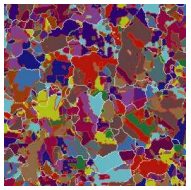


Gibbs Energy Minimization Challenges using Implicit Variables Solution Models

by

Jean-Philippe Harvey

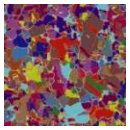
(jean-philippe.harvey@polymtl.ca)

Pr. Patrice Chartrand

Dr. Gunnar Eriksson

Pr. Dominique Orban

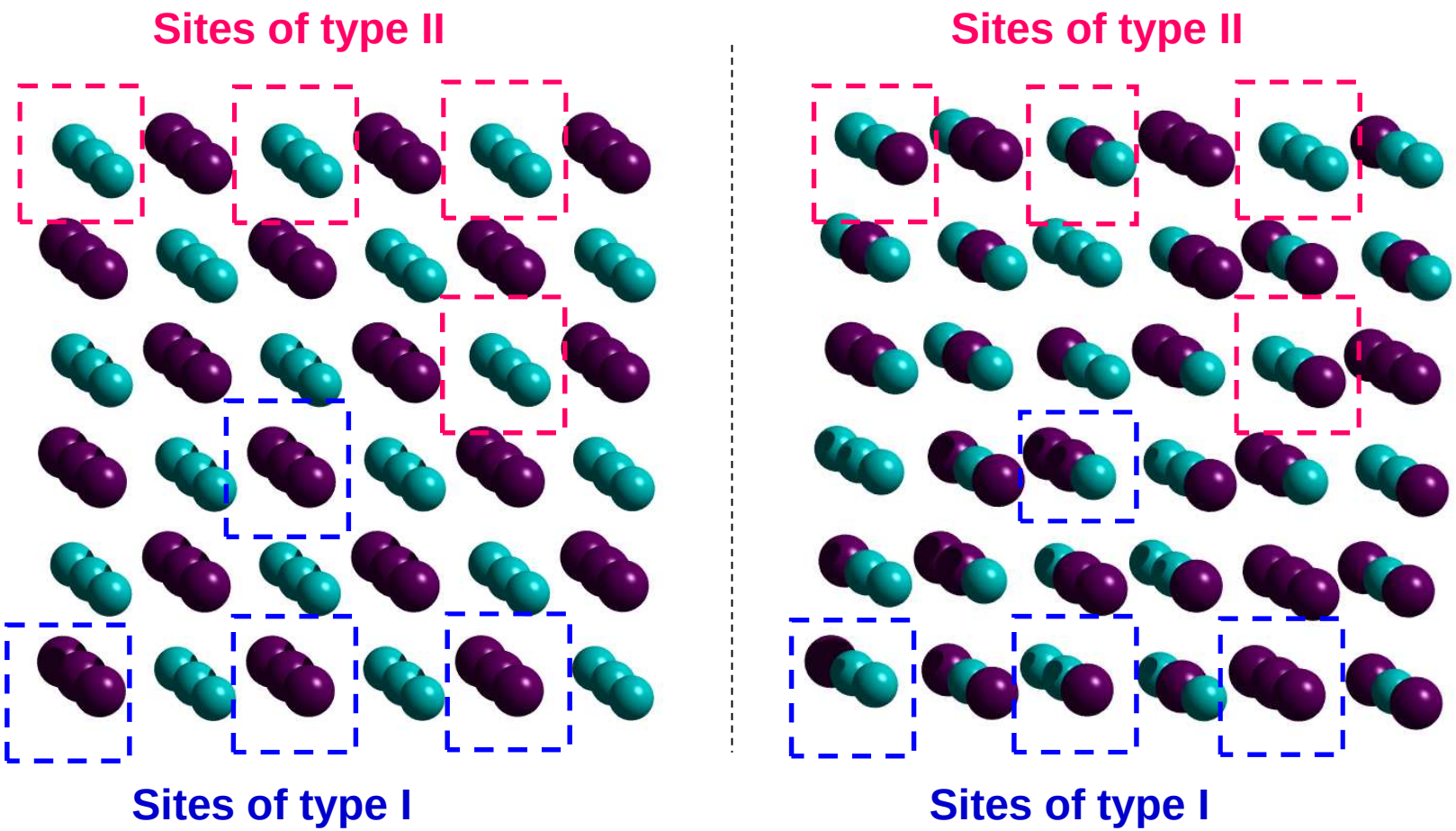
ÉCOLE POLYTECHNIQUE MONTRÉAL

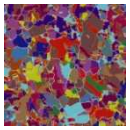


Presentation Overview

1. Importance of cluster approaches to model order/disorder in solid solutions
2. Gibbs energy minimization problematic (NLP): original SOLGASMIX
3. New first estimate technique and performance of various algorithms
4. Future work

The Problematic





Possible Approaches

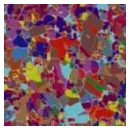
1. **Bragg and Williams** → Long Range Order parameter

2. **Compound Energy Formalism** → Excess parameters

SRO and LRO simultaneously considered

3. **Quasichemical Approach → Ising model → Cluster Site Approximation**

4. **Cluster variation method** → Correction of the configurational entropy of mixing using corrected probability (pairs, triangles, edges, quadruplets, tetrahedron, octahedron, etc.).



Quasichemical Approach

Fowler and Guggenheim, *Proc. R. Soc. London,* 1940:

Developed a thermodynamic model based on the idea of Ising according to the following quasichemical reaction:

A-A + B-B → 2 A-B Δg_{A-B}

Yang, *J. Chem. Phys.*, 1945:

Generalized this approach to superlattices.

Oates and Wenzl, *Src. Mater.*, 1996:

This led to the cluster site approximation (CSA). In the tetrahedron approximation, the Gibbs energy of a solution using the CSA can be written as followed:

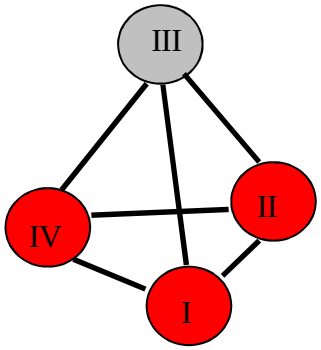
$$G^{CSA} = 4\left[\begin{array}{l}\gamma \cdot \sum_{ijkl=1}^{s}\left(g^{0}_{ijkl} \cdot n_{ijkl} + R \cdot T \cdot n_{ijkl} \ln\left(\frac{n_{ijkl}}{n_{total}}\right)\right) \\ -(\gamma - 0.25)\cdot R \cdot T \cdot n_{total} \cdot \sum_{i=1}^{q}\left(y_i^{I} \ln\left(y_i^{I}\right) + y_i^{II} \ln\left(y_i^{II}\right) + y_i^{III} \ln\left(y_i^{III}\right) + y_i^{IV} \ln\left(y_i^{IV}\right)\right)\end{array}\right]$$

Cluster Site Approximation (CSA)

$$G^{CSA} = 4\left[\gamma \cdot \sum_{ijkl=1}^{s}\left(g^{0}_{ijkl} \cdot n_{ijkl} + R \cdot T \cdot n_{ijkl} \ln\left(\frac{n_{ijkl}}{n_{total}}\right)\right) - (\gamma - 0.25) \cdot R \cdot T \cdot n_{total} \sum_{i=1}^{q}\left(y_i^I \ln\left(y_i^I\right) + y_i^{II} \ln\left(y_i^{II}\right) + y_i^{III} \ln\left(y_i^{III}\right) + y_i^{IV} \ln\left(y_i^{IV}\right)\right)\right]$$

Tetrahedra contribution

Site contribution



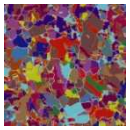
y_i^l : Site occupancy of species "*i*" on site "*l*"

g^0_{ijkl} : Standard Gibbs energy of the tetrahedron "*ijkl*"

γ : Semi-empirical parameter (0.8-1.6)

n_{ijkl} : Number of moles of the tetrahedron "*ijkl*"

n_{total} : Total number of moles of the solution



Minimization Procedure: SOLGASMIX

The CRCT (Center for Research in Computational Thermochemistry) has developed a thermodynamic software called ***FactSage*** and used for the past 30 years.

