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Efficient Evaluation of Vapour–Liquid Equilibria from Multi-parameter Thermodynamic Models Using Differential Algebra

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Abstract

An efficient method is proposed to evaluate the Vapour–Liquid Equilibrium (VLE) curve for complex multi-parameter technical and reference thermodynamic equations of state, in connection with Computational Fluid Dynamics (CFD) simulations of compressible flows of real gases. Differential algebra techniques are used to obtain an approximation of the VLE curve from the reference equation of state of carbon dioxide. Seven fourth-order Taylor polynomials are required to approximate the VLE curve for a reduced pressure between 0.7 and 1, with an error on density below 0.04%, except near the critical point where the error is around 0.1%. The proposed approach is proved to be a suitable alternative to standard Look-Up Table (LUT) techniques, with comparable accuracy and computational burden. Moreover, the explicit use of the model analytical expression in the determination of the polynomial expansions allows to reduce the number of expansion poles and it will possibly simplify the approximation of different fluids, including mixtures.

Keywords: Vapour–liquid equilibrium, Reference equation of state, Technical equation of state, Carbon dioxide, Differential Algebra, Computational fluid dynamics, Look-Up Table

1. Introduction

In most engineering applications, the numerical simulation of compressible flows is usually carried out under the assumption of an ideal gas. The ideal gas model is the paradigm of the majority of aeronautic and aerospace problems, such as the analysis of the flow-field around transonic-cruise aircraft and hypersonic re-entry vehicles or in turbomachinery applications. However, the

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ideal-gas approximation is not suitable for situations where the conditions of the fluid in terms of pressures and temperatures are close to the Vapour Liquid Equilibrium (VLE) curve or are of an order of magnitude close to the critical-point values. Remark that for some fluids the ideal gas model provides inaccurate results from an engineers' viewpoint at pressures near 1 bar already.

To account for so-called real gas effects, including two-phase flows and critical point phenomena, real-gas fluid models are to be included in Computational Fluid Dynamics codes. If fluid continuity and thermodynamic equilibrium can be assumed, an analytical thermodynamic equation of state (EOS) is sufficient to compute all real-gas properties required by the CFD solver, including e.g., the pressure, the temperature, the speed of sound and transport properties. The inclusion of such an EOS usually results in a significant increase of the computational costs, as discussed, e.g., in [1]. Due to the evaluation of non-ideal gas properties at each time step, the computational time increases, with respect to ideal gas simulations, up to three/four orders of magnitude for an explicit CFD code and one order of magnitude for an implicit one, since the latter usually requires a lower number of iterations to reach the steady state. For modern reference or technical multi-parameter EOS, see [2, 3, 4, 5], the computational burden related to EOS evaluations can be the main limiting factor of using CFD simulations.

Modern thermodynamic models are usually written in terms of a thermodynamic potential, to guarantee thermodynamic consistency and stability of all derived quantities. This is for example the Helmholtz free energy, which is written as a function of the temperature and of either the density or specific volume. The analytical expression of both technical and reference EOS generally includes a number of empirical functional terms, whereby these fluid-specific parameters are computed by fitting the functional relation to experimental data. In the case of a simpler technical EOS, the uncertainty associated to the evaluation of thermodynamic properties is within 1-2%, a range that is deemed sufficient for technical applications. Reference equations of state compute thermodynamics properties within the accuracy of the experimental measurements they are based upon [6].

The *direct* evaluation of the thermodynamic model, where any given property is computed from the two so-called natural variables—the temperature and density in the case of the Helmholtz potential—amounts to the direct evaluation of an algebraic non-linear function and therefore requires negligible CPU time. On the contrary, *inverse* evaluation, where one or both independent variables are not the natural ones, requires the (numerical) solution of an algebraic non-linear equation or a 2×2 system of algebraic non-linear equations. Unfortunately, the latter is usually the situation encountered in CFD, since typically the internal energy and the density are the independent variables. In particular, the identification of the fluid phase—be it vapour, liquid or two-phase—amounts to solving a 2×2 system of algebraic non-linear equations for the saturated liquid and vapour values of the density. Moreover, the evaluation of each term in the system requires the solution of inner inverse problems for the pressure and the temperature.

The identification of the fluid phase is mandatory to determine whether single-phase or two-phase models are to be applied and therefore in CFD computations such a test is carried out for all grid points and for all time steps; as a consequence, a significant reduction of the computational burden can be obtained by introducing a computationally efficient approximation of the VLE curve. Moreover, in inverse evaluations, the phase check is to be carried out at each sub-iteration.

So-called ancillary equations can be used to estimate the density and pressure along the VLE curve as a function of the temperature [2]. The functional form is valid for a given class of fluids and it includes a variable number of parameters fitted on VLE experimental data of the considered fluid. Alternatively, Look-Up Tables (LUT) can be used to compute saturated density and pressure along the VLE curve. LUT are tables containing the thermodynamic properties of the fluid, computed with accurate equations of state in a discrete number of points of the thermodynamic plane. The thermodynamic state in other points, including the VLE curve, can be retrieved by interpolation of these data. In the approximate evaluation of the thermodynamic properties of the fluid, particular care must be taken in guaranteeing thermodynamic stability [7]. As explained in [8], thermodynamic stability requires that the thermodynamic variables computed through the approximate model satisfy the constraints posed by Maxwell relations.

