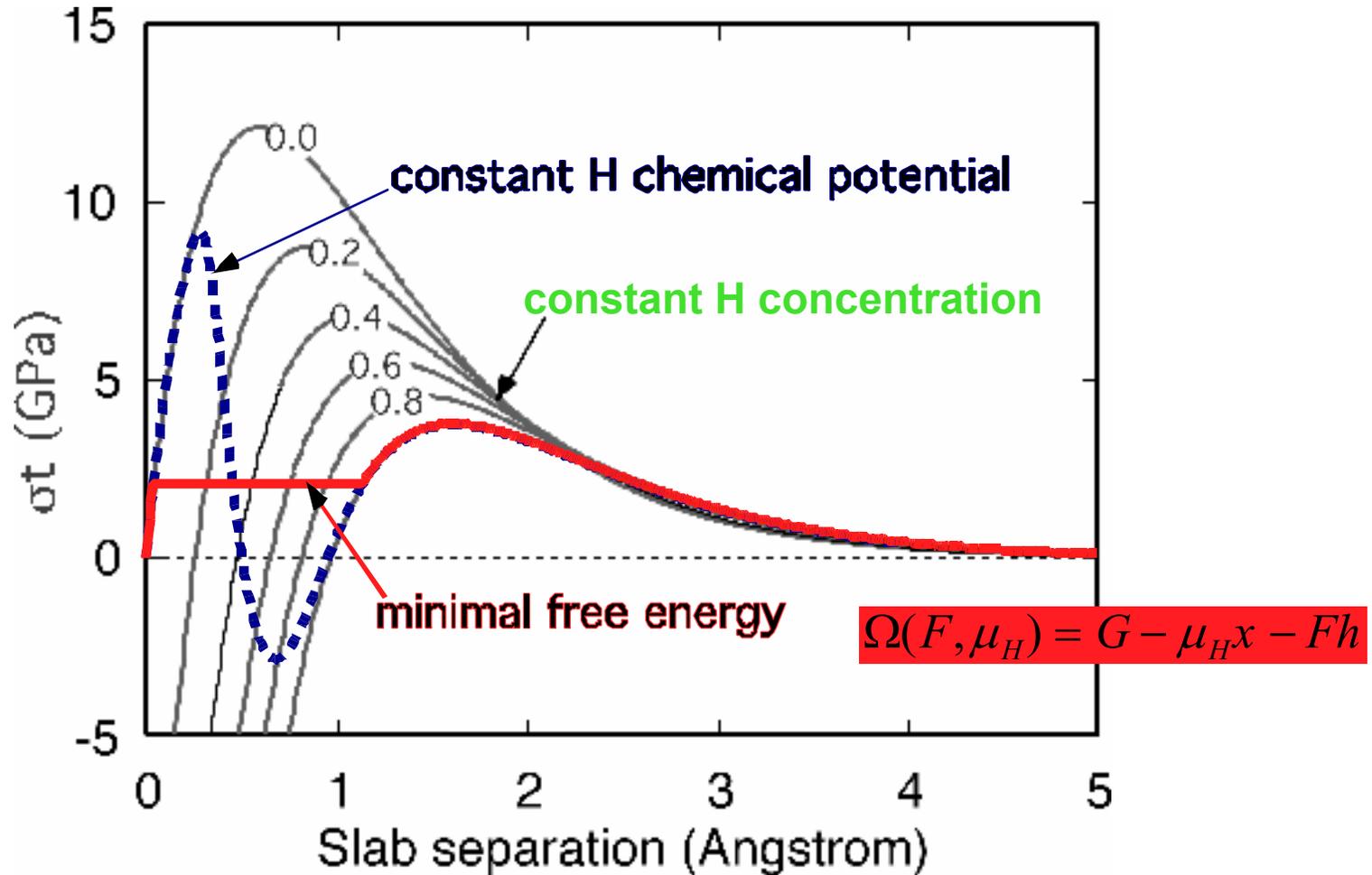
Cluster expand 

Perform Monte Carlo at each separation

Interactions



Apply force with constant H chemical potential



First order transition: Separation at constant force due to impurity inflow

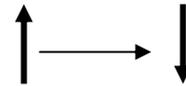
Why is Ising – like model such a good approximation for the real system. Look back at coarse-graining ideas