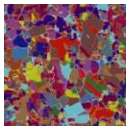
In this software, the Gibbs energy minimization is done using a routine called ***SOLGASMIX*** developed by Eriksson, *Acta Chem. Scand.* 1971.

A conventional thermodynamic equilibrium calculation can be mathematically defined as:

$$\min_{n \in \Re^n} G(n)$$

$$subject\ to\ \ c(n) = 0$$

Length of n ~2 $\rightarrow$ 2000



Constrained Minimization Problematic

The Gibbs energy of a multicomponent system is defined as:

$$G(n)=\sum_{i=1}^{s} n_i^{Compound}\cdot g_i^{Compound}(T,P)+\sum_{h=1}^{p} G_h^{Solution}(T,P,n_r)$$

$$(i=1,2,...,s)$$

Solution

$$(h=1,2,...,p)$$

$$(r=1,2,...,q)$$

Phase constituent

Ideal solution

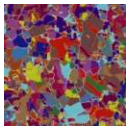
Sub-Regular solution

*Modified quasichemical models**

CSA

CVM

Etc…



Mass Balance Constraints

The **explicit linear constrains** associated to the minimization of the Gibbs energy of a system are the mass balances related to **each chemical species *"j"*** (ex.: Al, Li, Mg, Zn, Cu, etc…) present in the system:

Amount of species "j"

$$c_j(n) = \sum_{i=1}^{s} \left[\xi_{ij}^{Compound} \cdot n_i^{Compound} \right] + \left[\sum_{h=1}^{p} \sum_{r=1}^{q} \xi_{rj}^{(h)} \cdot n_r^{(h)} \right] - b_j \quad (r = 1,2,...,q)$$

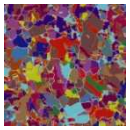
$$(h = 1,2,...,p)$$

Stoichiometric factor of **pure compound "*i*"**

Stoichiometric factor of component "*r*" in **solution "*h*"**

Example for Al_3Fe compound:

$$\xi_{Al_3Fe-Al} = 3 \qquad \xi_{Al_3Fe-Fe} = 1$$

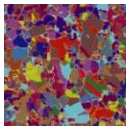


SOLGASMIX Algorithm

1. Use the **Newton technique (quadratic programming)** to solve the **NLP associated to the KKT condition (local minimum) and constraints**.

2. Express the **second order derivatives** of each solution associated to the NLP using an **ideal model**.

$$\left[X_1^{Comp.},\ldots,X_i^{Comp.},\left(\frac{X}{Y}\right)^{Sol.(1)},\ldots,\left(\frac{X}{Y}\right)^{Sol.(j)},\pi_1^{Species},\ldots,\pi_k^{Species} \right]$$

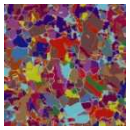


SOLGASMIX Drawbacks

The SOLGASMIX **Algorithm efficiency decreases** as the solution behavior is deviating from the ideal (second derivative hypothesis validity ↓). Applying it to the CSA model for ordered solutions can be problematic.

SOLGASMIX is **extremely sensitive to the first estimate** for strongly ordered solutions. The attractive strength of the disorder phase (local minimum) is high compared to other local minima involving ordered phases. Failure to converge to the global minimum can occur.

Cyclic and/or erratic convergence behavior are also observed in *SOLGASMIX* for strongly non-ideal solutions like the CSA model. This could have an impact on the phase equilibrium calculated by the algorithm.

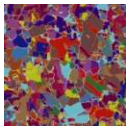


How to Solve this Problematic

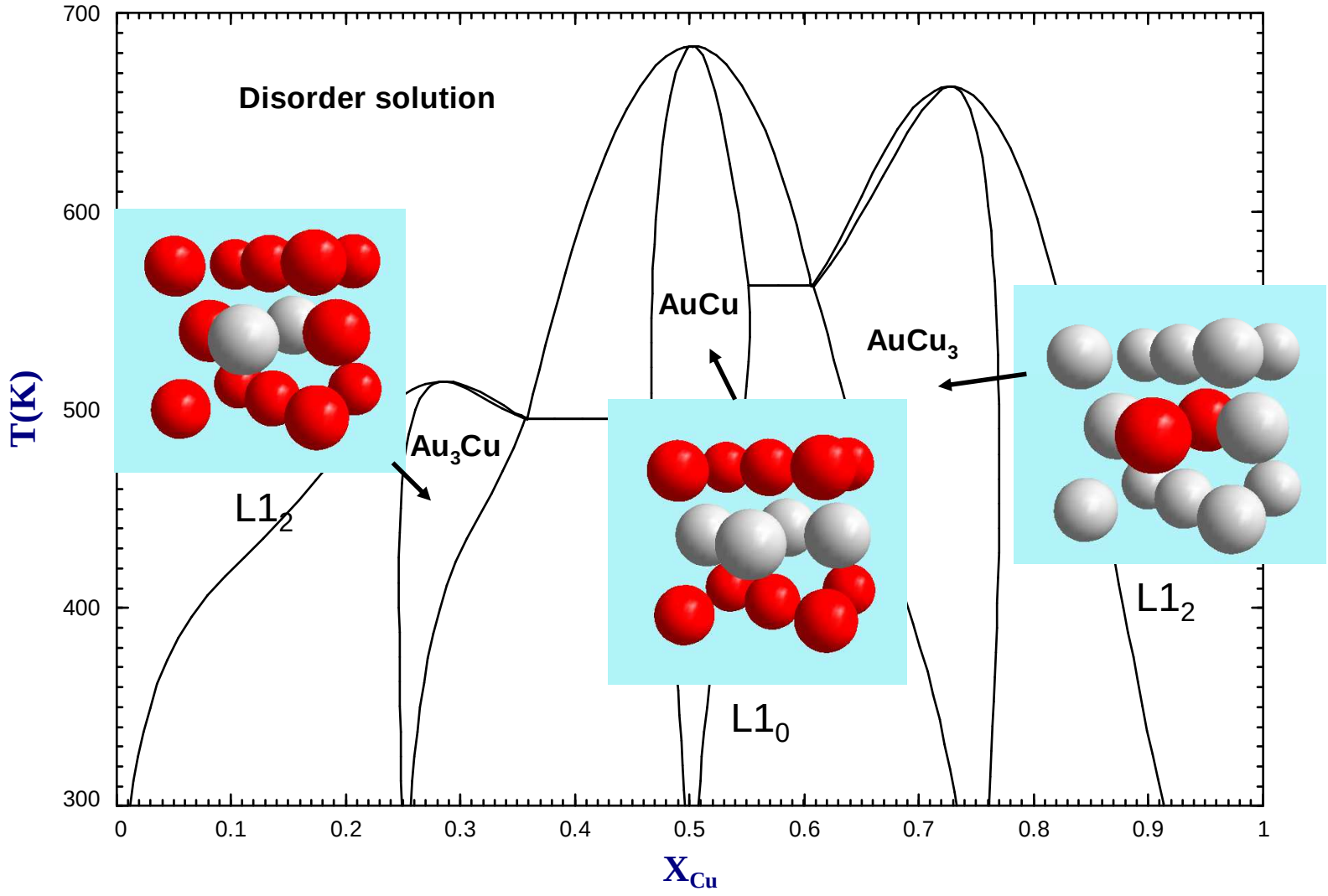
1. **Modification of the first estimate routine**

2. Implementation of a new non-linear quadratic programming minimization algorithm (**C**alculation **O**f **T**hermodynamic **E**quilibrium **S**ates). The exact second derivates are calculated for this new algorithm.

