TOPOLOGICAL ANALYSIS OF THE G^M FUNCTION IN LIQUID-LIQUID EQUILIBRIUM DATA CORRELATION FOR TERNARY AND BINARY SYSTEMS

(Thermodynamic Review)

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Keywords: Liquid-Liquid Equilibrium, Phase Equilibria Calculation, Gibbs Energy of Mixing, NRTL, UNIQUAC, Spinodal Curve, Hessian Matrix, Plait Point, Critical Solution Temperature, Data Correlation, Binary and Ternary Systems, Tie Line, Thermodynamic Models.

Introduction

Most chemical processes involve mass transfer operations between one or more streams. In fact, 60-80 % of the operating and fixed costs of a chemical plant are due to separation and purification processes. For this reason, proper design of equipment and processes, and the minimization of their cost and/or environmental impacts will play a vital role in the optimal performance and yield of the plant as a whole. Success will partially be determined by accurate correlation or prediction of the phase equilibria using some of the available models. Excess Gibbs energy models such as NRTL or UNIQUAC are potentially capable of representing liquid-liquid splitting. The application of these models to the correlation of liquid-liquid equilibrium (LLE) has yielded a close approximation to the experimental data for many systems. There are many difficulties associated with the complexity of the phase equilibrium behavior and phase equilibrium data correlations, such as convergence, objective function definition, initial parameters value dependence, and the existence of multiple or metastable solutions. Consequently, obtaining acceptable results can be very difficult for many systems, especially for those far from ideality [1-7]. In this sense, different possibilities to avoid inconsistent solutions are: to restrict for instance the NRTL iteration parameters during the correlation process depending on the characteristic and type of the system (number of binary pairs partially miscible), to limit the composition space for the LLE root determination (using the second derivative of the Gibbs energy of mixing function), to use geometrical methods to determine appropriate initial values of variables in LLE or LLLE calculation processes, etc [8-19].

Nevertheless, there is an additional and recurrent problem in the literature that is the occasional publication of incoherent parameters for different systems. The inconsistencies detected are the type of unrealistic Gibbs energy of mixing (G^M) surfaces or inconsistent behavior due to values for the parameters which predict LL splitting for a homogeneous binary subsystem. This problem could be handled for instance, by adopting a system as the Thermodata engine by NIST [20], but updated for liquid-liquid equilibrium data.

Thus, the aim of this work is to refresh the relevant role that has the topology analysis of the G^M/RT function to avoid false solutions and suggest a procedure that should be adopted by researchers on this topic or/and the reviewers and editors of the corresponding journals, in order to confirm the coherence of the correlation parameters obtained in the correlation process. The analysis of the G^M function can be easily done and modeled, taking into account the actual possibilities of computer calculations. This analysis should include the review of the total composition space, the analysis of the individual binary pairs, and the analysis of each experimental tie line.

Some examples

When a phase equilibrium calculation review is made, it is still possible to find in the literature some results that should be taken carefully. Figures 1a-c show some calculated Gibbs Mixture Energy Surface in the whole composition space using the published NRTL parameters, initially obtained for systems type 1

in the Treybal Classification [21] with only one pair of components partially miscible. As it is possible to observe, the surface obtained is not coherent with the expected behavior. The same conclusion can be obtained if the behavior of the binary subsystems and/or the evolution of the G^M/RT function along the experimental tie lines is analyzed ($G^{Mixture}/RT = G^{Ideal}/RT + G^{Excess}/RT$).

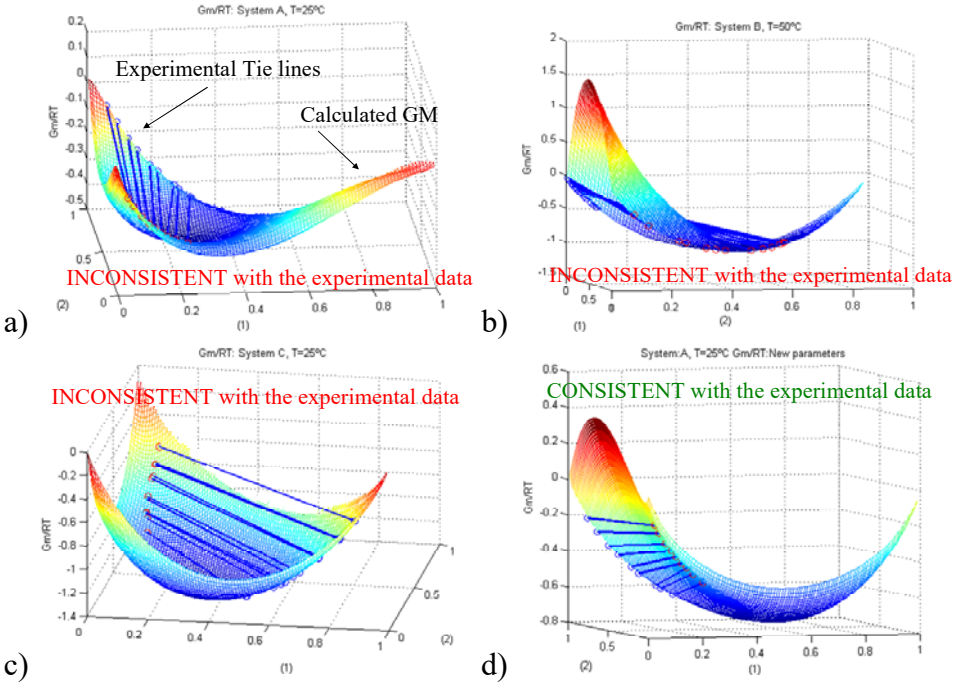

Figure 1. Calculated Gibbs Mixture Energy Surface using: a-c) Published NRTL parameters d) New consistent parameters for system A.

Thus, a single and very easy-to-use Graphical User Interface (GMcal_TieLinesLL) [22] based on the topological information contained in the Gibbs energy of mixing function has been developed for binary and ternary LLE systems, as a friendly tool to check the coherence of the parameters obtained in a correlation data procedure (the NRTL and UNIQUAC models are included by defect, however any other $G^{Excess}(L)/RT$ model could be easily implemented). This analysis of the $G^M(L)/RT$ surface in the whole range of composition, the $G^M(L)/RT$ for the binary subsystems and the $G^M(L)/RT$ curves in planes containing the liquid-liquid tie lines should be necessary to validate the obtained parameters for the different models for correlating phase equilibrium data. This simple analysis could be used by authors and journals in order to guarantee the adequate prediction of equilibrium [23-30]. In addition, restrictions on NRTL binary parameters have been used in the correlation procedure to guarantee the adequate prediction of the total or partial miscibility behavior of the binary subsystems [13,31].

Figure 2. Visual of the GMcal_TieLinesLL MATLAB GUI developed [22].

Version 2.2 of this friendly tool also allows, on the one hand, the analysis of the Hessian Matrix determinant (σ), the spinodal curve (σ=0), and the Plait Point location for LLE ternary systems, using additionally the δ and δ* matrix determinants [11], which have to be also equal to zero (eqs. 1). On the other hand, it is also possible to analyze binary LLE data at different temperatures, including the location, if there exits, of the Critical Solution Temperature (UCST, LCST or Closed Miscibility Loops) [31] (see Figures 3 and 4), using the NRTL, the UNIQUAC or "other" model. Additionally, the representation of the correlated miscibility boundaries (LLE or mLLE) for the NRTL model depending on the α_{ij} value [32,33] has been included in this new version.

$$\sigma = \begin{vmatrix} \frac{\partial^2 G^M}{\partial^2 x_1} & \frac{\partial^2 G^M}{\partial x_1 \partial x_2} \\ \frac{\partial^2 G^M}{\partial x_2 \partial x_1} & \frac{\partial^2 G^M}{\partial^2 x_2} \end{vmatrix} = 0;\ \delta = \begin{vmatrix} \frac{\partial \sigma}{\partial x_1} & \frac{\partial \sigma}{\partial x_2} \\ \frac{\partial^2 G^M}{\partial x_2 \partial x_1} & \frac{\partial^2 G^M}{\partial^2 x_2} \end{vmatrix} = 0;\ \delta^* = \begin{vmatrix} \frac{\partial \sigma}{\partial x_2} & \frac{\partial \sigma}{\partial x_1} \\ \frac{\partial^2 G^M}{\partial x_1 \partial x_2} & \frac{\partial^2 G^M}{\partial^2 x_1} \end{vmatrix} = 0 \quad (1)$$

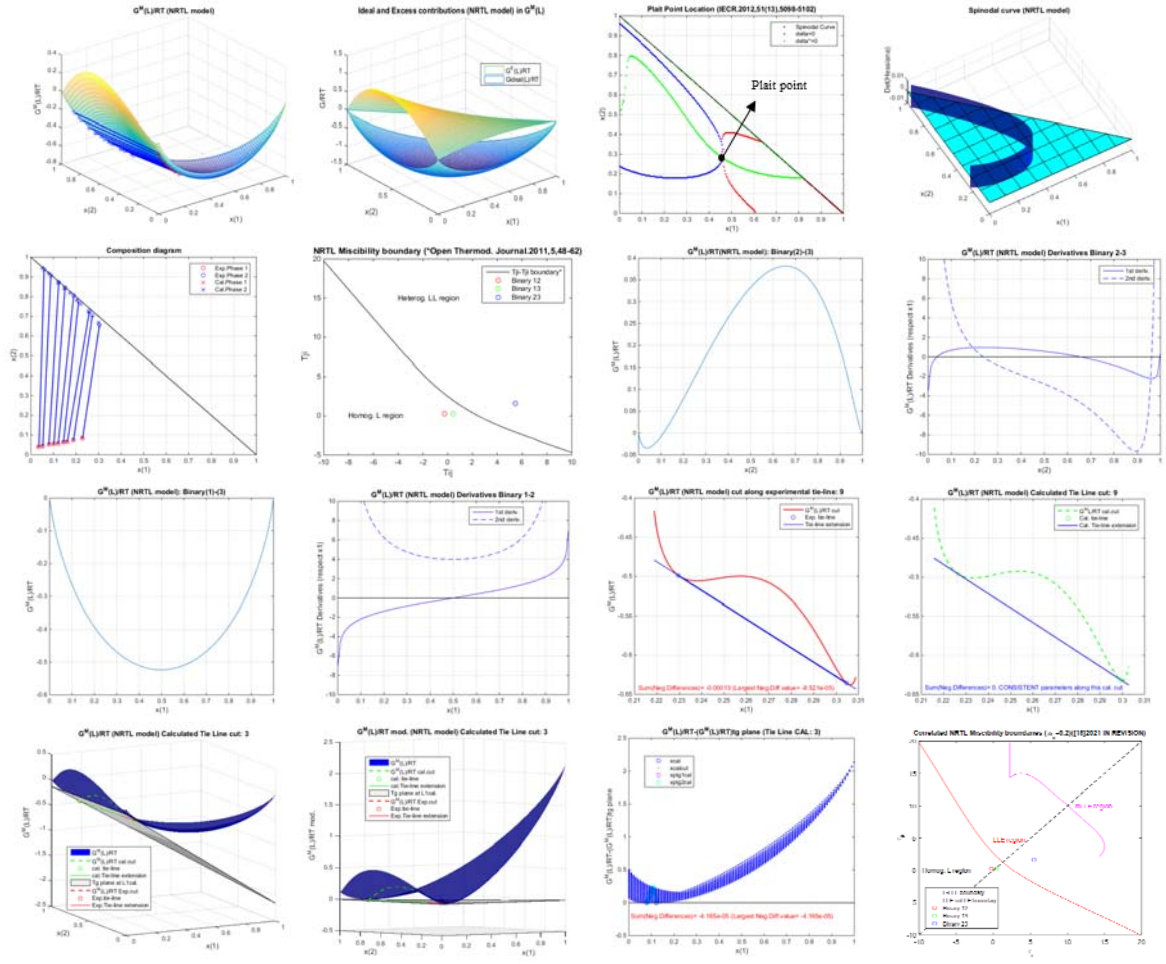

Figure 3. Examples of the graphs for ternary systems that can be generated with the developed GUI: GMcal_TieLinesLL [22].

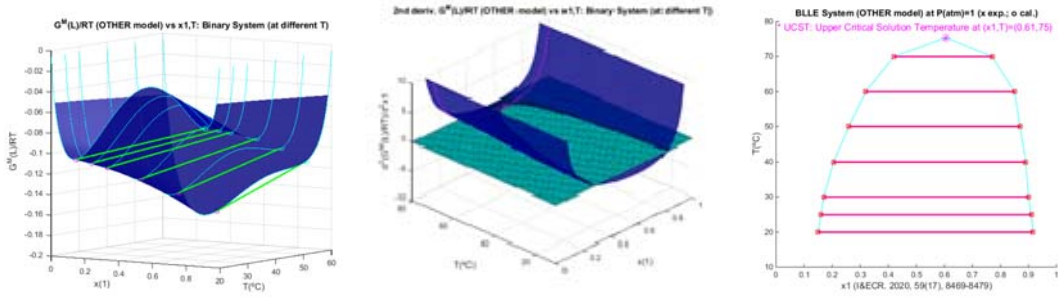

Figure 4. Examples of the graphs for binary systems that can be generated with the developed GUI: GMcal_TieLinesLL [22].

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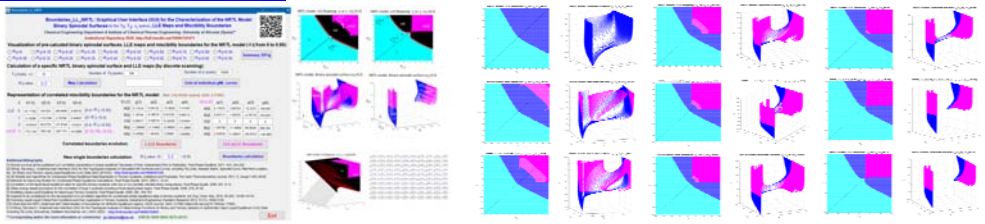

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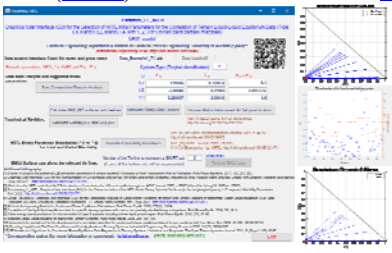

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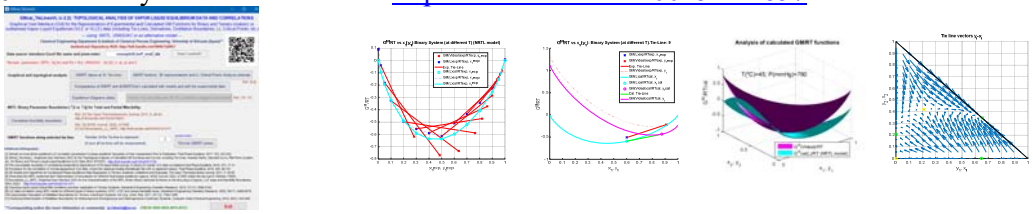

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TOPOLOGICAL ANALYSIS OF LIQUID-LIQUID EQUILIBRIUM CORRELATIONS

-Thermodynamic review

-Proposal of an easy methodology to ensure the coherence of correlation parameters

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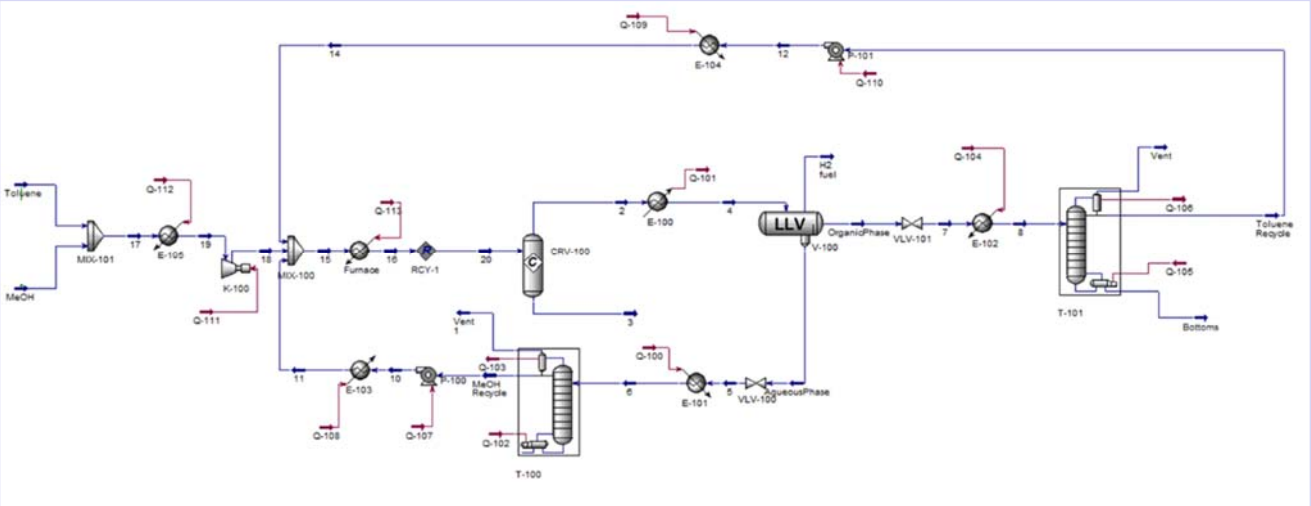
OUTLINE

- **Introduction. Thermodynamic foundation**
- **Equilibrium calculations: difficulties**
- **Binary and ternary examples (LL, LV, LS, LLS…)**
- **New Strategies to avoid convergence problems**
- **Bibliography**

1. Phase equilibrium calculations play a key role in the simulation of industrial processes by using commercial simulators



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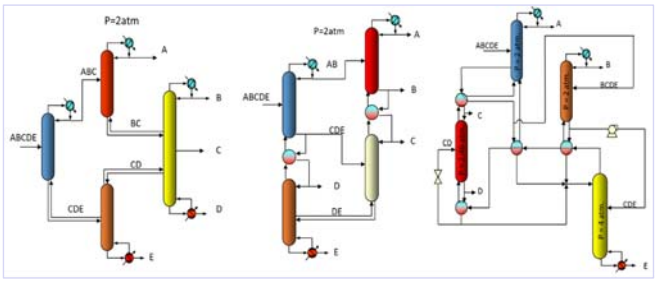
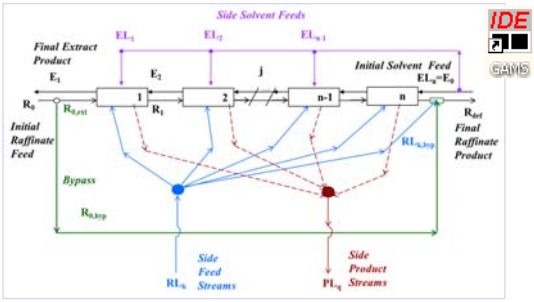
or in the optimal design of general superstructures of separation processes by mathematical programming (optimizing e.g. costs, environmental impacts, etc.)





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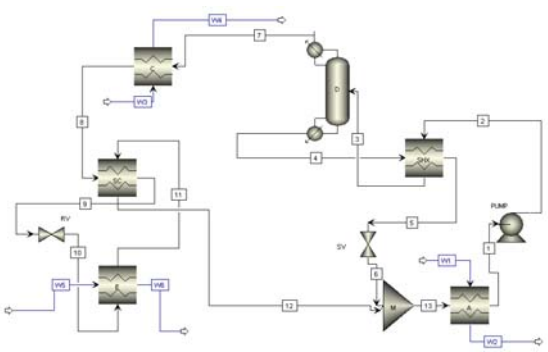

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INTRODUCTION

Phase equilibria is necessary to design separation processes

Thermodynamic basis are well stablished (Gibbs)

$$\mu_i^I = \mu_i^{II} = ... = \mu_i^F$$

LV

LL

LS, LLS, LLSh

LLV

THERMODYNAMIC FOUNDATION

For L-L equilibrium:

$$\begin{aligned} \mu_i^I &= \mu_i^{II} \\ f_i^I &= f_i^{II} \\ a_i^I &= a_i^{II} \end{aligned}$$

$$\gamma_i^I x_i^I = \gamma_i^{II} x_i^{II}$$

T, P
Phase II $x_1^{II}, x_2^{II}, ...x_C^{II}$
Phase I $x_1^I, x_2^I, ...x_C^I$

where the activity is given by:

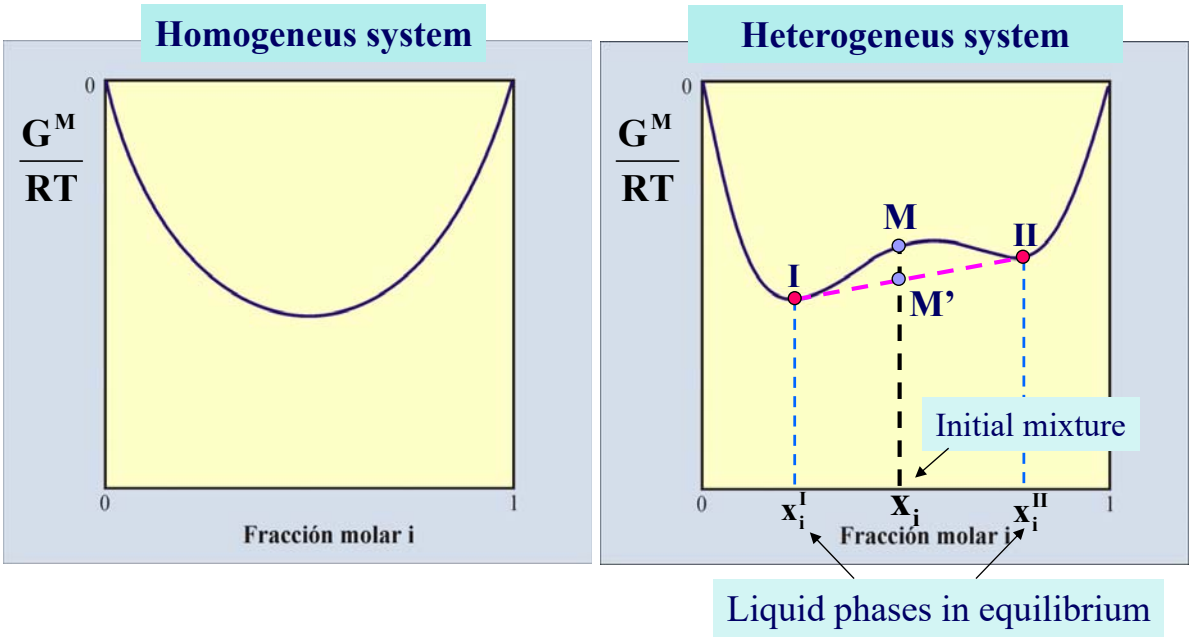
$$RT \ln a_i = G^M + \sum_j x_i \left(\frac{\partial G^M}{\partial x_i}_{c\,j} - \frac{\partial G^M}{\partial x_j} \right)$$

o alternatively, for the activity coefficient:

including all components

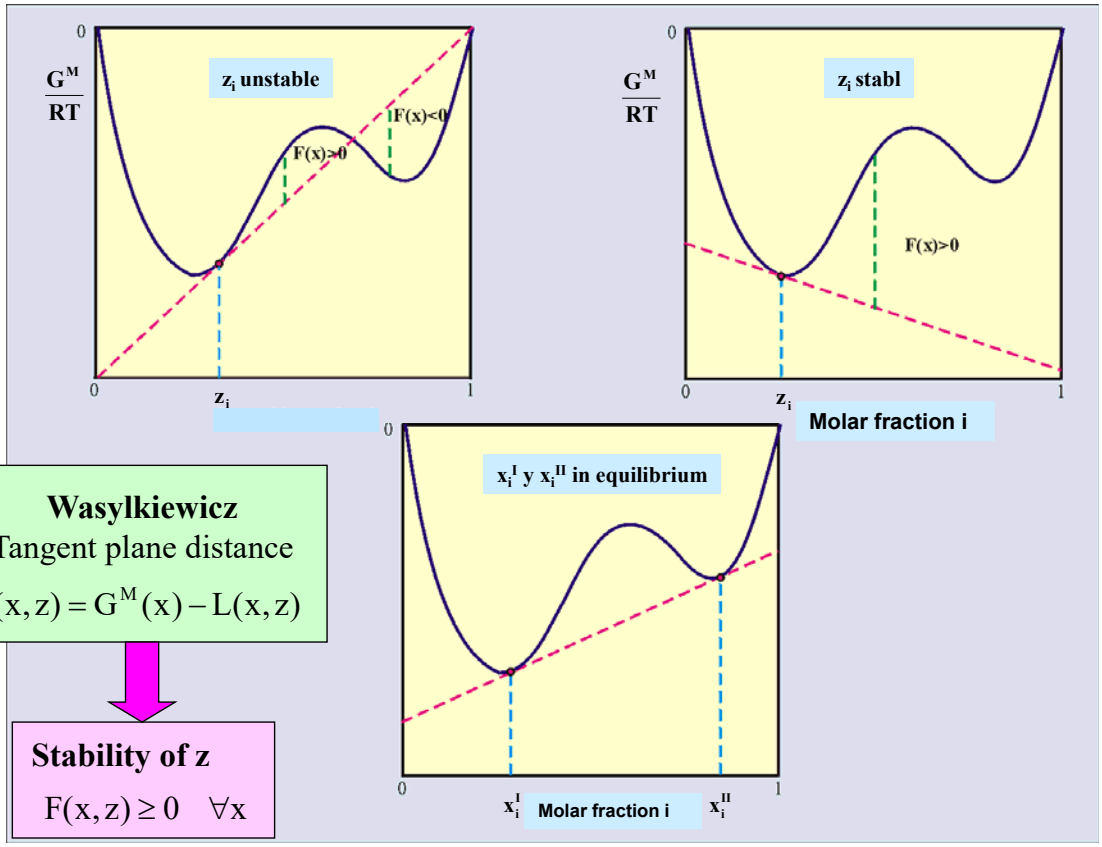
$$RT \ln \gamma_i = G^E + \sum_j^c x_j \left(\frac{\partial G^E}{\partial x_i} - \frac{\partial G^E}{\partial x_j} \right)$$

G^M and phase stability: *"Common Tangent Plane"*



- G^M information is unsufficiently used
- Is the key to completely solve the problem

Stability criterion



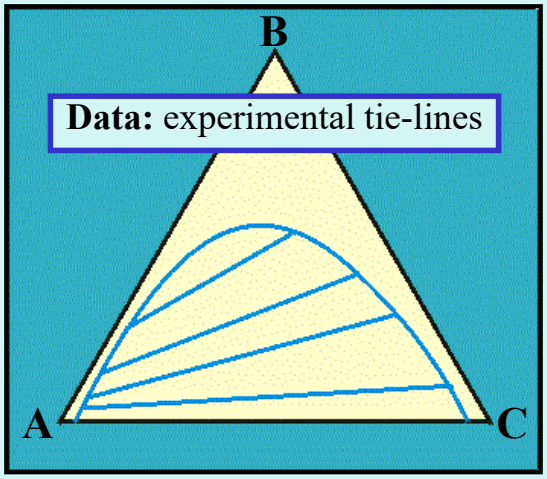
Wasylkiewicz
Tangent plane distance

$$F(x,z) = G^M(x) - L(x,z)$$

Stability of z

$$F(x,z) \geq 0 \quad \forall x$$

P and T=constant



A) Experimental Data Correlation

For each calculated tie line

$$\gamma_A^I x_A^I = \gamma_A^{II} x_A^{II}$$

$$\gamma_B^I x_B^I = \gamma_B^{II} x_B^{II}$$

$$\gamma_C^I x_C^I = \gamma_C^{II} x_C^{II}$$

$$\gamma_i^F = f(x_i^F, x_{j\neq i}^F, A_{ij})$$

Unknown variables: binary parameters $A_{AB}, A_{BA}, A_{AC}, A_{CA}, A_{BC}, A_{CB}$

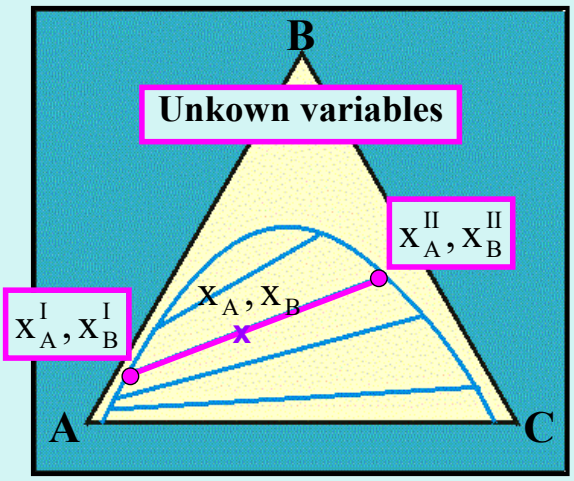
$$F.O(a) = \sum_{k=1}^{n}\sum_{i=1}^{c}\left(a_{i,k}^I - a_{i,k}^{II}\right)^2$$

$$F.O(c) = \sum_{k=1}^{n}\sum_{i=1}^{c}\left[\left(x_{i,k,exp}^I - x_{i,k,cal}^I\right)^2 + \left(x_{i,k,exp}^{II} - x_{i,k,cal}^{II}\right)^2\right]$$

B) LL Equilibrium Prediction

Initial Data: binary parameters $A_{AB}, A_{BA}, A_{AC}, A_{CA}, A_{BC}, A_{CB}$
global mixture composition (x_A, x_B)

P and T=constant



$$\gamma_A^I x_A^I = \gamma_A^{II} x_A^{II}$$

$$\gamma_B^I x_B^I = \gamma_B^{II} x_B^{II}$$

$$\gamma_C^I x_C^I = \gamma_C^{II} x_C^{II}$$

Isothermal flash calculation:

$$\begin{cases} L^I + L^{II} = 1 \text{ mol} \\ L^I x_A^I + L^{II} x_A^{II} = x_A \\ L^I x_B^I + L^{II} x_B^{II} = x_B \end{cases}$$

DIFFICULTIES: 1. Tolerance in the isoactivity criterion??

Example:

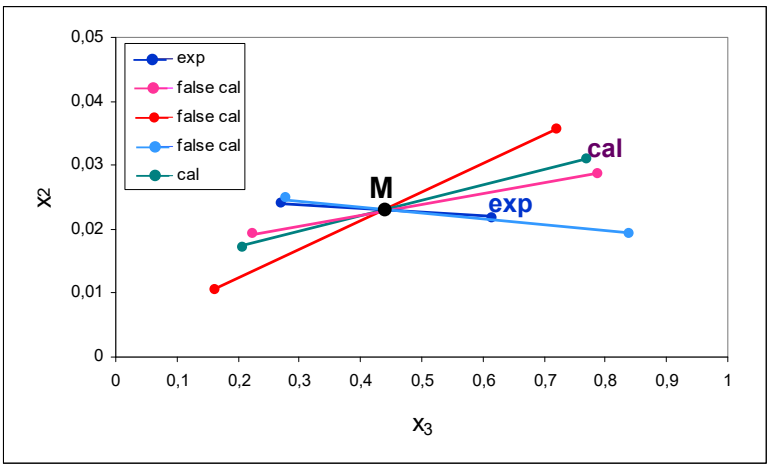
System: methanol (1) + diphenylamine (2) + cyclohexane (3) system at 25ºC.

Global mixture M: z_1=0.5365; z_2=0.0230; z_3=0.4405 (molar fractions)

Model: NRTL (α=0.2) and binary interaction parameters from DECHEMA Chemistry Data Series.

Many conjugated compositions can be calculated:

$$O.F.(a) = \sum_i \left(a_i^{I} - a_i^{II}\right)^2 \leq 10^{-12}$$



Many false LL tie-lines

Marcilla, A.; Reyes-Labarta J.A.; Serrano, M.D.; Olaya, M.M. Pitfalls on computing liquid-liquid phase equilibria using the k-value method. Institutional Repository RUA: http://hdl.handle.net/10045/26610

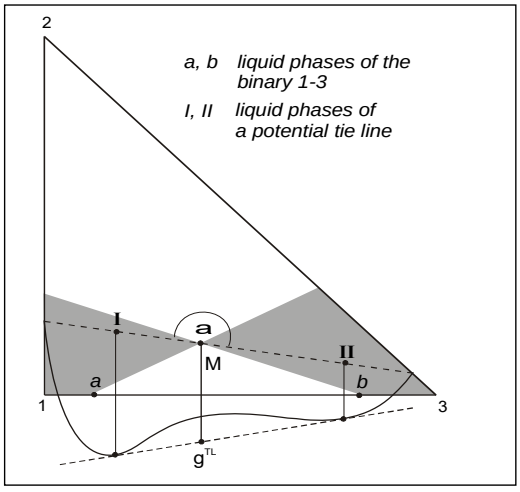
DIFFICULTIES: 1. Tolerance in the isoactivity criterion??

