

Geometry of Double Retrograde Vaporization

Prediction

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Abstract

Double retrograde vaporization is a phase behavior phenomenon that occurs close to the critical point of binary mixtures. Here we employ sophisticated modern numerical methodology to untangle the geometry of this complex phenomenon, based on the robust methodology of inversion of functions.

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 specific system temperature and composition. 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.¹ and Chen et al.² for binary mixtures involving methane + n-butane and methane + n-pentane, under specified temperature. More recently, Raeissi and Peters³ 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 Peters⁴ indicated that the Peng-Robinson equation of state⁵, with classical mixing rules, was capable to qualitatively predict this phenomenon. In order to detail the thermodynamic fundamentals of double retrograde vaporization, Raeissi and Peters⁶ 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.⁷. For this reason, the development of robust frameworks for this type 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.⁸, where they developed an extensive theory to handle functions in a generic class of functions defined in the whole plane to the plane. Their theory give precise statements about the solution of 2 by 2 systems of nonlinear equations, when the function is defined everywhere in the plane.

From their theory we select a few techniques which are applicable to our thermodynamic problem, namely the This technique⁸ proposes — considering a generic class of functions — the computation of critical curves in the mathematical sense¹, the construction of a bank of solved points (to be used as with good initial estimates for all the possibly multiple solutions) and, finally, the inversion of the desired point (calculation of all pre-images of a such image).

As far as we know, the first application of these techniques of the general methodology of numerical inversion of functions from the plane to the plane, adapting them to handle a chemical engineering problem was presented by Guedes et al.⁹, in the prediction of the azeotropic behavior in systems with double azeotropes. More recently, Libotte et al.¹⁰ presented some preliminary results regarding the application of the methodology proposed by Malta et al.⁸ in the prediction of double retrograde vaporization phenomenon in the system ethane + limonene.

However, several 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). As pointed previously, the solution of this kind of nonlinear system with typical derivative based root-finding algorithms (such as Newton's methods) is not a trivial task, even when using more sophisticated numerical tools⁷ and thus, one of the objectives of this work is to provide a geometrical view of this challenging nonlinear algebraic system, which can be useful in the development of numerical tools for solving high-pressure phase equilibrium problems.

In order to analyze these main points and provide an in-depth geometric study of the phase equilibrium problem in two-component systems, we present two case studies. The first one is the system composed of ethane + limonene at $T = 307.4$ K which is analyzed, fixing the molar fraction of the vapor phase of ethane at $y_1 = 0.998966$. Under these conditions,

¹The 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.

the system presents four distinct solutions, corresponding to the intersections of the dew point curve with the line of a given 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 of the function that defines the nonlinear system that are folds and cusps, and their relation with the degeneration of solutions of this problem.

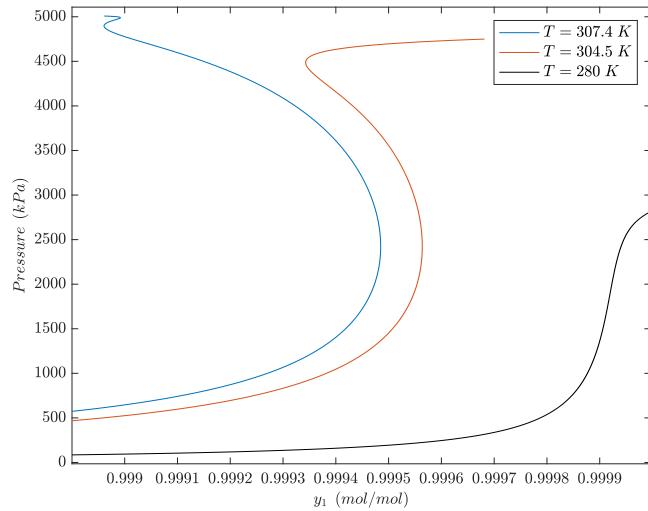


Figure 1: Dew point curves for the system ethane + limonene at several temperatures. LIBOTTE, VC PODERIA COLOCAR DUAS VERTICAIS nos pontos de y_1 mencionados no texto, para ver as interseções.....RETIRAR ESTA FRASE!!!

In the second case study, the temperature of the system composed of the same components of the previous case was set at $T = 304.5$ K and compared with the same system at $T = 280$ K. In these temperature scenarios, with $y_1 = 0.99945$ (among other conditions), the system has three and one solutions, respectively, as shown in Figure 1. Thus, it is 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

of the function defining the nonlinear 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.

The remaining of this work is organized as follows. First we discuss the thermodynamic model. Next we present the mathematical and numerical methodology, begining with an example of a function scalar function of one variable (1D case) and showing how the critical points and their images are used to break the equation in cases where the number of solutions is constant, followed by a discussion of functions of two variables (2D case), and fold and cusp critical points. The construction of the critical set and of the bank of solved problems is next. Finally we present and discuss the numerical examples, and conclusions.

Models and Methodology

Thermodynamic models and problem formulation

All the phase equilibrium calculations, as well as the critical point curves (in the thermodynamic sense), are 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.¹⁰.

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:

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

$$\hat{\phi}_2^L(1 - x_1) = \hat{\phi}_2^V(1 - y_1) . \quad (2b)$$

The vector of unknowns, considering the specification of temperature and vapor molar fractions, is $p = (x_1, P)$. Let the residue of the nonlinear equations be denoted by f_i , and define $F = F(x_1, P) = (f_1, f_2) = (\hat{\phi}_1^L x_1 - \hat{\phi}_1^V y_1, \hat{\phi}_2^L(1 - x_1) - \hat{\phi}_2^V(1 - y_1))$. Thus, in general, the nonlinear algebraic system can be re-stated as

$$F(p) = q , \quad (3)$$

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).

