

# Further Results on the Prediction of Double Retrograde Vaporization Using the Numerical Inversion of Functions from the Plane to the Plane

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## Abstract

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# Introduction

Double retrograde vaporization is a phase behavior phenomenon that occurs close to the critical point of binary mixtures, that is, the point where there are no phase boundaries and therefore the distinction between them does not exist, causing the mixture to cease to exist as well. It occurs in mixtures characterized by containing a solvent with high volatility relative to the solute contained in the mixture. More specifically in relation to the mixture to be studied, composed of ethane + limonene, the solvent boils at 184.6 K, while the boiling point of the solute is 448.2 K. This tendency towards evaporation of ethane in relation to limonene causes its volatility to be high, satisfying one of the conditions of occurrence.

The phenomenon corresponds to a special shape of the dew-point curve, exhibiting a “S” shape (with three dew points) or a double-dome structure (with four dew points), for a specific temperature and composition of the system. Especially in the case of double-dome manifestation, the phenomenon occurs within a very limited temperature range, which is slightly above to the critical temperature of the more volatile component. We must mention that the composition of vapor phase is arbitrarily chosen, in order to produce the thermodynamic phenomenon.

Its occurrence was firstly investigated by Chen et al.<sup>1</sup> and Chen et al.<sup>2</sup> for binary mixtures involving methane + n-butane and methane + n-pentane, under specified temperature. More recently, Raeissi and Peters<sup>3</sup> identified a double-dome behavior for the binary mixture ethane + limonene at  $T = 307.4$  K and in a narrow range of compositions (close to the pure ethane). Furthermore, Raeissi and Peters<sup>4</sup> indicated that the Peng-Robinson equation of state<sup>5</sup>, with classical mixing rules, was capable to qualitatively predict this phenomenon. In order to detail the thermodynamic fundamentals of double retrograde vaporization, Raeissi and Peters<sup>6</sup> also presented a detailed discussion of the volumetric properties of the fluids involved as defining the existence of the phenomenon.

In the vicinity of the mixture critical point, the robust calculation of dew point pressures (under specified temperature) is a very hard task. Furthermore, some roots of the phase

equilibrium problem show very small radius of convergence for Newton-type methods, as indicated by Platt et al.<sup>7</sup>. For this reason, the development of robust frameworks for this kind of problem is extremely relevant. Among several possibilities, we focus on the robust methodology of the numerical inversion of functions, proposed by Malta et al.<sup>8</sup>, for functions from the plane to the plane. This technique<sup>8</sup> proposes — considering a restrict set of functions — the generation of the critical curves in the mathematical sense<sup>1</sup>, the construction of a bank of solved points (to be used as with good initial estimates for the solution) and, finally, the inversion of the desired points (calculation of all pre-images of a such image).

As far as we can know, the first application of the methodology of numerical inversion of two-variable functions in a chemical engineering problem was presented by Guedes et al.<sup>9</sup>, in the prediction of the azeotropic behavior in systems with double azeotropes. More recently, Libotte et al.<sup>10</sup> presented some initial results regarding the application of the methodology proposed by Malta et al.<sup>8</sup> in the prediction of double retrograde vaporization phenomenon in the system ethane + limonene.

However, a few relevant aspects were not considered there and we discuss them in this work. Among these aspects, we can briefly mention: (i) the influence of the system temperature in the critical curves, and (ii) the analysis of the behavior of inversions near the critical image (where the number of pre-images — solutions of the system — change). Furthermore, one of the objectives of this work is to provide a mathematical view of this challenging nonlinear algebraic system, which can be useful in the development of numerical tools for solving high-pressure phase equilibrium problems. As pointed previously, the solution of this kind of nonlinear system with typical root-finding algorithms (such as Newton's methods) is not a trivial task, even when using more sophisticated numerical tools.<sup>7</sup>

In order to analyze these main points and provide an in-depth study (in the mathematical sense) of the phase equilibrium problem in two-component systems, the work was divided

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<sup>1</sup>The term “critical” assumes two meanings in this work: in the mathematical sense, a critical point of a function is a nonregular point (where the jacobian matrix is non-invertible); in the thermodynamic sense, the critical point is that where we cannot distinguish between the properties of the phases.

predominantly into two parts: first, the system composed of ethane + limonene at  $T = 307.4$  K was analyzed, fixing the molar fraction of the vapor phase of ethane at  $y_1 = 0.998966$ . Under these conditions, the system presents four distinct solutions, that is, the number of times the dew point curve is intercepted, for the chosen mole fraction, as can be seen in Figure 1. For this system, all the steps of the method of inversion of functions from the plane to the plane were performed and the solution degeneration was investigated by obtaining pre-images of a set of points located in the vicinity of the critical image. We also evaluated the critical points (in mathematical terms) that are folds and cusps, and their relation with the degeneration of solutions of this problem.