3. Translation of the thermodynamic problematic into a conventional non-linear constrained problematic (*Ipopt, Knitro, etc.*)



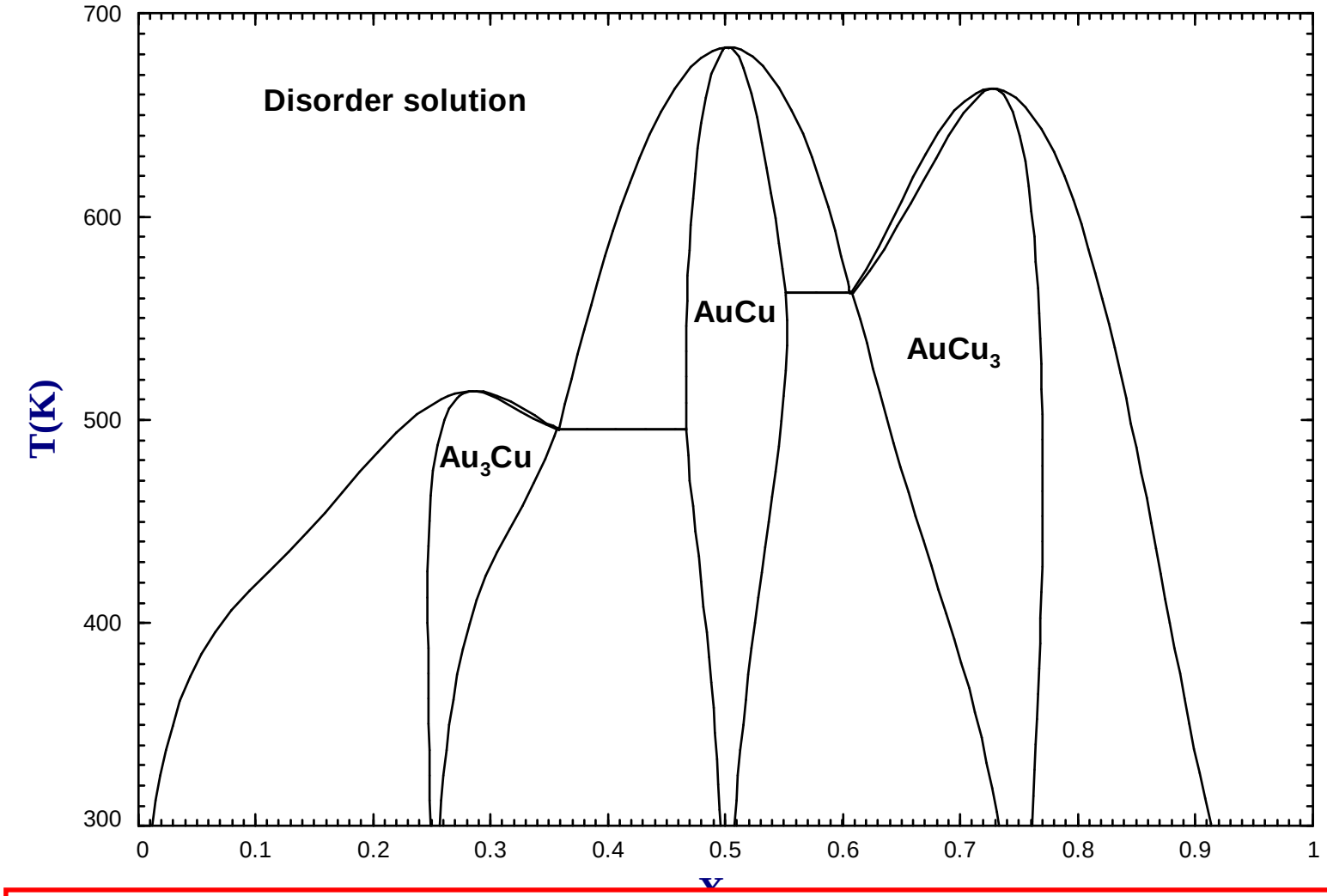
CSA applied to the Au-Cu System



Pure Gold

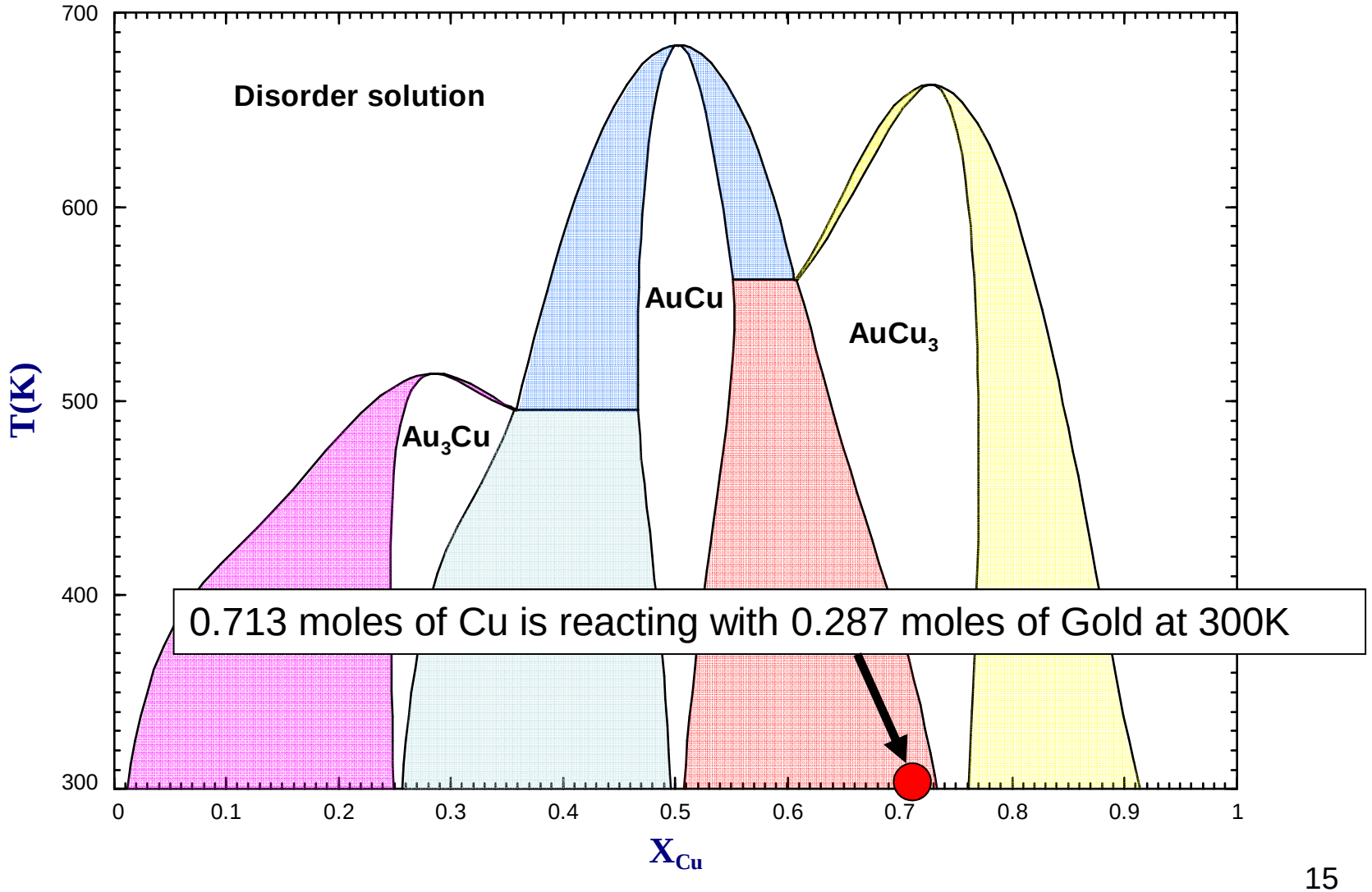
Pure Copper

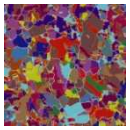
CSA applied to the Au-Cu System



Thermodynamic parameters obtained from Cao *et al.*, *Intermetallics*, 15, 2007, pp.1438

Equilibrium State: An Example





First Estimate Routine

At chemical equilibrium, all stable mixture models lie on a common hyper-plane, that is:

$$\frac{\partial G_{sln1}}{\partial n_i} = \frac{\partial G_{sln2}}{\partial n_i} = \frac{\partial G_{sln3}}{\partial n_i} = ... = \mu_i$$ For all species “i”

No mixture models can appear at lower Gibbs energy values than this hyper-plane (they would then be more stable than the equilibrium state). The first step to estimate the equilibrium state of a system is to **find a set of reference species**.

