

Publisher's note

Erratum to “On the computation of the fundamental derivative of gas dynamics using equations of state” [Fluid Phase Equilib. 286 (2009) 43–54]

P. Colonna ^{a,*}, N.R. Nannan ^a, A. Guardone ^b, T.P. van der Stelt ^a

^a Energy Technology Section, Process and Energy Department, Delft University of Technology, Leeghwaterstraat 44, 2628 CA Delft, The Netherlands

^b Dipartimento di Ingegneria Aerospaziale, Politecnico di Milano, Via La Masa 34, 20156 Milano, Italy

ARTICLE INFO

Article history:

Available online 27 November 2009

The publisher regrets that the article this was truncated in the printed version. Only the abstract and references were published. The full article is reprinted in the following pages.

Please note that the full article appears correctly in the original online version.

The publisher would like to apologise for any inconvenience this may have caused to the authors of this article and readers of the journal.

DOIs of original articles: [10.1016/j.fluid.2009.11.003](https://doi.org/10.1016/j.fluid.2009.11.003), [10.1016/j.fluid.2009.07.021](https://doi.org/10.1016/j.fluid.2009.07.021)

* Corresponding author. Tel.: +31 15 2782172.

E-mail address: p.colonna@tudelft.nl (P. Colonna).

Update

Fluid Phase Equilibria

Volume 288, Issue 1–2, 25 January 2010, Page 162–174

DOI: <https://doi.org/10.1016/j.fluid.2009.11.003>



Erratum to “On the computation of the fundamental derivative of gas dynamics using equations of state” [Fluid Phase Equilibr. 286 (1) (2009) 43–54]

P. Colonna^{a,*}, N.R. Nannan^a, A. Guardone^b, T.P. van der Stelt^a

^a Energy Technology Section, Process and Energy Department, Delft University of Technology, Leeghwaterstraat 44, 2628 CA Delft, The Netherlands

^b Dipartimento di Ingegneria Aerospaziale, Politecnico di Milano, Via La Masa 34, 20156 Milano, Italy

ARTICLE INFO

Article history:

Available online 1 December 2009

Keywords:

BZT fluid
Equation of state
Fundamental derivative of gas dynamics
Gas dynamics
Negative nonlinearity

ABSTRACT

The value of the fundamental derivative of gas dynamics, Γ , is a quantitative measure of the variation of the speed of sound with respect to density in isentropic transformations, such as those occurring, for example, in gas-dynamic nozzles. The accurate computation of its value, which is a constant for a perfect gas, is key to the understanding of real-gas flows occurring in a thermodynamic region where the polytropic ideal gas law does not hold. The fundamental derivative of gas dynamics is a secondary thermodynamic property and so far, no experiments have been conducted with the aim of measuring its value. Several studies document the estimation of Γ for fluids composed of complex molecules using mainly simple thermodynamic equations of state, e.g., that of Van der Waals. A review of these studies has revealed that the calculated values of Γ are affected by large uncertainties; these uncertainties are due to the functional form of the adopted equations and because of uncertainties in the available fluid property data on which these equations were fitted. In this work, the fundamental derivative of gas dynamics of molecularly simple fluids is computed with the aid of, among other models, modern reference equations of state. The accuracy of these computations has been assessed. Reference thermodynamic models however, are not available for molecularly complex fluids; some of these molecularly complex fluids are the substances of interest in studies on the so-called nonclassical gas dynamics. Therefore, results of the computation of Γ for few, molecularly simple hydrocarbons, like methane, ethane, etc., are used as a benchmark against which the performance of simpler equations of state, can be assessed. For the selected substances, the Peng–Robinson, Stryjek–Vera modified, cubic equation of state yields good results for Γ -predictions, while the modern multiparameter technical equations of state, e.g., the one in the Span–Wagner functional form, are preferable, provided that enough accurate thermodynamic data are available. Another notable result of this study, is that Γ for a fluid composed of complex molecules is less affected by the inaccuracy of C_v -information (C_v is the isochoric heat capacity), if compared to the estimation of Γ for simple molecules. Inspection of the results of the calculation of Γ in the proximity of the critical point confirms that analytical equations of state fail to predict the correct physical behavior, even if they include terms which allow for the correct estimation of thermodynamic properties.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Compressible flows occurring in the dense-vapor thermodynamic regime can exhibit qualitatively different features with respect to more conventional gaseous flows for which the thermodynamic properties are governed by the polytropic ideal gas law. The root cause of this deviation is the non-ideal dependence of the speed of sound on the density along isentropes. Both the value of the speed of sound and its isentropic variation with respect

to density depend on the complexity of the molecule and on the thermodynamic region where the flow occurs. As described, for example, in Refs. [1,2], three cases are possible. For substances of *low molecular complexity* (LMC), the speed of sound can only increase on isentropic compression and decrease on isentropic expansion, independently of the thermodynamic region where the process takes place, as far as phase change is excluded. Therefore, the qualitative features of fluid flows are always similar to the ones of a flow of an ideal gas. For substances of *high molecular complexity* (HMC) there exists a thermodynamic region in which the speed of sound decreases on isentropic compressions and increases upon isentropic expansions. This may lead, for example, to the non-monotone behavior of the Mach number and speed of sound in compressible flows through nozzles [3–6]. The third and more dramatic case occurs for fluids composed of even more

DOI of original articles: [10.1016/j.fluid.2009.07.021](https://doi.org/10.1016/j.fluid.2009.07.021), [10.1016/j.fluid.2009.11.002](https://doi.org/10.1016/j.fluid.2009.11.002)

* Corresponding author. Tel.: +31 15 2782172.

E-mail address: p.colonna@tudelft.nl (P. Colonna).

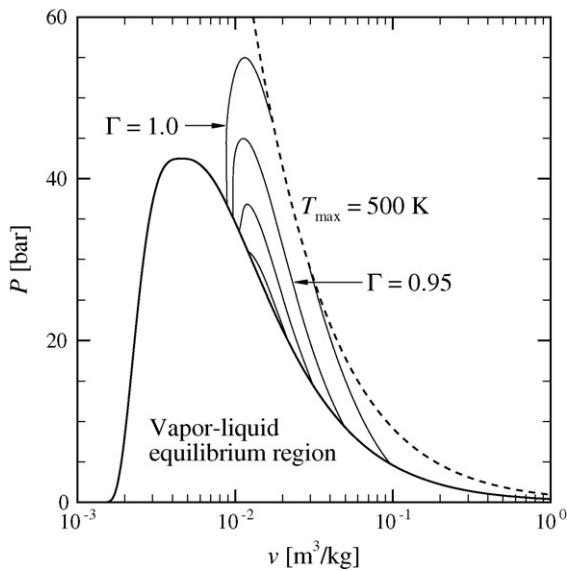


Fig. 1. The v - P thermodynamic plane of propane displaying the vapor-liquid equilibrium region, the maximum isotherm and several iso- Γ -lines, namely $\Gamma = 0.85, 0.90, 0.95, 1.0$. Computations are performed with the Buecker-Wagner reference EoS [12].

complex molecules for which nonclassical gas-dynamic effects in the dense-vapor region are predicted. These substances are called *Bethe-Zel'dovich-Thompson* (BZT) fluids [7–9] after the names of the scientists who first theoretically studied these phenomena. For these fluids, in a limited thermodynamic region at high reduced temperature and pressure near the dew-line, the reversed dependency of the speed of sound with respect to density in isentropic flows is so pronounced, that gas-dynamic behavior is reversed with respect to the gas dynamics of perfect gases; for example, rarefaction shock waves become theoretically permissible. No generally accepted experimental proof of nonclassical gas-dynamic behavior is available, as several attempts have failed to provide evidence (see, e.g., Ref. [10] for a short review). The authors are involved in a project aiming at generating and detecting a rarefaction shock wave and this study has been carried out within this framework.

The thermodynamic property which can be used to discriminate among these different (compressible) flow behaviors is the fundamental derivative of gas dynamics [1,11]

$$\Gamma \equiv 1 + \frac{\rho}{c} \left(\frac{\partial c}{\partial \rho} \right)_s = 1 + \frac{\rho}{2c^2} \left(\frac{\partial^2 P}{\partial \rho^2} \right)_s = \frac{v^3}{2c^2} \left(\frac{\partial^2 P}{\partial v^2} \right)_s. \quad (1)$$

Here, ρ , P , s , and $v \equiv \rho^{-1}$ denote respectively, the density, pressure, entropy, and specific volume, and c is the zero-frequency speed of sound defined as

$$c \equiv \sqrt{\left(\frac{\partial P}{\partial \rho} \right)_s}. \quad (2)$$

Note that for a perfect gas $\Gamma = (\gamma + 1)/2 = \text{constant} > 1$, where γ represents the ratio of the isobaric heat capacity with respect to the isochoric heat capacity, i.e., $\gamma = C_p/C_v$.

A fluid can be defined as an *LMC-fluid* if $\Gamma > 1$ throughout the entire super heated vapor thermodynamic region. An *H MC-fluid* exhibits a thermodynamic region in the vapor phase where $0 < \Gamma < 1$. Finally, BZT fluids feature a single-phase thermodynamic region at high reduced pressure and temperature close to the dew line where $\Gamma < 0$. Fig. 1 shows several iso- Γ lines in the v - P thermodynamic plane of propane. As evident from Fig. 1, propane can therefore be classified as an *HMC-fluid*. Recent studies [13,14,10] show that the minimum value of Γ for any of the

candidate BZT fluids should not be lower than -1 and this estimate is possibly non-conservative with respect to the minimum value.

The estimation of Γ and especially of thermodynamic states having $\Gamma < 0$, is most relevant in the study of nonclassical gas dynamics, as it is related to the process conditions which can determine phenomena like rarefaction shock waves [15].

The study of dense-vapor flows is pertinent to several engineering applications. Process expanders and compressors in the oil and chemical industry often operate, at least partly, in the dense-vapor region [16,17]. The nozzle of organic-Rankine-cycle turbines expands the working fluid starting from superheated states close to the critical point [18], and such turbines might benefit from non-classical gas-dynamic effects [19–21]. Conversely, compressors of refrigeration equipment feature the final phase of the compression process in the same thermodynamic region. The same holds for the compressor of supercritical heat pumps [22]. The compressor of the closed-cycle gas turbine proposed as the next-generation nuclear power plant [23–25,27–30] operates in the supercritical thermodynamic region [31]. Energy efficiency is crucial to all these applications and sophisticated fluid dynamic design by means of simulation is one of the most important tools to achieve this goal. Γ is a secondary (or derived) thermodynamic property, i.e., it can be obtained by partial differentiation from the primary properties pressure P , specific volume v , temperature T , together with the isochoric specific heat in the ideal-gas state C_v^0 , see, e.g., Ref. [32]. The direct measurement of Γ in the dense-gas region of interest is quite problematic, and more so for BZT fluids, as this would require experiments at high temperature and close to saturated conditions. The value of Γ for ideal-gas states can be inferred from experimental data for the heat capacity ratio γ . In principle Γ could be obtained indirectly from other measurable quantities. This can be clarified if Γ is written in terms of measurable variables as

$$\Gamma(T, P) = 1 + c\rho \left(\frac{\partial c}{\partial P} \right)_T + \frac{\beta cT}{C_P} \left(\frac{\partial c}{\partial T} \right)_P, \quad (3)$$

with β denoting the coefficient of volume expansion, which is defined as

$$\beta \equiv \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_P. \quad (4)$$

Each of the thermodynamic properties in Eq. (3) can be measured either directly, i.e., densities, speeds of sound and isobaric heat capacities, or indirectly, that is $(\partial c/\partial P)_T$, $(\partial c/\partial T)_P$ and β . Moreover, the functional relation expressed by Eq. (3) allows for an uncertainty to be assigned to Γ under the provision that the uncertainty in each thermodynamic property is known. Unfortunately the availability of these data, e.g., β and speed-of-sound along isobars, is insufficient, even for well-measured fluids like methane. The value of Γ is therefore usually predicted from the complete thermodynamic model of the fluid. Such a prediction is largely dependent on the accuracy of the thermodynamic model and on its functional form [13], because any uncertainty affecting primary properties amplifies the uncertainty with which secondary or derived properties are calculated.

