

# Robust Prediction of Double Retrograde Vaporization by Numerical Inversion of Functions

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**Abstract** – Double retrograde vaporization is a thermodynamic phenomenon that occurs in mixtures formed by a solute with low volatility when compared to the solvent. Specially in high pressures, when the mixture reaches a temperature which is higher than the critical temperature of the pure solvent, the phase equilibrium can exhibit four different solutions (dew point pressures and liquid phase compositions), characterizing a very unique behavior. Because of the difficulty in predicting liquid molar fractions and pressure in which this phenomenon occurs, it makes the problem a real challenge for the supercritical fluid and oil industry.

The occurrence of this physical phenomenon will be illustrated in a binary system formed by ethane + limonene. Under certain conditions, the problem can be modelled through a  $2 \times 2$  system of nonlinear algebraic equations.

This fact makes it possible to predict the phenomenon of double retrograde vaporization by numerical inversion of functions from a subset of the plane to the plane. This method can obtain all the solutions of the problem in a robust and efficient way, besides offering a basis for conducting a qualitative analysis of the function behavior. **Copyright © 2016 Praise Worthy Prize S.r.l. - All rights reserved.**

**Keywords:** System of Nonlinear Algebraic Equations, Phase Equilibrium, Double Retrograde Vaporization, Inversion of Functions from the Plane to the Plane

## Nomenclature

$P$	Pressure
$R$	Universal gas constant
$T$	Temperature
$\bar{V}$	Molar volume
$a_m$	Intermolecular force of attraction
$b_m$	Covolume
$Z$	Compressibility factor
$k_{ij}$	Binary interaction parameter
$x_i$	Molar fraction in liquid phase
$y_i$	Molar fraction in vapor phase
$\hat{f}$	Fugacity
$z_i$	Molar composition in a given phase

### Greek symbols

$\omega$	Acentric factor
$\hat{\phi}$	Fugacity coefficient
$\alpha$	Correction term

### Subscripts and superscripts

$m$	Mixture
$i$	Component
$c$	Critical
$r$	Reduced
$L$	Liquid
$V$	Vapor
$\alpha$	Phase

## I. Introduction

The accurate and robust prediction of fluid phase behavior at high pressures is extremely important in many engineering study fields. In this context, we can mention the simulation of fluid flow in oil reservoirs and the equipment design for supercritical fluid extraction.

Therefore, the existence of unusual thermodynamic phenomena such as the double retrograde vaporization (DRV) may be regarded as a challenging situation for many computational codes for prediction of fluid phase equilibria. Double retrograde vaporization was first identified by [1] in the binary mixture formed by methane + n-butane. In the same year, Chen et al. [2] observed the same thermodynamic phenomenon for the mixture methane + n-pentane. Raeissi [3] concluded that this behavior is usually found in mixtures at high pressures, when the relative amount of one component of the mixture (in binary systems) is close to zero and there are significant differences (in terms of molecular size) between the two components.

In binary systems, this particular behavior appears when the system temperature is slightly above the critical temperature of the mixture. Then, a “double dome” occurs in the dew point curve, resulting in four dew point pressures and liquid compositions for each vapor phase composition. In this work we will analyze some numerical features of this phenomenon in the binary system formed by ethane + limonene [4].

The problem will be modelled by the Peng-Robinson equation of state [5] for both phases (liquid and vapor), with classical van der Waals mixing rules. Raissi et al. [6] demonstrated that the Peng-Robinson model is capable to predict the DRV.

The dew point pressure calculation (in binary mixture) is characterized by a nonlinear algebraic system with size  $2 \times 2$ . The main goal of this work is to obtain accurate and robust solutions for this problem, through the adaptation of some steps of a numerical technique known as the numerical inversion of function from the plane to the plane, proposed by [7].

In a simplified view, the numerical inversion of functions from the plane to the plane consists in three steps. The first one is the description of the critical set of the problem (the domain points where the Jacobian matrix of the nonlinear system is singular; the critical set is formed by a set of critical curves). In the second step, a bank of solved points is produced (with good initial estimates, in order to ensure convergence).

This bank permits the solution of other similar nonlinear problems, using a homotopy-continuation strategy. The final phase is the inversion of a point in the image and the respective pre-image calculation.

Beside the solution of the nonlinear algebraic problem, this technique produces a useful qualitative picture of the physical phenomenon. Recently, Guedes et al. [8] employed the numerical inversion of functions from the plane to the plane in the azeotrope prediction.

Despite the apparently simple solution of this problem (considering the low dimension of the problem itself), the nonlinear algebraic system exhibits multiple physical solutions (in the present case, four solutions) and infinite trivial solutions (when the vapor phase composition and liquid phase are equal). Moreover, there are uncountable divergence possibilities (when considering classical methods, such as Newton type methods).

Since DRV occurs in the vicinities of the mixture critical point (at high pressures), highly nonlinear behavior is expected, considering that the phase coexistence problem is on the verge of disappearing.

In this scenario, the use of a robust technique – even with an increase in the computational cost – is justified considering the nonlinear system's complex structure.

In this context, this engineering problem can be viewed as a challenging problem and used as a benchmark for the validation of numerical algorithms.

The use of a hyperheuristic structure for solving this problem was detailed in [9]. Platt [10] presents numerical experiments with a recently proposed metaheuristic (the Flower Pollination Algorithm [11]) in the identification of the dew point pressures in the binary system ethane + limonene. The stochastic algorithm was capable of identifying on the neighborhood of the roots.

## II. Thermodynamic Modelling

Cubic equations of state (CEOS) are usually employed in vapor-liquid equilibrium.

