

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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1 Introduction

The double retrograde vaporization 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). This phenomenon was firstly investigated by [9] and [10] for the binary mixtures involving methane + n-butane and methane + n-pentane, under specified temperature. More recently, [7] identified a double-dome behaviour for the binary mixture ethane + limonene at $T = 307.4$ K and in a narrow range of compositions (close to the pure ethane). Furthermore, [8] indicated that the Peng-Robinson equation of state [6], with classical mixing rules, was capable to qualitatively predict the phenomenon.

The robust calculation of dew point pressures (under specified temperature) is a very hard task, mainly if we consider the vicinity of the mixture critical point. Furthermore, some roots of the phase equilibrium problem show very small radius of convergence for Newton-type methods, as indicated by [11]. For this reason, the development of robust frameworks for this kind of problem is extremely relevant. Among several possibilities, we can cite the robust methodology of the numerical inversion of functions from the plane to the plane, proposed by [3]. This technique [3] proposes – considering a restrict set of functions – the generation of

the critical curves ¹(here, not in the thermodynamic meaning, but referring to the points where the Jacobian of the nonlinear algebraic system is singular), the construction of a bank of solved points (with good initial estimates) and, finally, the inversion of the desired points (calculation of all pre-images of a such image).

As far as we can see, the first application of the numerical inversion of functions from the plane to the plane in a chemical engineering problem was presented by [2], in the prediction of the azeotropic behavior in systems with double azeotropes.

More recently, [1] presented the initial results regarding the application of the methodology proposed by [3] in the prediction of double retrograde vaporization phenomenon in the system ethane + limonene. However, some relevant aspects were not approached by [1] and will be detailed in this work. Among these aspects, we can cite: (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 will be altered). 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 [11].

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 noted, considering the data presented in Table 1, that one root corresponds to a low pressure root (Root 1) and the other roots are very close (high pressure roots). 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.

Root	x_1	P (kPa)
1	0.1567	619.26
2	0.9829	4859.46
3	0.9918	4931.22
4	0.9979	5007.25

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

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

¹the term “critical” will assume two meanings in this work: in the mathematical sense, a critical point 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.

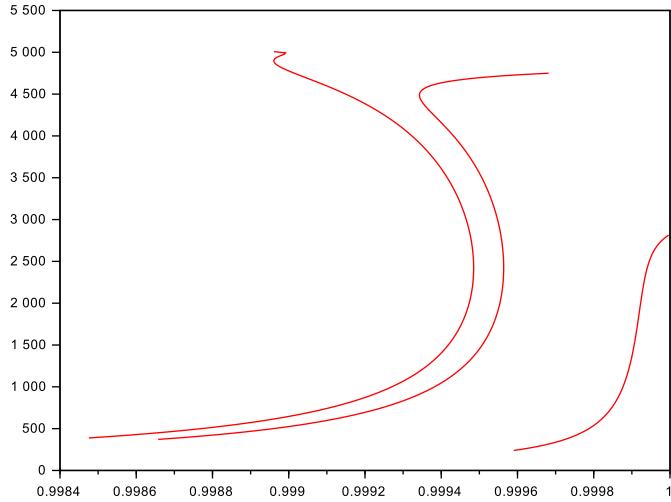


Figure 1: The thermodynamic critical curve in the system ethane + limonene.

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.

Root	x_1	P (kPa)
1	0.3064	1209.36
2	0.8442	3900.98
3	0.9917	4671.36

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

2 Models and Methodology

2.1 Thermodynamic models and problem formulation

All the phase equilibrium calculations, as well as the critical point curves (in the thermodynamic sense), will be conducted with 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 [1].

The phase equilibrium problem can be formulated as (considering a binary mixture):

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

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. Ordinarily, we are interested to solve $F(p) = (0, 0)$ (where $(0, 0)$ represents a null vector).

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

3 Numerical Results

The methodology of numerical inversion of functions from the plane to the plane [3] was employed in this phase equilibrium calculation by [1]. 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 [1]. Here, we will focus on some aspects not addressed by [1], mainly with respect of the quantity of pre-images for some 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.