Set of Reference Species

Starting from pure substances, the reference species are modified one at a time until all species of the system have positive standard Gibbs energies.

Iteration #0

Species	nb of moles	Standard Gibbs energy	Species Def.	
Solution: FCC				
Cu_Pure	1.78193E-001	0.00000E+000	1.00	0.00
Au_Pure	7.18075E-002	0.00000E+000	0.00	1.00
CuCuCuAu	0.00000E+000	-1.20201E+004	0.75	0.25
CuCuAuCu	0.00000E+000	-1.20201E+004	0.75	0.25
CuCuAuAu	0.00000E+000	-1.61617E+004	0.50	0.50
CuAuCuAu	0.00000E+000	-1.20201E+004	0.75	0.25
CuAuCuCu	0.00000E+000	-1.61617E+004	0.50	0.50
CuAuAuAu	0.00000E+000	-1.61617E+004	0.50	0.50
CuAuAuCu	0.00000E+000	-1.11129E+004	0.25	0.75
AuCuCuAu	0.00000E+000	-1.20201E+004	0.75	0.25
AuCuCuCu	0.00000E+000	-1.61617E+004	0.50	0.50
AuCuAuCu	0.00000E+000	-1.61617E+004	0.50	0.50
AuCuAuAu	0.00000E+000	-1.11129E+004	0.25	0.75
AuAuCuCu	0.00000E+000	-1.61617E+004	0.50	0.50
AuAuCuAu	0.00000E+000	-1.11129E+004	0.25	0.75
AuAuAuCu	0.00000E+000	-1.11129E+004	0.25	0.75

CuCuCuCu

AuAuAuAu

Each species contains 4 atoms:

(0.287 moles of Au / 4) = 0.07181

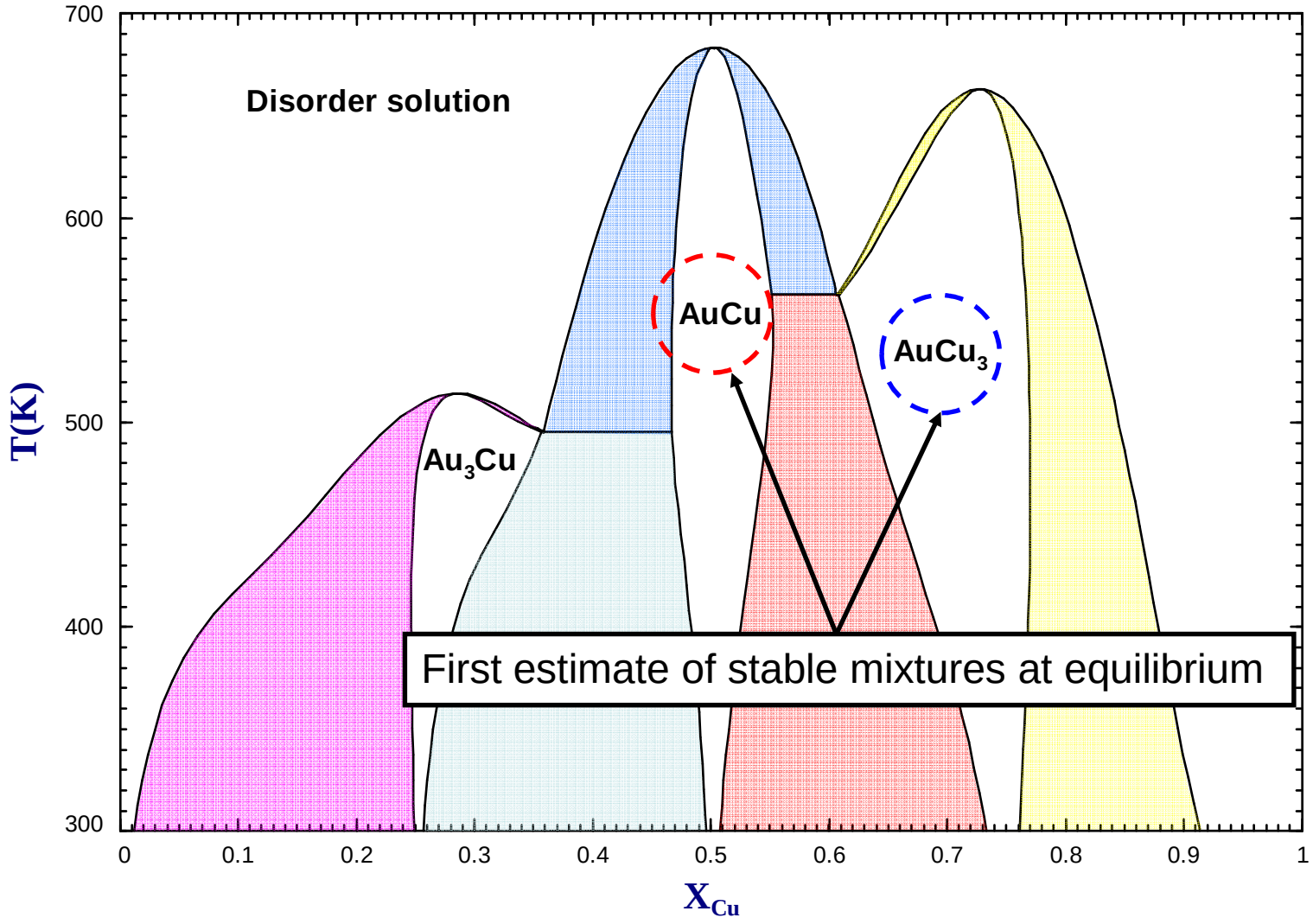
Species			Species Def.	
Solution: FCC				
Cu_Pure	0.00000E+000	7.87854E+003	2.00	-1.00
Au_Pure	0.00000E+000	2.44449E+004	-2.00	3.00
CuCuCuAu	2.12770E-001	0.00000E+000	1.00	0.00
CuCuAuCu	0.00000E+000	0.00000E+000	1.00	0.00
CuCuAuAu	3.72300E-002	0.00000E+000	0.00	1.00
CuAuCuCu	0.00000E+000	0.00000E+000	1.00	0.00
CuAuCuAu	00000E+000	0.00000E+000	0.00	1.00
CuAuAuCu	00000E+000	0.00000E+000	0.00	1.00
CuAuAuAu	00000E+000	9.19038E+003	-1.00	2.00
AuCuCuCu	00000E+000	0.00000E+000	1.00	0.00
AuCuCuAu	00000E+000	0.00000E+000	0.00	1.00
AuCuAuCu	00000E+000	0.00000E+000	0.00	1.00
AuCuAuAu	00000E+000	9.19038E+003	-1.00	2.00
AuAuCuCu	00000E+000	0.00000E+000	0.00	1.00
AuAuCuAu	0.00000E+000	9.19038E+003	-1.00	2.00
AuAuAuCu	0.00000E+000	9.19038E+003	-1.00	2.00

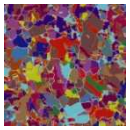
CuCuCuAu

CuCuAuAu

The reference species will define the stoichiometric factors of all the species of the system (mass balances)

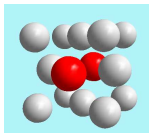
Equilibrium State: An Example





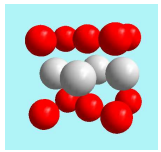
Mixture Composition Estimation

The reference species will reflect the ordering tendency of the system.



