

Real Gas Thermodynamics

and the isentropic behavior of substances

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by

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Abstract

A generalized isentropic gas model is derived following earlier work by Kouremenos et al. [1–3] by replacing the traditional adiabatic exponent γ by the real exponents γ_{Pv} , γ_{Tv} , and γ_{PT} , describing the isentropic pressure-volume, temperature-volume, and pressure-temperature relations respectively. The real adiabatic exponents are expressed as functions of state variables to take into account compressibility effects on the isentropic behavior of substances. Due to the implicit analytical nature of the real exponents, any equation of state or thermodynamic library can be used for their evaluation. The theoretical limits and overall behavior of the real isentropic gas model are explored for a Van der Waals substance. In the two opposing physical limits, the model is shown to reduce to the incompressible substance model for liquid densities and the ideal gas model as the temperature increases or the pressure goes to zero.

The relation of the generalized isentropic gas model with other thermodynamic properties is explored, leading to the development of specific heat relations and other thermodynamic properties in terms of the real exponents γ_{Pv} , γ_{Tv} , and γ_{PT} . Besides providing alternative schemes for their evaluation, special features of thermodynamic properties such as the state of maximum density and inversion temperature may be related to the value of the isentropic exponents determined by the local compressibility of the substance. Due to the exact definitions of the real adiabatic exponents at a state point, the relations between properties is thermodynamically consistent – another physical requirement.

The generalized isentropic gas model is then applied to isentropic flows to derive traditional gas dynamic relations such as speed of sound, stagnation properties, and choked flow conditions for non-ideal compressible fluid flows. Exact solutions are provided for Prandtl-Meyer expansion fans, and approximate Rankine-Hugoniot jump conditions are explored for real gases. Finally, attributes of the fundamental derivative of gas dynamics are explored under the generalized isentropic gas model to gain new insights into its mathematical properties. Under the generalized isentropic model, the fundamental derivative is shown to satisfy both liquid and gaseous physical limits. Non-classical behavior is attributed to higher-order derivatives of the real exponents.

The application of the generalized isentropic gas model is demonstrated and validated for use in non-ideal compressible fluid dynamic (NICFD) codes by simulation of the one-dimensional Euler equations for a standard shock tube problem. Several numerical schemes for the evaluation of thermodynamic properties of varying levels of accuracy are presented for evaluation of the isentropic gas model. In the application of the shock tube problem, the general equation for the speed of sound is demonstrated to be equivalent to the speed of sound of a Van der Waals gas, proving the validity of the model.

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Nomenclature

Physical Constants

R	universal gas constant
k_B	Boltzmann constant
N_A	Avogadro's constant
a	molecular attraction parameter
b	molecular volume parameter
f	molecular degrees of freedom

Thermodynamic Properties

P	pressure
T	temperature
Ζ	compressibility factor
ρ	density
v	specific volume
e	specific internal energy
h	specific enthalpy
s	specific entropy
c_v	specific isochoric heat capacity
c_p	specific isobaric heat capacity
γ	ideal isentropic exponent
γ_{Pv}	pressure-volume isentropic exponent
γ_{Tv}	temperature-volume isentropic exponent

- γ_{PT} pressure-temperature isentropic exponent
- β thermal expansion coefficient
- κ isothermal compressibility
- K adiabatic bulk modulus
- μ_{JT} Joule-Thomson coefficient
- μ_J Joule coefficient
- Γ fundamental derivative of gas dynamics

Gas Dynamic Variables

- u velocity c speed of sound
- M mach number
- A flow area
- \dot{m} mass flow rate
- α geometrical angle
- δ deflection angle
- ν Prandtl-Meyer angle

Superscripts and Subscripts

- c critical property
- r reduced property
- * critical flow property
- 0 stagnation property
- $1, 2, \dots$ thermodynamic state

Introduction

The burden placed upon the environment by the energy requirement of today's society urges humanity to develop new sustainable technologies to meet demands. An enormous potential lies in the exploitation of geothermal reservoirs, ocean thermal gradients, concentrated solar radiation, waste heat from prime movers and industrial processes, and biomass combustion [4–7], typically consisting of small to medium size thermal reservoirs at moderate temperature levels. Conventional thermal energy conversion technologies – whom over the years have been optimized to operate at ever higher temperature levels to improve conversion efficiency – are unsuitable for efficient thermal conversion of these energy sources mostly due to the incompatibility of the working fluid and the temperature profile of the thermal reservoir [8–11]. The critical point, saturation line, specific heat capacities, and heat of evaporation associated with the choice of working fluid translates directly into the size and temperature level of a thermal reservoir to which a system can efficiently operate [8, 10, 12].

