INTERVAL MATHEMATICS APPLIED TO CRITICAL POINT TRANSITIONS

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Abstract

The determination of critical points of mixtures is important for both practical and theoretical reasons in the modeling of phase behavior, especially at high pressure. The equations that describe the behavior of complex mixtures near critical points are highly nonlinear and with multiplicity of solutions to the critical point equations. Interval arithmetic can be used to reliably locate *all* the critical points of a given mixture. The method also verifies the *nonexistence* of a critical point if a mixture of a given composition does not have one. This study uses an interval Newton/Generalized Bisection algorithm that provides a mathematical and computational guarantee that all mixture critical points are located. The technique is illustrated using several example problems. These problems involve cubic equation of state models; however, the technique is general purpose and can be applied in connection with other nonlinear problems.

Keywords: Critical Points, Interval Analysis, Computational Methods.

Resumen

La determinación de puntos críticos de mezclas es importante tanto por razones prácticas como teóricas en el modelamiento del comportamiento de fases, especialmente a presiones altas. Las ecuaciones que describen el comportamiento de mezclas complejas cerca del punto crítico son significativamente no lineales y con multiplicidad de soluciones para las ecuaciones del punto crítico. Aritmética de intervalos puede ser usada para localizar con confianza todos los puntos críticos de una mezcla dada. El método también verifica la no–existencia de un punto crítico si una mezcla de composición dada no tiene dicho punto. Este estudio usa un algoritmo denominado Newton–Intervalo/Bisección–Generalizada que provee una garantía matemática y computacional de que todos los puntos críticos de una mezcla han sido localizados.

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Estos problemas cubren los modelos de ecuaciones cbicas de estado; sin embargo, la técnica es de propósito general y puede ser aplicada en el caso de otros problemas no lineales.

Palabras clave: Puntos Críticos, Análisis de Intervalos, Métodos Computacionales.

Mathematics Subject Classification: 65G30.

1   Introduction

Determination of critical points is an important problem in the chemical industry. There are numerous studies of this phenomenon (Deiters and Schneider, 1976; Boberg and White, 1962; Hurle *et al.*, 1977 (a,b); Nagarajan *et al.*, 1991 (a,b); Sadus, 1994; Stockfleth and Dorhn, 1998; Spear *et al.*, 1971; Enick *et al.*, 1985; Grieves and Thodos, 1962; Munoz and Chimowitz, 1993; Teja and Kropholler, 1975; Teja and Rowlinson, 1973), and a majority are related to the petroleum industry (Heidemann, 1975; Baker and Luks, 1980; Luks *et al.*, 1987; Boshkov *et al.*, 1997, Rochocz *et al.*, 1997). For a pure component, the critical point is at the intersection of the spinodal and binodal curves, this is at the end of the vapor pressure curve. In a binary mixture the liquid-vapor critical point is found at the maximum pressure of the dew-bubble envelope. Multicomponent mixtures also have critical points, but there is no prior knowledge of their thermodynamic coordinates (Rowlinson and Swinton, 1982). Computation of critical points for multicomponent mixtures is a difficult task due to the higher dimensionality of the problem (Heidemann, 1983; Michelsen, 1982; Modell and Reid, 1983) that increases with the number of components. The critical points computed may be stable, unstable or metastable.

The equations that describe critical points are highly non-linear and numerous techniques have been used to solve this problem. Two of the better known computational approaches are those by Heidemann and Khalil(1980) and Hicks and Young (1977). In general these methods cannot guarantee the existence or uniqueness of a critical point for a given mixture. Binary mixtures may have both low and high temperature critical points. These usually would correspond to vapor-liquid and liquid-liquid critical points. The classification of high-pressure binary mixtures (Scott and van Konynenburg, 1970; van Konynenburg, 1968) is based on the location and existence of critical points.