Studies dealing with the evaluation of the fundamental derivative of gas dynamics are concerned mainly with nonclassical gas-dynamic phenomena (see Section 2). Only recently the problem of the correctness of the predicted values has been pointed out [13,10]. It became clear that the thermodynamic models used in the past to calculate Γ (see Section 2) led to an unacceptably wide scatter in the resulting values, such that the possibility of designing nonclassical experiments or processes based on these predictions is questionable [33].

The scatter in the predicted Γ -values is due to both the thermodynamic parameters on which the model is based (e.g., critical

Table 1

Previous studies on the identification of BZT fluids. All these fluids are indicated as exhibiting a region of negative nonlinearity according to the employed thermodynamic model. Note: BWR: Benedict–Webb–Rubin EoS [38], HBMS: Hirschfelder–Buehler–McGee–Sutton EoS [37], MH: Martin–Hou EoS [39], mMH: modified Martin–Hou EoS [52], PRSV: Peng–Robinson EoS [51] modified by Stryjek and Vera [47], VdW: Van der Waals EoS, RK: Redlich–Kwong EoS [43], SRK: Soave–Redlich–Kwong EoS [50], CII: Clausius II EoS [49], WS: Wong–Sandler mixing rule [59], and SW: Span–Wagner functional form for the EoS [60].

Reference	Formula	Name	Thermodynamic model
Lambrakis and Thompson [36]	C ₄ H ₁₀ C ₅ H ₁₂ C ₆ H ₁₄ C ₇ H ₁₆ C ₈ H ₁₈ C ₉ H ₂₀ C ₁₀ H ₂₂ C ₆ F ₁₄ C ₁₀ F ₂₂ C ₈ F ₁₆ C ₇ F ₁₄ C ₆ F ₆ C ₁₀ F ₁₈ C ₁₁ F ₂₀ C ₁₅ H ₁₆ C ₈ F ₁₆ O	n-Butane n-pentane n-Hexane n-Heptane n-Octane n-Nonane n-Decane Perfluoro-n-hexane Perfluoro-n-decane 1,3-Perfluorodimethylcyclohexane Perfluoromethylcyclohexane Perfluorobenzene Perfluorodecalin Perfluoromethyldecalin 4-Isopropylbiphenyl Perfluoro-2-butyltetrahydrofuran	Tabulated data ^a ; virial Tabulated data ^a ; virial Tabulated data ^a ; virial HBMS HBMS; BWR HBMS; BWR HBMS; BWR; MH Tabulated data ^b ; HBMS HBMS; MH Tabulated data ^b ; HBMS; MH Tabulated data ^b ; HBMS Tabulated data ^b ; HBMS Tabulated data ^b ; HBMS; MH Tabulated data ^b ; HBMS; MH Tabulated data ^c ; HBMS; MH Tabulated data ^d
Thompson and Lambrakis [9]	C ₈ F ₁₇ HO ₂ C ₁₁ F ₂₃ HO ₃ C ₁₄ F ₂₉ HO ₄ C ₁₇ F ₃₅ HO ₅	Fluorinated ether E-2 Fluorinated ether E-3 Fluorinated ether E-4 Fluorinated ether E-5	HBMS; MH HBMS; MH HBMS; MH HBMS; MH
Cramer [45]	C ₁₂ F ₂₇ N C ₁₅ F ₃₃ N C ₁₈ F ₃₉ N C ₁₃ F ₂₂ C ₁₄ F ₂₄ C ₁₆ F ₂₆ C ₁₇ F ₃₀	FC-43, pf-tributylamine FC-70, pf-tripentylamine FC-71, pf-trihexylamine PP-10, pf-perhydrofluorene PP-11, pf-perhydrophenanthrene PP-24, pf-fluoranthenene PP-25, pf-benzyltetralin	MH MH MH MH MH MH MH
Colonna and Silva [32]	C ₁₂ H ₃₆ O ₄ Si ₅ C ₁₄ H ₄₂ O ₅ Si ₆ C ₈ H ₂₄ O ₄ Si ₄ C ₁₀ H ₃₀ O ₅ Si ₅ C ₁₂ H ₃₆ O ₆ Si ₆ Equimolar mixtures containing cyclic siloxanes of D _{i>4}	MD ₃ M, dodecamethylpentasiloxane MD ₄ M, tetradecamethylhexasiloxane D ₄ , octamethylcyclotetrasiloxane D ₅ , decamethylcyclopentasiloxane D ₆ , dodecamethylcyclohexasiloxane	PRSV PRSV PRSV PRSV PRSV PRSV + WS
Guardone and Argrow [14]	C ₁₂ F ₂₇ N C ₁₅ F ₃₃ N C ₁₈ F ₃₉ N C ₆ F ₁₄ C ₈ F ₁₆ O C ₁₀ F ₁₈ C ₁₁ F ₂₀ C ₁₃ F ₂₂ C ₁₄ F ₂₄ C ₁₆ F ₂₆ C ₁₇ F ₃₀ C ₁₁ F ₂₃ HO ₃ C ₁₄ F ₂₉ HO ₄ C ₁₇ F ₃₅ HO ₅	FC-43, pf-tributylamine FC-70, pf-tripentylamine FC-71, pf-trihexylamine FC-72, perfluorohexane FC-75 PP-5, perfluorodecalin PP-9, perfluoromethyldecalin PP-10, pf-perhydrofluorene PP-11, pf-perhydrophenanthrene PP-24, pf-fluoranthenene PP-25, pf-benzyltetralin Fluorinated ether E-3 Fluorinated ether E-4 Fluorinated ether E-5	VdW; RK; CII; PR; SRK; mMH VdW; RK; CII; PR; SRK; mMH VdW; RK; CII; PR; SRK; mMH VdW; RK VdW; RK; CII VdW; RK; CII; PR; SRK; mMH VdW; RK; CII; PR; SRK; mMH
Colonna et al. [10]	C ₁₂ H ₃₆ O ₄ Si ₅ C ₁₄ H ₄₂ O ₅ Si ₆ C ₁₂ H ₃₆ O ₆ Si ₆	MD ₃ M, Dodecamethylpentasiloxane MD ₄ M, Tetradecamethylhexasiloxane D ₆ , Dodecamethylcyclohexasiloxane	SW SW SW

^a L. N. Canjar and F. S. Manning. *Thermodynamic Properties and Reduced Correlations for Gases*. Gulf Publishing Company, Houston, TX, 1967.

^b Imperial Smelting Corporation, Ltd. *Tables of Thermodynamic Properties for Flutec*. Bristol, England.

^c Monsanto Chemical Company. *Computer Tables of Thermodynamic Properties for CP 9*. St. Louis, MO, 1965.

^d R. M. Yarrington and W. B. Kay. Thermodynamic properties of perfluoro-2-butyltetrahydrofuran. *J. Chem. Eng. Data*, 5(1): 24–29, 1960.

values, acentric factor, etc.), and to the functional form of the equation of state. Recently, highly accurate thermodynamic models of fluids based on the so-called reference equations of state became available [34,35]. An equation of state can be defined as a reference equation if it can represent the numerous and heterogeneous measurements on which it is fitted (like, P–v–T data, speed of sound, enthalpy of vaporization, etc., which are selected among the most accurate data available), with the same level of uncertainty affecting the measurements themselves. Such equations are currently available only for few fluids made of rather simple

molecules for which large data sets are available, e.g., methane and water.

This work stemmed from the need of evaluating Γ with an uncertainty which is suitable for the design of nonclassical gas-dynamic experiments, and from the observation that reference equation of state of simple substances can be used to test the possibility of accurately calculating the fundamental derivative of gas dynamics. In general, the correct estimation of Γ is also useful in the investigation of the features of flows occurring in the classical dense-gas thermodynamic region (see Refs. [78,33]). Reference

thermodynamic models can also be used as a benchmark to assess the performance of simpler thermodynamic models with regard to Γ -predictions.

This paper is structured as follows. After a review of previous work, refer to Section 2, Section 3.1 treats the calculation of Γ for several simple hydrocarbons by means of a reference and one or two multiparameter equations of state for each fluid, in order to assess the scatter in Γ -values of such calculations. Reference equations of state are used as a benchmark to evaluate the performance of simpler equations of state (see Section 3.2); such simple equations of state are currently the only option that is available for predicting Γ for fluids composed of more complex molecules (Section 4). Finally, Section 5 summarizes the findings and indicates the direction for future work in this area.

2. Critical review of previous studies

Thompson and Lambrakis were the first scientist to address the computation of the fundamental derivative of gas dynamics, specifically with the aim of identifying Bethe–Zel'dovich–Thompson (BZT) fluids [9,36]. In their work of 1972, they calculated the value of Γ along the critical isotherm for 16 organic fluids using two different methods. The first method consisted of interpolating published thermodynamic data in order to draw isentropes on a $P-v$ diagram. From Eq. (1), if the obtained isentrope exhibits downward concavity, this implies a region of negative Γ . This method is clearly prone to large uncertainties, as the computation of a second-order derivative from primary thermodynamic data, themselves effected by considerable uncertainties, leads to values of Γ which heavily depend upon the data selected for the interpolation and its functional form. As a consequence, this method has been abandoned. The second method involved the direct computation of Γ from a complete thermodynamic model of the fluid. In this case the authors employed the virial (up to the fourth virial coefficient), the Hirschfelder–Buehler–McGee–Sutton (HBMS) [37], the Benedict–Webb–Rubin (BWR) [38], and the Martin–Hou (MH) [39] multiparameter EoS's. However, many relevant properties which are required for the computation of the substance-specific parameters (e.g., the critical pressure P_c , the critical temperature T_c , the critical specific volume v_c , the acentric factor ω , and the normal boiling point T_B), together with the ideal-gas heat capacities, had to be determined using estimation techniques, because accurate and reliable experimental information was not available at that time. Depending on the estimation method and the substance itself, uncertainties in estimated critical properties can be as high as 10% [40,41] and up to 25% for heat capacities [40,41]. Moreover, the estimated critical properties can be inconsistent. No sensitivity analysis was performed, but it can be inferred that the calculated values of Γ , as well as the correct identification of BZT fluids, are effected by large uncertainties [13]. Table 1 reports the fluids selected in these studies and the method employed to determine Γ . The results presented by Lambrakis and Thompson indicated that all 16 fluids exhibit a region of negative nonlinearity, i.e., a region of $\Gamma < 0$. Among these 16 fluids, Lambrakis and Thompson considered n-alkanes from n-butane to n-decane. As an indication of the accuracy of such estimations, it can be noted that computations performed with the most recent and accurate thermodynamic models for hydrocarbons (Section 3) show that the minimum value of the fundamental derivative of gas dynamics (Γ_{\min}^V), which is along the dew-line, is 0.68 for n-butane (the thermodynamic model is that of Buecker and Wagner [12]), whereas for n-decane, employing the EoS of Lemmon and Span [42], $\Gamma_{\min}^V = 0.29$. Consequently, it can be asserted, based on the law of corresponding states that (n-)alkanes with a molecular complexity lower than or equal to that of n-decane, are not BZT fluids.