To adapt to the temperature profiles of renewable energy sources and waste heat streams, a major development in the field of power generation technologies is the selection of the working fluid as an additional degree of freedom to the design of energy conversion systems. The fluid can be chosen such that it is optimal from a thermodynamic and technical point of view [10, 11, 13]. Examples of such technologies are the application of Organic Rankine Cycles (ORC) for low-temperature renewable sources and waste heat utility applications [8, 12, 14, 15], supercritical carbon dioxide (sCO₂) power cycles for medium to high temperature solar or nuclear applications [9, 16–18], and supercritical CO₂ refrigeration cycles [19, 20].

Performance optimization of system components is of primary importance for the successful implementation of these innovations. The combination of unusual working fluid characteristics and the thermodynamic regime in which these technologies are to operate makes for fluid behavior to depart greatly from ideal behavior [21-23]. Due to the complexities of non-ideal compressible fluid dynamics (NICFD), the design and analysis of equipment operating dense gas regime is one that is mainly driven by computational fluid dynamics [24-27]. The development of NICFD codes, therefore, plays a crucial role in the overall advancement of this research field.

At the same time, the conventional classification between "ideal" and "non-ideal" fluids is distinctive for the lacking means to describe the behavior of fluids in a general sense. Whereas the behavior of ideal gases is fully resolved, our capabilities are severely limited when moving away from ideal conditions and force us to resort to thermodynamic libraries and equations of state of (semi)-empirical nature [28, 29]. Having to rely on thermodynamic libraries and complex multiparameter equations of state (MPEOS), imposes heavy computational costs in the modeling of non-ideal compressible fluid flows. Moreover, the absence or only partial availability of experimental data in the thermodynamic region of interest introduces a level of uncertainty that makes robust and accurate simulations of non-ideal fluid flows still a challenge [27, 30]. In this work, an analytical framework for the evaluation of non-ideal gas behavior is constructed, based on the generalized isentropic relations introduced by Kouremenos et al. in the 1980s [1–3, 31, 32]. In a series of papers, they proposed a method to include compressibility effects into the adiabatic constant γ used in classical ideal gas dynamics – a model that could potentially be very useful in the modeling of non-ideal compressible fluid flows. Though upon its introduction, the application of the isentropic model leaned more towards empirical substitution of equations of state into compressible ideal gases relations rather than analytical arguments. Isentropic flow relations for non-ideal gases were presumed to retain their ideal form, and their exponents empirically evaluated [31]. Demonstrating these concepts based on analytical arguments will be the objective of this work: "To analytically extend concepts of classical ideal compressible gas dynamics to non-ideal gases using the generalized isentropic model."

The extent to which ideal gas dynamics can be successfully extended to non-ideal fluids will be investigated by addressing the following related topics:

- *i*. Does the mathematical behavior of the generalized isentropic gas model comply with physical limits, and to what extent can the model capture real gas behavior between those limits?
- ii. Is the isentropic gas model consistent with other thermodynamic properties?
- *iii.* Can isentropic flow properties be extended to non-ideal fluids using the generalized isentropic gas model, and what are the limits of its application?

By adoption of the generalized isentropic model, we will consider a fluid exhibiting any gas dynamic behavior, henceforth referred to as a "*real*" fluid. The ideal gas equation will be demonstrated to be a subclass of the real model, as indeed are any other equations of state such as Van der Waals, Soave-Redlich-Kwong, Peng-Robinson, etc. Classical analytical ideal gas concepts such as the speed of sound, stagnation properties, choked flow conditions, and other thermodynamic identities, will be demonstrated to inherit their formulation from fundamental mass, momentum, and energy conservation equations that do not distinguish between ideal or non-ideal gases. These concepts will be shown to be shared properties of ideal gases and real gases alike. The kind of behavior that the substance exhibits is captured in the value of the adiabatic exponents of the real isentropic model.