Experience with commercial software indicates that it cannot easily compute multiple critical points without reinitializing and judicious initial guesses (Hytoft and Gani, 1996). There is no information as to how many critical points may be located in one region, thus there is no previous information to know how many initial guesses are necessary. As it will be shown later, we have found as many as three critical points for some binary mixtures. The solution procedure by Heidemann and Khalil (1980) was adopted in this paper to determine critical points. Their approach is dominant in the literature due to its simplicity of implementation and clear theoretical foundation, and it is available in the program *critpt* that is a part of the IVC-SEP simulation package (Hytoft and Gani, 1996; Michelsen, 1984). This algorithm is designed to determine only higher temperature critical points, and it uses a built-in selection for the initial values of the critical temperature and mole volume. However for multiple critical points, the algorithm needs to be reinitialized, and

the code altered to permit input of new initial guesses. In addition, there are no heuristics to guide our initial estimates to compute multiple critical points. We prefer this approach based on our experience implementing other strategies based on determinant forms (Modell and Reid, 1983). These resulted in slower and computationally more expensive options specially for mixtures with more than three components and multiple critical points. In none of the references cited here, there is a report of multiple critical points for mixtures. In our results section, there are several cases with more than one critical point and there is a case with three stable critical points for the H_2S-CH_4 binary system.

We present the computation of critical points by the Interval-Newton Generalized Bisection (IN/GB) method (Kearfott and Novoa, 1990) using the formulation of Heidemann and Khalil (1980). The advantages of our approach are: there is no need for an initial guess of temperature and volume, all critical points in a given domain can be determined without reinitializing the algorithm, and in absence of a critical point, there is a mathematical guarantee that there is no critical point. These characteristics exceed those of most other real arithmetic methods. We show the effectiveness of the algorithm with binary, ternary and a quaternary mixture. All computations were performed in a Ultra 30 Sun workstation.

2   Background

2.1   Interval mathematics

The IN/GB method (Neaumier, 1990; Moore, 1966; Hansen, 1992; Hua *et al.*, 1998; Knuppel, 1994; Schnepper and Stadtherr, 1996; Kearfott, 1987, 1989, 1990) can find the solutions to a system of non-linear equations with mathematical certainty and without the need of initial guesses. The only information needed is the domain of the variables.

A real interval, X, is the set of all real numbers lying between an upper and lower bound:

$$X = [l_1, l_2] = \{x \in \mathbb{R} | l_1 \leqslant x \leqslant l_2\}, \qquad \text{where } l_1, l_2 \in \mathbb{R} \text{ and } l_1 \leqslant l_2.$$

A n-dimensional real interval vector $X = \{X_1, X_2, \ldots, X_n\}^T$ has n real intervals. An inteval vector is also called n-dimensional box. In this section the lower case quantities are real numbers, and the upper case quantities are intervals. Underlined lower case letters identify vectors of real numbers.

We start with a system of non-linear equations $\underline{f}(\underline{x}) = \underline{0}$ with $\underline{x} \in X^{(0)}$ where $X^{(0)}$ is the initial n-dimensional box. The kth iteration in the IN/GB method computes $N^{(k)}$ by solving the following system of equations (Kearfott, 1996):

$$F'(X^{(k)})(N^{(k)} - \underline{x}^{(k)}) = -\underline{f}(\underline{x}^{(k)}) \tag{1}$$

$F'(X^{(k)})$ is the interval extension of the real-number jacobian matrix, $\underline{f}'(\underline{x})$, over the interval $X^{(k)}$. $\underline{x}^{(k)}$ is an array of real numbers that is usually the midpoint of $X^{(k)}$.

A range test is applied before evaluating Eq. 1. This test consists of evaluating the system of equations $\underline{f}(\underline{x}) = \underline{0}$ over the desired interval and if zero is contained inside the interval image $f(X)$ then Eq. 1 proceeds. Otherwise the interval box is discarded.

$N^{(k)}$ is computed and intersected with $X^{(k)}$. Any roots, $\underline{x}^*$, inside $X^{(k)}$ must be in their intersection, $\underline{x}^* \in \left\{ X^{(k)} \cap N^{(k)} \right\}$. There are three possible cases for the intersection of $N^{(k)}$ and $X^{(k)}$ as shown in Table 1.