Some features of the numerical inversion of functions

Here we present a few fundamental ideas on the solution of a nonlinear system by numerical inversion of the associated functions.

An 1D example

To get a grasp of the methodology of inversion of functions to solve nonlinear systems of equations, we first consider a simple 1D example. Let $F(p) = p^3 - 3p^2 + 2p = p(p-1)(p-2)$. Assume that for physical reasons p is always non-negative. By examining the graph of F it is possible to check that the equation for q ,

$$F(p) = q, \quad \text{that is, } p^3 - 3p^2 + 2p = q ,$$

has 0 to 3 solutions. If $\eta(q)$ denotes the number of solutions as a function of q , then,

$$\eta(q) = \begin{cases} 0, & \text{if } q < -2\sqrt{3}/9 \\ 1, & \text{if } q = -2\sqrt{3}/9 \text{ or } q > 2\sqrt{3}/9 \\ 2, & \text{if } -2\sqrt{3}/9 < q < 0 \\ 3, & \text{if } 0 \leq q < 2\sqrt{3}/9 \end{cases}.$$

The jumping points, where the number of solutions can change, are either the image of a critical point — a critical image — or an image of a boundary point of the domain of definition of F . The critical points (where the derivative is zero) satisfy

$$F'(p) = 3p^2 - 6p + 2 = 0, \text{ that is } p = 1 \pm \sqrt{3}/3.$$

Since 0 is the only boundary point of the domain, the jumping points are $F(1 \pm \sqrt{3}/3) = \mp 2\sqrt{3}/9$ and $F(0) = 0$. These points suggest a partition of the range of F in seven subsets, $\mathbb{R} = \mathcal{T}_1 \cup \mathcal{J}_2 \cup \mathcal{T}_3 \cup \mathcal{J}_4 \cup \mathcal{T}_5 \cup \mathcal{J}_6 \cup \mathcal{T}_7$,

$$\begin{aligned} \text{jumping sets} \quad & \mathcal{J}_2 = \left\{ -\frac{2\sqrt{3}}{9} \right\}, \quad \mathcal{J}_4 = \{0\}, \quad \mathcal{J}_6 = \left\{ \frac{2\sqrt{3}}{9} \right\}, \\ \text{tile sets} \quad & \mathcal{T}_1 =]-\infty, -\frac{2\sqrt{3}}{9}[, \quad \mathcal{T}_3 =]-\frac{2\sqrt{3}}{9}, 0[, \quad \mathcal{T}_5 =]0, \frac{2\sqrt{3}}{9}[, \quad \mathcal{T}_7 =]\frac{2\sqrt{3}}{9}, +\infty[. \end{aligned}$$

Note that the number of solutions is constant in each tile. The overall strategy for solving the equation $F(p) = q$ is to compute the jumping sets and, by taking the complementary set, decompose the range of F in its jumping and tile sets, have a bank of solved points with representatives more or less covering all the tile sets, and to solve the equation with the bank of solved points providing initial guesses for each solution.

Jumping and tiles in the 2D case

Now we consider 2×2 systems of equations, $F(p) = q$, with $q \in \mathbb{R}^2$ and F a function defined on a subset Ω of the plane to the plane, $F : \mathbb{R}^2 \supset \Omega \rightarrow \mathbb{R}^2$. Recall that the Jacobian $JF|_p$

at a point $p = (x, y) \in \mathbb{R}^2$ is

$$JF|_p = \begin{pmatrix} \frac{\partial f_1}{\partial x} & \frac{\partial f_1}{\partial y} \\ \frac{\partial f_2}{\partial x} & \frac{\partial f_2}{\partial y} \end{pmatrix}.$$

A point p in the domain is said a critical point if $JF|_p$ is not invertible, which is equivalent to say that $\det(JF|_p) = 0$. A critical point is non-degenerate if $\text{grad}(\det(JF|_p)) \neq 0$. Under such conditions, the Jacobian matrix is not the null matrix. Therefore, this matrix has rank equal to one in p and there is a nonzero vector that is tangent to the critical curve. As a consequence, if a function has only non-degenerate critical points — which we assume — their set is formed by curves, the critical curves,

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

and the image of \mathcal{C} , $F(\mathcal{C}) = \{q = F(p), \text{ for all } p \in \mathcal{C}\}$, is called the critical image. The set formed by the union of the critical image and the image of the boundary of the domain of F , $\mathcal{J} = F(\mathcal{C}) \cup F(\Omega)$, define the jumping curves. The tiles are the connected components on the complement of \mathcal{J} ; if there are k connected components, \mathcal{T}_i , then $\mathbb{R}^2 = (\cup_{i=1}^k \mathcal{T}_i) \cup \mathcal{J}$, just as in the 1D example. The number of solutions of the equation $F(p) = q$ is constant if $q \in \mathcal{T}_i$, and may jump when crossing \mathcal{J} .

One of the drawbacks to the application of the detailed theory presented in Malta et al.⁸ to problems coming from applications that involve the solution of nonlinear 2×2 systems of equations is not so much that it applies only to a special collection of functions, but that the functions have to be defined in all points in the plane. When that happens, the theory gives a fairly good amount of information on the solutions of the nonlinear system of equations. In applications, however, the domain of a function has to satisfy some restrictions due, for instance, to the lack of physical significance of certain values of the variables, or due to existence of singularities, which breaks the theory presented in Malta et al.⁸. This is the case in the problems we are considering since, *e.g.*, the volume cannot be less than a certain

quantity, and the pressure cannot be above certain critical value. Nonetheless the overall methodology that they discuss is preserved in the form of algorithms.