To effectively engage in this extensive collection of closely related topics, this work has been divided into four parts. In Part I, the real isentropic model by Kouremenos is formally introduced [1–3]. Its mathematical properties and limits are explored for the underlying physics that governs fluid behavior. In Part II, the isentropic model is put into the wider perspective of thermodynamic fluid properties concerning specific heat relations, compressibility effects and entropy itself. In Part III, the isentropic model is applied to extend familiar concepts of ideal gas dynamics to real fluid flows. The speed of sound, stagnation properties, and choked flow conditions are derived for non-ideal compressible isentropic flows. An attempt is made to derive shock wave properties in real fluid flows. Finally, in Part IV, the application of the isentropic model in NICFD codes is demonstrated by simulation of the shock tube problem for a real compressible gas.

PART I

REAL ISENTROPIC RELATIONS

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Part I of this work serves as an introduction of the generalized isentropic gas model to the reader, which will be applied to thermodynamic property relations and isentropic flows in subsequent parts. The isentropic relations of real substances will be introduced, their functions formally derived, and their mathematical properties thoroughly investigated.

The first two chapters will together substantiate the theoretical framework behind the generalized isentropic relations based on earlier work by Kouremenos et al. [1-3]. Their original derivation is expanded for clarity and completeness, whereby the equivalence between the real isentropic gas model and the ideal isentropic gas model is explicitly outlined. In the final chapter of this part, the behavior of the generalized isentropic functions are investigated for Van der Waals gasses, and their physical limits explored.

ONE

Real Isentropic Exponents

The isentropic relations for ideal gases will form our point of departure for the derivation of their real gas counterparts. The isentropic relations of an ideal gas are readily derived from the entropy equations [33, 34], given as

$$ds = c_p \frac{dT}{T} + R \frac{dP}{P},\tag{1.1}$$

where ds = 0 for an isentropic process. Let $R = c_p - c_v$ for an ideal gas. Integration of Eq. (1.1) yields

$$\ln T - \frac{c_p - c_v}{c_p} \ln P = const. \tag{1.2}$$

The integration constant is unique for each isentrope. Taking the exponential of Eq. (1.2) we arrive at the description of the pressure-temperature isentrope in its familiar form. Using the ideal gas relation Pv = RT the pressure-volume isentrope and temperature-volume isentrope are also obtained:

$$Pv^{\gamma} = const, \tag{1.3a}$$

$$Tv^{\gamma-1} = const, \tag{1.3b}$$

$$TP^{\frac{1-\gamma}{\gamma}} = const.$$
 (1.3c)

For the derivation of the isentropic relations for real gasses a solution in the form of Eqs. (1.3a–1.3c) will be assumed for now, where the exponents are replaced by γ_{Pv} , γ_{Tv} , and γ_{PT} . The purpose of this chapter will be to find implicit expressions for the exponents in terms of state variables, based on earlier work by Kouremenos et al. in the 1980s [1–3]. The original derivation is expanded by explicitly underlining the equivalence between the isentropic relations in the ideal and real case. Moreover, Chapter 2 will provide further closure of the problem by show that the assumed form of the isentropes is indeed correct.

A special notice is reserved for recent work by Baltadjiev, who had been able to independently come up with expressions for the real gas isentropes using a slightly different choice of notation in terms of compressibility coefficients [35, 36]. The original notation introduced by Kouremenos is preferred in this work as it conveniently adheres to the ideal gas notation, thereby preserving familiar notations and emphasizing the equivalence between the ideal and generalized isentropic gas models.