Case	Interpretation
$N^{(k)} \subset X^{(k)}$	A unique root exists and is estimated by Newton–Raphson method with real arithmetic.
$N^{(k)} \cap X^{(k)} = \{\emptyset\}$	There is no root in the interval box, and it can be safely discarded.
$N^{(k)} \not\subset X^{(k)}$ and $N^{(k)} \cap X^{(k)} \neq \{\emptyset\}$	If $N^{(k)} \cap X^{(k)}$ is sufficiently smaller (60% of original volume) then continue to apply IN/GB, otherwise bisect.

Table 1: Intersection of $N^{(k)}$ and $X^{(k)}$.

2.2   Critical point equations

The criticality conditions can be stated in terms of the Gibbs free energy (G). However for a pressure-explicit equation of state the Helmholtz free energy (A) is preferred. The basic equations to solve are given in Equations 2 and 3 (Heidemann and Khalil, 1980) in those A is the Helmholtz free energy. A_{ij} and A_{ijk} are the second and third order derivatives of A with respect to composition, C is the total number of components and $\Delta n_i, (i = 1..C)$ is the change in the number of moles of the ith component. These are the second and third order terms of the Helmholtz-free-energy Taylor's expansion with respect to composition.

$$\sum_{i=1}^{C} \sum_{j=1}^{C} A_{ij} \Delta n_i \Delta n_j = 0 \tag{2}$$

$$\sum_{i=1}^{C} \sum_{j=1}^{C} \sum_{k=1}^{C} A_{ijk} \Delta n_i \Delta n_j \Delta n_k = 0 \tag{3}$$

It is computationally more economic to write the condition Eq. 2 in a different form as follows:

$$\{\Delta n_1, \Delta n_2, \ldots, \Delta n_C\} \left\{ \begin{array}{ccccc} A_{11} & A_{12} & \cdots & & A_{1C} \\ A_{21} & A_{22} & & & \\ \vdots & & \ddots & & \vdots \\ & & & A_{(C-1)(C-1)} & \\ A_{nc1} & & \cdots & & A_{(C)(C)} \end{array} \right\} \left\{ \begin{array}{c} \Delta n_1 \\ \Delta n_2 \\ \vdots \\ \Delta n_C \end{array} \right\} = 0. \tag{4}$$

We assume that the first term of Eq. 4 is not a null vector. Then the remaining matrix-vector product must generate the null vector to satisfy the equality in Eq. 4, this is,

$$
\left\{
\begin{array}{cccc}
A_{11} & A_{12} & \cdots & A_{1C} \\
A_{21} & A_{22} & & \\
\vdots & & \ddots & \vdots \\
& & A_{(C-1)(C-1)} & \\
A_{C1} & \cdots & & A_{(C)(C)}
\end{array}
\right\}
\left\{
\begin{array}{c}
\Delta n_1 \\
\Delta n_2 \\
\vdots \\
\Delta n_C
\end{array}
\right\}
=
\left\{
\begin{array}{c}
0 \\
0 \\
\vdots \\
0
\end{array}
\right\}
\tag{5}
$$

which can be written as,

$$
\sum_{j=1}^{C} A_{ij}\Delta n_j = 0, \quad i = 1, \ldots, C.
\tag{6}
$$

Equations (3) and (6) are more computationally economic than (2) and (3). Nonetheless, we found that the computational time even for binary systems were of several minutes.

Dramatic improvements in computation times were achieved by making the following modifications 1) normalizing the volume domain using the van der Waals mole volume, 2) normalizing the temperature by a value of 200 K, and 3) using the expressions of Michelsen and Heidemann (1981) for the critical point conditions.