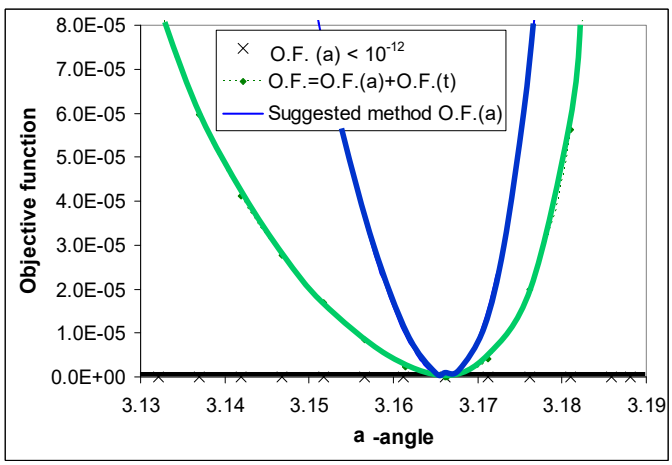
Comparison of the **values for three different objective function definitions**, close to the LLE solution:

a) *Isoactivity* $O.F.(a) = \sum_{i=1}^{3} \left(a_i^{I} - a_i^{II}\right)^2 = 0$

b) *Isoactivity + Minor common tangent condition* (Iglesias Silva et al., 2003)

c) A *modification of the initial vector method* (Eubank et al., 1992)



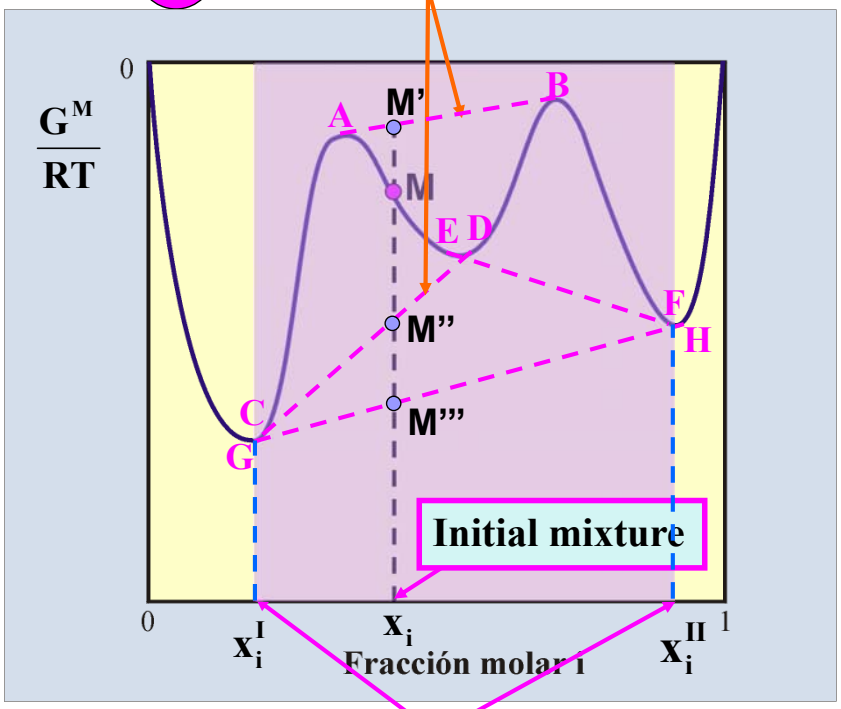


Olaya, M.M.; Ibarra, I.; Reyes-Labarta, J.A.; Serrano, M.D.; Marcilla, A. Computing Liquid-Liquid Phase Equilibria: An exercise to understand the nature of false solutions and how to avoid them. Chemical Engineering Education 2007, 41(3), 218-224. Institutional Repository RUA: http://hdl.handle.net/10045/14277

DIFFICULTIES:

2. Possibility of false solutions

e.g. Binary system:

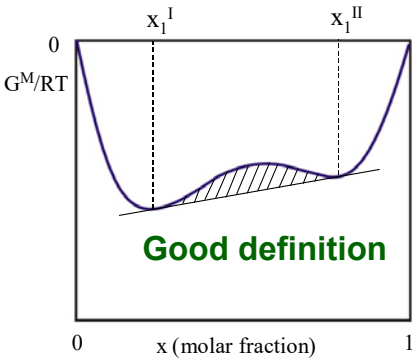


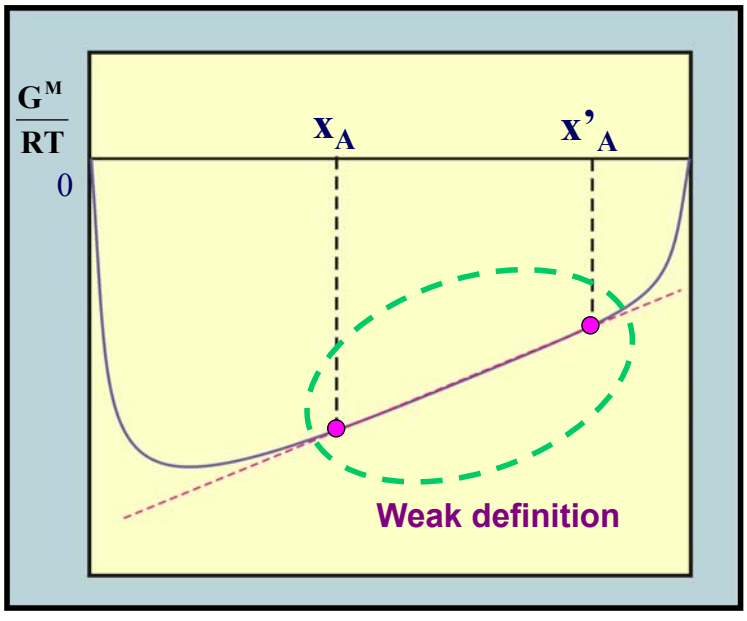
DIFFICULTIES:

3. Uncertainty in the solution

xA and x'A are equilibrium compositions (common tangent) but many other solutions can be obtained because the G^M curve is very linear between them.

e.g. Binary system:

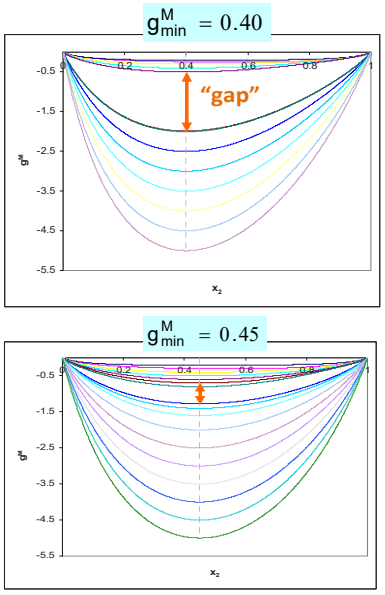


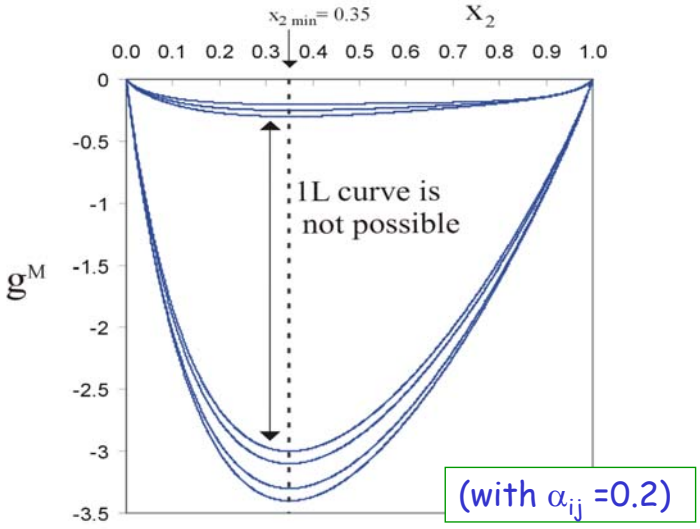


DIFFICULTIES:

4. Known and recognized limitations of the actual models

NRTL: If we carry out a systematic study of the G^M function for a totally miscible binary system, there exist a GAP where solutions for homogeneous binary behavior are not found.

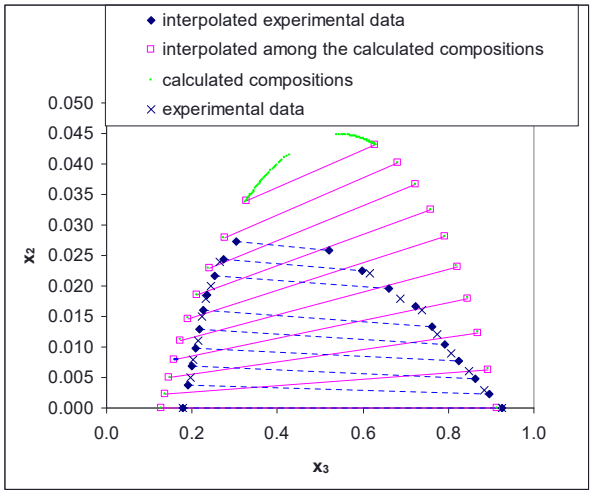




DIFFICULTIES:

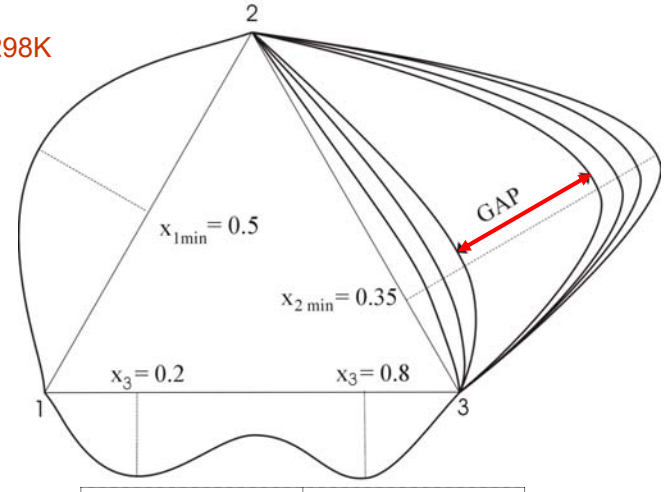
Illustrating example of a clear limitation for NRTL (constant alpha)

LLE inconsistency:
Methanol(1) + difenilamine(2) + cyclohexane(3) at 298K



Data and parameters from Dechema. Vol. V/2, p. 129.

opposite slopes!



A_{12}=873.57	α=0.2
A_{21}=-1245.0	σ=4.08
A_{13}=578.07	
A_{31}=578.07	
A_{23}=-987.32	
A_{32}=-856.11	

DIFFICULTIES:

Illustrating example of a clear limitation for NRTL

LVE inconsistency:

water + 1,2-propanediol at 25 mmHg

(DECHEMA, Vol 1, Part 1a, p. 256)

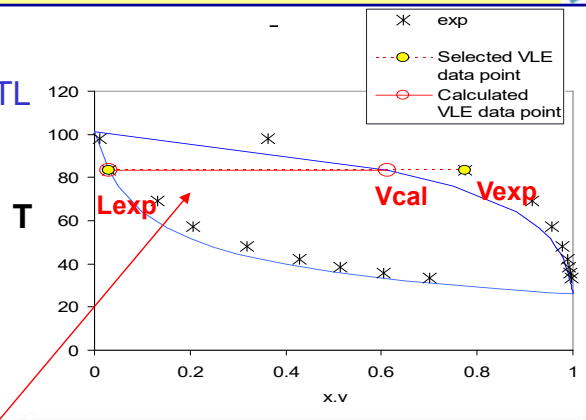
1 data	All data (DECHEMA)
A_{12} = -53.57 K	A_{12} = -136.05
A_{21} = 293.90 K	A_{21} = 402.92
α=3.0	α=2.8

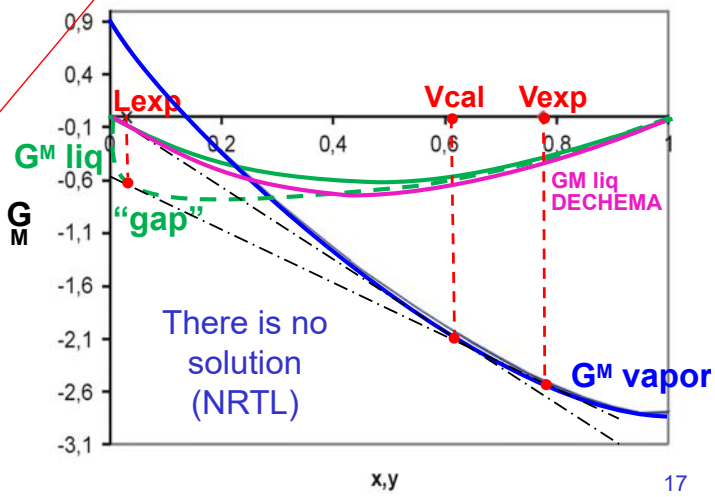
$$\frac{G^{M,V}}{RT} = \sum_i y_i \cdot \ln \frac{P}{p_i^o(T)} + \sum_i y_i \ln y_i$$

$$\left.\frac{d(G^{M,L}/RT)}{dx_1}\right|_{x\,exp} = -2.47$$

$$\left. G^{M,L}/RT \right|_{x\,exp} = -0.65$$

it is impossible to obtain a good correlation and also to correlate only one LVE point



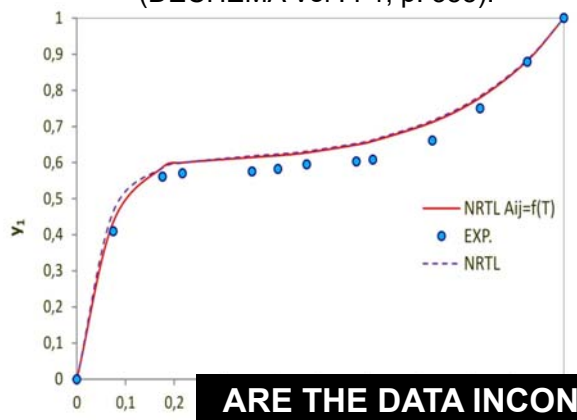


Illustrating example of a clear limitation for NRTL (constant alpha)

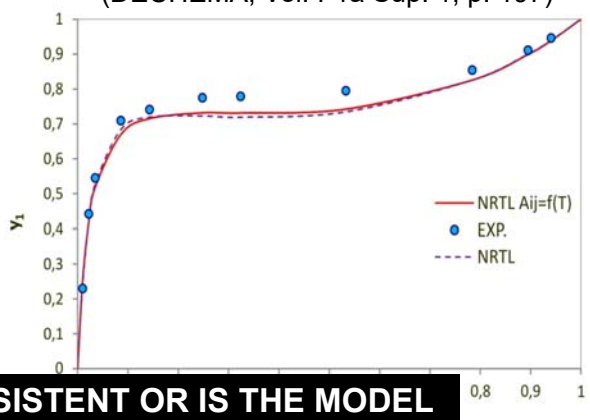
5. LVE: SOME CONSISTENCY TEST USE THERMODYNAMIC MODELS AS NRTL TO VALIDATE THE VLE EXPERIMENTAL DATA, e.g. Frenkel-NIST point-to-point test (van Ness)

BUT…. WHAT HAPPENDS IF WE CANNOT FIND A GOOD CORRELATION?

Metilvinilcetone (1) + water (2) at 743 mmHg (DECHEMA Vol . I-1, p. 355).



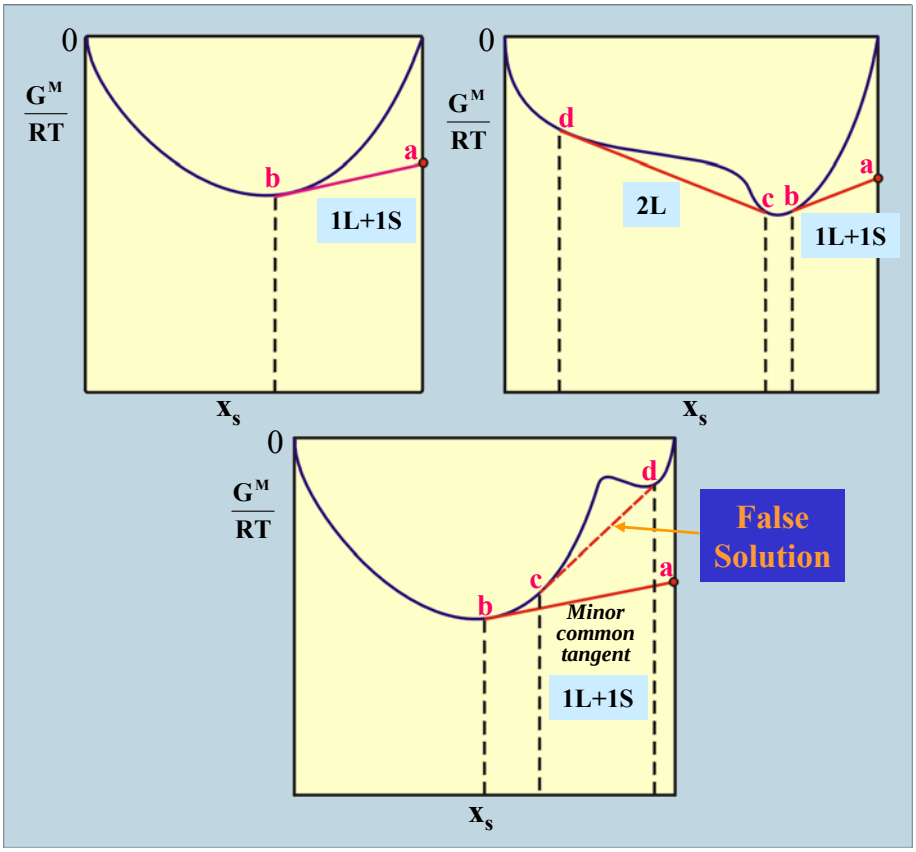
Acetone (1) + water (2) at 2570 mmHg (DECHEMA, Vol. I-1a Sup. 1, p. 197)



ARE THE DATA INCONSISTENT OR IS THE MODEL UNCAPABLE OF REPRESENTING THE EXPERMIENTAL BEHAVIOUR?

e.g. Other binary equilibriums:

-LS
-LL and LS
-LS (with a false LL solution)



E.g. Azeotropic binary system (non-ideal liquid and ideal vapour):

$$\frac{G^{M,Liq}}{RT} = \frac{G^{Liq,ideal}}{RT} + \frac{G^{Liq,excess}}{RT}$$

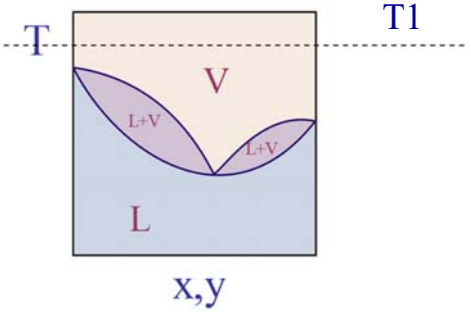
$$\frac{G^{Liq,ideal}}{RT} = \sum_{i=1}^{c} x_i \cdot \ln(x_i)$$

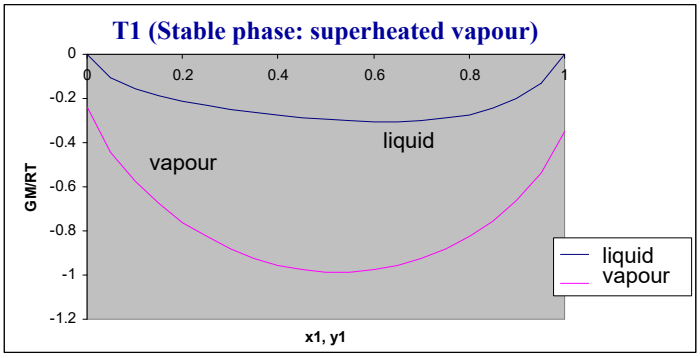
$$\frac{G^{Liq,excess\ (vanLaar)}}{RT} = \frac{A_{12} \cdot A_{21} \cdot x_1 \cdot x_2}{A_{12} \cdot x_1 + A_{21} \cdot x_2}$$

$$G^{M,V\ ideal} = \sum y_i \cdot G_i^{V,o\ (puro)} + RT \cdot \sum y_i \cdot \ln(y_i)$$

$$G_i^{V\ puro} = Ln\frac{P}{P_i^0}$$

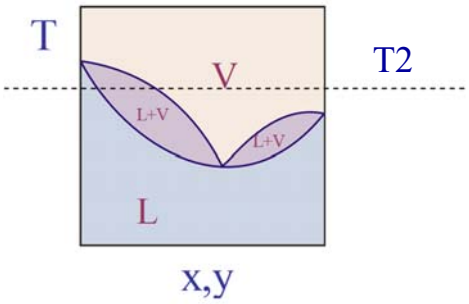
$$G^{V,M\,ideal} = y_1 G_1^{V\,puro} + y_2 G_2^{V\,puro} + RT(y_1 \ln y1 + y_2 \ln y_2)$$

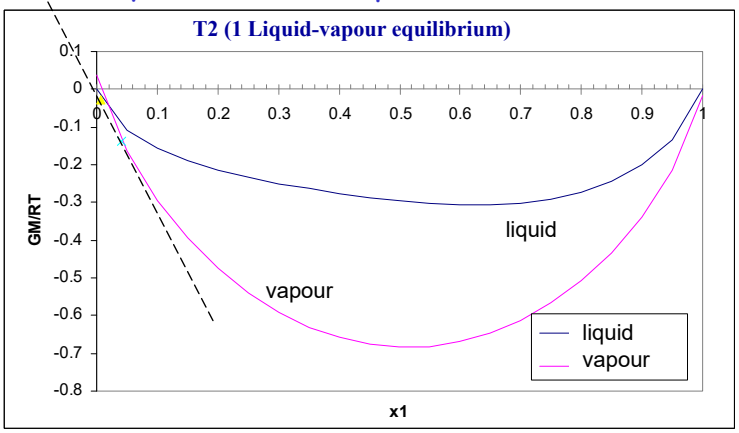


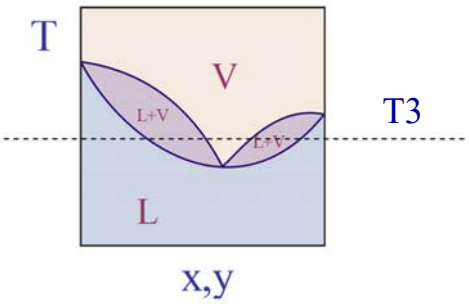


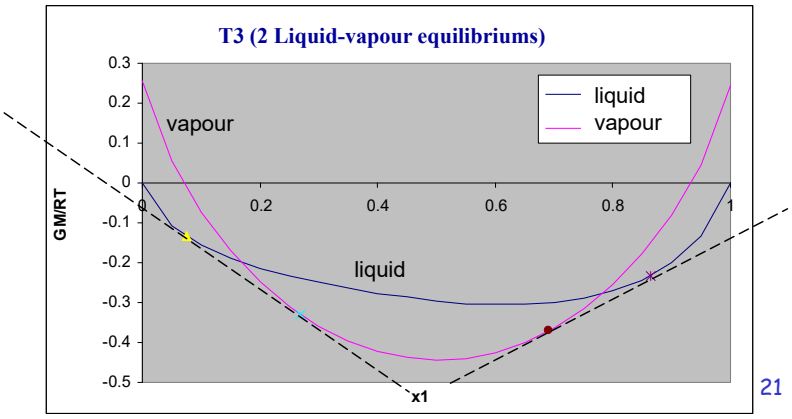
Olaya, M.M.; Reyes-Labarta, J.A.; Serrano, M.D.; Marcilla, A. Vapor-Liquid Equilibria using the Gibbs Energy and the Common Tangent Plane Criterion. Chemical Engineering Education. 2010, 44(3), 236-244. Institutional Repository RUA: : http://hdl.handle.net/10045/24677

E.g. Azeotropic binary system (non-ideal liquid and ideal vapour):

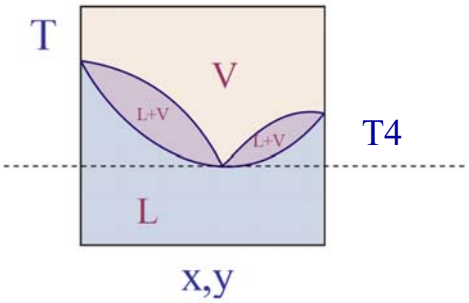


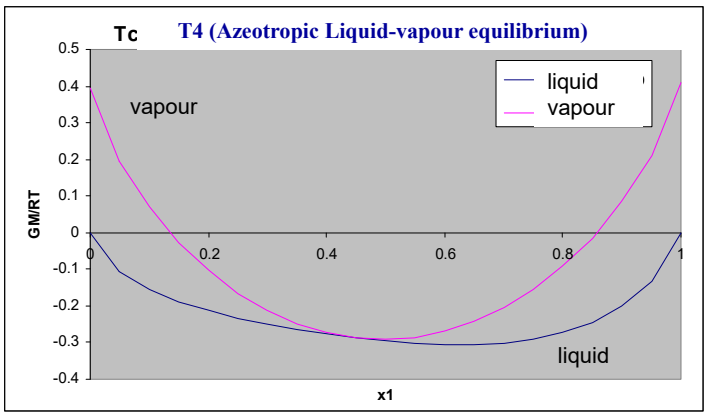


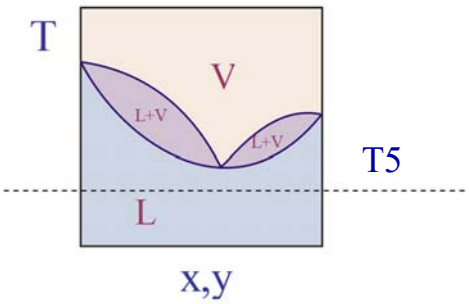


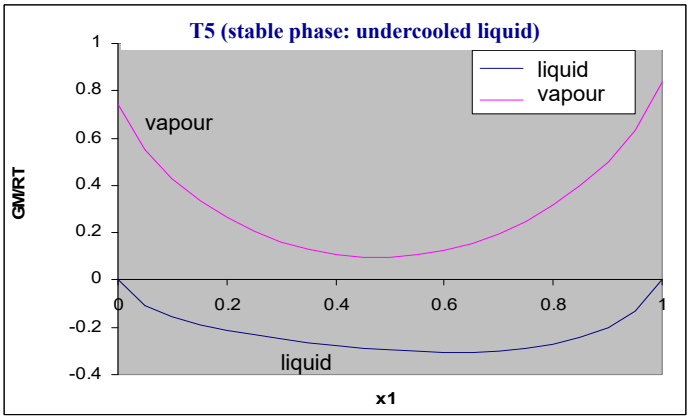


P.ej. Sistema líquido(no ideal)-vapor(ideal) binario:







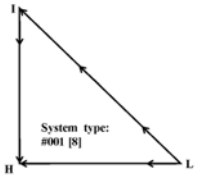


P.ej. Gibbs energy of mixing function in ternary azeotropic systems

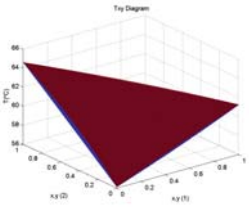
$$\Psi_{12}=\left[\left(\frac{\partial G^{E,L}(x_{1,2,3})}{\partial x_1}-\frac{\partial G^{E,L}(x_{1,2,3})}{\partial x_2}\right)-\left(\frac{\partial G^{E,V}(y_{1,2,3})}{\partial y_1}-\frac{\partial G^{E,V}(y_{1,2,3})}{\partial y_2}\right)\right]\cdot x_1\cdot x_2$$

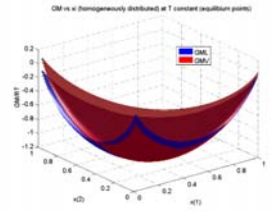
$$\Psi_{23}=\left[\left(\frac{\partial G^{E,L}(x_{1,2,3})}{\partial x_2}-\frac{\partial G^{E,L}(x_{1,2,3})}{\partial x_3}\right)-\left(\frac{\partial G^{E,V}(y_{1,2,3})}{\partial y_2}-\frac{\partial G^{E,V}(y_{1,2,3})}{\partial y_3}\right)\right]\cdot x_2\cdot x_3$$

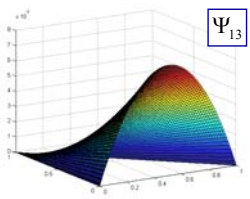
$$\Psi_{13}=\left[\left(\frac{\partial G^{E,L}(x_{1,2,3})}{\partial x_1}-\frac{\partial G^{E,L}(x_{1,2,3})}{\partial x_3}\right)-\left(\frac{\partial G^{E,V}(y_{1,2,3})}{\partial y_1}-\frac{\partial G^{E,V}(y_{1,2,3})}{\partial y_3}\right)\right]\cdot x_1\cdot x_3$$

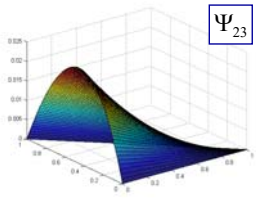


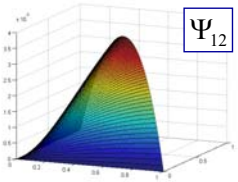
Ideal ternary system (no azeotropes, type #001 (type #105, Perry's Chemical Engineers' Handbook)

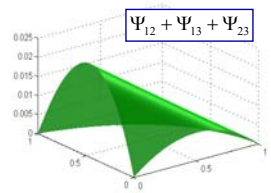


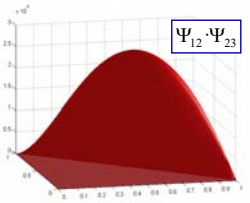












Marcilla, A.; Reyes-Labarta J.A; Olaya, M.M. Gibbs energy of mixing function: topological analysis in azeotropic systems. 27th European Symposium on Applied Thermodynamics ESAT 2014. http://hdl.handle.net/10045/42249.