1.1 Pressure-Volume Exponent

The isentropic pressure-volume relationship of an ideal gas is given by Eq. (1.3a). For the general case, we introduce the unknown adiabatic function γ_{Pv} which replaces the ideal adiabatic coefficient $\gamma = c_p/c_v$. The generalized isentropic pressure-volume relation becomes

$$Pv^{\gamma_{Pv}} = const. \tag{1.4}$$

To derive an expression for γ_{Pv} in terms of state variables, let entropy be defined as a function of pressure and specific volume s = s(P, v). In this case, the change in entropy is expressed as (App. A.1)

$$ds = \left(\frac{\partial s}{\partial P}\right)_{v} dP + \left(\frac{\partial s}{\partial v}\right)_{P} dv = 0, \tag{1.5}$$

where ds = 0 for an isentropic process. Rearranging the partial derivatives yields

$$\left(\frac{dP}{dv}\right)_{s} = -\frac{\left(\frac{\partial s}{\partial v}\right)_{P}}{\left(\frac{\partial s}{\partial P}\right)_{v}}.$$
(1.6)

The left-hand side of Eq. (1.6) can be evaluated by differentiation of the assumed isentropic pressure-volume relation Eq. (1.4) with respect to v, which becomes

$$\left(\frac{dP}{dv}\right)_s = -\gamma_{Pv}\frac{P}{v}.\tag{1.7}$$

The right-hand side of Eq. (1.6) can be re-expressed using Maxwell relations, and subsequently expanded using the triple product (App. A.1–A.2)

$$-\frac{\left(\frac{\partial s}{\partial v}\right)_{P}}{\left(\frac{\partial s}{\partial P}\right)_{v}} = \frac{\left(\frac{\partial P}{\partial T}\right)_{s}}{\left(\frac{\partial v}{\partial T}\right)_{s}},$$
(1.8a)

$$= \frac{\left(\frac{\partial P}{\partial s}\right)_T \left(\frac{\partial s}{\partial T}\right)_P}{\left(\frac{\partial v}{\partial s}\right)_T \left(\frac{\partial s}{\partial T}\right)_v},\tag{1.8b}$$

where $(\partial s/\partial T)_P = c_p/T$ and $(\partial s/\partial T)_v = c_v/T$ (App. A.3). Using the Maxwell relations once more, the remaining partial derivatives can be expressed as

$$-\frac{\left(\frac{\partial s}{\partial v}\right)_P}{\left(\frac{\partial s}{\partial P}\right)_v} = -\frac{c_p}{c_v} \left(\frac{\partial T}{\partial v}\right)_P \left(\frac{\partial P}{\partial T}\right)_v, \qquad (1.9a)$$

$$= \frac{c_p}{c_v} \left(\frac{\partial P}{\partial v}\right)_T.$$
(1.9b)

Equating the left-hand side and right-hand side results, we find an implicit function of γ_{Pv} in terms of state variables based on the assumed form of the isentropic pressure-volume relation [1]:

$$\gamma_{Pv} = -\frac{v}{P} \frac{c_p}{c_v} \left(\frac{\partial P}{\partial v}\right)_T.$$
(1.10)

To evaluate the function γ_{Pv} the expression must be made explicit by adopting an equation of state, or by using a thermodynamic library. This will be the subject of Part IV where the real isentropic gas model is used for modeling non-ideal compressible flows. For now, we will use this concept to demonstrate that the isentropic pressure-volume relation of an ideal gas is a subset of the solutions of Eq. (1.10). Evaluating the derivative $(\partial P/\partial v)_T$ for the ideal gas equation yields

$$\left(\frac{\partial P}{\partial v}\right)_T = -\frac{RT}{v^2}.\tag{1.11}$$

Elimination of the derivative in Eq. (1.10), we find that the function of γ_{Pv} reduces to the ratio of the specific heats, thereby demonstrating the equivalence between the ideal gas and real gas isentropic pressure-volume relation as

$$\gamma_{Pv} = \frac{c_p}{c_v}. \qquad (ideal \ gas) \tag{1.12}$$

1.2 Temperature-Volume Exponent

Similarly, let us assume the general temperature-volume relation to be of the from of Eq. (1.3b) where the adiabatic coefficient is replaced by the unknown function γ_{Tv} . The generalized temperature-volume relation along an isentrope becomes

$$Tv^{\gamma_T v^{-1}} = const. \tag{1.13}$$

The procedure for deriving an implicit expression for the function γ_{Tv} follows the same steps as previously for the pressure-volume exponent. We start out by defining entropy as a function of temperature and volume s = s(T, v). With ds = 0 for an isentropic process, the derivatives can be related as (App. A.1)

$$\left(\frac{dT}{dv}\right)_{s} = -\frac{\left(\frac{\partial s}{\partial v}\right)_{T}}{\left(\frac{\partial s}{\partial T}\right)_{v}}.$$
(1.14)

