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*

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USER INSTRUCTIONS*

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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:

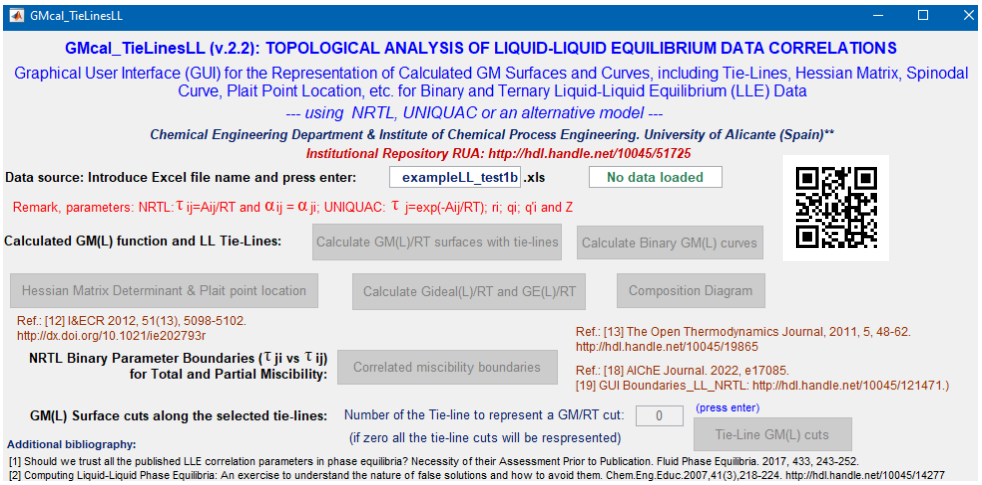
$$\frac{G^E}{RT} = \frac{G^E_{Combinatorial}}{RT} + \frac{G^E_{Residual}}{RT} = \sum_{i=1}^{C} x_i \cdot ln\frac{\phi_i}{x_i} + \frac{z}{2} \cdot \sum_{i=1}^{C} q_i \cdot x_i \cdot ln\frac{\theta_i}{\phi_i} - \sum_{i=1}^{C} q'_i \cdot x_i \cdot ln\left(\sum_{j=1}^{C} \theta'_j \cdot \tau_{j,i}\right)$$

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

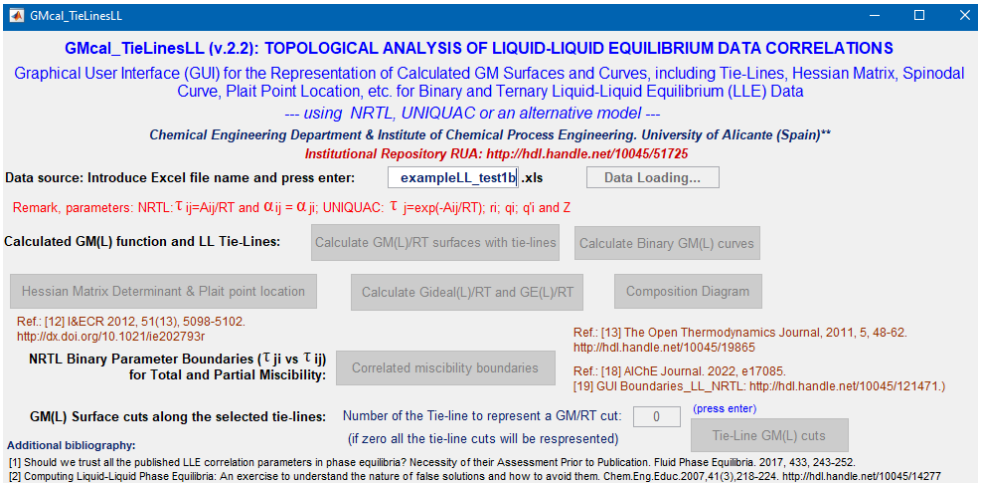
z = Coordination number (usually with a value of 10)
r_i = Volume parameter
q_i = Area parameter (or s_i)
q_i=q'_i for most of substances, except for water and some small alcohols.

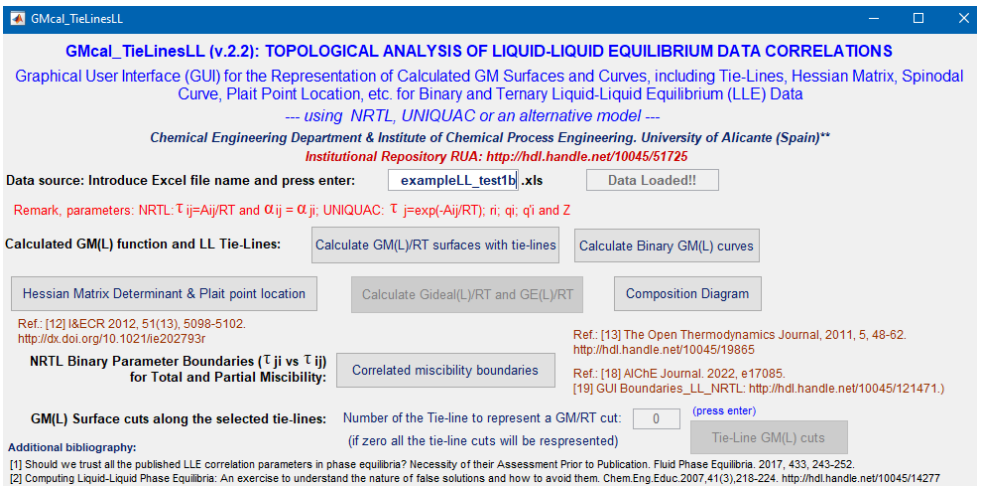
4. USING THE GUI GMcal_TieLinesLL

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).

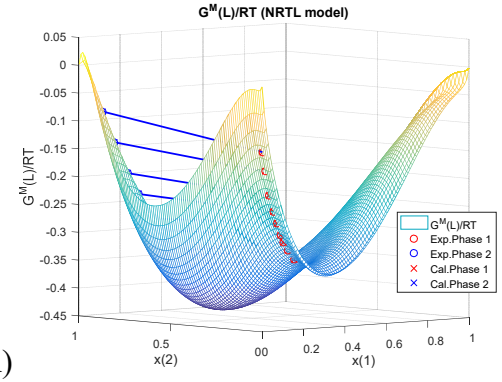
C) Composition diagram (in molar fractions).

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):

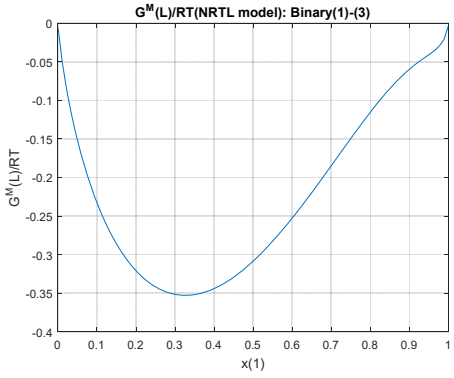
$$\sigma = \begin{vmatrix} \frac{\partial^2 G^M}{\partial^2 x_1} & \frac{\partial^2 G^M}{\partial x_1 \partial x_2} \\ \frac{\partial^2 G^M}{\partial x_2 \partial x_1} & \frac{\partial^2 G^M}{\partial^2 x_2} \end{vmatrix} = 0;\ \delta = \begin{vmatrix} \frac{\partial \sigma}{\partial x_1} & \frac{\partial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

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.