The expressions of Michelsen and Heidemann (1981) to compute critical points are:

$$
\sum_{j=1}^{C} A_{ij}\Delta n_j = \frac{RT}{n}\left(\frac{\Delta n_i}{y_i} + F_1\left(\beta_i\overline{N} + \overline{\beta}\right) + \beta_i\, F_1^2\,\overline{\beta}\right)
\tag{7}
$$
$$
+ \frac{a}{bn}\left(\beta_i\overline{\beta}F_3 - \frac{F_5}{a}\sum_{j=1}^{C} a_{ij}\Delta n_j + F_6\left(\beta_i\overline{\beta} - \alpha_i\overline{\beta} - \overline{\alpha}\beta_i\right)\right), \quad i = 1, \ldots, C
$$

$$
\sum_{i=1}^{C}\sum_{j=1}^{C}\sum_{k=1}^{C} A_{ijk}\Delta n_i\Delta n_j\Delta n_k = \frac{RT}{n^2}\left(-\frac{\displaystyle\sum_{i=1}^{C}\Delta n_i^3}{y_i^2} + 3\overline{N}(\overline{\beta}F_1)^2 + 2(\overline{\beta}F_1)^3\right)
\tag{8}
$$
$$
+ \frac{a}{n^2 b}(3\overline{\beta}^2(2\overline{\alpha} - \overline{\beta})(F_3 + F_6) - 2\overline{\beta}^3 F_4 - 3\overline{\beta}\overline{a}F_6).
$$

The last equation is the correct form of the third order term of the Taylor's expansion of the Helmholtz free energy. The original paper has an error in their last term. The terms are defined in the Appendix.

The values of Δn_i are normalized with the following requirement,

$$
\sum_{i=1}^{C}\Delta n_i^2 - 1 = 0.
\tag{9}
$$

We computed the values of temperature (T), volume (V) and composition variation vector (Δn_i) that satisfy Eqs. (7)-(9) at a given composition. Expressions for all of the terms are given in Stradi (2000) and in the Appendix. Variable ranges and parameters values are given in Table 2. Critical temperatures, pressures and acentric factors were taken from Reid *et al.* (1987). Equations (7)-(8) are more compact because a number of terms are cancelled out in the process of deriving the equations. The result is a smaller computational requirement and tighter bounds in the interval computations when compared to Eqs. (3) and (6).

Equations (7)-(9) are better suited for interval arithmetic. The derivatives with respect to temperature, T, and volume, V, and change in the number of moles, Δn_i, are given in Stradi (2000). In this short communication, there are the results for binary mixtures of methane and hydrogen sulfide, although the research project also looked at more complex systems successfully. The stability of the mixture, at pressures greater than zero, can be tested by tangent plane distance analysis (Hua *et al.*, 1996). The tangent plane distance for mixtures of methane and hydrogen sulfide are presented in this article.

An alternative procedure expresses Equations (2) and (3) in determinant forms. The expressions were developed by Reid and Beegle (1977) and are equivalent to those of Heidemann and Khalil (1980).

3   Results and discussion

We implemented Eqs. 7-9 with the IN/GB method. The variable ranges are given in Table 2. Negative pressures for critical points correspond to demixing of a liquid into two other liquid phases. Fluids at negative pressures are metastable or unstable with respect to the liquid at the same temperature and not in tension (Imre *et al.*, 1998, Debenedetti 1996). All of the critical points at positive pressures are stable unless indicated otherwise.

3.1   Methane/hydrogen sulfide binary mixture($k_{ij} = 0.08$)

The critical points of a series of binary mixtures of methane and hydrogen sulfide are shown in Table 3. The pressure versus temperature diagram, constructed with the computed critical points, for this binary mixture is shown in Fig. 1. The Redlich-Kwong-Soave equation of state (SRK-EOS) (Reid *et al.*, 1987) was used to model both liquid and gas phases. In the composition range of 0.53 to 0.84 mole fraction of methane, we found no critical points. Our results are in agreement with those of Heidemann and Khalil (1980). Computational times varied from 0.52 to 38.99 s.