In this work, we used the Peng-Robinson CEOS [5].

In the pressure-explicit ( $P$ ) form, this equation is expressed by:

$$P = \frac{RT}{\bar{V} - b_m} - \frac{a_m}{\bar{V}(\bar{V} + b_m) + b_m(\bar{V} - b_m)} \quad (1)$$

In this equation,  $T$  is the absolute temperature,  $R$  is the universal gas constant. The term  $a_m$  represents attractive forces and the covolume  $b_m$  is related to the repulsive forces.  $\bar{V}$  is the molar volume of such a phase [12].

Peng-Robinson CEOS can also be described as a cubic polynomial in terms of compressibility factor  $Z = P\bar{V}/RT$ :

$$Z^3 - (1 - B)Z^2 + (A - 3B^2 - 2B)Z - (AB - B^2 - B^3) = 0 \quad (2)$$

with  $A = a_m P / R^2 T^2$  and  $B = b_m P / RT$ . For mixtures (as treated here), we applied the classical van der Waals mixing rules:  $a_m = \sum_{i=1}^c \sum_{j=1}^c x_i x_j a_{ij}$  and  $b_m = \sum_{i=1}^c x_i b_i$ , where  $c$  is the number of components in the mixture. We also used the following combination rule  $a_{ij} = \sqrt{a_i a_j} (1 - k_{ij})$ , where  $k_{ij}$  is called the binary interaction parameter (in this work, binary interaction parameters are considered to be zero).

Furthermore,  $a(T) = a(T_c) \alpha(T_r, \omega)$  and  $b(T) = b(T_c)$ . For pure components, parameters  $a(T_c)$  and  $b(T_c)$  can be calculated by  $a(T_c) = 0.45724 R^2 T_c^2 / P_c$  and  $b(T_c) = 0.07780 R T_c / P_c$  [12].

The correction term  $\alpha(T_r, \omega)$  is a dimensionless function, depending on the reduced temperature ( $T_r$ ) and acentric factor ( $\omega$ ), through the formula  $\alpha(T_r, \omega) = [1 + \kappa(1 - \sqrt{T_r})]^2$ . The amount  $\kappa$  is obtained by the adjustment of vapor pressure data of pure components and is represented by  $\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2$  [12]. The solution of Eq. (2) produces one or three real roots, depending on the number of phases in the system. The fugacity coefficient for component  $i$  for the Peng-Robinson CEOS with van der Waals mixing rules is calculated by [12]:

$$\ln \hat{\phi}_i = \frac{b_i}{b_m} (Z - 1) - \ln(Z - B) + \frac{2}{2\sqrt{2}B} \left( \frac{\sum_{j=1}^c x_j a_{ij}}{a_m} - \frac{b_i}{b_m} \right) \ln \left( \frac{Z + (1 + \sqrt{2})B}{Z - (1 - \sqrt{2})B} \right) \quad (3)$$

## III. The Nonlinear Algebraic System

In order to apply ideas of the numerical inversion of functions from the plane to the plane, the thermodynamic problem must be formulated as a nonlinear algebraic system with dimension  $2 \times 2$ .

The phase coexistence implies in the isofugacity condition, i.e., for each component  $i$  in the system we have  $\hat{f}_i^V - \hat{f}_i^L = 0$  [12].

The fugacity of component  $i$  can be calculated by  $\hat{f}_i^\alpha = z_i^\alpha \hat{\phi}_i^\alpha P$ , where  $\alpha$  represents each phase in the system.

For a vapor-liquid equilibrium problem, the composition of each phase is usually described as  $z_i^V = y_i$  and  $z_i^L = x_i$ . Then, vapor-liquid equilibrium is represented as [12]:

$$y_i \hat{\phi}_i^V P - x_i \hat{\phi}_i^L P = 0 \quad (4)$$

Dividing Eqs. (4) by  $P$  and considering  $c = 2$ , the final expression for the nonlinear algebraic problem is:

$$\mathcal{F}(\theta) = \begin{cases} \hat{\phi}_1^V y_1 - \hat{\phi}_1^L x_1 = 0 \\ \hat{\phi}_2^V y_2 - \hat{\phi}_2^L x_2 = 0 \end{cases} \quad (3)$$

with fugacity coefficient calculated by Eq. (3).

Considering a specification of temperature and vapor compositions, the vector of unknown is represented by  $\theta = [x_1, P]^T$ , since  $x_1 + x_2 = 1$ . Clearly, we are dealing with a problem from the plane to the plane.

The numerical inversion of functions from the plane to the plane intends to obtain all the pre-images  $p$  (in the domain) such as  $\mathcal{F}(p) = q$ , where  $q$  is any value in the image of  $\mathcal{F}$ . Therefore, with a certain value  $q$  (in the image), the technique will calculate all the solutions (pre-images) in the domain of the problem. Alternatively, we can solve the nonlinear system when  $q$  is a null vector.

For the double retrograde vaporization phenomenon, we are interested in all values  $p = [\theta_1, \theta_2]^T = [x_1, P]^T$  when  $q = [\mathcal{F}_1, \mathcal{F}_2]^T = [0, 0]^T$ , or, in other words, values which guarantee the vapor-liquid coexistence condition, represented by Eqs. (5).

#### IV. Double Retrograde Vaporization Phenomena

As pointed out in Section I, in some mixtures formed by substances with large differences with respect to their molecular size, an unusual phenomenon called double retrograde vaporization (DRV) can occur, when the system's temperature is close to the critical temperature of the more volatile component. Under these conditions, the dew point curve can display four dew point pressures for each vapor molar fraction, in a "double-dome" structure [6].