Thermodynamic consistency is also to be guaranteed in the approximate framework. Consider the evaluation of the pressure P from the temperature T and density ρ by means of the pressure EOS $P = \Pi(T, \rho)$ provided by the model. If $T = \theta(P, \rho)$ is the temperature EOS, then $P \equiv \Pi(\theta(P, \rho), \rho)$. On the contrary, if the functions Π and θ are substituted by their approximate counterparts $\tilde{\Pi}$ and $\tilde{\theta}$, so that $P = \tilde{\Pi}(T, \rho) \pm \epsilon_{\Pi}$ and $T = \tilde{\theta}(P, \rho) \pm \epsilon_{\theta}$, with ϵ the approximation error, one in general has $P \neq \tilde{\Pi}(\tilde{\theta}(P, \rho), \rho)$. The difference $P - \tilde{\Pi}$ can be easily reduced by increasing the accuracy of the approximation $\tilde{\Pi}$: however, due to the high non-linearity of real gas thermodynamics and the number of inverse evaluations of the thermodynamic model in CFD computations, a relatively accurate approximation can produce significant inconsistencies that may eventually prevent the CFD solver to reach convergence. In the following, we will refer to the difference $P - \tilde{\Pi}$ as a measure of the thermodynamic consistency of the approximation.

In the present paper a novel technique for approximating the VLE curve is presented, which is at the same time computationally efficient and accurate. Differential algebra (DA) techniques are used, which allow to represent and operate on functions through their Taylor series expansions rather than their point-wise evaluations. For conciseness, this paper reports only the polynomial approximation of the VLE curve associated to the technical and the reference EOS of carbon dioxide, though the presented procedure was applied to four different fluids with comparable results.

The present paper is organized as follows. Section 2 describes the thermodynamic modelling of the VLE problem and reports also the reference EOS of carbon dioxide. Section 3 gives a brief explanation of DA techniques and

their application to the VLE problem. More specifically, sections 3.1 and 3.2 describe the algorithm for computing an approximate solution of the VLE system in terms of deviation from a reference temperature. Finally, the obtained results are presented and discussed in section 4. A summary of the work and an indication of possible further developments are presented in section 5.

2. Vapour-Liquid Equilibrium from thermodynamic models

The VLE curve of carbon dioxide is reported in Figure 1, where the density-temperature (ρ - T) thermodynamic planes is shown. With reference to Figure 1, each isotherm $T = \bar{T} < T_C$, with T_C the critical temperature, intersects the VLE curve at two points. The corresponding values of the specific volume $v_L = 1/\rho_L$ and $v_V = 1/\rho_V$, $v_L < v_V$, are called the saturated liquid and saturated vapour states, respectively. At $T = \bar{T} < T_C$, if $v < v_L$ the fluid state is liquid; if $v_L \leq v \leq v_V$ the liquid and vapour phase co-exist; if $v > v_V$ the fluid is in the vapour phase. At the critical pressure, $v_L \equiv v_C \equiv v_V$. Above the critical temperature and pressure, no phase transition can occur by iso-thermal compression of a gas. In the following, the subscript L, V and C refer respectively to thermodynamic properties along the liquid side, the vapour side and the critical state.

The saturated values of the specific volume can be computed by the following 2×2 system of non-linear equations, [7]

$$\begin{cases} P(\bar{T}, v_V) = P(\bar{T}, v_L) \\ \mu(\bar{T}, v_V) = \mu(\bar{T}, v_L) \end{cases} \quad (1)$$

which states that the pressure P and the chemical potential μ of saturated vapour and saturated liquid are equal at the same temperature $\bar{T} < T_C$.

The solution of the system (1) requires the specification of a thermodynamic model, which allows to compute P and μ from the temperature and the specific volume. Note that the definition of the VLE curve depends on the chosen thermodynamic model and therefore consistency issues may possibly arise if a different, simplified, model is used to compute the VLE curve.

In the present work, the reference EOS for carbon dioxide proposed by Span and Wagner in 1996 is considered [2]. This model allows to compute the reduced Helmholtz energy $\alpha = a/RT$, with a specific Helmholtz energy and R gas constant, as a function of the reduced density $\delta = \rho/\rho_C$ and the inverse of the reduced temperature $\tau = T_C/T$. The function α is written as the sum of a so-called ideal-gas contribution (indicated by the superscript ID) and of a second term describing the residual or real-gas behaviour (R) as follows

$$\alpha(\tau, \delta) = \alpha^{\text{ID}}(\tau, \delta) + \alpha^{\text{R}}(\tau, \delta). \quad (2)$$

The ideal-gas term α^{ID} of the Helmholtz energy solely depends upon the isobaric heat capacity in the ideal-gas state, i.e. C_P^{ID} , and it reads

$$\alpha^{\text{ID}}(\delta, \tau) = \frac{h_0^{\text{ID}} \tau}{RT_C} - \frac{s_0^{\text{ID}}}{R} - 1 + \ln \left(\frac{\delta \tau_0}{\delta_0 \tau} \right) - \frac{\tau}{R} \int_{\tau_0}^{\tau} \frac{C_P^{\text{ID}}}{\tau^2} d\tau + \frac{1}{R} \int_{\tau_0}^{\tau} \frac{C_P^{\text{ID}}}{\tau} d\tau \quad (3)$$

where h_0^{ID} and s_0^{ID} are the enthalpy and the entropy of the ideal gas in the reference state τ_0 and δ_0 [9].