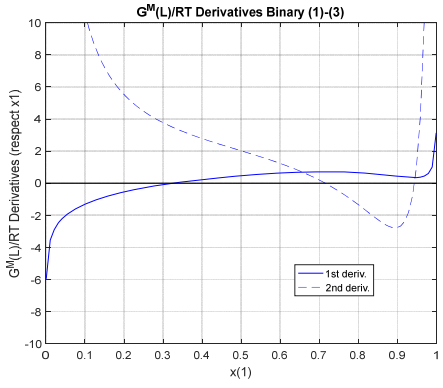
A)



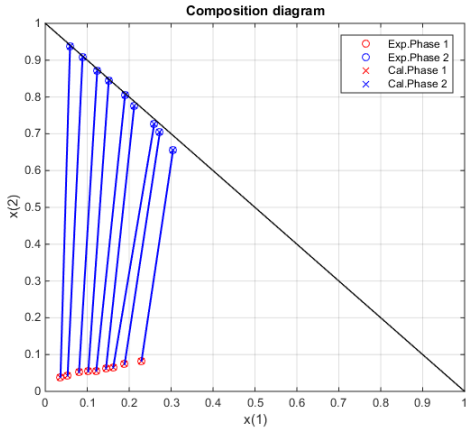
B1)

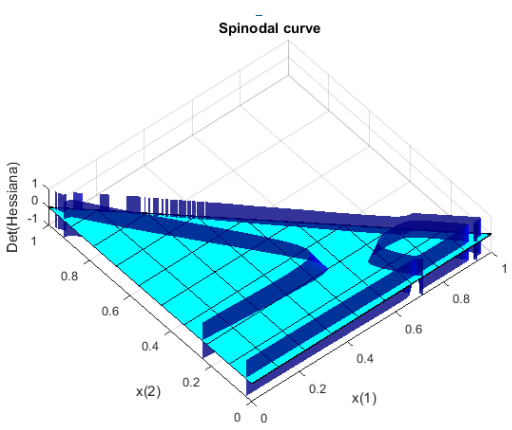


B2)

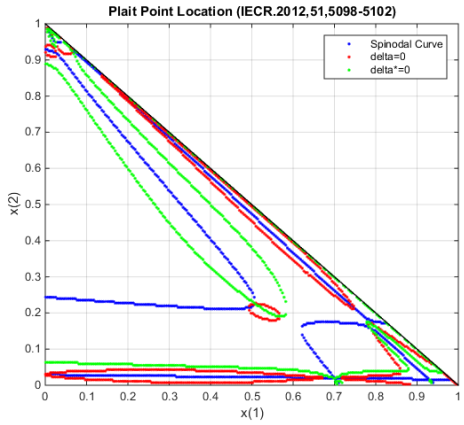


C)

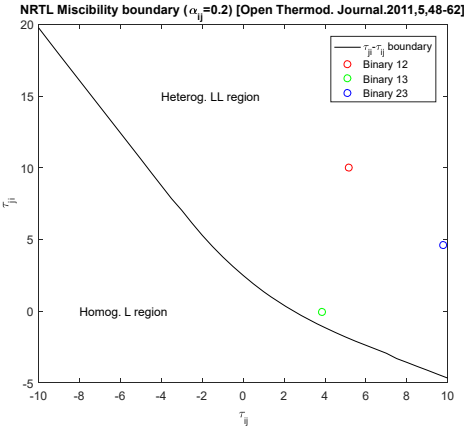




D1)



D2)



E)

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

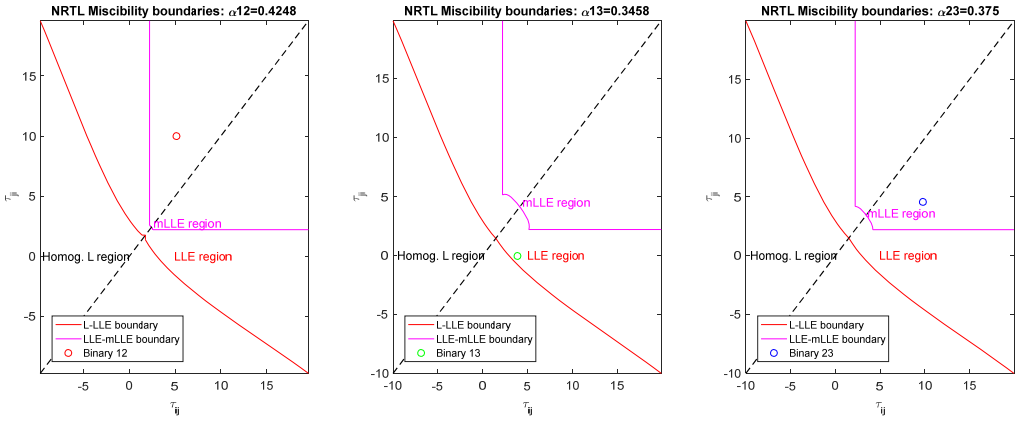
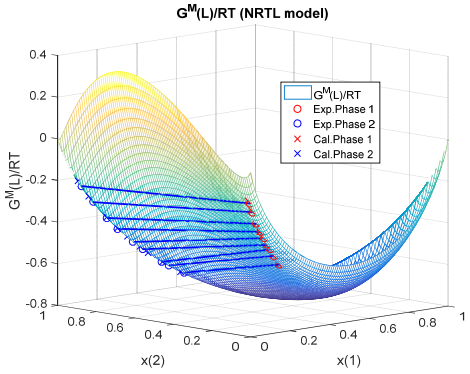
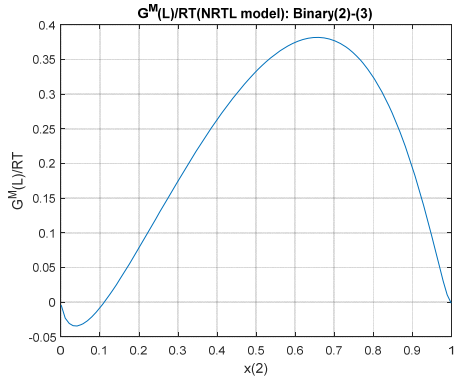


*Figure 1. Different diagrams corresponding to exampleLL_test1a.xls (LLE ternary system). In this example, the NRTL parameters used are **NOT COHERENT** with the experimental LL data.*

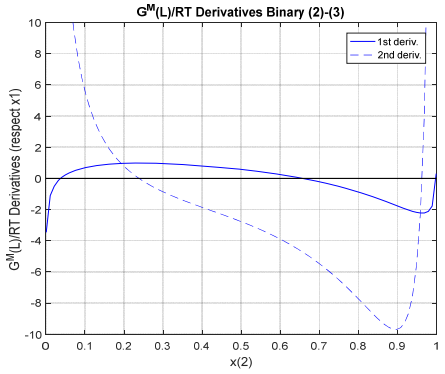
A)



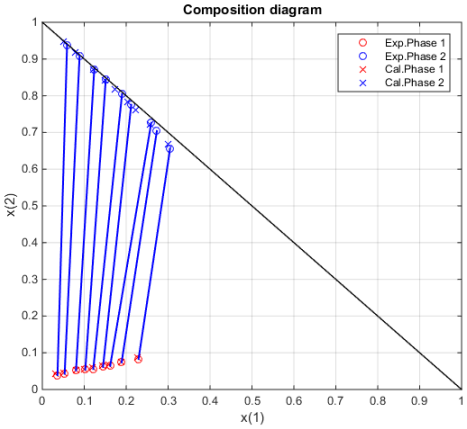
B1)



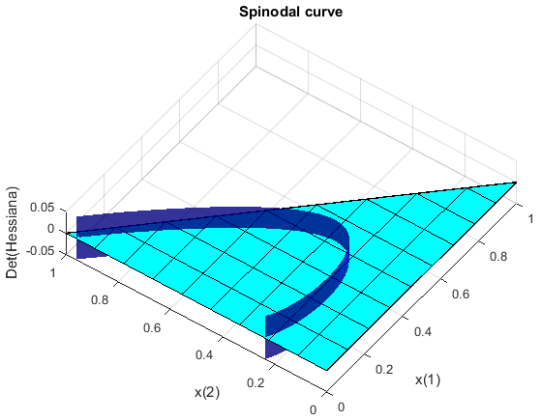
B2)



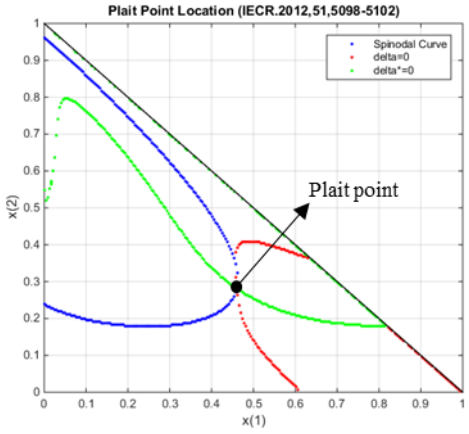
C)