$AuCu_3$ Solution

Initial Guess	n_{ijkl}
Cu_Pure	4.99866602032448E-004
Au_Pure	1.40023131402186E-012
CuCuCuAu	5.21454181413687E-002
CuCuAuCu	1.57488168678886E-005
CuCuAuAu	1.66569107038958E-004
CuAuCuCu	1.57488168678886E-005
CuAuCuAu	1.66569107038958E-004
CuAuAuCu	5.03067470950655E-008
CuAuAuAu	3.68507024156771E-008
AuCuCuCu	1.57488168678886E-005
AuCuCuAu	1.66569107038958E-004
AuCuAuCu	5.03067470950657E-008
AuCuAuAu	3.68507024156772E-008
AuAuCuCu	5.03067470950657E-008
AuAuCuAu	3.68507024156772E-008
AuAuAuCu	1.11295485678951E-011

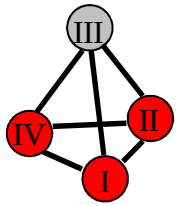


AuCu Solution

Cu_Pure	3.72804872600773E-009
Au_Pure	6.32636886634607E-009
CuCuCuAu	1.84241632982154E-005
CuCuAuCu	1.84241632982154E-005
CuCuAuAu	9.23163148487321E-003
CuAuCuCu	1.06050019639026E-009
CuAuCuAu	5.31375392426035E-007
CuAuAuCu	5.31375392426035E-007
CuAuAuAu	1.84401790562029E-005
AuCuCuCu	1.06050019639026E-009
AuCuCuAu	5.31375392426034E-007
AuCuAuCu	5.31375392426035E-007
AuCuAuAu	1.84401790562029E-005
AuAuCuCu	3.05861220888842E-011
AuAuCuAu	1.06142206807671E-009
AuAuAuCu	1.06142206807671E-009

Site probability= f (energetic interactions)

$$l_{ijkl} = y_i^I \cdot y_j^{II} \cdot y_k^{III} \cdot y_l^{IV}$$

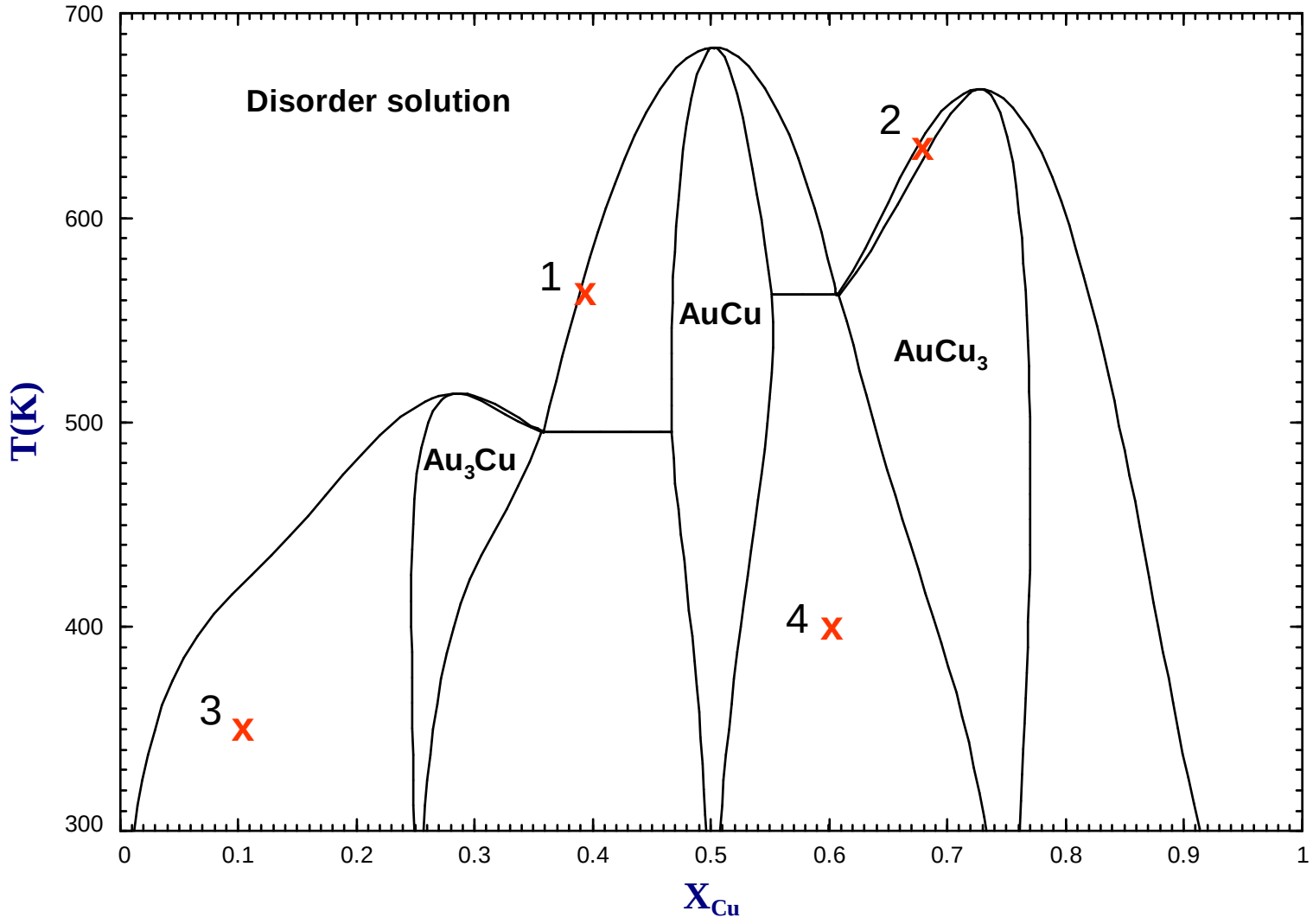


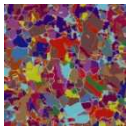
Molar composition

$$n_{ijkl} = \frac{l_{ijk}}{\sum_{ijkl} l_{ijkl}} \cdot n_{Mixture}$$

Amount of the reference species

Single Point Calculation Results





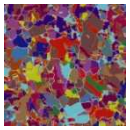
Preliminary Results

$$n_{Au}Au + n_{Cu}Cu \xrightarrow{T(K)} \sum_i n_i \left(Au_x Cu_y\right)_i$$

Point #	n_{Cu} (mol)	n_{Au} (mol)	T (K)	COTES	IPOPT	SOLGASMIX	PANDAT
1	0.39	0.61	565	Nb iter.: 16 ΔG:	Nb iter.: 12 ΔG:	Nb iter.: 224 ΔG:	Nb iter.: ? ΔG: -8272.94J Equilibrium: $L1_0$+ Disor.
2	0.68	0.32	635	Nb iter.: 11	Nb iter.: 12	Nb iter.: 407	Nb iter.: ? ΔG: -8935.6J Equilibrium: $L1_2$
3	0.10	0.90	350	Nb iter.: 18 ΔG: -2198.45J Equilibrium: $L1_2$+Disor.	Nb iter.: 54 ΔG: -2135.8J Equilibrium: Disor.	Nb iter.: 176 ΔG: -2198.39J Equilibrium: $L1_2$+Disor.	Nb iter.: ? ΔG: -2198.45J Equilibrium: $L1_2$+Disor.
4	0.60	0.40	400	Nb iter.: 19 ΔG: -8660.04J Equilibrium: $L1_2$+$L1_0$	Nb iter.: 71 ΔG: -8660.04J Equilibrium: $L1_2$+$L1_0$	Nb iter.: 194 ΔG: -8660.04J Equilibrium: $L1_2$+$L1_0$	Nb iter.: ? ΔG: -8660.04J Equilibrium: $L1_2$+$L1_0$