3.1 Thermodynamic critical point calculations

In this subsection we presented 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. In this subsection, we are dealing with thermodynamic critical points. Here, we used the approach of Heideman and Khalil [5], with a

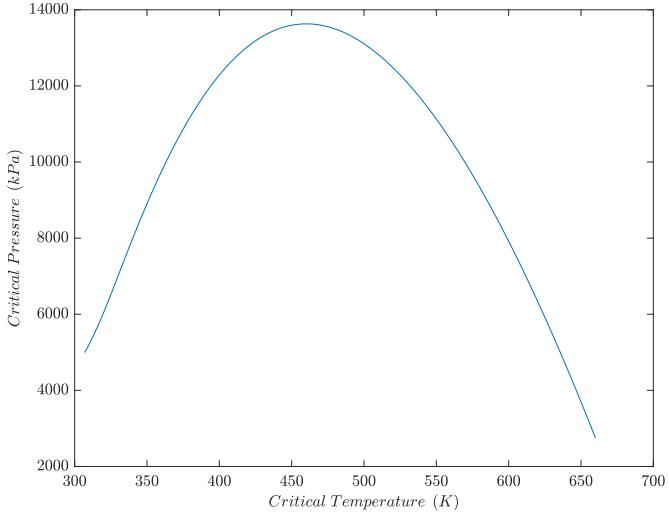


Figure 2: The thermodynamic critical curve in the system ethane + limonene.

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 observed a continuous and unique curve connecting the two pure components. Thus, this system can be classified as Type I, according to the classification of binary mixtures of Van Konynenburg and Scott [4].

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

3.2.1 A close examination on the critical curves

As pointed previously, the initial results regarding the application of the numerical inversion of functions to the prediction of double retrograde behaviour was presented by [1]. In this work, [1] studied some initial features of the critical curves. Here, we presented a more deeper analysis of the critical curves in this system.

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

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.

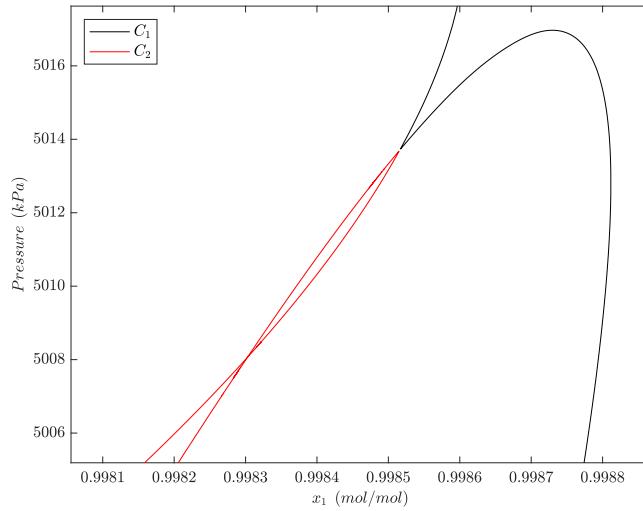


Figure 3: A detailed view of the critical curves.

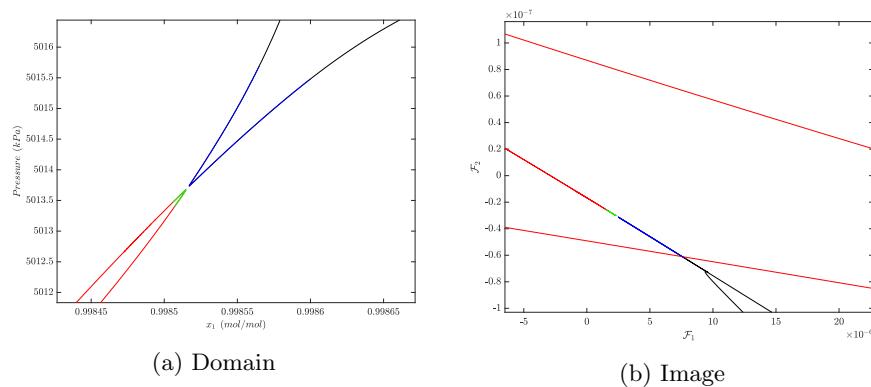


Figure 4: Amplification of the interest region of the critical curve and the critical image.