In Figure 2, the pressure versus composition diagram is shown at 208.15 K. The pressure versus composition diagrams were generated using `LNGFLASH`, which is a part of the `IVC-SEP` simulation package (Hytoft and Gani, 1996). The Gibbs energy of mixing is shown in Fig. 3. At a methane mole fraction of 0.49, the curve is close to horizontal what is usually the case at stable critical points. The tangent plane distance for a methane feed of 0.49 is shown in Fig. 4. The tangent plane distance is always positive, and it is zero only at the feed; therefore, the feed is stable. In Figure 5, the pressure versus composition diagram at 190.98 K is shown. The critical point at 22.5 bar is an unstable critical point

because the feed would split into liquid and gas phases. There is a three-phase line at 41.22 bar; above this pressure liquid-liquid and vapor-liquid envelopes are found. The liquid-liquid envelope does not have a critical point. The vapor-liquid locus has a critical point at 46.4 bar and a mole fraction of methane of 0.997.

The program `lngflash`, which is a part of the `IVC-SEP` simulation package (Hytoft and Gani, 1996), was used to generate the pressure versus composition diagrams.

4   Conclusions

This paper discussed the computation of critical points using the RKS equations of state and demonstrated that interval mathematics can be used to solve this highly non-linear problem. Via interval arithmetic, the problem was solved without the need of any kind of initial guess or reinitializing. This implementation can find both lower and higher temperature critical points. Additional results not presented here had computational times of less than 800 s for binary mixtures with a single critical point and less than 3200 s when there were several critical points. Inclusive in this development was the guarantee of convergence and existence within the variable domains. Consequently, in those cases where no critical points were found, we can assert with mathematical certainty that there are not any critical points within the chosen domain. A key step in our implementation was the implementation of compact expressions for the function computations and jacobian evaluations. These expressions minimized repetition of terms in the equations and permitted to compute tighter bounds for the functions and Jacobian elements.

Variable	Range	
Mole volume[1]	1.1-4.0 b	
Temperature (K)	110-800	
Δn_1	0-1	
Δn_i [2]	(-1)- 1	
Binary interaction parameters		
(k_{ij})		
	H_2S	CH_4
H_2S	0.0000	$0.08^{[3]}$
CH_4	$0.08^{[3]}$	0.0000

[1] 'b' is the van der Waals mole volume of the mixture.

[2] Δn_j is any of the 2nd-nth composition changes.

[3] parameters k_{ij} for the Redlich-Kwong-Soave equation of state.
Taken from Hua *et al.* (1996).

Table 2: Variable ranges and binary interaction parameters for the Redlich-Kwong-Soave equation of state.

Table 3: Critical points for mixtures of methane and hydrogen sulfide (CH_4-H_2S)

Feed Composition		vdWMV (cm^3/gmol)	Δn_1	Δn_2	Critical Volume (cm^3/gmol)	Critical Temperature (K)	Critical Pressure (bar)	Total time (s)
X_{CH_4}	X_{H_2S}	$b_{mixture}$						
0.998	0.002	29.82	0.9999	0.0042	114.26	190.82	46.3	0.522
0.97	0.03	29.82	0.9977	0.0682	107.70	196.74	50.4	1.422
0.9475	0.0525	29.83	0.9916	0.1292	102.18	201.37	53.9	3.154
0.94	0.06	29.83	0.9884	0.1517	100.30	202.86	55.1(*)	4.065
0.93	0.07	29.83	0.9830	0.1837	97.75	204.78	56.7(*)	5.640
			0.6185	0.7858	44.72	114.77	-283.6	
0.86	0.14	29.85	0.8651	0.5016	77.95	213.71	65.5(*)	20.912
			0.6003	0.7998	56.59	181.31	-1.7	
0.85	0.15	29.85	0.8189	0.5739	74.03	212.99	64.5(*)	25.368
			0.6239	0.7815	59.41	190.98	22.5(*)	
0.84	0.16	29.86			NCP			38.993
0.75	0.25	29.88			NCP			14.481
0.53	0.47	29.94			NCP			19.640
0.52	0.48	29.94	0.2017	-0.9795	59.26	270.02	146.1	35.049
			0.2874	-0.9578	54.94	260.27	149.0	
0.51	0.49	29.94	0.1352	-0.9908	63.37	279.25	145.0	27.800
			0.3896	-0.9210	50.31	249.01	160.1	
0.49	0.51	29.95	0.6814	-0.7319	34.89	208.15	1800.2	26.401
			0.5229	-0.8524	44.26	231.67	230.4	
			0.0846	-0.9964	67.59	288.86	144.0	
0.36	0.64	29.98	0.0628	-0.9999	83.21	323.07	132.6	8.866
0.229	0.771	30.00	0.0435	0.9999	95.58	345.50	117.1	4.869
0.24	0.76	30.01	0.0412	0.9999	94.58	343.86	118.4	5.142
0.09	0.91	30.05	0.0297	0.9999	107.91	363.58	100.0	1.953

