A New Algorithm for the Automation of Phase Diagram Calculation

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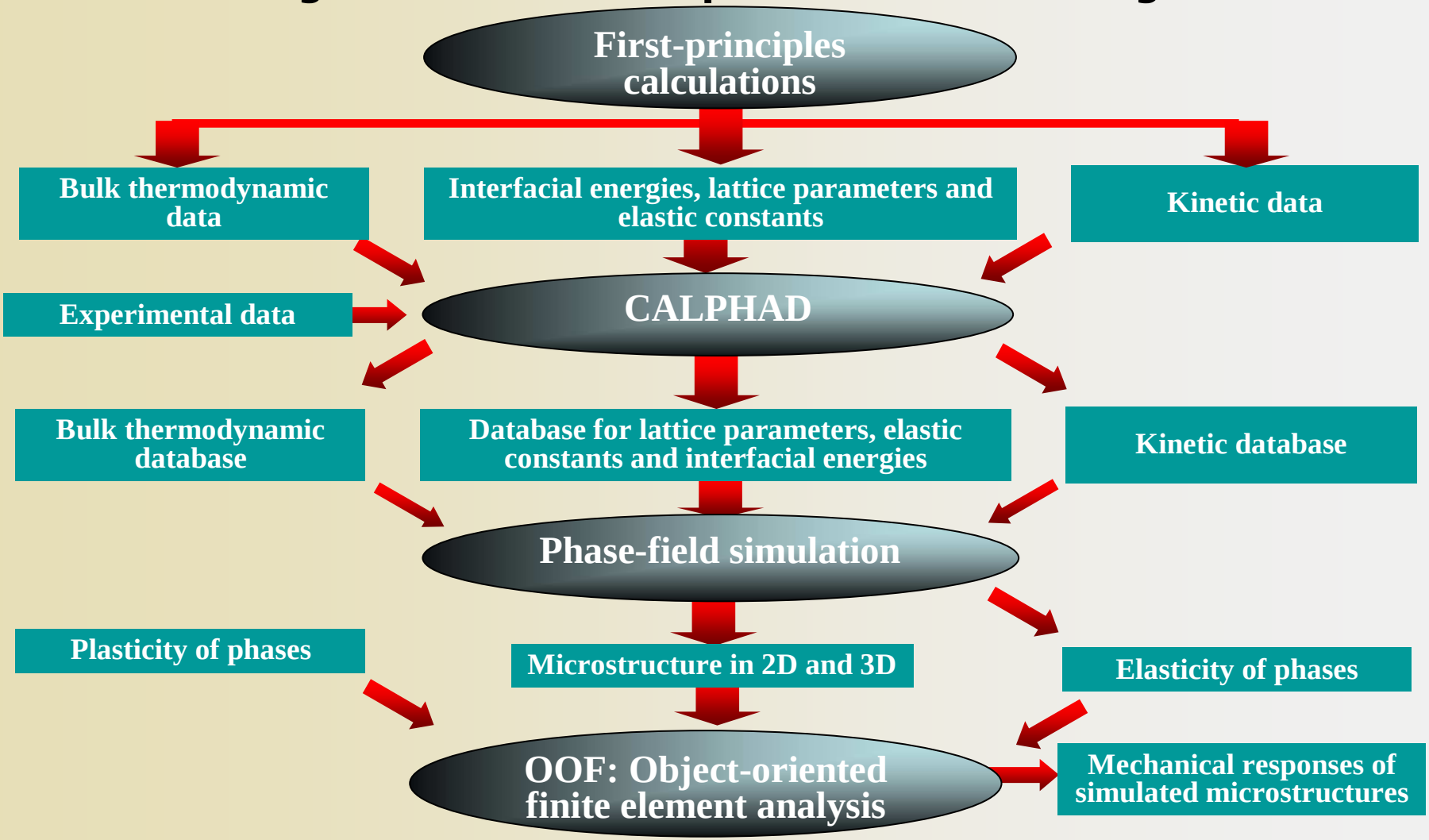
- Research is a part of the NSF-ITR Project MATCASE
  "Computational Tools for Materials Design"
  http://www.matcase.psu.edu
  Jointly with:
  Long-Qing Chen (PSU), Jorge Sofo (PSU), Padma Raghavan (PSU)
  Steve Langer (NIST), Chris Wolverton (Ford)

NSF ITR Project: MatCASE

(Materials Computation and Simulation Environment)

Integration of Four Computational Methodologies



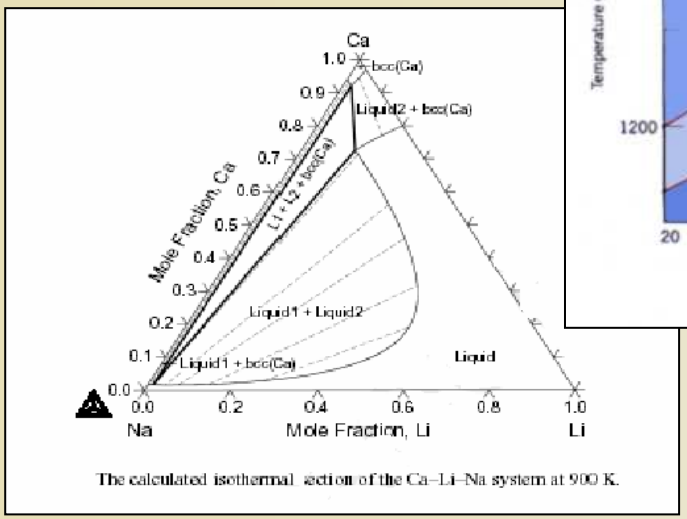
Outline

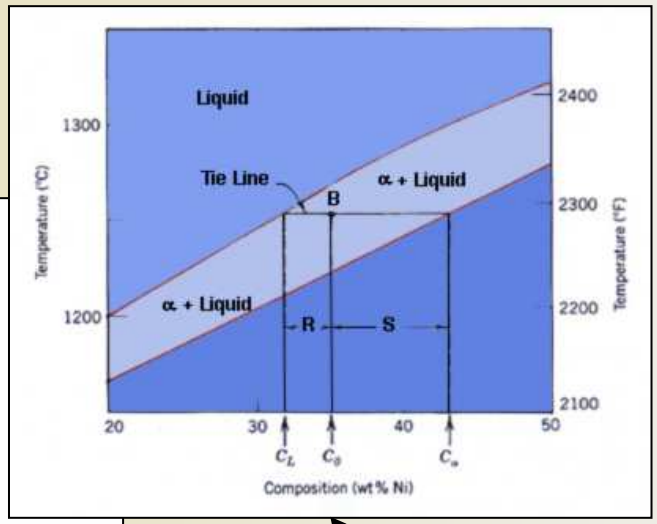
- Problem formulation
- Motivation
- Overview of the method for binary case
- Overview of the method for ternary case
- Computational complexity estimates
- Numerical examples
- Discussion and future work

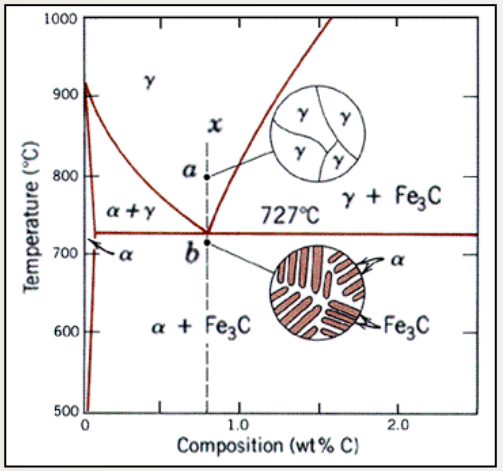
I. Problem formulation: phase diagrams

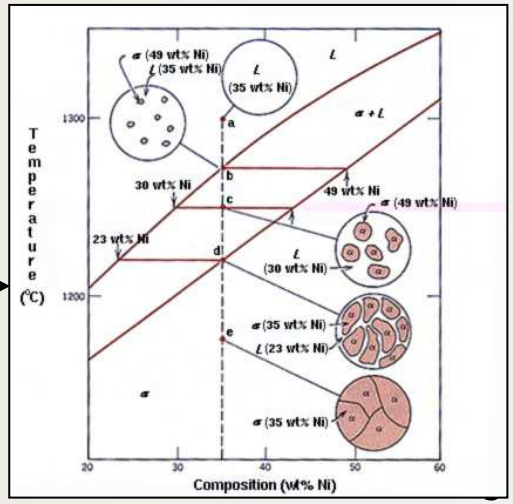
Phase diagrams are maps of the equilibrium phases associated with various combinations of temperature and composition