Considering now the real-gas correction $\alpha^{\text{R}} \equiv \alpha - \alpha^{\text{ID}}$, the latter is described by a function composed by 42 polynomial, exponential and Gaussian bell-shaped terms as follows

$$\begin{aligned} \alpha^{\text{R}}(\tau, \delta) = & \sum_{i=1}^7 n_i \delta^{d_i} \tau^{t_i} + \sum_{i=8}^{34} n_i \delta^{d_i} \tau^{t_i} \exp(-\delta^{c_i}) \\ & + \sum_{i=35}^{39} n_i \delta^{d_i} \tau^{t_i} \exp\left[-\alpha_i (\delta - \epsilon_i)^2 - \beta_i (\tau - \gamma_i)^2\right] \\ & + \sum_{i=40}^{42} n_i \Delta^{b_i} \delta \exp\left[-C_i (\delta - 1)^2 - D_i (\tau - 1)^2\right] \end{aligned} \quad (4)$$

where n_i , d_i , t_i , α_i , β_i , ϵ_i , γ_i , a_i , b_i , c_i , A_i , B_i and C_i , $i = 1, \dots, 42$ are substance-dependent constants and where

$$\Delta = \left\{ (1 - \tau) + A_i \left[(\delta - 1)^2 \right]^{\frac{1}{2\beta_i}} \right\}^2 + B_i \left[(\delta - 1)^2 \right]^{a_i}.$$

The numerical values of all constant parameters in (4) can be found in [2]. This equations was obtained through optimization of the functional form and simultaneous fit of high-accuracy experimental data of different thermodynamic properties. The resulting EOS is able to reproduce data within their experimental uncertainty, therefore it belongs to the class of reference EOS.

Since the function $\alpha(\tau, \delta)$ is a thermodynamic potential, all thermodynamic properties of the fluid can be calculated by evaluating its partial derivatives, see [7]. Some useful relations between common thermodynamic properties and partial derivatives of the reduced Helmholtz energy are listed in [3, Table II]. From relations in [3, Table II], it is possible to express the system (1) as

$$\begin{cases} \ln\left(\frac{\rho_{\text{L}}}{\rho_{\text{V}}}\right) + \alpha^{\text{R}}(\bar{\tau}, \delta_{\text{L}}) - \alpha^{\text{R}}(\bar{\tau}, \delta_{\text{V}}) + \delta_{\text{L}} \alpha_{\delta}^{\text{R}}(\bar{\tau}, \delta_{\text{L}}) - \delta_{\text{V}} \alpha_{\delta}^{\text{R}}(\bar{\tau}, \delta_{\text{V}}) = 0 \\ \delta_{\text{L}} [1 + \delta_{\text{L}} \alpha_{\delta}^{\text{R}}(\bar{\tau}, \delta_{\text{L}})] - \delta_{\text{V}} [1 + \delta_{\text{V}} \alpha_{\delta}^{\text{R}}(\bar{\tau}, \delta_{\text{V}})] = 0. \end{cases} \quad (5)$$

The system (5) provides the implicit definition of the VLE curve of carbon dioxide both under the reference and the technical Span-Wagner EOS.

2.1. Ancillary equations

Different types of so-called ancillary equations were proposed to approximate the VLE curve and avoid direct solution of system (5). These functions are generally composed of exponential terms and contain a variable number of parameters that are determined through correlations of experimental or reference data.

Table 1: Coefficients of the ancillary equations (6), representing VLE curve of carbon dioxide.

a_1	1.682959	b_1	-1.605071	c_1	-6.978589
a_2	0.897143	b_2	-2.926083	c_2	1.216980
a_3	0.353873	b_3	-7.379254	c_3	-7.025053
a_4	-6.476158	b_4	-6.000816	c_4	197.311927
		b_5	-453.936079	c_5	-6488.004466

In the present work, the following set of ancillary equations were used to obtain the values of density and pressure along the VLE curve as functions of temperature:

$$\frac{\rho_L}{\rho_C} = 1 + a_1\theta^{\frac{1}{3}} + a_2\theta^{\frac{2}{3}} + a_3\theta^{\frac{7}{3}} + a_4\theta^{\frac{20}{3}} \quad (6a)$$

$$\frac{\rho_V}{\rho_C} = \exp \left[b_1\theta^{\frac{1}{3}} + b_2\theta^{\frac{2}{3}} + b_3\theta^{\frac{5}{3}} + b_4\theta^{\frac{8}{3}} + b_5\theta^{\frac{22}{3}} \right] \quad (6b)$$

$$\frac{P}{P_C} = \exp \left[c_1\theta + c_2\theta^{1.5} + c_3\theta^{3.5} + c_4\theta^7 + c_5\theta^{10.5} \right] \quad (6c)$$

where $\theta = 1 - T/T_C$. The constant parameters a_i , b_i , c_i were determined by linear least-square fits to the reference data reported in [2] and are listed in Table 1.