NCP: no critical point was found.
vdWMV: van der Waals molar volume of the mixture.
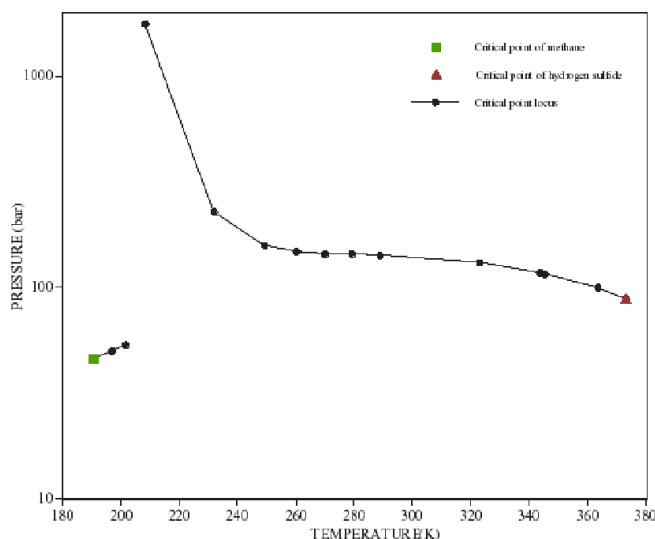(*) Unstable critical points.

Figure 1: Pressure versus temperature diagram for CH_4/H_2S binary mixtures.

Acknowledgment

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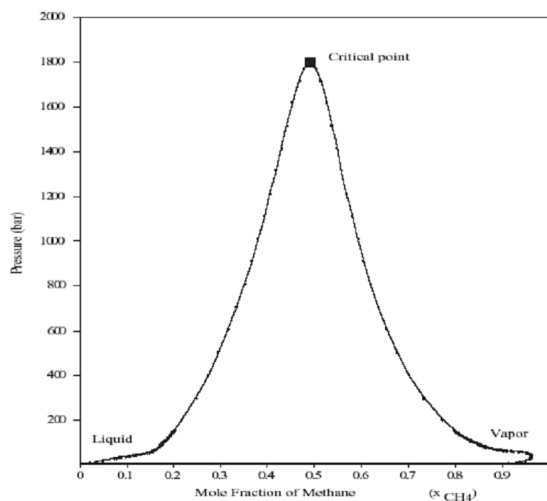[8] Hansen, E. (1992) *Global Optimization using Interval Analysis.* Marcel-Dekker, New York.

Figure 2: Pressure versus mole fraction of methane at 208.15 K.

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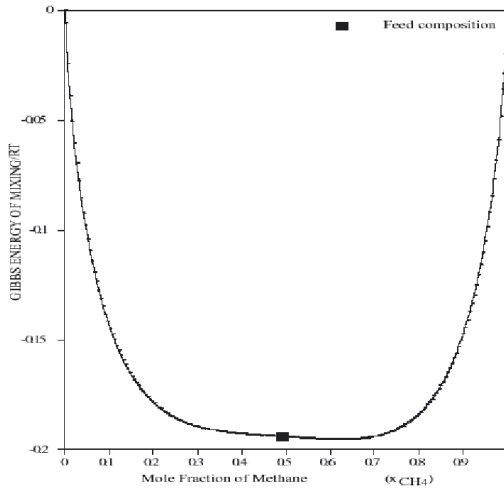
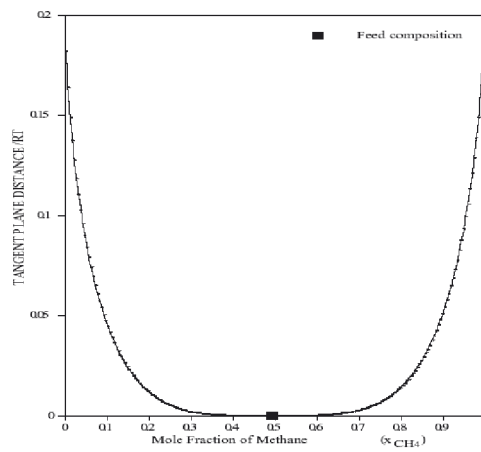Figure 3: Gibbs energy of mixing versus composition at 208.15 K.

