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 miscibles)

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INTRODUCTION AND USER INSTRUCTIONS*

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Keywords: NRTL model, phase equilibria, experimental data correlation, LLE, initial parameters.

1. INTRODUCTION

The correlation of liquid-liquid equilibrium data is still currently a problem not fully resolved, especially for complex systems such as, those involving ionic liquid (Rodríguez-Escontrela et al. 2016, Zhu et al. 2020, Zhang et al. 2020), etc., where the high nonlinearity and non-convexity of the equations involved produce convergence problems, with a strong dependence on the initialization values used of the obtained solution (Marcilla et al. 2017, Labarta et al. 2022a). To avoid this situation, for the NRTL model, we have analyzed more than 200 LLE ternary systems (including type I, II, III and 0 or island, following the Treybal classification, Figure 1) in order to obtain a good representation of the different possible binodal curves and tie triangles that this model can reproduce satisfactorily, in a wide enough interval of values of the different parameters ($\tau_{i,j}$, $\alpha_{i,j}$). All these systems have been parametrized regarding the main characteristics of the corresponding LLE, such as the number of binary subsystems partially miscible, the size and middle point of the binary tie-lines, the slope of the tie-lines, the location of the plate point (Marcilla et al. 2012), etc.

With this parametrization, we have created a database and a new graphical user interface, GUI (Labarta et al. 2022b-d) that allows loading a set of liquid-liquid experimental data to obtain, using optimization algorithms and machine learning techniques, a consistent set of initial NRTL parameters that predicts a parametrized LLE near the experimental one. This set of parameters can be used now in any correlation data algorithm (using the corresponding equilibrium condition: isoactivity, minimum of the global Gibbs energy of mixing, or the Gibbs energy of mixing minor common tangent plane) to obtain the final rigorous solution (Marcilla et al. 2011).

We believe that the present work can help researchers, professionals and students, in the task of correlating experimental liquid-liquid equilibrium data, in order to obtain consistent binary interaction parameters, taking into account that the correct calculation of the phase equilibrium is a key point in the optimal (efficient and sustainable) design of the corresponding processes and equipment.

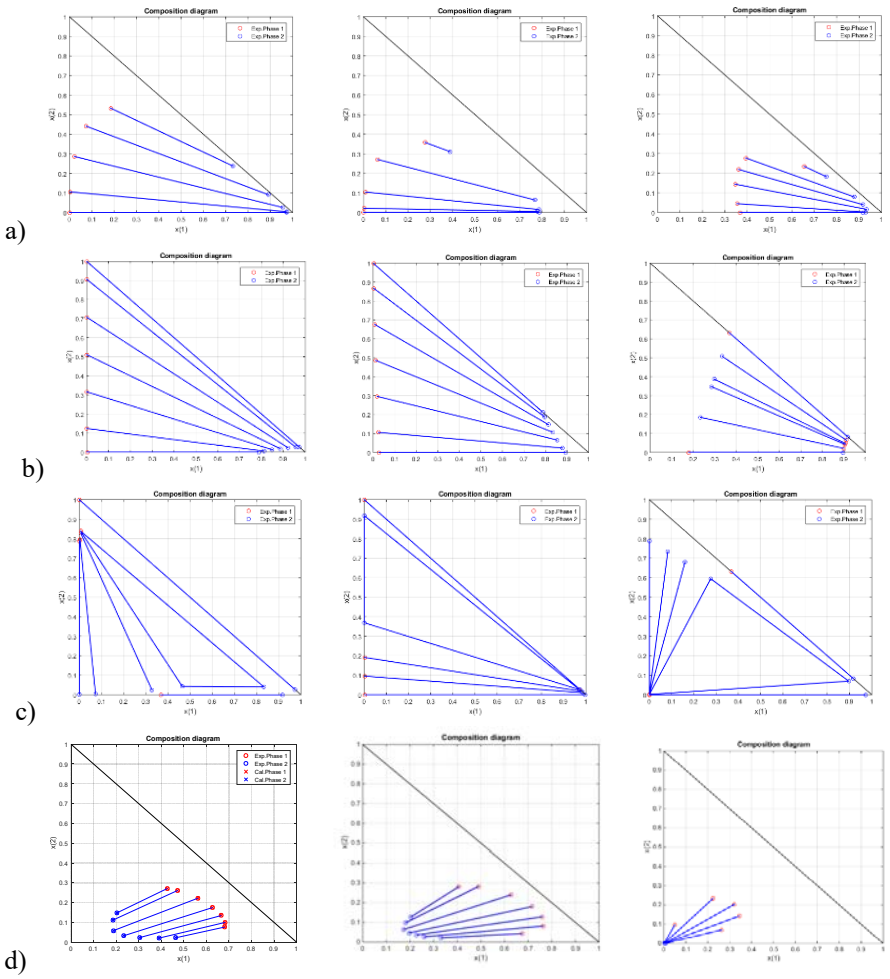


Figure 1. Examples of different LLE behaviors: a) Type I with only one binary partially miscible, b) Type II with two binaries partially miscible, c) Type III with three binaries partially miscible and a tie-triangle, d) Type 0 without binaries partially miscible but with an internal region of two liquids partially miscible.