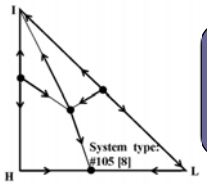
Topological Analysis of Liquid-Vapor Equilibrium Correlations

P.ej. Gibbs energy of mixing function in ternary azeotropic systems

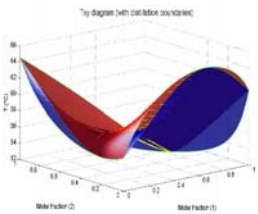
$$\Psi_{12}=\left[\left(\frac{\partial G^{E,L}(x_{1,2,3})}{\partial x_1}-\frac{\partial G^{E,L}(x_{1,2,3})}{\partial x_2}\right)-\left(\frac{\partial G^{E,V}(y_{1,2,3})}{\partial y_1}-\frac{\partial G^{E,V}(y_{1,2,3})}{\partial y_2}\right)\right]\cdot x_1\cdot x_2$$

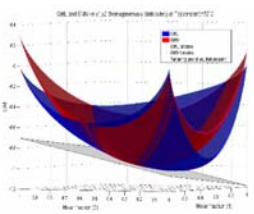
$$\Psi_{23}=\left[\left(\frac{\partial G^{E,L}(x_{1,2,3})}{\partial x_2}-\frac{\partial G^{E,L}(x_{1,2,3})}{\partial x_3}\right)-\left(\frac{\partial G^{E,V}(y_{1,2,3})}{\partial y_2}-\frac{\partial G^{E,V}(y_{1,2,3})}{\partial y_3}\right)\right]\cdot x_2\cdot x_3$$

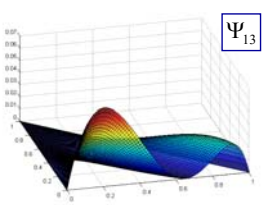
$$\Psi_{13}=\left[\left(\frac{\partial G^{E,L}(x_{1,2,3})}{\partial x_1}-\frac{\partial G^{E,L}(x_{1,2,3})}{\partial x_3}\right)-\left(\frac{\partial G^{E,V}(y_{1,2,3})}{\partial y_1}-\frac{\partial G^{E,V}(y_{1,2,3})}{\partial y_3}\right)\right]\cdot x_1\cdot x_3$$

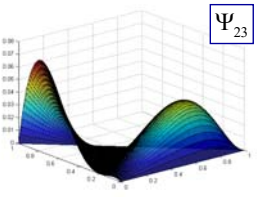


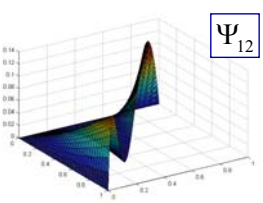
Example: Ternary system with 3 binary azeotropies (2 of minimum temperature and one of maximum temperature), 1 ternary azeotropy (saddle) and 4 distillation boundaries (type #105, Perry's Chemical Engineers' Handbook)

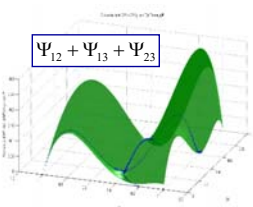


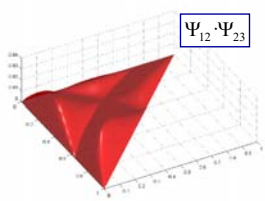








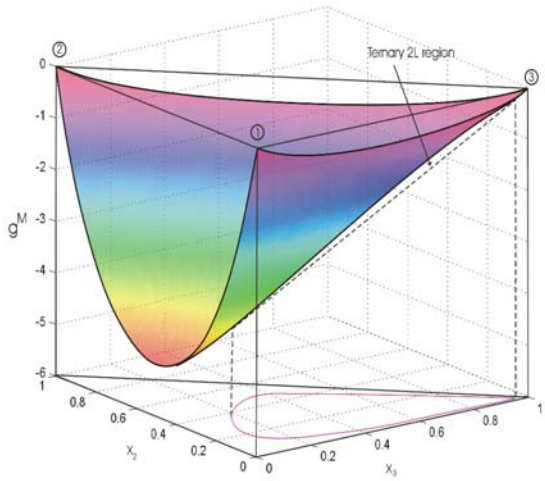




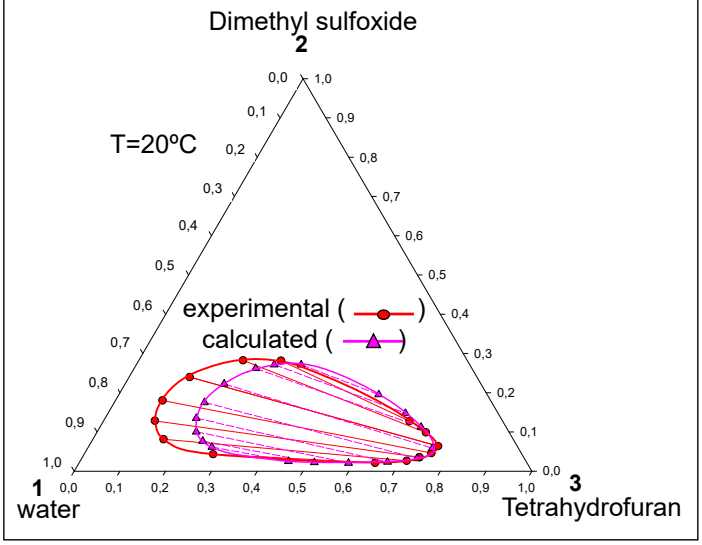
Ternary examples:

♦ Island type (type 0)

NRTL can give a Gibbs energy surface compatible with an island type ternary system (NRTL)



Example of an island correlation

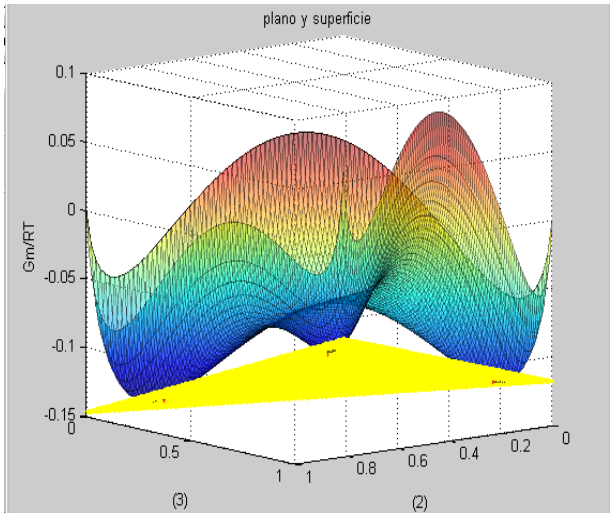


Olaya, M.M.; Reyes-Labarta, J.A.; Velasco, R.; Ibarra, I.; Marcilla A. Modelling Liquid-Liquid Equilibria for Island Type Ternary Systems. Fluid Phase Equilibria 2008, 265, 184-191 (doi: 10.1016/j.fluid.2007.12.010). Institutional Repository RUA: http://hdl.handle.net/10045/24681

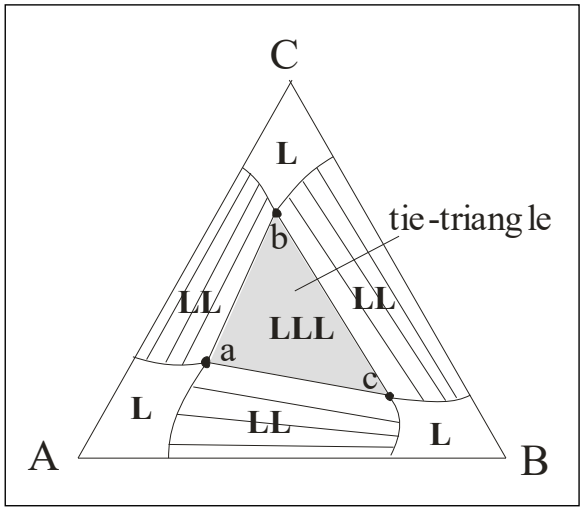
Ternary examples:

♦ Type 3 including LLLE region (tie-triangle)

Gibbs energy surface for a type 3 ternary system with LLLE (NRTL)

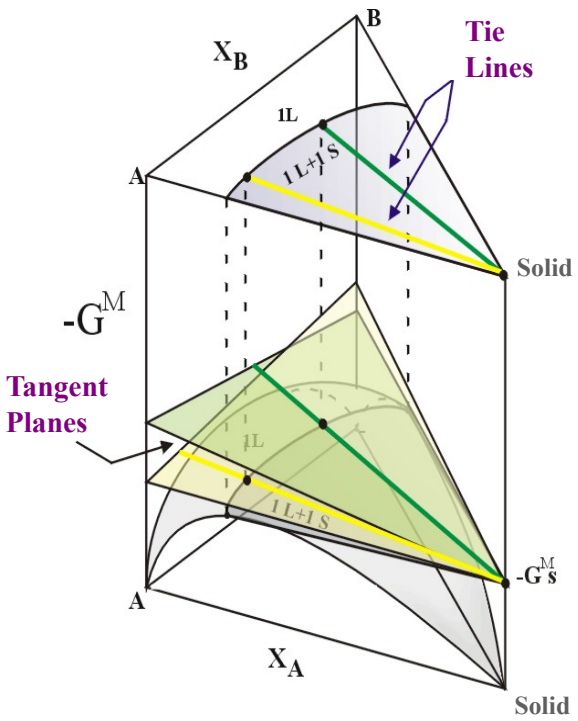


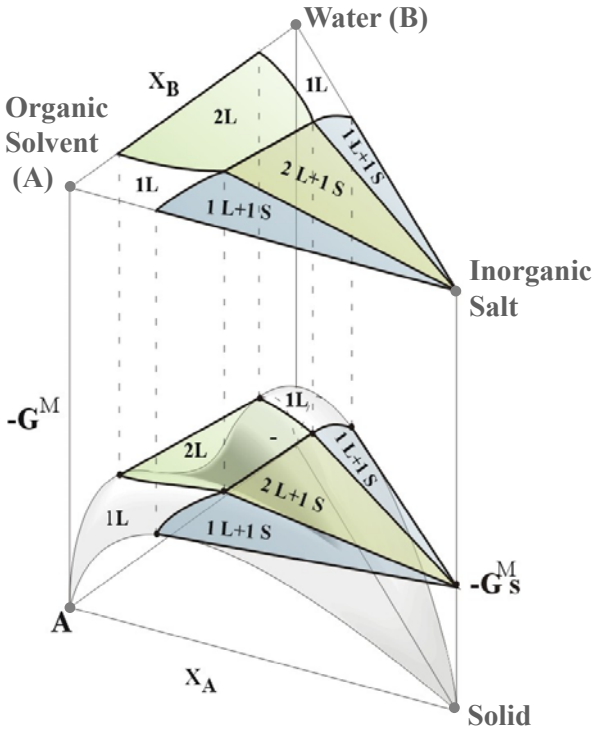
Phase diagram for a type 3 ternary system with LLLE



Marcilla, A; Olaya, M.; Serrano M.D.; Velasco, R.; Reyes-Labarta, J.A. Gibbs Energy Based Procedure for the Correlation of Type 3 Ternary Systems Including a Three-Liquid Phase Region. Fluid Phase Equilibria 2009, 281(1), 87-95 (doi: 10.1016/j.fluid.2009.04.005). Institutional Repository RUA: http://hdl.handle.net/10045/13315

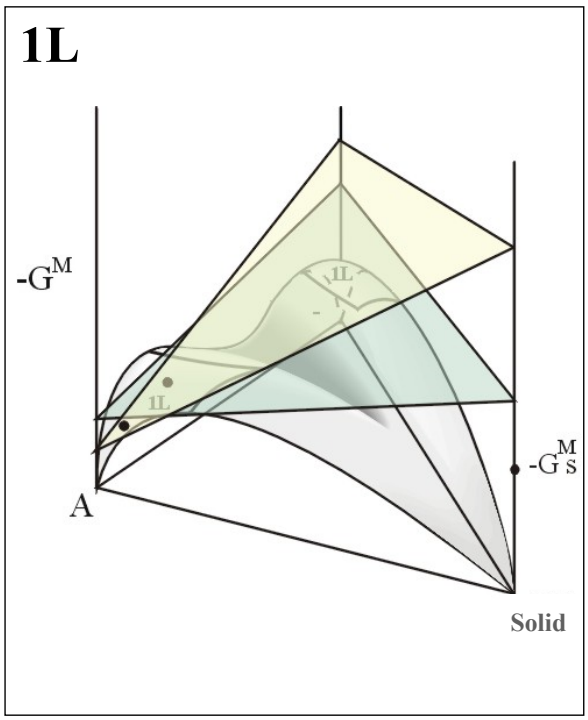
Ternary examples: ♦ Water + organic solvent + inorganic salt (LL, LS,LLS,..)

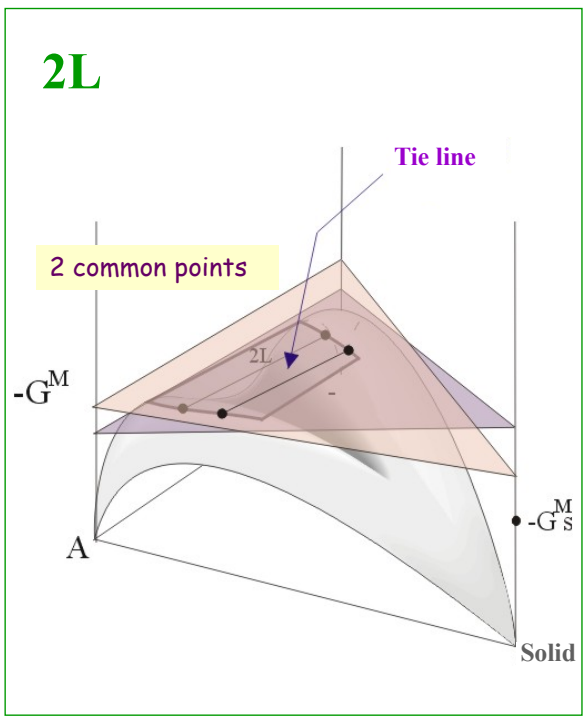




Olaya, M.M.; Marcilla, A.; Serrano,M.D.; Botella A.; Reyes-Labarta, J.A. Simultaneous Correlation of LL, LS and LLS Equilibrium Data for Water + Organic Solvent + Salt Ternary Systems. Anhydrous Solid Phase. Industrial & Engineering Chemistry Research 2007, 46, 7030-7037 (DOI: 10.1021/ie0705610).

Ternary examples: ♦ Water + organic solvent + inorganic salt (LL, LS,LLS,..)

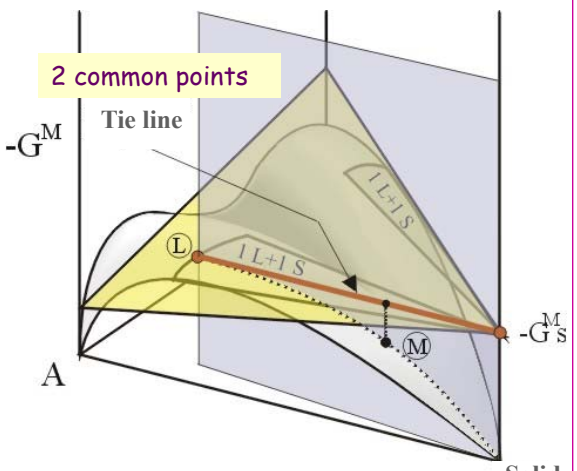




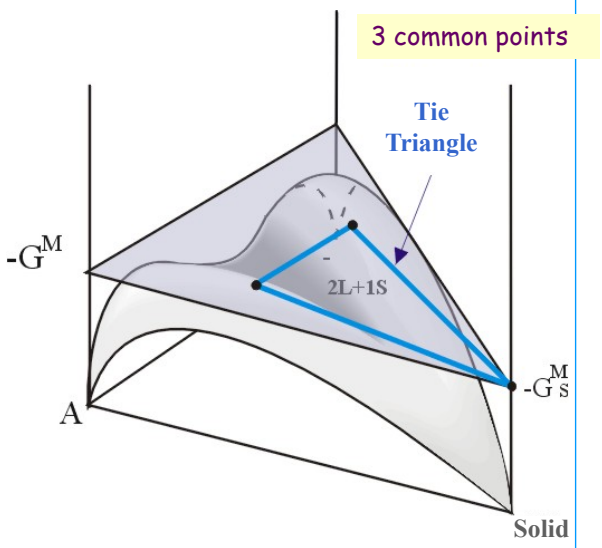
Reyes, J.A.; Conesa, J.A.; Marcilla, A.; Olaya, M.M. Solid-Liquid Equilibrium Thermodinamics: checking stability in multiphase systems using Gibbs Energy Function. Industrial & Engineering Chemistry Research. 2001; 40: 902-907 (http://dx.doi.org/10.1021/ie000435v)

Ternary examples: ♦ Water + organic solvent + inorganic salt (LL, LS,LLS,..)

1L+1S

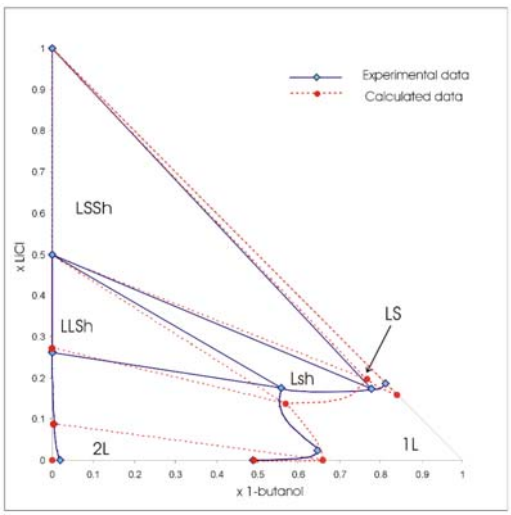


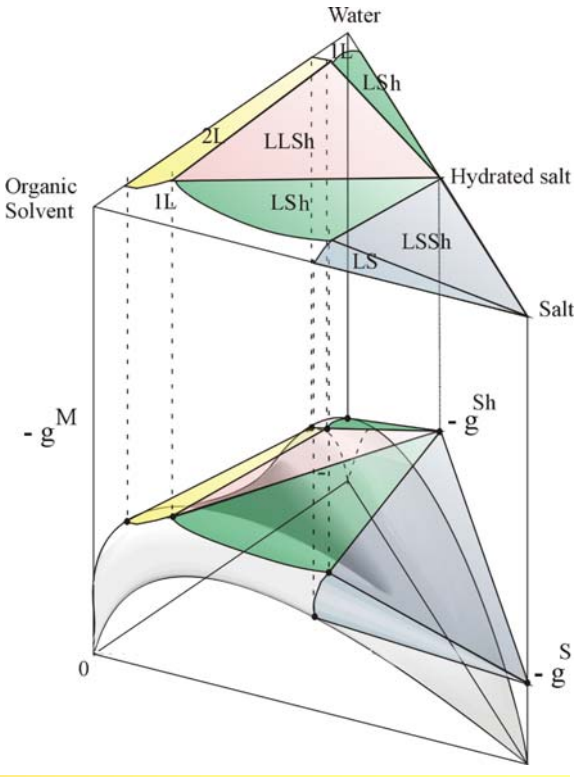
2L+1S



Ternary examples:

♦ Water + organic solvent + inorganic salt with hydatres (LL, LS, LSh, LLSh, LSSh, ..)





Marcilla, A.; Reyes-Labarta, J.A.; Olaya, M.M.; Serrano M.D. Simultaneous Correlation of LL, LS and LLS Equilibrium Data for Water + Organic Solvent + Salt Ternary Systems. Hydrated Solid Phase Formation. Industrial & Engineering Chemistry Research 2008, 47, 2100-2108 (DOI: 10.1021/ie071290w).

$$\mu_i^I = \mu_i^{II} = ... = \mu_i^F$$
$$f_i^I = f_i^{II} = ... = f_i^F$$
$$a_i^I = a_i^{II} = ... = a_i^F$$

Necessary criteria, **but not sufficient in complex systems**

For liquid phases considering the same reference state

NECESSARY and SUFFICENT criterion for phase stability at constant P and T

Minot Tangent Plane Test (to the Mixtures Gibbs function

NRTL model: "no random two liquid" (Renon y Prausnitz)

$$\overline{G}^E = RT\sum_i x_i \frac{\sum_j \tau_{ji} G_{ji} x_j}{\sum_k G_{ki} x_k}$$

$$\ln \gamma_i = \frac{\sum_j \tau_{ji} G_{ji} x_j}{\sum_k G_{ki} x_k} + \sum_j \frac{G_{ij} x_j}{\sum_k G_{kj} x_k}\left(\tau_{ij} - \frac{\sum_r \tau_{rj} G_{rj} x_r}{\sum_k G_{kj} x_k}\right)$$

$$G_{ji} = \exp\left(-\alpha_{ji}\tau_{ji}\right)$$

$$\tau_{ji} = \frac{g_{ji} - g_{ii}}{RT} = \frac{A_{ji}}{T}$$

$$\alpha_{ij} = \alpha_{ji}$$

$$g_{i,j} = g_{j,i}$$

$$A_{ij} \neq A_{ji}$$

$$g_{i,i} \neq g_{j,j}$$

2 parameters for binary subsystem:

- Binary: 2 parameters
- Ternary: 6 parameters
- Cuaternary: 12 parameters

For a binary system:

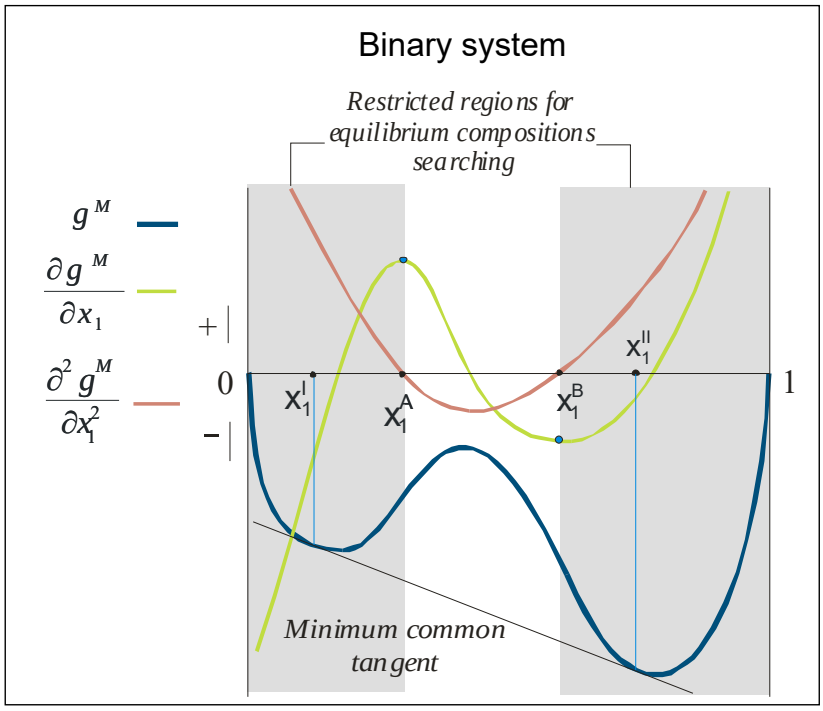
$$\ln \gamma_1 = \frac{1}{RT}\left\{x_2^2\left[\tau_{21}\frac{G_{21}^2}{(x_1 + x_2 G_{21})^2} + \tau_{12}\frac{G_{12}}{(x_2 + x_1 G_{12})^2}\right]\right\}$$

$$\ln \gamma_2 = \frac{1}{RT}\left\{x_1^2\left[\tau_{12}\frac{G_{12}^2}{(x_2 + x_1 G_{12})^2} + \tau_{21}\frac{G_{21}}{(x_1 + x_2 G_{21})^2}\right]\right\}$$

New Strategies to avoid convergence problems

♦ **Limited composition space for the LLE root determination**

a) Using the second derivative of the G^M



Advantages:

✓ Less time consuming

✓ Trivial solution is avoided

Marcilla, A; Olaya, M.; Serrano M.D.; Reyes-Labarta, J.A. Methods for Improving Models for Condensed Phase Equilibrium Calculations. Fluid Phase Equilibria 2010, 296(1), 15-24.

(http://dx.doi.org/10.1016/j.fluid.2009.12.026).

Institutional Repository RUA: http://hdl.handle.net/10045/13314

New Strategies to avoid convergence problems

♦ **Limited composition space for the LLE root determination**

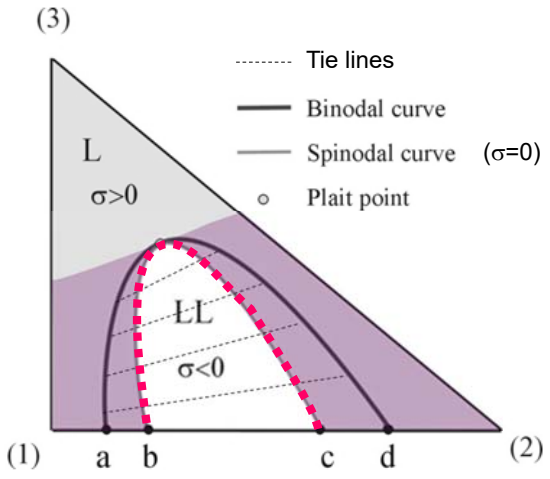
a) Using the second derivative of the G^M

➢ **Ternary LLE**

$$H(g^M)=\begin{bmatrix}\frac{\partial^2 g^M}{\partial x_1^2} & \frac{\partial^2 g^M}{\partial x_1 \partial x_2}\\ \frac{\partial^2 g^M}{\partial x_2 \partial x_1} & \frac{\partial^2 g^M}{\partial x_2^2}\end{bmatrix}$$

Determinant of the Hessian matrix of the g^M function

$$\sigma=\begin{vmatrix}\frac{\partial^2 g^M}{\partial x_1^2} & \frac{\partial^2 g^M}{\partial x_1 \partial x_2}\\ \frac{\partial^2 g^M}{\partial x_2 \partial x_1} & \frac{\partial^2 g^M}{\partial x_2^2}\end{vmatrix}$$



Marcilla, A; Olaya, M.; Serrano M.D.; Reyes-Labarta, J.A. Methods for Improving Models for Condensed Phase Equilibrium Calculations. Fluid Phase Equilibria 2010, 296(1), 15-24

New Strategies to avoid convergence problems

♦ **Extended ternary plait point condition to avoid false solutions:**

a) Using the second derivative of the G^M

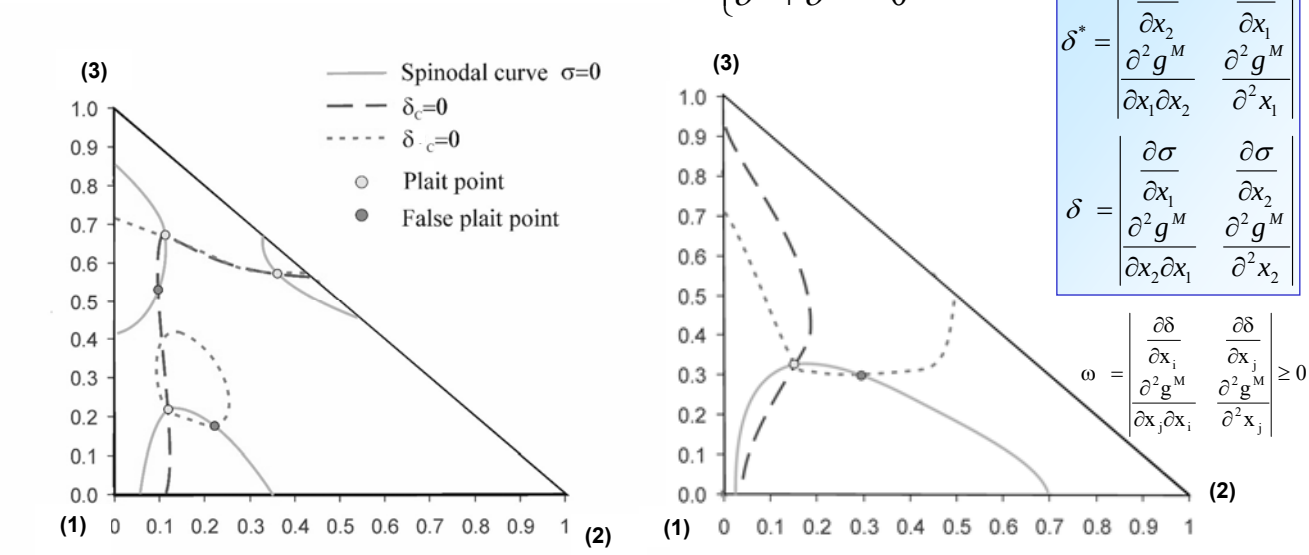
$$\begin{cases} \sigma = 0 \\ \delta^2 + \delta^{*2} = 0 \end{cases}$$

$$\sigma = \begin{vmatrix} \frac{\partial^2 g^M}{\partial x_1^2} & \frac{\partial^2 g^M}{\partial x_1 \partial x_2} \\ \frac{\partial^2 g^M}{\partial x_2 \partial x_1} & \frac{\partial^2 g^M}{\partial x_2^2} \end{vmatrix}$$

$$\delta^* = \begin{vmatrix} \frac{\partial \sigma}{\partial x_2} & \frac{\partial \sigma}{\partial x_1} \\ \frac{\partial^2 g^M}{\partial x_1 \partial x_2} & \frac{\partial^2 g^M}{\partial^2 x_1} \end{vmatrix}$$

$$\delta = \begin{vmatrix} \frac{\partial \sigma}{\partial x_1} & \frac{\partial \sigma}{\partial x_2} \\ \frac{\partial^2 g^M}{\partial x_2 \partial x_1} & \frac{\partial^2 g^M}{\partial^2 x_2} \end{vmatrix}$$

$$\omega = \begin{vmatrix} \frac{\partial \delta}{\partial x_i} & \frac{\partial \delta}{\partial x_j} \\ \frac{\partial^2 g^M}{\partial x_j \partial x_i} & \frac{\partial^2 g^M}{\partial^2 x_j} \end{vmatrix} \geq 0$$

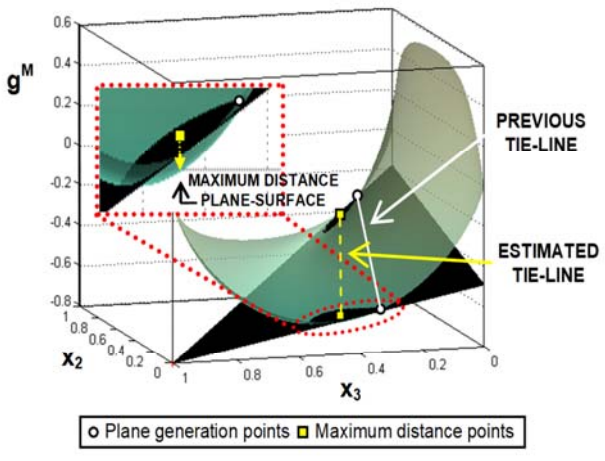


Marcilla, A.; Serrano, M.D.; Reyes-Labarta. J.A.; Olaya, M.M. Checking Liquid-Liquid Critical Point Conditions and their Application in Ternary Systems. Industrial & Engineering Chemistry Research 2012, 51(13), 5098-5102. http://dx.doi.org/10.1021/ie202793r

New Strategies to avoid convergence problems

b) Using a geometrical method to determine appropriate initial values of variables in LLE calculation processes → Sequential series of minor cutting planes: very good approximation to the ELL solution.

➢ **LLE data type 1**



1. Starting with the binary LLE, two separated zones, where the conjugated compositions must be located, are found by intersection between an adequate plane and the G^M surface.

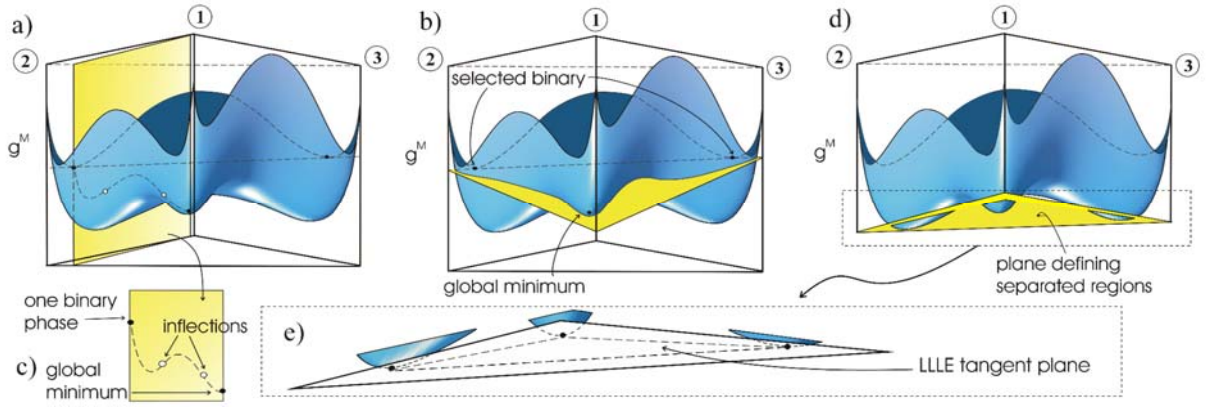
2. The maximum distance point to the intersection plane is located in each one of these zones.

3. The conjugated points obtained are used to generate a new plane and they are also a very good approximation to the tie-line.

Reyes-Labarta, J.A; Olaya, M.; Velasco, R.; Serrano M.D.; Marcilla, A. Correlation of the Liquid-Liquid Equilibrium Data for Specific Ternary Systems with One or Two Partially Miscible Binary Subsystems. Fluid Phase Equilibria 2009, 278, 9-14.

New Strategies to avoid convergence problems

b) <u>Using a geometrical method to determine appropriate initial values of variables in LLLE calculation processes</u> → very good approximation to the ELLL solution.



(sequential series of minor cutting planes)

e.g. 1-nonanol + nitromethane + water (23 ºC)
1-hexanol + nitromethane + water (21 ºC)

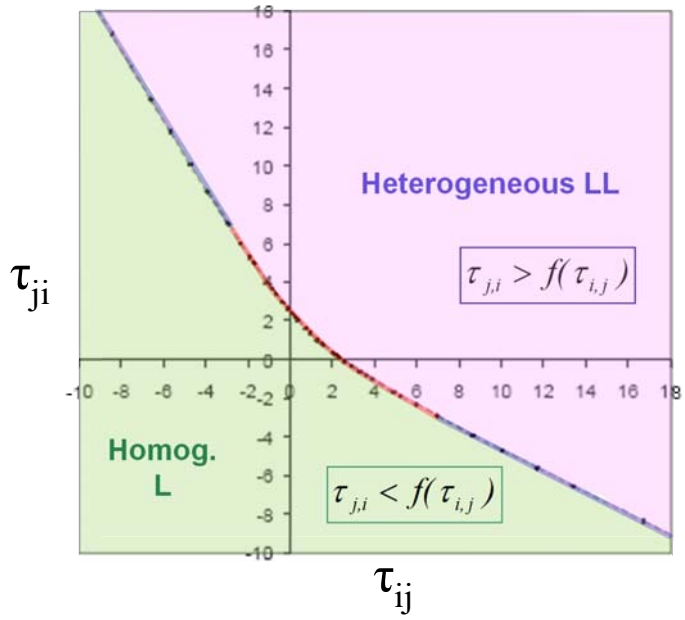
Marcilla, A.; Olaya, M.M.; Serrano, M.D.; Reyes-Labarta J.A. Institutional Repository RUA:. http://hdl.handle.net/10045/17574

Marcilla, A; Olaya, M.; Serrano M.D.; Velasco, R.; Reyes-Labarta, J.A. Gibbs Energy Based Procedure for the Correlation of Type 3 Ternary Systems Including a Three-Liquid Phase Region. Fluid Phase Equilibria 2009, 281(1), 87-95.