The inversion of functions from the plane to the plane

Next, we present the method of inversion of functions from the plane to the plane, as well as the main definitions that support the technique. A detailed description of the method can be found in Malta et al.⁸.

The method is intended to solve systems with two equations and two unknowns of type $F(p) = q$ with $p, q \in \mathbb{R}^2$ and F should be a smooth function.

In dealing specifically with critical points, they are assumed of just two types, either folds or cusps. A fold is a non-degenerate critical point such that:

- the kernel K of the Jacobian and the tangent line T to the critical set in p do not coincide.

In cases where the kernel K and the line T tangent to the critical set coincide, there is a cusp-like critical point. In general, cusps are non-degenerate critical points such that:

- the kernel K of the Jacobian and the tangent line T to the critical set in p coincide;
- for a smooth parametrization $\gamma : (-\epsilon, \epsilon) \rightarrow \mathbb{R}^2$ of C near p , with $\gamma(0) = p$ and $\gamma'(0) \neq 0$, the angle $\theta(\gamma(t))$ between the kernel $K(\gamma(t))$ of $J(\gamma(t))$ and the tangent line $T(\gamma(t))$ to C satisfies $\theta'(0) \neq 0$.

Within the scope of functions from the plane to the plane, we must introduce two descriptions of very important type of functions. A continuous function from a subset of the plane to the plane is proper if $\lim_{|(x, y)| \rightarrow \infty} |F(x, y)| = \infty$. This avoids to treat equations with infinitely many solutions. A 1D case, of an equation with infinite solutions, is $\sin x = 0$. This happens because $\sin x$ is not a proper function. A smooth proper function from the plane into itself is excellent if every critical point of F is a fold or a cusp. In essence, the

theory developed in Malta et al.⁸ aims at solving equations defined by excellent functions that satisfy yet another technical condition, the nice functions. For them, the theory asserts several results. An essential feature of the class of nice functions is that, under a suitable topology, they are generic in a mathematical sense. That means in particular that they are a dense set. From a simplified point of view, that property expresses that any smooth function can be approximated arbitrarily close by a nice functions. Therefore, the analysis can be restricted to this type of function. That is, in practice, it is enough to work with nice functions, thus the critical points are only cusps and folds.

The methodology of inversion of functions from a subset of the plane to the plane is composed of three fundamental steps: obtaining the critical set of F , creating the bank of solved points and calculating the pre-images from an arbitrary point. Each of these steps will be described next.

Generation of the critical set

Knowing the critical set is fundamental in the inversion process, since it allows the computation of the critical image which, as illustrated in the 1D example, are places where the number of solutions can change — in this cases we say that the solutions degenerate. In addition to tracing the regions where the continuation method does not face points of singularity in the inversion process, it also indicates the boundary of the different tiles, which is a primordial concept in the analysis of solution degeneration.

In the original procedure, Malta et al.⁸ proposes various calculations and verifications in order to establish that, strictly speaking, the critical points obtained form the critical set as a whole. In addition, the computational routine still sorts the critical points and locates points of intersection of the curves in the image. Due to the difficulties mentioned above regarding the application of the technique to solve real engineering problems, some adaptations were made to the original method, so that it could be simplified without affecting its main attributes.

Initially, the problem domain is fully mapped. An equally spaced rectangular mesh is constructed in the domain of the problem and the value of the determinant of the Jacobian matrix at each point is calculated. Since the critical points are those in which the determinant of the Jacobian is null, the mesh is traversed, and each time changes in the signal of the determinant are identified, an arbitrary point of the segment between the two points of the mesh with distinct signals is taken as initial guess of the root calculation. Therefore, a Newton-type routine is executed until the critical point within the segment of the mesh is obtained.

The previous procedure is executed until all the mesh is traversed, that is, until all the critical points of the domain are obtained, forming the critical set. The mesh must be sufficiently refined so that the whole set of critical curves can be obtained, with the desired accuracy. After obtaining the set \mathcal{C} of critical curves, the set of critical images $F(\mathcal{C})$ follows by calculating the value of the function of each of the critical points contained in \mathcal{C} .

Creation of the bank of solved points

The bank of solved points is a set of points in the image where all their respective pre-images in the domain are known since they have been carefully computed. These points are then used as initial guesses for the process of inversion of an arbitrary point in the image of the function. The bank of solved points can be as extensive as desired and obtaining the pre-images of each of the points can be performed by the continuation method (when at least one pre-image is known) or by using a numerical method capable of getting the whole set p_a when $F(p_a) = q_a$. Since the inversion method can fail if it approaches sufficiently close to the critical set, it is instrumental the creation of a bank of solved points, to effectively be able to solve the system of equations in general. It is a set of points in the image where all their respective pre-images in the domain are known.

Once the bank of solved points has been built, it is needed to adopt an appropriate criteria in choosing the point that is used as the beginning point in the path created by

the continuation method. Originally, the technique adopts different criteria based on the following properties: the calculated segments in the inversion process should stay away from critical points, especially from the cusp type, which are difficult to obtain pre-images. In addition, the segments should have few intersections with $F(\mathcal{C})$, due to the possible degeneration of solutions. Also, segments should be as short as possible. However, due to difficulties the criterion assumed for the choice of the bank point that will be taken as the initial guess of the continuation process in the inversion step is the calculation of the shortest path, since the critical points are not classified in the step of obtaining the critical curves and it is intended to avoid that the segment crosses the critical curve. In this way, the point q_0 of the bank with the least Euclidean distance in relation to q — the point to be inverted — is chosen.