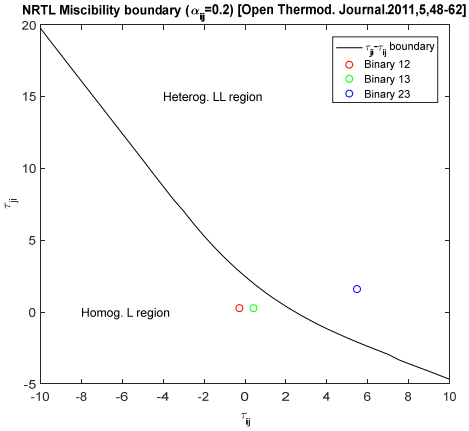
D1)



D2)



E)



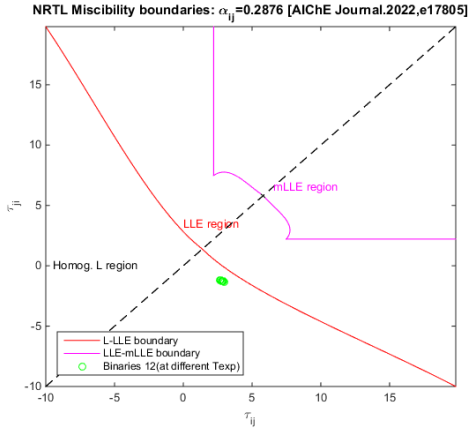
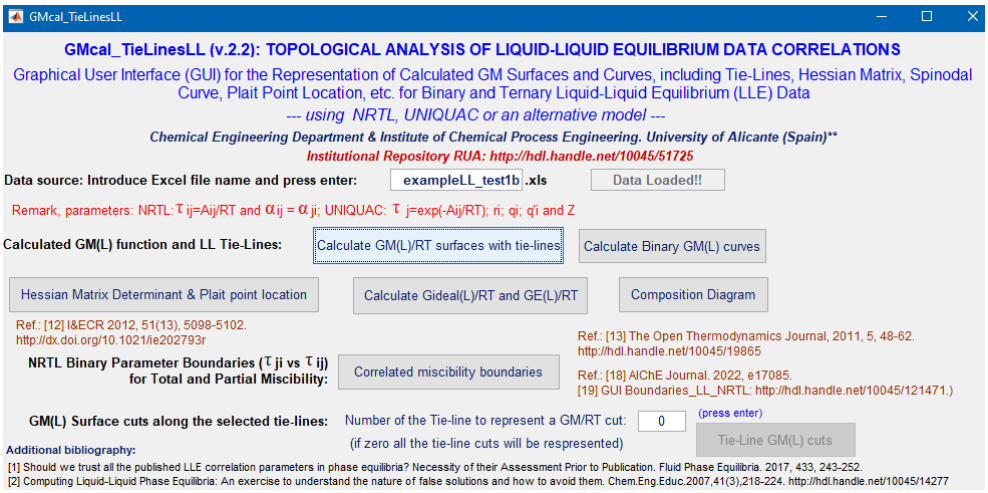


*Figure 2. Different diagrams corresponding to exampleLL_test1b.xls (LLE ternary system). In this example, the NRTL parameters used are **COHERENT** with the experimental LL data.*

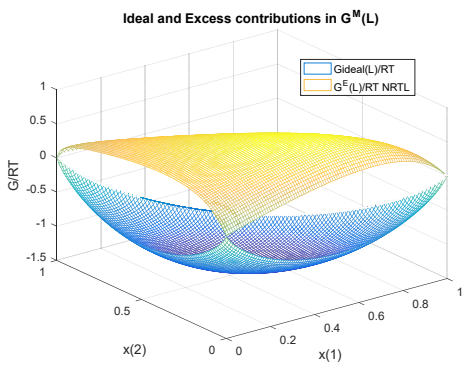
6. Once the $G^M(L)/RT$ surface (A) is calculated, two more options are active:



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)

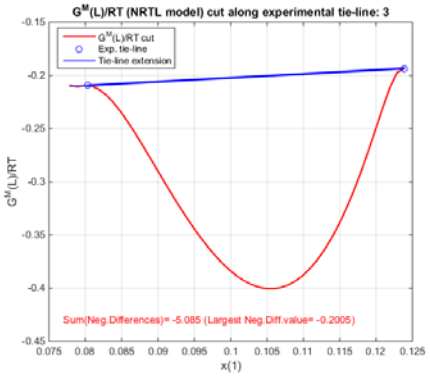
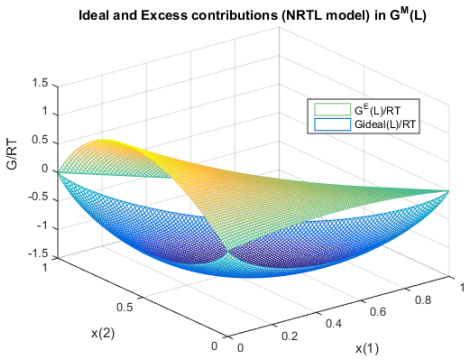
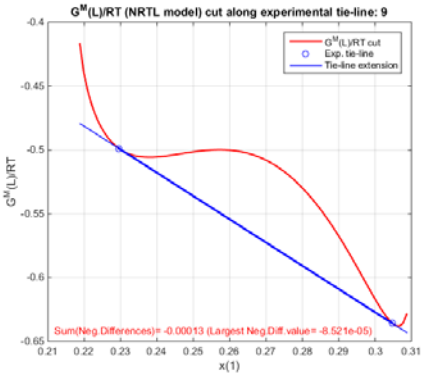


*Figure 3. Different diagrams corresponding to exampleLL_test1a.xls: Ideal and Excess contribution, and $G^M(L)/RT$ cut along a tie-line. In this example, the NRTL parameters used are **NOT COHERENT**.*

F)



G1)



G2)

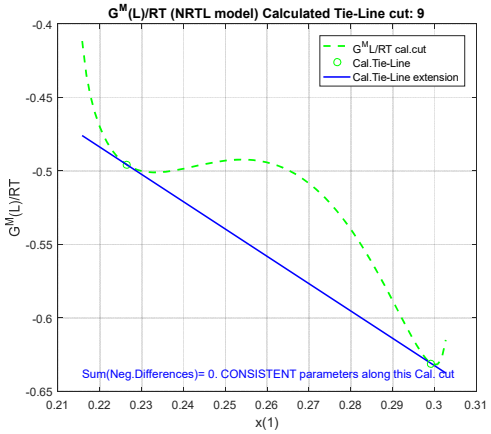
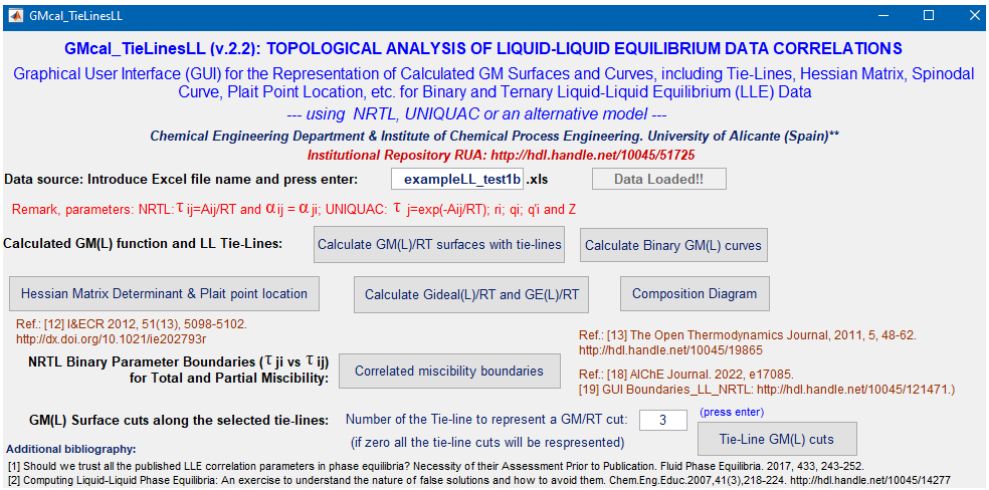


Figure 4. Different diagrams corresponding to exampleLL_test1b.xls: Ideal and Excess contribution, and $G^M(L)/RT$ cut along an exp. and cal. tie-line. In this example, the NRTL parameters used are ***COHERENT****.*

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.