Some typical binary and ternary phase diagrams (PDs)



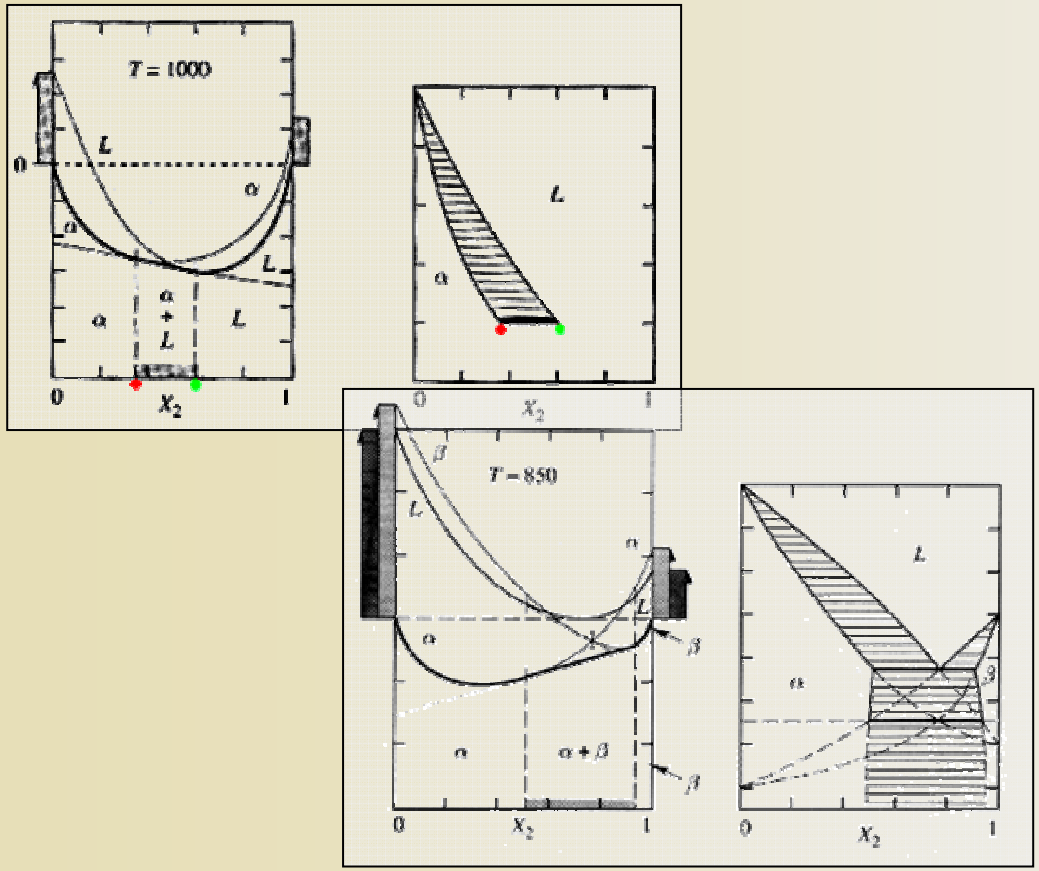




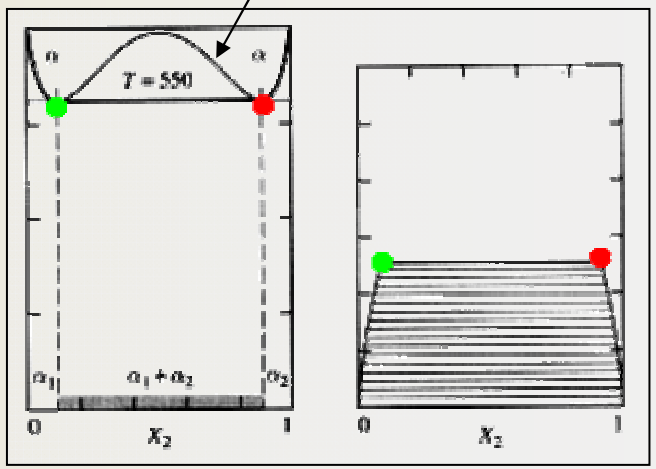


I. Problem formulation: PD construction

Geometrically: *common tangent construction*



Miscibility gap



Pictures courtesy of the Visual Analysis Lab, Virginia Tech

I. Problem formulation: Gibbs energy minimization

Mathematically, equilibrium analysis of a K-component system with n phases leads to the following minimization problem:

$$\min_{(f_i,\varphi_i^k)} \{G = \sum_{i=1}^{n} f_i G_i(\varphi_i^k)\}$$

$$\sum_{i=1}^{n} f_i = f_0$$

$$\sum_{i=1}^{n} f_i \varphi_i^k = f_0 \varphi_0^k, k = 1, \ldots, K$$

f_i is the number sites in phase i,
φ_i^k is volume fraction of k particles in phase i,
G_i is the Gibbs energy of phase i.

II. Motivation: existing commercial software

- Calphad-type iterative software
  - Thermo-Calc (TCC, TCW, DICTRA)
    Thermo-Calc Software
  - PANDAT (WinPhad, PanEngine)
    CompuTherm LLC
  - ChemSage family (FactSage, ChemApp)
    GTT Technologies
  - MTDATA
    National Physical Lab, UK

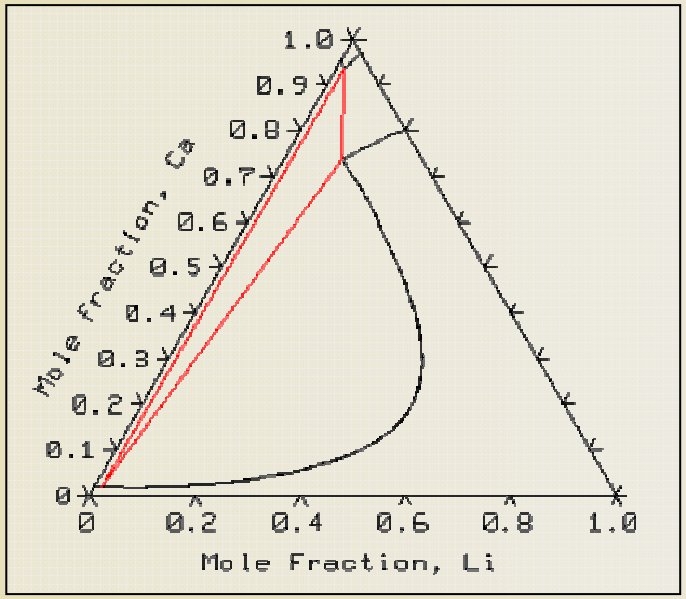
II. Motivation: existing software

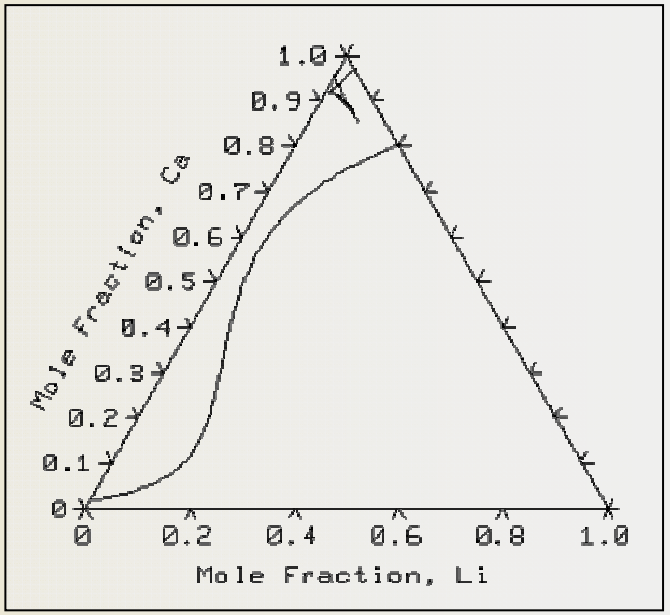
- Calphad-type iterative software drawbacks
  - **(user-dependent)** Use of prior knowledge of the system to generate a suitable starting point
  - **(unstable)** Possible divergence or convergence to metastable equilibria