Choosing the point that will generate the shortest path does not guarantee that the segment will not cross some critical curve. If q_0 is located on a different tile than q , the inversion process may have problems, since the segment will necessarily cross some image of a critical or boundary curve before q is reached. Therefore, it is convenient that the bank of solved points be formed by points contained in different tiles, according to the problem solving requirements.

From the point of view of user interference in relation to each of the steps of the method, the creation of the bank of solved points is the most expensive stage, especially when they are very extensive and there are several pre-images, according to each specific problem. However, the homotopy-continuation technique used in the inversion step (see more in Eugene L. Allgower¹¹) allows the use of a single bank in solving different problems of the same genre, that is, with variation of parameters, as shown in Guedes et al.⁹, which solved the double azeotropy problem of the system composed of benzene + hexafluorobenzene at different values of the system pressure, with the same bank of solved points generated at $P = 20kPa$.

Inversion of an arbitrary point

The calculation of the solutions of the system of equations is accomplished through the creation of L-shaped paths using the Euler-Newton continuation method. Initially, the element q_0 of the bank of solved points in the image that is closest to the point to be inverted q is selected. Then, the points are connected to each other through two perpendicular segments, joined by their ends, going from q_0 to q , which produces an intermediate point, called \tilde{q} . The respective path in the domain will be traversed through the continuation method, starting from p_0 , that is, the point of the bank of solved points in the domain referring to q_0 . Since each point of the image stored in the bank must have all of its respective pre-images also kept in the bank, the inversion step must be executed as many times as there are entries stored in the bank of solved points in the domain relative to q , in order that all the solutions of the system are found, producing different L-shaped paths, which start from the same initial guess.

The predictor-corrector method used to trace the L-shaped path is based on homotopy techniques. Eugene L. Allgower¹¹ offers a detailed approach to homotopy techniques. Here, only the main points of the methodology will be treated. In a rudimentary way, take $F : \mathbb{R}^n \rightarrow \mathbb{R}^n$ a smooth map. In an attempt to find the values of p that determine the solutions of $F(p) - q = 0$, numerical methods may fail when no prior knowledge of F is known and the initial guesses taken may not be good enough to solve the problem. One way to avoid this kind of problem is to deform the original function through a homotopy technique and try to trace an implicitly defined curve in order to reach the solution of the system through a starting point. Therefore, the homotopy $H : \mathbb{R}^n \times \mathbb{R} \rightarrow \mathbb{R}^n$ is a smooth. One can choose the convex homotopy, which is given by

$$H(p, \lambda) = F(p) - \lambda q - (1 - \lambda) q_0 ,$$

where q is the point in the image to be inverted, q_0 is the point of the bank of solved points

that will be taken as the initial guess in an attempt to trace an implicitly defined curve and λ is a real parameter, such that $\lambda \in [0, 1]$. Note that the original problem can be retrieved when λ assumes the extreme values of the range in which it is defined.

The purpose of the predictor-corrector method is to trace the curve by varying the λ value over the interval in which it is defined, generating a sequence of points and respecting a given tolerance. The scheme used employs the Euler method in the predictor step. This method obtains the point sequence that approaches the curve through the recurrence relation

$$v_{i+1} = u_i + ht(H'(u_i)) ,$$

where $h > 0$ represents the stepsize and $t(H'(u_i))$ is an unitary vector tangent to the solution curve at the point u_i , obtained by QR decomposition. The stepsize must be arbitrarily small in order to obtain a reasonable approximation. Also, if u_i is sufficiently close to the curve, then the predictor point v_{i+1} will also be sufficiently close to the curve and the minimization problem will have an unique solution, which will be refined in the corrector step.

In turn, the scheme used in the corrector step is the Newton's method. However, the jacobian matrix H' is not square, since the homotopy technique introduces the λ parameter into the function that describes the problem, and therefore the matrix is not invertible. Thus, Newton's method requires modifications to satisfy the dimension of the problem. Therefore, the problem of minimization motivates the introduction of an alternative to the inversion of non-square matrices: the Moore-Penrose inverse. Denoted by A^+ , the Moore-Penrose right inverse of a matrix A is defined by $A^+ = A^T (AA^T)^{-1}$, where A is a $n \times (n+1)$ matrix with maximal rank. Therefore, the recurrence relation that defines Newton's method in the corrector step is given by

$$w_{i+1} = v_{i+1} - H'(v_{i+1})^+ H(v_{i+1}) .$$

After calculating a point that approximates the curve of interest in each of the iterations of

the predictor-corrector method through the approach mentioned above, a stepsize adaptation strategy is adopted for the next iteration. It is convenient to adopt strategies of this type to avoid regions that contain singularities or to prevent the numerical method from making big jumps during the calculation of the curve. Using this artifice, it is also possible to perform a complementary evaluation of the convergence of the method. Thus, the first parameter of evaluation is the contraction rate of the corrector step, defined by the quotient of the Euclidean norm of two successive iterations of the Newton method. The stepsize should be adjusted if the sequence of contraction rate values are not decreasing.

The stepsize can also be adjusted by analyzing the angle between two consecutive iterations, that is, the slope of the segment formed by subsequent points. By setting nominal values, one can define the appropriate stepsize for each of the iterations by analyzing these parameters. With this, the continuation method is subject to a “deceleration factor”, which varies between predefined limits. The details of the methodology will be omitted and can be viewed at Eugene L. Allgower¹¹.