In the following study on BZT fluids [9], Thompson and Lambrakis analyzed the influence of the functional form of the EoS on the estimation of Γ in more detail, although the reliability of the input thermodynamic data was still left untreated. Using the Van der Waals, Redlich–Kwong [43], Clausius, and Abbott cubic EoS's [44], and the HBMS, the MH, and the BWR multiparameter EoS's, they reported the minimum value of Γ along the critical isotherm for the same fluids as in Ref. [36] and additionally for 5 fluorinated ethers (also included in Table 1). They noted that the minimum value of Γ in the vapor phase and far from the critical-point region lies on the dew line, nonetheless they calculated Γ only along the critical isotherm, most likely for simplicity, as evaluating phase-equilibrium is then not required. From these results, they concluded that values reported in Ref. [36] for Γ_{\min} along the critical isotherm (the reported values were obtained from the HBMS EoS) were too negative and that, if compared to the results of the cubic EoS's and the other multiparameter EoS's, the predictions of Γ from the Martin–Hou EoS were preferable. Thompson and Lambrakis also indicated that because the HBMS EoS has incorrect functional form if the critical compressibility Z_c is less than 0.302, it should not be used for calculating Γ (note that all potential BZT fluids have a $Z_c < 0.302$).

The list of candidate BZT fluids was extended in subsequent studies. Cramer [45] adopted the MH EoS complemented by an ideal-gas isochoric heat capacity correlation expressed as a power-law of the temperature, and valid only in the temperature range of interest for the computation of Γ . All the necessary fluid parameters were estimated, therefore the accuracy of the model is possibly low. Incidentally, it is worthwhile noting that the MH EoS has a quite limited validity range if the model data are all computed from few fluid parameters, namely, a single vapor–pressure data point and critical point data [46]. Ref. [45] reports negative values for Γ along the saturated vapor line for perfluorocarbons of the FC and PP families (see Table 1). However, the properties which were necessary for the computation of the substance-specific parameters of the MH EoS, e.g., critical and saturation properties, were provided by the fluid manufacturers and were not published in the open literature. It is therefore neither known if the fluid data were measured or estimated, nor can their accuracy be assessed; it can be inferred from common practice that the manufacturers estimated the data with ad hoc techniques, as measuring these data for fluids featuring high critical temperature is very challenging, even nowadays. Estimation techniques for these data can be effected by large uncertainties, as previously indicated. In the concluding remarks, the author suggests that the predictions of Γ from the Martin–Hou EoS are too conservative with respect to negative values of Γ . Anticipating the results of Section 3, it can be shown that this hypothesis is contrary to what has been observed herein.

In 2003, Colonna and Silva [32] considered cyclic and linear siloxanes as candidate BZT fluids and determined the value of Γ along the critical isotherm using the Peng–Robinson cubic equation of state, modified by Stryjek and Vera in order to obtain accurate predictions of vapor pressures (PRSV) [47]. This thermodynamic model is based on measured vapor pressures, critical values extrapolated from saturation-pressure measurements and on ideal-gas isobaric heat capacities obtained with a group contribution method [48], the latter being possibly the major source of uncertainty. The authors were also the first to test substance-specific multiparameter equations of state based on large experimental data sets, and they reported results of predictions of Γ in the vapor phase for water, nitrogen and n-octane. As expected, none of these fluids can be classified as a BZT substance, but comparisons of values of Γ along the critical isotherms calculated with various thermodynamic models, clearly show to which extent the functional form of the equation

of state influences the results. Based on their preliminary results, Colonna and Silva anticipated that dodecamethylpentasiloxane (MD_3M , $C_{12}H_{36}O_4Si_5$) and linear siloxanes of greater complexity, and octamethylcyclotetrasiloxane (D_4 , $C_8H_{24}O_4Si_4$) and cyclic siloxanes of greater complexity might have a region of negative nonlinearity. In this work they also examined for the first time values of Γ for mixtures calculated by means of the modern mixing rules of Wong and Sandler in combination with the PRSV EoS. The exemplary results showed that equimolar mixtures of cyclic siloxanes might have a region of negative nonlinearity.

More recently, a study on the identification of BZT fluids was carried on by Guardone and Argrow [14]. They analyzed the influence of substance-specific parameters, namely, the acentric factor, critical compressibility, fluid complexity, etc., on the calculation of Γ using six different thermodynamic EoS's. The selected EoS's were: Van der Waals, Redlich–Kwong [43], Clausius II [49], Soave–Redlich–Kwong [50], Peng–Robinson [51], and Martin–Hou according to Ref. [52], herein denoted by mMH EoS. As for the ideal-gas heat capacity correlation [48], they chose the same functional form as the one adopted by Cramer [45]. In addition to the perfluorocarbons investigated by Cramer in Ref. [45], they included in their analysis PP-5, PP-9, FC-72, and FC-75. Also in this study, most of the relevant fluid parameters were obtained from manufacturers or from the previously indicated Refs. [45,36]. The reported results indicated that PP-5 and PP-9 feature a region where $\Gamma < 0$; FC-72 and FC-75 display a BZT region only if rather simple EoS's are used, namely, the Van der Waals, Redlich–Kwong, and Clausius II EoS's. These models are known to be quantitatively inaccurate in the dense-vapor region.

Finally, the study by Colonna et al. [10] shows an investigation of siloxanes as candidate BZT fluids. In this work, the authors employed state of the art multiparameter equations of state fitted on numerous data, either experimental or carefully estimated [53,54]. As stated by all other authors, the ideal-gas heat capacity is one of the major source of uncertainty in the estimation of the fundamental derivative of gas dynamics. The thermodynamic model adopted in this study is based on the most accurate data for the ideal-gas isobaric heat capacity of siloxanes [55], obtained from ad hoc measurements and molecular simulations. The results show that linear and cyclic dimethylsiloxanes, namely, dodecamethylpentasiloxane (MD_3M , $C_{12}H_{36}O_4Si_5$) and dodecamethylcyclohexasiloxane (D_6 , $C_{12}H_{36}O_6Si_6$), respectively (and fluids of the same family but of greater complexity) display a vapor region where Γ becomes negative. A sensitivity analysis to the estimation of the ideal-gas heat capacity is also included, while the authors point out that other sources of uncertainty still remain due to lack of information.

One last important remark is that, apart from Refs. [32,10], none of the previous studies on fluids that might exhibit a region of negative nonlinearity addressed the problem of the thermal stability of the fluid. This issue was first highlighted by Thompson and Lambrakis [9]. The thermodynamic region where Γ might be negative for some fluids composed of complex molecules lies in a range of temperatures for which organic molecules tend to decompose, if, for instance, they are in contact with metals (see, e.g., Ref. [56]). For most of the fluids listed in Table 1, no information on their thermal stability is available, and therefore the Γ -negative region might be located at temperatures for which the molecules decompose, if the fluid is contained in metal or if it is not completely degassed and dehydrated. Some preliminary experimental results indicate that siloxanes in contact with stainless steel are indeed thermally stable at the temperatures characterizing states with negative Γ , if the fluid is sufficiently purified [57,58].

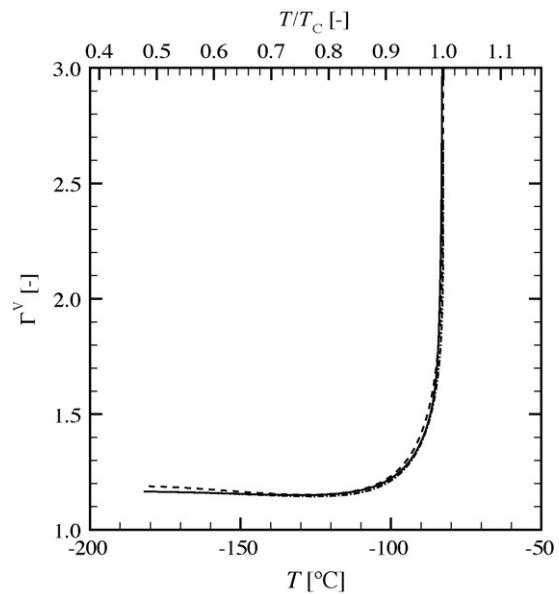


Fig. 2. The fundamental derivative of gas dynamics along the saturated vapor line of methane (CH_4) as a function of T and T/T_c , where T_c is the critical temperature. Results of computations performed with the Wagner–Setzmann reference equation of state [61] (solid line) are in excellent agreement with Γ^V computed with the Span–Wagner EoS [60] (dash-dotted line) and with the Friend–Ingham–Ely EoS [63] (dashed line), from the triple point ($-182.46^\circ C$) up to almost the critical point ($-82.59^\circ C$).

3. The fundamental derivative of gas dynamics for selected alkanes

3.1. Reference equations of state

As the prediction of Γ by means of equations of state currently appears to be the only viable option, reference equations of state, which are the most accurate and complete thermodynamic models,

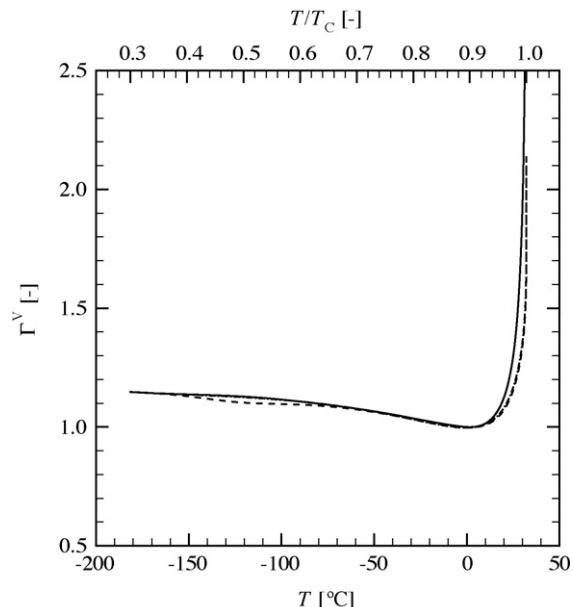


Fig. 3. The fundamental derivative of gas dynamics along the saturated vapor line of ethane (C_2H_6) as a function of T and T/T_c , where T_c is the critical temperature. Values calculated with the Buecker–Wagner reference EoS [64] (solid line) are almost coincident with those computed with the Span–Wagner EoS [60] (dash-dotted line) and with the Friend–Ingham–Ely EoS [65] (dashed line), from the triple point ($-182.78^\circ C$) up to almost the critical point ($32.17^\circ C$).