2. DOWNLOAD INSTRUCTIONS

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

3. BEFORE USING THE GUI ParamIni_LL_NRTL

1. In order to use this GUI it is necessary to have an excel file with an adequate structure for each type of LLE (I, II, III or 0) system, 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 Data_Examplei_Ti.xls included, as a draft for others similar case studies (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 model)

   c. The total number of experimental tie-lines (Nt) (max. value: 40).

d. Experimental molar fractions

e. Specific information depending on the type of system (such as plate point or tie triangle)

4. CLASIC G^M MODELS RESUME

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

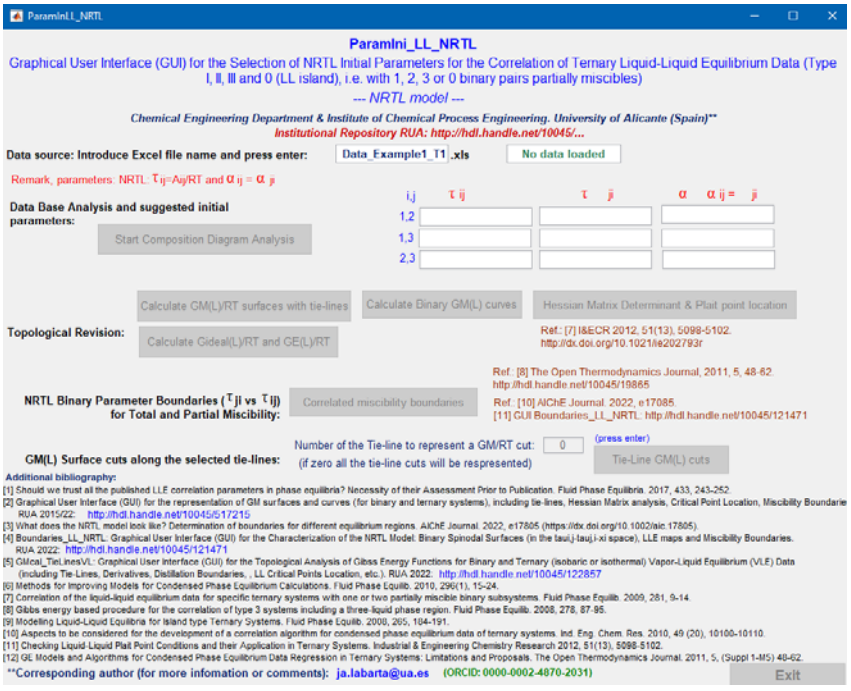
NRTL model:

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

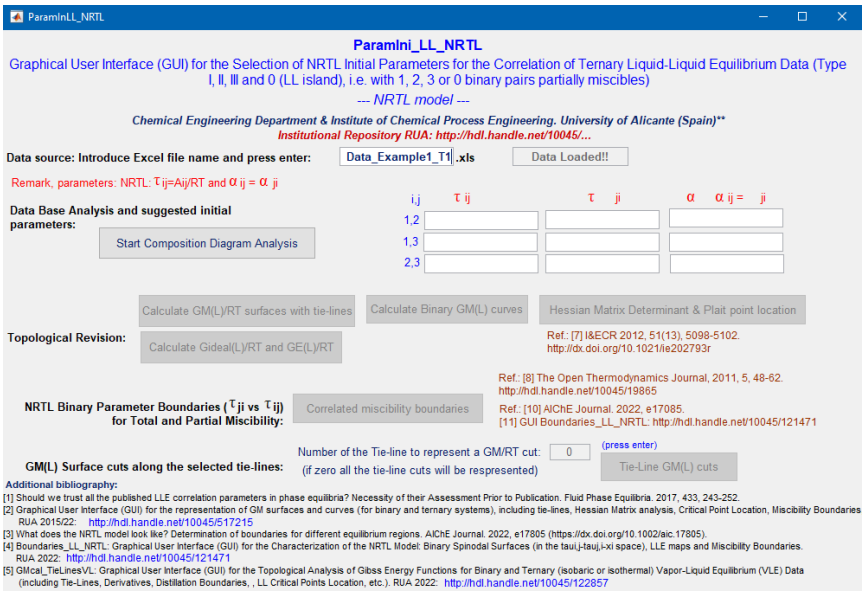
and $\alpha_{i,j} = \alpha_{j,i}$

5. USING THE GUI ParamIni_LL_NRTL

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

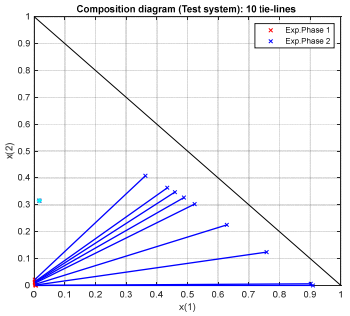


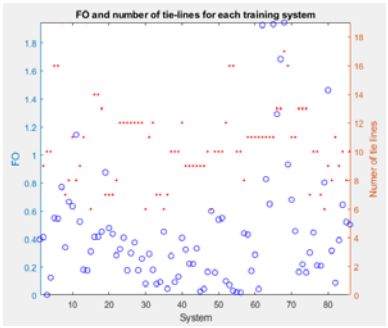
4. At this moment only the windows of the excel file name is active. Introduce the name of the excel data file corresponding to the system under study type 1, 2, 3, or 0 (e.g. Data_Example1_T1) and ***press enter***. Please wait a moment for the data load process.

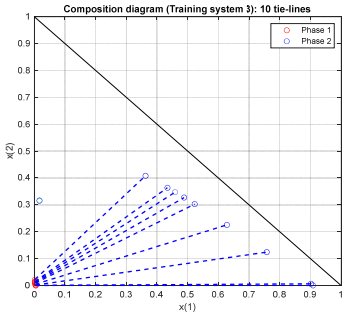


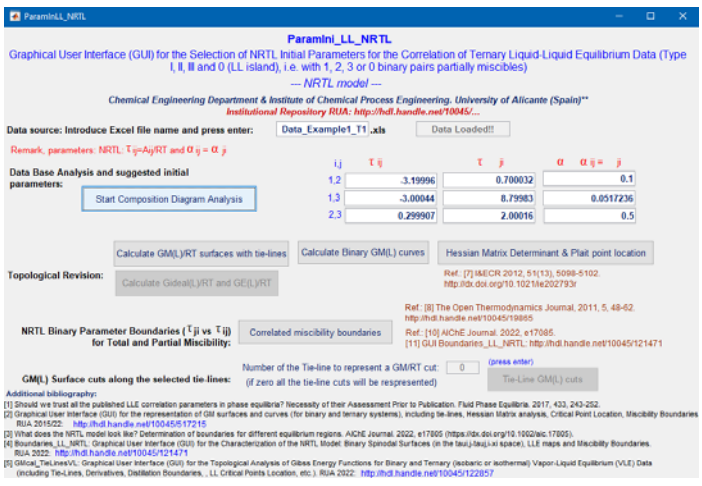
5. Now it is possible to start with the database analysis in order to obtain a consistent set of initial guest NRTL parameters for the correlation of the LLE under study by using the corresponding push buttons.

   Once this analysis finish, the suggested set of initial NRTL parameters appears. Additionally, three figures are shown: the ternary composition diagram (in molar fractions) of the system under study, a revision of the results regarding the system analysed, and the ternary composition diagram of the system included in the database with the biggest percentage of similitude (taking into account the parametrization done to characterize the corresponding LLE and solubility curves).









6. At this point it is possible to check the consistency of the suggested parameters by analyzing the topology of the calculated Gibbs Energy of Mixing Function [1,2], the calculated plait point [3], and the corresponding miscibility boundaries of the NRTL model [4-6], by pushing the push buttons:

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

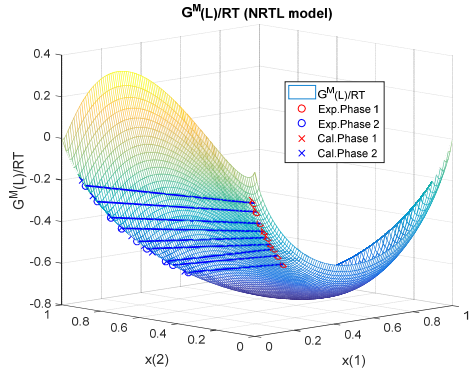
B) Calculated Binary G^M(L) curves, including 1st and 2nd derivatives (to facilitate the topological analysis).