Numerical Results

The methodology of numerical inversion of two-variable functions, adapted from Malta et al.⁸ which considered the special case of function from the plane to the plane, is employed in this phase equilibrium calculation. Some details regarding the construction of the bank of solved points and the numerical steps of the inversion process are given by Libotte et al.¹⁰. We present an in-depth analysis of the quantity of pre-images in limit-situations (for instance, when the critical image is approached). Furthermore, we 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 not only to find all roots, but also to find the high pressure roots in a robust way.

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

In order to better understand the geometry of the nonalgebraic system of equilibrium, we consider some modified problems (perturbed versions of the original one) — which bear no immediate physical meaning — and use the same numbering of the roots (1 to 4).

We also test 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

Here 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 and the thermodynamic. Here we deal with thermodynamic

critical points, and we use the approach of Heidemann and Khalil¹², 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, according to the classification of binary mixtures of Van Konynenburg and Scott.¹³

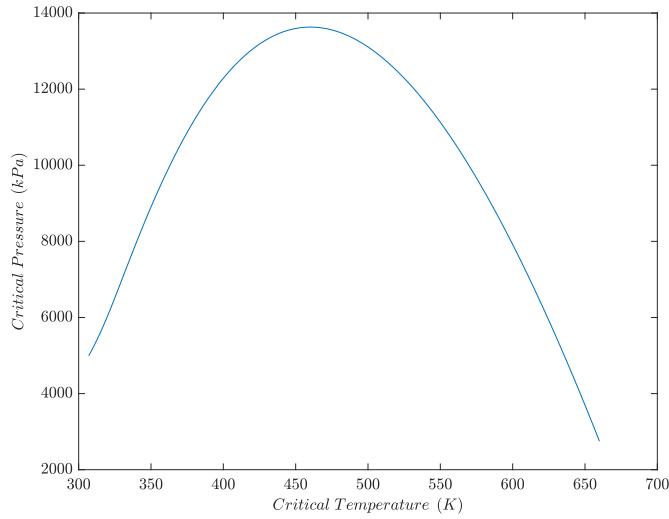


Figure 2: The thermodynamic critical curve in the system ethane + limonene.

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

An in-depth examination of the critical curves

Here, we present a deeper analysis of the mathematical critical curves in this system. Clearly, we note that — in the highlighted region — the critical curves exhibit one self-intersection, as exhibited 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.

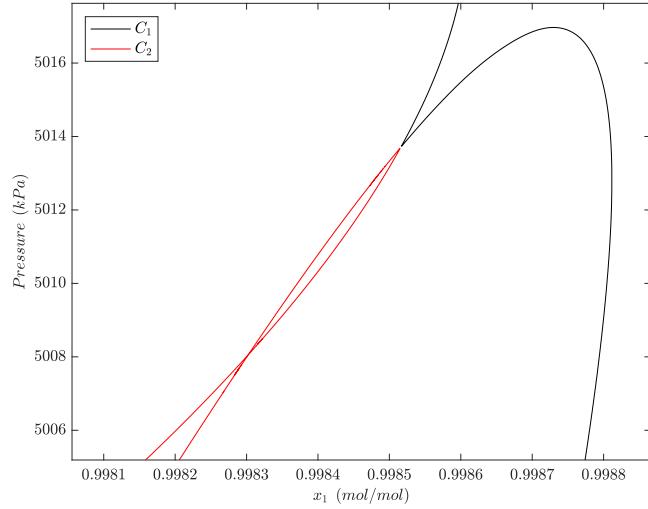


Figure 3: A detailed view of the critical curves.

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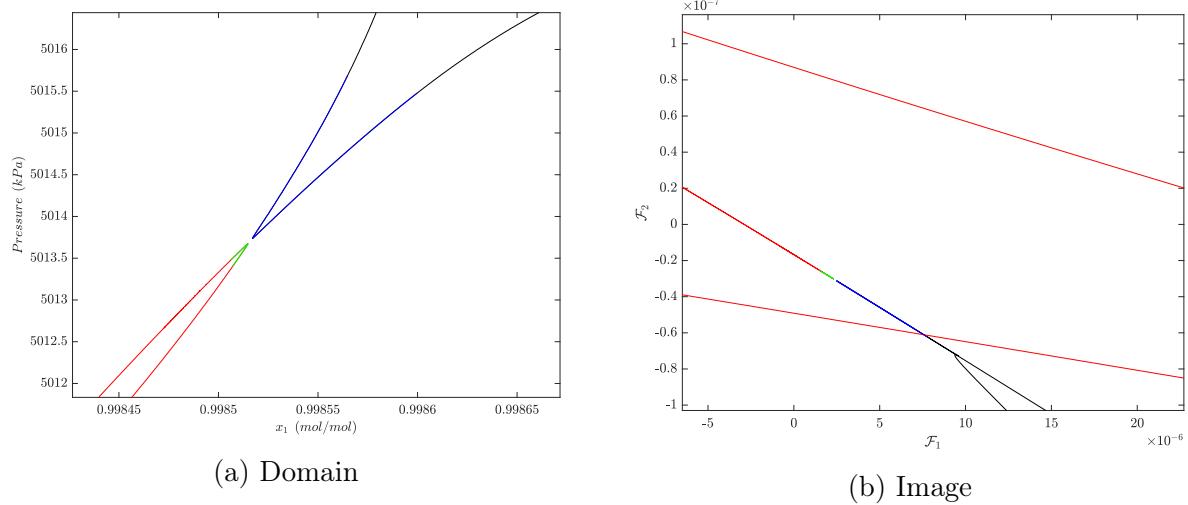


Figure 4: Amplification of the interest region of the critical curve and the critical image.