Correct diagram
Miscibility gap is specified

Failure !
Miscibility gap is not specified

Ca-Li-Na system at T=900K





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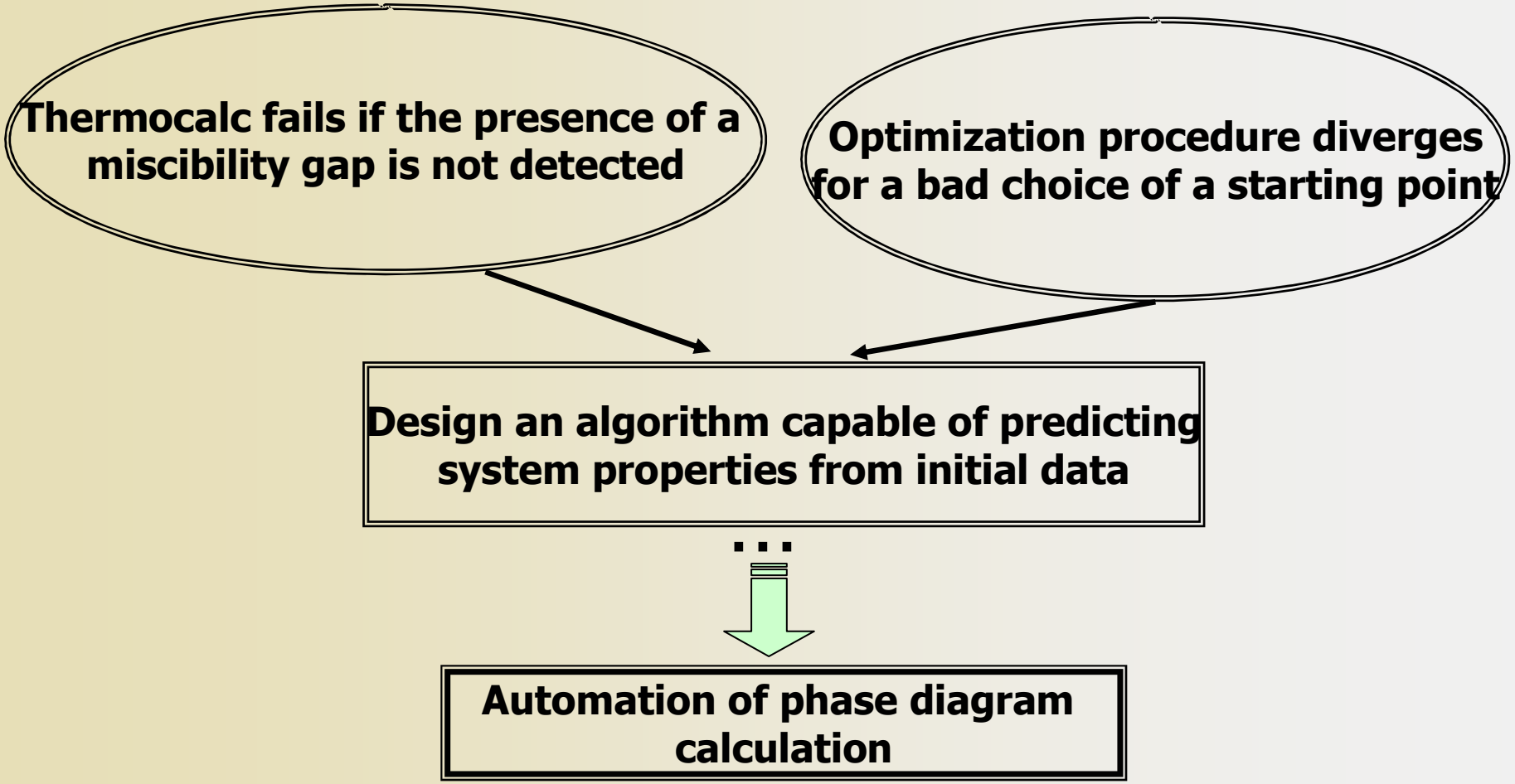
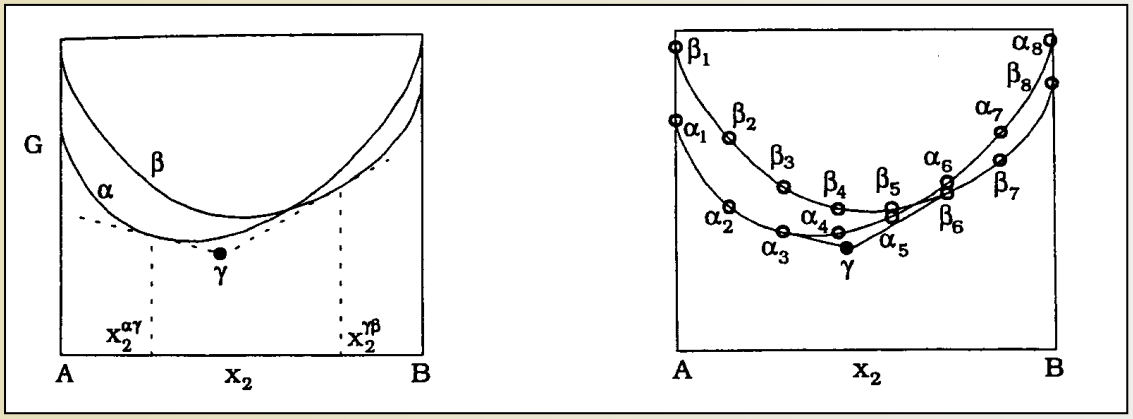


II. Motivation: PANDAT algorithm

S.-L. Chen et al, CALPHAD, 1993

Outline:

1) Subdivide the composition axis
2) Check stability, throw out points of higher energy
3) Check coplanarity condition on the remaining ones
4) Carry out optimization



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$$\frac{\begin{vmatrix} G_s & G_i & G_j \\ x_{1,s} & x_{1,i} & x_{1,j} \\ x_{2,s} & x_{2,i} & x_{2,j} \end{vmatrix}}{\begin{vmatrix} x_{1,i} & x_{1,j} \\ x_{2,i} & x_{2,j} \end{vmatrix}} \geq 0$$

for any of the compounds $A_{x_{1,s}}, B_{x_{2,s}}$, $s = 1, \ldots, N, s \neq i, j.$

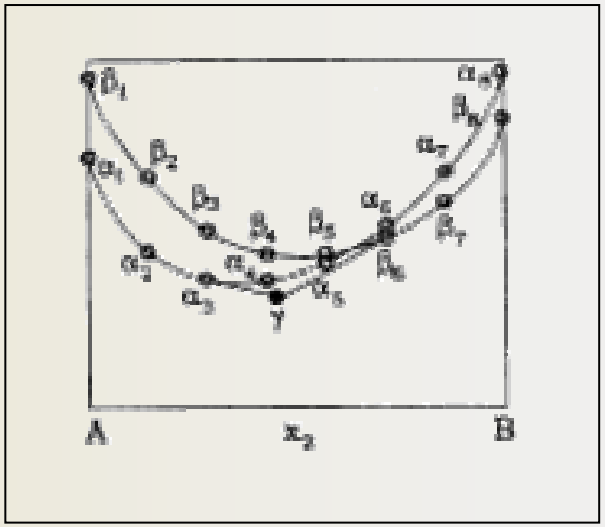
II. Motivation: PANDAT algorithm

S.-L. Chen et al, CALPHAD, 1993

- Better initial guess, BUT
- Computational cost is too high:

Coplanarity checks alone require
- *N-2 calculations of the determinant*
- *for a total of N(N-1)/2 pairs*

) $O(N^3)$ operations in binary case



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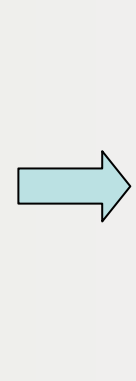
    Thermo-Calc Software — *user-dependence*

  - PANDAT (WinPhad, PanEngine)
    CompuTherm LLC — *complexity issues*



Can we improve the efficiency of the existing algorithms without sacrificing the accuracy and generality of the method?