2.2. Look-up tables

Thermodynamic Look-Up Tables (LUT) can be used in numerical simulations to reduce computational costs when an accurate thermodynamic model is required to correctly represent the fluid. For instance, References [10, 11, 12, 13] discuss LUT applications to take into account real gas effects in turbo-machinery flows and high-temperature gas effects in simulations of a hypersonic boundary layer. In [8], Swesty proposed a bi-quintic interpolation scheme for Helmholtz free energy LUT which guarantees that thermodynamic consistency is fulfilled.

In LUT methods, thermodynamic properties are computed during a pre-processing step by mapping the thermodynamic region of interest onto a bi-dimensional grid. In the CFD simulation, the required thermodynamic variables are computed through an interpolation of these tabulated values. The computational time and the accuracy depend on grid dimensions, search algorithm and interpolation scheme.

A one-dimensional LUT is used in the present work to approximate the VLE curve of carbon dioxide. The values of density and pressure are continuously retrieved from the LUT for any value of temperature in the computed range. Two different interpolation algorithms—a linear and a cubic—have been tested, as in [12].

3. VLE approximation using Differential Algebra

This section gives a brief overview of Differential Algebra (DA) and related techniques adopted in the present work. To introduce the following, it is useful to recall briefly that in the DA framework, a given function f is represented by its k -th order Taylor series expansion F , obtained by the extracting operation indicated by \mathcal{T} . More precisely, \mathcal{T} is an equivalence relation, and the application of \mathcal{T} corresponds to the transition from the function to the equivalence class comprising all those functions with identical Taylor series expansion to order k . The set of equivalence classes can be endowed with well-defined operations, leading to the definition of so-called truncated power series algebra (TPSA) [14]. For a detailed description of DA techniques the reader is referred to [15].

In the present work, DA techniques and their implementation in the software COSY-INFINITY by Martin Berz and Kyoko Makino [16] are used to solve system (5), which is a particular case of a system of parametric implicit equations. In Section 3.1, the procedure to find the solution of a scalar parametric equation is discussed in more details. In Section 3.2, DA techniques are applied to the system of parametric non-linear equations (5) to determine the saturation curve.

3.1. Solution of a scalar parametric implicit equation

The parametric non-linear equation

$$f(x, p) = 0 \quad (7)$$

where $x \in \mathbb{R}$ is the independent variable, $p \in \mathbb{R}$ is a parameter and $f \in \mathbb{R}$ is a k -differentiable function, is considered first. In particular, the solution of (7) amounts to the determination of the function $x = x(p) \in \mathbb{R} | f(x(p), p) = 0 \forall p \in \mathbb{R}$.

DA techniques allow to determine the function $x(p)$ in terms of its Taylor series expansion with respect to the parameter p . To this purpose, it is necessary to choose a nominal value of the parameter p^* and to compute the corresponding reference solution x^* of equation (7), namely,

$$f(x^*, p^*) = 0. \quad (8)$$

The solution pair (x^*, p^*) can be obtained by standard solution techniques such as the Newton-Raphson method. The values are required in order to initialize the state and the parameter as the so-called k -th order DA variables. In this respect, DA variables are defined as the sum of the reference values and the deviations from them

$$\begin{aligned} [x] &= x^* + \Delta x \\ [p] &= p^* + \Delta p. \end{aligned} \quad (9)$$

In the DA framework the function f can be expressed as

$$\Delta f = \mathcal{M}_f(\Delta x, \Delta p) \quad (10)$$

where \mathcal{M}_f is the Taylor series map of f . This map is origin-preserving since x^* is a solution of equation (7). Therefore, Δf represents the deviation of f from its reference value. The map defined in (10) is then augmented by introducing the map corresponding to the identity function on the parameter, i.e., $\Delta p = \mathcal{I}_p(\Delta p)$. Finally, the map is inverted by using ad hoc polynomial algorithms implemented in COSY-INFINITY. Since the goal is to compute the k -th order Taylor series expansion of the solution of equation (7), the function f is required to have a null deviation from its reference value, which is zero. Thus, the resulting inverse map is evaluated for $\Delta f = 0$ as

$$\begin{bmatrix} \Delta x \\ \Delta p \end{bmatrix} = \begin{bmatrix} \mathcal{M}_f \\ \mathcal{I}_p \end{bmatrix}^{-1} \begin{bmatrix} 0 \\ \Delta p \end{bmatrix}. \quad (11)$$

The first row of the map (11) reads $\Delta x = \mathcal{M}_x(\Delta p)$ and therefore it describes, through a k -th order Taylor series polynomial, the function $x = x(p)$. Finally, the expression of Δx can be substituted into the first equations of (9) to obtain

$$[x] = x^* + \mathcal{M}_x(\Delta p). \quad (12)$$

which is the k -th order Taylor series expansion of the solution of the implicit parametric equation (7). For each Δp , the approximated solution to (7) can be computed directly by evaluating this polynomial. The accuracy of the approximation depends on both the order k of the Taylor series expansion and the relative variation Δp with respect to the reference value p^* .