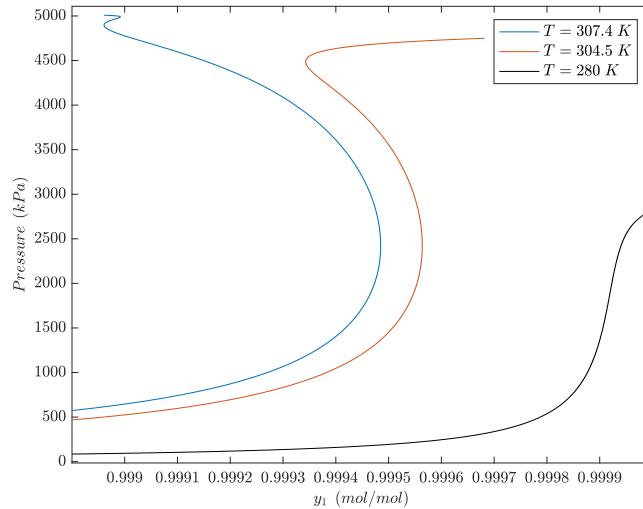


Figure 1: Dew point curves for the system ethane + limonene at several temperatures.

Then, the temperature of the system composed of the same components of the previous case was defined as  $T = 304.5$  K and analyzed together with the same system at  $T = 280$  K. In these two conditions, when  $y_1 = 0.99945$  (among other conditions), the systems have three and one solutions, respectively, as shown in Figure 1. Thus, it was possible to evaluate the degeneracy of solutions in both systems, varying only one of the parameters of the problem.

The possibility of solving the problem - and therefore obtaining the pre-images of a given point in the image - was also evaluated from a mathematical perspective: the critical curves (in the mathematical sense) of the system were obtained for different temperatures and their

respective critical images . Through this variation, for a fixed molar fraction of ethane in the vapor phase, it was possible to verify the influence of the critical curves in obtaining the solutions of the problem through methods that use derivatives.

## Models and Methodology

### Thermodynamic models and problem formulation

All the phase equilibrium calculations, as well as the critical point curves (in the thermodynamic sense), will be conducted for the Peng-Robinson equation of state with classical mixing rules and null binary interaction parameters. Critical properties and acentric factors of pure components can be found, for instance, in Libotte et al.<sup>10</sup>.

For a binary mixture, the phase equilibrium problem can be formulated as:

$$\hat{\phi}_i^L x_i = \hat{\phi}_i^V y_i \quad i = 1, 2 \quad (1)$$

In the last equation  $\hat{\phi}$  represents the fugacity coefficient for component  $i$  (using the Peng-Robinson model),  $x_i$  is the molar fraction in the liquid phase,  $y_i$  represents the vapor phase. The superscripts  $L$  and  $V$  refer to the liquid and vapor phases, respectively.

Using  $x_2 = 1 - x_1$  and  $y_2 = 1 - y_1$ , the nonlinear algebraic problem (in the plane) is then:

$$\hat{\phi}_1^L x_1 = \hat{\phi}_1^V y_1 \quad (2)$$

$$\hat{\phi}_2^L (1 - x_1) = \hat{\phi}_2^V (1 - y_1) \quad (3)$$

The vector of unknowns, considering the specification of temperature and vapor molar fractions, is  $p = (x_1, P)$ . Each residue of the nonlinear equations will be referred as  $f_i$ , since  $F = (f_1, f_2)$ .

The nonlinear algebraic system can be re-stated as:

$$F(p) = q, \quad (4)$$

where  $p$  is a point in the domain and  $q$  is a point in the image (range) of  $F$ . Ordinarily, we are interested to solve  $F(p) = (0, 0)$  (where  $q = (0, 0)$  represents the null vector in the Euclidean plane).

## TO BE DELETED - a few ideas on the inversion of functions

To understand the methodology of inversion of functions to solve nonlinear systems of equations, we first consider a simple 1D example.

**Example 1.** Let  $F(p) = 3p^3 - p$ . By examining the graph of  $F$  it is possible to check that the equation for  $q$ ,

$$F(p) = q, \quad \text{that is, } 3p^3 - p = q,$$

has three possibilities as far as the number of solutions,  $\eta(q)$ , is concerned,

$$\eta(q) = \begin{cases} 1, & \text{if } q < -2/9 \\ 2, & \text{if } q = -2/9 \\ 3, & \text{if } -2/9 < q < 2/9 \\ 2, & \text{if } q = 2/9 \\ 1, & \text{if } q > 2/9 \end{cases}$$

One way to determine the transition points where the number of solutions change is to look at the image of the critical points. The critical points (where the derivative is not invertible)

satisfy

$$F'(p) = 9p^2 - 1 = 0, \text{ that is } p = \pm 1/3.$$

Therefore, the transition points are  $F(\pm 1/3) = \mp 2/9$ .