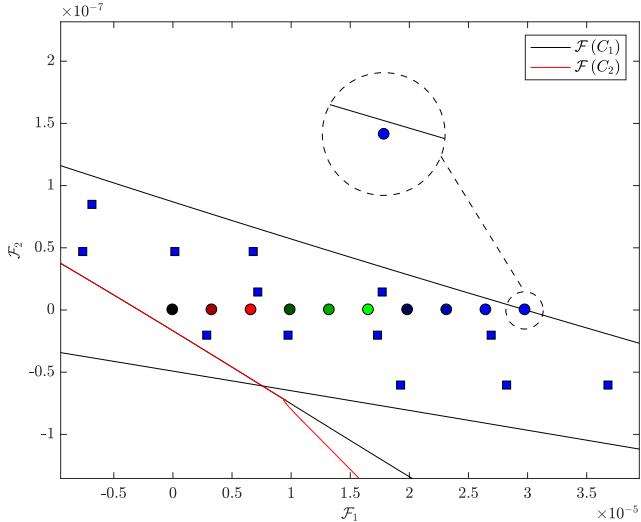


Figure 5: Sequence of inverted points (image).

3.2.2 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.

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,

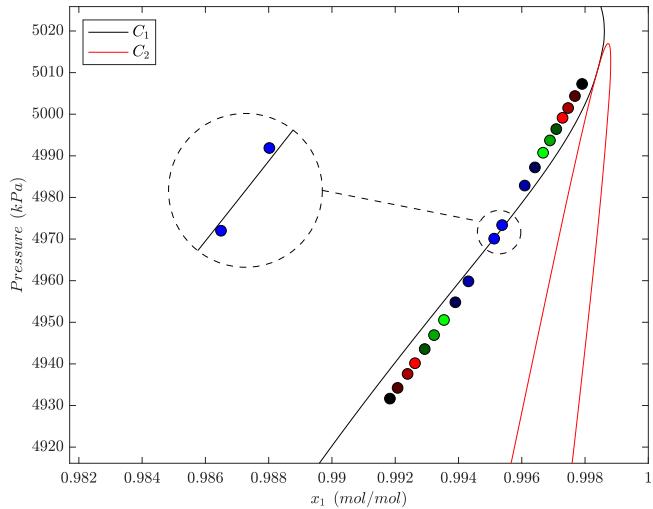


Figure 6: Sequences of inverted points (domain), Roots 3 and 4.

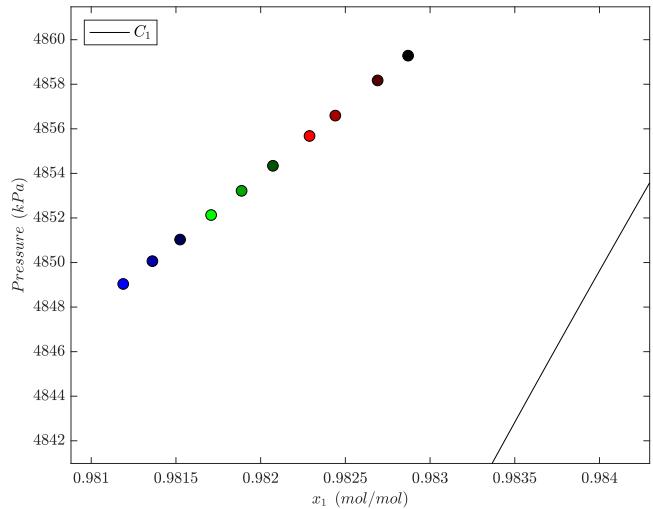


Figure 7: Sequence of inverted points (domain), Root 2.