3.2. DA techniques applied to the VLE curve

To apply DA techniques to the solution of system (5), the latter is written in the following compact form

$$\mathbf{f}(\boldsymbol{\delta}, \tau) = \mathbf{0} \quad \text{with} \quad \boldsymbol{\delta} = \begin{bmatrix} \delta_L \\ \delta_V \end{bmatrix} \quad (13)$$

where $\boldsymbol{\delta}$ is the vector of independent variables and τ is the parameter. The solution is sought in the reduced pressure range $0.7 \leq P/P_C \leq 1$. Since in the critical region a small variation of the temperature results in significant changes in relevant thermodynamic properties, a scale factor $\sigma < 1$ is introduced to guarantee that the variations are of the order of unity. To this purpose, the initialization of the DA variables (9) is modified as follows

$$\begin{aligned} [\delta_L] &= \delta_L^* + \sigma \Delta \delta_L \\ [\delta_V] &= \delta_V^* + \sigma \Delta \delta_V \\ [\tau] &= \tau^* + \sigma \Delta \tau \end{aligned} \quad (14)$$

and therefore the Taylor expansions of the solution are

$$\begin{aligned} [\delta_L] &= \delta_L^* + \sigma \mathcal{M}_{\delta_L}(\Delta \tau) \\ [\delta_V] &= \delta_V^* + \sigma \mathcal{M}_{\delta_V}(\Delta \tau). \end{aligned} \quad (15)$$

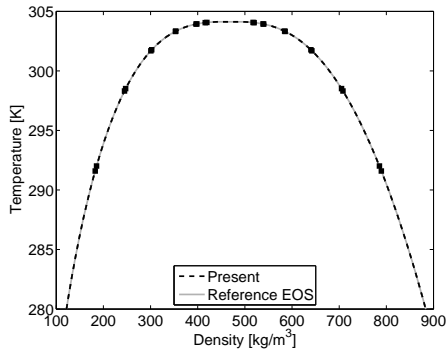


Figure 1: Polynomial approximation of the VLE curve of carbon dioxide obtained using the reference EOS [2]; black marks indicate the bounds of each polynomial and the overlap regions.

The reference solutions δ_L^* , δ_V^* and τ^* in (15) are computed using the software FluidProp [17] and RefProp [18]. These tools allow for the computation of the thermodynamic properties for a large variety of fluids and have implemented therein different EOS, including technical and reference ones. The approximation accuracy depends on the order k of the polynomial reconstruction. Second and third order polynomials prove to be insufficient to represent the VLE curve, because the coefficients of the Taylor polynomial are of about the same order of magnitude, thus indicating that higher-order terms may be needed to be considered. The magnitude of the coefficients of fourth-order polynomials obtained from COSY-INFINITY reduces as the order of the corresponding term increases. In particular, by selecting a sufficiently small scale factor, fourth-order coefficients of about 10^{-7} are obtained. Since the accuracy of the approximations (15) decreases as the distance from the poles δ_L^* and δ_V^* increases, an accurate representation of the VLE curve requires the definition of a number of different Taylor series expansions centred at different values of τ^* . Seven fourth-order polynomials are necessary to accurately represent the VLE curve for $0.7 < P_R < 1$ within 0.1% of uncertainty. Numerical experiments were performed by considering higher-order polynomials. In these cases, the accuracy of the approximation slightly increases, but a larger number of polynomials is required to approximate the same portion of the VLE curve since the representation error increases very rapidly with the distance from the poles.

4. Results and discussion

Differential Algebra techniques are now applied to represent the VLE curve of carbon dioxide obtained from the reference equation of state. Figure 1 shows the approximation of the VLE curve in the T - ρ thermodynamic plane, compared with the one obtained by the reference EOS [2]. The bounds of the interval of validity of each polynomial are indicated by black marks. An overlap of 5% between the intervals is introduced to facilitate transitions from one polynomial

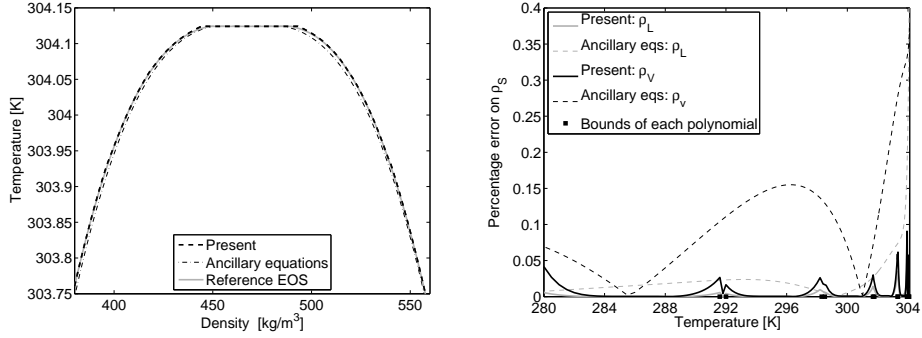


Figure 2: Comparison between the approximations of the VLE curve of carbon dioxide obtained by polynomials (present) and ancillary equations. Left: Detail of the VLE curve in the region near the critical point. Right: Percentage errors on saturated density computed in both cases: $\%error = 100(\rho - \rho_{REF})/\rho_{REF}$, where the subscript REF relates to the values computed by the software RefProp using the reference EOS [2].