III. New algorithm: goals and ideas

Emelianenko M.G., Liu Z.K., Du Q., Computational Materials Science, 2005

Goals:

- Calculate equilibria in multicomponent multiphase systems
- Minimize the number of trial points
- Get comparable accuracy of solution with lower complexity

Ideas:

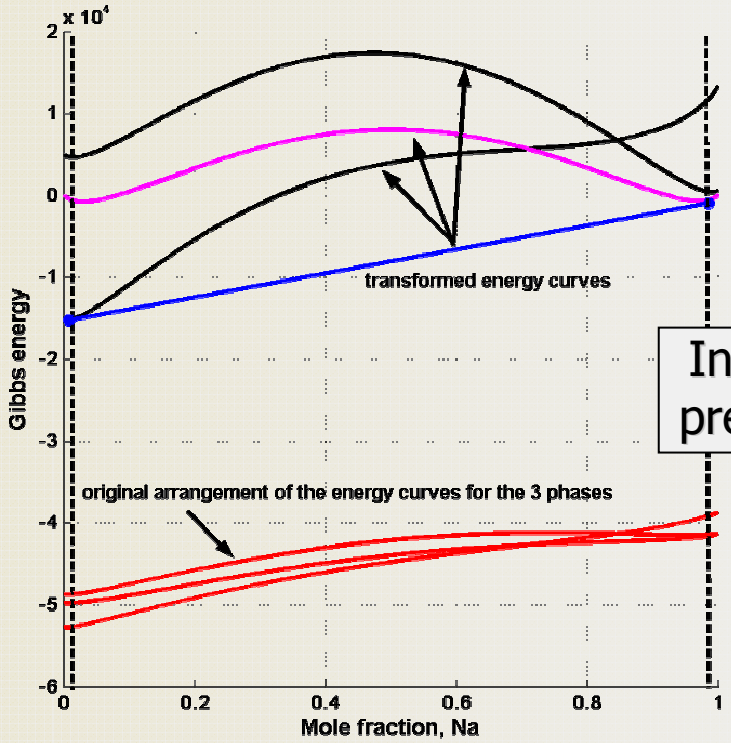
- Rely on the geometrical properties of the Gibbs energies to find better starting points
- Use adaptive approach with effective sampling techniques

III. New algorithm: binary case

Preliminary axis transformation:

$$y_{new}(x) = M(y(x) - (y_m(1) - y_m(0))x - y_m(0))$$

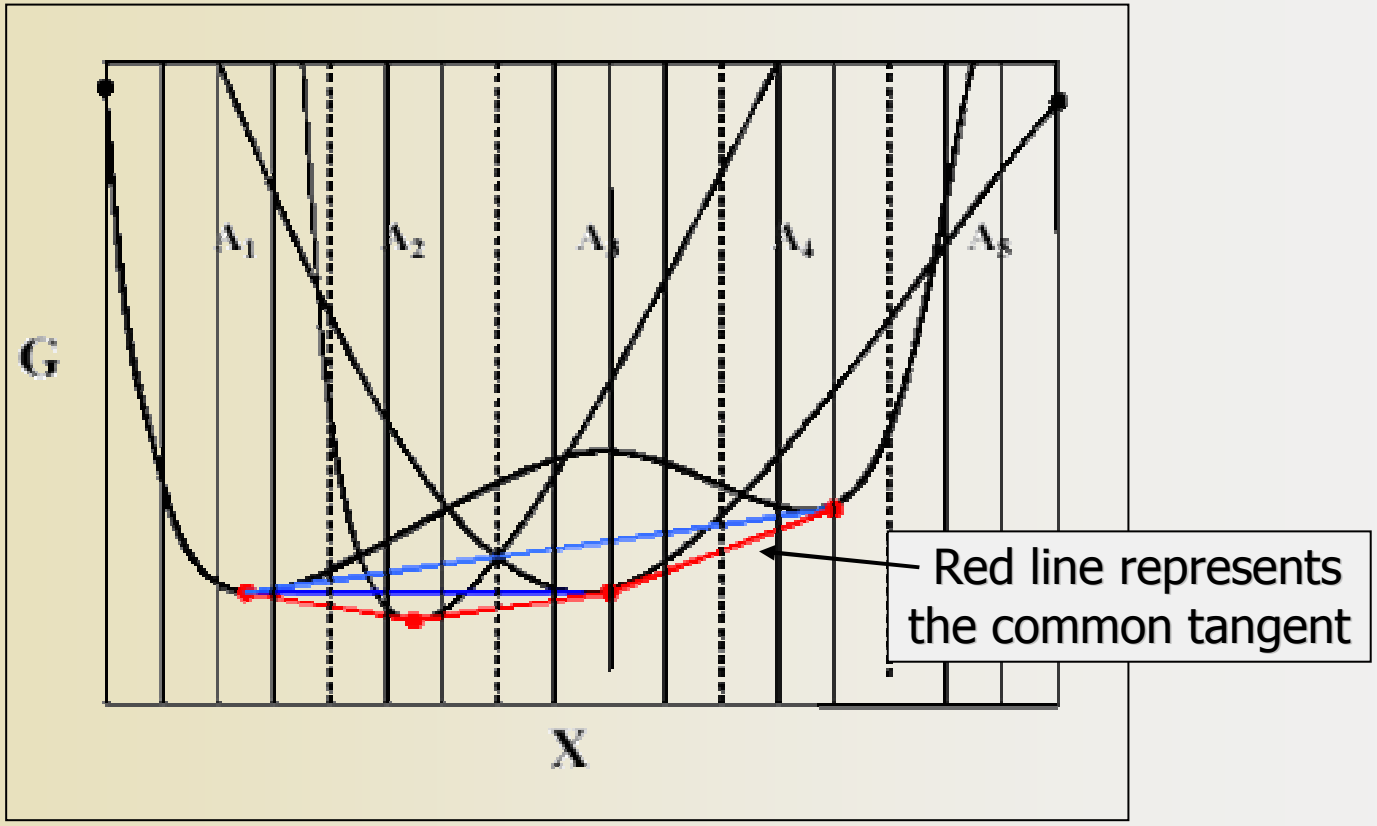
Curve having minimal value at the right end



Increasing curvature while preserving relative extrema

III. New algorithm: binary case

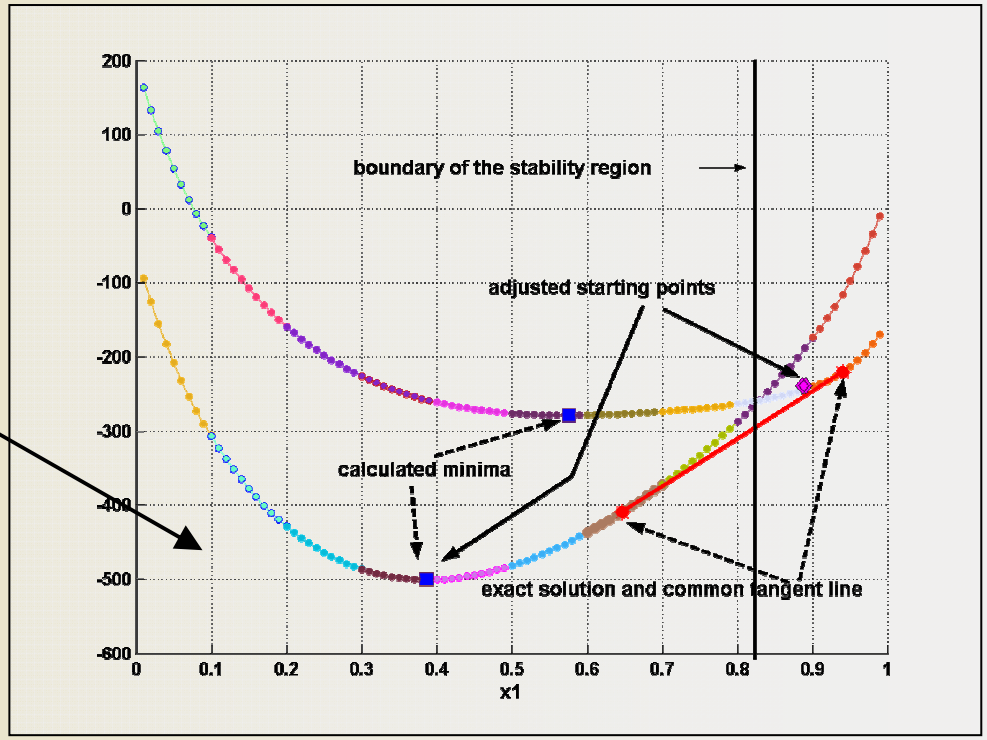
1. Fix *N* – the number of grid points in major axis subdivision
2. Identify stability regions



III. New algorithm: binary case

1. Fix *N* – the number of grid points in major axis subdivision
2. Identify stability regions
3. Calculate starting points for optimization

Adaptive search procedure is used to find local minima



Function minima =AdaptiveSearch (*a,b,phase,iter*)

while *(iter<=Niter)*

(1) Sample n points on [a,b]

(2) For *(iter==1)* % finding concavity regions

(a) Calculate $G^{(phase)00}(x_j)$ for x_j, $j=1,\ldots,N$

(b) Locate inflection points by finding indices, such that

$$G^{(phase)00}(x_s)\, G^{(phase)00}(x_{s+1})<0$$

(c) Identify interval(s) for refinement by counting inflection points.