Again, a function for γ_{Tv} can be found by evaluating both sides of Eq. (1.14). The lefthand side of Eq. (1.14) can be evaluated by differentiation of the assumed temperaturevolume relation with respect to v

exponent γ_{Pv}

$$\left(\frac{dT}{dv}\right)_s = -(\gamma_{Tv} - 1)\frac{T}{v}.$$
(1.15)

The partial derivatives on the right-hand side of Eq. (1.14) can be expanded using Maxwell relations (App. A.2)

$$-\frac{\left(\frac{\partial s}{\partial v}\right)_T}{\left(\frac{\partial s}{\partial T}\right)_v} = -\frac{\left(\frac{\partial P}{\partial T}\right)_v}{\left(\frac{\partial s}{\partial T}\right)_v},\tag{1.16a}$$

 $= -\frac{1}{c_v} \left(\frac{\partial P}{\partial T}\right)_v. \tag{1.16b}$

Equating the left-hand side and right-hand side in Eq. (1.14), the function for the exponent γ_{Tv} for an real isentropic process becomes [1]:

$$\gamma_{Tv} = 1 + \frac{v}{c_v} \left(\frac{\partial P}{\partial T}\right)_v.$$
(1.17) exponent γ_{Tv}

Like in the case of γ_{Pv} , the ideal adiabatic exponent can be shown to be a subset of the solutions of γ_{Tv} by evaluating the derivative $(\partial P/\partial T)_v$ using the ideal gas relation which yields

$$\left(\frac{\partial P}{\partial T}\right)_v = \frac{R}{v}.$$
(1.18)

Elimination of the partial derivative in Eq. (1.17) the exponent γ_{Tv} is demonstrated to reduce to the ratio of the specific heats in the ideal case

$$\gamma_{Tv} = 1 + \frac{R}{c_v} = \frac{c_p}{c_v}. \qquad (ideal \ gas) \tag{1.19}$$

1.3 Pressure-Temperature Exponent

Finally, we introduce the function γ_{PT} to relate the isentropic pressure-temperature relation in the general case. Again, the purpose is to find an implicit expression for γ_{PT} in terms of state variables. The general pressure-temperature relation for an isentropic process becomes

$$TP^{\frac{1-\gamma_{PT}}{\gamma_{PT}}} = const. \tag{1.20}$$

We start by expressing entropy as an exact differential in terms of pressure and temperature s = s(P,T) (App. A.1). Again, with ds = 0 the following relation between the partial derivatives is obtained

$$\left(\frac{dP}{dT}\right)_{s} = -\frac{\left(\frac{\partial s}{\partial T}\right)_{P}}{\left(\frac{\partial s}{\partial P}\right)_{T}}.$$
(1.21)

The left-hand side of Eq. (1.21) is evaluated by differentiating the assumed pressuretemperature relation with respect to temperature, giving

$$\left(\frac{dP}{dT}\right)_s = \frac{\gamma_{PT}}{\gamma_{PT} - 1} \frac{P}{T}.$$
(1.22)

The right-hand side of Eq. (1.21) can be expanded using Maxwell relations (App. A.2)

$$-\frac{\left(\frac{\partial s}{\partial T}\right)_P}{\left(\frac{\partial s}{\partial P}\right)_T} = \frac{\left(\frac{\partial s}{\partial T}\right)_P}{\left(\frac{\partial v}{\partial T}\right)_P},\tag{1.23a}$$

$$= \frac{c_p}{T} \left(\frac{\partial T}{\partial v}\right)_P.$$
(1.23b)