In order to promote a qualitative analysis of the phenomenon, as well as an investigation of some of the problem's features, we chose a binary mixture of ethane + limonene. Ethane exhibits a high volatility (normal boiling point close to 184.6 K) when compared to limonene (normal boiling point: 448.2 K).

Therefore, the nonlinear problem that characterizes the double retrograde vaporization phenomenon corresponds to finding the roots of the function  $\mathcal{F}(\theta)$ , such that  $\mathcal{F}: D \subset \mathbb{R}^n \rightarrow \mathbb{R}^n$ . For the binary mixture studied here, evidently  $n = 2$ , and the domain of the problem is then  $D = \{(x_1, P) \in \mathbb{R}^2 \mid 0 < x_1 < 1, P > 0\}$ .

One of the assumptions for the phenomenon is that the system temperature must be close to the critical temperature of the pure solvent (the more volatile compound in the binary mixture).

Critical properties and acentric factors for ethane and limonene are presented in Table I. Considering these data, we used  $T = 307.4 \text{ K}$  as the system temperature (slightly above the critical temperature of pure ethane), in order to provoke the existence of the double retrograde phenomenon.

TABLE I  
CRITICAL PROPERTIES AND ACENTRIC FACTORS [6]

Component	Critical temperature (K)	Critical pressure (kPa)	Acentric factor
Ethane	305.3	4872	0.100
Limonene	660	2750	0.313

Fig. 1 presents the dew point curve for the binary mixture ethane + limonene at  $T = 307.4 \text{ K}$ .

We can see that, in a small portion of the diagram, in the region between the dashed lines, we obtain four dew point pressures with a specification of vapor composition.

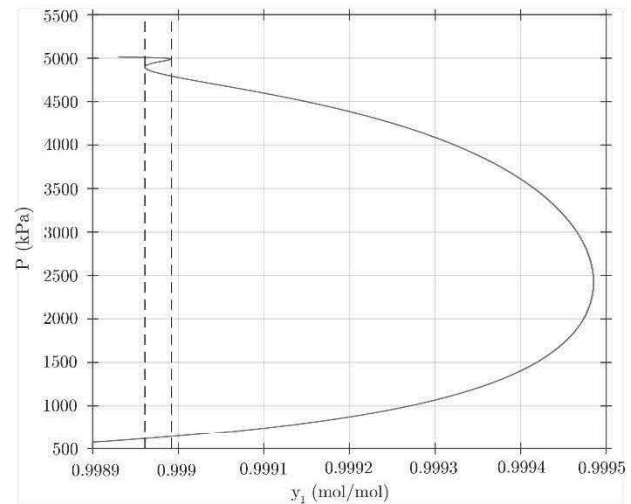


Fig. 1. The "double-dome" dew point curve in the system ethane + limonene at  $T = 307.4 \text{ K}$ .

The double dome is clearly evidenced in Fig. 1, for molar fractions in the interval  $0.998961 < y_1 < 0.998992$ . Therefore, any molar fraction in this interval will produce a dew point problem with four physical solutions. We chose, arbitrarily, the value  $y_1 = 0.998966$  in the numerical experiments conducted here.

#### V. Numerical Inversion of Functions

The global behavior of functions from a subset of the plane to the plane can be extremely relevant for the problem's solution. For functions of one variable, a common practice is to obtain the critical points. In the same way, for functions from the plane to the plane, we must consider critical curves, instead of critical points.

By definition, a point  $p$  is called a regular point of a function  $\mathcal{F}: D \subset \mathbb{R}^2 \rightarrow \mathbb{R}^2$  if the Jacobian matrix  $J$  is invertible at this point, or, equivalently,  $\det J(p) \neq 0$ . A point  $p$  in the domain is a pre-image of a point  $q$  in the image if  $\mathcal{F}(p) = q$ . Furthermore, a point in the image of  $\mathcal{F}$  is a regular value if all its pre-images are regular points. A point that is not regular is a critical point [7]. Considering this last definition, critical curves are formed by critical points of a such function  $\mathcal{F}$ .

We say that a curve is regular if it admits a smooth parametrization with non-null derivatives; and we said that a curve is simple when it does not present auto-intersection points. Considering that the Jacobian matrix is formed by partial derivatives of the function  $\mathcal{F}$ , an assumption of this methodology is that the function is smooth in a subset of the domain.

The set of critical points (or critical set) of a function  $\mathcal{F}: \mathbb{R}^2 \rightarrow \mathbb{R}^2$  will be a union of simple and regular disjoint curves if the gradient of the determinant of the Jacobian matrix of  $\mathcal{F}$  never vanishes [7]. We would like to emphasize that the whole procedure of the inversion of functions from the plane to the plane [7] is not fully considered here. For instance, Malta et al. [7] employed a word criterion to establish the critical set.

In our computational experiments, we conduct a search in the feasible domain (in a physical sense) in order to obtain the critical curves.

### V.1. Obtaining the Critical Set

Smooth functions  $\mathcal{F}: \mathbb{R}^2 \rightarrow \mathbb{R}^2$  are called nice if they obey the following properties:  $\mathcal{F}$  is proper; the critical set  $C$  of  $\mathcal{F}$  is bounded; any critical point is a fold or a cusp;  $\mathcal{F}(C)$  is a normal set of curves.

More details on nice functions (and about folds and cusps) can be found in [13]. The knowledge of the critical set is an important step in the numerical inversion of  $\mathcal{F}$ . Since nice functions exhibit a limited critical set  $C$ , these curves are closed and finite.