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 maintain the same numbering of the roots (1 to 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 drops from four to two, since these pre-images tend to the critical curve.

Figures 7 and 8 contain the sequence of inverted points regarding Roots 1 and 2, respectively. In these cases, the inverted points are not close to the critical curves.

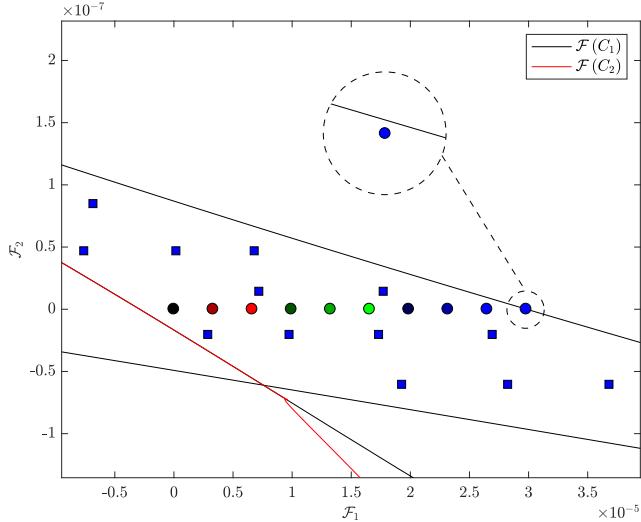


Figure 5: Sequence of inverted points (image).

We detail the inversion process 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 indicated and the critical curve has a fold at this point.

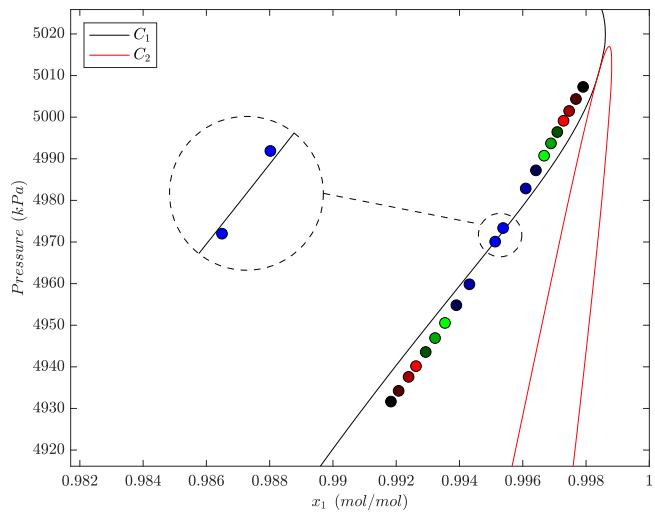


Figure 6: Sequences of inverted points (domain), Roots 3 and 4.

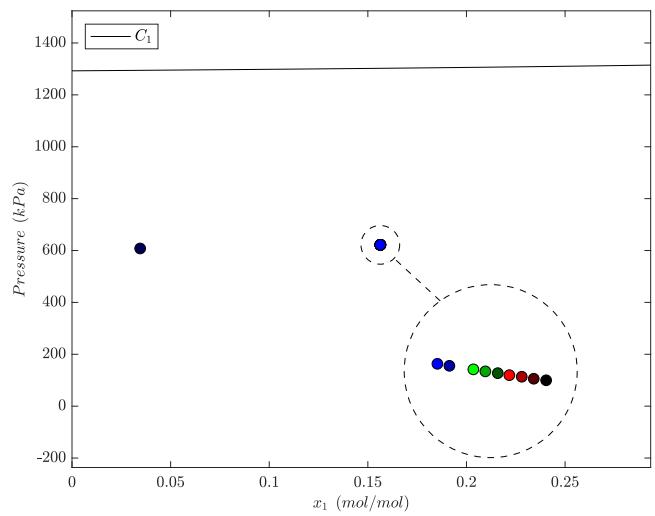


Figure 7: Sequence of inverted points (domain), Root 1.

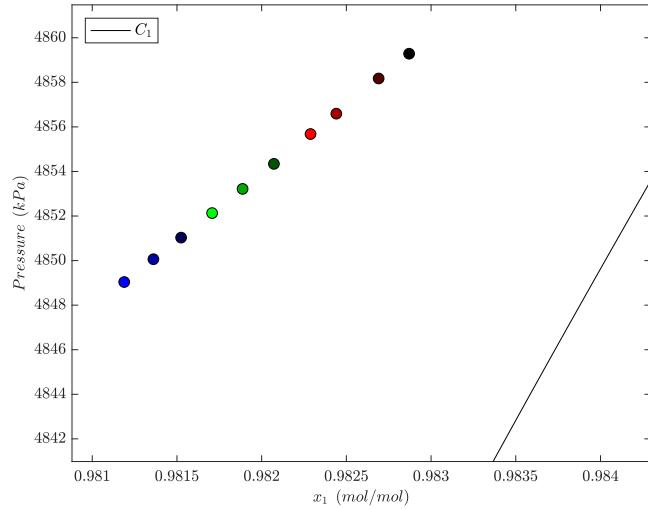


Figure 8: Sequence of inverted points (domain), Root 2.