If no inflection points found, put $k=1,\ a(1)=a,\ b(1)=b,$

If one inflection point found and $G^{(phase)00}(x_j)>0$, put $k=1,\ a(1)=a,\ b(1)=x_s,$

If one inflection point found and $G^{(phase)00}(x_j)<0$, put $k=1,\ a(1)=x_s,\ b(1)=b,$

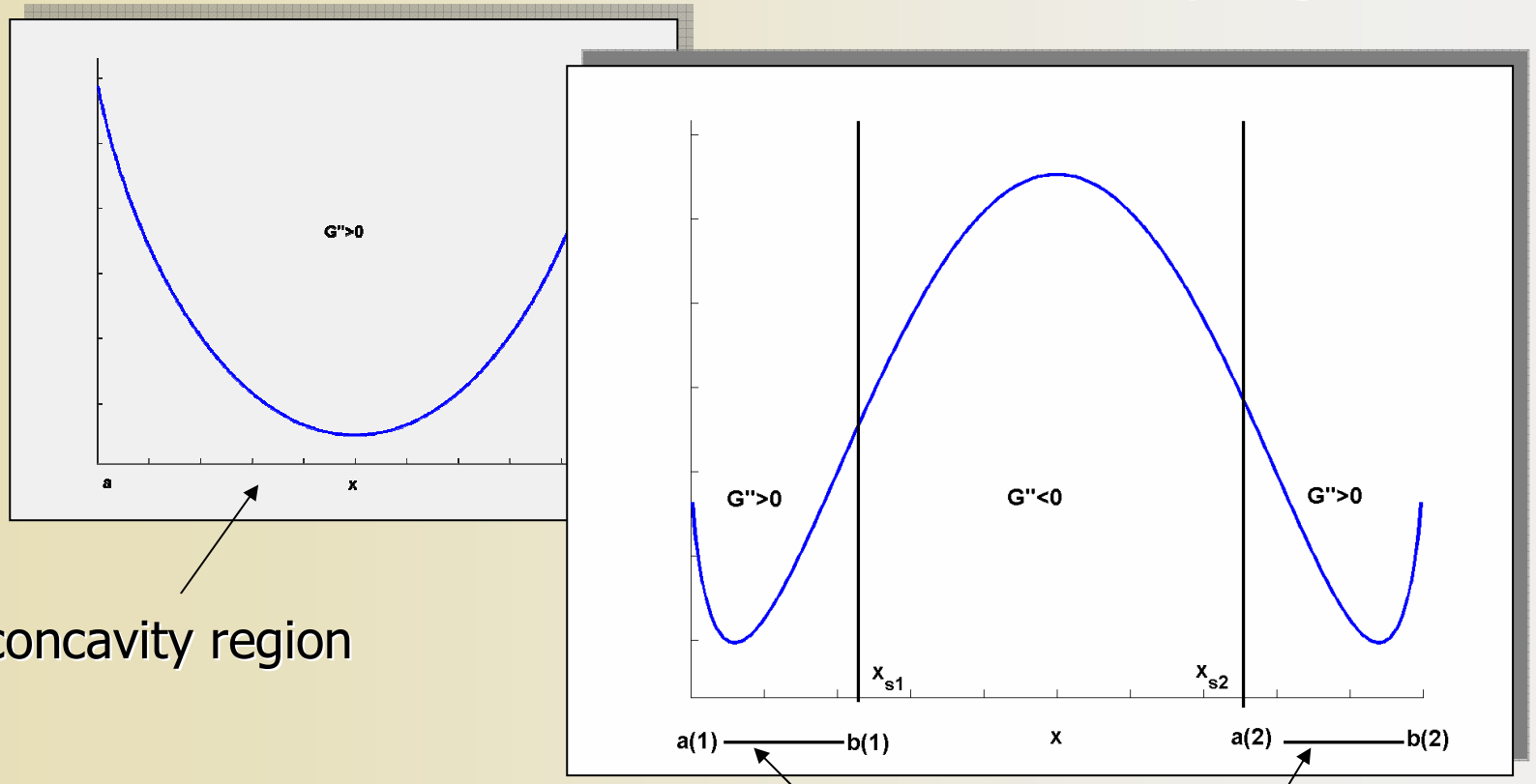
If two inflection points found, put $k=2,\ a(1)=a,\ b(1)=x_{s1},\ a(2)=x_{s2},\ b(2)=b,$

(d) Perform recursive search on each of the identified intervals *(a(j),b(j)):*

minima(j)=AdaptiveSearch(*a(j),b(j),phase,2*)

III. New algorithm: binary case

Schematic view of the search for concavity regions



1 concavity region

2 concavity regions

Function minima =AdaptiveSearch (a,b,phase,iter)

(contunued)

(3) For *(iter>1)* % recursive search procedure

(a) Calculate $G^{(phase)0}(x_j)$ for x_j, $j=1,\ldots,N$

(b) Find s = argmin $G^{(phase)0}(x_j)$ for x_j, $j=1,\ldots,N$

(c) If $(G^{(phase)0}(x_s)<\varepsilon)$ or *(iter>Niter)* % met stopping criteria

x_s=*minima*, return *minima*

else for $\delta=(b-a)/2N$ do % recursive refinement

minima =AdaptiveSearch($x_s-\delta, x_s+\delta, phase, iter+1$)

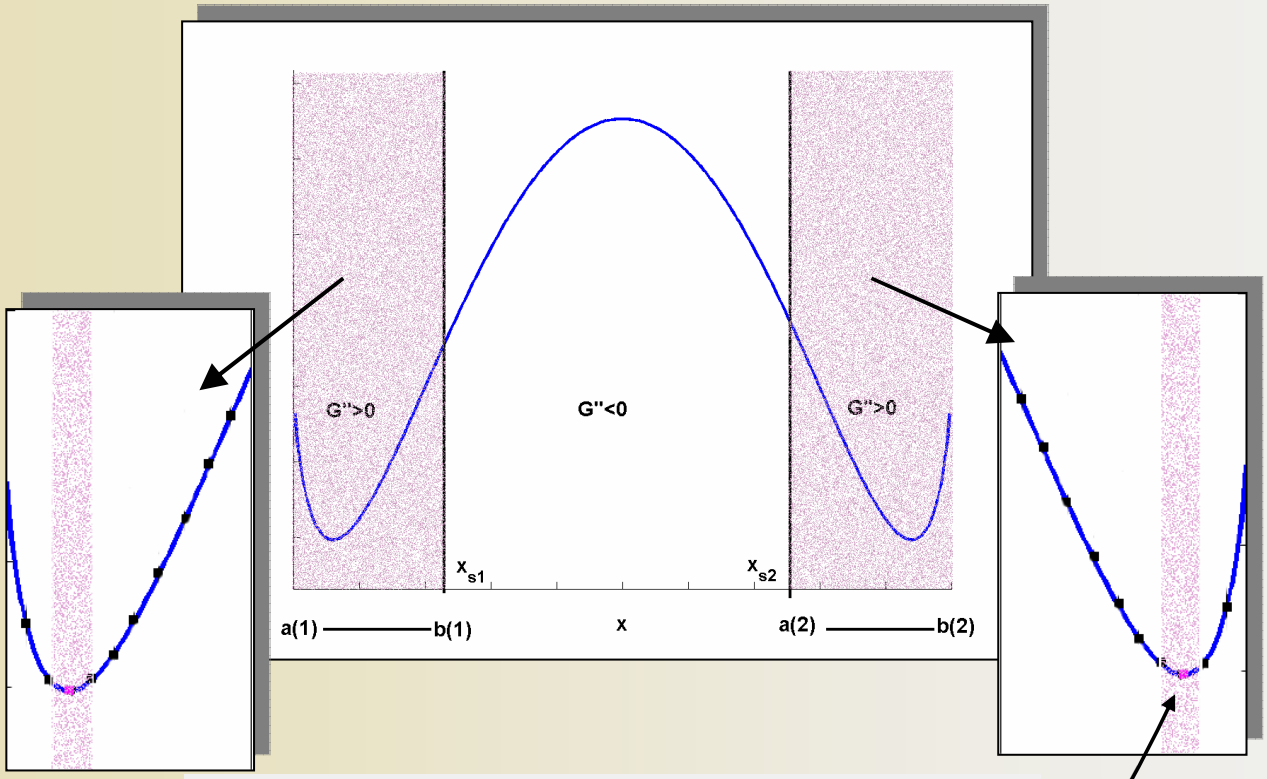
end if

End while

III. New algorithm: binary case

Schematic view of the adaptive refinement

Continue until some stopping criterion is met (tolerance or maxIter is reached)



Sample N points after each refinement and locate lowest derivative value

III. New algorithm: binary case

1. Fix N – the number of grid points in major axis subdivision
2. Identify stability regions
3. Calculate possible starting points for optimization
4. Perform coplanarity checks to get the convex hull of points
5. Carry out optimization for all remaining pairs of points
6. Check result for consistency
7. Construct phase diagram using solution obtained in step 6