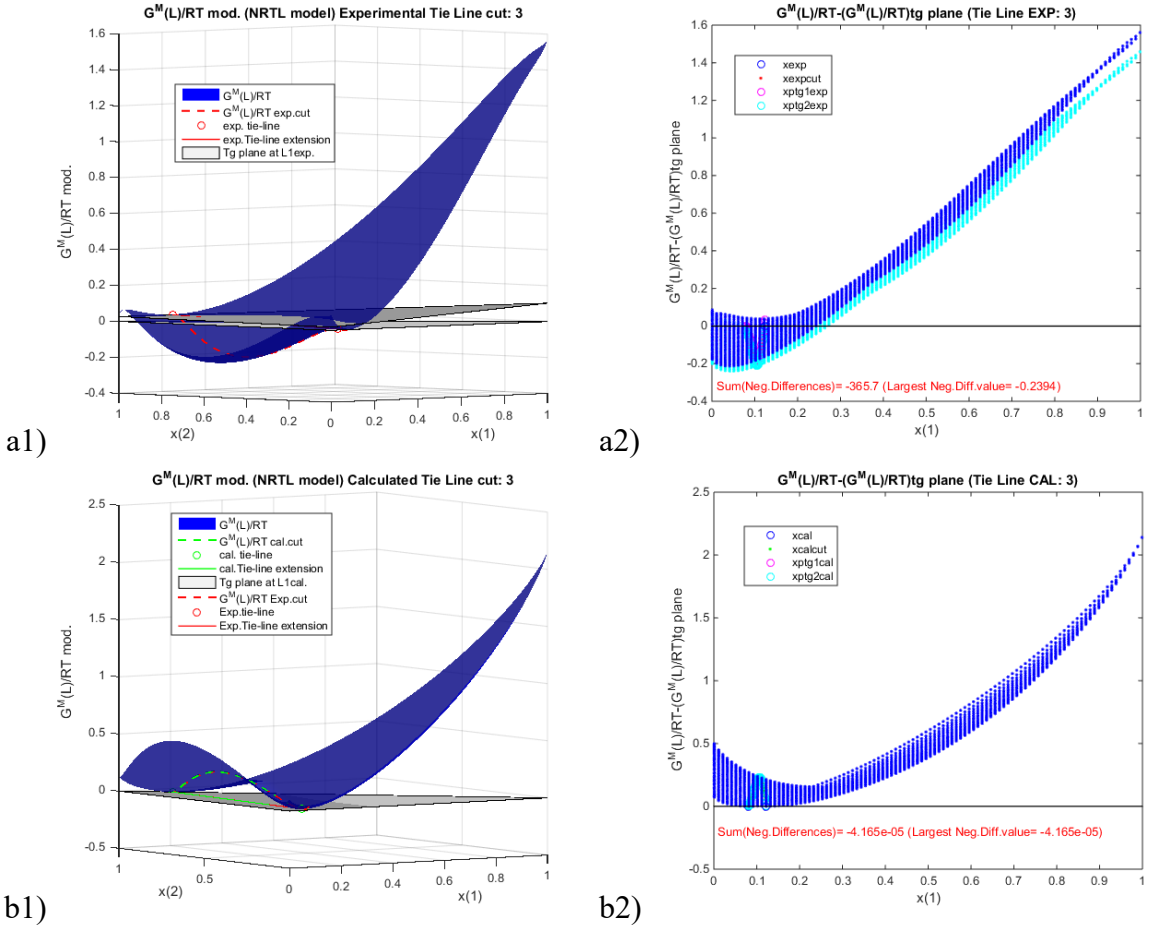


*Figure 5. Complete $G^{M}(L)/RT$ surface including the selected tie-line and the tangent planes at both extremes of the tie-line. Remark: the values of the $G^{M}(L)/RT$ surface have been modified to draw horizontal tangent planes to facilitate the viewing. a) Example with **NOT COHERENT** NRTL parameters,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

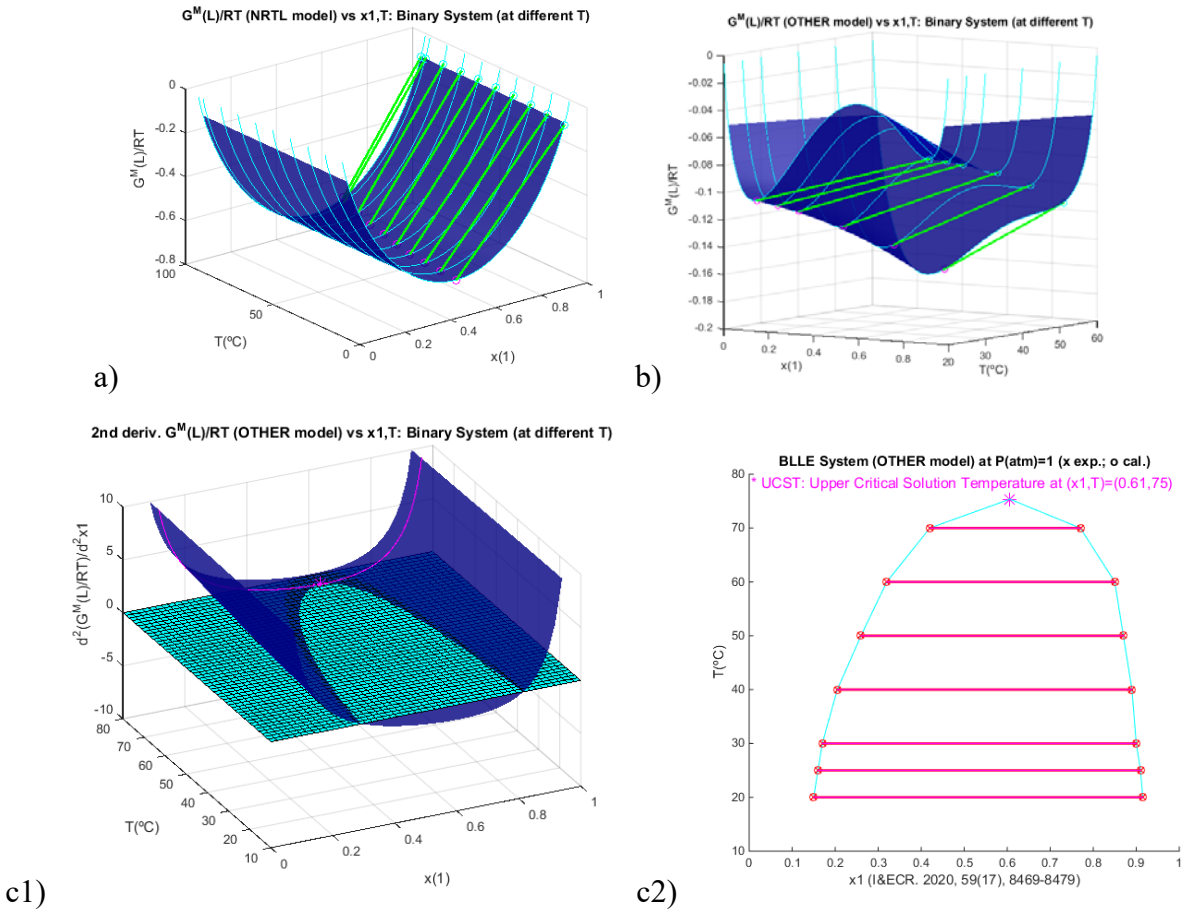


Figure 7. Additional graphics for ***LLE binary systems at different temperatures****: Evolution of the $G^M(L)/RT$ surface with the composition and temperature (including experimental tie-lines). a) Example with* ***not coherent*** *NRTL parameters (e.g. exampleLL_test4a.xls). b) Example with* ***coherent***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