The numerical inversion of the functions from the plane to the plane demands, in its original proposal, that the functions at hand be nice. In that case, a complete topological characterization of the inversion is attained. Naturally, in engineering problems there is no guarantee that the models turn out to be represented by nice functions. In fact, in complex thermodynamic models we are dealing with functions that are not nice. For instance, they are not defined in the whole  $\mathbb{R}^2$  (since, say, the concentration must be between zero and one); on the other hand, the set of tools introduced in [7] to study the problem with nice functions, can be judiciously re-assembled and we apply some steps of the method to our problem, keeping in mind that some assumptions will not be valid. The determination of the critical set continues to be needed, in this case.

The critical curves generation begins with the definition of a rectangular grid in the domain of the problem. Then, a computational routine finds neighbor points (in both directions) with opposite signs for  $\det(J)$ .

A second routine finds the critical point in the segment connecting the two points. The Intermediate Value

Theorem guarantees that if we obtain some change in the sign of the determinant of the Jacobian matrix then there will be a point in the interval where  $\det(J) = 0$ , i.e., a critical point.

Therefore, we can use a numerical method in order to obtain this root (for instance, the bisection algorithm).

Following with the procedure, each one of the critical points is used as an initial point for a continuation method (with an adaptive steplength strategy), obtaining a set of critical points. The steplength strategy is necessary considering that frequently the critical curves display different curvatures and, even in the same curve, sometimes a small portion of the curve is especially relevant [2]. A detailed description of the continuation procedure is presented by [14] and [15].

### V.2. Bank of Solved Points

The bank of solved points is composed by a list of points in the image and their respective pre-images (in the domain). The number of pre-images depends on the problem and the region where the point is located in the image of the function. The goal of this step is to provide initial points for the inversion process (conducted by an Euler-Newton technique). Malta et al. [7] employed an Euler-Newton [16] method in order to obtain all the pre-images of a point in the image. In the approach of Malta et al. [7], several points in the image are organized in squares and, then, the sides of these squares are traversed in an anticlockwise orientation using the continuation method. The process is repeated until all the pre-images are obtained.

In this work, we used a Newton-Raphson method with several initial estimates. For each initial estimate, the Newton method converges for a particular pre-image. In all points in the bank, we obtained four pre-images (the same number of roots of the dew point problem).

### V.3. Generation of the Pre-Images of an Arbitrary Point

With the determination of the critical set and the bank of solved points, we are able to conduct the inversion process of an arbitrary point.

Once again, we will consider  $q$  as a point in the image of  $\mathcal{F}$ , and the procedure starts with the connection of the point  $q$  to a point in the bank  $q_0$  through a "L" path, i.e., a path formed by two line segments, a horizontal one and a vertical one, oriented from  $q_0$  to  $q$  (the order of the segments is irrelevant) [7]. Since the bank of solved points exhibits a large amount of points, we need some criterion in order to establish which solved point will be used in the path connecting  $q_0$  and  $q$ . Here, we chose the shortest path as the selection criterion.

Furthermore, we must guarantee that the path does not present intersections with the critical image (since this condition represents problems in the inversion process



using the continuation method and a change in the number of pre-images). Thus, admitting that  $q_0$  is the closest point to  $q$  in the bank of solved points, the intermediary point in the “L” is denoted by  $\tilde{q}$ , which is represented by the abscissa of  $q_0$  and by the ordinate of  $q$ . As pointed previously, the orientation of the “L” path is arbitrary, but some care must be exercised in order to avoid intersections with the critical image (preventing a change in the number of pre-images). The determination of the solutions (pre-images)  $p$  in the domain through the inversion of  $q$  at  $\mathcal{F}(p) = q$  is conducted by an Euler-Newton procedure, considering  $p_0$  (pre-images of the solved point) as the initial condition for the algorithm.

The first part of the “L” path is constructed by the continuation method beginning at  $p_0$  and ending at  $\tilde{p}$  (a pre-image of  $\tilde{q}$ ).

Then, the procedure follows, and the second part of the “L” path is obtained, linking  $\tilde{p}$  top. This procedure (in the image) is illustrated in the Fig. 2. It must be stressed that this procedure occurs simultaneously for all pre-images (in the domain) of the point  $q_0$ .

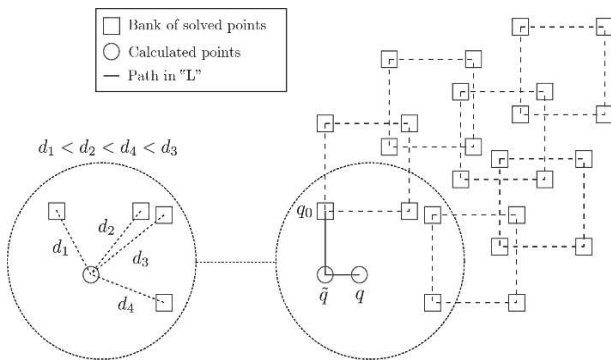


Fig. 2. The “L” path in the image

## VI. Numerical Results of the Inversion Procedure

### VI.1. Critical Curves in the Dew Point Calculation Problem

We define, a priori, the search interval for both variables of the problem, i.e.,  $x_1(\text{mol/mol}) \in [0,1]$  and  $P(\text{kPa}) \in [500,5500]$ , based on thermodynamic properties of the pure substances.

Obviously, the search interval for pressures can be modified in other situations. Moreover, we consider  $ni = 500$ , where  $ni$  is the number of subintervals in the domain, in order to evaluate the sign of the determinant of the Jacobian matrix in the search space. Fig. 3 illustrates the regions of the domain with different signs of the determinant of Jacobian. This result emulates, in a simplified form, the shape of the critical curves of the nonlinear system. The critical curves can also be obtained in a more convenient way (and more accurately): when two consecutive points in the array that contains the sign of  $\det(J)$  present different values, a root-finding procedure was ran.