Large-scale non linear optimization algorithm

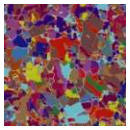
Gibbs energy minimization software



Preliminary Results

$$n_{Au}Au + n_{Cu}Cu \xrightarrow{T(K)} \sum_i n_i \left(Au_x Cu_y\right)_i$$

Point #	n_{Cu} (mol)	n_{Au} (mol)	T (K)	COTES	IPOPT	SOLGASMIX	PANDAT
1	0.39	0.61	565	Nb iter.: 16 ΔG: -8272.94J Equilibrium: $L1_0$+ Disor.	Nb iter.: 12 ΔG: -8272.93J Equilibrium: Disor.	Nb iter.: 224 ΔG: -8272.94J Equilibrium: $L1_0$+ Disor.	Nb iter.: ? ΔG: -8272.94J Equilibrium: $L1_0$+ Disor.
2	0.68	0.32	635	Nb iter.: 11 ΔG: -8936.66J Equilibrium: $L1_2$+Disor.	Nb iter.: 12 ΔG: -8935.2J Equilibrium: Disor.	Nb iter.: 407 ΔG: -8936.66J Equilibrium: $L1_2$+Disor.	Nb iter.: ? ΔG: -8935.6J Equilibrium: $L1_2$
3	0.10	0.90	350	Nb iter.: 18 ΔG: -2198.45J Equilibrium: $L1_2$+Disor.	Nb iter.: 54 ΔG: -2135.8J Equilibrium: Disor.	Nb iter.: 176 ΔG: -2198.39J Equilibrium: $L1_2$+Disor.	Nb iter.: ? ΔG: -2198.45J Equilibrium: $L1_2$+Disor.
4	0.60	0.40	400	Nb iter.: 19 ΔG: -8660.04J Equilibrium: $L1_2$+$L1_0$	Nb iter.: 71 ΔG: -8660.04J Equilibrium: $L1_2$+$L1_0$	Nb iter.: 194 ΔG: -8660.04J Equilibrium: $L1_2$+$L1_0$	Nb iter.: ? ΔG: -8660.04J Equilibrium: $L1_2$+$L1_0$

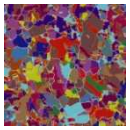


Preliminary Results

$$n_{Au}Au + n_{Cu}Cu \xrightarrow{T(K)} \sum_i n_i \left(Au_x Cu_y\right)_i$$

Point #	n_{Cu} (mol)	n_{Au} (mol)	T (K)	COTES	IPOPT	SOLGASMIX	PANDAT
1	0.39	0.61	565	Nb iter.: 16 ΔG:	Nb iter.: 12 ΔG: -8272.93J Equilibrium: Disor.	Nb iter.: 224 ΔG: -8272.94J Equilibrium: $L1_0$+ Disor.	Nb iter.: ? ΔG: -8272.94J Equilibrium: $L1_0$+ Disor.
2	0.68	0.32	635	Nb iter.: 11 ΔG: -8936.66J Equilibrium: $L1_2$+Disor.	Nb iter.: 12 ΔG: -8935.2J Equilibrium: Disor.	Nb iter.: 407 ΔG: -8936.66J Equilibrium: $L1_2$+Disor.	Nb iter.: ? ΔG: -8935.6J Equilibrium: $L1_2$
3	0.10	0.90	350	Nb iter.: 18 ΔG: -2198.45J Equilibrium: $L1_2$+Disor.	Nb iter.: 54 ΔG: -2135.8J Equilibrium: Disor.	Nb iter.: 176 ΔG: -2198.39J Equilibrium: $L1_2$+Disor.	Nb iter.: ? ΔG: -2198.45J Equilibrium: $L1_2$+Disor.
4	0.60	0.40	400	Nb iter.: 19 ΔG: -8660.04J Equilibrium: $L1_2$+$L1_0$	Nb iter.: 71 ΔG: -8660.04J Equilibrium: $L1_2$+$L1_0$	Nb iter.: 194 ΔG: -8660.04J Equilibrium: $L1_2$+$L1_0$	Nb iter.: ? ΔG: -8660.04J Equilibrium: $L1_2$+$L1_0$

Necessity to customize this algorithm



Future Work

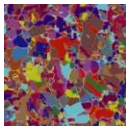
Model disorder solid solutions using the CSA model and take advantage of the **modified quasichemical model with the pair approximation for liquid solutions** to see the impact of considering simultaneously in solid and liquid phases SRO effects on the Gibbs energy of the system. (ex.: Al-FCC in Al-Li)

Run Monte Carlo simulations (N,V,T) (N,P,T) on specific systems to have a better understanding of configurational and non configurational entropy effects, g(r) functions, mixing enthalpies, volumetric properties, etc using the modified embedded atom model with the 2nn approximation.

Add new excess parameters (ex.: $g^E = f(n_{ijkl})$) to the CSA model according to the Monte Carlo results.

Add vacancies to the CSA model.

CVM implemention.



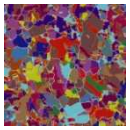
Thank you for your attention!

Any questions?

jean-philippe.harvey@polymtl.ca

Génie chimique POLYTECHNIQUE

ÉCOLE POLYTECHNIQUE MONTRÉAL



Systems of Interests

Benchmark systems:

Cu-Au-Ag

Al-Ni-Re

Fe-Al-Co

Fe-Si-Co

Fe-Al-Ge

Fe-Si-Al

Cd-Hg

Cd-Mg

Cd-Ca

Ga-In-P

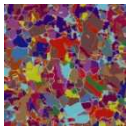
Ga-As-Sb

Co-Pt

Ti-Al-Mo

Ti-Al-Nb

Ti-Al-W

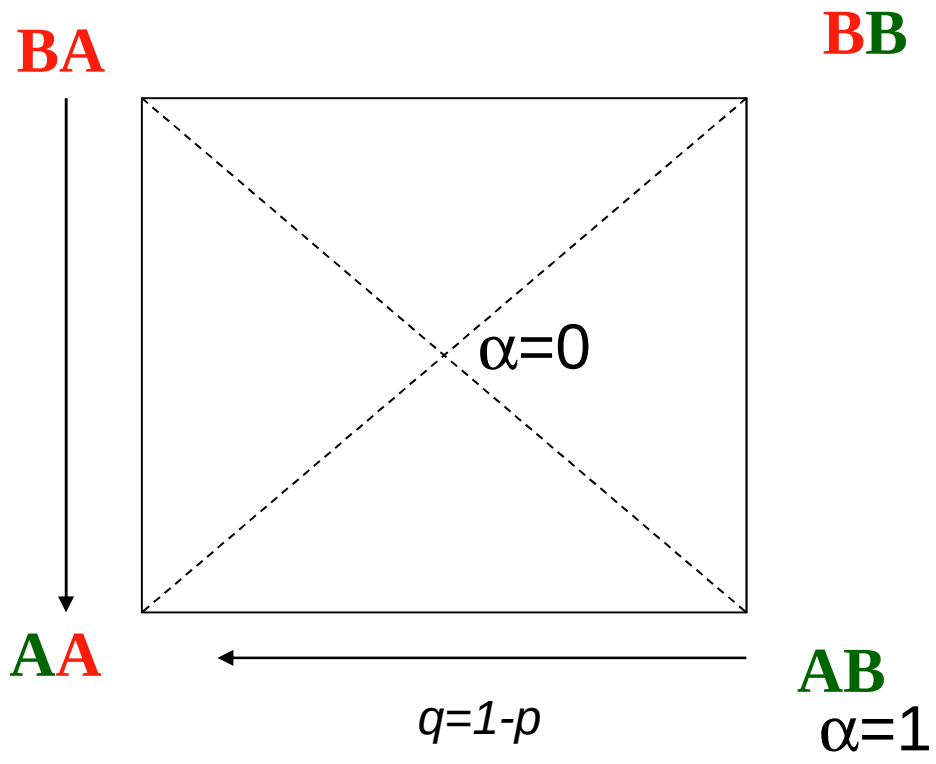


Supplementary Slides

Original work of Bragg and Williams

Lets assume that an **equimolar** solid solution is modeled using two sublattices:

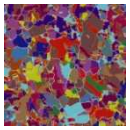
$(\mathbf{A},\mathbf{B})^{I}\,(\mathbf{A},\mathbf{B})^{II}$



Probability that site *I* is occupied by an *A* atom p

Probability that site *II* is occupied by an *A* atom

$$\alpha = \frac{p - 1/2}{1 - 1/2}$$



Original work of Bragg and Williams

$$\Delta S^{config.} = -2R\left[\left(x_A + \frac{\alpha}{2}\right)\ln\left(x_A + \frac{\alpha}{2}\right) + \left(1 - x_A + \frac{\alpha}{2}\right)\ln\left(1 - x_A + \frac{\alpha}{2}\right)\right]$$