Table 2

The minimum value of fundamental derivative of gas dynamics along the dew-line and the corresponding reduced temperature, as predicted by reference equations of state and multiparameter EoS's for several alkanes. Note: SW: Span–Wagner functional form, MW: Miyamoto–Watanabe functional form, FIE: Friend–Ingham–Ely functional form.

	Reference EoS		SW EoS		MW/FIE EoS	
	T_r [-]	Γ_{\min}^V [-]	T_r [-]	Γ_{\min}^V [-]	T_r [-]	Γ_{\min}^V [-]
CH ₄	0.75	1.15	0.77	1.14	0.76	1.15
C ₂ H ₆	0.90	1.00	0.89	1.00	0.90	1.00
C ₃ H ₈	0.93	0.82	0.93	0.83	0.94	0.83
C ₄ H ₁₀	0.95	0.68	0.95	0.70	0.95	0.70
HC-(CH ₃) ₃	0.95	0.68	0.95	0.69	0.96	0.68

are used to calculate the fundamental derivative of gas dynamics and to assess the best accuracy that can be obtained with respect to the evaluation of Γ . Reference equations of state exist only for few simple molecules, like water, argon, nitrogen and simple hydrocarbons [34]. Methane, ethane, propane, n-butane, and iso-butane are the fluids selected for this study. To provide an indication of the accuracy of these thermodynamic models, the reference equation of state for methane [61] for example, is able to predict densities with an uncertainty of 0.03% for pressures below 12 MPa. For the speed of sound in the vapor phase the uncertainty is 0.03%. Heat capacities may be generally calculated within an uncertainty of 1% (higher uncertainties up to 5% can be expected in the close-to-critical region) [61,62].

The functional form of the reference equations are expressed in terms of the reduced Helmholtz free energy, $\psi \equiv \Psi(T, \rho)/RT$, as a function of the reduced density, $\delta \equiv \rho/\rho_c$, and the inverse of the reduced temperature, $\tau \equiv T_c/T = 1/T_r$. The Helmholtz free energy can be written as a part describing the ideal-gas contribu-

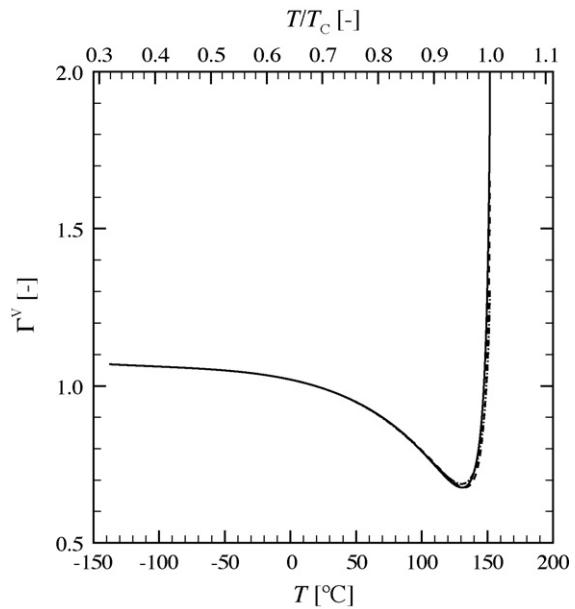


Fig. 5. The fundamental derivative of gas dynamics along the saturated vapor line of n-butane (C_4H_{10}) as a function of T and T/T_c , where T_c is the critical temperature. Values calculated with the Buecker–Wagner reference EoS [12] (solid line) are almost coincident with those computed with the Span–Wagner EoS [60] (dash-dotted line), and with the Miyamoto–Watanabe EoS (dashed line) [67], from the triple point ($-138.26^\circ C$) up to almost the critical point ($151.98^\circ C$).

tion, namely

$$\begin{aligned} \psi^{IG}(\tau, \delta) = & \frac{h_0^{IG}\tau}{RT_c} - \frac{s_0^{IG}}{R} - 1 + \ln\left(\frac{\tau_0\delta}{\delta_0\tau}\right) - \frac{\tau}{R} \int_{\tau_0}^{\tau} \frac{C_p^{IG}}{\tau^2} d\tau \\ & + \frac{1}{R} \int_{\tau_0}^{\tau} \frac{C_p^{IG}}{\tau} d\tau, \end{aligned} \quad (5)$$

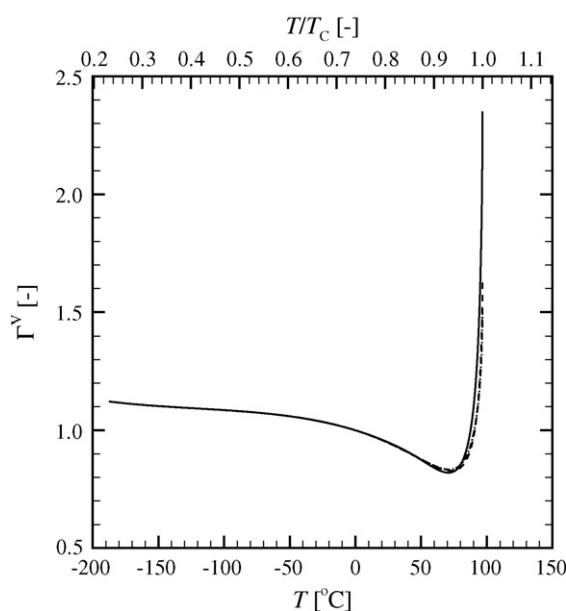


Fig. 4. The fundamental derivative of gas dynamics along the saturated vapor line of propane (C_3H_8) as a function of T and T/T_c , where T_c is the critical temperature. Results of computations performed with the Buecker–Wagner reference EoS [12] (solid line) are in excellent agreement with Γ^V computed with the Span–Wagner EoS [60] (dash-dotted line) and with the Miyamoto–Watanabe EoS (dashed line) [66], from the triple point ($-187.67^\circ C$) up to almost the critical point ($96.68^\circ C$).

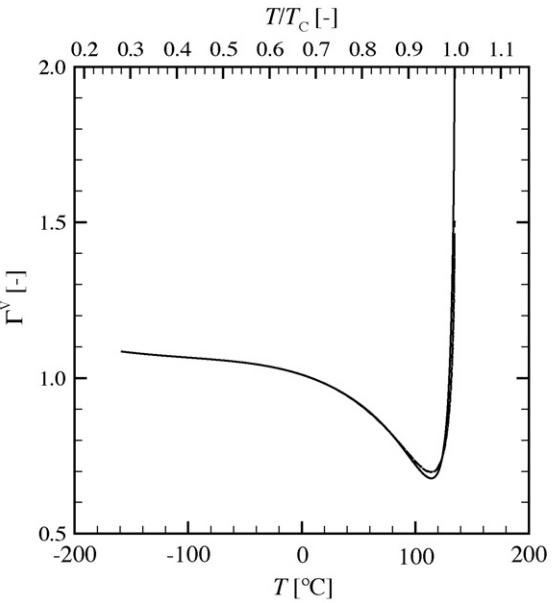


Fig. 6. The fundamental derivative of gas dynamics along the saturated vapor line of isobutane ($HC-(CH_3)_3$) as a function of T and T/T_c , where T_c is the critical temperature. Results of computations performed with the Buecker–Wagner reference EoS [12] (solid line) are in excellent agreement with Γ^V computed with the Span–Wagner EoS [60] (dash-dotted line) and with the Miyamoto–Watanabe EoS (dashed line) [68], from the triple point ($-159.42^\circ C$) up to almost the critical point ($134.66^\circ C$).

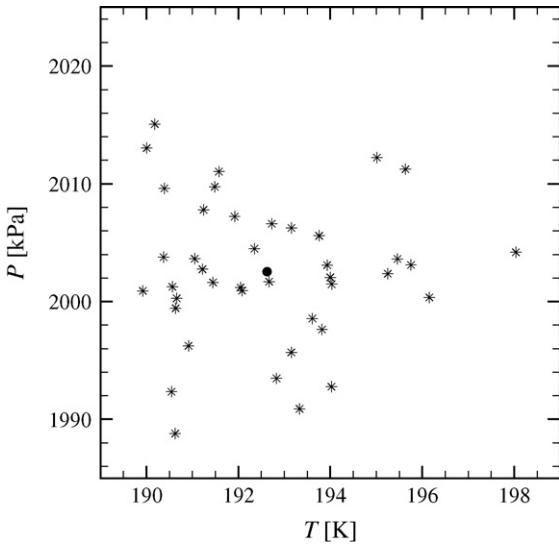


Fig. 7. An example of one collection of (P, T)-points of methane for which ρ -, c - and C_p -data are simulated. •: represents the center-point of the simulated data.

which only depends on the ideal-gas (isobaric) heat capacity, C_p^{IG} , of the substance, and a residual part which takes the intermolecular forces into account. In Eq. (5), $\delta_0 = \rho_0/\rho_c$ and $\tau_0 = T_c/T_0$ represent the reduced density and the inverse of the reduced temperature, respectively at a pre-defined or prescribed reference state (T_0, ρ_0). Parameters h_0^{IG} and s_0^{IG} denote the ideal-gas enthalpy and entropy, respectively at (T_0, P_0) , and are chosen according to common convention in industry or recommendations of, e.g., the International Institute of Refrigeration (IIR) or the International Union of Pure and Applied Chemistry (IUPAC) [42]. For hydrocarbons for example, h_0^{IG} and s_0^{IG} are chosen such that both the enthalpy h and entropy s for the saturated liquid-phase at the normal boiling point are zero.

The residual part can again be separated in two sets of terms, namely, a set of regular terms and a set of critical-point terms which is intended to describe the thermodynamics of the region in the close proximity of the critical point. For the alkanes selected for this study, the residual reduced Helmholtz free energy has the functional form

$$\psi^R = \underbrace{\sum_{i=1}^j n_i \delta^{d_i} \tau^{t_i} + \sum_{i=j+1}^k n_i \delta^{d_i} \tau^{t_i} \exp(-\delta c_i)}_{\text{Regular terms}} + \underbrace{\sum_{i=k+1}^m n_i \delta^{d_i} \tau^{t_i} \exp(-\alpha_i(\delta - \Delta_i)^2 - \beta_i(\tau - \gamma_i)^2)}_{\text{Critical-point terms}}. \quad (6)$$

Here, n_i are substance specific parameters and are determined by fitting the functional form of the EoS to weighted experimental or estimated data. Parameters $d_i, t_i, c_i, \alpha_i, \beta_i, \gamma_i$ and Δ_i as well as the total number of terms, namely, j, k and m , are specific to an EoS. These parameters can therefore be the same for various fluids which are modeled with the same EoS, like, for example, in the case of the reference EoS for propane, n-butane, and isobutane [12].