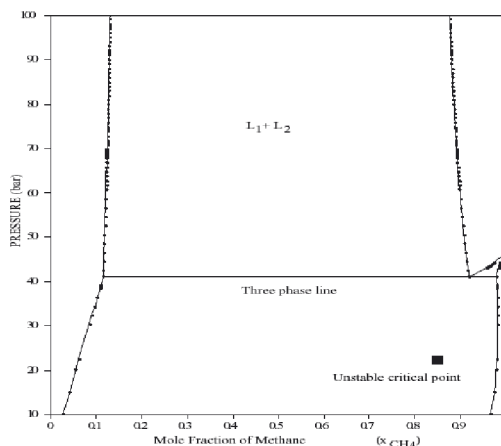Figure 4: Tangent plane distance versus composition at 208.15 K.

Figure 5: Pressure versus mole fraction of methane at 190.98 K.

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A   Appendix

We have the following equations used in the computation of critical points,

$$\sum_{j=1}^{C} A_{ij}\Delta n_j \;=\; \frac{RT}{n}\left(\frac{\Delta n_i}{y_i} + F_1\left(\beta_i\overline{N} + \overline{\beta}\right) + \beta_i F_1^2\overline{\beta}\right)$$

$$+\frac{a}{bn}\left(\beta_i\overline{\beta}F_3 - \frac{F_5}{a}\sum_{j=1}^{C} a_{ij}\Delta n_j + F_6\left(\beta_i\overline{\beta} - \alpha_i\overline{\beta} - \overline{\alpha}\beta_i\right)\right),\; i=1,\ldots,C. \tag{10}$$

$$\sum_{i=1}^{C}\sum_{j=1}^{C}\sum_{k=1}^{C} A_{ijk}\Delta n_i \Delta n_j \Delta n_k \;=\; \frac{RT}{n^2}\left(-\frac{\sum\limits_{i=1}^{C}\Delta n_i^3}{y_i^2} + 3\overline{N}(\overline{\beta}F_1)^2 + 2(\overline{\beta}F_1)^3\right) \tag{11}$$

$$+\frac{a}{n^2 b}(3\overline{\beta}^2(2\overline{\alpha} - \overline{\beta})(F_3 + F_6) - 2\overline{\beta}^3 F_4 - 3\overline{\beta}\overline{a}F_6).$$

where,

C: total number of components.

A_{ij}: second order derivative of the Helmholtz free energy with respect to the number of moles of species i and j.

Δn_j: change in total number of moles of species j. This is used in the context of a Taylor series expansion of the Helmholtz free energy in terms of composition.

R: ideal gas constant.

T: absolute temperature.

n: total number of moles.

n_i: number of moles of species i. Analogous meaning for other subindices.