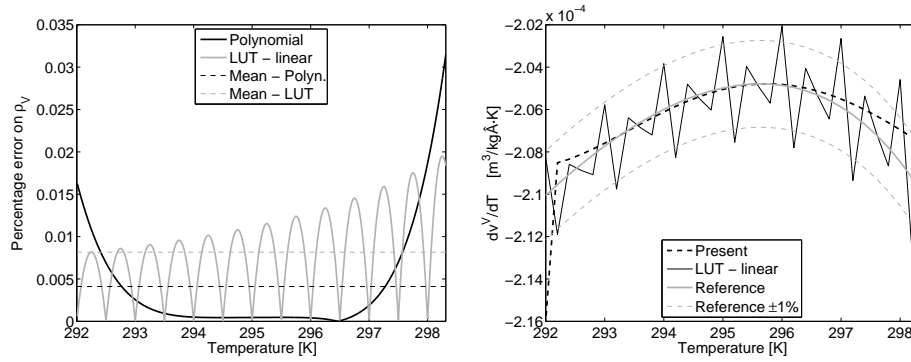


Figure 3: Comparison between the approximations of the VLE curve of carbon dioxide obtained by polynomials (present) and by a LUT along with a linear interpolation scheme, in a range of temperature between $T = 292\text{K}$ and $T = 298.3\text{K}$, which is approximated by only one Taylor polynomial. Left: Percentage errors on saturated density ρ_s along the vapour side of the VLE curve. Right: Derivative of specific volume with respect to temperature along the vapour side of the VLE curve dv_V/dT .

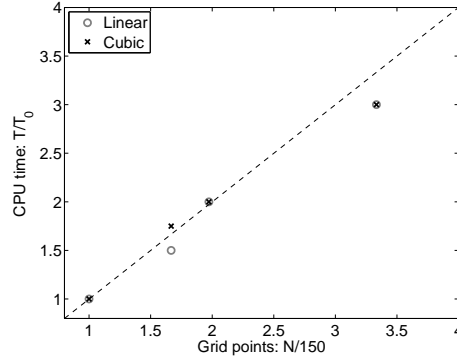


Figure 4: Dependence of the computational time on the number of LUT points. The CPU time refers to the interpolation of 1000 points between $T = 292\text{K}$ and $T = 298.3\text{K}$ both with a linear and a cubic scheme. Both quantities are normalized to the respective smallest value and the dashed line represent the linear dependence.

	CPU time	% Error on ρ_L		% Error on ρ_V	
		Mean	Max	Mean	Max
REFERENCE EOS					
RefProp	14.67				
Polynomial approximation	1.33	0.00137	0.01180	0.00411	0.03144
LUT linear interpolation	1.33	0.00240	0.00683	0.00816	0.01950
LUT cubic interpolation	1.34	0.00003	0.00012	0.00010	0.00034
TECHNICAL EOS					
RefProp	14.33				
Polynomial approximation	1.00	0.00065	0.00806	0.00154	0.01784
LUT linear interpolation	1.46	0.00247	0.00719	0.00786	0.01857
LUT cubic interpolation	1.46	0.00003	0.00013	0.00009	0.00032

Table 2: Computational time required to evaluate ρ_L and ρ_V in 1000 points between $T = 292\text{K}$ and $T = 298.3\text{K}$ along the VLE curve of carbon dioxide by the polynomial approximation proposed in the present work, by the software RefProp [18] and by a LUT method for two different equations of state. The LUT consists in 150 points—which cover a range of temperature between 231 K and the critical point—computed by RefProp. First rows of the table refer to the reference EOS [2] and the latter ones to the technical Span-Wagner EOS [5]. The table reports also the mean and the maximum errors on densities in the considered range, with respect to the values computed by RefProp. The unit CPU time corresponds to 0.0468 s on an Intel Core i7-2620M (2.0GHz), with 8 GB RAM. The values of CPU time refer only to the evaluation of the thermodynamic properties and they do not include the time required by the determination of the polynomial expansions and by the computation of LUT data.

to the next one. Inside these overlapping regions, the solution is obtained by combining the overlapping polynomials through an error function. At the critical point, the two approximations ρ_L and ρ_V for the liquid and vapour densities, respectively, do not overlap. Moreover, since the polynomial expansions are not centred at the critical point, the critical value is general different from the reference one.

Figure 2(right) shows the percentage errors on reduced densities with respect to the temperature. It can be noticed that the resulting curve approximates fairly well the reference one. The choice of using seven fourth-order polynomials resulted in a maximum error of 0.1% on reduced densities near the critical point and 0.04% elsewhere. The errors are larger near the bounds of the validity regions and, if needed, they can be reduced by using more Taylor series polynomials.