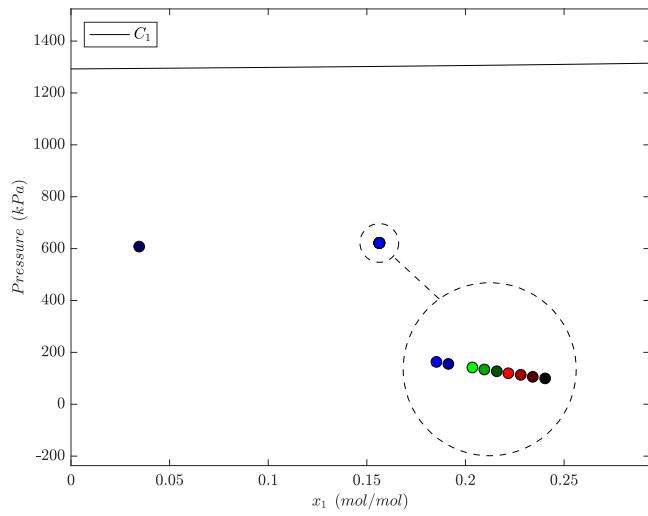


Figure 8: Sequence of inverted points (domain), Root 1.

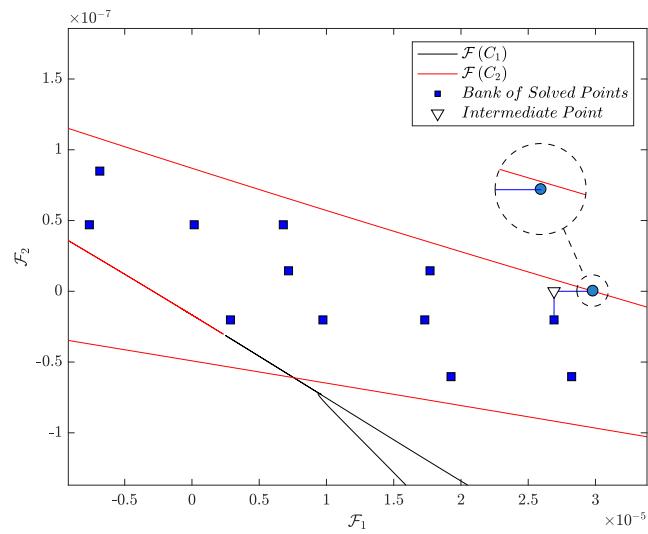


Figure 9: The “L” path in the image.

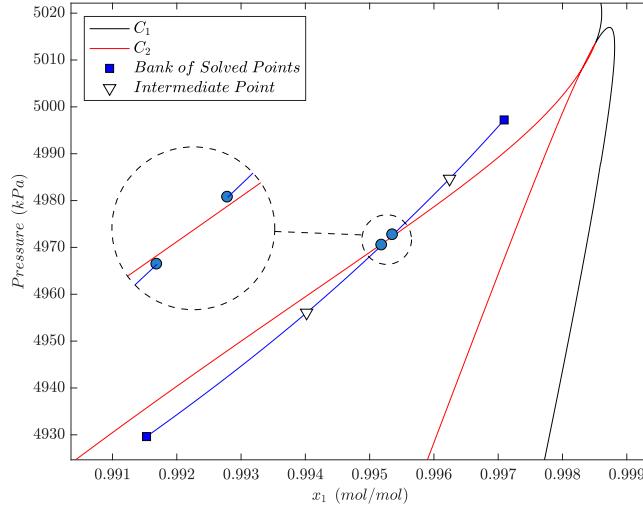


Figure 10: The “L” path in the domain, Roots 3 and 4.

the degeneration process is clearly indicated and the critical curve has a fold at this point.

3.3 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.

3.3.1 Inversion Process – Approaching to the critical image

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.