α=1

$$\Delta S^{config.} = 0$$

Completely ordered solution

α=0

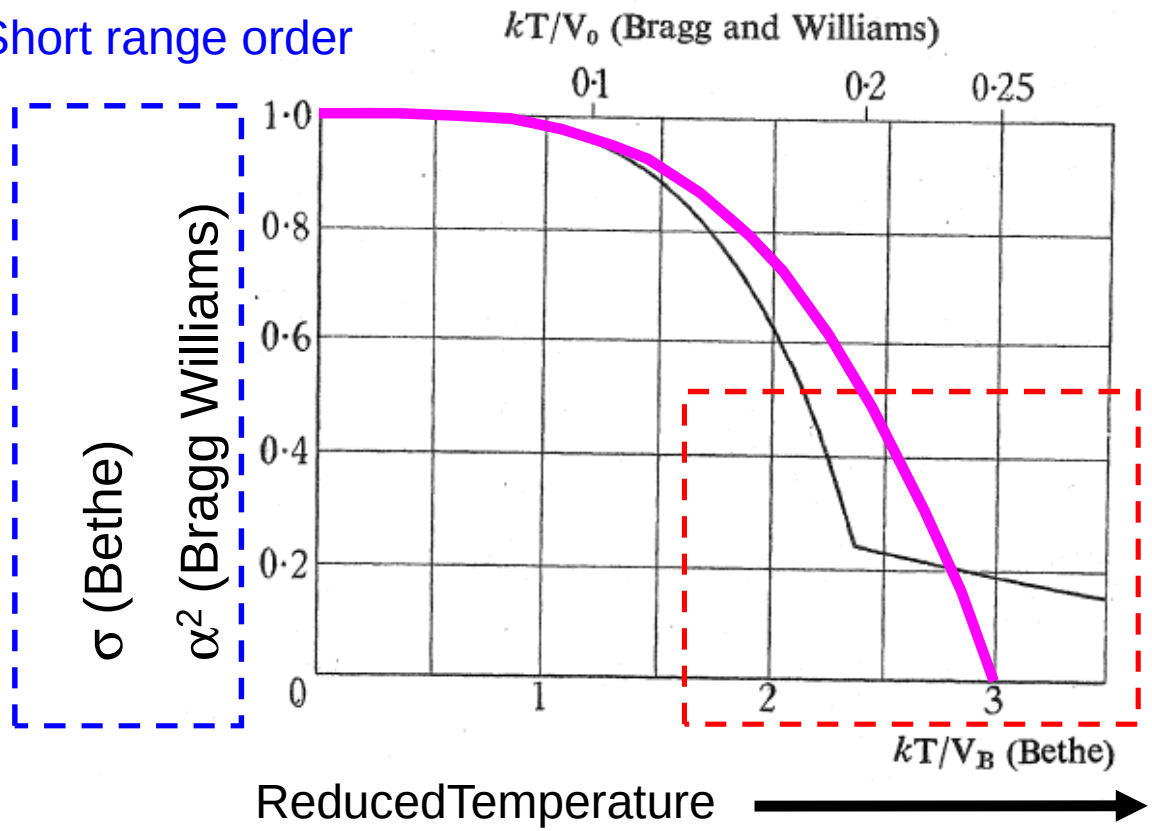
$$\Delta S^{config.} = -2R\ln\left(\frac{1}{2}\right)$$

random solution

Original work of Bragg and Williams

Bragg and Williams, Proc. R. Soc. London, Ser. A, 1934

Short range order



Short range order effects

(SRO)

1) Shift in the order / disorder temperature
2) Presence of SRO after $T_{critical}$

Compound Energy Formalism (CEF)

The compound energy formalism which is extensively used in the thermodynamic modelling of multicomponent phase is based on the general idea of Bragg and Williams:

$$G = \sum_i \sum_j \sum_k \sum_l y_i^I y_j^{II} y_k^{III} y_l^{IV} g_{ijkl}^o$$

4 sublattices model

$$+ RT \sum_i \left[y_i^I \ln\left(y_i^I\right) + y_i^{II} \ln\left(y_i^{II}\right) + y_i^{III} \ln\left(y_i^{III}\right) + y_i^{IV} \ln\left(y_i^{IV}\right) \right]$$

$$+ G^E + G^{magnetism}$$

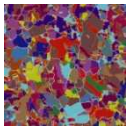
$$G^E = \sum_{i_1} \sum_{i_2} \sum_j \sum_k \sum_l y_{i_1}^I y_{i_2}^I y_j^{II} y_k^{III} y_l^{IV} L_{i_1,i_2:j:k:l} + .. +$$

2nd nearest neighbour terms (LRO)

$$\sum_{i_1} \sum_{i_2} \sum_{j_1} \sum_{j_2} \sum_k \sum_l y_{i_1}^I y_{i_2}^I y_{j_1}^{II} y_{j_2}^{II} y_k^{III} y_l^{IV} L_{i_1,i_2:j_1,j_2:k:l} + \ldots$$

Reciprocal excess terms (SRO)

Recent application: $D0_3$ in Sundman *et al.*, *Acta Mater.*, 2009



Compound Energy Formalism (CEF)

As explained by Sundman *et al., Calphad*, 1998, the CEF has serious limitations when it is used to model order / disorder phenomena:

1. Numerous **excess parameters** must be introduced in the Gibbs energy function when SRO influences the configurational entropy.

2. The "*L*" excess parameters are dependant and strongly correlated.

3. As a consequence, the thermodynamic software implementing the CEF **should restrain the choice and magnitude of excess parameters** (ex.: symmetrical excess parameters) to avoid artificial order/disorder transitions.

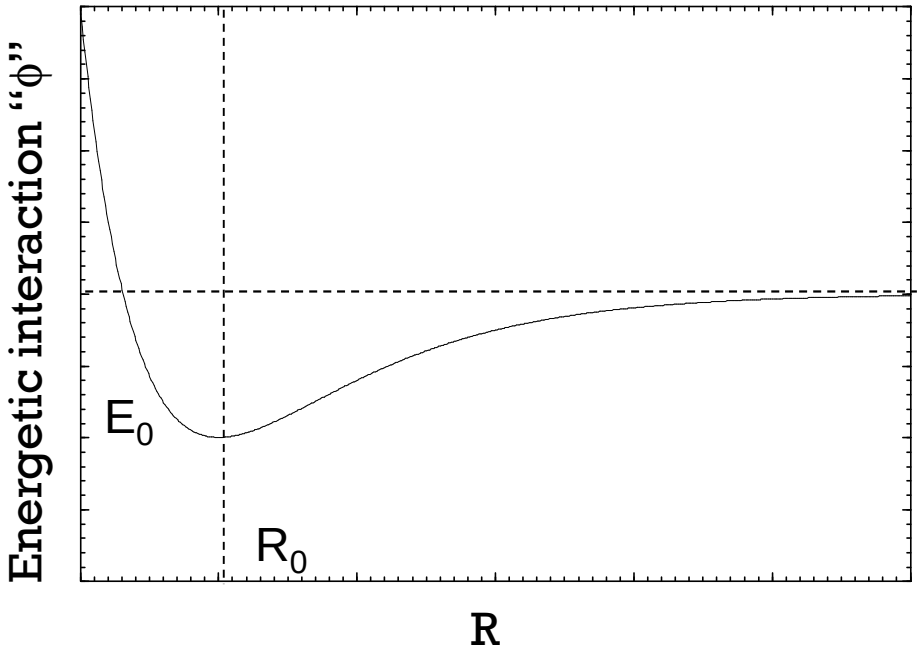
4. The **predictive capability** of the model in multicomponent systems is reduced by the introduction of numerous excess parameters that have to be interpolated.