Now, the range of  $F$  is partitioned in five subsets,  $\mathbb{R} = R_1 \cup T_2 \cup R_3 \cup T_4 \cup R_5$ ,

$$\begin{aligned} \text{transitional sets: } & T_2 = \left\{-\frac{2}{9}\right\}, \quad T_4 = \left\{\frac{2}{9}\right\}, \\ \text{non-transitional sets: } & R_1 = ]-\infty, -\frac{2}{9}[, \quad R_3 = ]-\frac{2}{9}, \frac{2}{9}[, \quad R_5 = ]\frac{2}{9}, +\infty[. \end{aligned}$$

The overall strategy for solving the equation  $F(p) = q$  is to decompose the range of  $F$  in its transitional and non-transitional sets, have a bank of solved points with representatives more or less covering the non-trasitional sets, and to solve the system with the bank of solved points as initial guesses. ■

Similarly, with functions from the plane to the plane,  $F : \mathbb{R}^2 \rightarrow \mathbb{R}^2$ , satisfying certain technical regularity requirements,<sup>8</sup> one defines the critical curves, where the jacobian  $JF$  is not invertible,

$$\mathcal{C} = \{p \in \mathbb{R}^2 \mid \det(JF|_q) = 0\},$$

and the image of  $\mathcal{C}$ ,  $\mathcal{T} = F(\mathcal{C}) = \{q = F(p), \text{ for all } p \in \mathcal{C}\}$ , the critical image, which defines the curves in the range of  $F$  delimiting regions where transitions on the number of pre-images may occur.

One of the drawbacks to the application of the theory presented in Malta et al.<sup>8</sup> to problems coming from applications that involve the solution of nonlinear  $2 \times 2$  systems of equations is not so much that it applies only to a collection of “regular” functions, but that the functions have to be defined in all points in the plane. In this case, the theory then gives

a fairly good amount of information on the solutions of the nonlinear system of equations. In applications usually, however, the domain of a function has to satisfy some restrictions due, for instance, to the lack of physical significance of certain values, or due to existence of singularities, which breaks the theory presented in Malta et al.<sup>8</sup>, but preserves the overall methodology that they discuss. We illustrate some aspects of this issue in the next example.

**Example 2.** Let  $F(p) = -\frac{1}{p+1/2} \frac{1}{p-1/2}(p + \frac{1}{4})(p - \frac{1}{4})$ , and consider the nonlinear equation  $F(p) = q$  for given  $q$ . A simple examination of the graph of  $F$  shows that the number of solutions as a function of  $q$  is

$$\eta(q) = \begin{cases} 2, & \text{if } q < -1 \\ 0, & \text{if } -1 \leq q < -1/4 \\ 1, & \text{if } q = -1/4 \\ 2, & \text{if } q > -1/4 \end{cases}.$$

Again we have the range of  $F$  partitioned in regions,

$$\text{non-transitional sets: } R_1 = ]-\infty, 1[ , R_4 = ]-1/4, +\infty[ ,$$

$$\text{transitional set: } T_3 = \{-1/4\} ,$$

$$\text{mixed set: } M_2 = [-1, -1/4[ .$$

The only critical point,  $F'(p) = \frac{3p/8}{(p^2-1/4)^2} = 0$ , is 0, and the critical image  $F(0) = -1/4$ .

This is a transitional set, however, we are not able to determine the mixed set from this calculation. ■

## A brief description for some features of the numerical inversion of functions from the plane to the plane

### Numerical Results

The methodology of numerical inversion of two-variable functions, adapted from Malta et al.<sup>8</sup> which considered the special case of function from the plane to the plane, was employed in this phase equilibrium calculation by Libotte et al.<sup>10</sup>. In this sense, all details regarding the production of the bank of solved points and the numerical steps of the inversion process are detailed by Libotte et al.<sup>10</sup>. Here, we will focuses on some aspects not addressed by Libotte et al.<sup>10</sup>, mainly with regard to the quantity of pre-images in limit-situations (for instance, when we approached to the critical image). Furthermore, we will present the thermodynamic calculation of the critical points for the binary mixture ethane + limonene for the entire range of compositions.