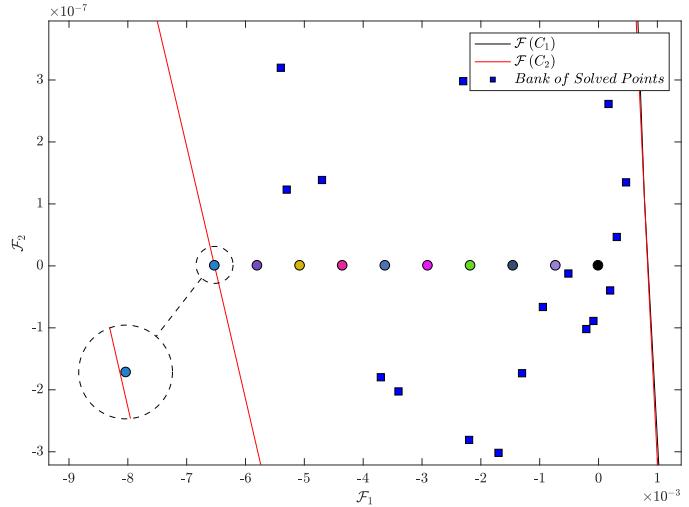


Figure 11: Sequence of inverted points (image) for $T = 304.5$ K and $y_1 = 0.99945$.

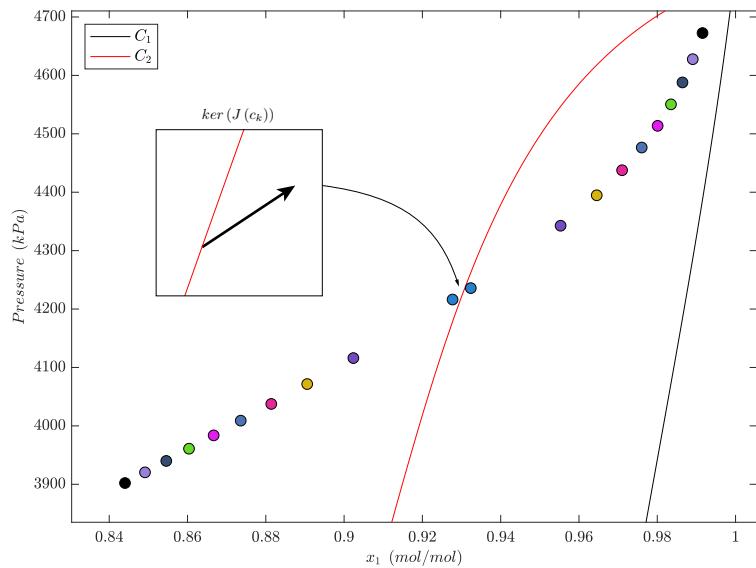


Figure 12: Sequence of inverted points (domain) for $T = 304.5$ K and $y_1 = 0.99945$ (Roots 2 and 3).

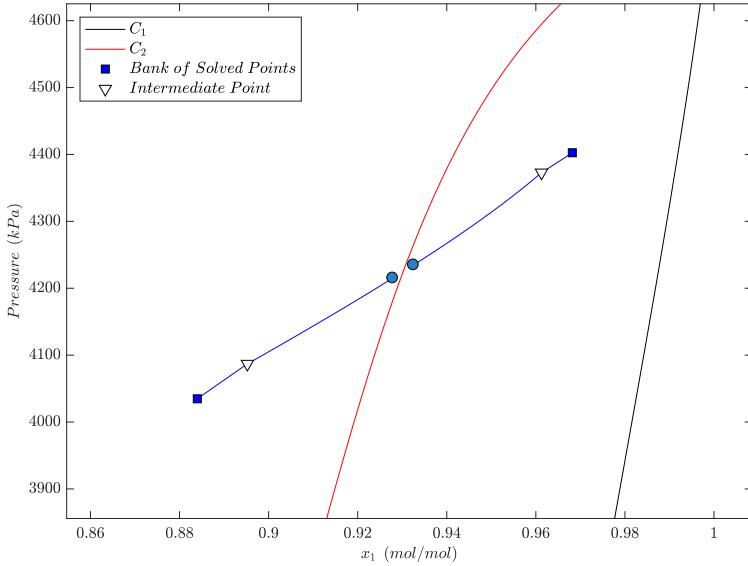


Figure 13: The “L” path in the domain, Roots 2 and 3, for $T = 304.5$ K and $y_1 = 0.99945$.

3.4 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.

4 Conclusions

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