IV. New algorithm: ternary case

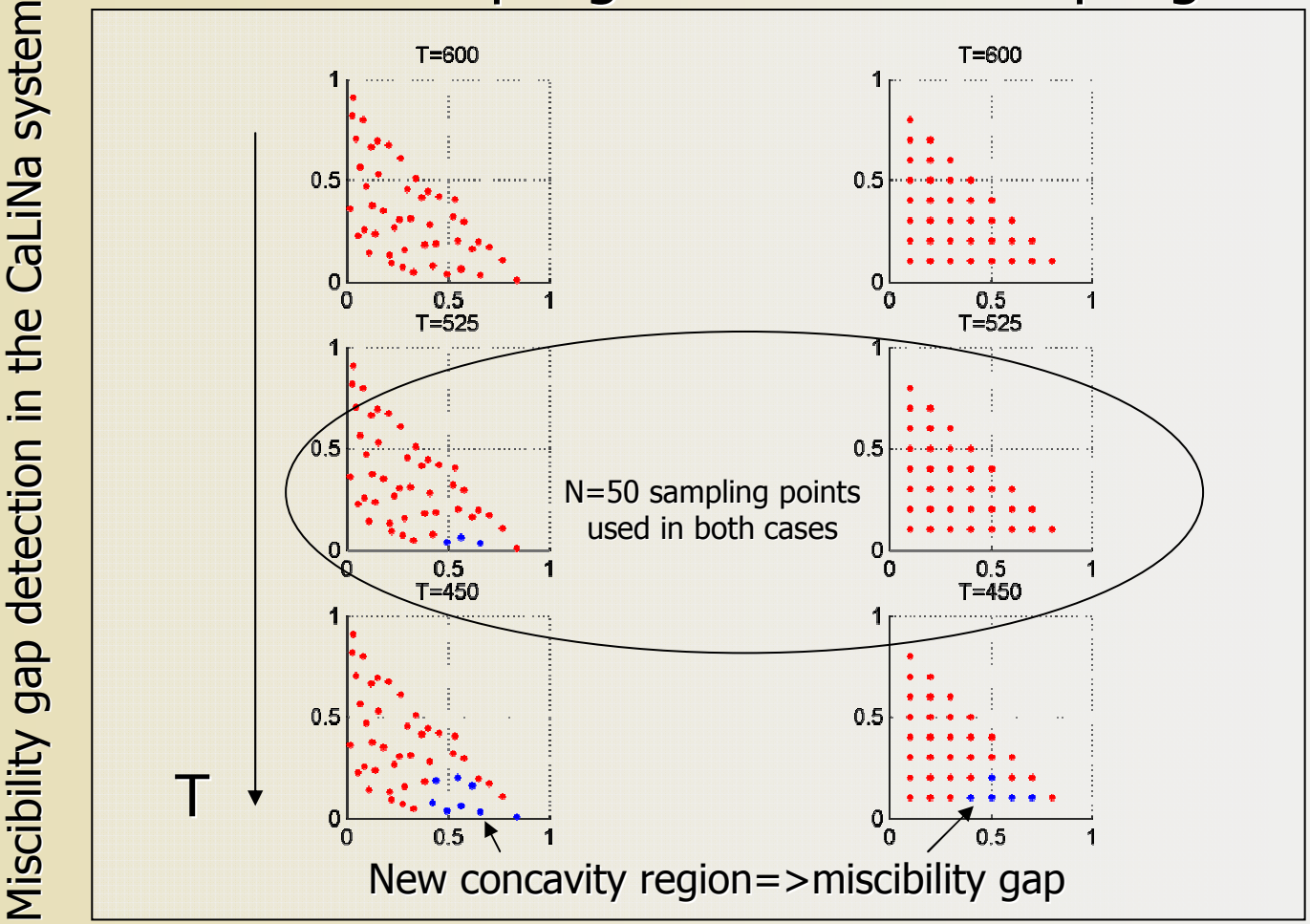
Changes comparing to the binary case:

- Stability regions calculation is not cost effective, so resort to adding sample points on the boundary
- Better sampling techniques need to be used in the interior to lower the complexity of finding critical points

  Quasirandom sampling approach (via Halton, Hammersley or Sobol sequencing) can be one possible alternative to the uniform distribution.

IV. New algorithm: ternary case

Sobol sampling vs. uniform sampling



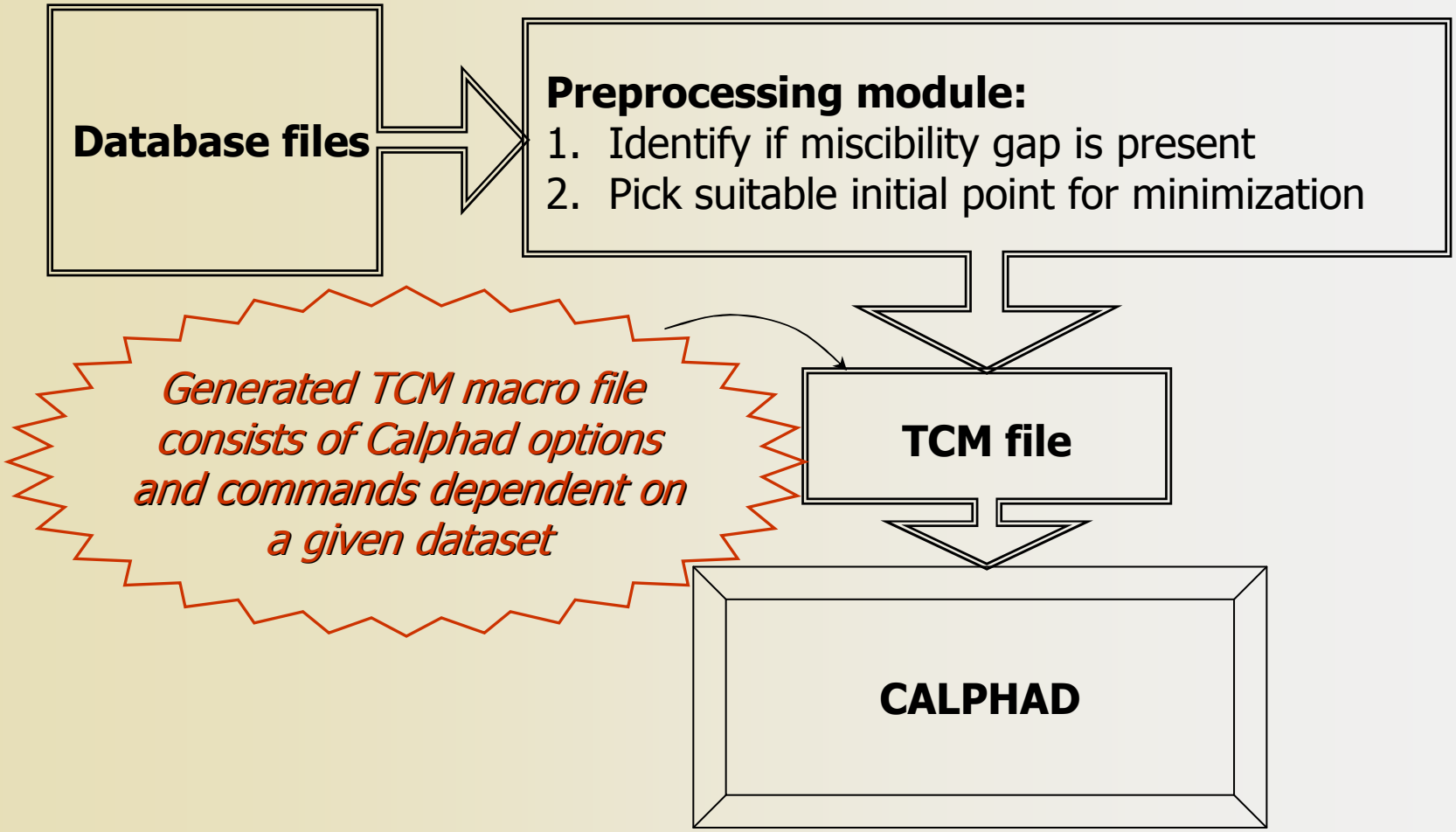
IV. New algorithm: ternary case

1. Fix original domain as $V=\{(x,y)|\ x+y<1,x,y>0\}$, N – the number of grid points in major axis subdivision, ε- tolerance, *Niter* - maximum number of allowed refinements

2. For *phase=1,…,K* do
   (a) *minima = AdaptiveSearch2d(V,phase,1)*
   CÃ (minima, phase)
   (b) Sample *N* points *bdrypts* on the boundary of domain *V,*
   CÃ (bdrypts, phase)
   end

3. Perform coplanarity checks to get the convex hull of points in *C*
4. Carry out optimization for all remaining pairs of points, check result for consistency
5. Complete the phase diagram

IV. New algorithm: flow chart



V. Computational complexity estimates: binary case

h - the smallest mesh size to identify starting points with a given accuracy ε.