Table 1 presents the compositions and pressures for the dew point calculation in the system ethane + limonene at  $T = 307.4$  K and  $y_1 = 0.998966$ , where the “double-dome” structure appears, with four dew point pressures (and compositions of the liquid phase). We note, considering the data presented in Table 1, that one root corresponds to a low pressure root (Root 1) and the others are high pressure roots (which are close to each other). From the point of view of the calculation techniques – using classical numerical methods, such as Newton-Raphson methods – we are interested in robust methodologies capable to find all roots, but mainly with some features to find in a robust way the high pressure roots.

Table 1: Dew point compositions and pressures for  $T = 307.4$  K and  $y_1 = 0.998966$ . (Case 1)

Root	$x_1$	$P$ (kPa)
1	0.1567	619.2575
2	0.9829	4859.4621
3	0.9918	4931.2247
4	0.9979	5007.2503

We will use the same numbering to the roots (1, 2, 3 and 4) even for some modified nonlinear problems (without physical significance).

We also tested the dew point calculation at  $T = 304.5$  K and  $y_1 = 0.99945$ , where a “S” shape dew curve appears, with three physical roots. The roots are detached in Table 2.

Table 2: Dew point compositions and pressures for  $T = 304.5$  K and  $y_1 = 0.99945$  (Case 2).

Root	$x_1$	$P$ (kPa)
1	0.3064	1209.3572
2	0.8442	3900.9812
3	0.9917	4671.3568

## Thermodynamic critical point calculations

In this subsection we present the critical curve for the mixture ethane + limonene for the entire range of compositions. As reported previously, the term “critical curve” can exhibit two different meanings: the mathematical sense (points where the jacobian is singular) and the thermodynamic sense. Here we deal with thermodynamic critical points, and we use the approach of Heideman and Khalil<sup>11</sup>, with a double-loop structure in temperature-molar volume, for the critical point calculation.

Figure 2 illustrates the critical curve, in the temperature-pressure plane, for the mixture at hand. We observe a continuous and unique curve connecting the two pure components. Thus, this system can be classified as Type I, accordingly to the classification of binary mixtures of Van Konynenburg and Scott.<sup>12</sup>

## Results at $T = 307.4$ K and $y_1 = 0.998966$

### An in-depth examination of the critical curves

As pointed out previously, the initial results regarding the application of the numerical inversion of functions to the prediction of double retrograde behavior was presented by<sup>10</sup>.

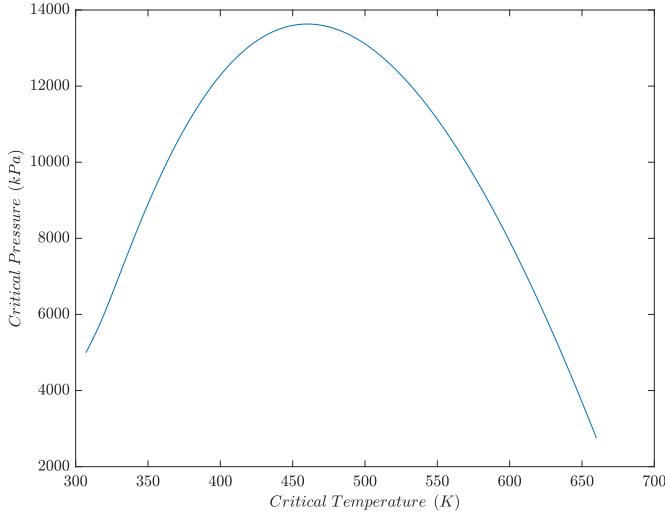


Figure 2: The thermodynamic critical curve in the system ethane + limonene.

In that work they investigated some basic features of the critical curves. Here, we present a deeper analysis of the critical curves in this system.

Clearly, we note that — in the highlighted region — the critical curves exhibit one self-intersection, as represented in Figure 3. Furthermore, the two critical curves show a “quasi-tangent” point (or a meeting point).

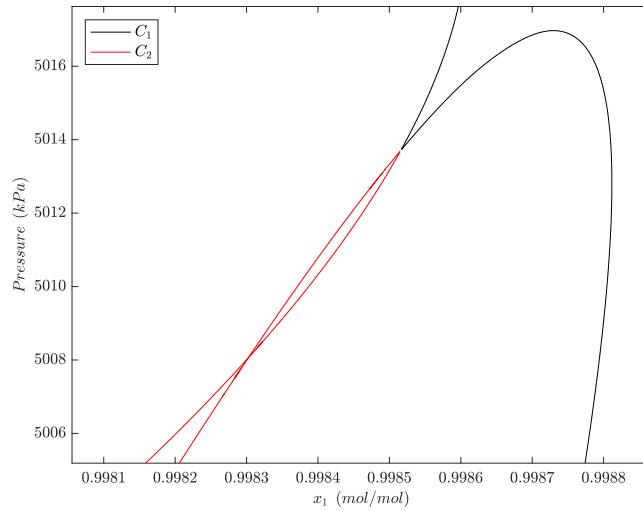


Figure 3: A detailed view of the critical curves.