Electronic

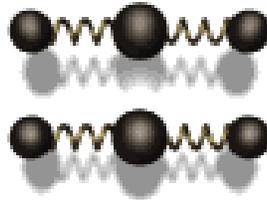
Occupation

$$\Psi \longrightarrow \hbar$$

Magnetic (electron spin)



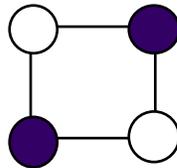
Vibrational



Molecular Dynamics: can not reach configurational excitations

Monte Carlo: too many energy evaluations required

Configurational



We can use lattice models for studying mixing and ordering of atoms in crystalline materials. But why is this a good approximation ?

Coarse-graining: The concept

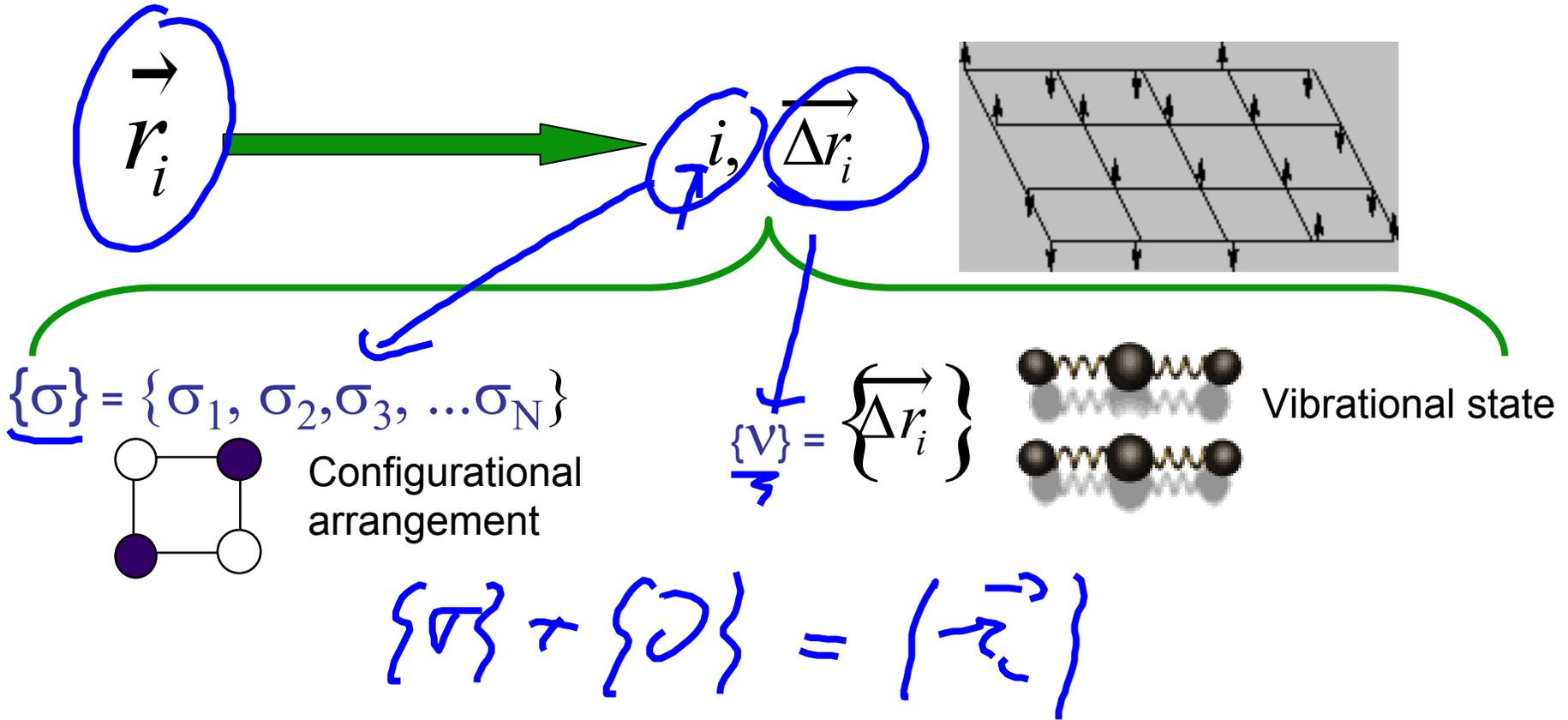
Can we integrate partition function over fast degrees of freedom to obtain an effective Hamiltonian for the slower degrees of freedom ?

e.g. **for an alloy**: Can we find an effective free energy function for the **substitutional** arrangement of an alloy that includes the entropic effect of vibrations and electronic excitations ?