New Strategies to avoid convergence problems

♦ **To use relations between the $A_{i,j}$ or $\tau_{i,j}$ parameters to ensure the correct phase behavior for the systems**

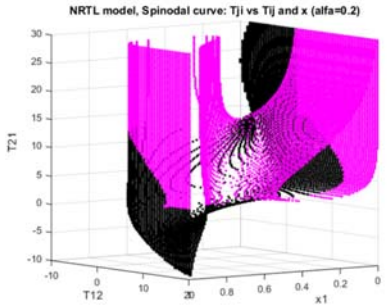
e.g. Border line $\tau_{j,i} = f(\tau_{i,j})$ between L and LL regions for the NRTL model



τ_{ij}<-3 $\quad \tau_{ji} = -1.833 \cdot \tau_{ij} + 1.423$

-3<τ_{ij}<7 $\quad \tau_{ji} = -4.191 \cdot 10^{-3} \cdot \tau_{ij}^3 + 9.089 \cdot 10^{-2} \cdot \tau_{ij}^2 - 1.206 \cdot \tau_{ij} + 2.481$

τ_{ij}>7 $\quad \tau_{ji} = -0.545 \cdot \tau_{ij} + 0.7758$

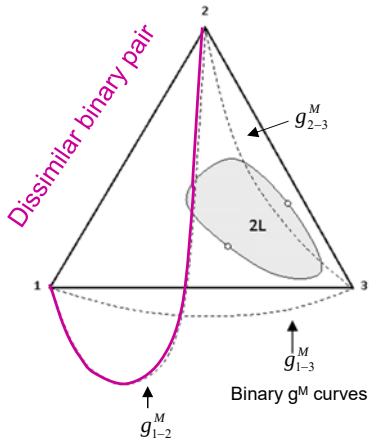


Marcilla, A.; Reyes-Labarta, J.A.; Serrano M.D.; Olaya, M.M. GE Models and Algorithms for Condensed Phase Equilibrium Data Regression in Ternary Systems: Limitations and ProposalsThe Open Thermodynamics Journal, 2011, 5, (Suppl 1-M5) 48-62. http://www.benthamscience.com/open/totherj/articles/V005/SI0016TOTHERJ/48TOTHERJ.pdf
http://hdl.handle.net/10045/19865

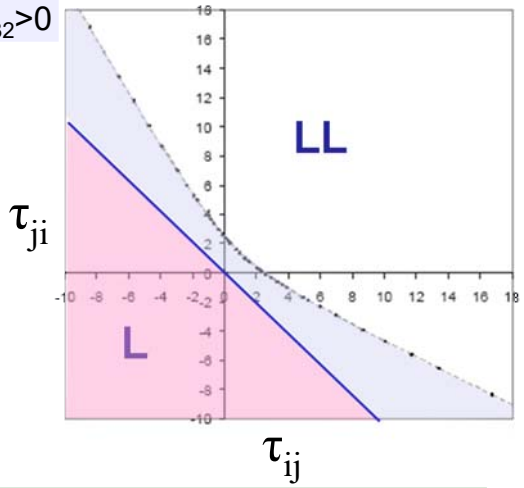
New Strategies to avoid convergence problems

- To use relations between the Ai,j or ti,j parameters to ensure the correct phase behavior for the systems

e.g. Type island ternary systems $A_{i,j}$ or $\tau_{i,j}$ NRTL Constraints



$\tau_{12}+\tau_{21}<0$ (dissimilar binary pair)
$\tau_{13}+\tau_{31}>0$
$\tau_{23}+\tau_{32}>0$



Olaya, M.M.; Reyes-Labarta, J.A.; Velasco, R.; Ibarra, I.; Marcilla A. Modelling Liquid-Liquid Equilibria for Island Type Ternary Systems. Fluid Phase Equilibria 2008, 265, 184-191.

New Strategies to avoid convergence problems

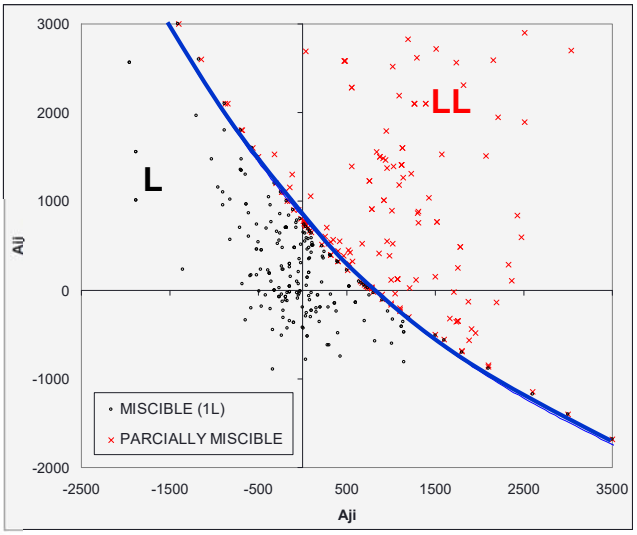
- To limit the A_{ij} values to ensure correct phase behaviour for the binaries

Border line between L and LL regions for the NRTL model (at 25ºC)

$$A_{ij} = f(A_{ji}) = -4.46564\cdot10^{-8}\,A_{ji}^{3} + 2.95745\cdot10^{-4}\,A_{ji}^{2} + 1.20662\,A_{ji} + 766.908$$

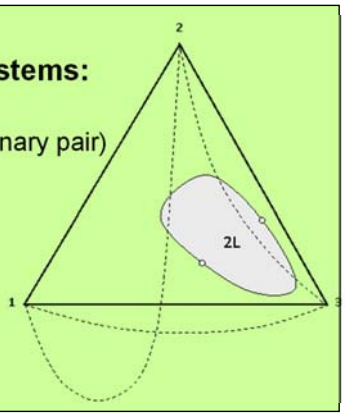
Homogeneous (L) $A_{ij} < f(A_{ji})$

Heterogeneous (LL) $A_{ij} > f(A_{ji})$



Type island ternary systems:

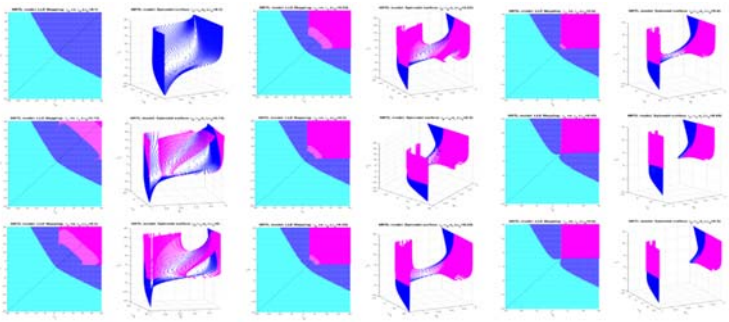
A12+ A21<0 (dissimilar binary pair)
A13+ A31>0
A23+ A32>0

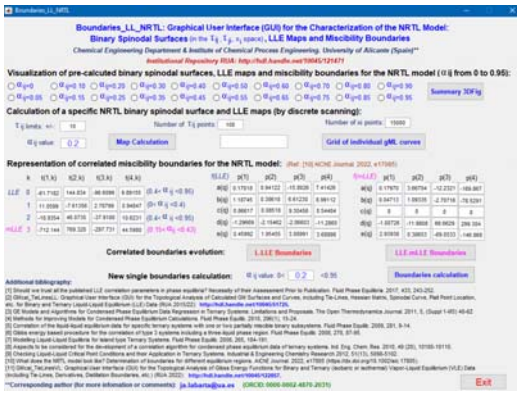


New Strategies to avoid convergence problems

♦ **To limit the τ_{ij} values to ensure correct phase behaviour for the binaries**

Border line between L and LL regions for the NRTL model (for different α_{ij} values)



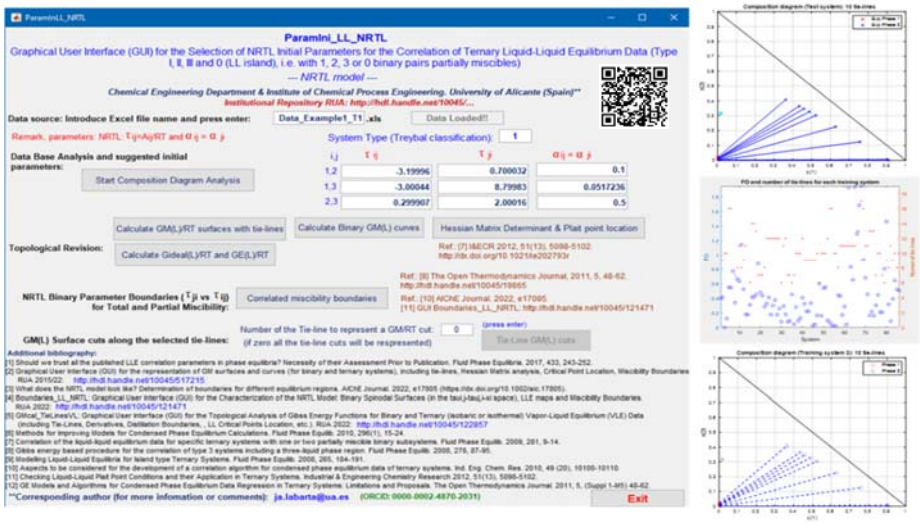


Labarta, J.A.; Olaya, M.M.; Marcilla, A. What does the NRTL model look like? Determination of boundaries for different fluid phase equilibrium regions. AIChE Journal. 2022, e17805. https://dx.doi.org/10.1002/aic.17805.

Labarta, J.A.; Olaya, M.M.; Marcilla, A. Boundaries_LL_NRTL Graphical User Interface (GUI) for the characterization of the NRTL model: Binary Spinodal Surfaces (in the $\tau_{i,j}$-$\tau_{j,i}$-x_i space), LLE maps and Miscibility Boundaries. Institutional Repository of the University of Alicante (RUA) 2022. Available at: http://hdl.handle.net/10045/121471.

♦ **Selection of a initial set of consistent NRTL parameters**

ParamIni_LL_NRTL: Graphical User Interface (GUI) for the Selection of NRTL Initial Parameters for the Correlation of Ternary Liquid-Liquid Equilibrium Data (Type I, II, III and 0 (LL island), i.e. with 1, 2, 3 or 0 binary pairs partially miscible). Institutional Repository of the University of Alicante (RUA), 2023, publicly available at: http://hdl.handle.net/10045/130017.



Labarta, J.A.; Caballero, J.A.; Marcilla, A. Liquid-Liquid Equilibrium Data Correlation: Predicting a robust and consistent set of initial NRTL parameters. Computer Aided Chemical Engineering (ESCAPE 33). 2023, 52, 3457-3462. DOI: https://doi.org/10.1016/B978-0-443-15274-0.50552-7. Inst. Rep. of the Univ. of Alicante (RUA) 2023: http://hdl.handle.net/10045/134753.

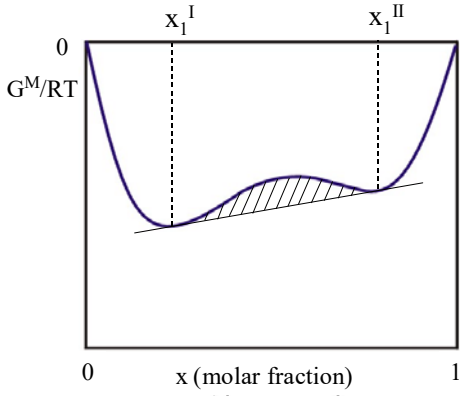
New Strategies to avoid convergence problems

♦ **Isoactivity criteria is substituted by other equilibrium conditions for LLE calculations**

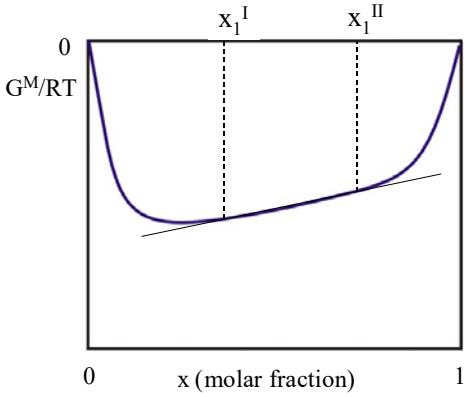
The isoactivity criteria can lead to **false LLE solutions**. We propose **modifications of the objective functions** that improve the convergence efficiency and overcome inconsistencies.

The good or poor definition of the LLE solution depends on the G^M curvature

Good definition



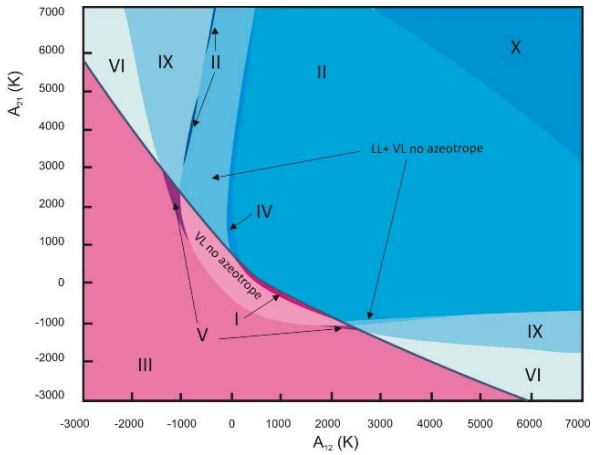
Poor definition

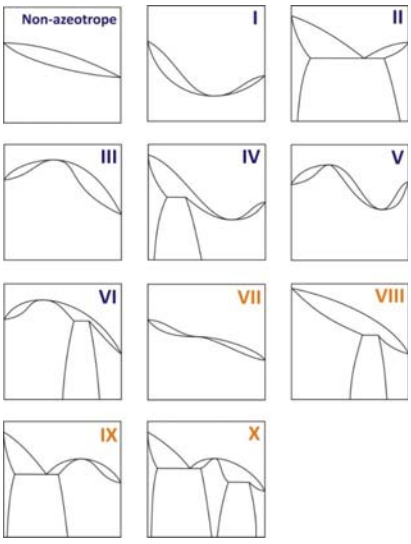


Marcilla, A.; Reyes-Labarta J.A.; Serrano, M.D.; Olaya, M.M. Pitfalls on computing liquid-liquid phase equilibria using the k-value method. Institutional Repository RUA: http://hdl.handle.net/10045/26610

New Strategies to avoid convergence problems

♦ **Mapping Binary Liquid-vapor Or Liquid-liquid-vapor Equilibria Regions, Including The Different Azeotropic Behaviours, as a function of the NRTL Binary Parameters**





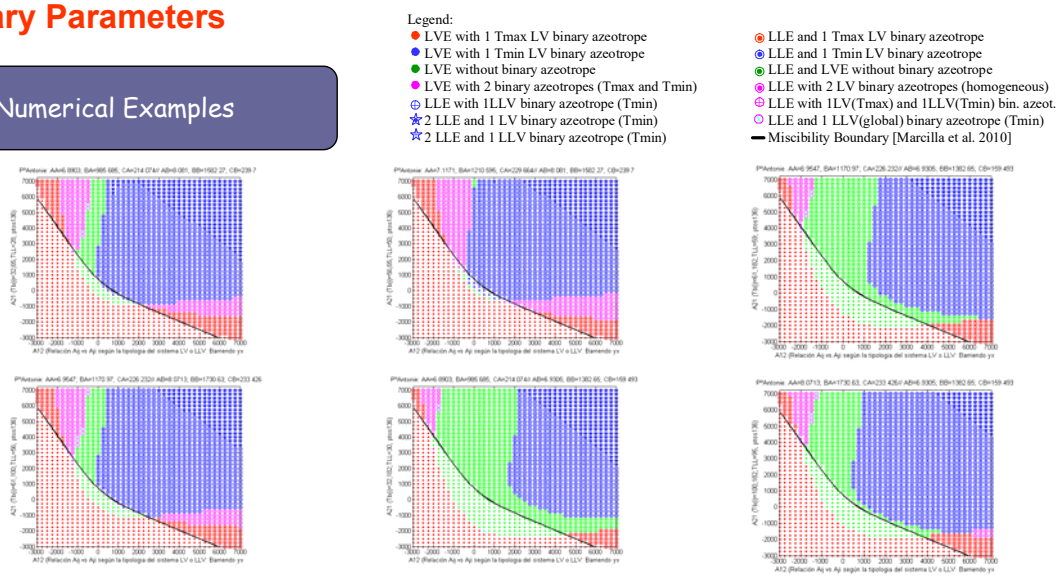
Types I to VI had been previously classified in literature. Types VII to X have been added to this classification in the present work, because all of them (and others) are possible, as a function of the NRTL parameter values.

Reyes-Labarta, J.A.; Olaya, M.M.; Marcilla, A. Mapping Binary Liquid-Vapor or Liquid-Liquid-Vapor Equilibria Regions, including the Different Azeotropic Behaviours, as a Function of the NRTL Binary Parameters. 13th Mediterranean Congress of Chemical Engineering. 2014. Institutional Repository RUA: http://hdl.handle.net/10045/42248

New Strategies to avoid convergence problems

♦ **Mapping Binary Liquid-vapor Or Liquid-liquid-vapor Equilibria Regions, Including The Different Azeotropic Behaviours, As A Function Of The Nrtl Binary Parameters**

Numerical Examples

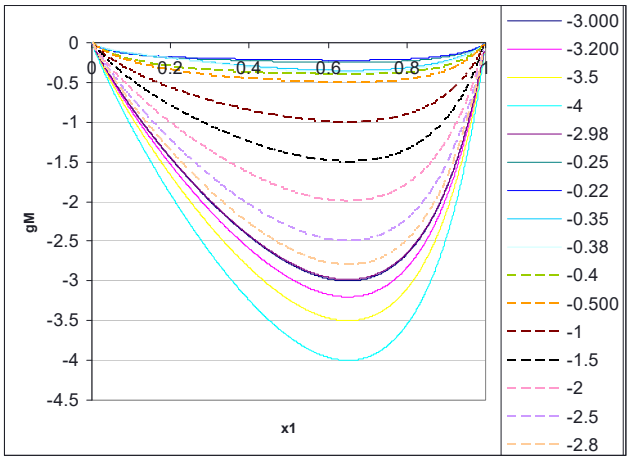


Labarta, J.A.; Olaya, M.M.; Marcilla, A. What does the NRTL model look like? Determination of boundaries for different fluid phase equilibrium regions. AIChE Journal. 2022, e17805. https://dx.doi.org/10.1002/aic.17805.

More proposed solutions

1) To introduce specific modifications in the models. E.g.:

➢ **LLE & LLLE. Incorporation of new contribution factors in the NRTL model:**



New factors
"Effective molecular weights"

$$\frac{G^E}{RT} = \sum_i F_i \cdot x_i \frac{\sum_j \tau_{ji} G_{ji} x_j}{\sum_l G_{li} x_l}$$

The initial GAP is completed!

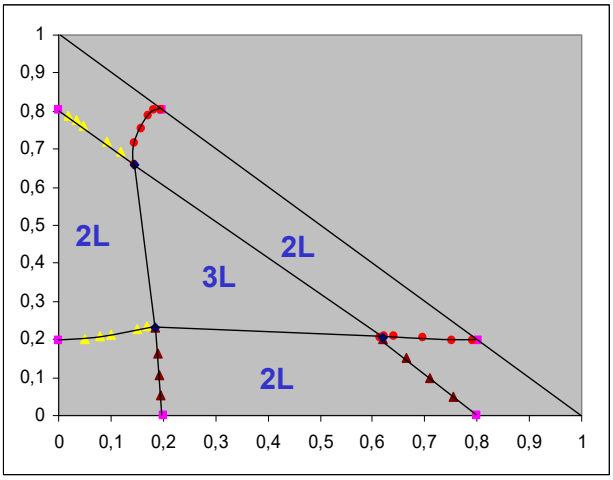
Marcilla, A; Olaya, M.M.; Serrano M.D.; Reyes-Labarta, J.A. Aspects to be considered for the development of a correlation algorithm for condensed phase equilibrium data for ternary systems. Industrial & Engineering Chemistry Research 2010, 49(20), 10100-10110.

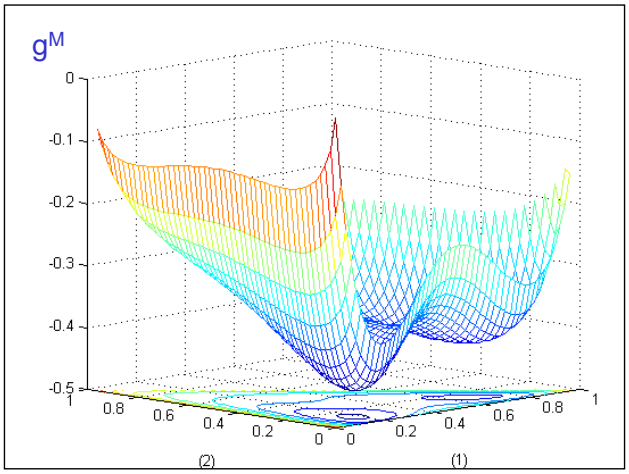
More proposed solutions

2) To introduce specific modifications in the models. E.g.:

- **LLLE. Incorporation of a dependence of the NRTL parameters with the composition:**

$$A_{i,j} = A_{i,j,i} \cdot \frac{x_i}{x_i + x_j} + A_{i,j,j} \cdot \frac{x_j}{x_i + x_j}$$



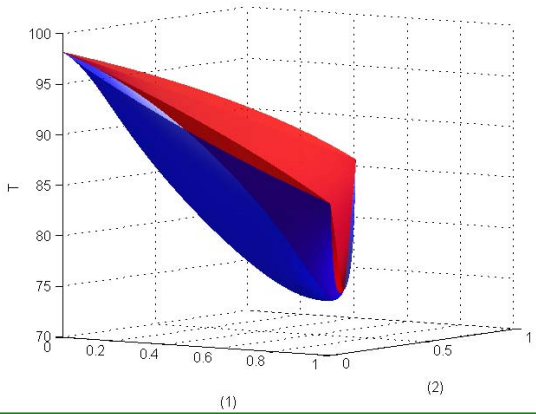


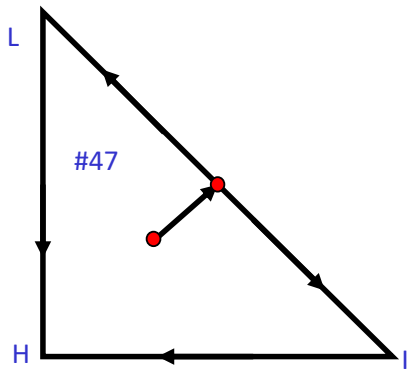
More proposed solutions

3a) To introduce specific modifications in the models. E.g.:

- **LVE. Incorporation of a ternary contribution.** E.g. for predicting ternary systems with one minimum boiling point binary azeotrope and two ideal binaries (#47 type, Perry's Handbook of Chemical Engineering)

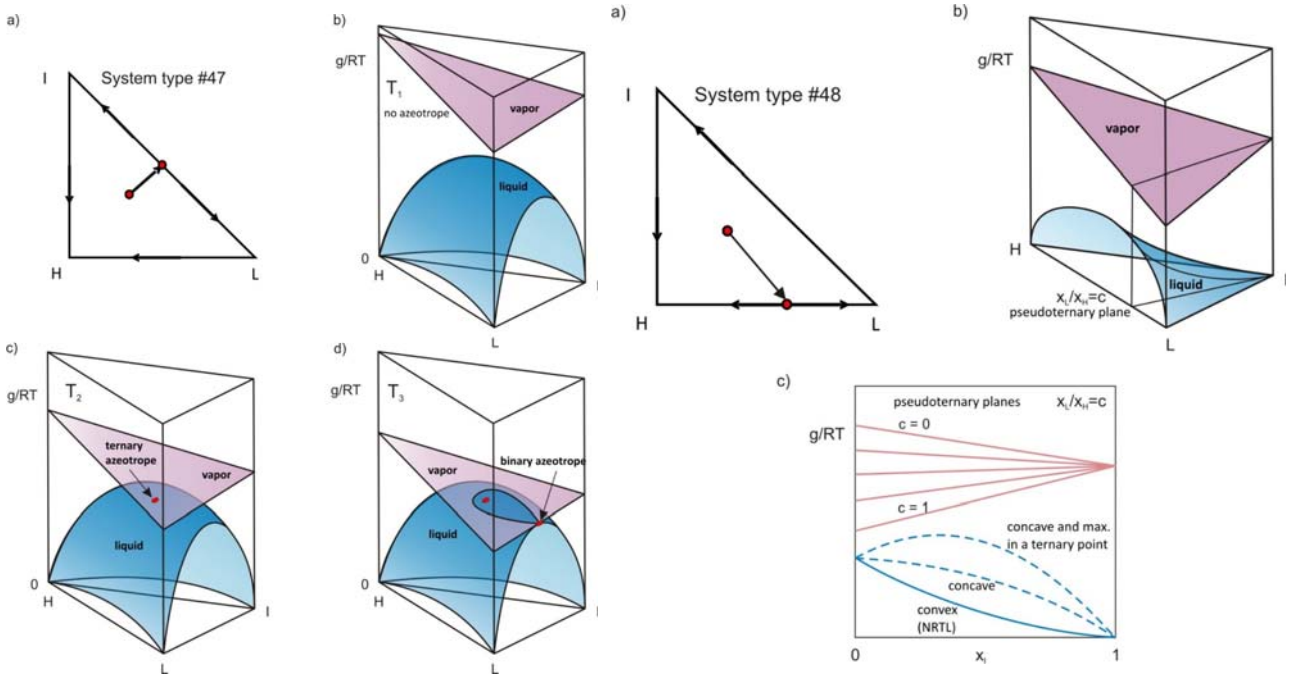
$$\frac{G^E}{RT} = \sum_i x_i \cdot \frac{\sum_j \tau_{ji} G_{ji} x_j}{\sum_l G_{li} x_l} + x_1 \cdot x_2 \cdot x_3 \cdot \frac{t_1 \cdot x_1 + t_2 \cdot x_2 + t_3 \cdot x_3}{1 + t_4 \cdot x_1 \cdot x_2 \cdot x_3}$$





Marcilla, A.; Olaya, M.M.; Reyes-Labarta, J.A. Comments on the Correlation of Vapor-Liquid Equilibrium (VLE) Data in Azeotropic Ternary Systems. Fluid Phase Equilibria 2016, 426, 110-118.

♦ Comments on the Correlation of Vapor-Liquid Equilibrium Data



A. Marcilla, M.M. Olaya and J.A. Reyes-Labarta. Comments on the Correlation of Vapor-Liquid Data. Fluid Phase Equilibria (Elsevier) 2016, 426, 110-118. http://dx.doi.org/10.1016/j.fluid.2016.02.010

More proposed solutions

3b) Simultaneous VLLE data correlation for ternary systems: Modification of the NRTL equation for improved calculations

➢ **LLVE. Incorporation of a ternary contribution (based on the Wohl model):**

$$\frac{G^{M,L}}{RT}=\frac{G^{M,Lideal}}{RT}+\frac{G^{E,L}}{RT}=\frac{G^{M,Lideal}}{RT}+\frac{G^{E,L,NRTL}}{RT}+\frac{G^{E,L,add}}{RT}$$

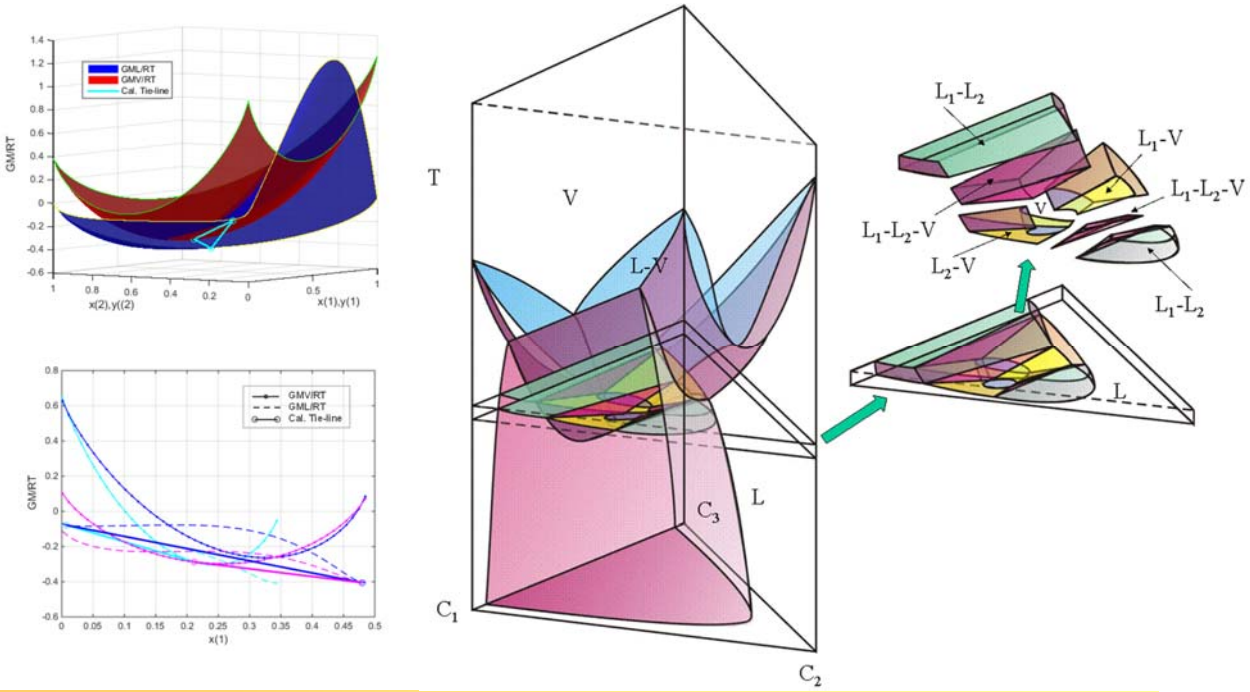
$$\frac{G^{M,Lideal}}{RT}=\sum_{i=1}^{3}x_i\cdot\ln x_i$$

$$\frac{G^{E,L,NRTL}}{RT}=x_1\cdot x_2\cdot\left(\frac{\tau_{21}G_{21}}{x_1+G_{21}x_2+G_{31}x_3}+\frac{\tau_{12}G_{12}}{G_{12}x_1+x_2+G_{32}x_3}\right)+x_1\cdot x_3\cdot\left(\frac{\tau_{31}G_{31}}{x_1+G_{21}x_2+G_{31}x_3}+\frac{\tau_{13}G_{13}}{G_{13}x_1+G_{23}x_3+x_3}\right)+$$
$$+x_2\cdot x_3\cdot\left(\frac{\tau_{32}G_{32}}{G_{12}x_1+x_2+G_{32}x_3}+\frac{\tau_{23}G_{23}}{G_{13}x_1+G_{23}x_2+x_3}\right)$$

$$\frac{G^{E,L,add}}{RT}=x_1\cdot x_2\cdot x_3\cdot\frac{t_1\cdot x_1+t_2\cdot x_2+t_3\cdot x_3}{1+t_4\cdot x_1\cdot x_2\cdot x_3}+x_1\cdot x_2\cdot\frac{a_1\cdot x_1+a_2\cdot x_2}{1+a_3\cdot x_1\cdot x_2}+x_1\cdot x_3\cdot\frac{b_1\cdot x_1+b_2\cdot x_3}{1+b_3\cdot x_1\cdot x_3}+$$
$$+x_2\cdot x_3\cdot\frac{c_1\cdot x_2+c_2\cdot x_3}{1+c_3\cdot x_2\cdot x_3}$$

Marcilla, A.; Olaya, M.M.; Reyes-Labarta, J.A. Simultaneous VLLE data correlation for ternary systems: Modification of the NRTL equation for improved calculations. Fluid Phase Equilibria (Elsevier) 2016, 426, 47-55.. DOI: 10.1016/j.fluid.2015.12.047

♦ Simultaneous VLLE data correlation for ternary systems: Modification of the NRTL equation for improved calculations



Marcilla, A.; Olaya, M.M.; Reyes-Labarta, J.A. Simultaneous VLLE data correlation for ternary systems: Modification of the NRTL equation for improved calculations. Fluid Phase Equilibria (Elsevier) 2016, 426, 47-55. DOI: 10.1016/j.fluid.2015.12.047

New Strategies to avoid convergence problems

All these ideas have been used to improve the algorithm to correlate LLE data for ternary systems (type I and II)

Reyes-Labarta, J.A; Olaya, M.; Velasco, R.; Serrano M.D.; Marcilla, A. Correlation of the Liquid-Liquid Equilibrium Data for Specific Ternary Systems with One or Two Partially Miscible Binary Subsystems. Fluid Phase Equilibria 2009, 278, 9-14 (doi: 10.1016/j.fluid.2008.12.002). Institutional Repository RUA: http://hdl.handle.net/10045/24683.