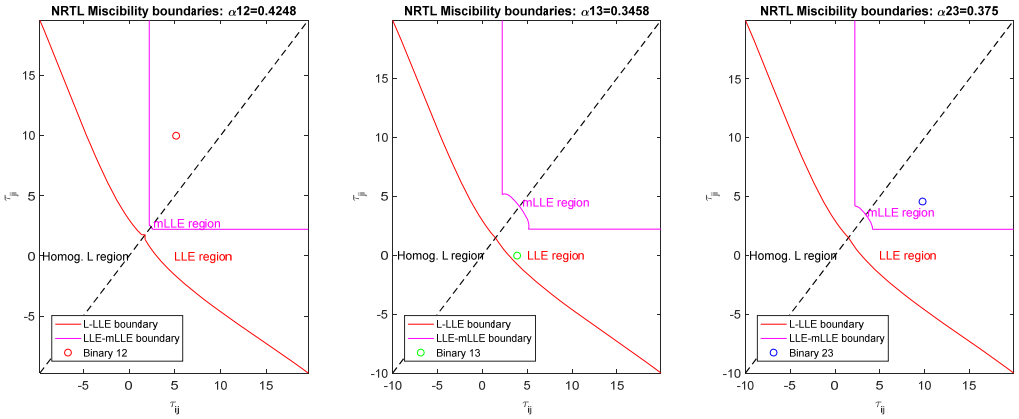
✓ **If calculated tie-lines are not available, the corresponding cells have to be empty.**

List of test files included (exampleLL_test.xls

LLE TERNARY SYSTEMS

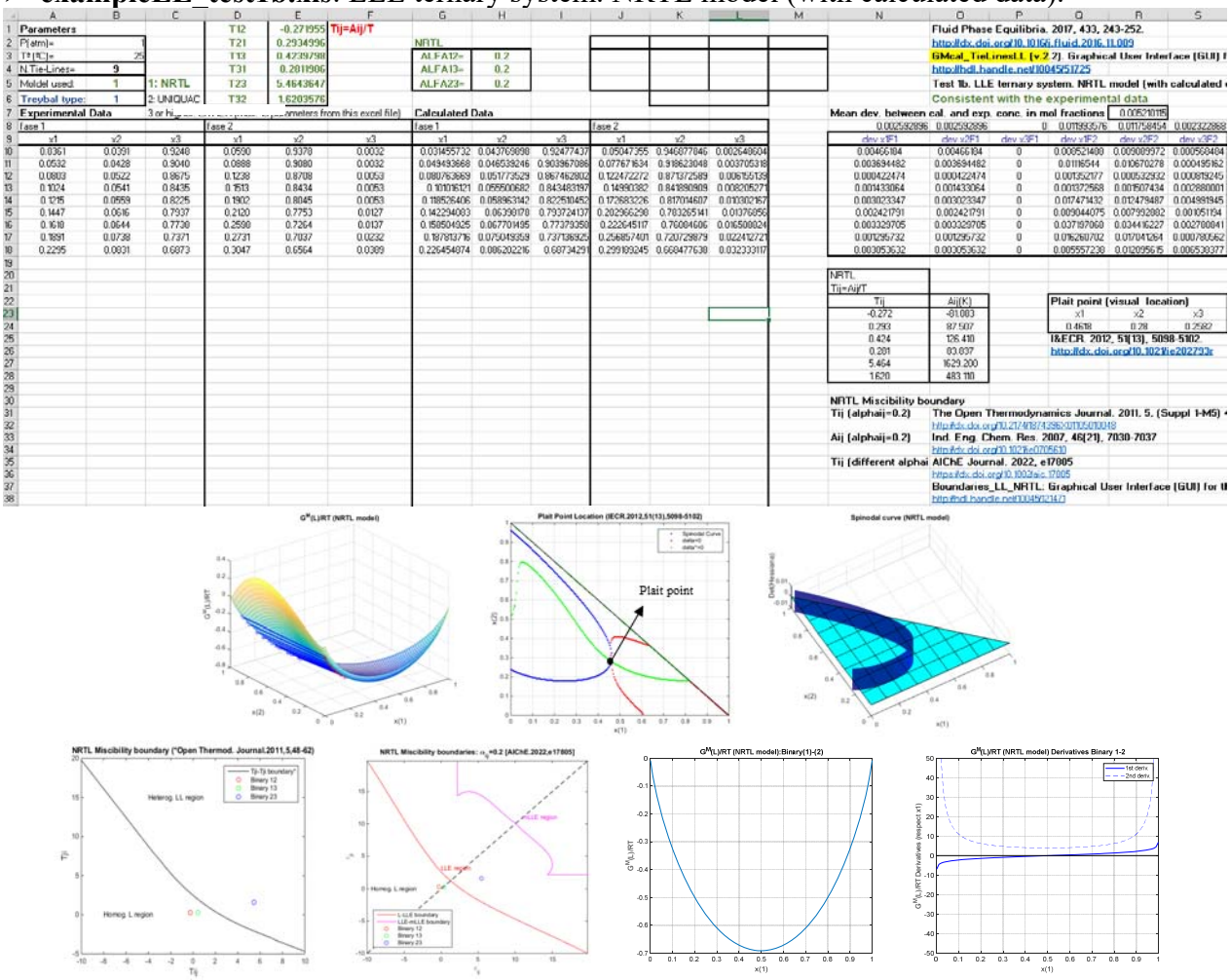
➢ **exampleLL_test1a.xls**: LLE ternary system. NRTL model (without calculated data).

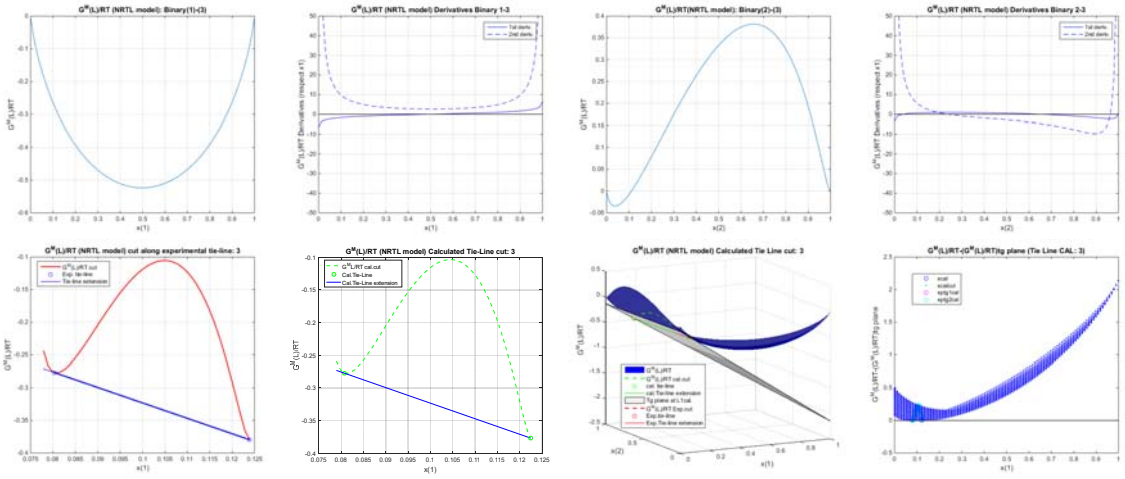
	A	B	C	D	E	F	G	H	I	J	K	L	M
1	**Parameters**			T12	5,149	Tij=Aij/(R·T)							
2	P(atm)=	1		T21	9,999		NRTL						
3	T ª (ºC)=	25		T13	3,868		ALFA12=	0,42					
4	N.Tie-Lines=	9		T31	-0,068		ALFA13=	0,35					
5	Moldel used:	1	1: NRTL	T23	9,771		ALFA23=	0,38					
6			2: UNIQUAC	T32	4,578								
7	**Experimental 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.