To assess the significance of the functional form with respect to the prediction of Γ , values calculated with the reference equations of state are compared with one or two highly-accurate multiparameter EoS's, depending on the availability, for each one of the selected fluids. These additional EoS's are the EoS formulated by Miyamoto and Watanabe, the EoS by Span and Wagner, and the

EoS by Friend, Ingham and Ely. They are also expressed in terms of the Helmholtz free energy. The functional form of the residual reduced Helmholtz free energy for these thermodynamic models is

$$\psi^R = \sum_{i=1}^j n_i \delta^{d_i} \tau^{t_i} + \sum_{i=j+1}^k n_i \delta^{d_i} \tau^{t_i} \exp(-\delta c_i), \quad (7)$$

where for the functional form proposed by Span and Wagner, $j = 6$ and $k = 12$, for the functional form proposed by Miyamoto and Watanabe, $j = 8$ and $k = 19$, and for the functional form used by Friend et al., $j = 13$ and $k = 32$. The interested reader is referred to the respective papers for the value of parameters d_i, t_i and c_i . Contrary to the reference EoS's where the entire functional form can be optimized for a specific fluid, the functional forms of the Span–Wagner (SW), Miyamoto–Watanabe (MW), and Friend et al. EoS's are fixed and the substance-specific parameters n_i are determined by fitting the functional form to weighted experimental or estimated data. Consequently, the latter EoS's are applicable to an entire family of fluids, e.g., non-polar fluids, although this is only rigorously tested for the Span–Wagner functional form.

The procedure for obtaining Γ as an algebraic function of the pressure P , the temperature T , the specific volume v and the isochoric specific heat C_v from a thermodynamic model formulated in terms of the reduced Helmholtz free energy can be found in the Appendix of Ref. [10].

Fig. 2 shows the results of calculations of the fundamental derivative of gas dynamics along the dew-line (Γ^V) for methane as predicted by the reference equation of state [61], by the Span–Wagner EoS [60], and by the Friend–Ingham–Ely EoS [63]. Values are calculated from the triple point (-182.46°C) up to the critical point (-82.59°C). It can be noted that the Γ^V -lines superimpose to an excellent degree. The minute difference between the value of Γ^V calculated with the Friend–Ingham–Ely EoS and the values calculated with the other two EoS's at low temperature is believed to be due to the difference in the estimation of the ideal gas specific heat [62], and the correlations employed by the two more recent EoS's are to be preferred.

Figs. 3–6 display similar results for propane, ethane, n-butane and iso-butane. The reference equation of state and the other multiparameter thermodynamic models predict almost the same Γ^V , from the triple point up to temperatures very close to the critical point. In the close vicinity of the critical point where the variation of Γ^V is very large, the difference between the calculated Γ^V 's tends to become comparatively larger. A quantitative indication of the difference in the calculated Γ^V is provided in Table 2, which reports the minimum value of the fundamental derivative of gas dynamics and the corresponding reduced temperature for the selected alkanes, as calculated by the reference equation of state and the two other thermodynamic models.

The first important observation is that the functional form has very limited influence on the computation of Γ in the vapor phase, if highly accurate thermodynamic models are employed. Highly accurate thermodynamic models predict, for a given thermodynamic state, Γ -values that differ of at maximum few hundredths, except in the close proximity of the critical point.

If reference equations of state were available for fluids made of molecules that are complex enough for Γ to be negative, it can be expected that the predictions of Γ made with these models would be accurate enough (because the scatter in the Γ -values is at maximum few hundredths) for the design and interpretation of nonclassical gas-dynamic experiments, see, e.g., Refs. [69,21,15,33], and processes, see, e.g., Refs. [19,70,20,21]. In Refs. [33,26] for example, it is shown that an uncertainty in the evaluation of Γ

due to the EoS and due to that of the isobaric heat capacity correlation would still allow to reach conclusive evidence with respect to the existence of a rarefaction shock wave, given the accuracy of the adopted measuring and control instruments. This however intrinsically implies that in order to develop such reference equations of state, numerous accurate heterogeneous thermodynamic property data must be available, which is currently not the case.

To assess the uncertainty in the values of Γ in the vapor phase, if calculated with reference equations of state, it can be observed that predictions of Γ deviate from the true values because of two aspects, namely, (1) the uncertainty in the experimental data on which the parameters of the functional form are fitted (formulated differently, this implies that the substance-specific parameters of the EoS have an uncertainty), and (2) the bias introduced by the functional form. The influence of the functional form of the EoS on predictions of Γ , i.e., the estimation of the bias error, can be analyzed by applying the procedure illustrated in the following, valid only under the assumption that: (1) the reference EoS is truly capable of predicting thermal and caloric properties within their experimental uncertainty (this is a necessary assumption only if

the reference EoS is used to simulate experimental data; if sufficient experimental data are available, this assumption can be abandoned), (2) that the single-phase thermodynamic surface in the P - T -plane is smooth, and (3) the analyzed thermodynamic state is outside the so-called critical region [71].

First of all, the reference EoS is used to simulate experimental data for densities, speeds of sound, and isobaric heat capacities. These simulated experimental data, like for example the speed of sound, are computed from the reference EoS at a given pressure P and temperature T , and then randomly perturbed using a uniform distribution based on the maximum expected deviation that the EoS exhibits with respect to experimental data (for the Wagner–Setzmann reference EoS for methane for example, speeds of sound, densities and isobaric heat capacities display an average deviation with respect to experimental data of 0.03%, 0.03%, and 1% respectively). Fig. 7 shows just one collection of data points in terms of T and P (these are the *'s) for which ρ -, c - and C_p -values are simulated and randomly perturbed. In total 40 *'s for each • are used per collection. The simulated-and-perturbed data are then fitted to the Taylor series expansion around (P^*, T^*) using the method of least-squares. No weights are assigned to the data. The Taylor series

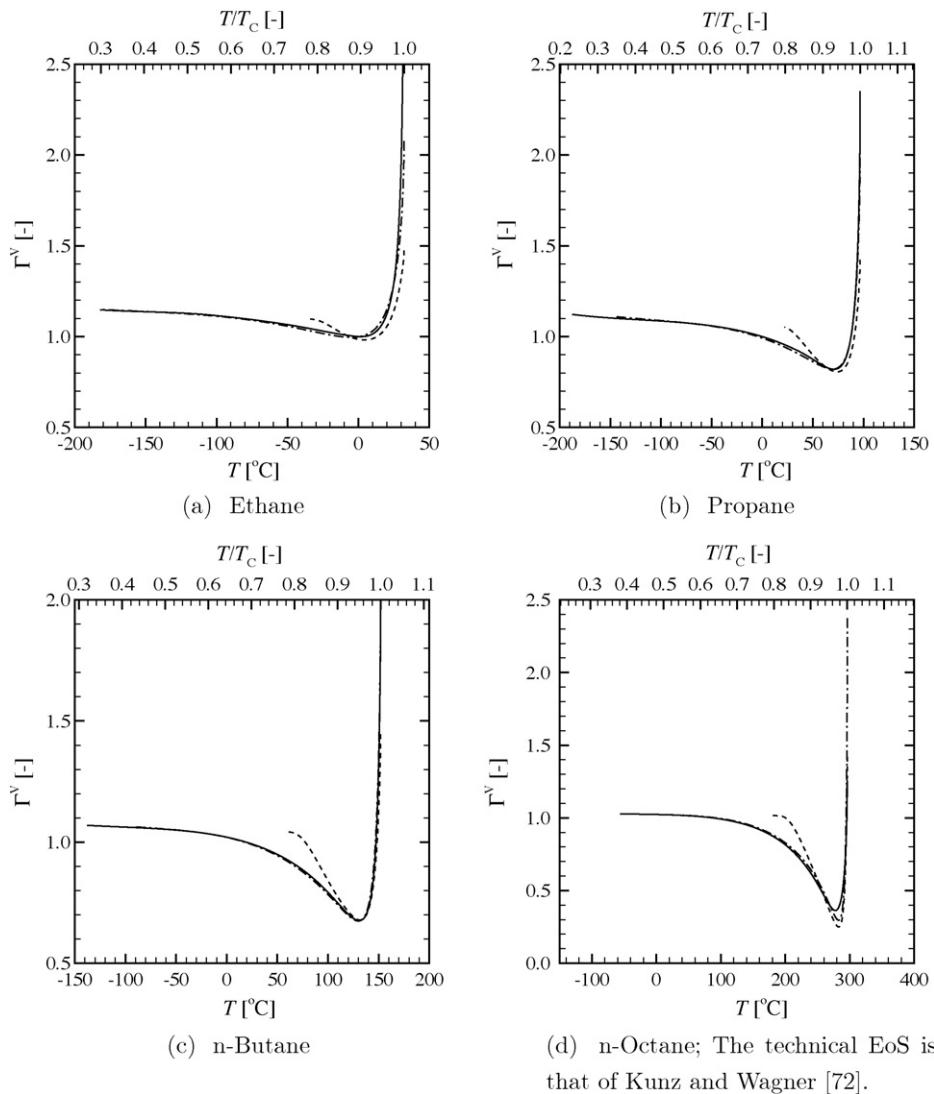


Fig. 8. The fundamental derivative of gas dynamics along the dew-line of selected n-alkanes. Continuous lines represent computations with the reference EoS (see Section 3.1), dashed lines represent computations with the MH EoS, and the dash-dotted lines represent computations with the PRSV EoS. (a) Ethane, (b) propane (c) n-butane, (d) n-octane. The technical EoS is that of Kunz and Wagner [72].

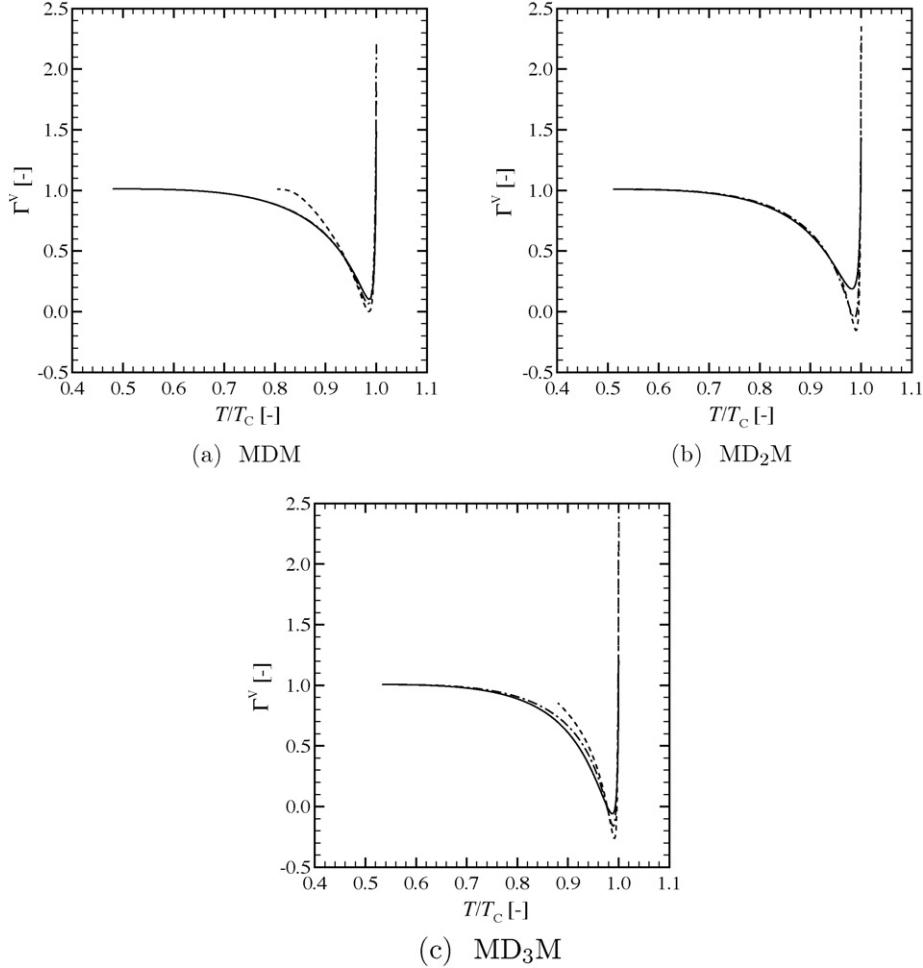


Fig. 9. The fundamental derivative of gas dynamics along the dew-line of selected linear dimethylsiloxanes. The solid line represents computations with the multiparameter EoS using the SW functional form [54], the dashed line represents computations with the MH EoS, and the dash-dotted line represents computations with the PRSV EoS. (a) MDM, (b) MD₂M, (c) MD₃M.