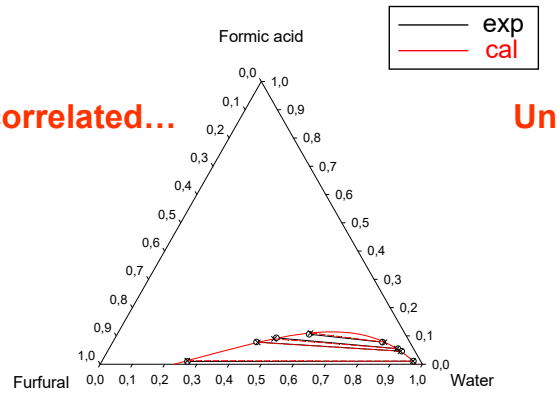
	System	Data	T (ºC)
I	Furfural (1) + formic acid (2) + water (3)[15]	4	35
II	Water (1) + acetic acid (2) + dichloromethane (3)[16]	4	19
III	Toluene (1) + acetaldehyde (2) + water (3)[17]	6	17
IV	Propyl acetate (1) + formic acid (2) + water (3)[18]	4	35
V	1-Butanol (1) + methanol (2) + water (3)[19]	4	60
VI	4-Methyl-2-pentanone (1) + acetonitrile (2) + water (3)[20]	7	30
VII	Propenoic acid (1) + propanoic acid (2) + water (3)[21]	4	70
VIII	Hexane (1) + 2,5-dimethyl-THF (2) + 1,2-ethanodiol (3)[22]	3	120
IX	Trichloroethene (1) + furfural (2) + water (3)[23]	6	20
X	Acetonitrile (1) + 1-propanol (2) + hexane (3)[24]	6	25
XI	1-hexanol (1) + nitromethane (2) + water (3)[25]	10	40

9 systems not correlated previously

2 systems with inconsistent parameters

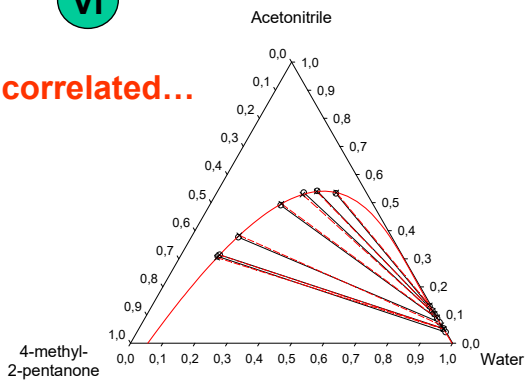
Topological Analysis of Liquid-liquid Equilibrium Correlations

I



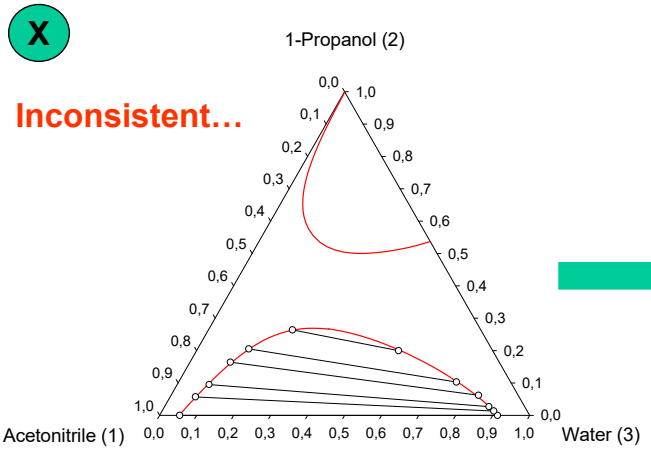
Uncorrelated…

VI

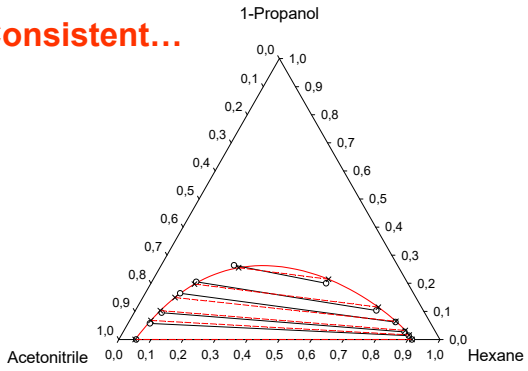


Uncorrelated…

X



Inconsistent…



Consistent…

Topological Analysis of simultaneous LLE-LLLE Correlations

New Strategies to avoid convergence problems

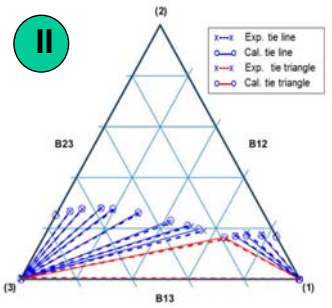
All these ideas have been used to improve the algorithm for the simultaneous correlation of LLE and LLLE data ternary systems (including ionic liquids)

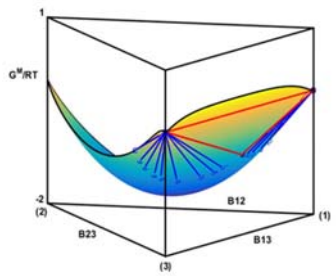
Rodríguez-Escontrela, I.; Arce, A.; Soto, A.; Marcilla, A; Olaya, M.M.; Reyes-Labarta, J.A. Correlation of Three-Liquid-Phase Equilibria involving Ionic Liquids. Physical Chemistry Chemical Physics (Royal Society of Chemistry). 2016, 18, 21610-21617 (http://dx.doi.org/10.1039/C6CP03467E).

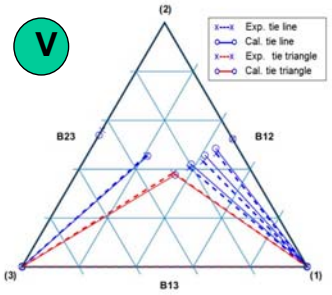
	System	Data	T (ºC)
I	Water (1) + [P6 6 6 14][DCA] (2) + hexane (3)	10	25
		11	50
II	Water (1) + [P6 6 6 14]Cl (2) + dodecane (3)	16	25
		12	75
III	Water (1) + [P6 6 6 14][NTf_2] (2) + dodecane (3)	11	25
		14	75
IV	Water (1) + [P6 6 6 14][$(iOc)_2PO_2$] (2) + dodecane (3)	8	25
V	Water (1) + [P6 6 6 14][DCA] (2) + dodecane (3)	9	25
		10	75
VI	Water (1) + [C_{10}mim][NTf_2] (2) + dodecane (3)	7	25
		9	75
VII	Water (1) + [C_{12}mim][NTf_2] (2) + dodecane (3)	9	25
		10	75

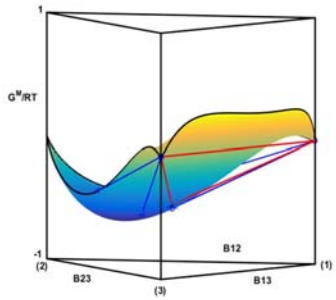
7 systems LLE and LLLE ((including ionic liquids) not correlated previously

Topological Analysis of simultaneous LLE-LLLE Correlations









GMcal_TieLinesLL (v.2.2): Graphical User Interface (GUI) for the Topological Analysis of Calculated GM Surfaces and Curves, including Tie-Lines, Hessian Matrix, Spinodal Curve, Plait Point Location, etc. for Binary and Ternary Liquid-Liquid Equilibrium (LLE) Data. 2015-22. Institutional Repository RUA: http://hdl.handle.net/10045/51725

Topological Analysis of Liquid-liquid Equilibrium Correlations

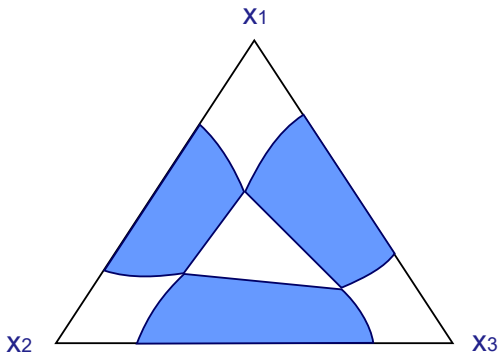
NECESSITY OF A STRATEGY TO AVOID THESE PROBLEMS

The solution must be found in the analysis of the topology of the G^M/RT function

suggested procedure

1. **Know qualitatively the shape of the G^M/RT vs composition function**
2. **Check the binaries**
3. **Inspect the topology of the G^M/RT vs composition function provided by the parameters calculated of the model**
4. **Validate the parameters (in the whole range of compositions)**

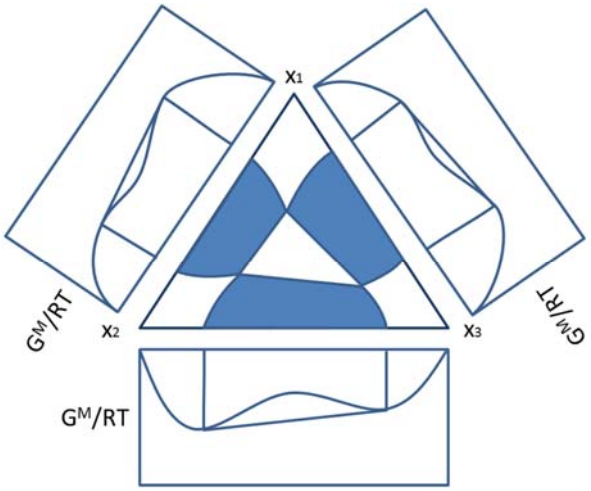
Marcilla, A.; Reyes-Labarta, J.A.; Olaya, M.M. Should we trust all the published LLE correlation parameters in phase equilibria? Necessity of their Assessment Prior to Publication. Fluid Phase Equilibria. 2017, 433, 243-252. DOI: http://dx.doi.org/10.1016/j.fluid.2016.11.009.

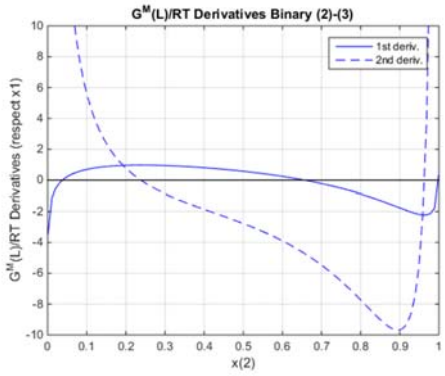


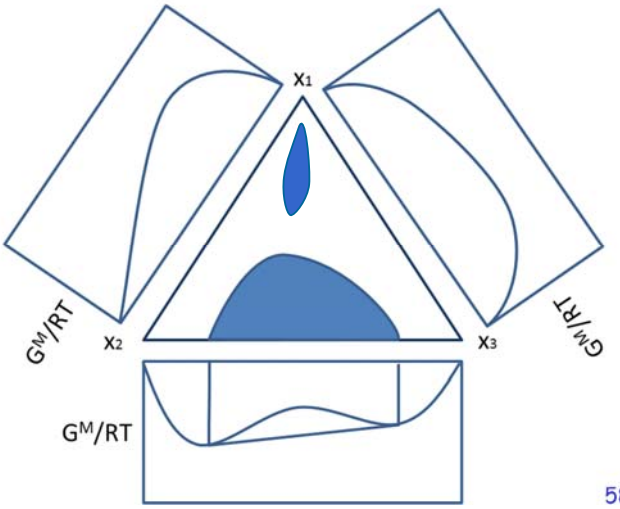
1. Know qualitatively the shape of the G^M/RT vs composition function

- **E.g. Type 3 ternary LLLE**

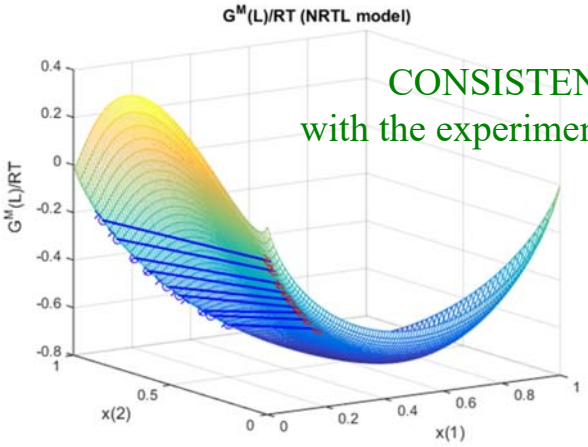
2. Checking the binaries



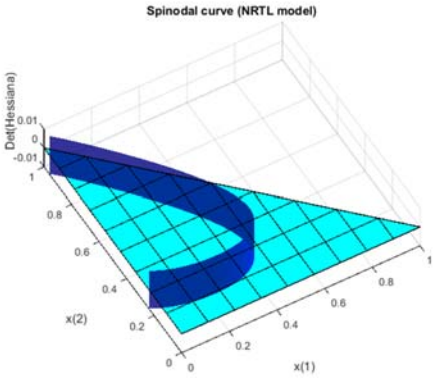


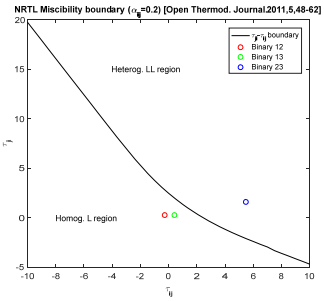


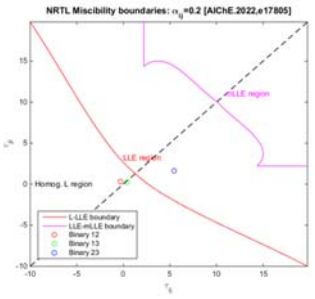
3. Inspect the topology of the G^M/RT vs composition function provided by the parameters calculated of the model (LLE ternary system at constant T)

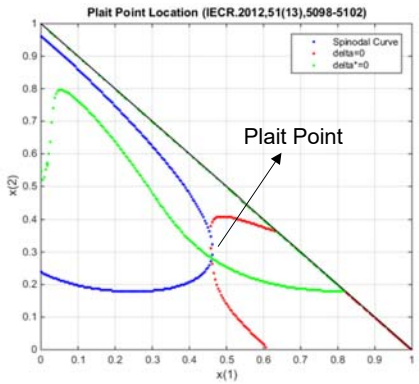


CONSISTENT
with the experimental data



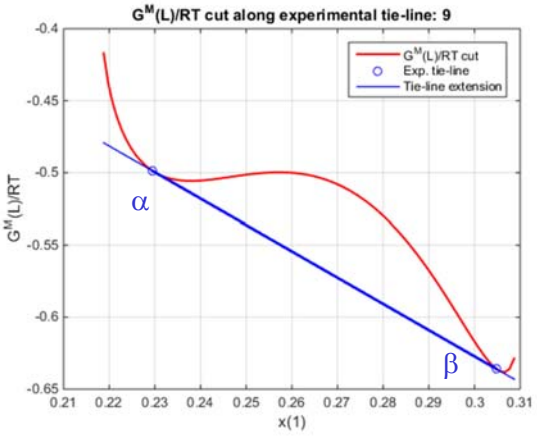






3. Inspect the topology of the $g^M=G^M/RT$ vs composition function provided by the parameters calculated of the model

➢ **Checking the individual tie-lines:**

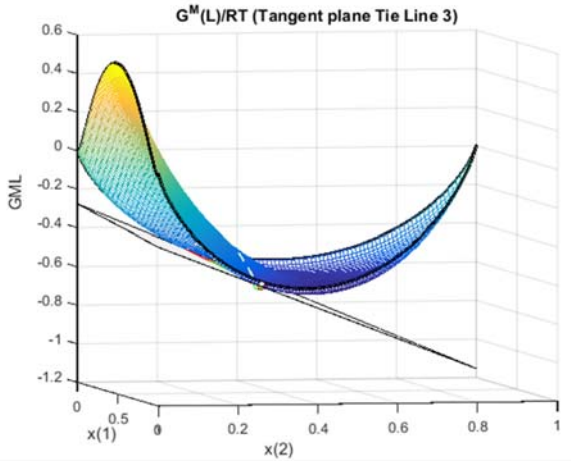


$$F_1 \equiv \left(\frac{\partial g^M}{\partial x_1}\right)^{\alpha}_{T,P,x_2} - \left(\frac{\partial g^M}{\partial x_1}\right)^{\beta}_{T,P,x_2} = 0$$

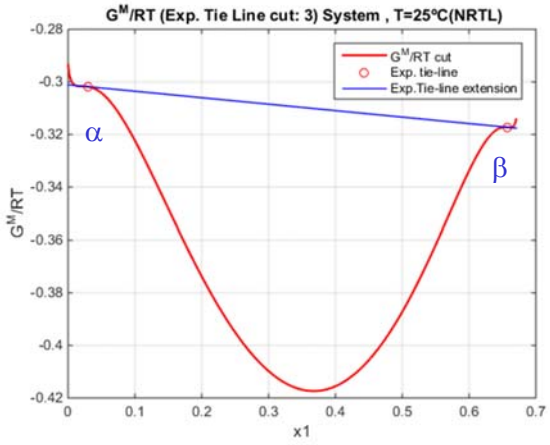
$$F_2 \equiv \left(\frac{\partial g^M}{\partial x_2}\right)^{\alpha}_{T,P,x_1} - \left(\frac{\partial g^M}{\partial x_2}\right)^{\beta}_{T,P,x_1} = 0$$

$$F_3 \equiv (g^{M,\beta} - g^{M,\alpha}) - (x_1^{\beta} - x_1^{\alpha})\left(\frac{\partial g^M}{\partial x_1}\right)^{\alpha}_{T,P,x_2} - (x_2^{\beta} - x_2^{\alpha})\left(\frac{\partial g^M}{\partial x_2}\right)^{\alpha}_{T,P,x_1} = 0$$

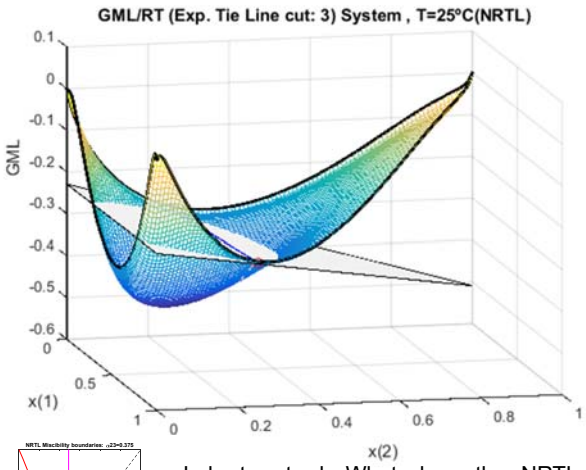
CONSISTENT
with the experimental data

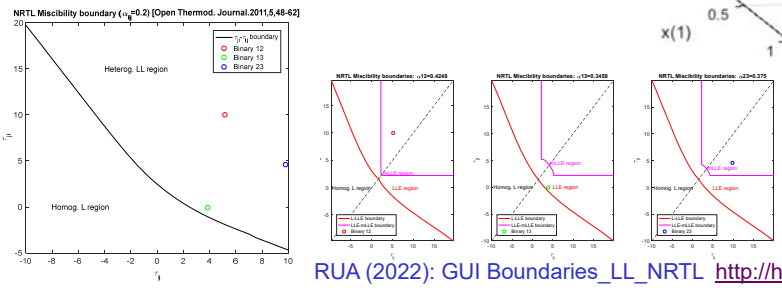


3. Inspect the topology of the G^M/RT vs composition function provided by the parameters calculated of the model



INCONSISTENT
with the experimental data





Labarta et al. What does the NRTL model look like? Determination of boundaries for different equilibrium regions. *AIChE Journal*. 2022, e17805. https://dx.doi.org/10.1002/aic.17805.

RUA (2022): GUI Boundaries_LL_NRTL http://hdl.handle.net/10045/121471.

3. Inspect the topology of the $g^M=G^M/RT$ vs composition function provided by the parameters calculated of the model

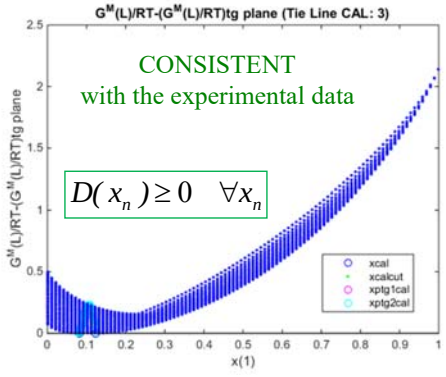
- **Extension for multicomponent systems (tangent hyperplanes):**

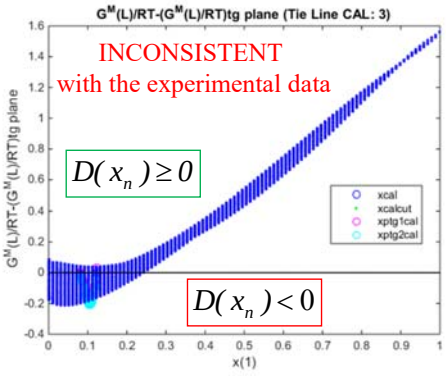
$$F_i \equiv \left(\frac{\partial G^M}{\partial x_i}\right)^{\alpha}_{T,P,x_{i\neq j}} - \left(\frac{\partial G^M}{\partial x_i}\right)^{\beta}_{T,P,x_{i\neq j}} = 0 \quad \forall i \in \{1,\ 2,\ ...,\ C-1\}$$

$$F_C \equiv (G^M - G^{M,\alpha}) - \sum_{i=1}^{C-1}(x_i - x_i^{\alpha}) \cdot \left(\frac{\partial G^M}{\partial x_i}\right)^{\alpha}_{T,P,x_{i\neq j}} = 0$$

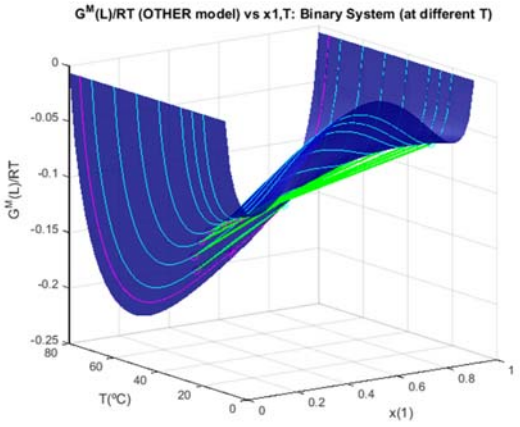
Extension of the Wasylkiewicz's stability test

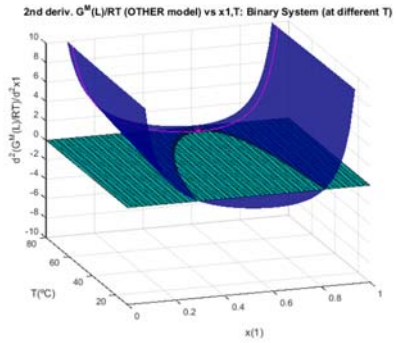
- **Representation of the distance (D) between GM(thermodynamic model)-GM (tg hyperplane) at each point of the whole range of compositions:**

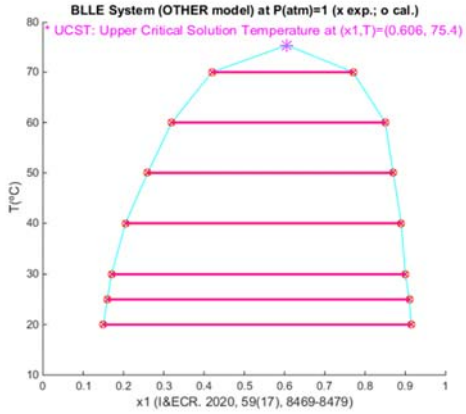




3. Inspect the topology of the G^M/RT vs composition function provided by the parameters calculated of the model (LLE binary system at different T)



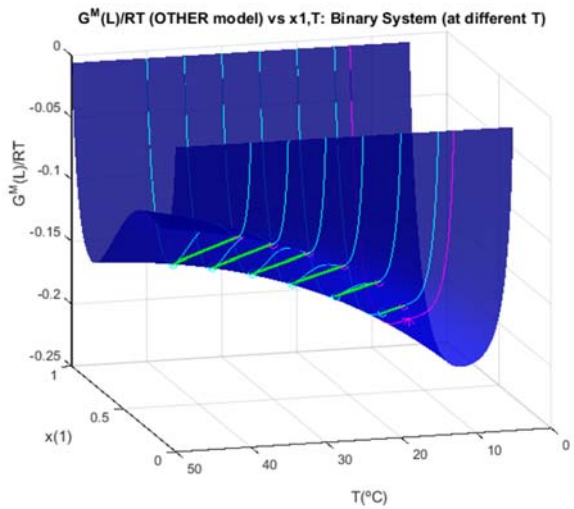


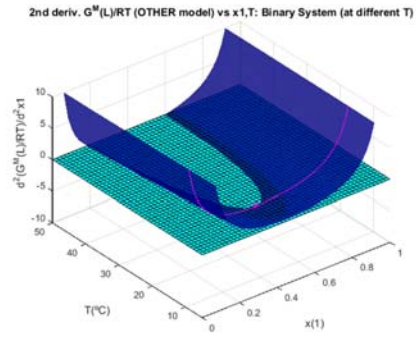


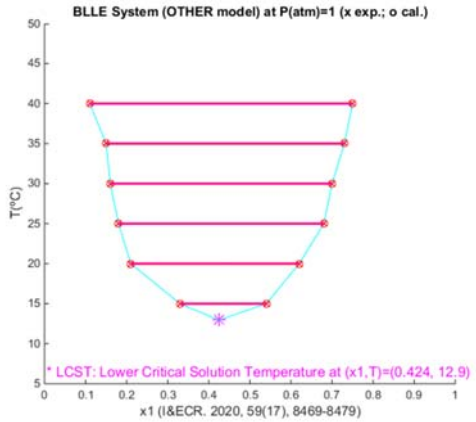
CONSISTENT
with the experimental data
(UCST)

Topological Analysis of Liquid-liquid Equilibrium Correlations

3. Inspect the topology of the G^M/RT vs composition function provided by the parameters calculated of the model (LLE binary system at different T)

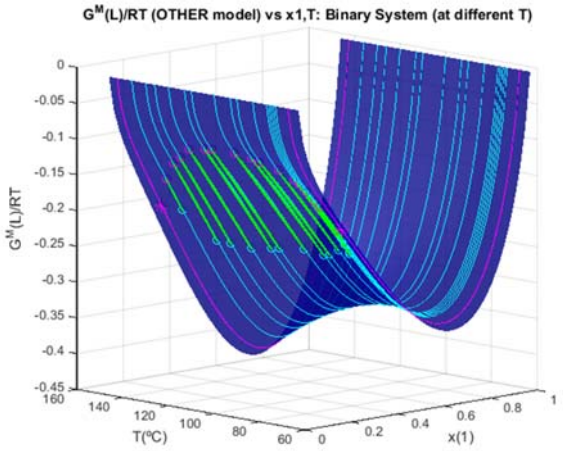


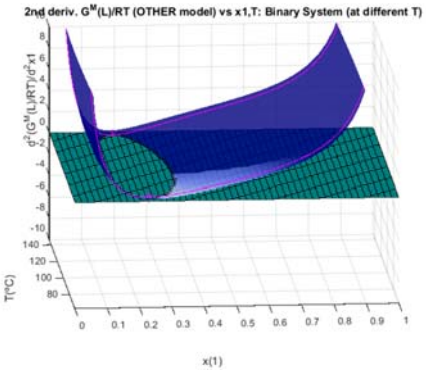


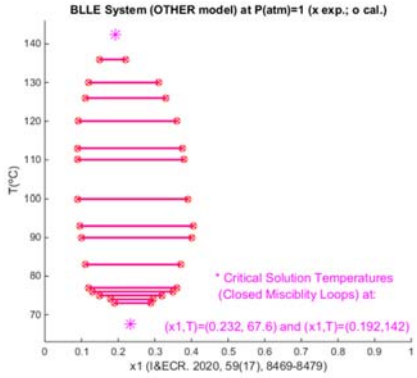


CONSISTENT
with the experimental data
(LCST)

3. Inspect the topology of the G^M/RT vs composition function provided by the parameters calculated of the model (LLE binary system at different T)







CONSISTENT
with the experimental data
(Closed Miscibility Loop)

CONCLUSIONS (I)

✓ **Be careful with the OF used:** $O.F._{total} = O.F._{x,LL} + O.F._{x,LLL} + O.F._{y,LV} + \ldots$

$$O.F._{x,L_1L_2} = \sum_{j=1}^{NTL}\sum_{k=1}^{2}\sum_{i=1}^{C}\left(x_{i,j}^{Lk,exp} - x_{i,j}^{Lk,cal}\right)^2 \quad \text{subject to:} \quad \left\{\sum_{j=1}^{NTL}\sum_{i=1}^{C}\left(a_{i,j}^{L1,cal} - a_{i,j}^{L2,cal}\right)^2 < \varepsilon \quad \ldots\right.$$

$$O.F._{x,L_1L_2L_3} = \sum_{k=1}^{3}\sum_{i=1}^{C}\left(x_{i}^{Lk,exp} - x_{i}^{Lk,cal}\right)^2 \quad \text{subject to:} \quad \left\{\sum_{p=1}^{2}\sum_{k>p}^{3}\sum_{i=1}^{C}\left(a_{i}^{Lp,cal} - a_{i}^{Lk,cal}\right)^2 < \varepsilon \quad \ldots\right.$$

$$O.F._{y,LV} = \begin{cases} \sum_{j=1}^{NTL}\sum_{i=1}^{C}\left(y_{i,j}^{exp} - y_{i,j}^{cal}\right)^2 \\ \sum_{j=1}^{NTL}\sum_{i=1}^{C}\left(T_{i,j}^{exp} - T_{i,j}^{cal}\right)^2 \\ \sum_{j=1}^{NTL}\sum_{i=1}^{C}\left(G_{i,j}^{ML,exp} - G_{i,j}^{ML,cal}\right)^2 \\ \sum_{j=1}^{NTL}\sum_{i=1}^{C}\left(\dfrac{\gamma_{i,j}^{exp} - \gamma_{i,j}^{cal}}{\gamma_{i,j}^{exp}}\right)^2 \quad \ldots \end{cases}$$

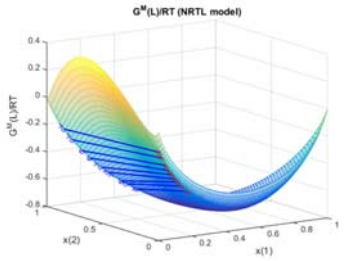
$$\text{subject to:} \quad \begin{cases} \sum_{j=1}^{NTL}\left(\sum_{i=1}^{C} y_{i,j}^{cal} - 1\right)^2 < \varepsilon \\ \sum_{j=1}^{NTL}\sum_{i=1}^{C-1}\left(\dfrac{\partial G_j^{M,V}}{\partial y_{i,j}^{cal}} - \dfrac{\partial G_j^{M,L}}{\partial x_{i,j}^{exp}}\right)^2 < \varepsilon \quad \ldots \end{cases}$$

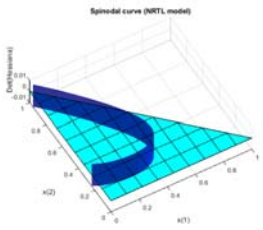
Marcilla, A.; Reyes-Labarta, J.A.; Olaya, M.M. Phase Equilibrium Correlation. Regarding the full consistency of the thermodynamics. 10th World Congress of Chemical Engineering. Barcelona (SPAIN), 1t-5th October, 2017. RUA: http://hdl.handle.net/10045/70035

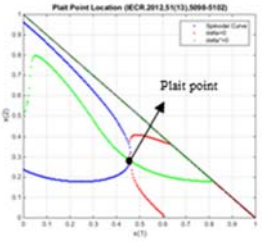
CONCLUSIONS (II)

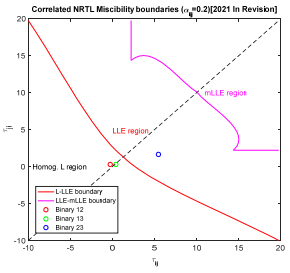
✓ Stability criterion must be always checked

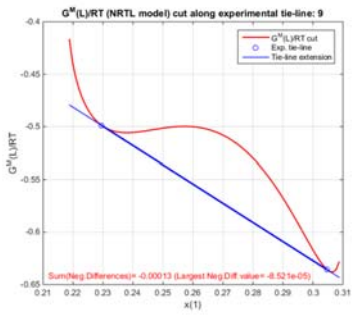
➢ The analysis of the GM function (and derivatives) can be very useful

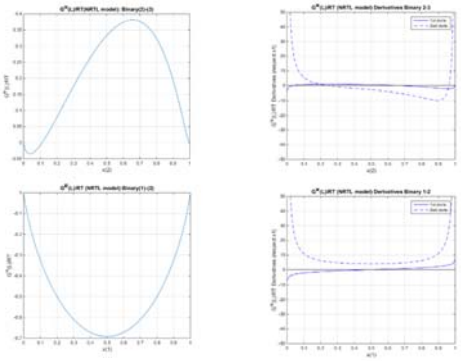












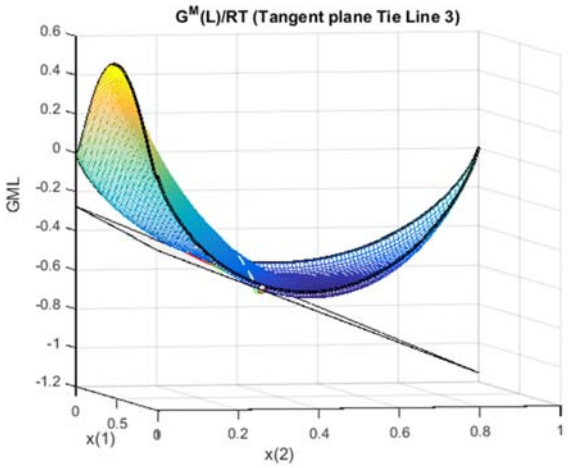
RUA (2015-2022): GUI GMcal_TieLinesLL (v.2.2) http://hdl.handle.net/10045/51725.

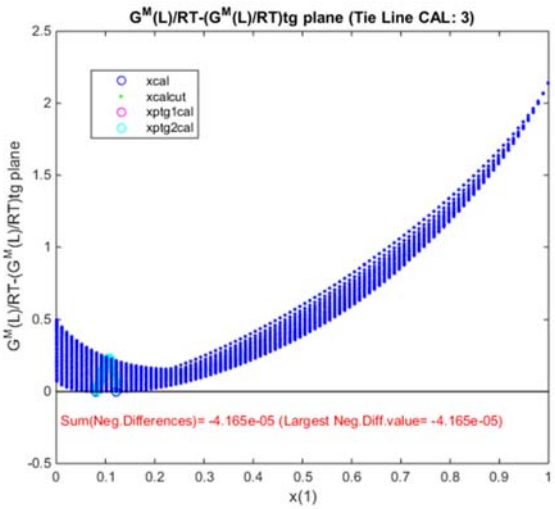
Topological Analysis of Liquid-liquid Equilibrium Correlations

CONCLUSIONS (II)

✓ Stability criterion must be always checked

➢ Validate the parameters in the whole range of compositions





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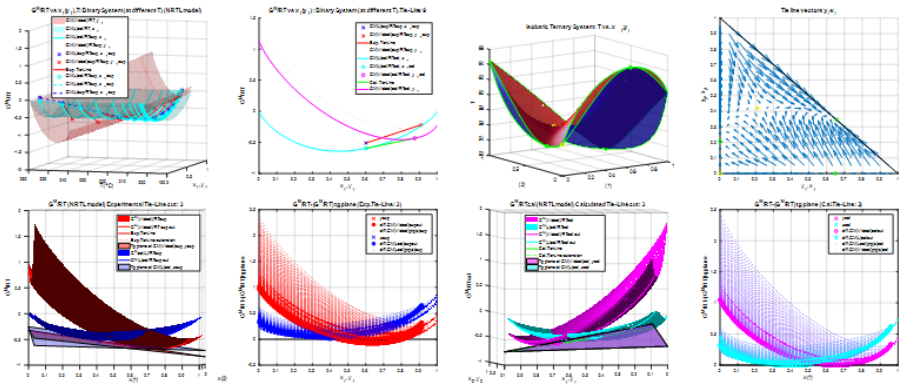

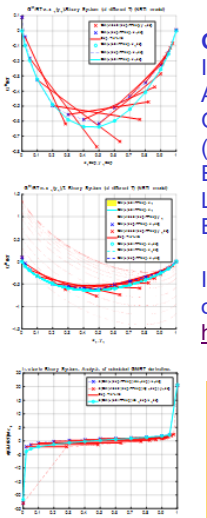

GMcal_TieLinesVL: Graphical User Interface (GUI) for the Topological Analysis of Experimental and Calculated GM Functions for Binary and Ternary (Isobaric or Isothermal) Vapor-Liquid Equilibrium (VLE) Data (including Tie-Lines, Derivatives, Distillation Boundaries, etc.).