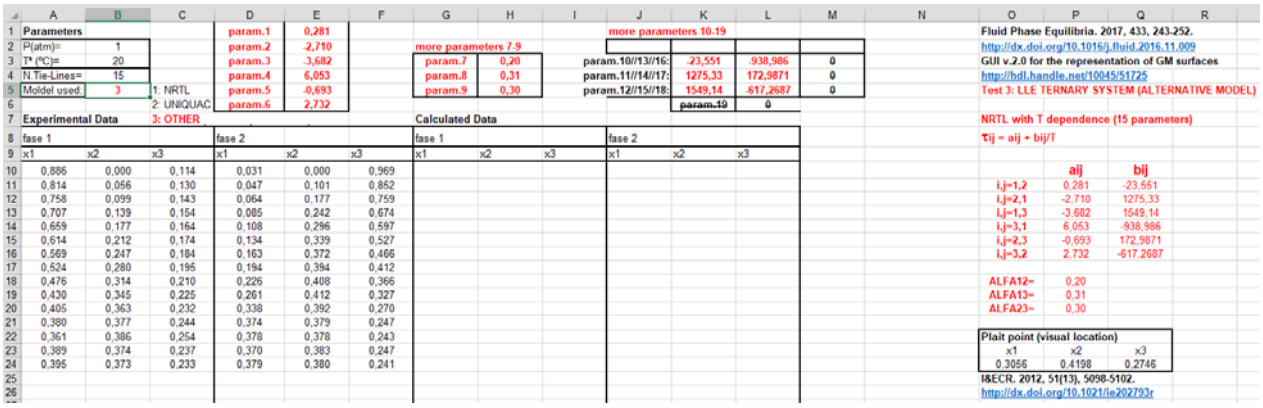
As commented before, in an alternative way, cells E1:E6; H3:H5; K3:K5; L3:L5; M3:M5 and L6 (in this order) could be used to introduce a maximum of 19 parameters directly from the excel file for any OTHER model (different to NRTL or UNIQUAC) to calculate the Gibbs Excess Function using the corresponding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

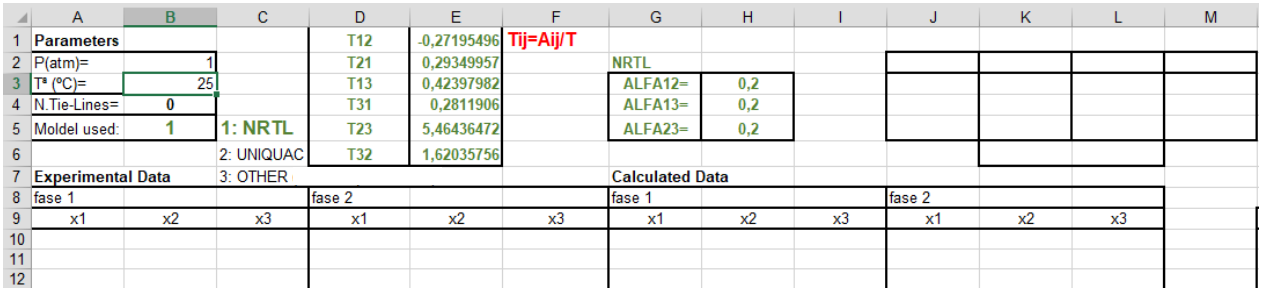
As example of the introduction of an additional model, in the exampleLL_test3.xls test file, a modified version of the NRTL model (e.g. used in Aspen Plus Software) for ternary systems with temperature dependent parameters: $\tau_{ji} = a_{ji} + b_{ji}/T$ (15 parameters: 6 a_{ij}, 3 α_{ij}, 6 b_{ij}) 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).

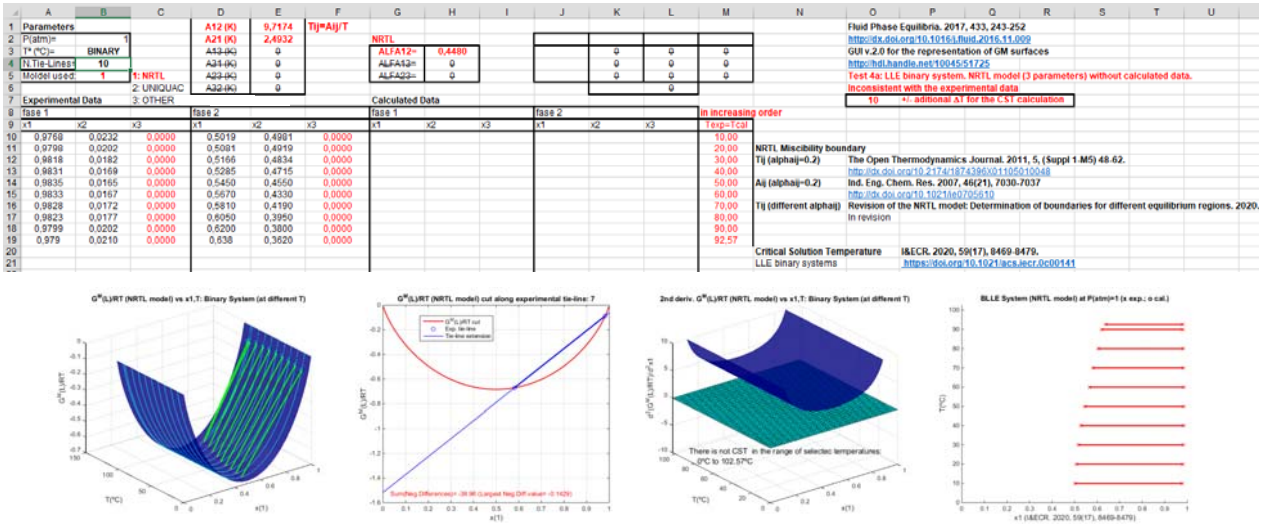


LLE BINARY SYSTEMS

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.

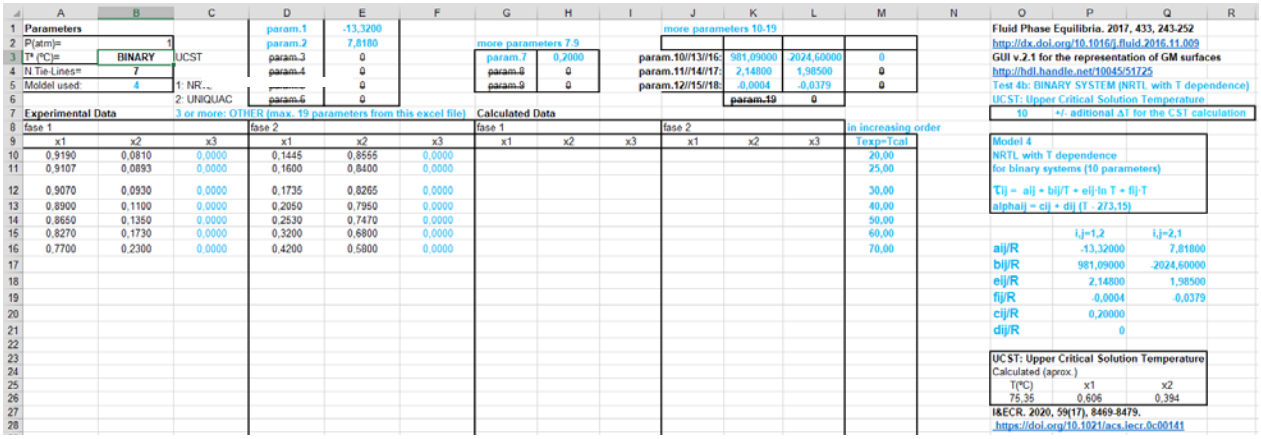


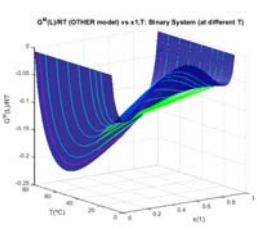
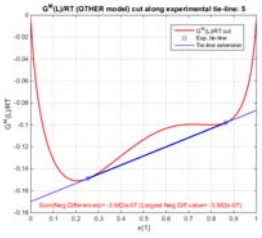
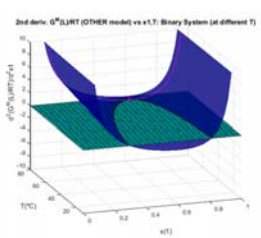
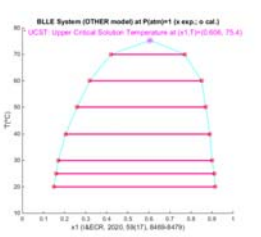
- **exampleLL_test4b-d.xls:** Using as "other model (max. 19 parameters directly from the excel file)", the NRTL model for a binary system with temperature dependent parameters (10 parameters):