C) 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:

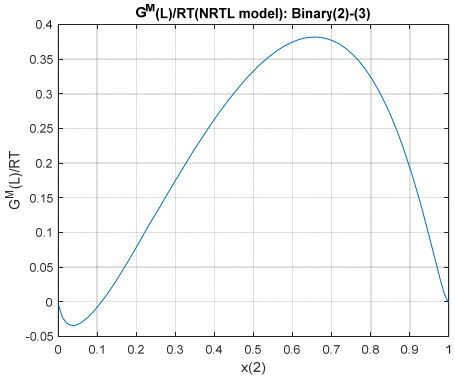
$$\sigma = \begin{vmatrix} \frac{\partial^2 G^M}{\partial^2 x_1} & \frac{\partial^2 G^M}{\partial x_1 \partial x_2} \\ \frac{\partial^2 G^M}{\partial x_2 \partial x_1} & \frac{\partial^2 G^M}{\partial^2 x_2} \end{vmatrix} = 0;\ \delta = \begin{vmatrix} \frac{\partial \sigma}{\partial x_1} & \frac{\partial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

D) Correlated NRTL binary Miscibility Boundaries (e.g. for Total and Partial Miscibility): $\tau_{j,i}$ vs $\tau_{i,j}$ (for α_{ij}=0.2) and for α_{ij} between 0 and 0.95). The obtained $\tau_{i,j}$ binary parameters are also represented, to check their adequate location.

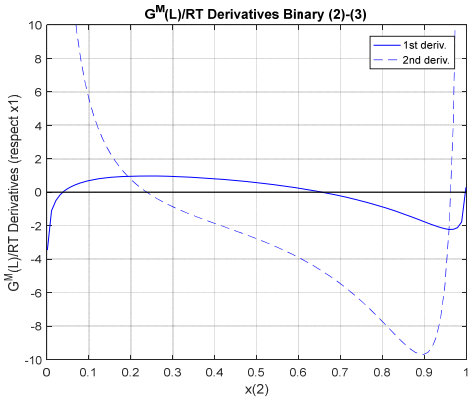
A)



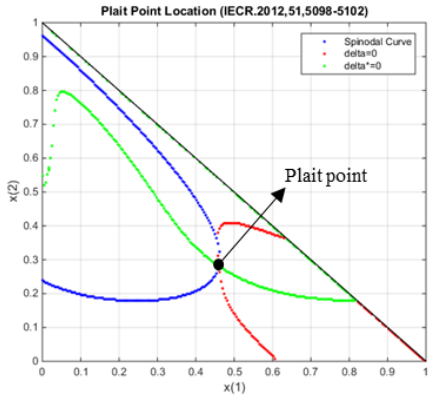
B1)



B2)



C)



D)

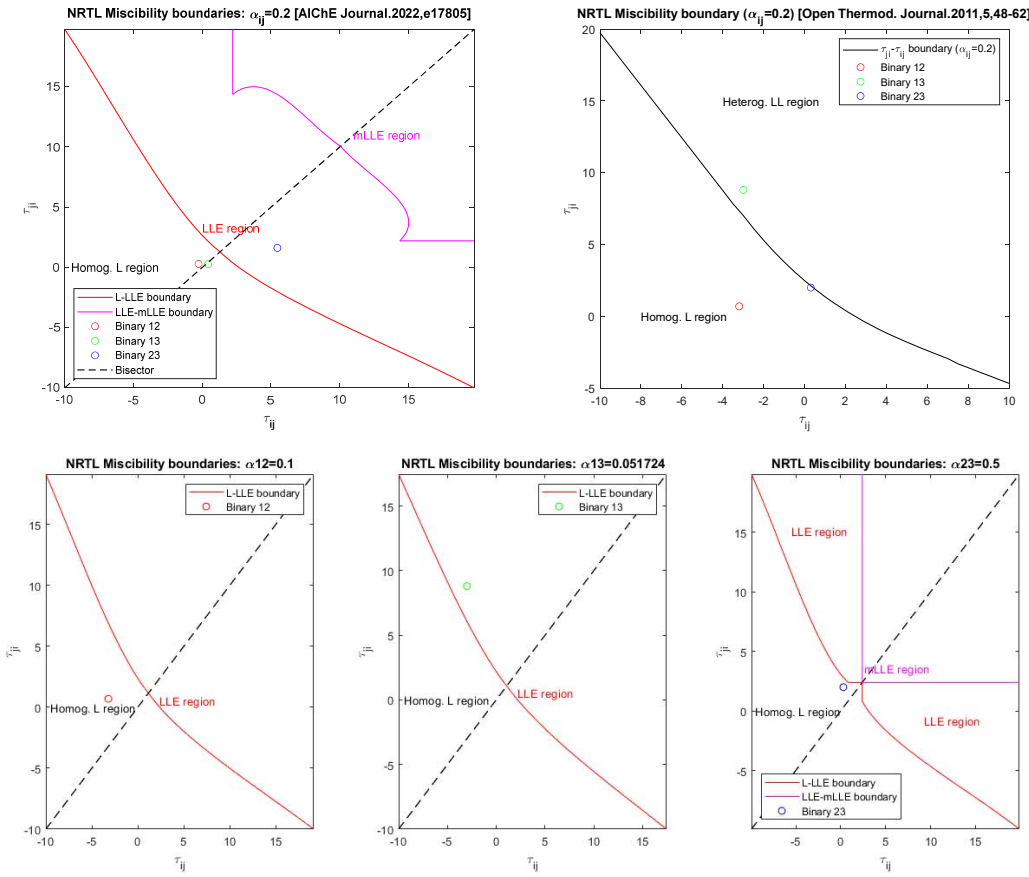
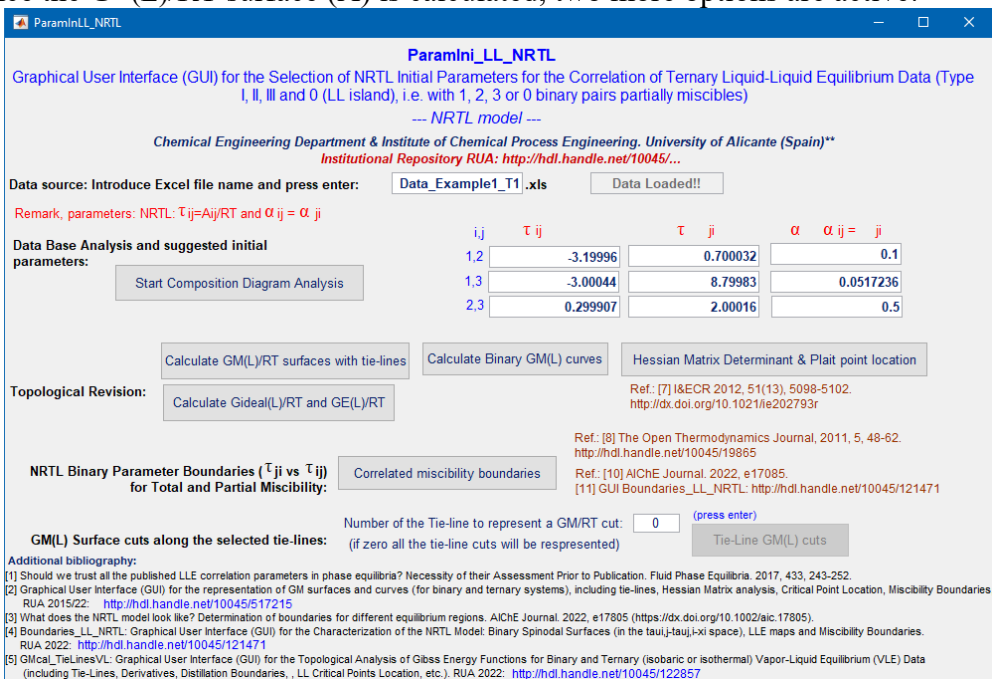