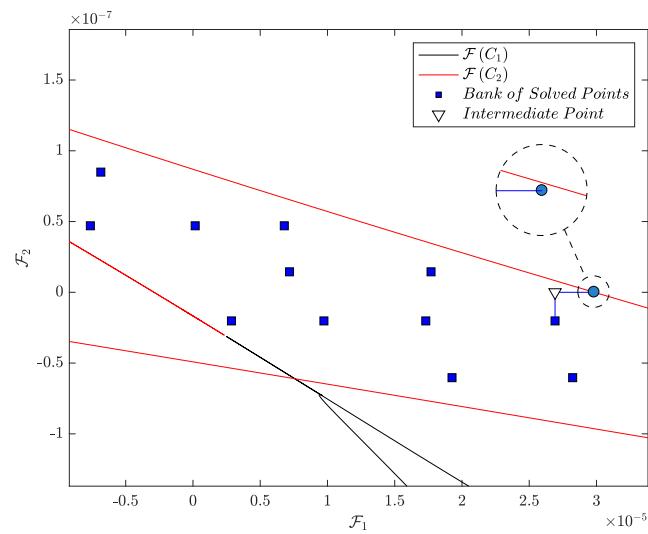


Figure 9: The “L” path in the image.

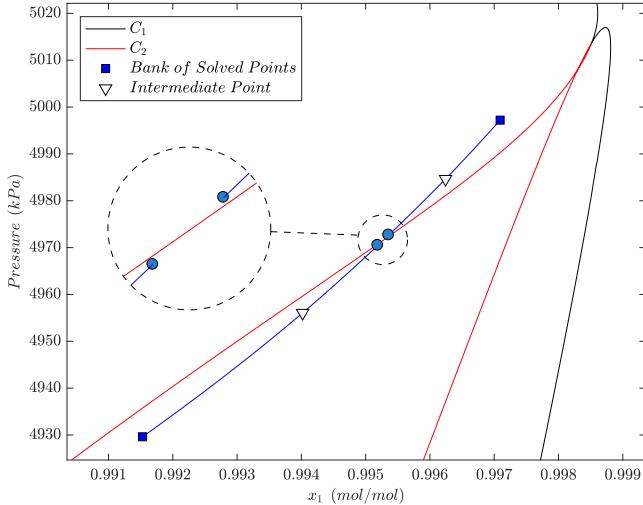


Figure 10: The “L” path in the domain, Roots 3 and 4.

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 observe 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 the critical image.

Inversion process — approaching the critical image

The movement of the pre-images obtained in the inversion process is illustrated in Figure 12. We note that, when q approaches 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 the domain for the last point (marked in blue in the two previous figures). Again, we note that the two pre-images corresponding to Roots 2 and 3 tend degenerate into a single pre-image.

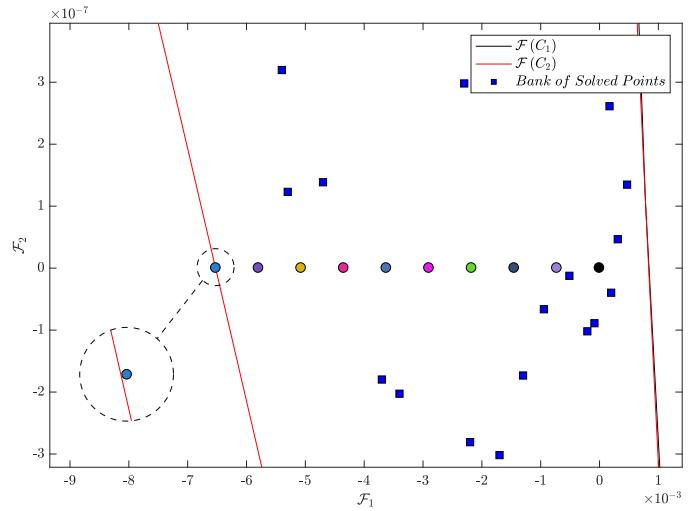


Figure 11: Sequence of inverted points (image) for $T = 304.5$ K and $y_1 = 0.99945$.

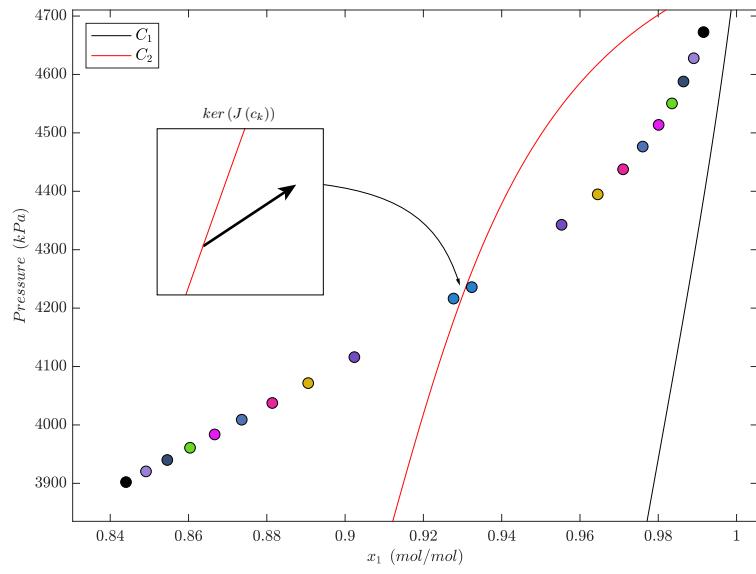


Figure 12: Sequence of inverted points (domain) for $T = 304.5$ K and $y_1 = 0.99945$ (Roots 2 and 3).

