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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.

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 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

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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 [2–5], 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 Fig. 1, where the density–temperature (ρ–T) thermodynamic planes is shown. With reference to Fig. 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