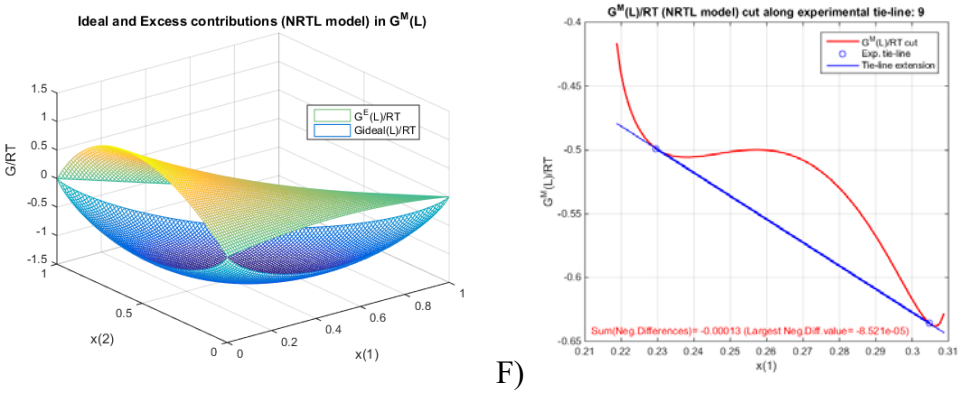
Figure 2. Examples of different diagrams for the topological analysis of NRTL parameters.

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



E) $G^{Ideal}(L)/RT$ and $G^E(L)/RT$ surfaces (ideal and excess contributions of the $G^M(L)/RT$ function calculated with the suggested NRTL: Push button.