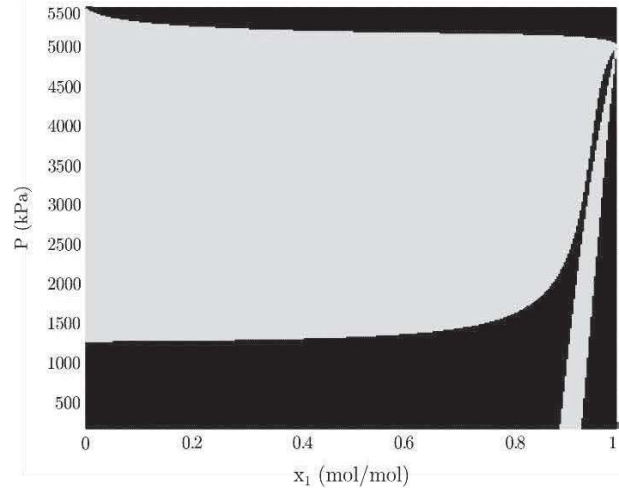


Fig. 3. Signs of the determinant of the Jacobian matrix in the feasible domain of the problem

Thus, from this point, a continuation method (as pointed out in the previous section) is used in order to calculate the critical curves.

An exhaustive search for critical curves was conducted in order to describe the critical set in the feasible domain. Fig. 4 contains the two critical curves,  $C_1$  and  $C_2$ , in the domain of the problem.

After the critical set's determination in the domain of the function, we can obtain the critical image, substituting the critical points in the domain in Eq. (5).

We can see that, in the image, we are mainly interested in the vicinities of the point  $q = (0,0)$ , which is the point that solves the nonlinear algebraic problem.

The determination of these vicinities is important for the construction of the bank of solved points. As pointed by [7], it is not desirable that the paths of the inversion procedure intersect (with uncontrolled frequency) the critical image, promoting a variation in the number of pre-images.

### VI.2. Bank of Solved Points

As pointed out in Section I, the main goal of the numerical inversion of functions technique adaptation [7] (to functions defined on a subset of the plane to the plane) is the accurate solution of the system represented by Eqs. (5), i.e., the calculation of solutions of  $\mathcal{F}(p) = q$ , with  $q = (0,0)$ . Moreover, we need to avoid intersections between the critical image and the paths in the inversion process. Thus, it is convenient to obtain the bank of solved points within the limits established by the critical image in the neighborhood of the point  $q = (0,0)$ .

The first step in the construction of the bank of solved points consists in disposing an arbitrary number of points in the function image, accordingly to Fig. 5.

At this moment, it must be emphasized that we do not use the procedure as proposed by [7]. With the points as displayed in Fig. 5, the generation of the bank of points in the domain of  $\mathcal{F}$  demands that all pre-images of the points in Fig. 5 have been calculated.

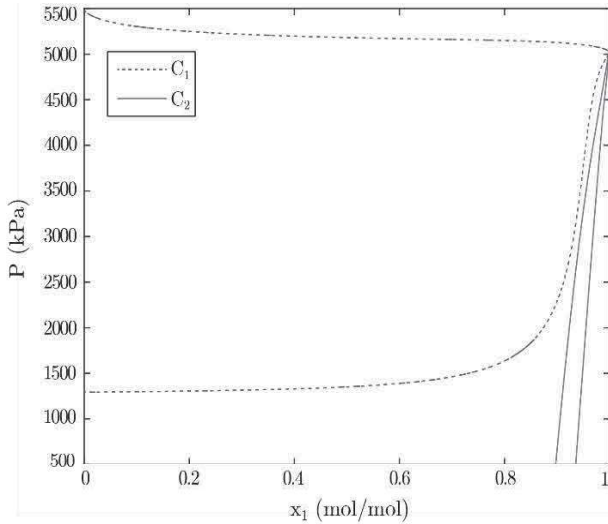


Fig. 4. Critical curves for the dew point problem in the system ethane + limonene

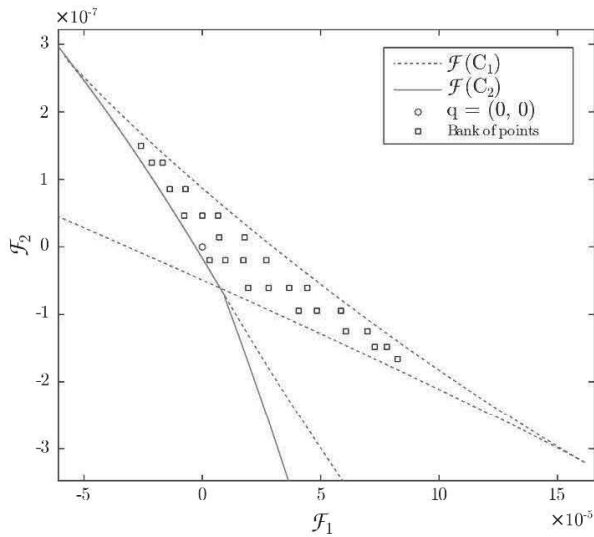


Fig. 5. Bank of solved points in the image of the function

For this task, we can use any numerical technique in order to calculate  $p$  at  $\mathcal{F}(p) = q$ . Figs. 6 and 7 illustrate the pre-images of the bank of points at low and high pressures, respectively. As pointed out in Section V, we use a Newton-Raphson procedure, with different initial estimates, in order to obtain the pre-images of a point  $q$ .