Equating the left-hand side and right-hand side in Eq. (1.21), the following expression is found for the function γ_{PT} in terms of state variables [1]:

$$\gamma_{PT} = \frac{1}{1 - \frac{P}{c_p} \left(\frac{\partial v}{\partial T}\right)_P}.$$
(1.24)

In agreement with the previous sections, the isentropic pressure-temperature relation for an ideal gas can be demonstrated to be a subset of the solutions of Eq. (1.24). The partial derivative $(\partial v / \partial T)_P$ for an ideal gas becomes

$$\left(\frac{\partial v}{\partial T}\right)_P = \frac{R}{P}.\tag{1.25}$$

Elimination of the partial derivative in Eq. (1.24), the exponent γ_{PT} can be shown to reduce to the ratio of the specific heats in the ideal gas case

$$\gamma_{PT} = \frac{c_p}{c_p - R} = \frac{c_p}{c_v}. \qquad (ideal \ gas) \tag{1.26}$$

exponent γ_{PT}

1.4 Summary of the Isentropic Functions

In summary, the generalized isentropic relations for real substances introduced in the previous sections for are expressed as [1]

$$Pv^{\gamma_{Pv}} = const, \tag{1.27}$$

$$Tv^{\gamma_{Tv}-1} = const, \tag{1.28}$$

$$TP^{\frac{1-\gamma_{PT}}{\gamma_{PT}}} = const, \tag{1.29}$$

where the isentropic exponents are functions of state variables summarized as

$$\gamma_{Pv} = -\frac{v}{P} \frac{c_p}{c_v} \left(\frac{\partial P}{\partial v}\right)_T,\tag{1.30}$$

$$\gamma_{Tv} = 1 + \frac{v}{c_v} \left(\frac{\partial P}{\partial T}\right)_v,\tag{1.31}$$

$$\gamma_{PT} = \frac{1}{1 - \frac{P}{c_p} \left(\frac{\partial v}{\partial T}\right)_P}.$$
(1.32)

The isentropic functions Eqs. (1.30-1.32) are state variables that can be evaluated using any thermodynamic library or equation of state. Moreover, the accuracy of the generalized isentropic functions is determined only by the accuracy of the equation of state using to relate the state variables [3].

Additionally, as each of the isentropic functions has some derivative of pressure, temperature, or volume, they can be shown to be interdependent using the chain rule. One can use the cyclic P-v-T relation and eliminate the partial derivatives by Eqs. (1.30–1.32) to relate the isentropic exponents

$$\left(\frac{\partial P}{\partial v}\right)_s = \left(\frac{\partial T}{\partial v}\right)_s \left(\frac{\partial P}{\partial T}\right)_s.$$
(1.33)

Elimination of the partial derivatives using Eq. (1.7), Eq. (1.15) and Eq. (1.22), we find [1]:

$$\frac{\gamma_{Pv}}{\gamma_{Tv} - 1} = \frac{\gamma_{PT}}{\gamma_{PT} - 1}.$$
(1.34) relation between exponents

TWO

Approximate Real Isentropes

In the previous chapter, the isentropic relations for real gases were derived based on the presumed form of the pressure, volume, and temperature relation along an isentrope, Eqs. (1.27–1.29). The legitimacy of this assumption will be demonstrated in this chapter. However, we shall begin with a general notion on the ability of the real isentropic gas model to describe isentropic state changes.

Each of the isentropic exponents introduced in the previous chapter possesses a multivariate dependency on state variables, whose values change continuously along an isentrope. The isentropic exponents are therefore themselves state variables. However, we may think of thermodynamic regions where the values of the isentropic exponents are locally constant – such is the case of ideal gases for example where the adiabatic ratio is assumed constant. Similarly, to evaluate isentropic state changes of real gases, the isentropic exponents γ_{Pv} , γ_{Tv} , and γ_{PT} may assumed to be *locally constant functions*. This approximation is of a somewhat higher order than the assumption of constant specific heat ratio of ideal gases, as the latter indirectly imposes restrictions on the variation of the isobaric heat capacity c_p . The assumption locally constant values of the isentropic state changes.