An amplification of the region in the neighborhood of the “quasi-tangent” point, using a

color pattern (in order to clarify the relationship between domain and image) is presented in Figure 4.

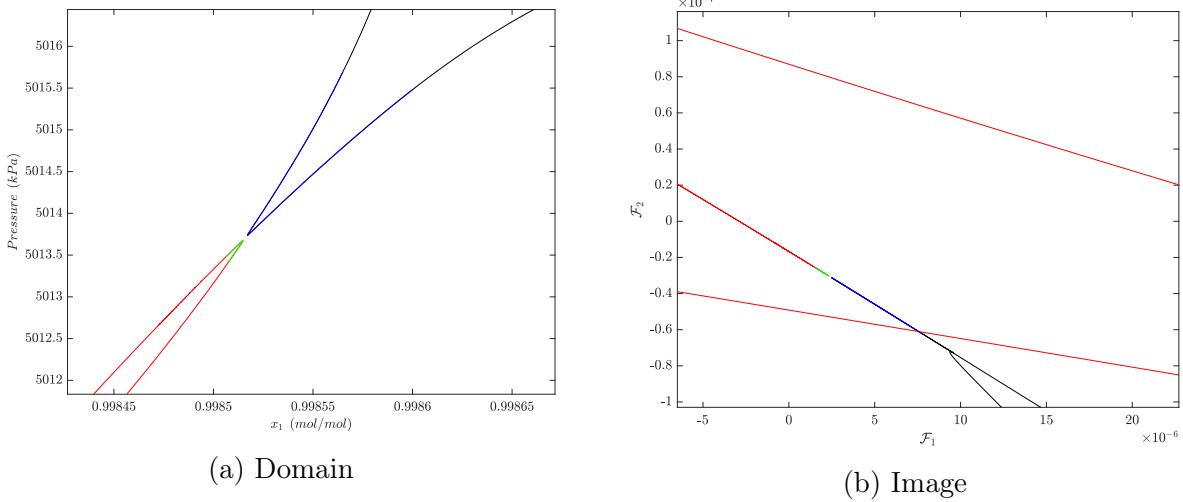


Figure 4: Amplification of the interest region of the critical curve and the critical image.

### Inversion Process – Approaching to the critical image

Figure 5 presents the sequence of points inverted in the image, beginning at  $q = (0, 0)$  and ending close to the critical image (moving to the right side of the image). The squares in the figure are the bank of solved points. The inversion process is then applied, producing the pre-images of the inverted points, in the domain. In this situation, four pre-images are observed (in accordance with the number of solutions of the original nonlinear problem). Obviously, these solutions are not roots of the original problem, since we have  $q = (0, 0)$  for the physical nonlinear problem. On the other hand, as pointed previously, we will maintain the same numbering of the roots (1, 2, 3 and 4).

The sequence of inverted points – in the domain – for Roots 3 and 4 (high pressure roots) is represented by Figure 6. The final point inverted is detailed in the zoom (the blue circles). Clearly, we are facing a degeneration process: the number of roots will decay from four to two, since these pre-images tend to the critical curve.

Figures 8 and 7 contain the sequence of inverted points regarding the Roots 1 and 2,

respectively. In these cases, the inverted points are not close to the critical curves.

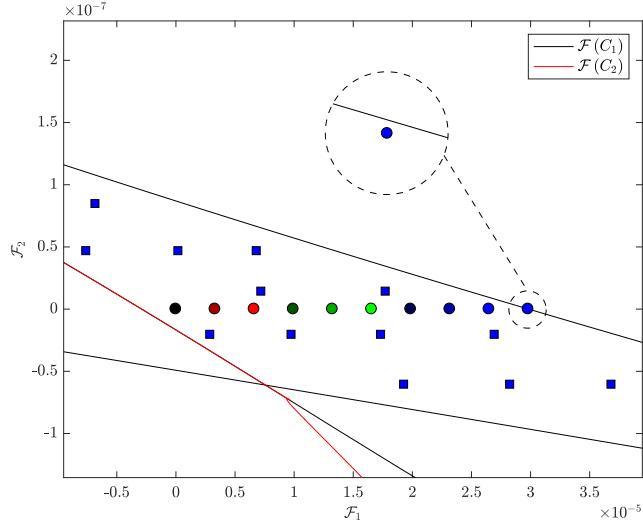


Figure 5: Sequence of inverted points (image).