Figure 2 compares the approximation of the VLE curve obtained by DA techniques and the one obtained by the ancillary equations (6). The former yields a smaller deviation from the reference VLE curve than the latter, especially in the critical region, see Figure 2(left). This is confirmed also by data in Figure 2(right), which displays the percentage errors on reduced density along the liquid and vapour sides of the VLE curve.

An evaluation of the computational time is reported in Table 2. The values of saturated liquid and vapour density in 1000 points between $T = 292\text{K}$ and $T = 298.3\text{K}$ have been computed using both the polynomial Taylor series approximations proposed here and RefProp, using the same reference equation of state. The computational time does not include the time required by the computation of the Taylor polynomials but only their evaluation. The proposed approximation has been proved to be almost ten time faster than the evaluation by RefProp.

A similar comparison was performed between the proposed approximation and a LUT-based method [10]. A preliminary analysis was carried out to predict the dependence of the computational time on the number of points. For this purpose, different mono-dimensional LUT have been built by means of RefProp for carbon dioxide, computing the thermodynamic properties with the same reference EOS in a different number of points within different temperature ranges. The computational time for LUT evaluation—both with linear and cubic interpolation schemes—grows linearly with the number of grid points, as can be seen in Figure 4, while it seems to be unaffected by the temperature range. This is probably due to the binary search algorithm used to locate the nearest data values required by interpolation, which discards half of the range at each iteration. The comparison between the polynomial approximation and the interpolation of LUT values has been performed using a table composed by 150 points between $T = 231\text{K}$ and the critical point. This LUT allowed to compute the values of saturated density in the same 1000 points in the same computational time. The computational time required by the linear and the cubic interpolation is reported in Table 2, which summaries also the percentage errors on density. The two interpolation schemes requires the same computational effort, while the cubic one yields a reduction of approximately two order of magnitude in the

percentage errors.

For the reference EOS, the proposed method seems to bring no advantages in terms of computational time or accuracy with respect to linear interpolation of LUT data. Nevertheless, a more detailed analysis reveals that the approximation obtained by Taylor polynomials exhibits a more regular behaviour. This is displayed by Figure 3(left) which shows the error on density on the vapour side of VLE curve in the temperature range between $T = 292\text{K}$ and $T = 298.3\text{K}$, which is approximated by only one Taylor polynomial. This behaviour leads to an inaccurate approximation of the derived quantities. For instance, Figure 3(right) shows the derivative of specific volume with respect to temperature on the vapour side in the same range of temperatures. It can be noticed that the derivative of the approximation obtained by the LUT exhibits an oscillatory behaviour. Such a behaviour, which has been observed also on the liquid side and for the derivative of the volume with respect to pressure, strongly affects the thermodynamic consistency. The same derivatives computed by means of the polynomial approximation present as well discontinuities, but only where two different polynomials join together, so in a well defined region. The cubic interpolation of LUT data does not present this drawback.

Similar results have been obtained for technical EOS for different fluids. More specifically, the present method has been applied also to the VLE curve obtained using the technical Span-Wagner EOS [3, 4, 5] for four different fluids (carbon dioxide, butane, methane, propane). In all these cases, seven fourth-order polynomials have proved to be sufficient to approximate the VLE for $0.7 < P_R < 1$, with a maximum error on the reduced density of 0.02% for carbon dioxide, 0.005% for butane, 0.03% for methane and 0.006% for propane. Figure 5 shows the exact and the approximated VLE curve of the four fluids in the plane T - ρ obtained using the technical Span-Wagner EOS and the percentage errors on reduced densities. For carbon dioxide only, Table 2 contains also the comparison between the polynomial and LUT-based approximations applied to the twelve-parameter technical Span-Wagner EOS. In this case, the polynomial approximation yields a reduction of the computational cost and an error on saturated densities comparable to the one obtained by linear interpolation of LUT.

5. Conclusions

Differential Algebra techniques were applied to approximate the Vapour-Liquid Equilibrium curve of carbon dioxide obtained from the reference equation of state of Span-Wagner [2], for a reduced pressure in the interval $0.7 < P/P_C < 1$. DA techniques implemented in the software COSY-INFINITY delivered two sets of seven fourth-order polynomials for the reduced saturated liquid and vapour density as a function of the inverse reduced temperature. Each fourth-order polynomial is defined over a limited range of temperature. Errors on reduced saturated density are less than 0.1% with respect to values computed with the reference EOS. The maximum value of the error is observed close to the