YES

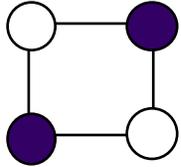
Use Monte Carlo, Molecular Dynamics, or analytical methods to integrate effect of temperature on fast degrees of freedom

Change coordinates

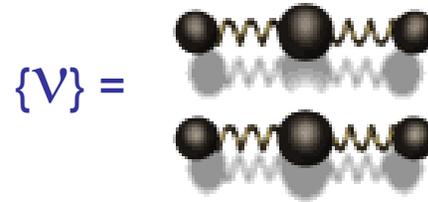


Coarse-graining by reduction of degrees of freedom

$$\{\sigma\} = \{\sigma_1, \sigma_2, \sigma_3, \dots, \sigma_N\}$$



Configurational arrangement



$$\{v\} =$$

Vibrational state

$$Q = \sum_{\{\sigma\}} \sum_{\{v\}} \exp(-\beta E(\{\sigma\}, v(\{\sigma\})))$$

$$\exp(-\beta F)$$

$$Q = \sum_{\{\sigma\}} \exp(-\beta F(\{\sigma\}))$$

Partition Function of an Ising-like Model

Two approximations for F

$$F(\{\sigma\}) = -kT \ln \left[\sum_{\{v\}} \exp(-\beta E(v(\{\sigma\}))) \right]$$

F is Effective Hamiltonian for $\{\sigma\}$ degree of freedom

G. Ceder, *Computational Materials Science* **1**, (1993) 144-150.

Approximations to $F(\{\sigma\})$ determine which excitations (entropies) are included in the total free energy

1. Approximate $F(\{\sigma\})$ by $E(\{\sigma\})$

$$F(\{\sigma\}) = -kT \ln \left[\sum_{\{v\}} \exp(-\beta E(v(\{\sigma\}))) \right]$$

when doing Monte Carlo and free energy integration, only get configurational entropy

2. Approximate $F(\{\sigma\})$ by $E(\{\sigma\}) - TS_{\text{electronic}}(\{\sigma\})$

when doing Monte Carlo and free energy integration, get configurational entropy and electronic

3. $F(\{\sigma\}) = E(\{\sigma\}) - TS_{\text{electronic}}(\{\sigma\}) - TS_{\text{vib}}(\{\sigma\})$

when doing Monte Carlo and free energy integration, get configurational entropy + electronic + vibrational

Summary

The model on the time scale of the substitutional excitations is an Ising-like model (i.e. excitations are changes of occupation variables)