Ising Model

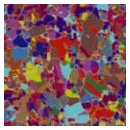
$$E = \sum_{i} \sum_{j \neq i} \phi_{ij} S_i S_j$$

For metals, ϕ_{ij} can be modelled using:

- Tight-binding approach (closed packed structures)
- Finnis-Sinclair (BCC,….)
- Modified embedded atomic method (MEAM for all type of structures)



It is well recognized that the **Ising model is able to predict second order transitions** when at least two dimensions are considered **(Z>2)**. Thermodynamic models have been constructed based on the Ising approach neglecting all energetic contributions except first nearest neighbours.



Cluster Site Approximation (CSA)

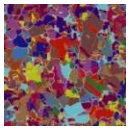
In the **present** representation of the CSA model, **(n^4) component variables have to be introduced** in the system for each potentially stable solution described by the CSA in order to calculate the Gibbs energy of the system.

The number of components in the system increases exponentially as species are added to the system. However, because of the nature of the CSA model, it is possible to **introduce Lagrange multipliers called μ_i related to each *"i"* site of the structural entity** (in this case the tetrahedron). The phase constituent molar fractions of the solution are computed from the following expression at equilibrium (ex.: A-B binary system):

$$\left(\mu_j, y_i^l\right) \longrightarrow x_{ijkl} = \frac{\exp\left[\left(\sum_{s=1}^{4}\mu_A^s\right)_{ijkl} - g_{ijkl}^0\right]}{\sum_{ijkl=1}^{2^4}\exp\left[\left(\sum_{s=1}^{4}\mu_A^s\right)_{ijkl} - g_{ijkl}^0\right]}$$

Minimization

Results



Cluster Site Approximation (CSA)

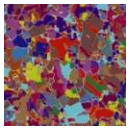
The advantages of using the CSA are the following:

1. **SRO and LRO are simultaneously considered** in the evaluation of the Gibbs energy of the solution. It is reasonable to believe that this improves the physical description of the solution.

2. In the original version of the CSA, the definition of the **standard Gibbs energy of the clusters** are the **only parameters** needed to describe the solution.

3. As for other thermodynamic models, **excess parameters can be added** to the original CSA model to better fit experimental data.

4. Using a tetrahedron as the cluster entity defining the solution, 3 order compositions can be modelled simultaneously.



Lagrangian Function Formulation

The Lagrangian function of the system is expressed as:

$$L(n,\lambda) = G(n) - \sum_j \lambda_j c_j(n)$$

At a local minimum, the first order necessary optimality condition (KKT) is:

$$\nabla L(n^*,\lambda^*) = \nabla G(n^*) - \sum_j \lambda_j^* \cdot \nabla c_j(n^*) = 0$$

To be a valid local minimum, the solution must respect the feasibility condition:

$$c_j(n^*) = 0$$

SOLGASMIX Algorithm

The fundamental idea of *SOLGASMIX* is to use the **Newton technique to solve the non linear set of equations** obtained from the KKT condition and the feasibility condition in order to improve the system equilibrium estimate:

$$W_k = \nabla^2_{nn} L(n_k, \lambda_k) \qquad A = \left[\nabla c_j (n_k)^T\right]$$

$$\begin{bmatrix} W_k & A_k \\ A_k^T & 0 \end{bmatrix} \begin{pmatrix} \delta n_k \\ \delta \lambda_k \end{pmatrix} = -\begin{pmatrix} \nabla G(n_k) - A_k \cdot \lambda_k \\ c_k \end{pmatrix}$$

$$\downarrow$$

$$(n_{k+1}, \lambda_{k+1}) \leftarrow (n_k, \lambda_k) + (\delta n_k, \delta \lambda_k)$$

SOLGASMIX Algorithm

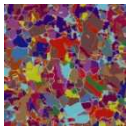
The **Hessian matrix** of each solution is calculated using an **ideal solution model approximation**. The ideal solution model is a convex function. **Moreover, at an infinite temperature, any solution model must degenerate to the ideal solution model (2nd law of thermodynamics).** This hypothesis leads to a greatly simplified set of equations to be solved which is exact for a system containing only ideal solutions and/or stoichiometric compounds.

$$\left[X_1^{Comp.},\ldots,X_i^{Comp.},\left(\frac{X}{Y}\right)^{Sol.(1)},\ldots,\left(\frac{X}{Y}\right)^{Sol.(j)},\pi_1^{Species},\ldots,\pi_k^{Species} \right]$$

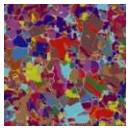
$$\downarrow$$

$$x_{Component(l)}^{Sol.(j)} = x_l^{Sol.(j)} = y_l^{Sol.(j)}\left[\left(\frac{g^o}{RT}\right)_l^{Sol.(j)} + \ln\left(\frac{y_l^{Sol.(j)}}{Y^{Sol.(j)}}\right)\right]$$

$$+ y_l^{Sol.(j)}\left[\left(\frac{X}{Y}\right)^{Sol.(j)} + \sum_{k=1}^{m}\pi_k\xi_{kl}^{Sol.(j)}\right]$$



COTES algorithm



New Minimization Algorithm

1. **Start the iterative process by emphasis on obtaining a first feasible solution (merit function ϕ)**

$$\phi(n,\nu) = G(n) + \nu\|c\|_2$$

Factoring the full KKT system (PARDISO)

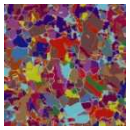
$$(dn_k, d\lambda_k) \longrightarrow \phi'(0; dn_k) < 0 \longrightarrow \nu > \frac{\nabla G^T \cdot dn_k}{\|c\|_2}$$

Armijo condition

$$\phi(n_k,\nu,\tau) \le \phi(n_k) + C_1 \cdot \tau \cdot \phi'(0; dn_k) \longrightarrow n_{k+1} = n_k + \tau \cdot \varepsilon \cdot dn_k$$

Damping (ε) is used to prevent convergence to a disordered mixture.

(Disordered mixtures are insensitive to the initial estimate while ordered mixtures are strongly sensitive to it)



New Minimization Algorithm

2. <u>After obtaining a first feasible solution, the following procedure is applied</u>

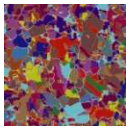
Factoring the full KKT system using PARDISO.

Important note: the Hessian of the Lagrangian matrix inertia was in a first attempt always analyzed (at every iteration). For a bad matrix inertia, the following procedure was applied:

$$H_K = W_k + \alpha \cdot I$$

→ Incremental steps until H_k is positive-definite

The disordered mixture was most of the time favored when perturbations of W_K were introduced. **No perturbation of the Hessian of the Lagrangian are thus used** in the actual minimization algorithm**.**



New Minimization Algorithm

3. The calculation of the new estimate (n_{k+1}) is :

$$n_{k+1} = n_k + \alpha_{Armijo} \cdot \alpha_{negative} \cdot dn_k$$

$$\lambda_{k+1} = \lambda_k + \alpha_{Armijo} \cdot \alpha_{negative} \cdot d\lambda_k$$

The inequality constraints related to positive amounts are indirectly considered by reducing the Newton step.

	n_k	dn_k
Cu_Pure	3.728048E-009	2.75244E-008
Au_Pure	6.326368E-009	-1.14819E-008
CuCuCuAu	1.842416E-005	9.36782E-005
CuCuAuCu	1.842416E-005	9.36782E-005
CuCuAuAu	9.231631E-003	2.57193E-002
CuAuCuCu	1.060500E-009	5.39010E-009
CuAuCuAu	5.313753E-007	1.47939E-006
CuAuAuCu	5.313753E-007	1.47939E-006
CuAuAuAu	1.844017E-005	8.95335E-006
AuCuCuCu	1.060500E-009	5.39010E-009
AuCuCuAu	5.313753E-007	1.47939E-006
AuCuAuCu	5.313753E-007	1.47939E-006
AuCuAuAu	1.844017E-005	8.95335E-006
AuAuCuCu	3.058612E-011	8.50950E-011
AuAuCuAu	1.061422E-009	5.13313E-010
AuAuAuCu	1.061422E-009	5.13313E-010

The biggest step that can be used to obtain only positive amounts.

$$\alpha_{negative} = \mathbf{0.55043}$$

Post-Iteration Procedure