### VI.3. Inversion Procedure and Solutions Generation

Following the generation of an adequate bank of solved points, containing the coordinates in the image and their respective pre-images in the domain of  $\mathcal{F}$ , we are now able to make the inversion of an arbitrary point.

Specifically, we are interested in the inversion of  $q = (0, 0)$ , that solves the nonlinear algebraic system  $\mathcal{F}(p) = q$ , as represented by Eq. (5). Considering the thermodynamic problem features, we expect to obtain four solutions. The first step is to create the “L” path in the function image.

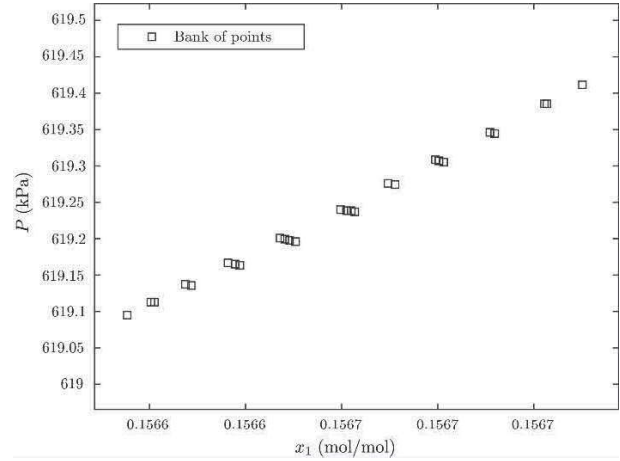


Fig. 6. Bank of solved points in the domain of the function (low pressures)

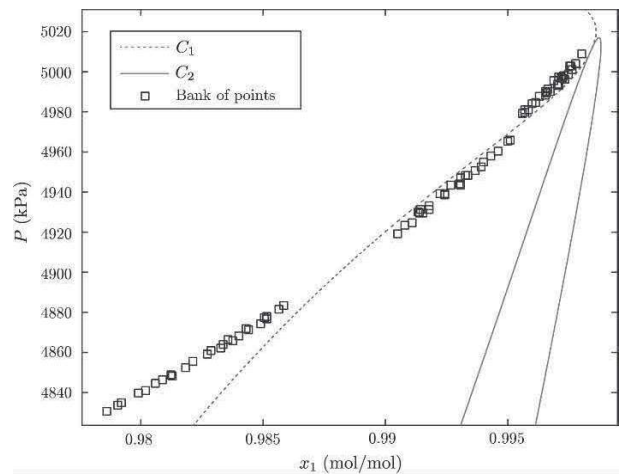


Fig. 7. Bank of solved points in the domain of the function (high pressures)

Since we know the bank point used in the creation of the “L” path in the image, we also know the coordinates of its respective pre-images in the domain (also stored in the bank). These paths in domain also behave as “L” paths, but with some deformation.

The final results are depicted in Table II, in terms of molar fractions for ethane and dew point pressures in  $kPa$ . The results are fully compatible to those obtained, for instance, by [9] and [10].

Moreover, Figs. 8 contain the paths in the domain. The squares in the figure represent the bank points used in the inversion process. The triangles are the intermediary points, connecting the two segments obtained by the Euler-Newton procedure. Finally, the circles are the final coordinates obtained at the solution.

TABLE II  
APPROXIMATE SOLUTIONS AND THEIR IMAGES

$i$	$p_i$	$\mathcal{F}(p_i)$
1	(0.156668, 619.257576)	$(5.142 \times 10^{-10}, 2.352 \times 10^{-12})$
2	(0.982905, 4859.462142)	$(2.118 \times 10^{-8}, -2.76 \times 10^{-11})$
3	(0.991826, 4931.224652)	$(1.613 \times 10^{-9}, -2.08 \times 10^{-12})$
4	(0.997938, 5007.250285)	$(7.436 \times 10^{-9}, 1.015 \times 10^{-11})$

The analysis of Figs. 8(a) and 8(d) indicates that the “L” paths are almost rectilinear, with a slight inclination.

This behavior is justified, probably, by the proximity of the bankpoint and the solution (in the image).

## VII. Relationship between Basins of Attraction and Critical Curves in the Calculation of Double Retrograde Phenomenon

The goal of this section is to obtain the relationship between the critical curve and the basins of attraction for the roots when using a Newton-type method to solve the dew point problem. In this sense, the calculation of the critical curve can be used for another purpose, besides the numerical inversion of the function. Some initial ideas regarding this issue were presented by [17]. Furthermore, a detailed algorithm devoted to the construction of the critical curve was presented by [18].