The limits of this assumption may be clarified by Figure 2.1, which shows the discrepancy between the isentropic constant in Eq. (1.27) calculated with variable and constant values of the isentropic exponent γ_{Pv} . As the value of the constant in Eq. (1.27) is unique along each isentrope, the contours of the isentropic constant outline the contours of the isentropes by requirement. In Figure 2.1 the isentropes are approximated by their values of γ_{Pv} at the critical pressure. The critical pressure level has been chosen to demonstrate the ability of the continuous isentropic pressure-volume relation – the solid lines in Figure 2.1 – to demonstrate the ability of the model Eq. (1.27) to capture the highly non-linear fluid behavior at critical conditions. Note for example the curvature of the isentropes theoretically encountered in dense gases in Figure 2.1b [37–41], which is the subject of Chapter 10. The polytropic Van der Waals equation of state has been used to evaluate the function of γ_{Pv} , Eq. (1.30). The details of this procedure are discussed in Chapter 11.

Two important physical aspects can be outlined from this figure. Firstly, the approximate isentropes – the dashed lines in Figure 2.1 – form an increasingly better fit moving away from the critical point, in the limit where the solid and dashed lines will eventually coincide in the ideal limit for increasingly higher temperatures. Secondly, the discrepancy between the approximate and continuous isentropes increases with increasing molecular weight. The deviations are caused by higher order compressibility effects caused by the increased molecular complexity as the molecular size increases [37–41]. However, note that Figure 2.1 only displays the contours of the isentropic constants



Figure 2.1: Pressure-volume is entropes Eq. (1.27) with variable (—) and constant (– –) exponents for a molecular light and heavy Van der Waals substance.

regardless of their actual values. In the next chapter, we will see that the variation of the exponents γ_{Pv} , γ_{Tv} and γ_{PT} reduces with increased molecular weight.

Nevertheless, the message conveyed by Figure 2.1 on the validity of the assumption of constant isentropic exponents must be bared in mind throughout the subsequent chapters of this work. It presents the context in which the application of the approximated isentropic relations in later chapters are to be viewed.

2.1 Pressure-Volume Isentrope

In this and the following sections, the validity of the form of the isentropic relations assumed in Chapter 1 will be demonstrated, starting with the pressure-volume relationship. The form of the pressure-volume isentrope of section 1.1, can be shown to be correct by expressing the exact differential of entropy in terms of pressure and volume

$$ds = \left(\frac{\partial s}{\partial P}\right)_{v} dP + \left(\frac{\partial s}{\partial v}\right)_{P} dv.$$
(2.1)

The partial differentials of Eq. (2.1) can be rewritten using Maxwell relations (App. A.2). The resulting derivatives $-(\partial v/\partial T)_s$ and $(\partial P/\partial T)_s$, in turn, may be evaluated as the derivative of the isentropes in terms of temperature and volume Eq. (1.15), and pressure and temperature Eq. (1.22), summarized as

$$\left(\frac{\partial v}{\partial T}\right)_s = -\frac{1}{\gamma_{Tv} - 1} \frac{v}{T},\tag{2.2a}$$

$$\left(\frac{\partial P}{\partial T}\right)_{s} = \frac{\gamma_{PT}}{\gamma_{PT} - 1} \frac{P}{T}.$$
(2.2b)

Here we introduce the assumption of a locally constant value for the isentropic functions. From a mathematical point of view, the isentropes derived in this chapter may be viewed as approximation of an exponential function by a power function. Substitution of the partial derivatives back into Eq. (2.1) yields

$$ds = \frac{1}{\gamma_{Tv} - 1} \frac{v}{T} dP + \frac{\gamma_{PT}}{\gamma_{PT} - 1} \frac{P}{T} dv.$$

$$(2.3)$$

Introducing the real gas relation Pv = ZRT into the equation we obtain

$$ds = \frac{1}{\gamma_{Tv} - 1} ZR \frac{dP}{P} + \frac{\gamma_{PT}}{\gamma_{PT} - 1} ZR \frac{dv}{v}.$$
(2.4)