L – number of levels for the adaptive scheme to reach this mesh size) $h=1/N^L$ i.e. $L = \ln(1/h)/\ln N$

	Chen et al method	Proposed method
N_T = total # of subdivisions required to reach mesh size ***h***	$N_T = 1/h$	$N_T = N + 2(N-1)L =$ O(ln *1/h*)
Total complexity estimated in terms of ***h***	$KN_T+0.5N_T(N_T-1)¢$ $(2+12(N_T-2))$	$2NK+3NC + 4NCL$
	O($1/h^3$)	O(ln *1/h*)

V. Computational complexity estimates: binary case

O(*1/h*^{3}) vs. O(ln *1/h*)

VI. Numerical examples

In the examples that follow we use the following form of the Gibbs energy:

$$G_m^{\Phi} = \sum_i x_i {}^0G_i^{\Phi} + RT \sum_i x_i \ln x_i + {}^{xs}G_m^{\Phi}$$

$${}^{xs}G_m^{\Phi} = \sum_{j>i} x_i x_j \sum_{k=0}^{n} L_{i,j}^{\Phi} (x_i - x_j)^k$$

The excess energy here is given in the form of the Redlich-Kister polynomial.

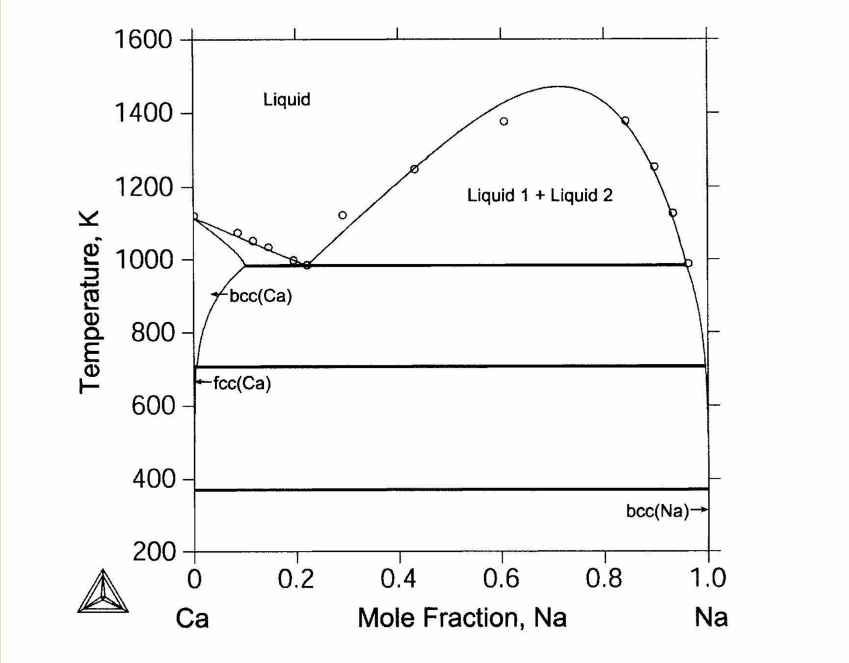
The reference phase diagrams are reproduced from

S. J. Zhang, D. W. Shin and Z. K. Liu, Thermodynamic modeling of the Ca-Li-Na system, CALPHAD, Vol.27, 2003, 235-241.

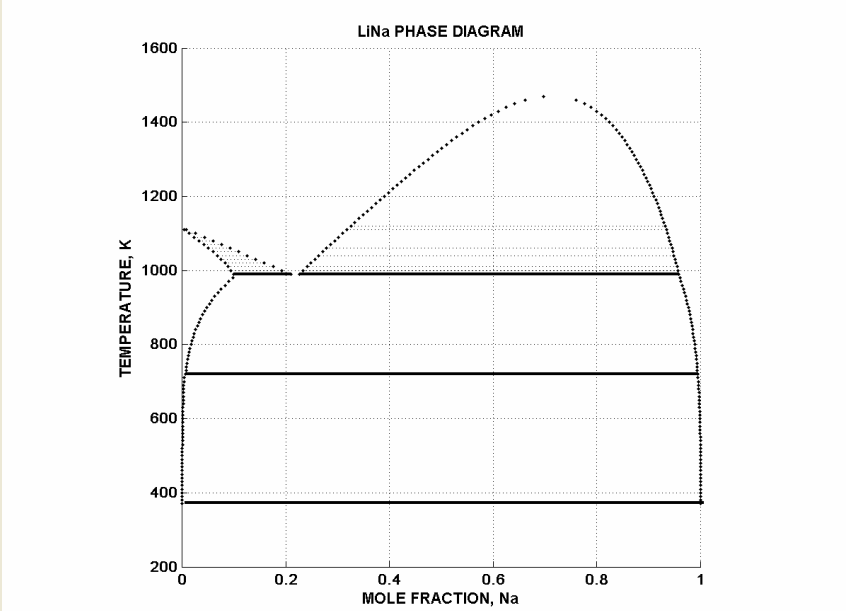
VI. Numerical examples

Example 1: Binary Ca Na system

ThermoCalc result obtained using the a priori information



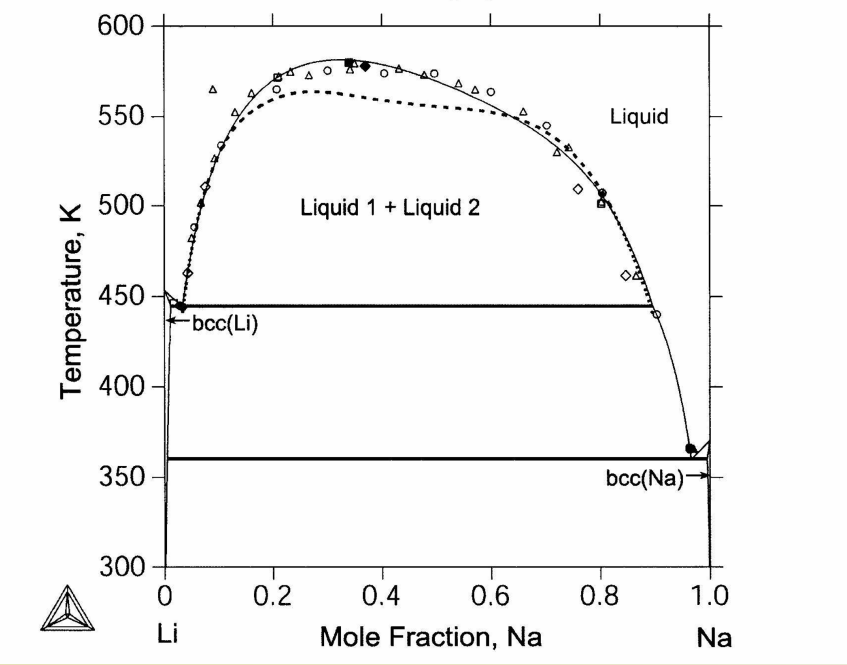
The corresponding phase diagram obtained automatically