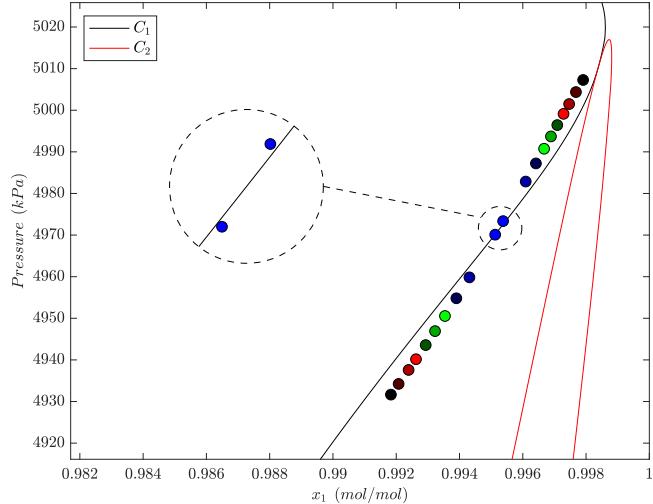


Figure 6: Sequences of inverted points (domain), Roots 3 and 4.

The inversion process will be detailed for the point close to the critical image. Figure 9 indicates the “L” path in the image. Again, the square is a point in the bank of solved points and the desired point is represented by a circle.

The paths in the domain are detached in Figure 10. We can note that the “L” paths were deformed and are virtually straight lines. Once again, the degeneration process is clearly

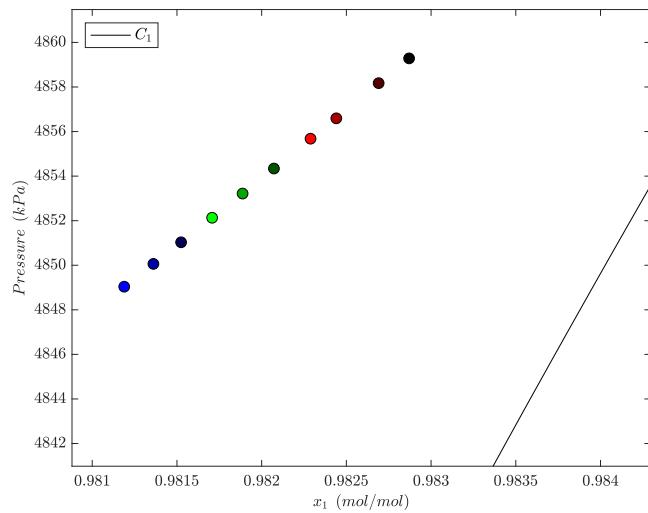


Figure 7: Sequence of inverted points (domain), Root 2.

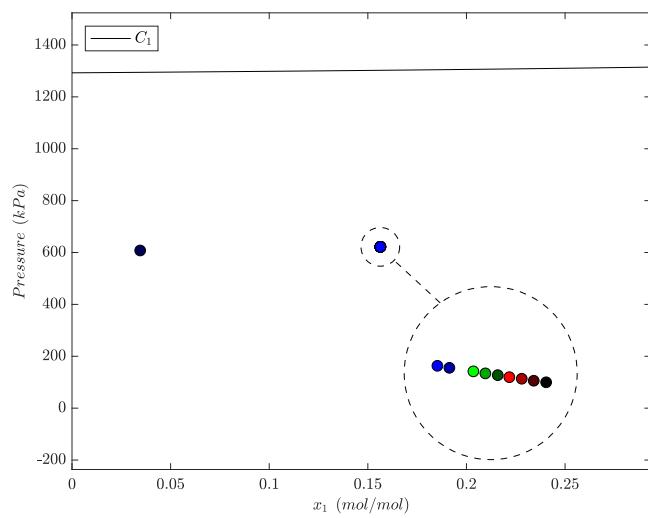


Figure 8: Sequence of inverted points (domain), Root 1.

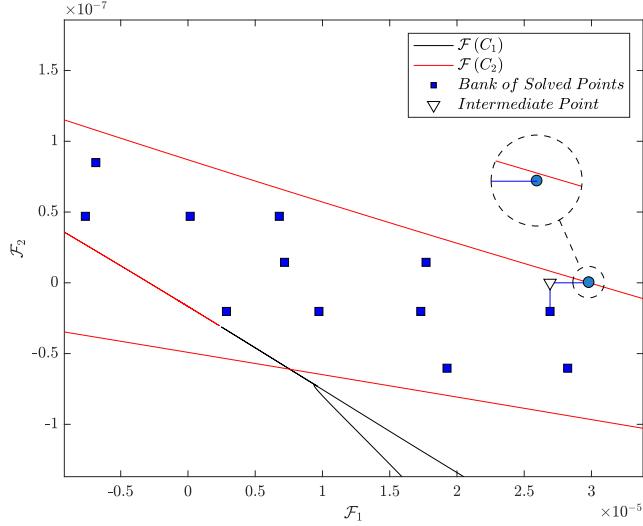


Figure 9: The “L” path in the image.

indicated and the critical curve has a fold at this point.