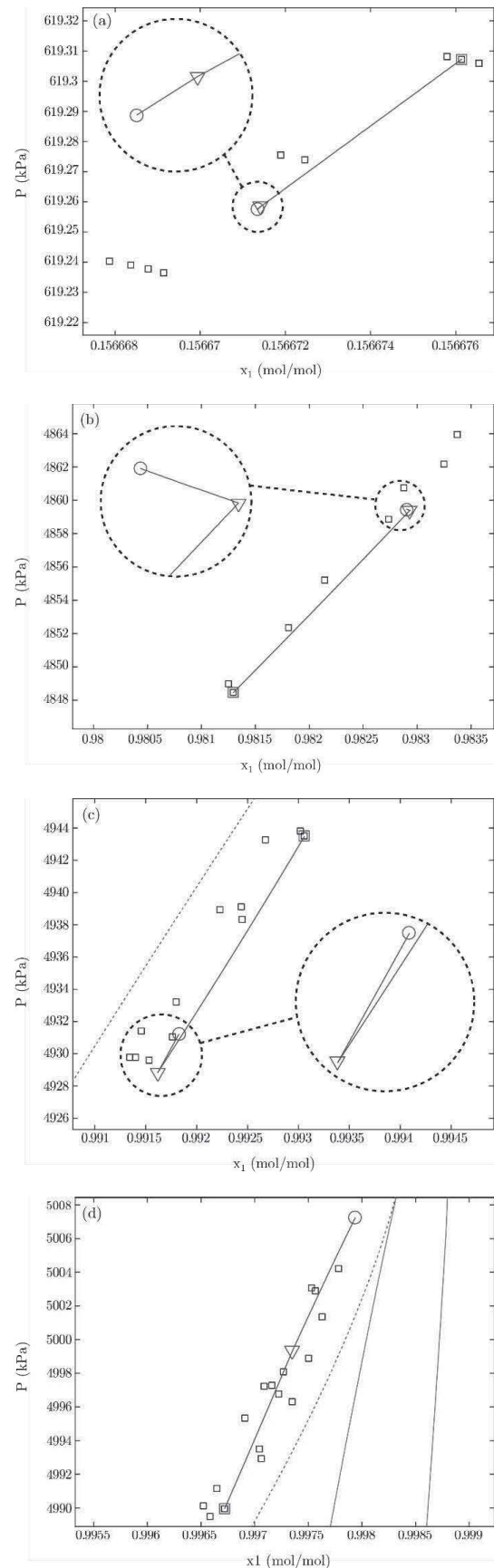
Basins of attraction are commonly employed in the study of dynamical systems, particularly in chaotic motion [19], [20]. This kind of diagram can also be used to evaluate convergence patterns for Newton-type methods in nonlinear algebraic systems with multiple solutions [21] (which is the issue focused in this work).

The main idea in the basin of attraction construction is to provide a rectangular grid of initial estimates for the Newton-type method and, then, the final results are displayed using different colors for each solution found.

The first – and obvious – evidence of the existence of a correlation among the critical curve and basins of attraction is based on the fact that both are strictly related to the inversion of the Jacobian matrix (when considering Newton-type methods). The creation of basins of attraction requires all the convergence possibilities to be considered in the task at hand. Thus, we must take into account, besides the physical solutions, two other cases: the non-convergence condition and the existence of trivial solutions (without physical interest). In the first case, we can obtain, in some situations, singular Jacobian matrices, which will stop the algorithm (since a Newton method requires the inversion of the Jacobian matrix).

Furthermore, the algorithm can be in an infinite loop, again without convergence (this situation is easily identified, considering the number of iterations of the method). The trivial solutions occur when the composition of the liquid phase is identical to the vapor phase. In this case, for any pressure, the coexistence equations will be attained (but without any physical relevance). Once again, the results are easily identified, when the absolute difference between the molar fraction of liquid and vapor phases is less than a tolerance.

The basin of attraction for this problem using a Newton method with natural monotonicity check [22] is represented in Fig. 9. Each point in the figure represents an initial estimate for the Newton method. Since the problem exhibits multiple roots, different initial estimates produce different final results.



Figs. 8. Results of the inversion of the point  $q = (0,0)$  (a)  $p_1 \approx (0.156668, 619.257576)$  (b)  $p_2 \approx (0.982905, 4859.462142)$  (c)  $p_3 \approx (0.991826, 4931.224652)$  (d)  $p_4 \approx (0.997938, 5007.250285)$

The ratio between colors and roots/situations is presented in Table III. The critical curve in Fig. 9 is represented as a black line. It must be stressed that the critical curve and the basin of attraction are produced using different methodologies.

TABLE III  
RELATION BETWEEN RESULTS AND COLOR  
IN THE BASIN OF ATTRACTION

Result	Color
(0.156668,619.257576)	Magenta
(0.982905,4859.462142)	Green
(0.991826,4931.224652)	Yellow
(0.997938,5007.250285)	Red
Without convergence	Blue
Trivial solution	Cyan

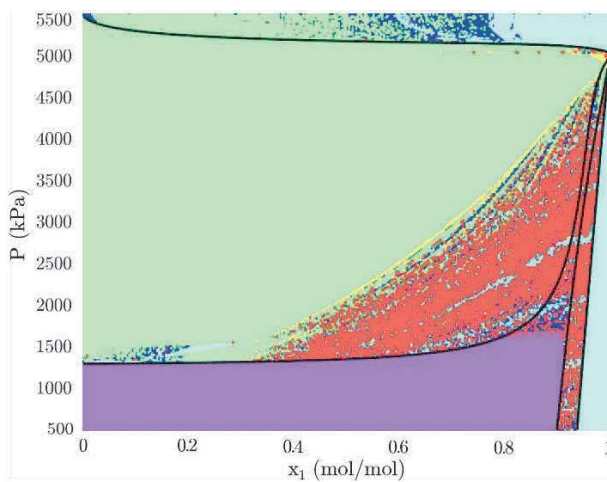


Fig. 9. The critical curve (continuous line in black) superposed to the basin of attraction for the dew point calculation in the system ethane + limonene

An analysis of Fig. 9 clearly indicates a relationship between these two elements (the critical curve and the basin of attraction). The critical curve appears to delimit the regions with different colors in the basin of attraction.

Thus, we consider that the calculation of the critical curve can be a useful tool in the analysis of Newton methods convergence. As far as we know, this strategy has not been used before.