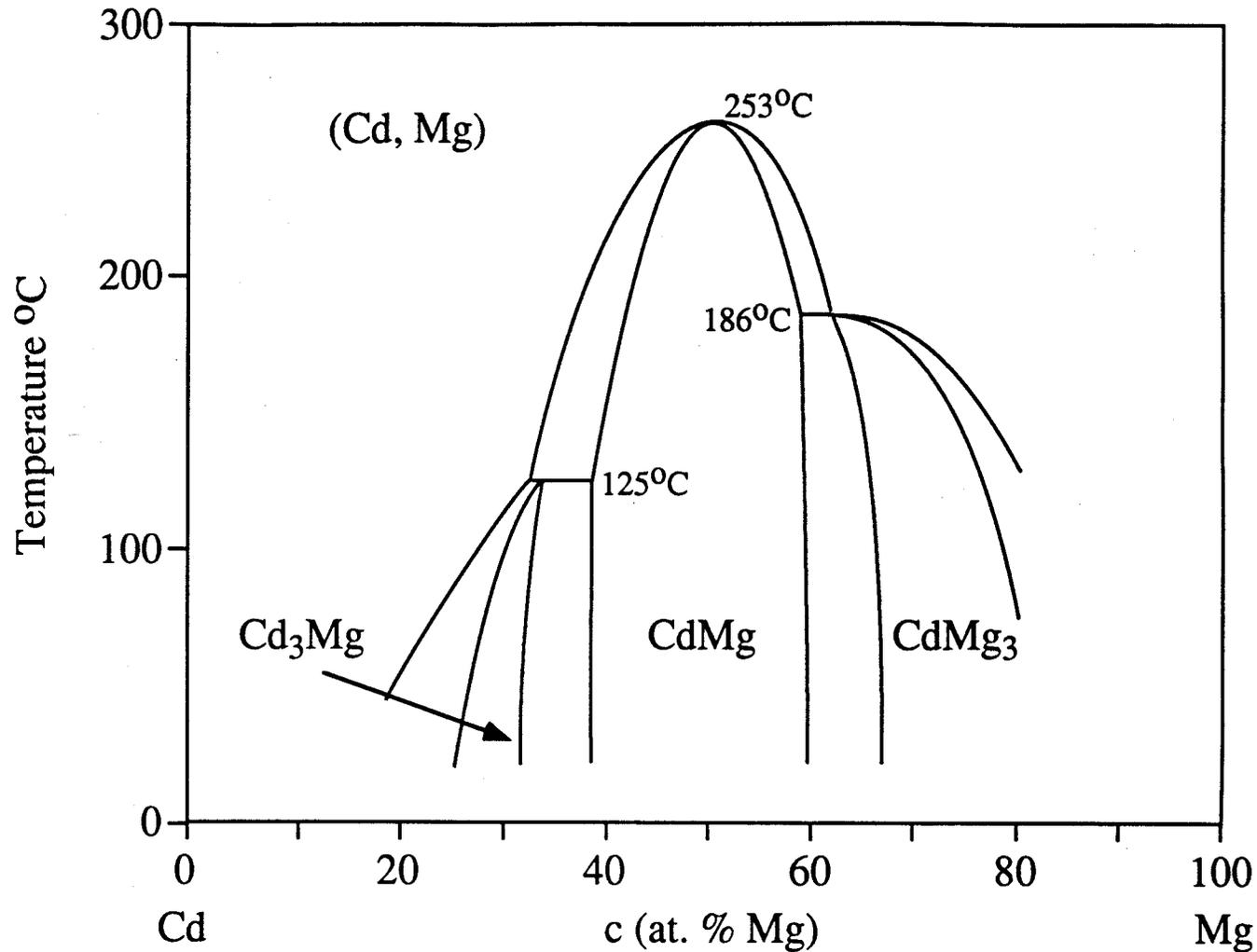
The Hamiltonian of the Ising-like model is the free energy of the faster excitations (e.g. vibrations, electronic excitations).

Only approximation is separation of time scales



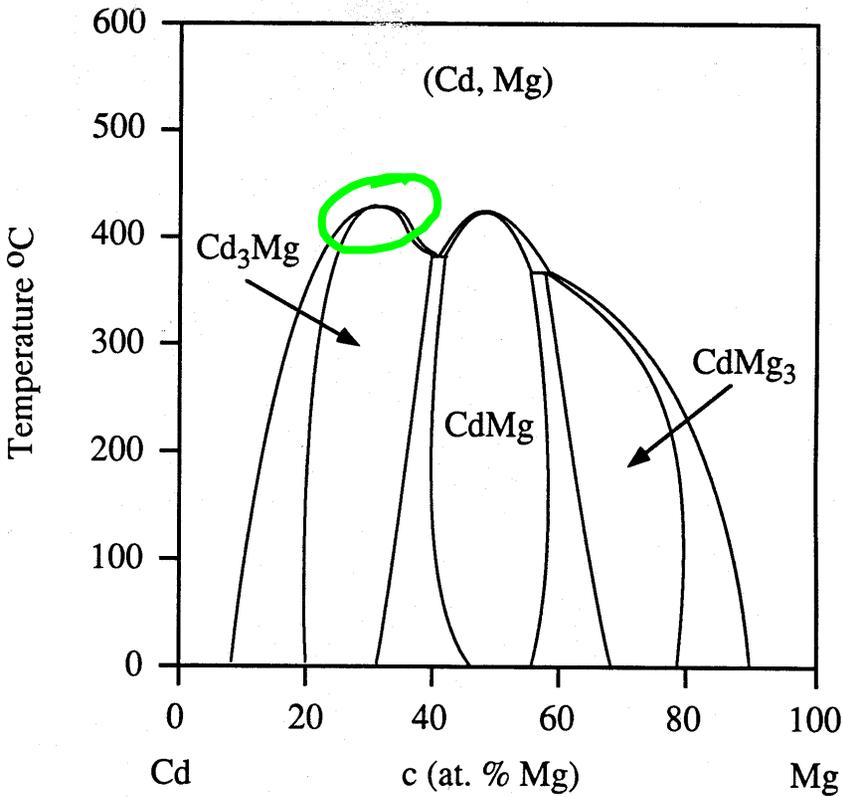
Cluster Expansion is a practical form for the Ising-like Hamiltonian