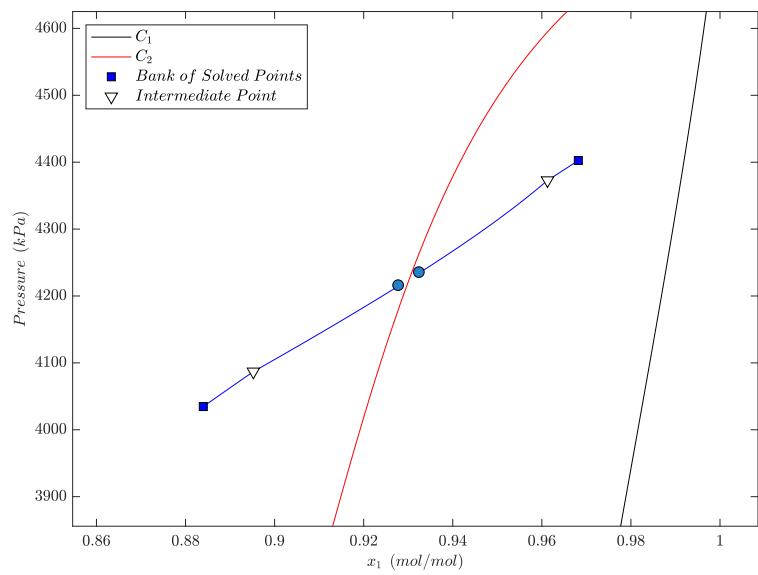


Figure 13: The “L” path in the domain, Roots 2 and 3, for $T = 304.5$ K and $y_1 = 0.99945$.

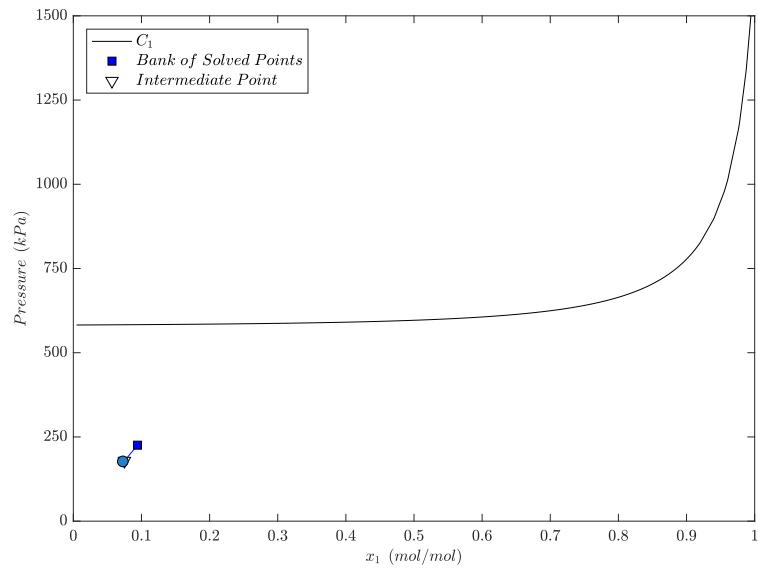


Figure 14: The “L” path in the domain, Root 1, for $T = 280.0$ K and $y_1 = 0.99945$.

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

The influence of temperature on the critical curve

The last feature to be investigated 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.

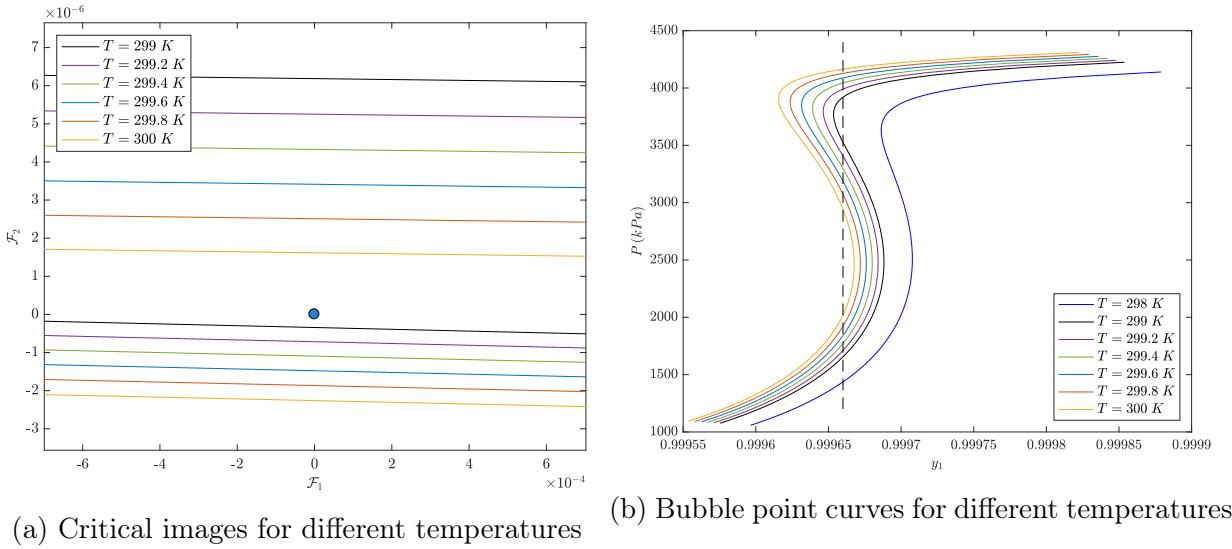


Figure 15: Influence of system temperature variation on the critical images of the problem. The molar fraction of the vapor phase of ethane is set at $y_1 = 0.99966$ for all cases, as shown in the dashed line.

Conclusions

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feedback on the class, which is reflected in all of the different demonstrations shown in this document.

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