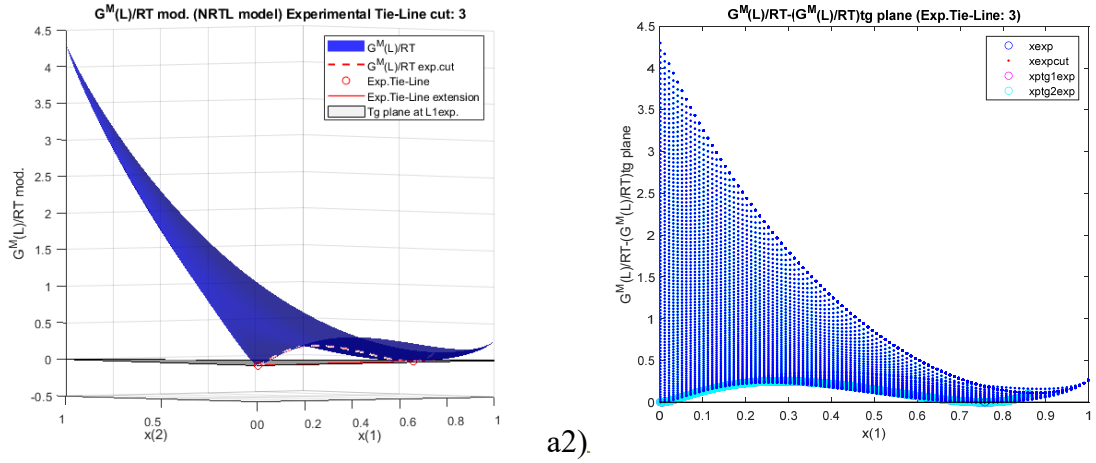
F) $G^M(L)/RT$ surface cuts along the selected Experimental Tie-Lines. In this case, the ordinal number corresponding to a tie-line (from 0 to Nt) has to be introduced (the value 0 will select the representation of the different cuts along all the experimental tie-lines). Then ***press enter***. After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



E) F)

Figure 3. Different diagrams: Ideal and Excess contribution, and $G^M(L)/RT$ cut along an exp. tie-line.

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 4). 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 experimental (Figure 4.a1). 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 Figure 4.a2). Evidently, this difference in the equilibrium compositions should be equal to zero.



a1) a2)

Figure 4. Complete $G^M(L)/RT$ surface including the selected tie-line and the tangent planes at both extremes of the experimental tie-line. Remark: the values of the $G^M(L)/RT$ surface have been modified to draw horizontal tangent planes to facilitate the viewing.

In order to complement this visual analysis in a rigorous way, 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 5). 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 5. Example of the additional information that appears at the Command Window after pushing the "Tie-Line GM(L) cuts" button.

Finally, a new excel file for other 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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REMARK: IF YOU WANT TO RECEIVE A NOTIFICATION WITH POSSIBLE UPDATES OF THIS GUI. PLEASE SENT AN E-MAIL TO: ja.labarta@ua.es

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

It is essential to respect the correct structure of the excel file. It is possible to use the file Data_Examplei_Ti.xls included as a draft for other case studies or systems. (Note that this structure is totally compatible with the excel test files for the GUI GMcal_TieLinesLL: http://hdl.handle.net/10045/51725).

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. It is important to remark that for type 1 systems, the binary 13 has to be the binary partially miscible, and for type 2 systems, the binary subsystems that have to be partially miscible are de 13 and 23:

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)	B5
Treybal type: (0, 1, 2 or 3)	B6
For Treybal type 1 systems: Plait point location	---
Molar fraction component 1	Q24
Molar fraction component 2	R24
Molar fraction component 3	S24
For Treybal type 3 systems: Tie triangle or Plait points location (x1 increasing order)	---
Molar fraction component 1 (lowest)	Q24
Molar fraction component 2	R24
Molar fraction component 3	S24
Molar fraction component 1 (intermediate)	Q25
Molar fraction component 2	R25
Molar fraction component 3	S25
Molar fraction component 1 (higher)	Q26
Molar fraction component 2	R26
Molar fraction component 3	S26
For Treybal type 0 systems: Plait points (x1 increasing order)	---
Molar fraction component 1 (lowest)	Q24
Molar fraction component 2	R24
Molar fraction component 3	S24
Molar fraction component 1 (higher)	Q25
Molar fraction component 2	R25
Molar fraction component 3	S25

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

(**) Initially, the maximum value of the total number of tie-lines admitted is: 40.

List of test files included (Data_Examplei_Ti.xls.xls)

- **Data_Example1_T1.xls.xls**: LLE ternary system (Type 1).
- **Data_Example2_T2.xls.xls**: LLE ternary system (Type 2).
- **Data_Example3_T3.xls.xls**: LLE ternary system (Type 3).
- **Data_Example4_T0.xls.xls**: LLE ternary system (Type 0).