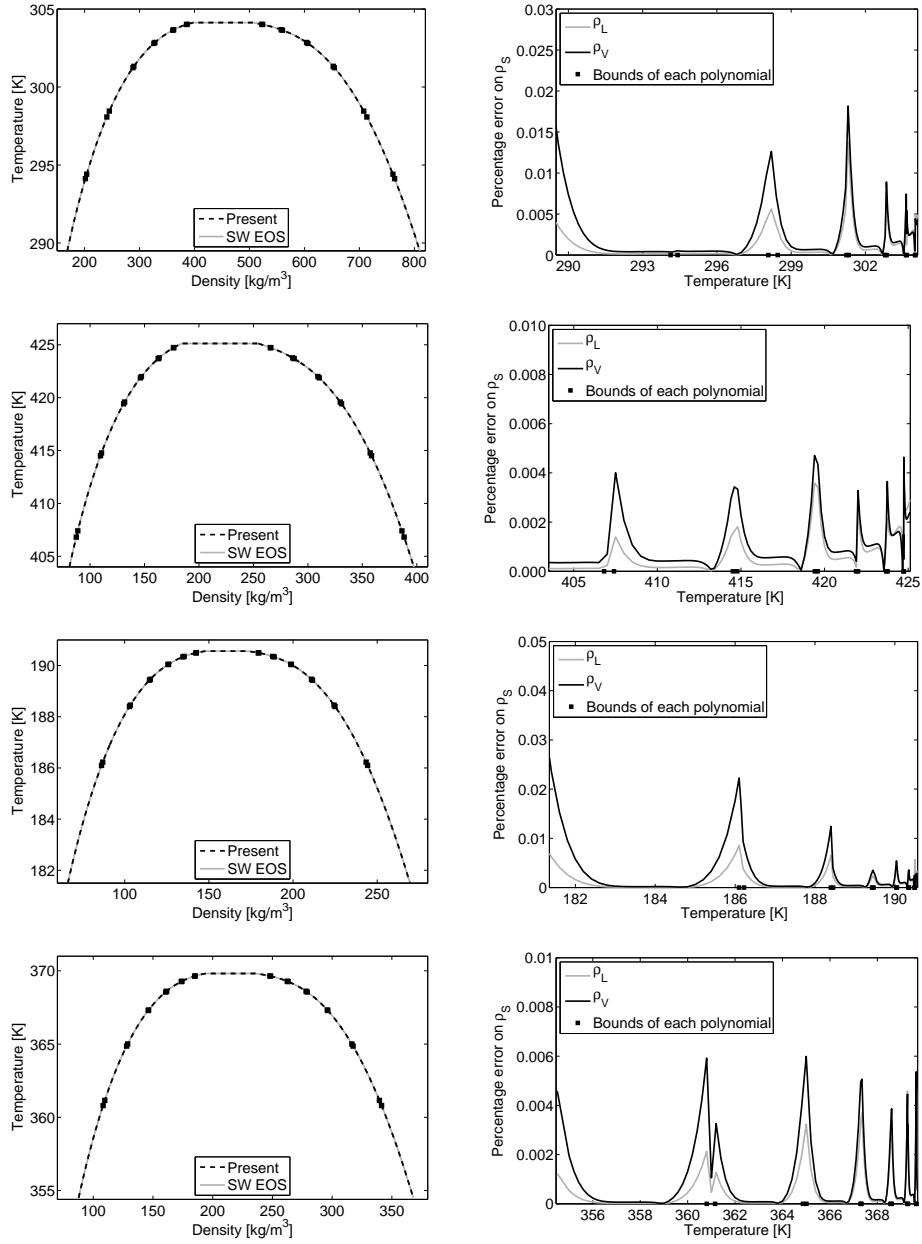


Figure 5: Polynomial approximation of the VLE curve of different fluids obtained using the technical EOS of Span-Wagner [4, 5]; black marks indicate the bounds of each polynomial and the overlap regions. Left: VLE curve in the $T - \rho$ thermodynamic plane. Right: Percentage errors on saturated density: $\%error = 100(\rho - \rho_{SW})/\rho_{SW}$, where the subscript SW relates to the values computed by the software RefProp using the technical Span-Wagner EOS. First row refers to carbon dioxide, the second one to butane, the third one to methane and the fourth to propane

boundary of the interval associated to each polynomial, where two neighbouring polynomials are combined using an error function.

A comparison between the computational time required by evaluating saturated density values using the exact implementation of the reference EOS in RefProp and the present approach showed that the latter allows for a one-order-of-magnitude reduction of the computational costs. The polynomial approximation was found to be more accurate than so-called ancillary equations, though admittedly the latter are characterized by very simple functional form—which allows for an almost instantaneous evaluation—and were not devised for accurate CFD computations.

A comparison with a mono-dimensional LUT method showed that the polynomial approximation brings few notable advantages with respect to linear interpolation of LUT data. One of this concerns regularity, at least in the centred part of the validity region of each polynomial. This allows to compute the derivative of thermodynamic quantities more accurately and therefore to increase thermodynamic consistency. Furthermore, a similar comparison revealed that the polynomial approximation offers no advantages in computational time or accuracy with respect to cubic interpolation, even if it allows to approximate the VLE curve with a less amount of stored information.

In the opinion of the authors, the polynomial approximation proposed here is suitable for phase check, especially in CFD code which allows to choose between different thermodynamic models or in simulations that involve different fluids or mixtures. The proposed approximation can, in fact, be easily implemented and the functional form does not change even if thermodynamic model changes. This possibility could circumvent the drawback of performing time-consuming phase check in LUT methods.

Further developments will concern a more detailed analysis on the effects of the polynomial approximation on the thermodynamic consistency and the implementation of such approximation also to mixtures. Moreover the proposed approach based on DA techniques will be extended to the approximation of additional thermodynamic quantities needed in CFD computations, including further portion of the P - v - T diagram.

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