expansion reads

$$\begin{aligned} \rho(T^* + \Delta T, P^* + \Delta P) &= \rho^*(T^*, P^*) + \left(\frac{\partial \rho}{\partial P}\right)_{T^*, P^*} \Delta P + \left(\frac{\partial \rho}{\partial T}\right)_{T^*, P^*} \Delta T \\ &\quad + \frac{1}{2} \left[\left(\frac{\partial^2 \rho}{\partial P^2}\right)_{T^*, P^*} \Delta P^2 + 2 \left(\frac{\partial^2 \rho}{\partial P \partial T}\right)_{T^*, P^*} \Delta P \Delta T + \left(\frac{\partial^2 \rho}{\partial T^2}\right)_{T^*, P^*} \Delta T^2 \right] + \dots \end{aligned} \quad (8)$$

$$\begin{aligned} C_P(T^* + \Delta T, P^* + \Delta P) &= C_P^*(T^*, P^*) + \left(\frac{\partial C_P}{\partial P}\right)_{T^*, P^*} \Delta P + \left(\frac{\partial C_P}{\partial T}\right)_{T^*, P^*} \Delta T \\ &\quad + \frac{1}{2} \left[\left(\frac{\partial^2 C_P}{\partial P^2}\right)_{T^*, P^*} \Delta P^2 + 2 \left(\frac{\partial^2 C_P}{\partial P \partial T}\right)_{T^*, P^*} \Delta P \Delta T + \left(\frac{\partial^2 C_P}{\partial T^2}\right)_{T^*, P^*} \Delta T^2 \right] + \dots \end{aligned} \quad (9)$$

$$\begin{aligned} c(T^* + \Delta T, P^* + \Delta P) &= c^*(T^*, P^*) + \left(\frac{\partial c}{\partial P}\right)_{T^*, P^*} \Delta P + \left(\frac{\partial c}{\partial T}\right)_{T^*, P^*} \Delta T \\ &\quad + \frac{1}{2} \left[\left(\frac{\partial^2 c}{\partial P^2}\right)_{T^*, P^*} \Delta P^2 + 2 \left(\frac{\partial^2 c}{\partial P \partial T}\right)_{T^*, P^*} \Delta P \Delta T + \left(\frac{\partial^2 c}{\partial T^2}\right)_{T^*, P^*} \Delta T^2 \right] + \dots \end{aligned} \quad (10)$$

and the thermodynamic properties necessary for Eq. (3) and therefore Γ , are determined. It was decided to extend the Taylor series expansion for C_P and c to an order of smallness which was greater than that required for determining the thermodynamic properties necessary for Eq. (3), however, it was checked and confirmed that

in principle, the higher-order terms in Eqs. (9) and (10) can be left out. This method allows for predicting Γ without a prescribed functional form for an EoS. Moreover, the difference between

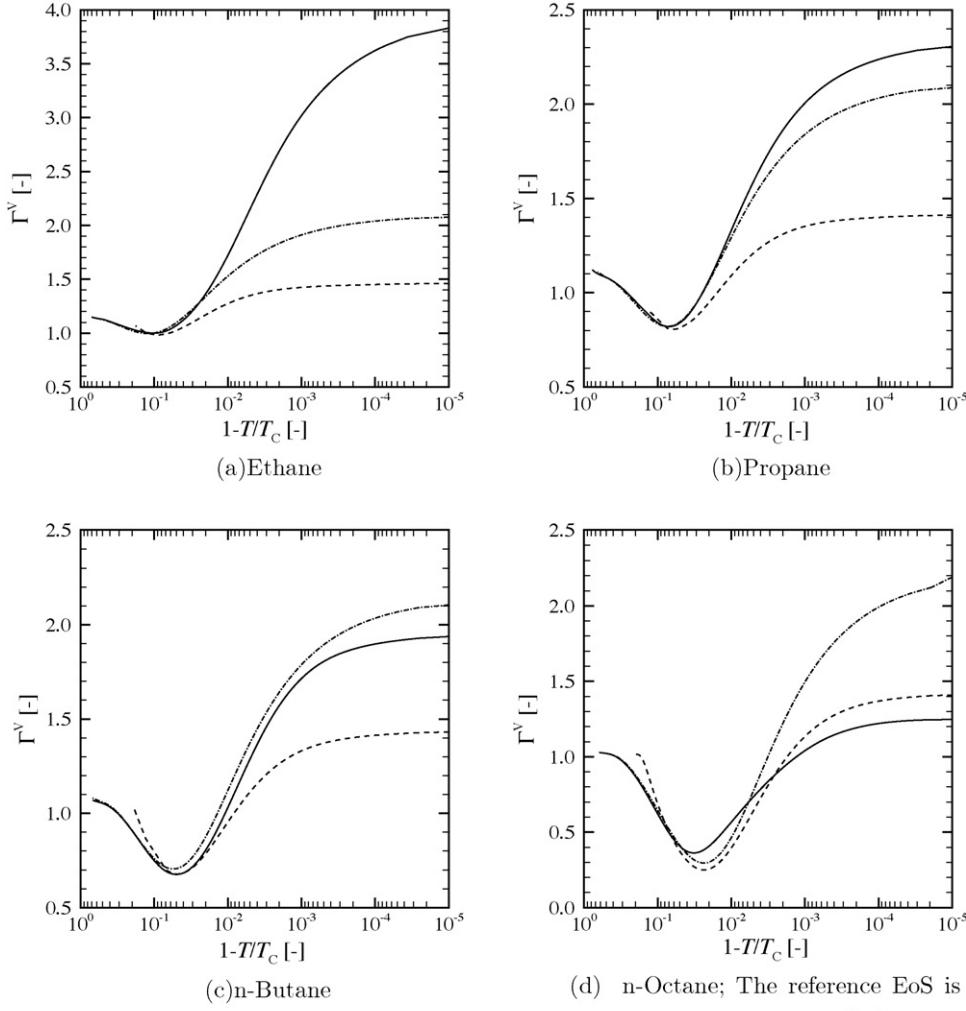


Fig. 10. The fundamental derivative along the dew-line of selected n-alkanes close to the critical point. The solid line represents computations with the reference EoS, the dashed line represents computations with the MH EoS, and the dash-dotted line represents computations with the PRSV EoS. Note that the horizontal coordinate has been chosen to better visualize the region near the critical point: $1 - T/T_c = 10^{-2}$ correspond to approximately 3–4 K. (a) Ethane, (b) propane, (c) n-butane, (d) n-octane. The reference EoS is that of Kunz and Wagner [72], which does not contain critical-point terms.

Γ from an EoS with respect to Γ from the fit to simulated data can be considered as an estimate of the precision of the EoS for this specific collection of points. To get an unbiased estimate of the precision, more than one configuration of data-points has to be considered. In total five random configurations of 40 *'s per • were checked. It was found that, if the • was sufficiently far from the critical point, the five Γ -values from the fit differed from each other by no more than 0.01. Note that a convergence study taking into account the number of *'s per • were checked, as well as whether the Taylor series should be truncated up to the first-order derivative terms or up to second-order terms, has been performed. For example, for ethane, if the • was taken at a pressure of 4347.15 kPa and a temperature of 316.227 K, fits showed that the value of Γ varied between 1.05 and 1.08 for the number of *'s taken between 30 and 40, with the inclusion or exclusion of the second-order terms in the Taylor series expansion. The value predicted from the reference EoS at a pressure of 4347.15 kPa and a temperature of 316.227 K is 1.06, therefore the Γ obtained from the fits to the Taylor series expansion differ by at maximum 2%. If the number of *'s per • is 25, much larger differences.

In this study, three center-points (•'s) were considered for methane, all located in the vapor region, namely ($P^\bullet = 2002.5$ kPa,

$T^\bullet = 192.62$ K, $Z = 0.84$; ($P^\bullet = 3487.3$ kPa, $T^\bullet = 192.65$ K, $Z = 0.68$; ($P^\bullet = 3405.0$ kPa, $T^\bullet = 192.70$ K, $Z = 0.62$. For all these points it was found that the bias of the estimation of Γ randomly varied between ± 0.01 (computations with ethane yielded similar results).

3.2. Simpler equations of state

For the vast majority of fluids, reference equations of state are not available. In general terms, the availability of accurate multiparameter equations of state is inversely proportional to the molecular complexity characterizing the fluid. The main reason is that large experimental data sets are available only for simple fluids, because measurements become comparatively more difficult and uncertain for fluids made of more complex molecules.

In all previous studies related to the evaluation of the fundamental derivative of gas dynamics, except for the one documented in Ref. [10], simpler and relatively inaccurate thermodynamic models were adopted, because this was the only option. It becomes therefore interesting to evaluate the performance of simpler equations of states with respect to the computation of Γ , in comparison with reference equations of state. This assessment provides an indica-

tion with respect to the relative accuracy that can be expected from simpler models.

To this purpose, the cubic PRSV and the multiparameter MH equations of state are selected, because these thermodynamic models were adopted in many of the previous studies on nonclassical gas dynamics (see Section 2). It can be noted that the PRSV EoS is inconsistent at the critical temperature, i.e., iso-property lines exhibit discontinuities if the critical isotherm is crossed [47], and the MH EoS is self-inconsistent [46].

Fig. 8 presents a comparison between the values of Γ along the dew line calculated with the PRSV and MH EoS's with respect to values calculated with reference EoS's for ethane, propane, n-butane and n-octane. A relevant remark is that the EoS of n-octane is that of Kunz and Wagner [72] and classifies as a technical EoS rather than a reference EoS, therefore, although accurate, it does not fulfill all the requirements of a reference EoS [34,35]. Note that the Γ^V curve calculated with the MH EoS is truncated at a temperature higher than the triple point, because saturation properties are affected by large errors on the computation of v^V . Such behavior is well known and it is due to the fact that only the normal boiling point and the critical point data are used to set the substance-specific parameters of the EoS (see Section 2). From the inspection of **Fig. 8** it can be observed that, while the performance of the PRSV equation of state is very satisfactory, and only in the case of n-octane it slightly underpredicts the minimum value of Γ , the MH EoS displays fairly large deviations in the lower temperature range.