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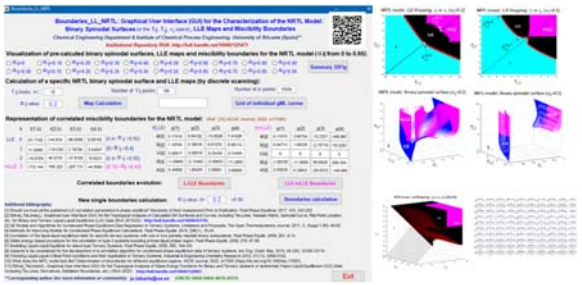

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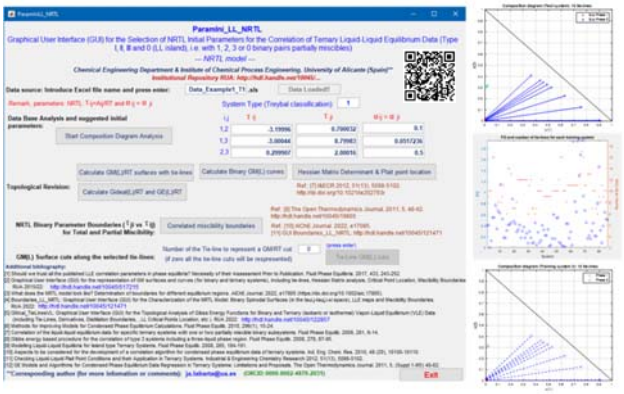

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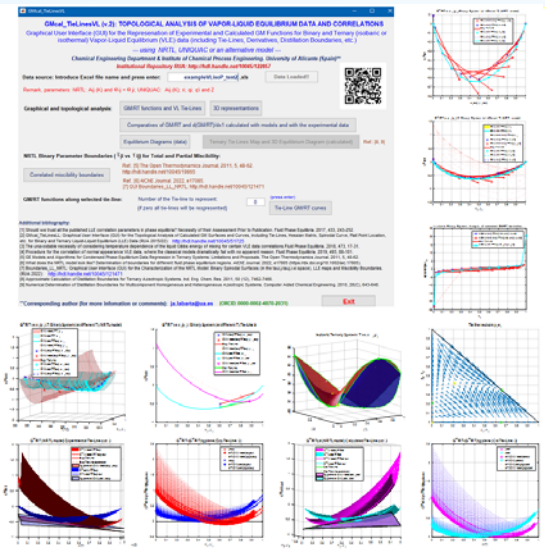

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facebook:
http://www.facebook.com/GUI-for-the-analysis-of-the-Gibbs-stability-criteria-1861744990767271/

GMcal_TieLinesLL (v.2.3): Graphical User Interface (GUI) for the Topological Analysis of Calculated $G^{M(L)}$ Surfaces and Curves, including Tie-Lines, Hessian Matrix, Spinodal Curve, Critical Point Location, etc. for Binary and Ternary Liquid-Liquid Equilibrium (LLE) Data

(Topological Analysis of Liquid-Liquid Equilibrium Correlations)

Institutional Repository RUA: http://hdl.handle.net/10045/51725*

Department of Chemical Engineering & Institute of Chemical Process Engineering
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USER INSTRUCTIONS*

**Contact details for more information and/or comments.*
Corresponding author: ja.labarta@ua.es ORCID: http://orcid.org/0000-0002-4870-2031

1. Download instructions

1. Download the file to your computer in a known folder: **GMcal_TieLinesLL.zip**
2. Unzip the file

2. Before using the GUI GMcal_TieLinesLL

1. In order to use this GUI it is necessary to have an excel file with an adequate structure, with the following information corresponding to the system under study. It is essential to respect the correct structure of the excel file. It is possible to use the different files exampleLL_test.xls included, as a draft for other similar case study or system (see **Appendix A: Structure of the excel data file**):

   a. Values of $T^{(*)}$ and P for the corresponding LLE system.

   b. $G^{Excess}(L)/RT$ Model selection variable: 1=NRTL, 2=UNIQUAC, 3 or higher=OTHER (that could be implemented by the user)

   c. $G^{E}(L)/RT$ Model parameters:

   - For the **NRTL** model, the parameters used are: $\tau_{i,j}$(dimensionless)$=A_{i,j}/(R\cdot T)$, $\alpha_{i,j}=\alpha_{j,i}$. i.e.: **9 parameters for a ternary system**: τ_{12}, τ_{21}, τ_{13}, τ_{31}, τ_{23}, τ_{32}, α_{12}, α_{13}, α_{23}.
   - For the **UNIQUAC** model, the parameters used are: $\tau_{i,j}=exp(-A_{i,j}/(R\cdot T))$, r_i, $q_i=s_i$, q'_i, Z. i.e.: **16 parameters for a ternary system**: τ_{12}, τ_{21}, τ_{13}, τ_{31}, τ_{23}, τ_{32}, r_1, r_2, r_3, q_1, q_2, q_3, q'_1, q'_2, q'_3, Z.
   - Classic NRTL or UNIQUAC models are the ones that can directly be used to calculate the GExcess. However, it is possible to use any other model by including in the MatLab function file: ModelGExcess.m the corresponding model (Model selection variable: **3 or higher= OTHER**). This alternative model could directly use a maximum of 19 parameters by using in the excel file the cells corresponding to the NRTL model plus the cells corresponding to the UNIQUAC model, cells, i.e.: E1:E6; H3:H5; K3:K5, L3:L6 and M3:M5. (see **Appendix A: Structure of the excel data file**). In the case of not using all the 19 parameters of the excel file, the

ones not used have to be equal to zero due to the fact that this function is called as:

```
function
y=ModelGExcess(ModelF,TEMP,x1,x2,x3,PARAM1,PARAM2,PARAM3,PARAM4,PARAM5,PARAM6,PARAM7
,PARAM8,PARAM9,PARAM10,PARAM11,PARAM12,PARAM13,PARAM14,PARAM15,PARAM16,PARAM17,PARAM
18,PARAM19).
```

* As examples of the introduction of an additional model, three different examples are already implemented:

Model 3: a modified version of the NRTL model (e.g. used in Aspen Plus Software) for ternary systems with temperature dependent parameters ($\tau_{j,i} = a_{j,i} + b_{j,i}/T$ with 15 parameters: 6 $a_{i,j}$, 3 $\alpha_{i,j}$, 6 $b_{i,j}$).

Model 4: a modified version of the NRTL model (e.g. used in Aspen Plus Software) for binary systems with temperature dependent parameters (with 10 parameters).

Model 5: a modified version of the UNIQUAC model (e.g. used in Aspen Plus Software) for binary systems with temperature dependent parameters (with 13 parameters.

See Appendix A: Structure of the excel data file: **exampleLL_test3.xls**, **exampleLL_test4b-d.xls** and **exampleLL_test5.xls**, respectively.

*** In any case, just to remember that any model with no limitations in the number of parameters could be used by including the model and the specific parameters directly in the MatLab function file: ModelGExcess.m.**

*** Additionally, if the temperature of the system is constant, any dependence on the temperature of the temperature dependent parameters ($\tau_{j,i}$) could also be used by recalculating the constant values of $\tau_{j,i}$ at the given temperature.**

d. The total number of experimental tie-lines (Nt) (max. value: 40). This value can be equal to **0** for ternary and binary LLE systems, to analyse only the corresponding parameters and model. In the case of binary systems, it is also necessary to write in cell B3 of the excel file the word **BINARY**(*) (see the corresponding indications in sections 4.1 and 4.2 respectively).

e. Experimental molar fractions

f. Calculated molar fractions

➢ **Remark:** The proposed GUI GMcal_TieLinesLL can also be used to represent additionally the evolution of a **binary system** at different temperatures, including the calculation of the **critical solution temperature** (UCST, LCST or CML) if there exists (Ref.: *Ind. Eng. Chem. Res. 2020, 59, 17, 8469-8479.* https://doi.org/10.1021/acs.iecr.0c00141). In this case, an additional column including the temperature of each binary data (in increasing order) has also to be included with location = (M10:M50). Additionally, just in the case of the NRTL or UNIQUAC models, the parameters that have to be introduced are the $A_{j,i}(K)$ parameters (temperature independent variables).

A) **exampleLL_test4a.xls** (Figure 7a) using the NRTL model for a binary system (3 parameters)

B) **exampleLL_test4b(c and d).xls** (Figures 7b,c) using as "other model (max. 19 parameters directly from the excel file)", the NRTL model for a binary system with temperature dependent parameters (10 parameters):

$$\tau_{ji} = a_{ji} + b_{ji}/T + e_{ji} \cdot ln\ T + f_{ji} \cdot T$$

$$\alpha_{ji} = c_{ji} + d_{ji}\ (T - 273.15)$$

C) **exampleLL_test5.xls** using as "other model (max. 19 parameters directly from the excel file)", the UNIQUAC model for a binary system with temperature dependent parameters (13 parameters):

$$\tau_{ji} = exp\ (a_{ji} + b_{ji}/T + c_{ji} \cdot ln\ T + d_{ji} \cdot T)$$

(For more information see: **Appendix A: Structure of the excel data file**)

3. CLASIC GM MODELS RESUME

➢ $\boldsymbol{G^{Mixture}/RT} = G^{Ideal}/RT + G^{Excess}/RT) = x_i \cdot ln\ (x_i) + G^E/RT$

NRTL model:

$$\frac{G^E}{RT} = \sum_{i=1}^{C} x_i \cdot \frac{\sum_{j=1}^{C} \tau_{j,i} \cdot G_{j,i} \cdot x_j}{\sum_{k=1}^{C} G_{k,i} \cdot x_k}; \quad \text{with} \quad \tau_{j,i}(\text{dimensionless}) = \frac{A_{j,i}}{RT}; \quad G_{j,i} = exp\left(-\alpha_{j,i} \cdot \tau_{j,i}\right); \quad A_{i,i}=0$$

and $\alpha_{i,j} = \alpha_{j,i}$

UNIQUAC model:

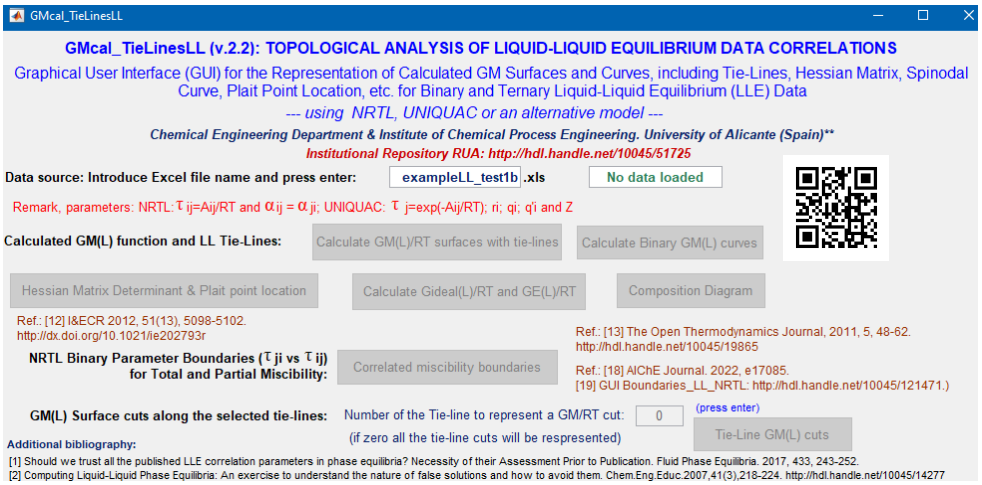
$$\frac{G^E}{RT} = \frac{G^E_{Combinatorial}}{RT} + \frac{G^E_{Residual}}{RT} = \sum_{i=1}^{C} x_i \cdot ln\frac{\phi_i}{x_i} + \frac{z}{2} \cdot \sum_{i=1}^{C} q_i \cdot x_i \cdot ln\frac{\theta_i}{\phi_i} - \sum_{i=1}^{C} q'_i \cdot x_i \cdot ln\left(\sum_{j=1}^{C} \theta'_j \cdot \tau_{j,i}\right)$$

with: $\phi_i = \frac{r_i \cdot x_i}{\sum_{j=1}^{C} r_j \cdot x_j}$; $\theta_i = \frac{q_i \cdot x_i}{\sum_{j=1}^{C} q_j \cdot x_j}$; $\theta'_i = \frac{q'_i \cdot x_i}{\sum_{j=1}^{C} q'_j \cdot x_j}$; $\tau_{j,i}(\text{dimensionless}) = \exp\left(-\frac{A_{j,i}}{RT}\right)$

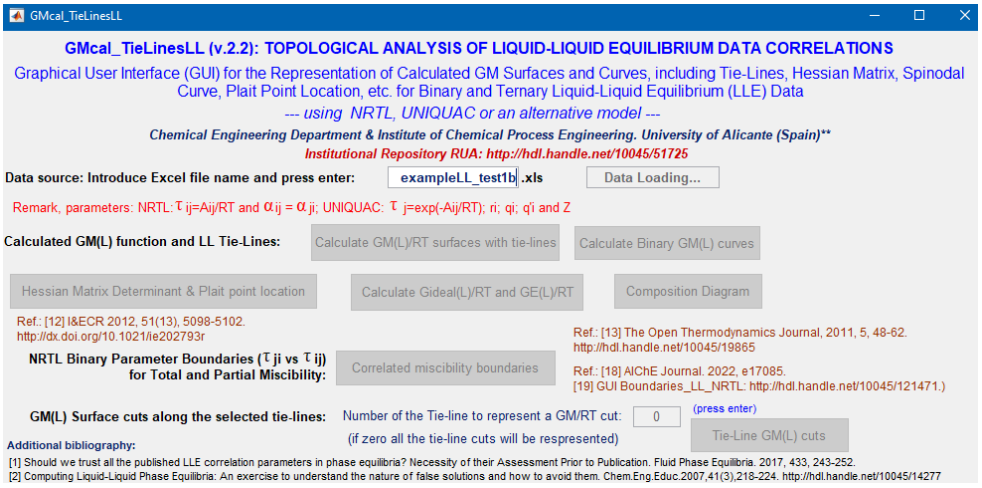
z = Coordination number (usually with a value of 10)
r_i = Volume parameter
q_i = Area parameter (or s_i)
q_i=q'_i for most of substances, except for water and some small alcohols.

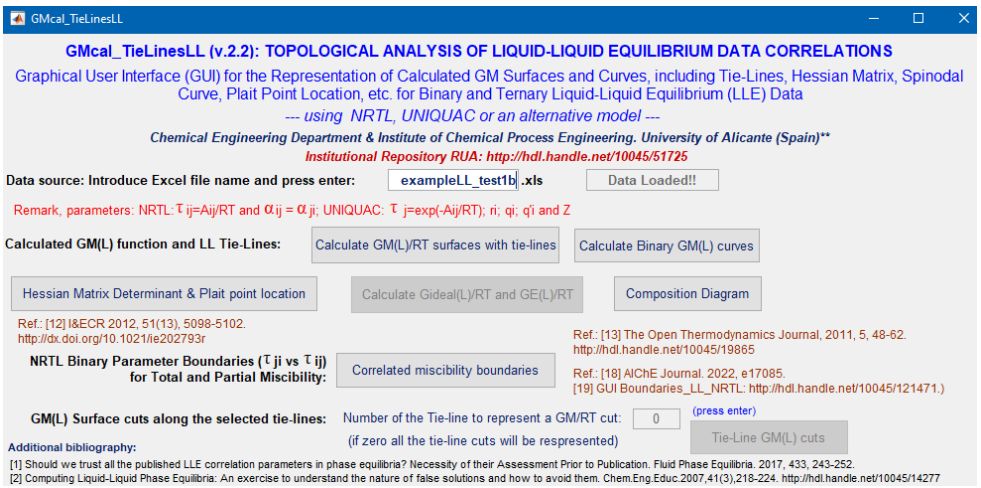
4. USING THE GUI GMcal_TieLinesLL

1. Open Matlab software
2. Once in MatLab, select the folder where the file **GMcal_TieLinesLL.zip** was unzipped as "current folder".
3. Localize and execute the file GMcal_TieLinesLL.p from the MatLab Command Window (i.e.: writing GMcal_TieLinesLL in the Command Window, and pressing enter)



4. At this moment only the windows of the excel file name is active. Introduce the name of the excel data file corresponding to the system under study (e.g. exampleLL_test1b) and ***press enter***. Please wait a moment for the data load process.





5. Now it is possible to create different diagrams by using the corresponding push buttons.

4.1) Ternary LLE systems at a constant temperature

A) G^M(L)/RT surface (calculated with the model and parameters defined), including also tie-lines (i.e. the corresponding experimental and calculated data included in the excel file loaded).

B) Calculated Binary G^M(L) curves, including 1st and 2nd derivatives (to facilitate the topological analysis).

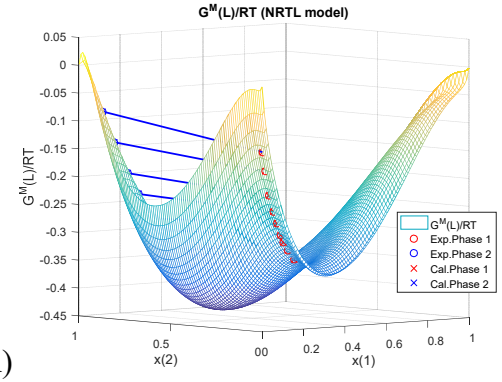
C) Composition diagram (in molar fractions).

D) Hessian matrix determinant (σ), spinodal curve ($\sigma=0$), and Plait point visual location using additionally δ and δ^* matrix determinants, which have to be also equal to zero. (*Ref.: Industrial & Engineering Chemistry Research. 2012, 51 (13), 5098-5102.* http://dx.doi.org/10.1021/ie202793r):

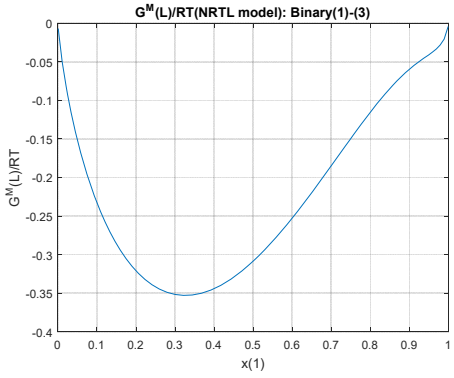
$$\sigma = \begin{vmatrix} \frac{\partial^2 G^M}{\partial^2 x_1} & \frac{\partial^2 G^M}{\partial x_1 \partial x_2} \\ \frac{\partial^2 G^M}{\partial x_2 \partial x_1} & \frac{\partial^2 G^M}{\partial^2 x_2} \end{vmatrix} = 0;\ \delta = \begin{vmatrix} \frac{\partial \sigma}{\partial x_1} & \frac{\partial \sigma}{\partial x_2} \\ \frac{\partial^2 G^M}{\partial x_2 \partial x_1} & \frac{\partial^2 G^M}{\partial^2 x_2} \end{vmatrix} = 0;\ \delta^* = \begin{vmatrix} \frac{\partial \sigma}{\partial x_2} & \frac{\partial \sigma}{\partial x_1} \\ \frac{\partial^2 G^M}{\partial x_1 \partial x_2} & \frac{\partial^2 G^M}{\partial^2 x_1} \end{vmatrix} = 0$$

E) Correlated NRTL binary Miscibility Boundaries (e.g. for Total and Partial Miscibility): $\tau_{j,i}$ vs $\tau_{i,j}$ (*Ref.: The Open Thermodynamics Journal, 2011, 5, 48-62*: http://dx.doi.org/10.2174/1874396X01105010048 (for α_{ij}=0.2) and *AIChE 2022, e17805*: https://dx.doi.org/10.1002/aic.17805-*RUA, 2022:* http://hdl.handle.net/10045/121471, for α_{ij} between 0 and 0.95). The $\tau_{i,j}$ binary parameters (included in the excel file) are also represented, to check their adequate location.

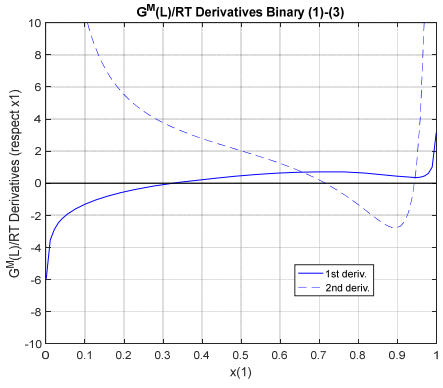
A)



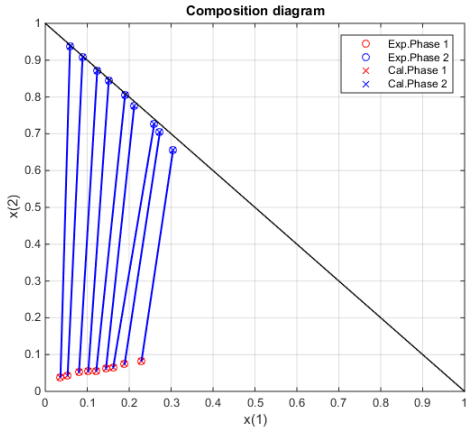
B1)

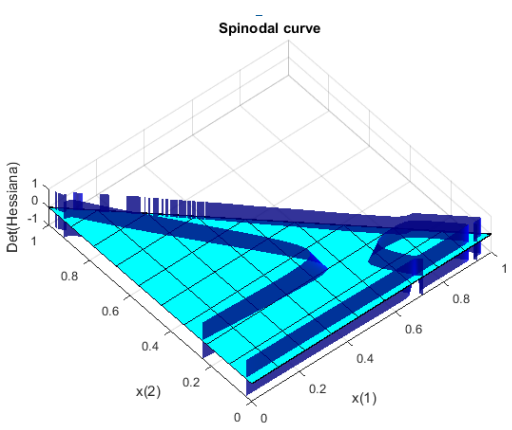


B2)

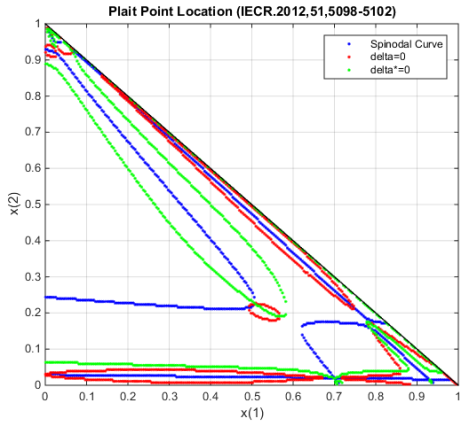


C)

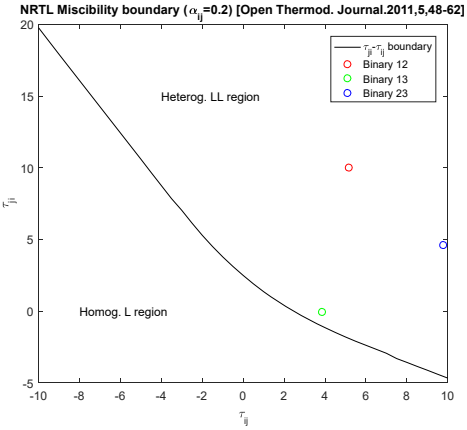




D1)



D2)



E)

0 < $\alpha_{i,j}$ < 0.95: AIChE Journal. 2022, e17805 (https://dx.doi.org/10.1002/aic.17805)

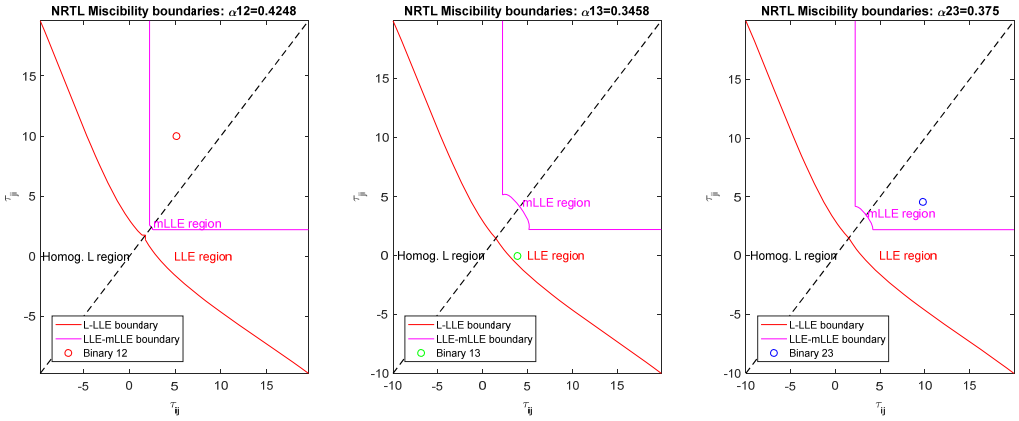
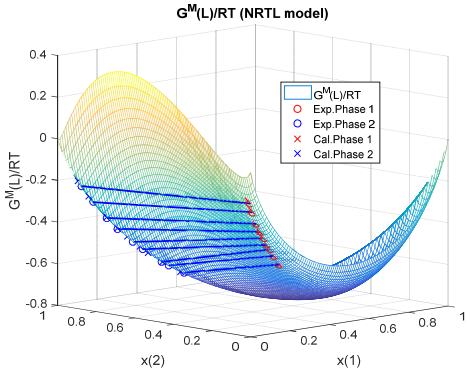


*Figure 1. Different diagrams corresponding to exampleLL_test1a.xls (LLE ternary system). In this example, the NRTL parameters used are **NOT COHERENT** with the experimental LL data.*

A)



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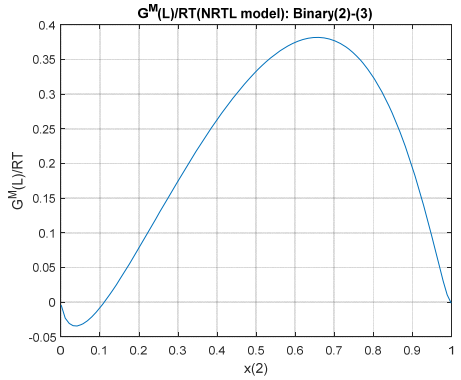
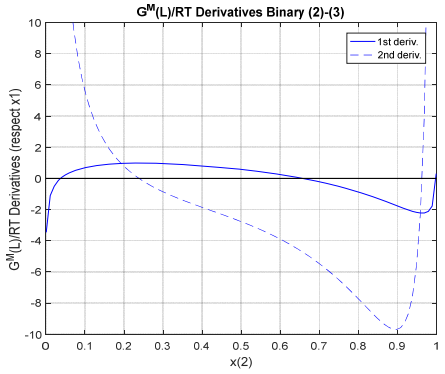
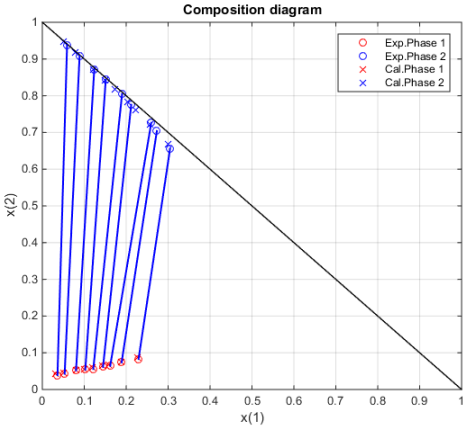


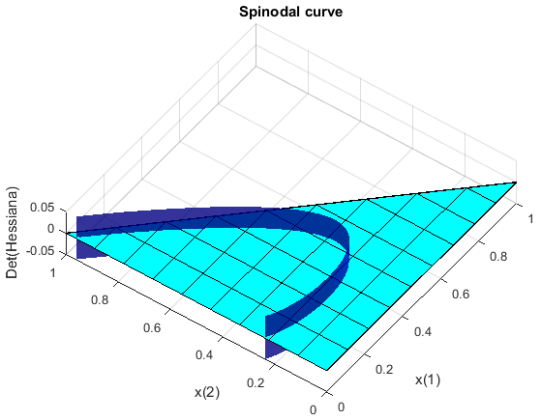
B2)



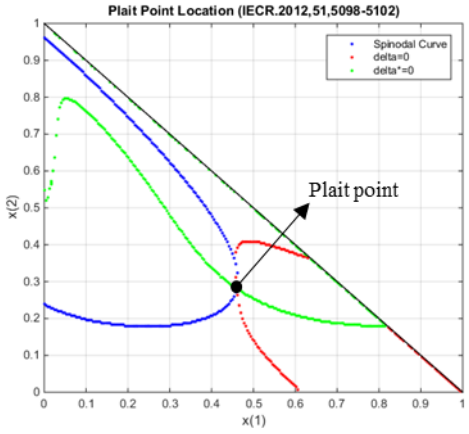
C)



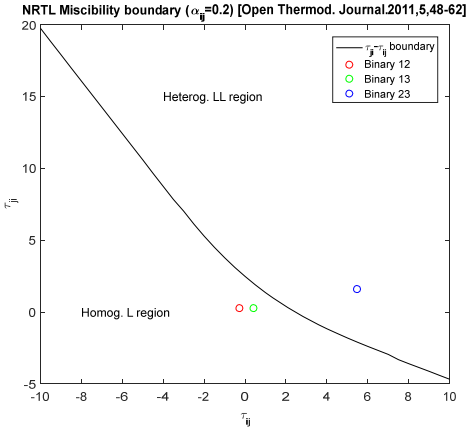
D1)



D2)



E)



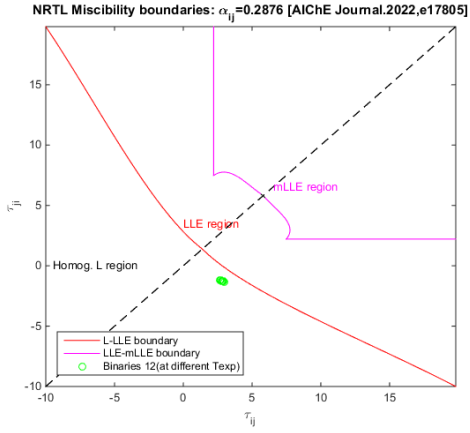
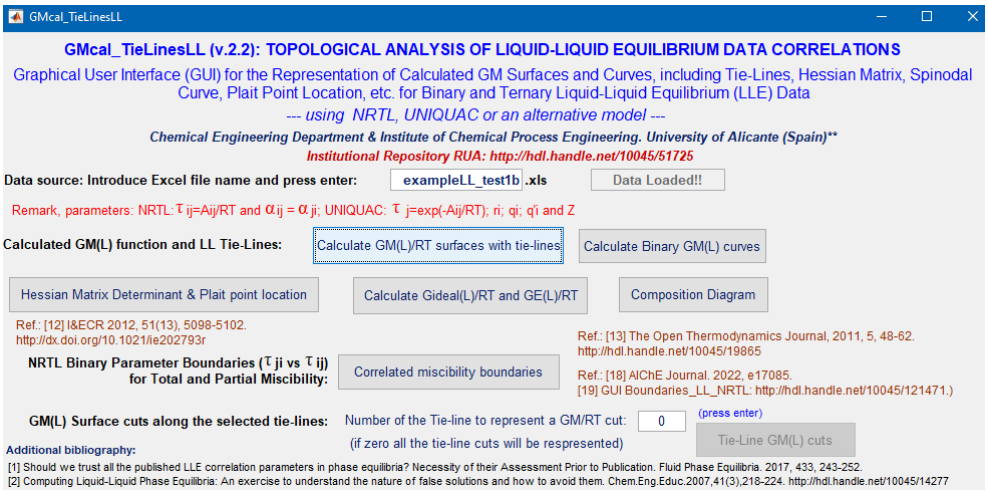


*Figure 2. Different diagrams corresponding to exampleLL_test1b.xls (LLE ternary system). In this example, the NRTL parameters used are **COHERENT** with the experimental LL data.*

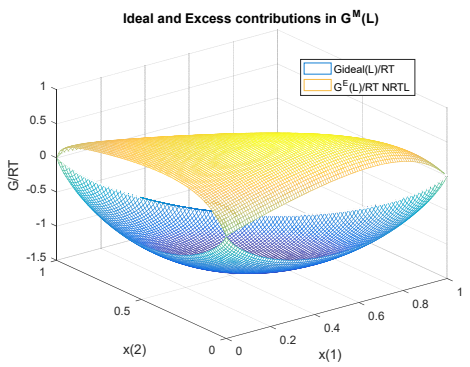
6. Once the $G^M(L)/RT$ surface (A) is calculated, two more options are active:



F) $G^{Ideal}(L)/RT$ and $G^E(L)/RT$ surfaces (ideal and excess contributions of the $G^M(L)/RT$ function calculated with the model parameters included in the excel data file): Push button.