Can investigate effect of various approximations: Cd-Mg system

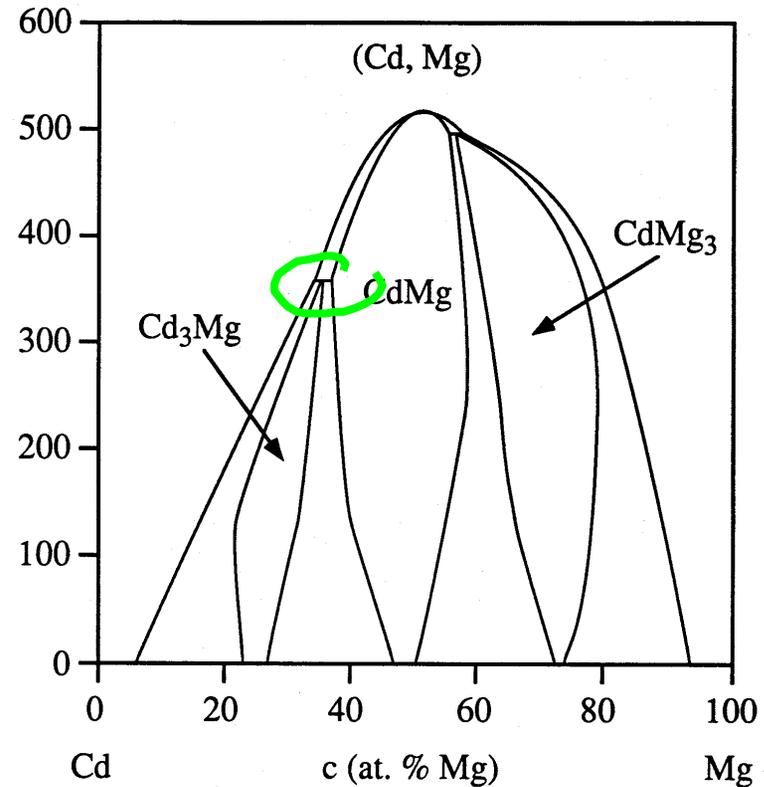


After from M. Asta et al. *Physical Review B* **48**, (1993) 748-766.