4. Computation of Γ for fluids made of complex molecules

The estimation of the value of the fundamental derivative of gas dynamics is of special interest in the case of fluids made of complex molecules, because for these fluids the inversion of gas dynamic phenomena is predicted in the thermodynamic region where Γ is negative.

As an example, the results of the calculation of Γ^V as a function of T/T_c for MDM, MD_2M and MD_3M made with the SW, the PRSV and the MH EoS's are shown in **Fig. 9**. It can be observed that the MH EoS consistently predicts a significantly lower value of Γ_{\min}^V compared to the PRSV and the technical EoS's [54], respectively. Finally, for all siloxanes it can be noted that $\Gamma_{\min,MH\text{ EoS}}^V < \Gamma_{\min,SW,\text{EoS}}^V$. This is also the case for all alkanes.

As a last remark, it is interesting to assess the influence of molecular complexity on the estimation of the fundamental derivative of gas dynamics. Note that Γ can be written as the summation of three terms as

$$\Gamma = \frac{v^3}{2c^2}(\bar{\Gamma}_1 + \bar{\Gamma}_2 + \bar{\Gamma}_3), \quad (11)$$

where,

$$\bar{\Gamma}_1 = \left(\frac{\partial^2 P}{\partial v^2} \right)_T \quad (12a)$$

$$\bar{\Gamma}_2 = -3 \frac{T}{C_v} \left(\frac{\partial P}{\partial T} \right)_v \left(\frac{\partial^2 P}{\partial v \partial T} \right)_{T,v} \quad (12b)$$

$$\bar{\Gamma}_3 = \left[\frac{T}{C_v} \left(\frac{\partial P}{\partial T} \right)_v \right]^2$$

$$\times \left[3 \left(\frac{\partial^2 P}{\partial T^2} \right)_v + \frac{1}{T} \left(\frac{\partial P}{\partial T} \right)_v \left(1 - \frac{T}{C_v} \left(\frac{\partial C_v}{\partial T} \right)_v \right) \right] \quad (12c)$$

In the dense-gas region, but outside the critical region, as the isochoric heat capacity increases, the contributions of both $\bar{\Gamma}_2$ (due to the factor C_v^{-1}) and $\bar{\Gamma}_3$ (due to the factor C_v^{-2}) are reduced. For this

reason, in the case of a complex molecule, the estimation of Γ is more sensitive to the accuracy of $P-v-T$ experimental data (because of the $\bar{\Gamma}_1$ -term) rather than to the terms affected by C_v . This, as well as the principle of corresponding states, suggests that simple EoS's (with a low bias error) can be used to reliably predict Γ -values for molecularly complex fluids.

Recent work on the estimation of ideal gas heat capacities of siloxanes [55] demonstrated that, by combining experimental measurements with molecular simulations, ideal gas heat capacities of molecularly complex fluids can be determined with approximately 5% uncertainty. The availability of accurate $P-v-T$ data in the dense-vapor region of molecularly complex fluids and the correct estimation of their critical parameters remains still an issue, as far as accurate values of Γ are concerned.

5. Conclusions

This work addresses the possibility of calculating the fundamental derivative of gas dynamics by means of equations of state. Its prediction is relevant in the study of the gas dynamic of dense vapors, as its value is related to the main features of the flow field. At present, no experimental measurements of Γ are available and its direct experimental determination in the dense-vapor region of interest appears difficult. Previous studies have shown a wide scatter in values if rather simple thermodynamic models are employed.

In order to obtain the most accurate values of the fundamental derivative of gas dynamics, reference equations of state were employed, limited to fluids made of simple molecules for which such models are available. In order to test the performance of these equations with respect to the estimation of the fundamental derivative of gas dynamics, values of Γ were calculated along the dew line for several alkanes and compared to values calculated with other highly accurate thermodynamic models. The accuracy of the obtained predictions has been assessed under several assumptions. Furthermore, simpler thermodynamic models adopted in the past for the computation of Γ of more complex fluids were used to perform the same calculations, using reference equations as a benchmark. This allows for an indication of the uncertainty involved in the use of simpler models. Finally, the calculation of Γ for fluids made of complex molecules was also addressed by comparing values calculated with three different thermodynamic models. The influence of molecular complexity on the accuracy of Γ has been highlighted. The following observations can be made:

- (1) Herein, the PRSV cubic equation of state compared to the MH equation of state, predicts values of Γ that are closer to the values of modern, reference multiparameter equations of state. Moreover, predictions of the minimum value of Γ with the PRSV equation of state are conservative with respect to predictions from the MH equation of state.
- (2) For fluids made of complex molecules, it is possible to achieve a comparatively higher level of accuracy in the estimation of Γ with respect to molecularly simpler fluids if experimental data are available, because of the fact that, for molecularly complex substances, C_v is large. The accuracy of the estimation of Γ depends on both the accuracy of $P-v-T$ data and that of C_v . A large value of C_v subdues the dependency of the accuracy of Γ with respect to the isochoric heat capacity.

As a last remark, it is important to notice that the treatment of the fundamental derivative of gas dynamics in the critical region deserves special attention. By exploring the results of the computations of Γ in the close proximity of the critical point made with various thermodynamic models, large deviations can be observed. **Fig. 10** reports the same lines as in **Fig. 8**, but an appropriate scale

has been chosen for the horizontal axis, in order to amplify the difference between the computed values close to the critical point. The reference equations of state contain critical-point terms to achieve good accuracy in the estimation of primary properties, while cubic equations of state are known to be inaccurate close to the critical point. Nonetheless, even reference equations of state, which are analytic in the Helmholtz free energy at the critical point, fail to correctly predict many critical anomalies [73–75] and therefore, also the trend of Γ along the dew-line is inaccurate/incorrect. In fact, Γ should diverge at the critical point [76,77]. The authors are currently investigating close-to-critical gas-dynamic phenomena using scaling laws for the calculation of the fundamental derivative of gas dynamics and results will be available in an upcoming publication. Anticipating these results, $\Gamma^V \propto |(T - T_c)/T|^{-0.89} \rightarrow +\infty$ as the critical point is approached along the dew-line.

Acknowledgments

This research is supported in part by the Dutch Technology Foundation STW, applied science division of NWO and the Technology Program of the Ministry of Economic Affairs, the Netherlands.