G) $G^M(L)/RT$ surface cuts along the selected Experimental Tie-Lines. In this case, the ordinal number corresponding to a tie-line (from 0 to Nt) has to be introduced (the value 0 will select the representation of the different cuts along all the experimental and calculated tie-lines). Then ***press enter***. After that, push the button "*Tie Line GM(L)*" to represent the $G^M(L)/RT$ surface cut is active and can be used.

F)



G)

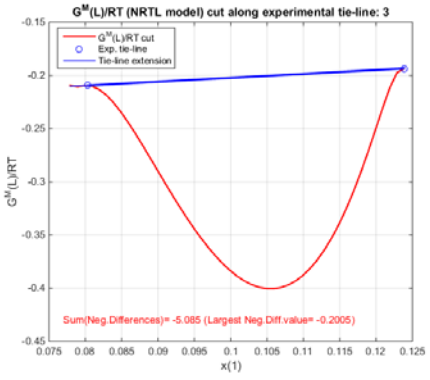
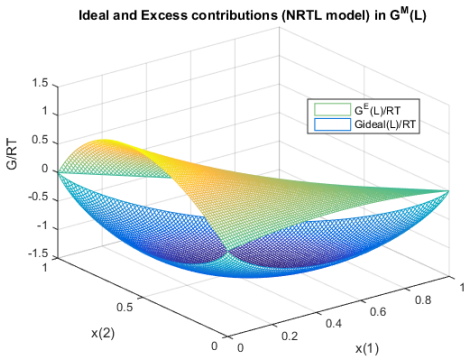
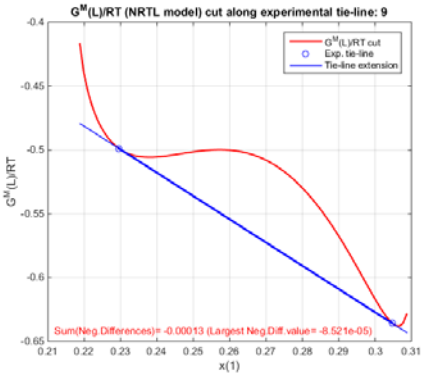


*Figure 3. Different diagrams corresponding to exampleLL_test1a.xls: Ideal and Excess contribution, and $G^M(L)/RT$ cut along a tie-line. In this example, the NRTL parameters used are **NOT COHERENT**.*

F)



G1)



G2)

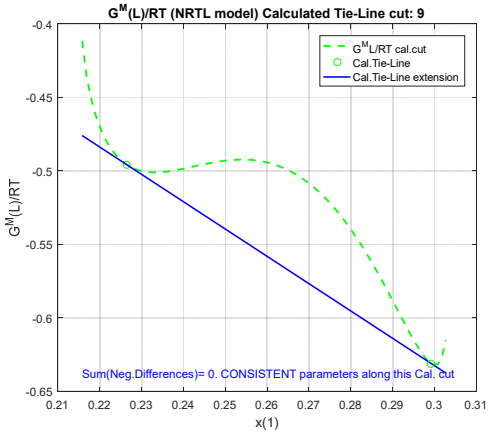
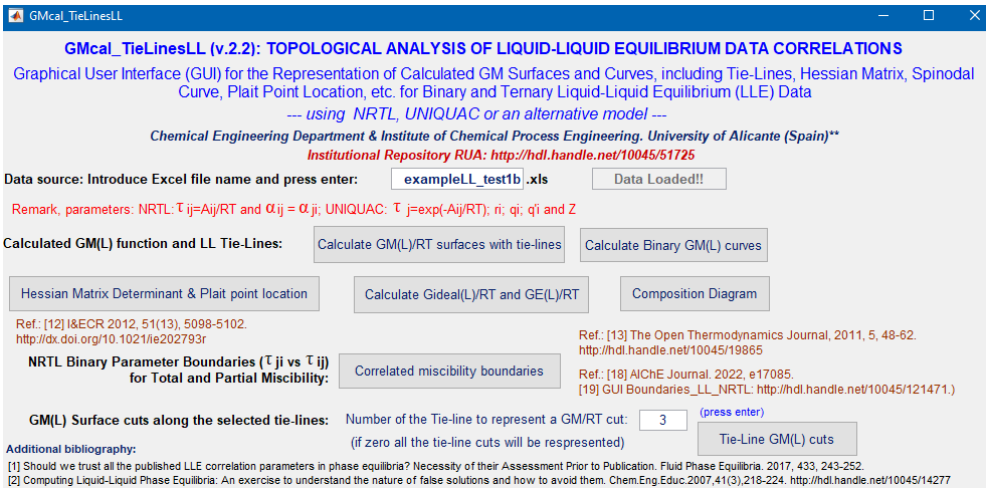


Figure 4. Different diagrams corresponding to exampleLL_test1b.xls: Ideal and Excess contribution, and $G^M(L)/RT$ cut along an exp. and cal. tie-line. In this example, the NRTL parameters used are ***COHERENT****.*

When the number of the Tie Line is different from 0, two additional figures are also generated in ternary systems to facilitate and complete the visual analysis (Figures 5). On one hand, a new 3D figure representing the complete $G^M(L)/RT$ surface (in modified units for drawing horizontal the tangent planes for the selected tie line, to facilitate the viewing and the coherence of the results). This figure includes the selected tie-line and the tangent planes at both extremes of the corresponding calculated or experimental (Figures 5.a1 and 5.b1). The second figure represents additionally the difference between $(G^M(L)/RT)_{Surface(model)}$ and $(G^M(L)/RT)_{tangent\ plane}$ in the whole range of compositions, including the way along the tie line cut and the tangent planes at its both extremes (see Figures 5.a2 and 5.b2). Evidently, this difference in the equilibrium compositions should be equal to zero.



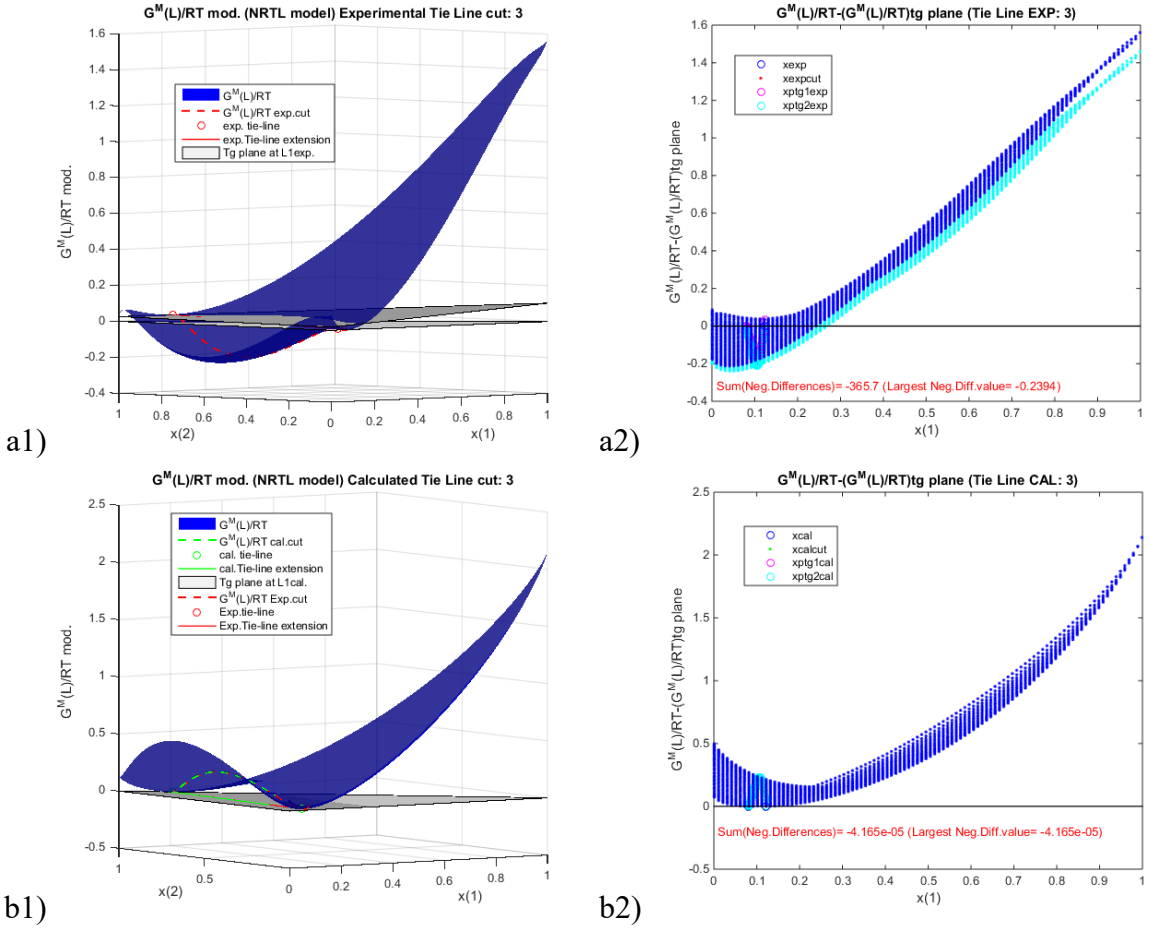


*Figure 5. Complete $G^{M}(L)/RT$ surface including the selected tie-line and the tangent planes at both extremes of the tie-line. Remark: the values of the $G^{M}(L)/RT$ surface have been modified to draw horizontal tangent planes to facilitate the viewing. a) Example with **NOT COHERENT** NRTL parameters, b) Example with **COHERENT** parameters.*

In order to complement this visual analysis in a rigorous way, from the version v.2.2. of this GUI, the summation of all the negative differences $[(G^{M}(L)/RT)_{Surface(model)}-(G^{M}(L)/RT)_{tangent\ plane}]$, and the largest negative difference, for each tie line (and the global for all the tie lines) are also calculated and showed in the Command Windows of MatLab (Figure 6). This calculation is

carried out in the cut along the tie lines and additionally in ternary systems, in the whole range of composition. Obviously, these summations should be zero for totally consistent parameters with the expected experimental behaviour.

Figure 6. Example of the additional information that appears at the Command Window after pushing the "Tie-Line GM(L) cuts" button.

As commented before, this GMcal_TieLinesLL GUI can be also used without any experimental data, just to analyse only the corresponding parameters and model. In the case of ternary LLE systems, this can be done only by indicating that the total number of experimental tie-lines (Nt) is equal to 0 (cell B4 in the excel file). E.g. **exampleLL_test0T.xls**.

4.2) Binary LLE systems at different temperatures

As commented before, the proposed GMcal_TieLinesLL GUI can also be used to represent additionally the evolution of a **binary system** at different temperatures, including the calculation of the **critical solution temperature** (UCST, LCST or CML) in a predefined range of temperatures, if there exists (*Ref.: Ind. Eng. Chem. Res. 2020, 59, 17, 8469–8479.* https://doi.org/10.1021/acs.iecr.0c00141). e.g. Figure 7 and exampleLL_test4a-4d.xls.

In this case, it is necessary to write in cell B3 of the excel file the word BINARY. Additionally, the components used have to be 1 and 2, and an additional column including the temperature of each binary data (in increasing order) has also to be included with location=(M10:M50). And also, in the case of the NRTL or UNIQUAC models, the parameters that have to be introduced are the A_{ji} (K) parameters (temperature independent variables). See **Appendix A: Structure of the excel data file.**

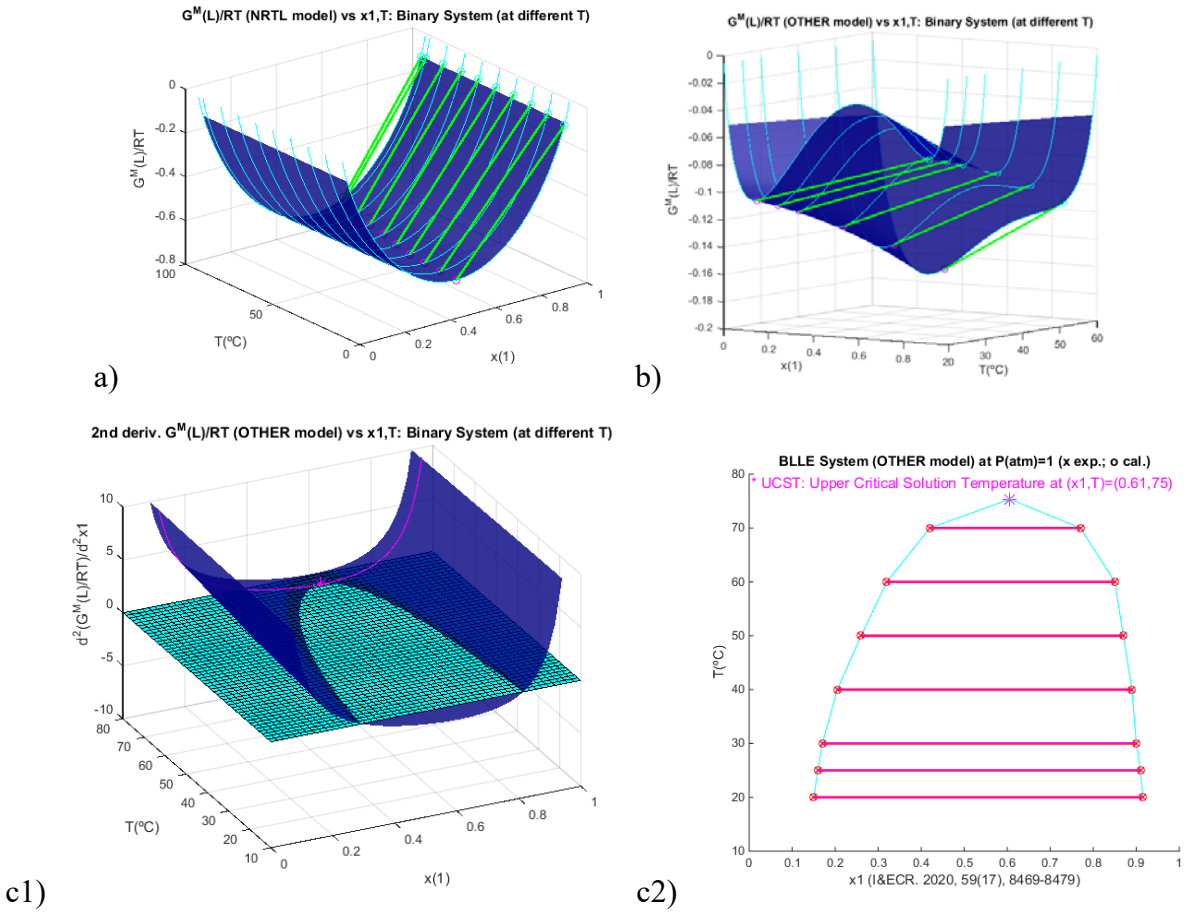


Figure 7. Additional graphics for ***LLE binary systems at different temperatures****: Evolution of the $G^M(L)/RT$ surface with the composition and temperature (including experimental tie-lines). a) Example with* ***not coherent*** *NRTL parameters (e.g. exampleLL_test4a.xls). b) Example with* ***coherent*** *parameters (e.g. exampleLL_test4b.xls). c) Determination of the critical solution temperature [18] (e.g. exampleLL_test4b.xls).*

In the case of using this GUI GMcal_TieLinesLL for binary systems without any experimental data just to analyse only the corresponding parameters and model, it is necessary:

-to write in the cell B3 of the excel file the word BINARY, and also

-to indicate that the total number of experimental tie-lines (Nt) is equal to 0 (cell B4 in the excel file).

-It is possible additionally to establish a range of temperatures to look for Critical Solution Temperatures. To do that can be used cells M10 and M11 (in increasing order). The range of temperatures defined by defect is 0-150ºC.

E.g. **exampleLL_test0B.xls**.

Finally, a new excel file for other binary or ternary case of study can be loaded to start again, or exit to the applications by using the exit push button.

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(ORCID: http://orcid.org/0000-0002-4870-2031)

After using this GUI GMcal_TieLinesLL, please complete the following quick inquiry to know your opinion about the graphical user interface developed:

English version. general user:
https://docs.google.com/forms/d/e/1FAIpQLSc_N4Oq0EMCkRjRgA1KeAwG8R8ZaxfZQ4lw-H3EjkMfruJvsw/viewform?c=0&w=1&usp=mail_form_link

Spanish version. Specific for Spanish students
https://docs.google.com/forms/d/e/1FAIpQLSfYkFzPrWK9iMummo210phzd3sgfEI-M-4U7TPIywc8ZpEmLw/viewform?c=0&w=1

Facebook:
http://www.facebook.com/GUI-for-the-analysis-of-the-Gibbs-stability-criteria-1861744990767271/

REMARK: IF YOU WANT TO RECEIVE A NOTIFICATION WITH POSSIBLE UPDATES OF THIS GUI. PLEASE SENT AN E-MAIL TO: ja.labarta@ua.es

APPENDIX A: STRUCTURE OF THE EXCEL DATA FILE FOR THE GMcal_TieLinesLL GUI

It is essential to respect the correct structure of the excel file. It is possible to use the file exampleLL_test.xls included as a draft for other case studies or systems.

1.- The active sheet of the excel file has to call it: **Example**
2.- The different data needed for the calculations and graphical representations has to be located in the following concrete cells of the active excel sheet:

Variable	Concrete cell location in the active (loaded) excel sheet
Pressure (atm)	B2
T(ºC)(*)	B3
Total number of experimental tie-lines (Nt<=40) (**)	B4
Model Used: (1: NRTL; 2: UNIQUAC; 3 or higher: OTHER MODEL (that has to be implemented previously in the ModelGExcess.m file)	B5
For NRTL model	---
NRTL binary parameter $T_{12}=A_{12}/RT$	E1 (** PARAM1)
NRTL binary parameter $T_{21}=A_{21}/RT$	E2 (** PARAM2)
NRTL binary parameter $T_{13}=A_{13}/RT$	E3 (** PARAM3)
NRTL binary parameter $T_{31}=A_{31}/RT$	E4 (** PARAM4)
NRTL binary parameter $T_{23}=A_{23}/RT$	E5 (** PARAM5)
NRTL binary parameter $T_{32}=A_{32}/RT$	E6 (** PARAM6)
NRTL binary parameter $\alpha_{12}=\alpha_{21}$	H3 (** PARAM7)
NRTL binary parameter $\alpha_{13}=\alpha_{31}$	H4 (** PARAM8)
NRTL binary parameter $\alpha_{23}=\alpha_{32}$	H5 (** PARAM9)
For UNIQUAC model	---
$T_{12}=\exp(-A_{12}/RT)$	E1
$T_{21}=\exp(-A_{21}/RT)$	E2
$T_{13}=\exp(-A_{13}/RT)$	E3
$T_{31}=\exp(-A_{31}/RT)$	E4
$T_{23}=\exp(-A_{23}/RT)$	E5
$T_{32}=\exp(-A_{32}/RT)$	E6
r_1	K3 (** PARAM10)
r_2	K4 (** PARAM11)
r_3	K5 (** PARAM12)
q_1	L3 (** PARAM13)
q_2	L4 (** PARAM14)
q_3	L5 (** PARAM15)
q'_1	M3 (** PARAM16)
q'_2	M4 (** PARAM17)
q'_3	M5 (** PARAM18)
Z	L6 (** PARAM19)

EXPERIMENTAL TIE-LINES*	
Molar fraction component 1 in Phase 1	A10:A50
Molar fraction component 2 in Phase 1	B10:B50
Molar fraction component 3 in Phase 1	C10:C50
Molar fraction component 1 in Phase 2	D10:D50
Molar fraction component 2 in Phase 2	E10:E50
Molar fraction component 3 in Phase 2	F10:F50
CALCULATED TIE-LINES✓	
Molar fraction component 1 in Phase 1	G10:G50
Molar fraction component 2 in Phase 1	H10:H50
Molar fraction component 3 in Phase 1	I10:I50
Molar fraction component 1 in Phase 2	J10:J50
Molar fraction component 2 in Phase 2	K10:K50
Molar fraction component 3 in Phase 2	L10:L50

(**) Initially, the maximum value of the total number of tie-lines admitted is: 40. This value can be equal to **0** for ternary and binary LLE systems, to analyze only the corresponding parameters and model. In the case of binary systems, it is also necessary to write in cell B3(*) of the excel file the word **BINARY** (see the corresponding examples: exampleLL_test0T.xls and exampleLL_test0B.xls).

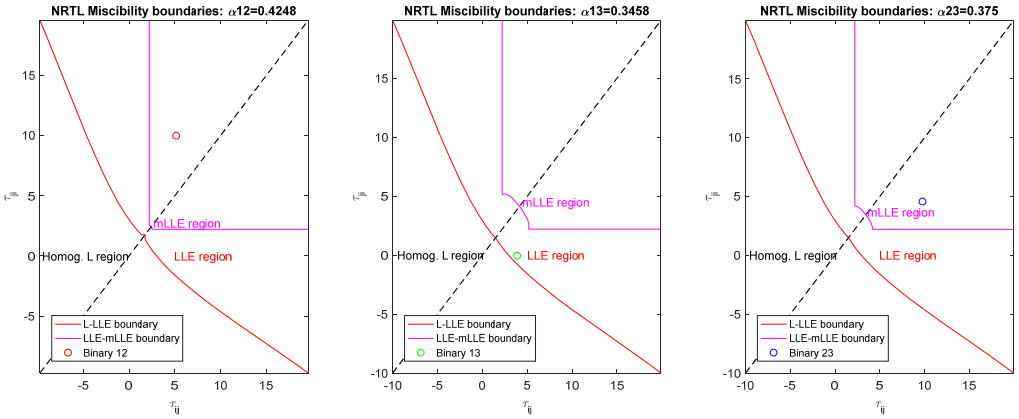
✓ **If calculated tie-lines are not available, the corresponding cells have to be empty.**

List of test files included (exampleLL_test.xls

LLE TERNARY SYSTEMS

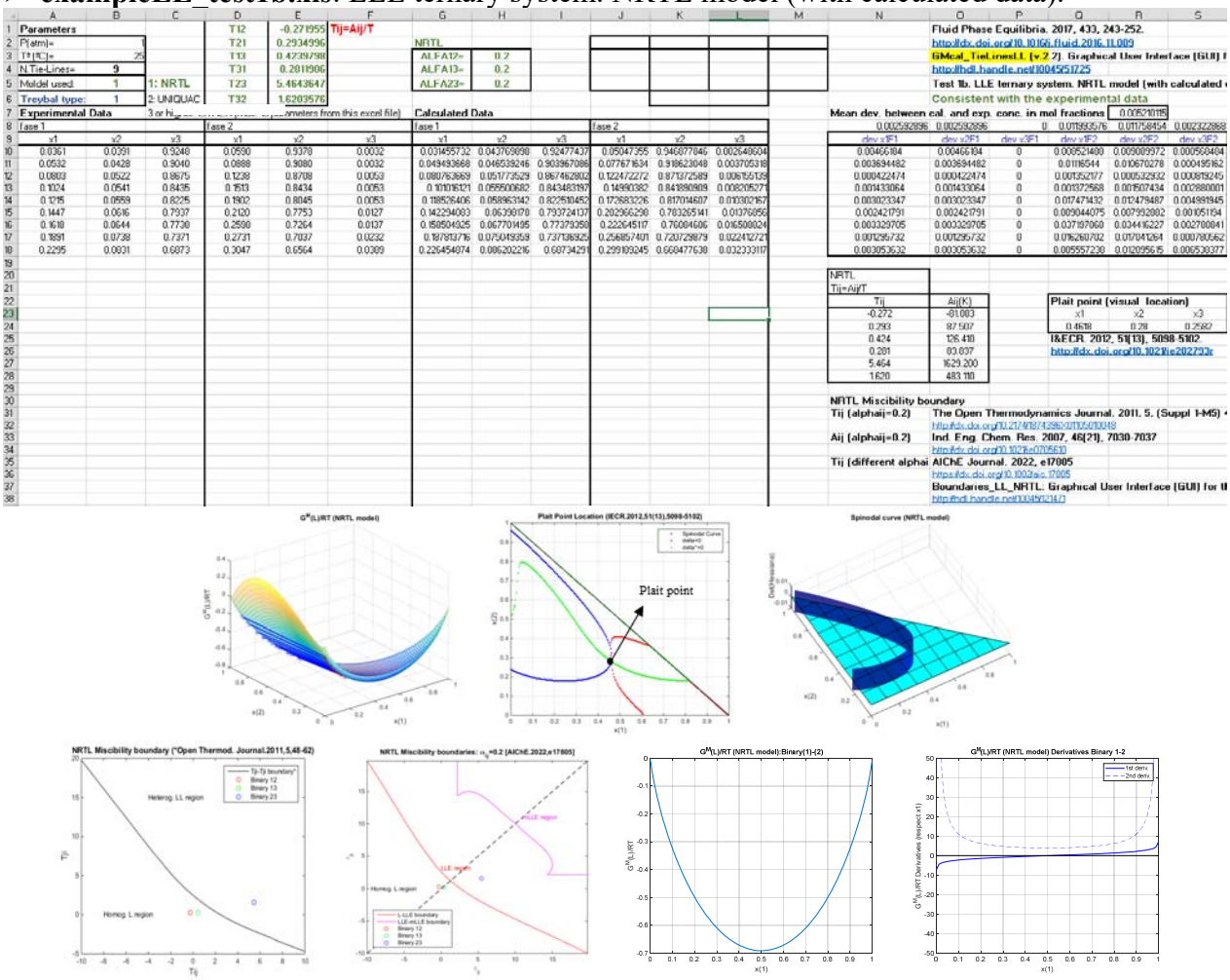
➢ **exampleLL_test1a.xls**: LLE ternary system. NRTL model (without calculated data).

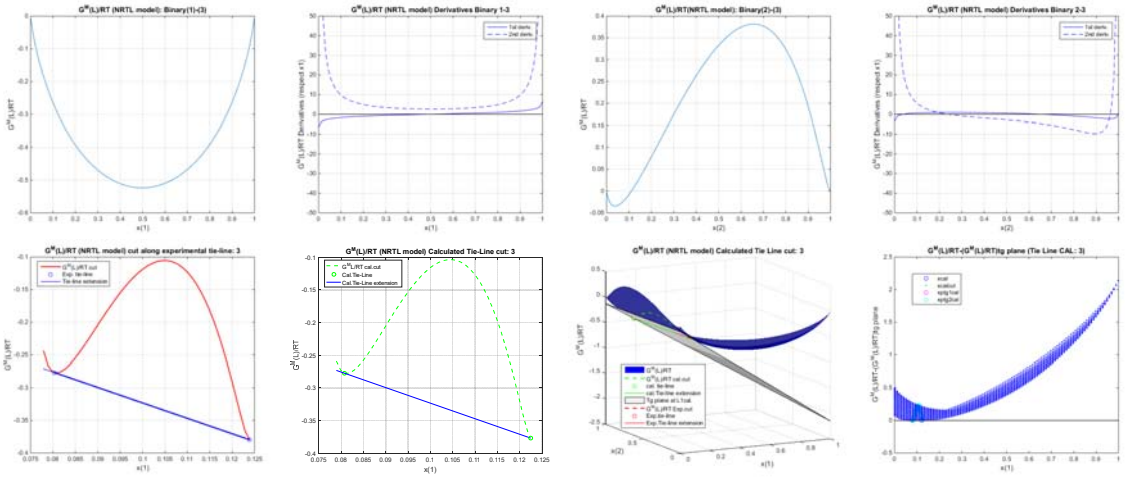
	A	B	C	D	E	F	G	H	I	J	K	L	M
1	**Parameters**			T12	5,149	Tij=Aij/(R·T)							
2	P(atm)=	1		T21	9,999		NRTL						
3	T ª (ºC)=	25		T13	3,868		ALFA12=	0,42					
4	N.Tie-Lines=	9		T31	-0,068		ALFA13=	0,35					
5	Moldel used:	1	1: NRTL	T23	9,771		ALFA23=	0,38					
6			2: UNIQUAC	T32	4,578								
7	**Experimental Data**		3: OTHER				**Calculated Data**						
8	fase 1			fase 2			fase 1			fase 2			
9	x1	x2	x3	x1	x2	x3	x1	x2	x3	x1	x2	x3	
10	0,036	0,039	0,925	0,059	0,938	0,003							
11	0,053	0,043	0,904	0,089	0,908	0,003							
12	0,080	0,052	0,867	0,124	0,871	0,005							
13	0,102	0,054	0,843	0,151	0,843	0,005							
14	0,122	0,056	0,823	0,190	0,805	0,005							
15	0,145	0,062	0,794	0,212	0,775	0,013							
16	0,162	0,064	0,774	0,260	0,726	0,014							
17	0,189	0,074	0,737	0,273	0,704	0,023							
18	0,230	0,083	0,687	0,305	0,656	0,039							



$0 < \alpha_{i,j} < 0.95$: AIChE Journal. 2022, e17805 (https://dx.doi.org/10.1002/aic.17805)

➢ **exampleLL_test1b.xls**: LLE ternary system. NRTL model (with calculated data).





➢ e.g. **exampleLL_test2.xls**: LLE ternary system. UNIQUAC model (without calculated data).

	A	B	C	D	E	F	G	H	I	J	K	L	M	N
1	**Parameters**			T12	1,43844874	Tij=exp(-Aij/T)				Remark: qi and q'i are different only for water and some small alcohols				
2	P(atm)=	1		T21	2,16509148					UNIQUAC	ri	qi	q'i	
3	T° (°C)=	25		T13	0,40101354					1	0,92	1,4	1,4	
4	N.Tie-Lines=	5		T31	0,10300668					2	2,1055	1,972	1,972	
5	Moldel used:	2	1: NRTL	T23	1,12206826					3	3,9228	2,968	2,968	
6			2: UNIQUAC	T32	0,69486078						z	10		
7	**Experimental Data**		3: OTHER				**Calculated Data**							
8	fase 1			fase 2			fase 1			fase 2				
9	x1	x2	x3	x1	x2	x3	x1	x2	x3	x1	x2	x3		
10	0,9997	0,0000	0,0003	0,0102	0,0000	0,9898								
11	0,8303	0,1667	0,0030	0,0151	0,0389	0,9461								
12	0,7351	0,2570	0,0079	0,0224	0,0860	0,8916								
13	0,6141	0,3644	0,0215	0,0382	0,1716	0,7902								
14	0,4754	0,4684	0,0561	0,0689	0,2963	0,6348								

➢ **exampleLL_test3.xls**: LLE ternary system. Alternative model (NRTL with $\tau_{ij} = a_{ij} + b_{ij}/T$). 15 parameters: 6 a_{ij}, 3 α_{ij}, 6 b_{ij}. Without calculated data.

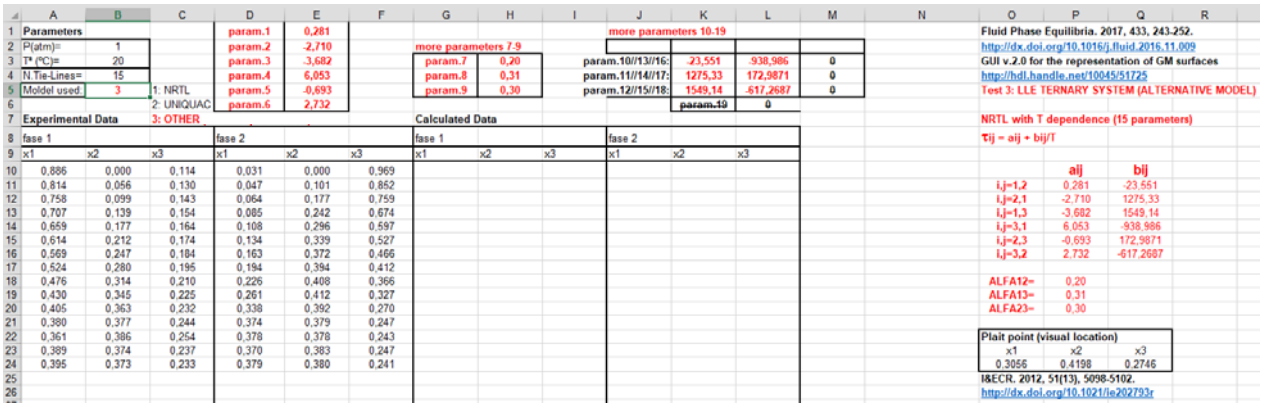
As commented before, in an alternative way, cells E1:E6; H3:H5; K3:K5; L3:L5; M3:M5 and L6 (in this order) could be used to introduce a maximum of 19 parameters directly from the excel file for any OTHER model (different to NRTL or UNIQUAC) to calculate the Gibbs Excess Function using the corresponding matlab function file (named: ModelGExcess.m) and keeping the following structure, variables and name:

```
Function
y=ModelGExcess(modelF,TEMP,x1,x2,x3,PARAM1,PARAM2,PARAM3,PARAM4,PARAM5,PARAM6,PARAM7,PARAM8,PARAM9
,PARAM10,PARAM11,PARAM12,PARAM13,PARAM14,PARAM15,PARAM16,PARAM17,PARAM18,PARAM19)
```

In any case, just to remember that if the temperature of the system is constant, any dependence of possible temperature dependent parameters (τ_{ij}) could also be used by recalculating the constant values of τ_{ij} at the given temperature. Additionally, also remark that any model with no limitations in the number of parameters could be use by including the model and the specific parameters directly in the MatLab function file: ModelGExcess.m.