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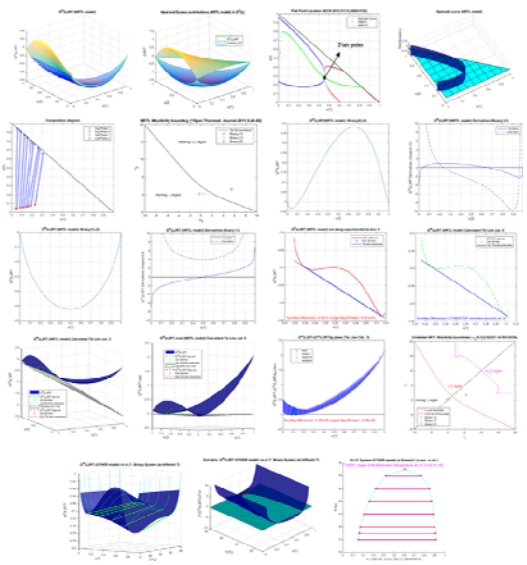

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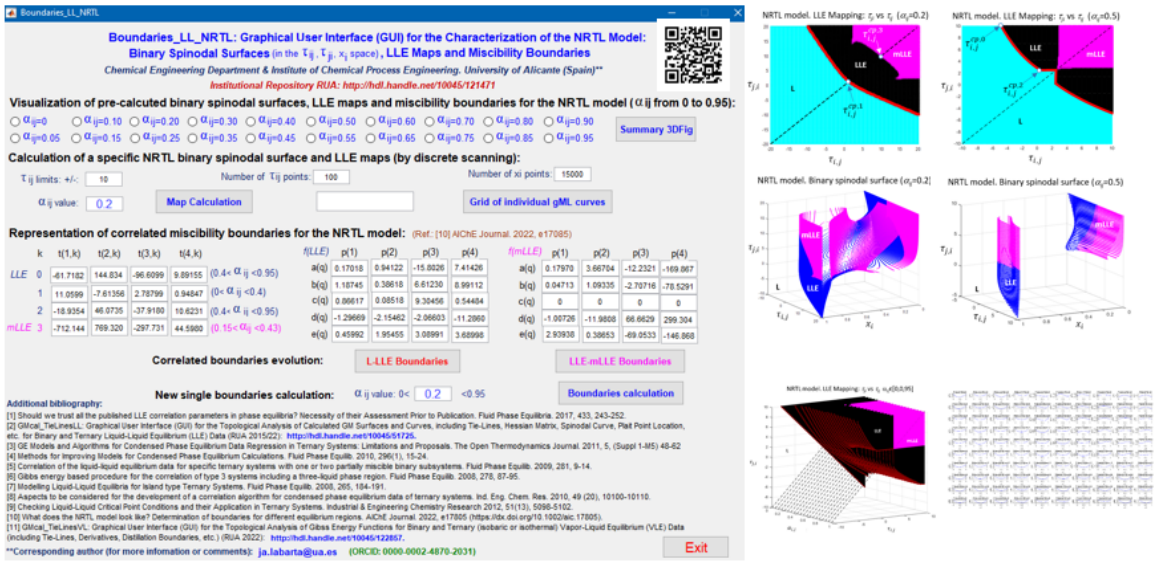

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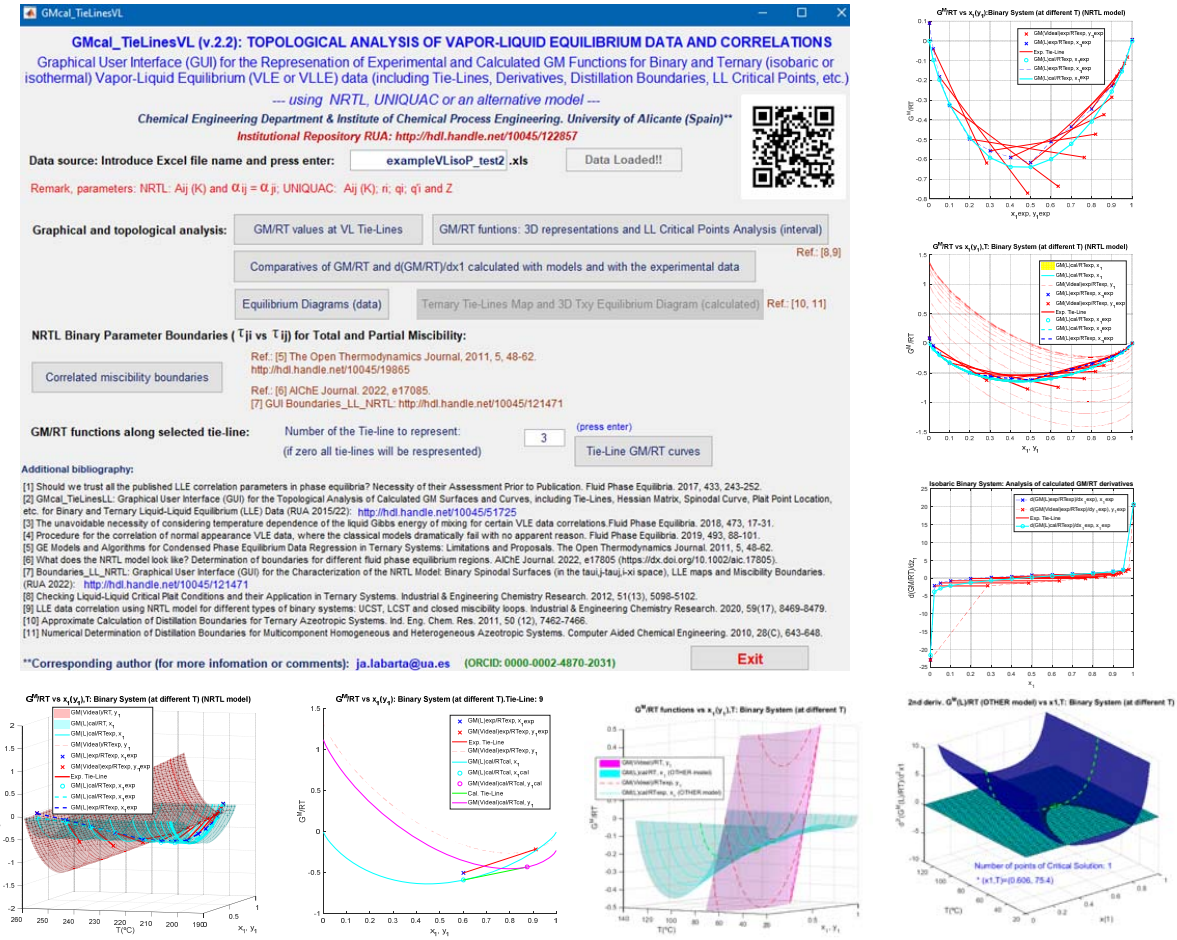