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

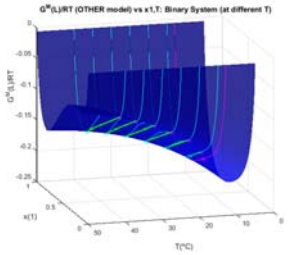
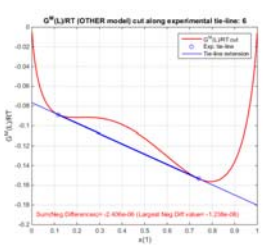
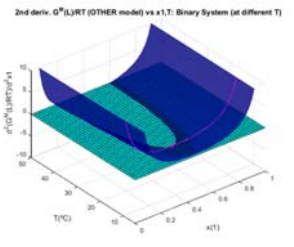
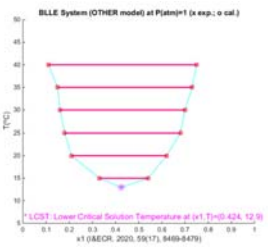
$$\alpha_{ji} = c_{ji} + d_{ji}\,(T - 273.15)$$

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

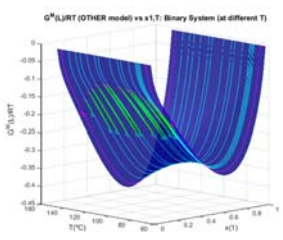
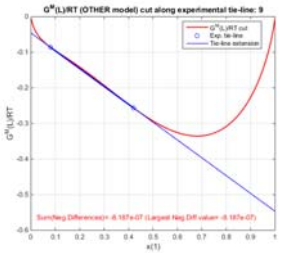
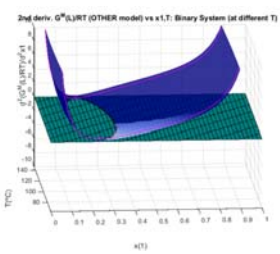
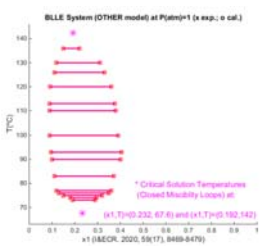


Parameters			param.1	-95,6300					more parameters 10-19				Fluid Phase Equilibria. 2017, 433, 243-252		
P(atm)=	1		param.2	-102,7000		more parameters 7-9							http://dx.doi.org/10.1016/j.fluid.2016.11.009		
T* (ºC)=	BINARY	LCST	param.3	0		param.7	0,2000		param.10//13//16:	-6,30280	-6,54080	0	GUI v.2.1 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

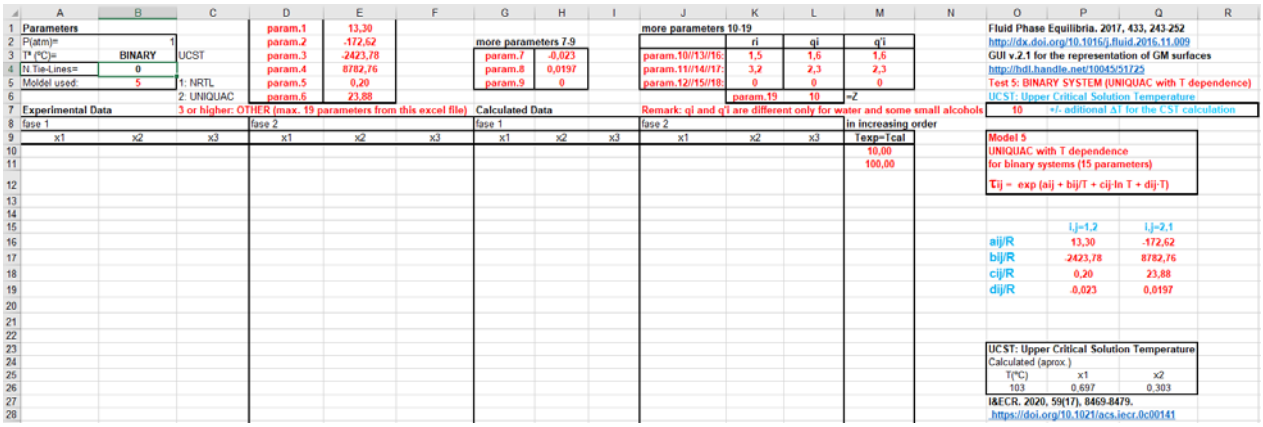





- **exampleLL_test5.xls:** Using as "other model (max. 19 parameters directly from the excel file)", the UNIQUAC model for a binary system with temperature dependent parameters (13 parameters):

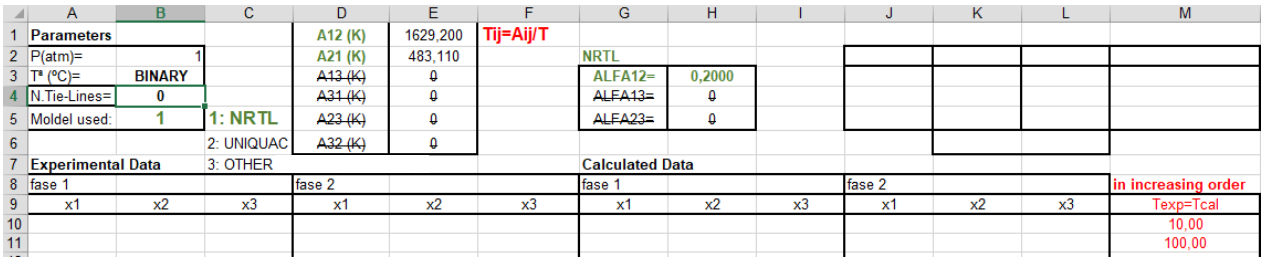
$$\tau_{ji} = \exp\left(a_{ji} + b_{ji}/T + c_{ji}\cdot \ln T + d_{ji}\cdot T\right)$$

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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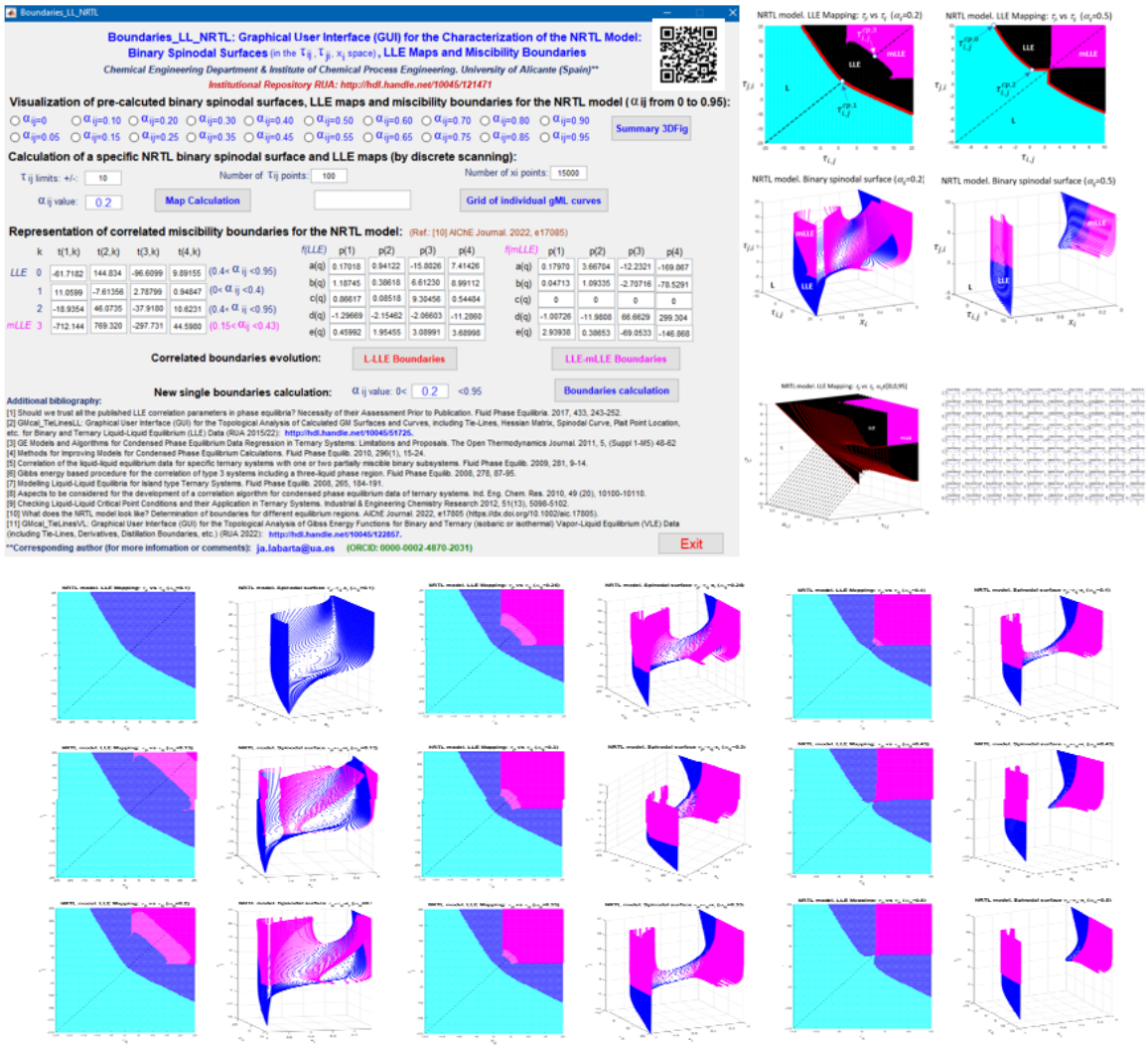