References

- [1] P.A. Thompson, A fundamental derivative in gas dynamics, *Phys. Fluids* 14 (9) (1971) 1843–1849.
- [2] P. Colonna, A. Guardone, Molecular interpretation of nonclassical gas dynamics of dense vapors under the Van der Waals model, *Phys. Fluids* 18 (2006) 056101–1–05610114–05610114.
- [3] M.S. Cramer, N.R. Fry, Nozzle flows of dense gases, *Phys. Fluids A* 5 (5) (1993) 1246–1259.
- [4] G.H. Schnerr, P. Leidner, Diabatic supersonic flows of dense gases, *Phys. Fluids A* 3 (10) (1991) 2445–2458.
- [5] A. Kluwick, Internal flows of dense gases, *Acta Mech.* 169 (2004) 123–143.
- [6] P. Colonna, S. Rebay, J. Harinck, A. Guardone, Real-gas effects in ORC turbine flow simulations: influence of thermodynamic models on flow fields and performance parameters, in: P., Wesseling, E., Onate, J., Périau, (Eds.), European Conference on Computational Fluid Dynamics (ECCOMAS CFD 2006), pages 1–18, September 2006.
- [7] H.A. Bethe, The theory of shock waves for an arbitrary equation of state. Technical paper 545, Office Sci. Res. & Dev., 1942.
- [8] Ya.B. Zel'dovich, On the possibility of rarefaction shock waves, *Zh. Eksp. Teor. Fiz.* 4 (1946) 363–364.
- [9] P.A. Thompson, K.C. Lambrakis, Negative shock waves, *J. Fluid Mech.* 60 (1973) 187–208.
- [10] P. Colonna, A. Guardone, N.R. Nannan, Siloxanes: a new class of candidate Bethe–Zel'dovich–Thompson fluids, *Phys. Fluids* 19 (2007) 086102–1–08610212–08610212.
- [11] W.D. Hayes, The basic theory of gas dynamic discontinuities, in: H.W. Emmons (Ed.), Fundamentals of Gas Dynamics, High Speed Aerodynamics and Jet Propulsion, vol. 3, Princeton University Press, 1958.
- [12] D. Buecker, W. Wagner, Reference equations of state for the thermodynamic properties of fluid n-butane and isobutane, *J. Phys. Chem. Ref. Data* 35 (2) (2006) 929–1019.
- [13] A. Guardone, L. Vigevano, B.M. Argrow, Assessment of thermodynamic models for dense gas dynamics, *Phys. Fluids* 16 (November 11) (2004) 3878–3887.
- [14] A. Guardone, B.M. Argrow, Nonclassical gasdynamic region of selected fluorocarbons, *Phys. Fluids* 17 (11) (2005) 116102.
- [15] C. Zamfirescu, A. Guardone, P. Colonna, Admissibility region for rarefaction shock waves in dense gases, *J. Fluid Mech.* 599 (March 2008) 363–381.
- [16] H.P. Bloch, C. Soares, Turboexpanders and Process Applications, Gulf Professional Publishing, 2001.
- [17] N.G. Kirillov, Analysis of modern natural gas liquefaction technologies, *Chem. Petrol. Eng.* 40 (7–8) (2004) 401–406.
- [18] J. Hoffren, T. Talonpoika, J. Larjola, T. Siikonen, Numerical simulation of real-gas flow in a supersonic turbine nozzle ring, *J. Eng. Gas Turb. Power* 124 (2) (April 2002) 395–403.
- [19] B.P. Brown, B.M. Argrow, Application of Bethe–Zel'dovich–Thompson fluids in organic Rankine cycle engines, *J. Propul. Power* 16 (November–December 6) (2000) 1118–1123.
- [20] J.F. Monaco, M.S. Cramer, L.T. Watson, Supersonic flows of dense gases in cascade configurations, *J. Fluid Mech.* 330 (1997) 31–59.
- [21] P. Colonna, S. Rebay, Numerical simulation of dense gas flows on unstructured grids with an implicit high resolution upwind Euler solver, *Int. J. Numer. Meth. Fl.* 46 (7) (2004) 735–765.
- [22] G. Angelino, C. Invernizzi, Supercritical heat pump cycles, *Int. J. Refrig.* 17 (8) (1994) 543–554.
- [23] G. Angelino, Carbon dioxide condensation cycles for power production, *J. Eng. Power-T. ASME* (July 1968) 287–295.
- [24] G. Angelino, Real gas effects in carbon dioxide cycles, *J. Eng. Power-T. ASME* 10 (13) (1969) 272–287.
- [25] V. Dostal, A supercritical carbon dioxide cycle for next generation nuclear reactors. PhD thesis, Massachusetts Institute of Technology, 2004.
- [26] N.R. Nannan, Advancements in nonclassical gas dynamics. PhD thesis, Delft University of Technology, 2009.
- [27] V. Dostal, M. Driscoll, P. Hejzlar, Y. Wang, Supercritical CO₂ cycle for fast gas-cooled reactors, ASME, in: Proceedings of the ASME Turbo Expo 2004, Vienna, 17 June, 2004.
- [28] H. Yamaguchi, X.R. Zhang, K. Fujima, M. Enomoto, N. Sawada, Solar energy powered Rankine cycle using supercritical CO₂, *Appl. Therm. Eng.* 26 (17–18) (2006) 2345–2354.
- [29] P. Hejzlar, V. Dostal, M.J. Driscoll, A supercritical CO₂ cycle—a promising power conversion system for generation IV reactors, in: Proceedings of the 2006 International Congress on Advances in Nuclear Power Plants (ICAPP'06), Reno, Nevada, June 4–8, 2006.
- [30] A. Steven, P. Wright, S. Pickard, M.E. Vernon, Initial status and test results from a supercritical CO₂ Brayton cycle test loop, in: Proceedings of the 2008 International Congress on Advances in Nuclear Power Plants (ICAPP '08), Anaheim, CA, June 8–12, 2008.
- [31] Y. Wang, G. Guenette, P. Hejzlar, M. Driscoll, Compressor design for the supercritical CO₂ Brayton cycle, in: Proceedings of the 2nd International Energy Conversion Engineering Conference, Providence, Rhode Island, 16–19, August, 2004, pp. 1–13, AIAA.
- [32] P. Colonna, P. Silva, Dense gas thermodynamic properties of single and multi-component fluids for fluid dynamics simulations, *J. Fluid Eng. -T. ASME* 125 (3) (2003) 414–427.
- [33] P. Colonna, A. Guardone, N.R. Nannan, C. Zamfirescu, Design of the dense gas Flexible Asymmetric Shock Tube, *J. Fluids Eng. -T. ASME* 130 (March 3) (2008) 034501-1–0345016–0345016.
- [34] R. Span, Multiparameter Equations of State—An Accurate Source of Thermodynamic Property Data, Springer-Verlag, Berlin, 2000.
- [35] R. Span, W. Wagner, E.W. Lemmon, R.T. Jacobsen, Multiparameter equations of state—recent trends and future challenges, *Fluid Phase Equilib.* 183–184 (2001) 1–20.
- [36] K.C. Lambrakis, P.A. Thompson, Existence of real fluids with negative fundamental derivative, *Phys. Fluids* 15 (5) (1972) 933–935.
- [37] J.O. Hirschfelder, R.J. Buehler, H.A. McGee, J.R. Sutton Jr., Generalized equation of state for gases and liquids, *Ind. Eng. Chem.* 50 (3) (1958) 375–385.
- [38] M. Benedict, G.B. Webb, L.C. Rubin, An empirical equation for thermodynamic properties of light hydrocarbons and their mixtures I. Methane, ethane, propane and n-butane, *J. Chem. Phys.* 8 (1940) 334–345.
- [39] J.J. Martin, Y.C. Hou, Development of an equation of state for gases, *AIChE J.* 1 (June 2) (1955) 142–151.
- [40] R.L. Rowley, W.V. Wilding, J.L. Oscarson, Y. Yang, N.A. Zundel, T.P. Daubert, R.P. Danner, DIPPR Data Compilation of Pure Chemical Properties, Taylor & Francis Publishing Company, New York, NY, 2004.
- [41] B.E. Poling, J.M. Prausnitz, J.P. O'Connell, The properties of gases and liquids. Chemical Engineering Series, 5th edition, McGraw-Hill, New York, 2001.
- [42] E.W. Lemmon, R. Span, Short fundamental equations of state for 20 industrial fluids, *J. Chem. Eng. Data* 51 (3) (2006) 785–805.
- [43] O. Redlich, J.N.S. Kwong, On the thermodynamics of solutions. V. An equation of state, fugacities of gaseous solutions, *Chem. Rev.* 44 (1949) 233–244.
- [44] M.M. Abbott, Cubic equations of state, *AIChE J.* 19 (1973) 596–601.
- [45] M.S. Cramer, Negative nonlinearity in selected fluorocarbons, *Phys. Fluids A* 11 (1) (1989) 1894–1897.
- [46] G. Emanuel, Assessment of the Martin–Hou equation for modeling a nonclassical fluid, *J. Fluids Eng. -T. ASME* 116 (December) (1994) 883–884.
- [47] R. Stryjev, J.H. Vera, PRSV: An improved Peng–Robinson equation of state for pure compounds and mixtures, *Can. J. Chem. Eng.* 64 (1986) 323–333.
- [48] B.K. Harrison, W.H. Seaton, Solution to missing group problem for estimation of ideal gas heat capacities, *Ind. Eng. Chem. Res.* 27 (1988) 1536–1540.
- [49] G. Emanuel, Advanced classical thermodynamics. AIAA Education Series, AIAA, New York, 1987.
- [50] G. Soave, Equilibrium constants from a modified Redlich–Kwong equation of state, *Chem. Eng. Sci.* 27 (6) (June 1972) 1197–1203.
- [51] D.Y. Peng, D.B. Robinson, A new two-constant equation of state, *Ind. Eng. Chem. Fundam.* 15 (1976) 59–64.
- [52] J.J. Martin, R.M. Kapoor, N. De Nevers, An improved equation of state for gases, *AIChE J.* 5 (2) (1959) 159–160.
- [53] P. Colonna, N.R. Nannan, A. Guardone, E.W. Lemmon, Multiparameter equations of state for selected siloxanes, *Fluid Phase Equilib.* 244 (2006) 193–211.
- [54] P. Colonna, N.R. Nannan, A. Guardone, Multiparameter equations of state for siloxanes: $[(CH_3)_2Si-O_{1/2}]_2-[O-Si-(CH_3)_2]_{i=1,\dots,3}$, and $[O-Si-(CH_3)_2]_6$, *Fluid Phase Equilib.* 263 (2) (2008) 115–130.
- [55] N.R. Nannan, P. Colonna, C.M. Tracy, R.L. Rowley, J.J. Hurly, Ideal-gas heat capacities of dimethylsiloxanes from speed-of-sound measurements and ab initio calculations, *Fluid Phase Equilib.* 257 (2007) 102–113.
- [56] L. Calderazzi, P. Colonna, Thermal stability of R-134a, R-141b, R-1311, R-7146, R-125 associated with stainless steel as a containing material, *Int. J. Refrig.* 20 (6) (1997) 381–389.
- [57] G. Angelino, C. Invernizzi, Cyclic methylsiloxanes as working fluids for space power cycles, *J. Sol. Energ. -Trans. ASME* 115 (3) (1993) 130–137.
- [58] P. Colonna, Fluidi di lavoro multi componenti per cicli termodinamici di potenza (Multicomponent working fluids for power cycles). PhD thesis, Politecnico di Milano, October 1996.

- [59] D.S.H. Wong, S.I. Sandler, A theoretically correct mixing rule for cubic equations of state, *AIChE J.* 38 (1992) 671–680.
- [60] R. Span, W. Wagner, Equations of state for technical applications. II. Results for nonpolar fluids, *Int. J. Thermophys.* 24 (1) (January 2003) 41–109.
- [61] U. Setzmann, W. Wagner, A new equation of state and tables of thermodynamic properties for methane covering the range from the melting line to 625 K at pressures up to 1000 MPa, *J. Phys. Chem. Ref. Data* 20 (6) (1991) 1061–1151.
- [62] E.W. Lemmon, M.O. McLinden, M.L. Huber, REFPROP – REference fluid PROPeries software, © NIST 2002.
- [63] D.G. Friend, J.F. Ely, H. Ingham, Thermophysical properties of methane, *J. Phys. Chem. Ref. Data* 18 (2) (1989) 583–638.
- [64] D. Buecker, W. Wagner, A reference equation of state for the thermodynamic properties of ethane for temperatures from the melting line to 675 K and pressures up to 900 MPa, *J. Phys. Chem. Ref. Data* 35 (1) (2006) 205–266.
- [65] D.G. Friend, H. Ingham, J.F. Ely, Thermophysical properties of ethane, *J. Phys. Chem. Ref. Data* 20 (2) (1991) 275–347.
- [66] H. Miyamoto, K. Watanabe, A thermodynamic property model for fluid-phase propane, *Int. J. Thermophys.* 21 (5) (2000) 1045–1072.
- [67] H. Miyamoto, K. Watanabe, A thermodynamic property model for fluid-phase n-butane, *Int. J. Thermophys.* 22 (2) (2001) 459–475.
- [68] H. Miyamoto, K. Watanabe, A thermodynamic property model for fluid-phase isobutane, *Int. J. Thermophys.* 23 (2) (2002) 477–499.
- [69] S. Fergason, A. Guardone, B. Argrow, Construction and validation of a dense gas shock tube, *J. Thermophys. Heat Transfer* 17 (3) (2003) 326–333.
- [70] G.H. Schnerr, P. Leidner, Two-dimensional nozzle flows of dense gases. In: *Fluids Engineering Conference*, number ASME Paper No. 93-FE-8, 1993.
- [71] M.A. Anisimov, S.B. Kiselev, J.V. Sengers, S. Tang, Crossover approach to global critical phenomena in fluids, *Physica A* 188 (1992) 487–525.
- [72] O. Kunz, B. Klimeck, W. Wagner, M. Jaeschke, The GERG-2004 wide-range reference equation of state for natural gases and other mixtures GERG TM, Fortschr. -Ber. VDI, VDI-Verlag 557 (2007) 15.
- [73] J.M.H. Levelt-Sengers, Scaling predictions for thermodynamic anomalies near the gas-liquid critical point, *Ind. Eng. Chem. Fundam.* 9 (3) (1970) 470–480.
- [74] J.M.H. Levelt Sengers, G. Morrison, R.F. Chang, Critical behavior in fluids and fluid mixtures, *Fluid Phase Equilib.* 14 (1983) 19–44.
- [75] J.V. Sengers, J.M.H. Levelt Sengers, Thermodynamic behavior of fluids near the critical-point, *Annu. Rev. Phys. Chem.* 37 (1986) 189–222.
- [76] S.C. Gulen, P.A. Thompson, H.J. Cho, Rarefaction and liquefaction shock waves in regular and retrograde fluids with near-critical end states, in: G.E.A. Meier, P.A., Thompson, (Eds.), *IUTAM Symposium: Adiabatic Waves in Liquid-Vapor Systems*, pp. 281–290, Berlin Heidelberg, Germany, 1989. Springer-Verlag 1990.
- [77] G. Emanuel, Analysis of a critical point with application to fluid mechanics. AME Report 96-1, University of Oklahoma, Norman, OK, USA, 1996.
- [78] P. Colonna, J. Harinck, S. Rebay, A. Guardone, Real-gas effects in organic Rankine cycle turbine nozzles, *J. Propul. Power* 24 (2) (2008) 282–294.