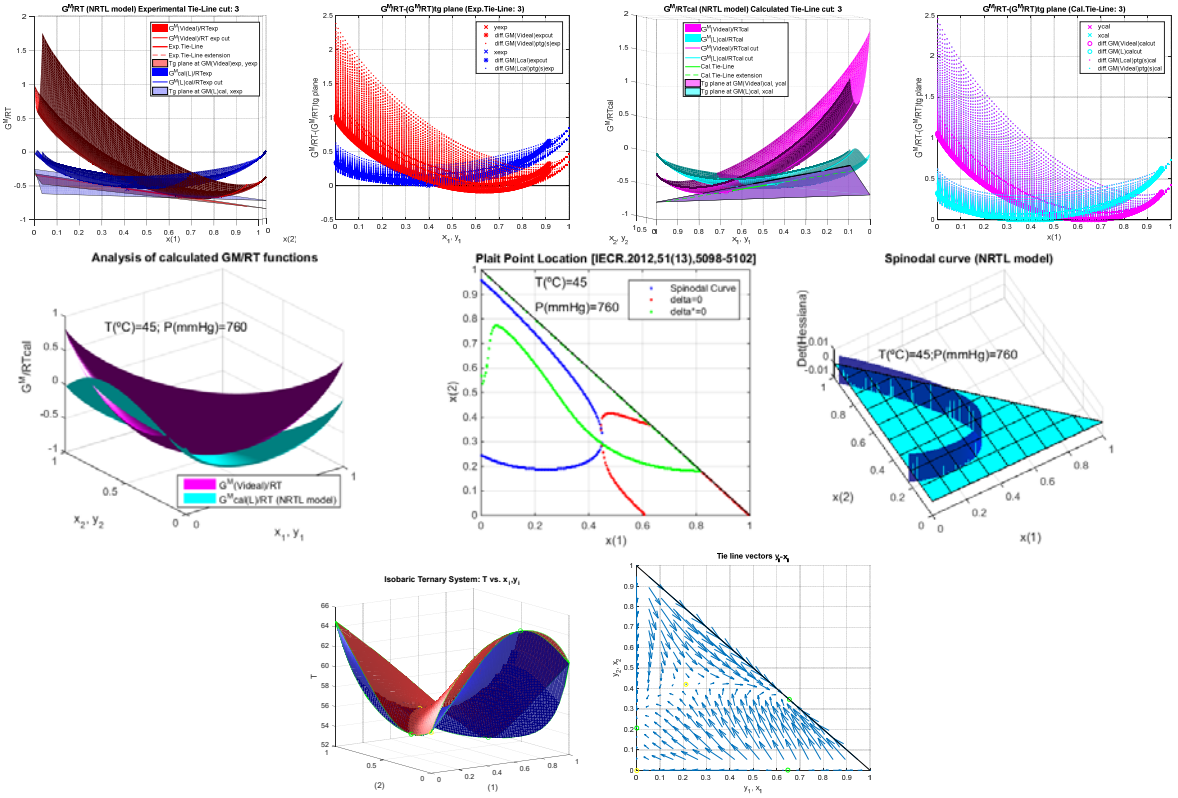

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