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GMcal_TieLinesVL
GMcal_TieLinesVL (v.2.2): TOPOLOGICAL ANALYSIS OF VAPOR-LIQUID EQUILIBRIUM DATA AND CORRELATIONS
Graphical User Interface (GUI) for the Represenation of Experimental and Calculated GM Functions for Binary and Ternary (isobaric or isothermal) 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
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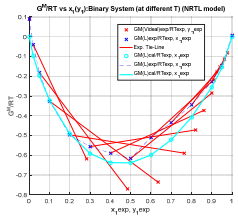
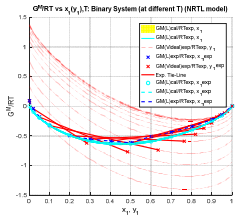
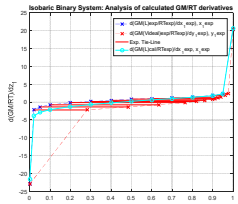
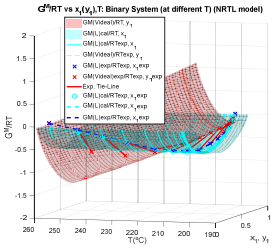
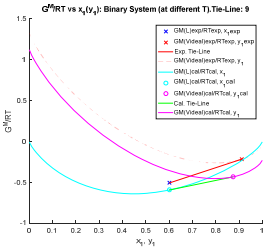
**Corresponding author (for more infomation or comments): ja.labarta@ua.es (ORCID: 0000-0002-4870-2031)
Exit

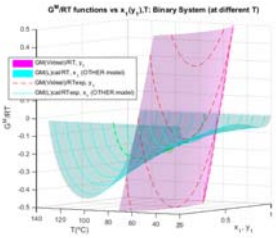


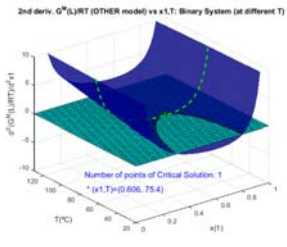


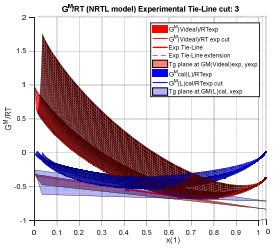


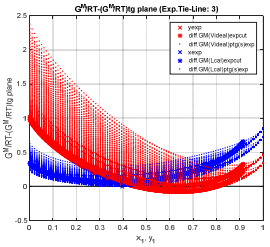


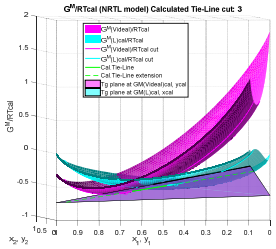


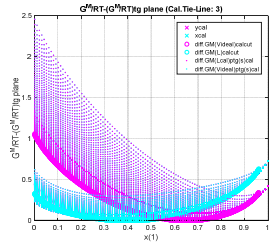


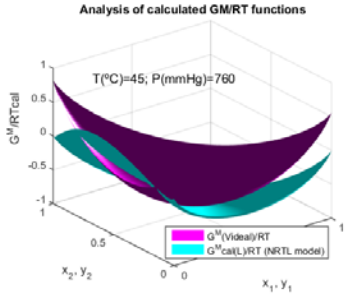


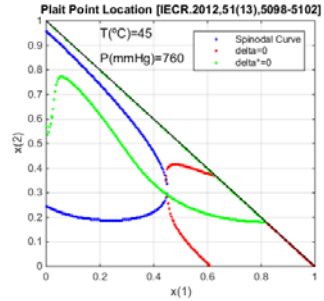


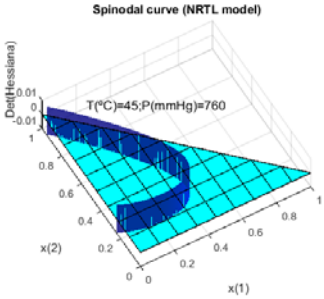


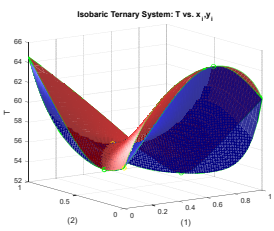


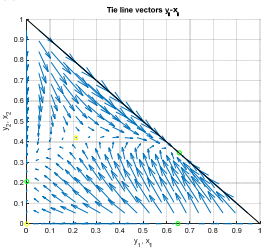



Analysis of calculated GM/RT functions
T(ºC)=45; P(mmHg)=760
GM(Videal)/RT
GMcal(L)RT (NRTL model)


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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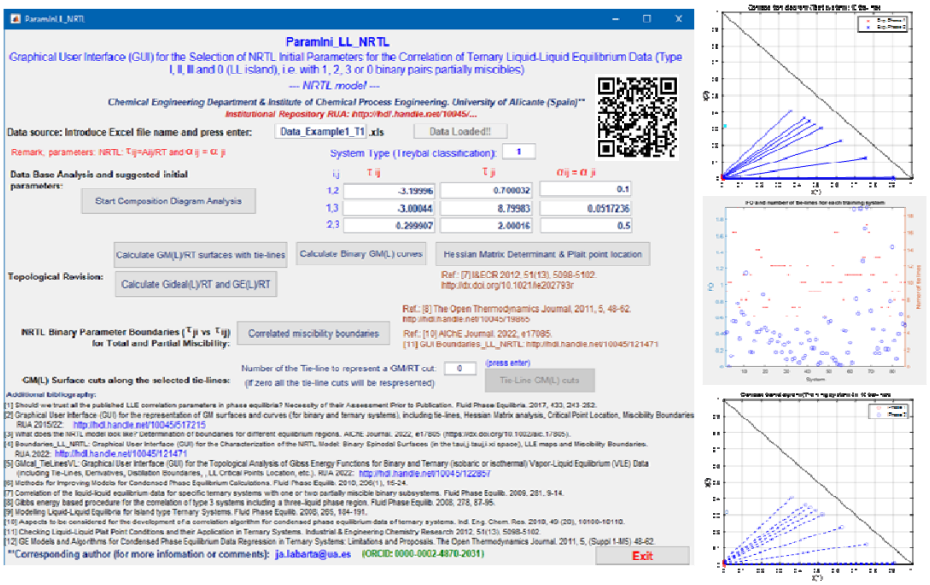

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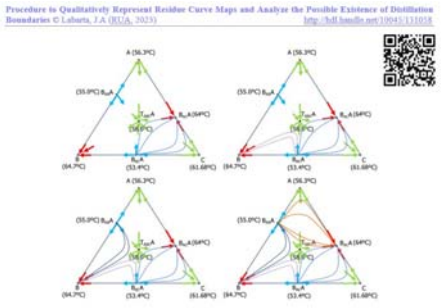

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