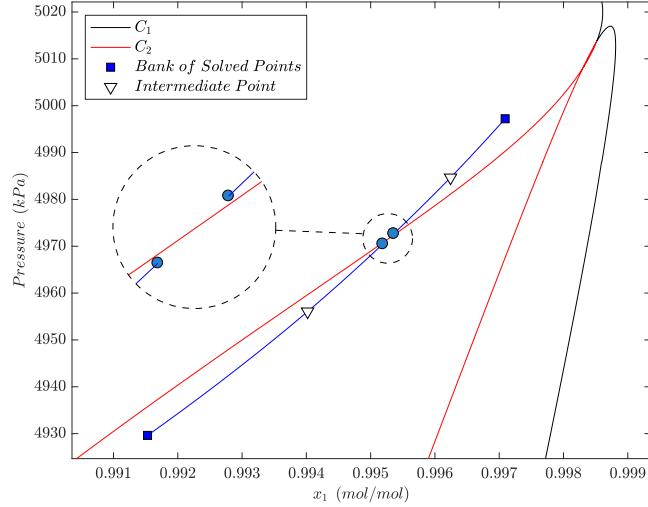


Figure 10: The “L” path in the domain, Roots 3 and 4.

## Results at $T = 304.5$ K and $y_1 = 0.99945$

At  $T = 304.5$  K and  $y_1 = 0.99945$ , the dew point curve still exhibits a double retrograde behavior, but now as a “S” shape (instead of a double dome). In this situation, we observed three dew point pressures (and liquid compositions) for a narrow range of molar fractions.

Figure 11 shows the path of the inversion processes, beginning at  $q = (0, 0)$  and approaching to the critical image.

### Inversion Process – Approaching to the critical image

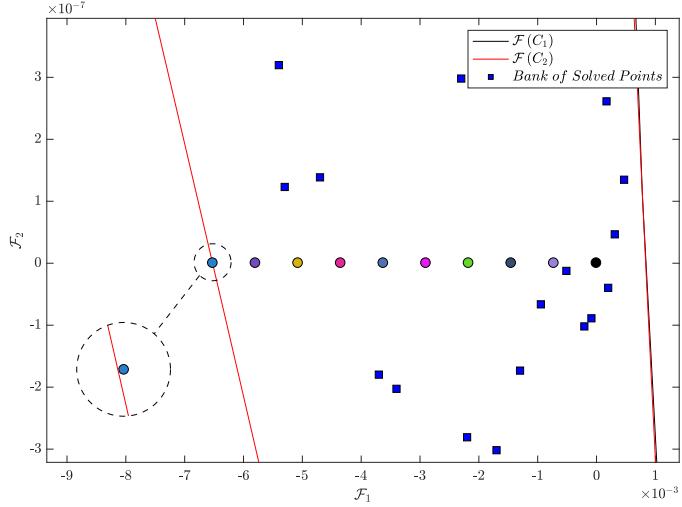


Figure 11: Sequence of inverted points (image) for  $T = 304.5$  K and  $y_1 = 0.99945$ .

The movement of the pre-images obtained in the inversion process is illustrated in Figure 12. We noted that, when  $q$  approaches to the critical image, two pre-images tend to disappear in a fold. We also displayed the kernel of the Jacobian matrix ( $\ker(J)$ ).

Finally, Figure 13 illustrates the “L” path of the inversion process in domain for the last point (marked in blue in the two previous figures). Again, we can note the two pre-images corresponding to the Roots 2 and 3 tend to degenerate to a unique pre-image.

### Results at $T = 280.0$ K and $y_1 = 0.99945$

#### The influence of the temperature in the critical curve

The last feature to be approached in this work corresponds to the influence of the system temperature (specified) in the critical curve. Obviously, the DRV phenomenon is a function of the temperature.