$\overline{N}$: parameter used in the equations for the computation of critical points, it is defined as,

$$\overline{N} = \sum_{i=1}^{C}\Delta n_i$$

y_i: mole fraction of component i. Analogous meaning for other subindices.

a: average energy parameter of the equation of state for the mixture of components. This is computed using standard van der Waals mixing rules:

$$a = \sum_{i=1}^{C}\sum_{j=1}^{C}\frac{n_i n_j}{n^2}a_{ij}$$

$$a_{ij} = (a_i a_j)^{0.5}(1 - k_{ij})$$

a_{ij}: energy of interaction parameter between species i and j.

a_i: energy parameter of species i. The meaning is the same for other subindices. It is computed using the following correlation:

$$a_i = \left(\frac{(RT_{c_i})^2 \eta}{P_{c_i}}\right)\left[1 + c_i\left(1 - \left(\frac{T}{T_{c_i}}\right)^{0.5}\right)\right]$$

$\eta = 0.45748$ and $c_i = 0.48 + 1.574w_i - 0.176w_i^2$, for the Redlich-Kwong-Soave Equation of State.

w_i: accentric factor of species i.

T_{ci}: critical temperature of species i.

P_{ci}: critical pressure of species i.

k_{ij}: binary interaction parameter between species i and j.

α_k: parameter used in the equations for the computation of critical points, it is defined as,

$$\alpha_k = \frac{\sum\limits_{i=1}^{C} y_i a_{ik}}{a}.$$

$\overline{\alpha}$: parameter used in the equations for the computation of critical points, it is defined as,

$$\overline{\alpha} = \sum_{i=1}^{C} \Delta n_i \alpha_i.$$

$\overline{a}$: parameter used in the equations for the computation of critical points, it is defined as,

$$\overline{a} = \frac{1}{a}\sum_{i=1}^{C}\sum_{j=1}^{C} \Delta n_i \Delta n_j a_{ij}.$$

b: average van der Waals mole volume of the Equation of State. This is computed using standard van der Waals mixing rules,

$$b = \sum_{i=1}^{nc} \left(\frac{n_i}{n}\right) b_i.$$

b_i: van der Waals mole volume of species i. This is computed as follows,

$$b_i = 0.08664RT_{c_i}/P_{c_i}, \text{ for the Redlich-Kwong-Soave equation of state.}$$

β_i: parameter used in the equations for the computation of critical points, it is defined as,

$$\beta_i = \frac{b_i}{b}.$$

$\overline{\beta}$: parameter used in the equations for the computation of critical points, it is defined as,

$$\overline{\beta} = \sum_{i=1}^{C} \Delta n_i \beta_i.$$

F_{1-6}: auxiliary functions used in the computation of critical points, they are defined as,

$$
\begin{aligned}
F_1 &= \frac{1}{K-1} \\
F_2 &= \frac{2}{D_1 - D_2}\left(\frac{D_1}{K+D_1} - \frac{D_2}{K+D_2}\right) \\
F_3 &= \frac{1}{(D_1 - D_2)}\left(\left(\frac{D_1}{K+D_1}\right)^2 - \left(\frac{D_2}{K+D_2}\right)^2\right) \\
F_4 &= \frac{1}{(D_1 - D_2)}\left(\left(\frac{D_1}{K+D_1}\right)^3 - \left(\frac{D_2}{K+D_2}\right)^3\right) \\
F_5 &= \frac{2}{(D_1 - D_2)}\ln\left(\frac{K+D_1}{K+D_2}\right) \\
F_6 &= \left(\frac{2}{(D_1 - D_2)}\right)\left(\left(\frac{D_1}{K+D_1} - \frac{D_2}{K+D_2}\right) - \ln\left(\frac{K+D_1}{K+D_2}\right)\right).
\end{aligned}
$$

K: dimensionless volume, it is defined as,

$$K = \frac{V}{nb}.$$

D_{1-2}: parameters of the equation of state. Their values are calculated with the following formulas,

$$D_1 = \frac{u_o + \sqrt{u_o^2 - 4w_o}}{2}$$

$$D_2 = \frac{u_o - \sqrt{u_o^2 - 4w_o}}{2}$$

where, $u_o = 1$ and $w_o = 0$, for the Redlich-Kwong-Soave equation of state.

δ_{ij}: Kronecker delta operator, which is defined as,

$$\delta_{ij} = \begin{cases} i = j, & \delta_{ij} = 1 \\ i \neq j, & \delta_{ij} = 0. \end{cases}$$