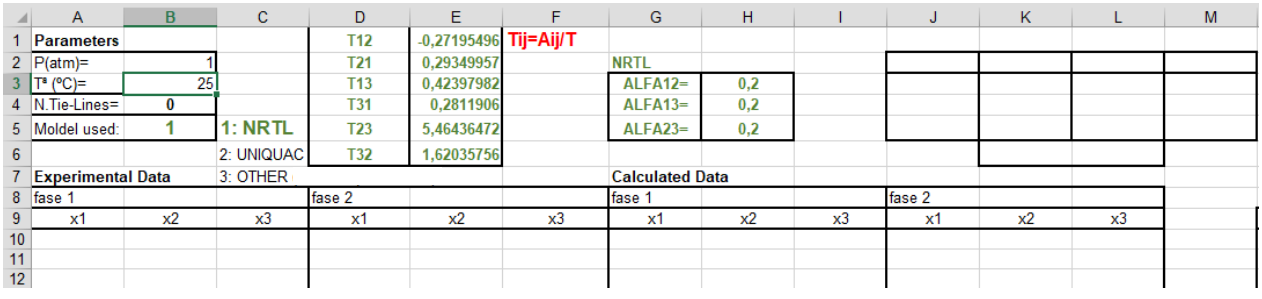
As example of the introduction of an additional model, in the exampleLL_test3.xls test file, a modified version of the NRTL model (e.g. used in Aspen Plus Software) for ternary systems with temperature dependent parameters: $\tau_{ji} = a_{ji} + b_{ji}/T$ (15 parameters: 6 a_{ij}, 3 α_{ij}, 6 b_{ij}) has also been introduced (this "other model" has been numbered in the ModelGExcess.m file as Model 3), following the previous indications where:

a_{12}	E1 (** PARAM1)
a_{21}	E2 (** PARAM2)
a_{13}	E3 (** PARAM3)
a_{31}	E4 (** PARAM4)
a_{23}	E5 (** PARAM5)
a_{32}	E6 (** PARAM6)
$\alpha_{12}=\alpha_{21}$	H3 (** PARAM7)
$\alpha_{13}=\alpha_{31}$	H4 (** PARAM8)
$\alpha_{23}=\alpha_{32}$	H5 (** PARAM9)
b_{12}	K3 (** PARAM10)
b_{21}	K4 (** PARAM11)
b_{13}	K5 (** PARAM12)
b_{31}	L3 (** PARAM13)
b_{23}	L4 (** PARAM14)
b_{32}	L5 (** PARAM15)



Just to remark the notation used for Aspen Plus in the case of the UNIQUAC model: $\tau_{ji} = \exp(a_{ji} + b_{ji}/T + \ldots) = \exp(-u_{ji}/RT) = \exp(-(g_{ji}-g_{ii})/RT) = \exp(-A_{ji}/RT)$.

- **exampleLL_test0T.xls**: LLE ternary system. NRTL model. Without exp. and calculated data (to analyze only the corresponding parameters and model).

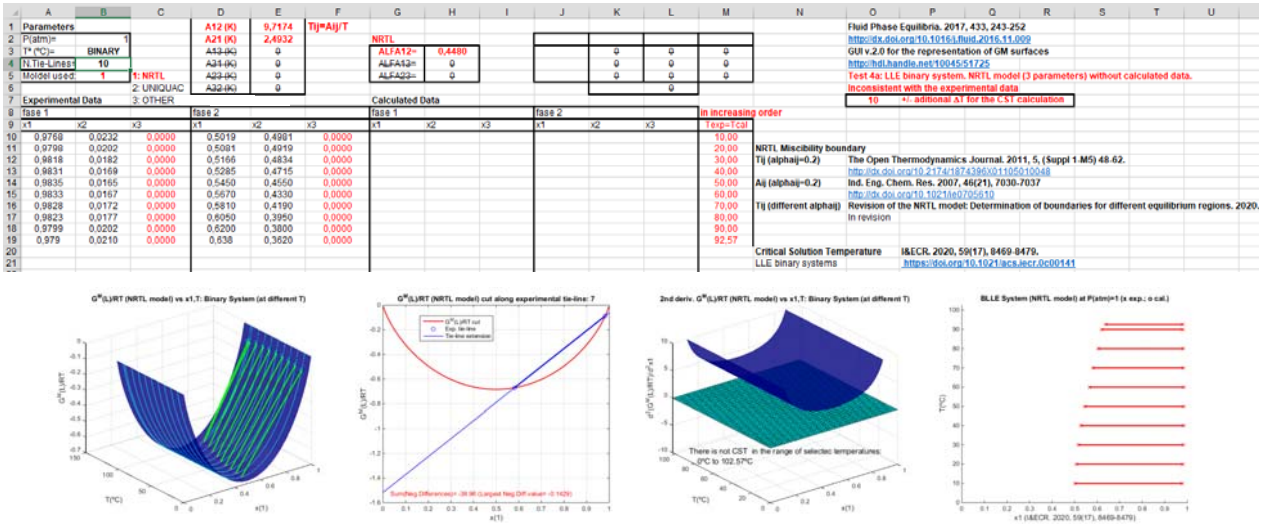


LLE BINARY SYSTEMS

As commented previously, the proposed GMcal_TieLinesLL GUI can also be used to represent additionally the evolution of a **binary system** at different temperatures (max. 40 points), including the location of the **critical solution temperature** (UCST, LCST or CML) if there exists (Ref.: Ind. Eng. Chem. Res. 2020, 59, 17, 8469–8479. https://doi.org/10.1021/acs.iecr.0c00141).

In this case, it is necessary to write in cell B3 of the excel file the word **BINARY,** and also an additional column including the temperature of each binary data (in increasing order) has also to be included with location = (**M10:M50**). Additionally, just in the case of the NRTL or UNIQUAC models, the parameters that have to be introduced are the A_{ji} (K) parameters (temperature independent variables). In cell **O6** of the corresponding excel file, it is possible to include an additional ΔT for the Critical Solubility Temperature calculation in the range of the experimental temperatures (by defect this ΔT=10).

- **exampleLL_test4a.xls:** NRTL model for the binary system (3 parameters) without calculated data.

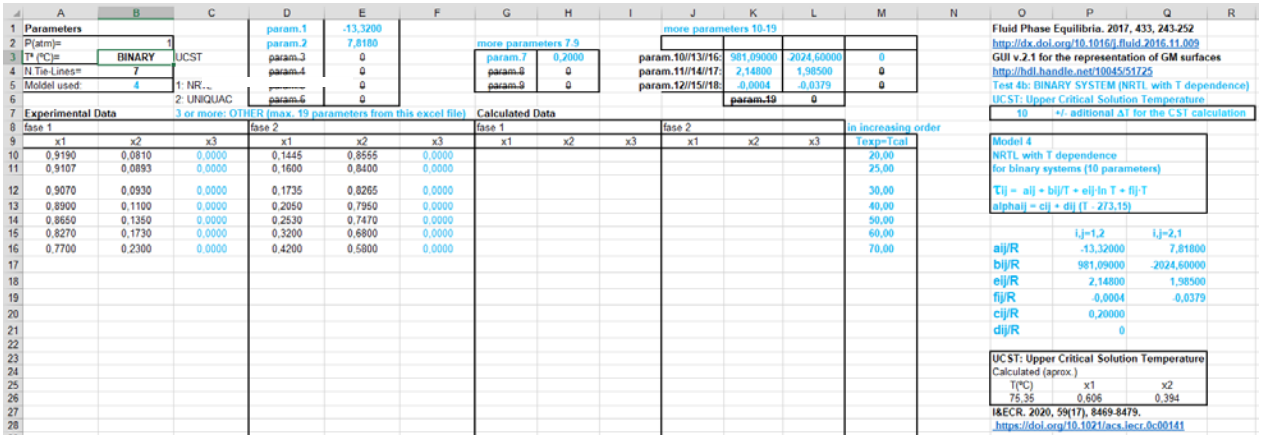


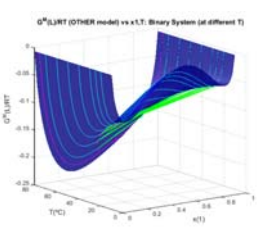
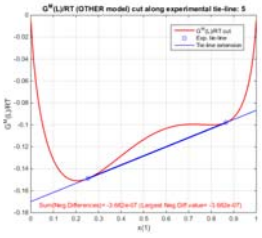
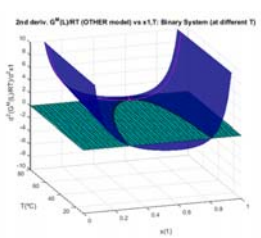
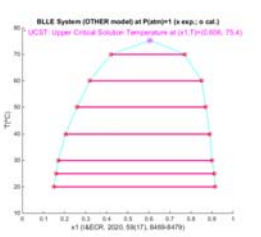
- **exampleLL_test4b-d.xls:** Using as "other model (max. 19 parameters directly from the excel file)", the NRTL model for a binary system with temperature dependent parameters (10 parameters):

$$\tau_{ji} = a_{ji} + b_{ji}/T + e_{ji}\cdot \ln T + f_{ji}\cdot T$$

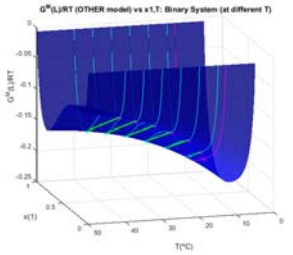
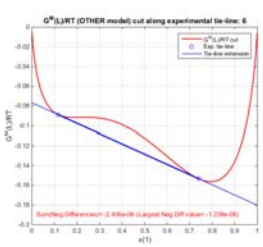
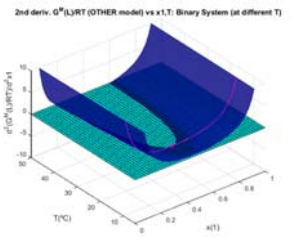
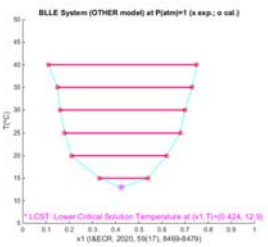
$$\alpha_{ji} = c_{ji} + d_{ji}\,(T - 273.15)$$

- This "other model" has been numbered in the ModelGExcess.m file as Model 4.

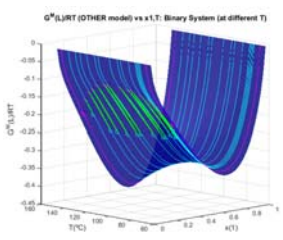
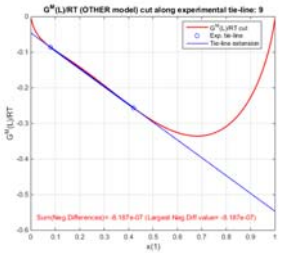
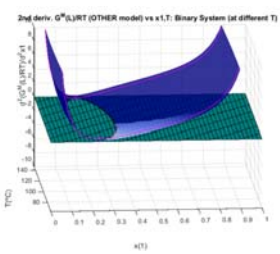
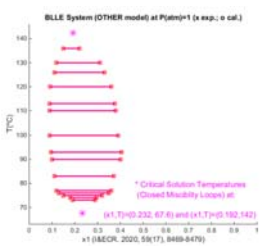


Parameters			param.1	-95,6300					more parameters 10-19				Fluid Phase Equilibria. 2017, 433, 243-252		
P(atm)=	1		param.2	-102,7000		more parameters 7-9							http://dx.doi.org/10.1016/j.fluid.2016.11.009		
T* (ºC)=	BINARY	LCST	param.3	0		param.7	0,2000		param.10//13//16:	-6,30280	-6,54080	0	GUI v.2.1 for the representation of GM surfaces		
N.Tie-Lines=	6		param.4	0		param.8	0		param.11//14//17:	20,49000	21,04000	0	http://hdl.handle.net/10045/51725		
Moldel used:	4	1: NRTL	param.5	0		param.9	0		param.12//15//18:	-0,0685	-0,0511	0	Test 4c: BINARY SYSTEM (NRTL with T dependence)		
		2: UNIQUAC	param.6	0						param.19	0		LCST: Lower Critical Solution Temperature		
Experimental Data		3 or more: OTHER (max. 19 parameters from this excel file)				**Calculated Data**							10 +/- aditional ΔT for the CST calculation		
fase 1			fase 2			fase 1			fase 2						
x1	x2	x3	x1	x2	x3	x1	x2	x3	x1	x2	x3	Texp-Tcal			
0,5300	0,4700	0,0000	0,3050	0,6950	0,0000							15,00	Model 4		
0,6250	0,3750	0,0000	0,2250	0,7750	0,0000							20,00	NRTL with T dependence		
0,6800	0,3200	0,0000	0,1820	0,8180	0,0000							25,00	for binary systems (10 parameters)		
0,7000	0,3000	0,0000	0,1550	0,8450	0,0000							30,00	$\tau_{ij} = aij + bij/T + eij \cdot \ln T + fij \cdot T$		
0,7300	0,2700	0,0000	0,1330	0,8670	0,0000							35,00	$alphaij = cij + dij\ (T - 273,15)$		
0,7400	0,2600	0,0000	0,1170	0,8830	0,0000							40,00			
														i,j=1,2	i,j=2,1
													aij/R	-95,63000	-102,70000
													bij/R	-6,30280	-6,54080
													eij/R	20,49000	21,04000
													fij/R	-0,0685	-0,0511
													cij/R	0,20000	
													dij/R	0	
													LCST: Lower Critical Solution Temperature		
													Calculated (aprox.)		
													T(ºC)	x1	x2
													12,95	0,4243	0,5757
													I&ECR. 2020, 59(17), 8469-8479.		
													https://doi.org/10.1021/acs.iecr.0c00141		

Parameters			param.1	-122,1000					more parameters 10-19				Fluid Phase Equilibria. 2017, 433, 243-252		
P(atm)=	1		param.2	-147,3000		more parameters 7-9							http://dx.doi.org/10.1016/j.fluid.2016.11.009		
T* (ºC)=	BINARY	CML	param.3	0		param.7	0,2000		param.10//13//16:	-6,33160	-6,56700	0	GUI v.2.1 for the representation of GM surfaces		
N.Tie-Lines=	15		param.4	0		param.8	0		param.11//14//17:	25,04000	30,01000	0	http://hdl.handle.net/10045/51725		
Moldel used:	4	1: NRTL	param.5	0		param.9	0		param.12//15//18:	-0,0722	-0,0712	0	Test 4d: BINARY SYSTEM (NRTL with T dependence)		
		2: UNIQUAC	param.6	0						param.19	0		Closed Miscibility Loops		
Experimental Data		3 or more: OTHER (max. 19 parameters from this excel file)				**Calculated Data**							10 +/- aditional ΔT for the CST calculation		
fase 1			fase 2			fase 1			fase 2			in increasing order			
x1	x2	x3	x1	x2	x3	x1	x2	x3	x1	x2	x3	Texp-Tcal			
0,2900	0,7100	0,0000	0,1900	0,8100	0,0000							73,00	Model 4		
0,2950	0,7050	0,0000	0,1800	0,8200	0,0000							74,00	NRTL with T dependence		
0,3200	0,6800	0,0000	0,1500	0,8500	0,0000							75,00	for binary systems (10 parameters)		
0,3500	0,6500	0,0000	0,1300	0,8700	0,0000							76,00	$\tau_{ij} = aij + bij/T + eij \cdot \ln T + fij \cdot T$		
0,3600	0,6400	0,0000	0,1200	0,8800	0,0000							77,00	$alphaij = cij + dij\ (T - 273,15)$		
0,3700	0,6300	0,0000	0,1100	0,8900	0,0000							83,00			
0,4200	0,5800	0,0000	0,1000	0,9000	0,0000							90,00		i,j=1,2	i,j=2,1
0,4250	0,5750	0,0000	0,0950	0,9050	0,0000							93,00	aij/R	-122,10000	-147,30000
0,4200	0,5800	0,0000	0,0800	0,9200	0,0000							100,00	bij/R	-6,33160	-6,56700
0,3800	0,6200	0,0000	0,0890	0,9110	0,0000							110,00	eij/R	25,04000	30,01000
0,3750	0,6250	0,0000	0,0895	0,9105	0,0000							113,00	fij/R	-0,0722	-0,0712
0,3600	0,6400	0,0000	0,0920	0,9080	0,0000							120,00	cij/R	0,20000	
0,3300	0,6700	0,0000	0,1100	0,8900	0,0000							126,00	dij/R	0	
0,3100	0,6900	0,0000	0,1200	0,8800	0,0000							130,00			
0,2200	0,7800	0,0000	0,1500	0,8500	0,0000							136,00	UCST: Upper Critical Solution Temperature		
													Calculated (aprox.)		
													T(ºC)	x1	x2
													142,4	0,1920	0,8080
													I&ECR. 2020, 59(17), 8469-8479.		
													https://doi.org/10.1021/acs.iecr.0c00141		
													LCST: Lower Critical Solution Temperature		
													Calculated (aprox.)		
													T(ºC)	x1	x2
													67,59	0,2324	0,7676

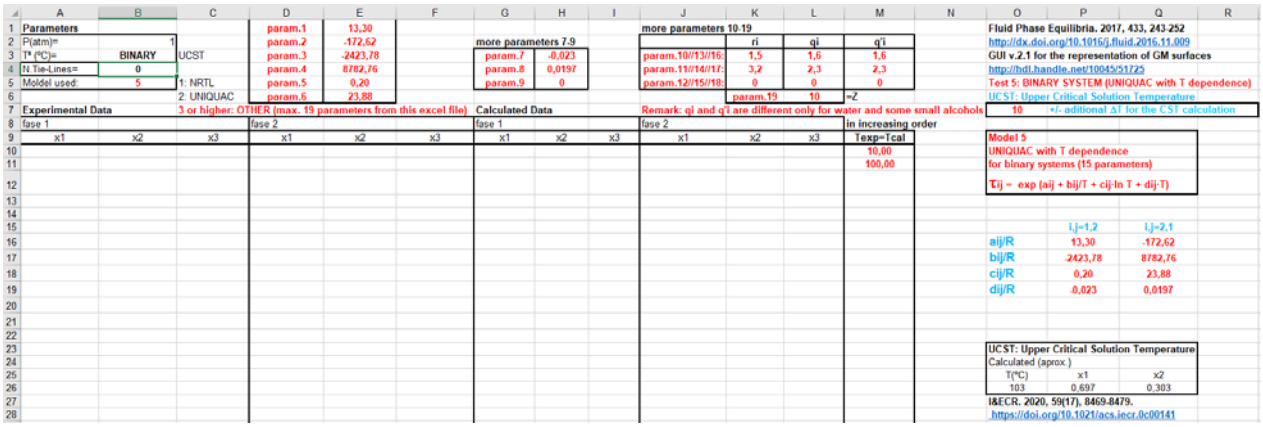





- **exampleLL_test5.xls:** Using as "other model (max. 19 parameters directly from the excel file)", the UNIQUAC model for a binary system with temperature dependent parameters (13 parameters):

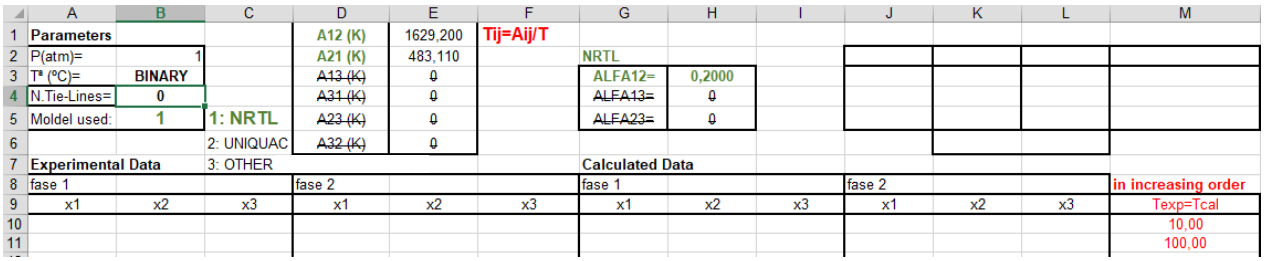
$$\tau_{ji} = \exp\left(a_{ji} + b_{ji}/T + c_{ji}\cdot \ln T + d_{ji}\cdot T\right)$$

Just to remark the notation used for Aspen Plus in the case of the UNIQUAC model: $\tau_{ji} = \exp(a_{ji} + b_{ji}/T + \ldots) = \exp(-u_{ji}/RT) = \exp(-(g_{ji}-g_{ii})/RT) = \exp(-A_{ji}/RT)$.

This "other model" has been numbered in the ModelGExcess.m file as Model 5.



- **exampleLL_test0B.xls:** LLE binary system. NRTL model with temperature dependence. Without exp. and calculated data (to analyze only the corresponding parameters and model).



**After using this GUI GMcal_TieLinesLL, please complete the following quick inquiry to know your opinion about the graphical user interface developed:

English version
General user

Spanish version
Specific for Spanish students

Facebook

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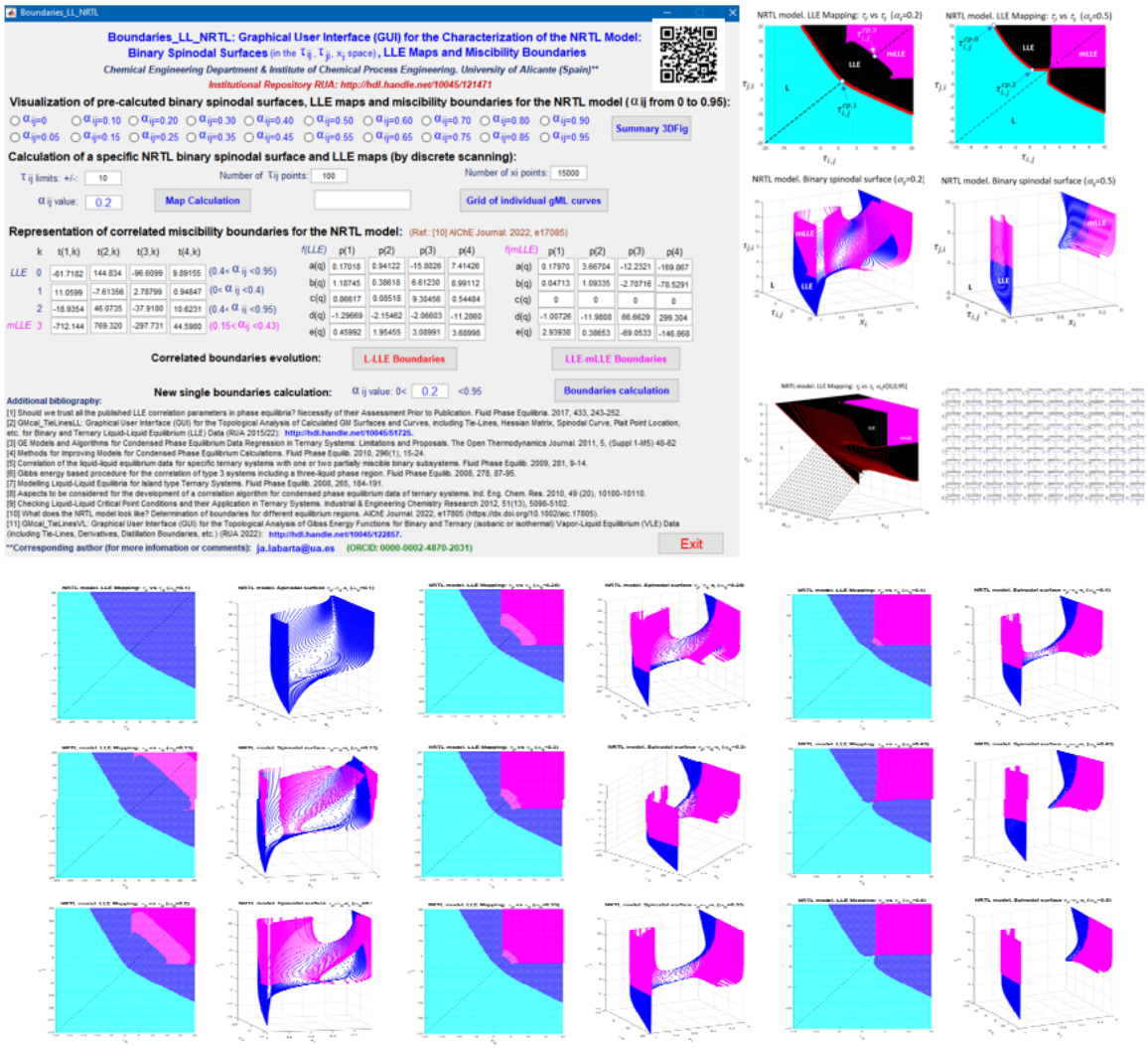

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GMcal_TieLinesVL
GMcal_TieLinesVL (v.2.2): TOPOLOGICAL ANALYSIS OF VAPOR-LIQUID EQUILIBRIUM DATA AND CORRELATIONS
Graphical User Interface (GUI) for the Represenation of Experimental and Calculated GM Functions for Binary and Ternary (isobaric or isothermal) Vapor-Liquid Equilibrium (VLE or VLLE) data (including Tie-Lines, Derivatives, Distillation Boundaries, LL Critical Points, etc.)
--- using NRTL, UNIQUAC or an alternative model ---
Chemical Engineering Department & Institute of Chemical Process Engineering. University of Alicante (Spain)**
Institutional Repository RUA: http://hdl.handle.net/10045/122857
Data source: Introduce Excel file name and press enter:
exampleVLisoP_test2 .xls
Data Loaded!!
Remark, parameters: NRTL: Aij (K) and αij = αji; UNIQUAC: Aij (K); ri; qi; q'i and Z
Graphical and topological analysis:
GM/RT values at VL Tie-Lines
GM/RT funtions: 3D representations and LL Critical Points Analysis (interval)
Ref.: [8,9]
Comparatives of GM/RT and d(GM/RT)/dx1 calculated with models and with the experimental data
Equilibrium Diagrams (data)
Ternary Tie-Lines Map and 3D Txy Equilibrium Diagram (calculated)
Ref.: [10, 11]
NRTL Binary Parameter Boundaries (τji vs τij) for Total and Partial Miscibility:
Correlated miscibility boundaries
Ref.: [5] The Open Thermodynamics Journal, 2011, 5, 48-62.
http://hdl.handle.net/10045/19865
Ref.: [6] AIChE Journal. 2022, e17085.
[7] GUI Boundaries_LL_NRTL: http://hdl.handle.net/10045/121471
GM/RT functions along selected tie-line:
Number of the Tie-line to represent:
(if zero all tie-lines will be respresented)
3
(press enter)
Tie-Line GM/RT curves
Additional bibliography:
[1] Should we trust all the published LLE correlation parameters in phase equilibria? Necessity of their Assessment Prior to Publication. Fluid Phase Equilibria. 2017, 433, 243-252.
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[6] What does the NRTL model look like? Determination of boundaries for different fluid phase equilibrium regions. AIChE Journal. 2022, e17805 (https://dx.doi.org/10.1002/aic.17805).
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**Corresponding author (for more infomation or comments): ja.labarta@ua.es (ORCID: 0000-0002-4870-2031)
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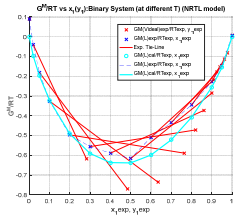
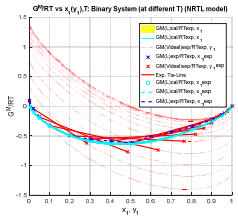
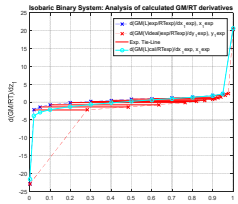
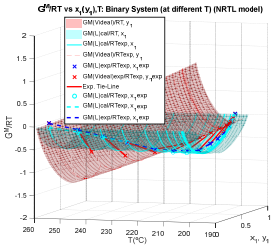
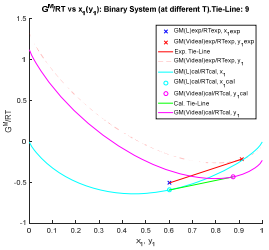
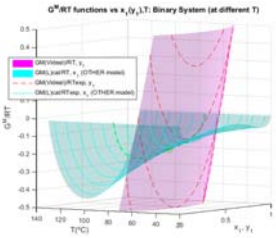


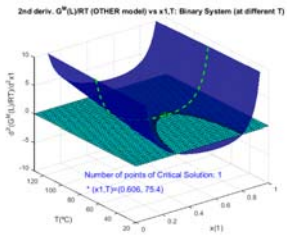


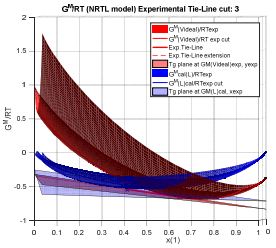


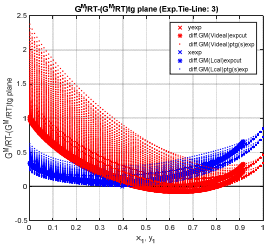


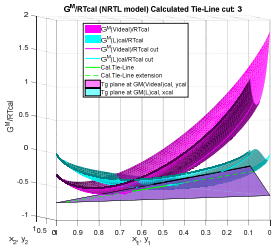


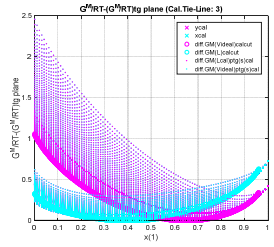


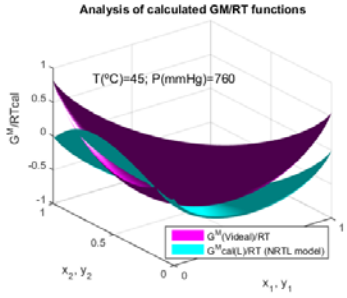


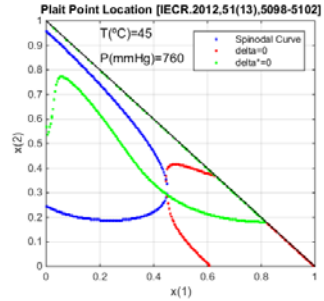


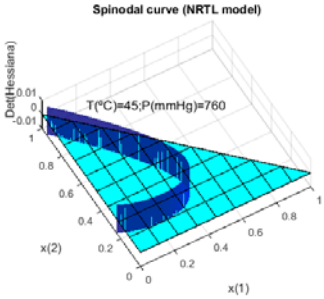


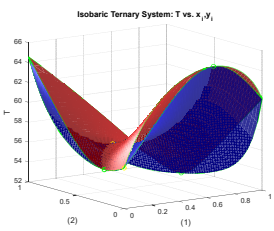


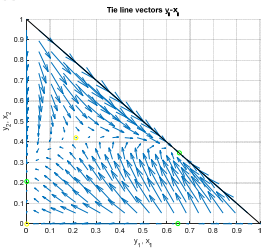



Analysis of calculated GM/RT functions
T(ºC)=45; P(mmHg)=760
GM(Videal)/RT
GMcal(L)RT (NRTL model)


Plait Point Location [IECR.2012,51(13),5098-5102]
T(ºC)=45
P(mmHg)=760
Spinodal Curve
delta=0
delta*=0


Spinodal curve (NRTL model)
T(ºC)=45;P(mmHg)=760


Isobaric Ternary System: T vs. x1,y1


Tie line vectors x1-x1

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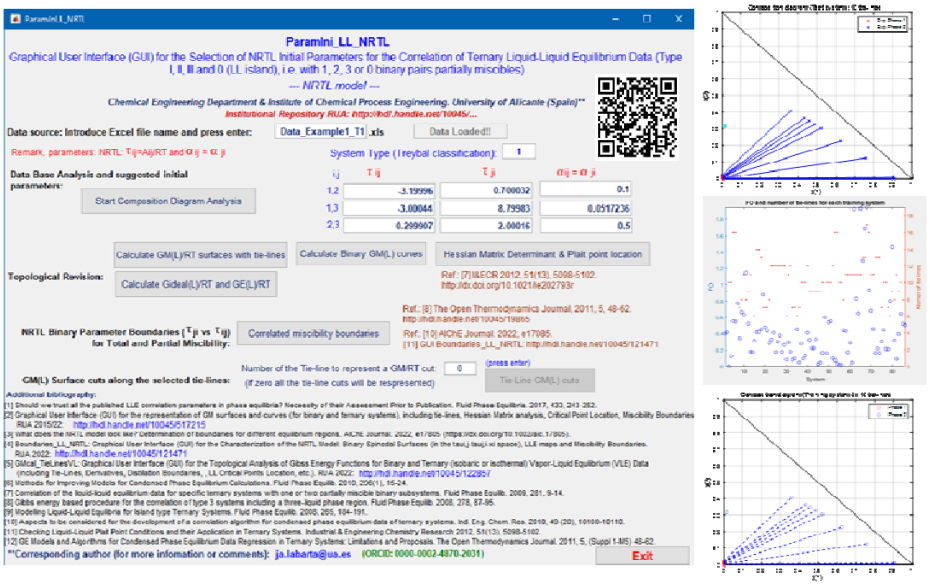

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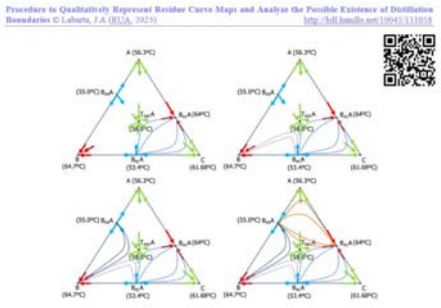

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