VI. Numerical examples

Example 2: Binary Li Na system

ThermoCalc result obtained using the a priori information



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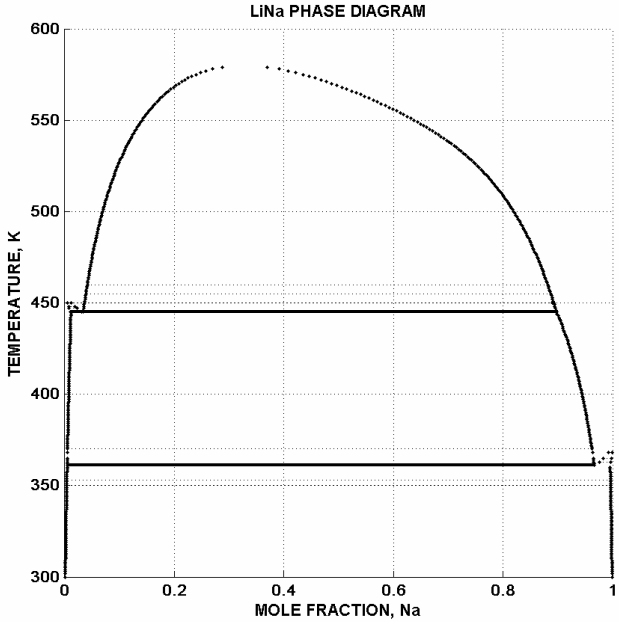
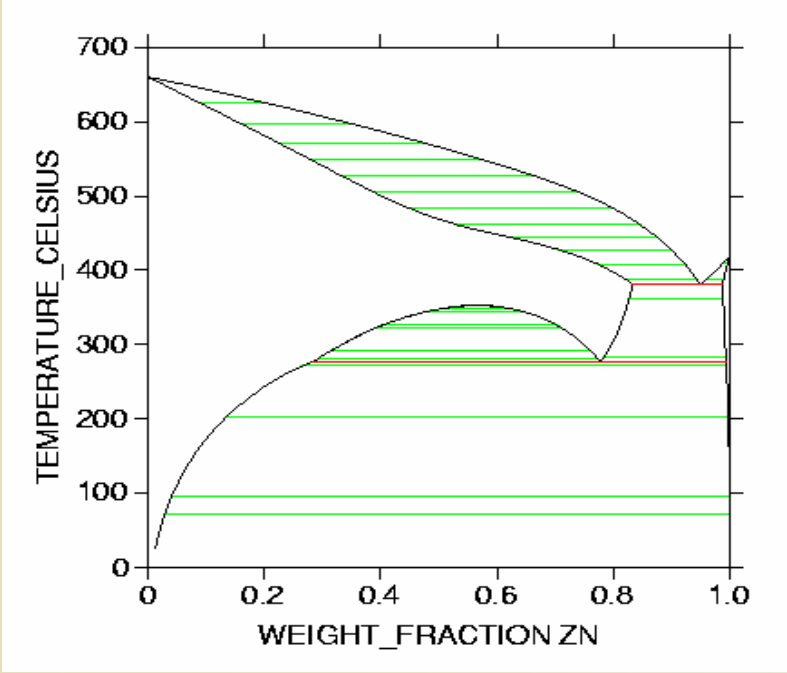


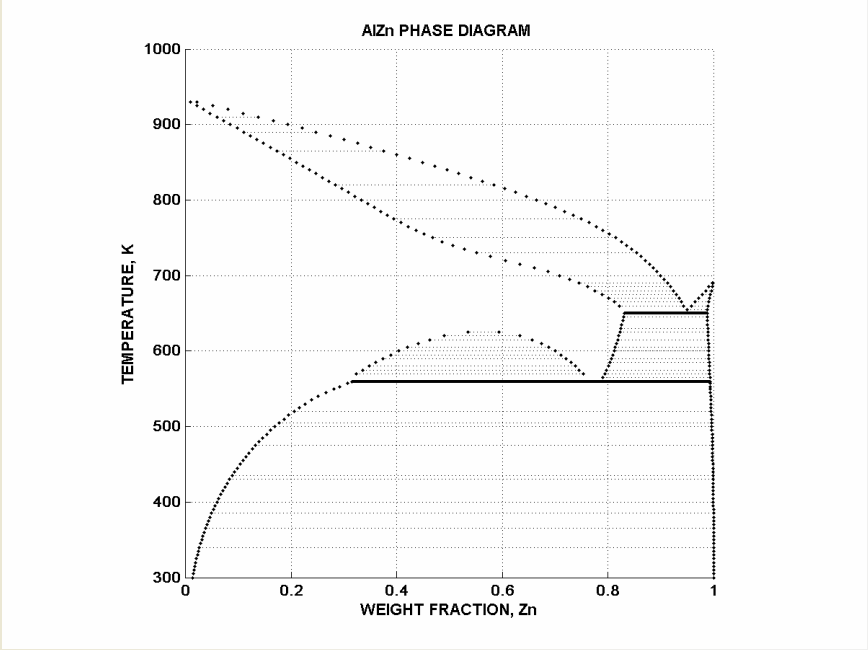
VI. Numerical examples

Example 3: Binary Al Zn system

ThermoCalc result obtained using the a priori information



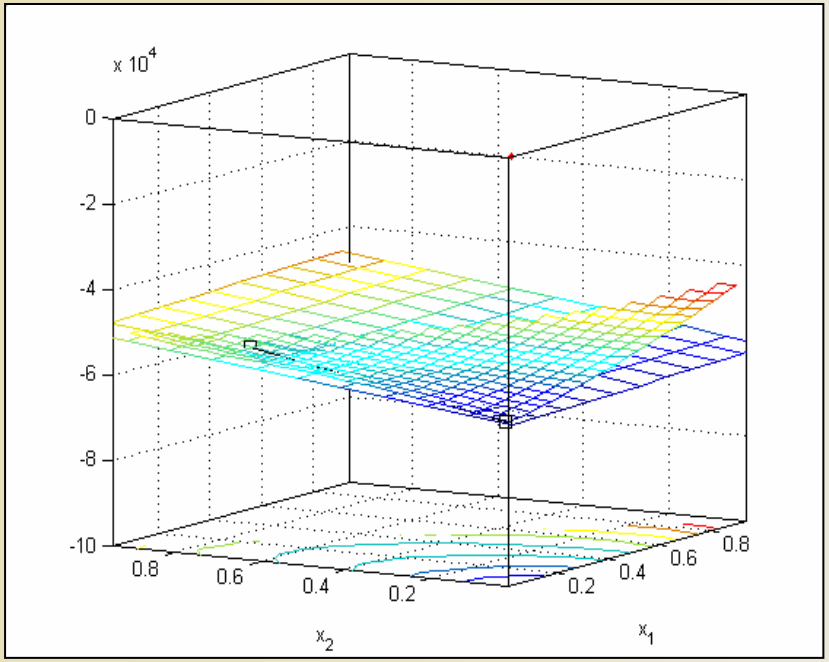
The corresponding phase diagram obtained automatically

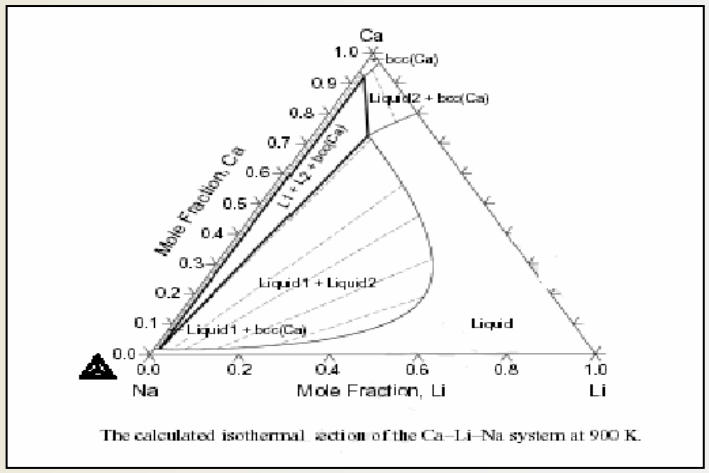


VI. Numerical examples

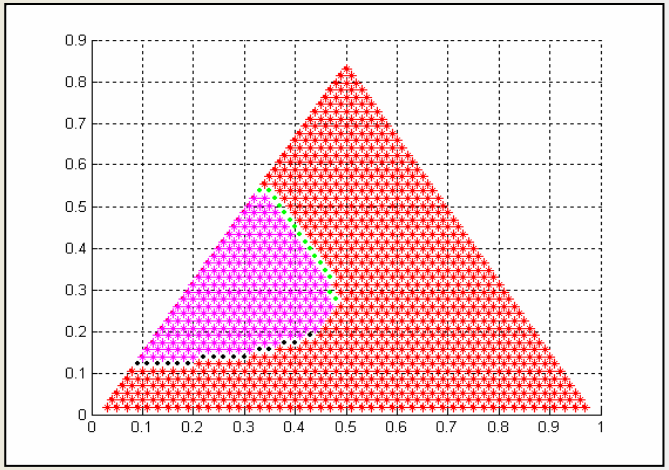
Example 4: Ternary Ca-Li-Na system at T=900K

Gibbs energy profile with the miscibility gap and a corresponding common tangent plane





The calculated isothermal section of the Ca–Li–Na system at 900 K.



VII. Discussion and future work

Conclusions:

- The new algorithm possesses advantages over existing methods in terms of the computational complexity and the robustness.
- It can be used to automate the calculation of phase equilibria in complicated systems.
- Numerical results for binary and ternary systems show good agreement of automatic calculations with prior results.

Future work:

1. Generalizations to higher dimensions
2. Analysis of other possible sampling strategies
3. Development of an independent software package

THANKS!