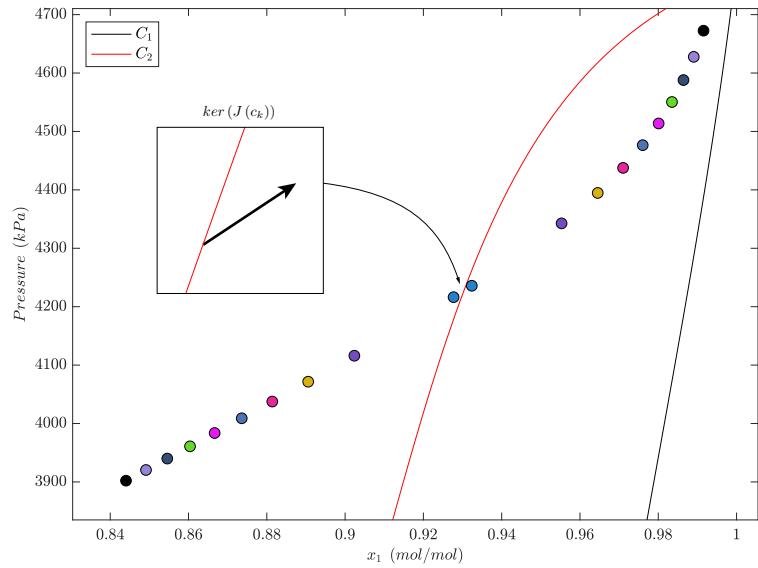


Figure 12: Sequence of inverted points (domain) for  $T = 304.5$  K and  $y_1 = 0.99945$  (Roots 2 and 3).

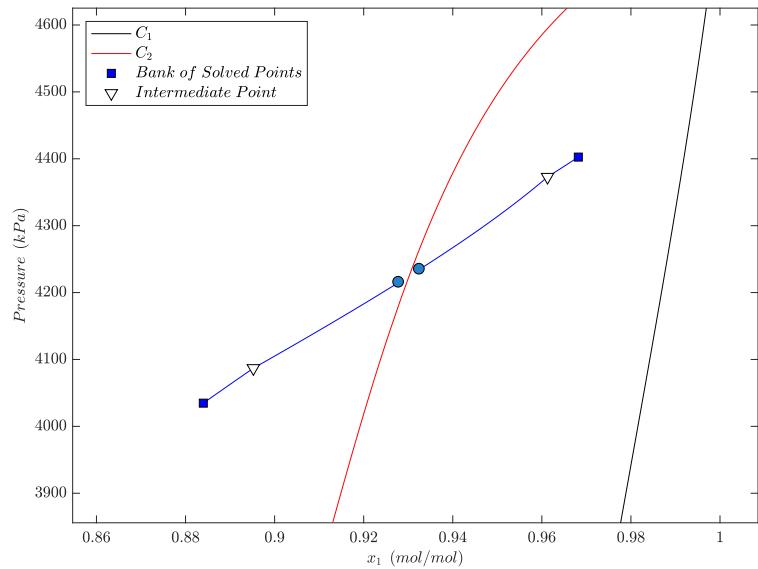


Figure 13: The “L” path in the domain, Roots 2 and 3, for  $T = 304.5$  K and  $y_1 = 0.99945$ .

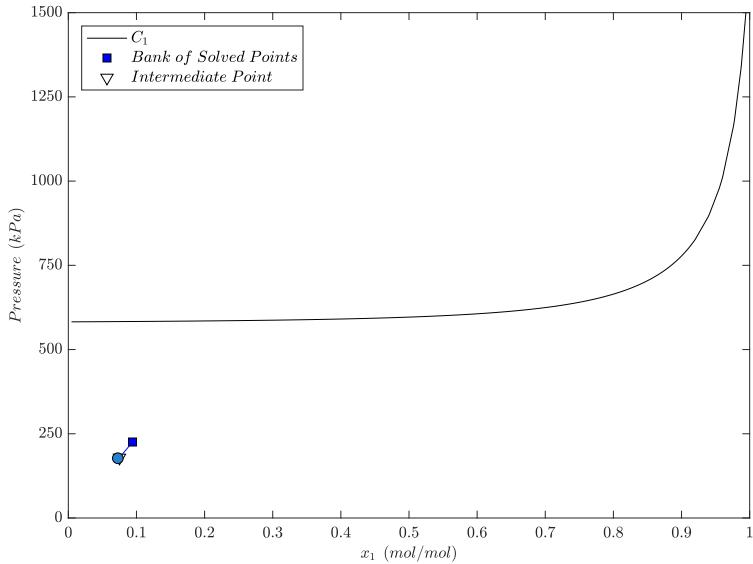


Figure 14: The “L” path in the domain, Root 1, for  $T = 280.0$  K and  $y_1 = 0.99945$ .

## Conclusions

## Acknowledgement

Please use “The authors thank …” rather than “The authors would like to thank …”.

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