## VIII. Conclusion

In this work we presented computational results regarding the application of some strategies applied in the numerical inversion of functions from the plane to the plane in the calculation of dew point pressures in a binary system (under specification of temperature) with double retrograde vaporization. The results obtained were good when it comes to accuracy and robustness. Naturally, the bank of solved points construction is a “slow step” from the computational time and user-interference point of view. However, the same bank can be used to solve different problems. Furthermore, we showed the existence of a relationship between the critical curve and the basin of attraction for a Newton-type method.

In future work, we will show that we can calculate dew point pressures and liquid phase compositions for other problems, using the same bank of solved points.

Moreover, the number of pre-images variation analysis (when a path approaches the critical image) will be conducted. Finally, we should emphasize that this procedure is restricted to the functions from the plane to the plane, i.e., nonlinear systems with only two unknowns.

## Acknowledgements

The authors acknowledge the financial support of Brazilian agencies FAPERJ, CAPES and CNPq.

## References

- [1] R. J. J. Chen, P. S. Chappelaar, R. Kobayashi, Dew point loci for methane-n-butane binary system, *Journal of Chemical and Engineering Data*, Vol. 19, pp. 53-58, 1974.
- [2] R. J. J. Chen, P. S. Chappelaar, R. Kobayashi, Dew point loci for methane-n-pentane binary system, *Journal of Chemical and Engineering Data*, Vol. 19, pp. 58-61, 1974.
- [3] S. Raeissi, On the phenomenon of double retrograde vaporization: within a study on supercritical deterpenation of orange oils with ethane. Ph.D. dissertation, TU Delft, Delft University of Technology, Holland, 2004.
- [4] S. Raeissi, C. J. Peters, On the phenomena of double retrograde vaporization: multi dew point behavior in the binary system ethane + limonene, *Fluid Phase Equilibria*, Vol. 191, pp. 33-40, 2001.
- [5] D. Peng, D. Robinson, A new two-constant equation of state, *Industrial & Engineering Chemistry Fundamentals*, Vol. 15, n. 1, p. 59-64, 1976.
- [6] S. Raeissi, C. J. Peters, Simulation of double retrograde vaporization using the Peng-Robinson equation of state, *Journal of Chemical Thermodynamics*, Vol. 35, pp. 573-581, 2003.
- [7] I. P. Malta, N. C. Saldanha, C. Tomei, The numerical inversion of functions from the plane to the plane, *Mathematics of Computation*, Vol. 65, n. 216, p. 1531-1552, 1996.
- [8] A. L. Guedes, F. D. Moura Neto, G. M. Platt, Prediction of azeotropic behaviour by the inversion of functions from the plane to the plane, *The Canadian Journal of Chemical Engineering*, Vol. 93, pp. 914-928, 2015.
- [9] G. M. Platt, I. N. Bastos, R. P. Domingos, Calculation of double retrograde vaporization: Newton's methods and hyperheuristic approach, *Journal of Nonlinear Systems and Applications*, Vol. 3, n. 2, pp. 107-120, 2012.
- [10] Platt, G., Computational Experiments with Flower Pollination Algorithm in the Calculation of Double Retrograde Dew Points, (2014) *International Review of Chemical Engineering (IRECHE)*, 6 (2), pp. 95-99.
- [11] X.-S. Yang, Flower Pollination algorithm for global optimization, *Lecture Notes in Computer Science*, Vol. 7445, pp. 240-249, 2012.
- [12] J. M. Smith, H. C. Van Ness, M. M. Abbott, *Introduction to Chemical Engineering Thermodynamics* (7th edition, McGraw-Hill International Edition, 2005).
- [13] I. P. Malta, N. C. Saldanha, C. Tomei, *Geometria e análise numérica de funções do plano no plano*. Proc. 19º Brazilian Colloquium of Mathematics, Rio de Janeiro, 1993 (in Portuguese).
- [14] E. T. Silva, wx2x2 – um software para sistemas não-lineares, M.Sc. Dissertation (in Portuguese), Dept. Mathematics, Pontifícia Universidade Católica, Rio de Janeiro, Brazil, 2007.
- [15] G. B. Libotte, *Método de inversão de funções do plano no plano aplicado ao problema de vaporização retrógrada dupla*, M.Sc. Dissertation (in Portuguese), Computational Modeling Dept., Rio de Janeiro State University, Nova Friburgo, Brazil, 2016.



- [16] Allgower, E. L., Georg, K. *Introduction to numerical continuation methods*. (1st edition, SIAM, 2003).
- [17] G. B. Libotte, G. M. Platt, *Estudo da relação de convergência nas bacias de atração com a curva crítica do problema de vaporização retrógrada dupla*, Proc. XVIII Brazilian Meeting on Computational Modelling (in Portuguese), Salvador-Brazil, 2015.
- [18] G. B. Libotte, G. M. Platt, *Experimentação numérica no fenômeno de vaporização retrógrada dupla: um estudo sobre a curva crítica do sistema não-linear*, Proc. CIBIM XII – Congreso Iberoamericano de Ingeniería Mecánica (in Portuguese), Guayaquil – Ecuador, 2015.
- [19] H.-W. Lorenz, *Nonlinear dynamical economics and chaotic motion* (1st edition, Springer, 1993).
- [20] C. Grebogi, E. Ott, J. A. Yorke, Fractal basin boundaries, long-live chaotic transients and unstable-unstable pair bifurcation, *Physical Review Letters*, Vol. 50, n. 13, 1983.
- [21] B. I. Epaneanu, H. S. Greenside, Fractal basins of attraction with a damped Newton's method, *SIAM Review*, Vol. 40, n. 1, pp. 102-109, 1998.
- [22] P. Deuflhard, *Newton methods for nonlinear problems: affine invariance and adaptive algorithms* (1st edition, Springer, 2011).

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