Calculated



No vibrational entropy



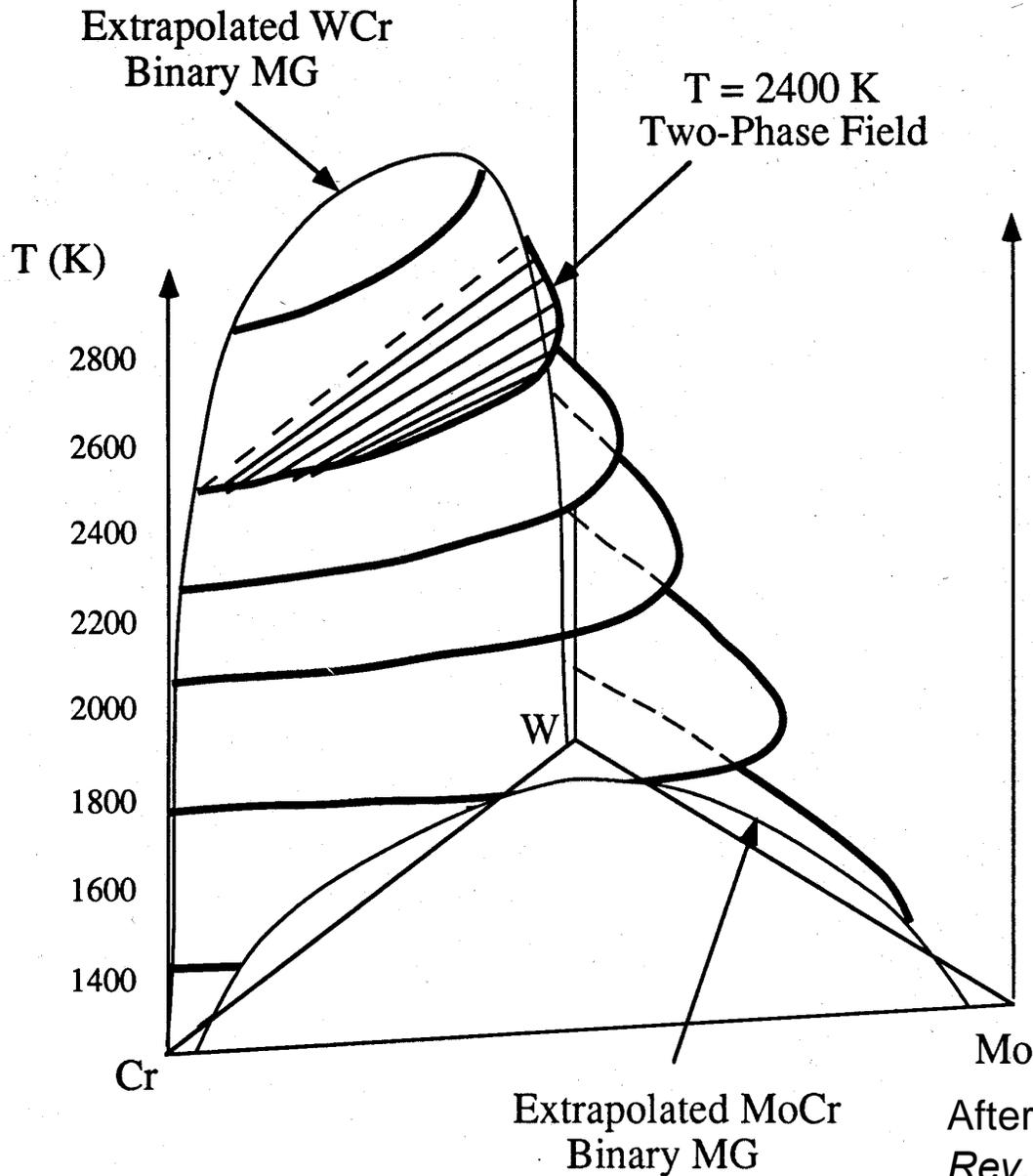
With vibrational entropy

After M. Asta et al. *Physical Review B* **48**, (1993) 748-766.

Systems as 1994

Table removed for copyright reasons.

Simple Ternaries



After R. McCormack et al. *Phys. Rev. B* **51**, (1995) 15808-15822.

References

- 1. D. de Fontaine, in *Solid State Physics* H. Ehrenreich, D. Turnbull, Eds. (Academic Press, 1994), vol. 47, pp. 33-176.
- 2. G. Ceder, A. Van der Ven, C. Marianetti, D. Morgan, *Modeling and Simulation in Materials Science and Engineering* **8**, (2000) 311-321.
- 3. A. Zunger, in *Statics and Dynamics of Alloy Phase Transformations* P. E. A. Turchi, A. Goniss, Eds., pp. 361-419 (1994).
- 4. A. Van de Walle, G. Ceder, *J. of Phase Equilibria* **23**, (2002) 348-359.
- 5. J. M. Sanchez, D. de Fontaine, *Phys. Rev. B* **25**, (1982) 1759-1765.
- 6. J. M. Sanchez, F. Ducastelle, D. Gratias, *Physica* **128A**, (1984) 334-350.