Rearranging terms, and introducing the relation between the isentropic exponents, Eq. (1.34), yields

$$\frac{\gamma_{Tv} - 1}{ZR} ds = \frac{dP}{P} + \gamma_{Pv} \frac{dv}{v}.$$
(2.5)

The ratio $ZR/(\gamma_{Tv} - 1)$, will be shown to be equal to the isochoric heat capacity c_v in Chapter 4. With respect to Eq. (4.13), the above equation does not include any

derivative terms following from the assumption of a constant value for the isentropic exponent γ_{Pv} . Integration of Eq. (2.5) between state zero and the arbitrary state s(P, v) gives

$$\frac{\Delta s}{c_v} = \ln P + \gamma_{Pv} \ln v + C. \tag{2.6}$$

Rearranging terms, we arrive at

$$Pv^{\gamma_{Pv}} = e^{\frac{\Delta s}{c_v} + C}.$$
(2.7)

When relating states along an isentrope, the change in entropy $\Delta s = 0$, for which the right-hand side of Eq. (2.7) becomes a constant whose value is unique for each isentrope. Moreover, as the isentropic exponent γ_{Pv} reduces to the ratio of the specific heats in the ideal case, it is easily verified that the ideal isentropes are a subset of the solutions of Eq. (2.7).

2.2 Temperature-Volume Isentrope

Similarly, the assumed form of the temperature-volume isentrope in section 1.2 can be demonstrated to be correct. Let the change in entropy be expressed as an exact differential in terms of temperature and volume

$$ds = \left(\frac{\partial s}{\partial T}\right)_v dT + \left(\frac{\partial s}{\partial v}\right)_T dv, \qquad (2.8)$$

where the partial derivative $(\partial s/\partial T)_v = c_v/T$ according to Maxwell relations. The right-hand side term of Eq. (2.8) is expanded using the triple product (App. A.1–A.2)

$$\left(\frac{\partial s}{\partial v}\right)_T = -\frac{c_v}{T} \left(\frac{\partial T}{\partial v}\right)_s.$$
(2.9)

Again, the partial derivative term $(\partial T/\partial v)_s$ is evaluated as the derivative of the Tv-isentrope, Eq. (1.15) in section 1.2

$$\left(\frac{\partial T}{\partial v}\right)_s = -(\gamma_{Tv} - 1)\frac{T}{v}.$$
(2.10)

Substitution of the derivatives into Eq. (2.9), the entropy change for real gasses can be expressed as

$$ds = c_v \frac{dT}{T} + c_v (\gamma_{Tv} - 1) \frac{dv}{v}.$$
 (2.11)

Integration between state zero an arbitrary state s(T, v) gives

$$\frac{\Delta s}{c_v} = \ln T + (\gamma_{Tv} - 1) \ln v + C.$$
(2.12)

Rearranging terms, we finally arrive at

$$Tv^{\gamma_{Tv}-1} = e^{\frac{\Delta s}{c_v} + C}.$$
(2.13)

It appears that for an isentropic process, for which $\Delta s = 0$, the right-hand side of Eq. (2.13) becomes constant along an isentrope, whose value is uniquely determined by the integration constant C that is unique for each isentrope.

2.3 Pressure-Temperature Isentrope

Lastly, the form of the isentropic pressure-temperature relation assumed in section 1.3 can be demonstrated to be correct in a very similar way as it was done for the temperature-volume isentrope. The only difference between the two will be the introduction of the isobaric specific heat capacity instead of the isochoric specific heat capacity. Again, let the entropy be a function of pressure and temperature. The change in entropy can be expressed as

$$ds = \left(\frac{\partial s}{\partial T}\right)_P dT + \left(\frac{\partial s}{\partial P}\right)_T dP, \qquad (2.14)$$

where the partial derivative $(\partial s/\partial T)_P = c_p/T$ following Maxwell relations. Like previously, the right-hand side term of Eq. (2.14) can be expanded using the triple product (App. A.1–A.2)

$$\left(\frac{\partial s}{\partial P}\right)_T = -\frac{c_p}{T} \left(\frac{\partial T}{\partial P}\right)_s.$$
(2.15)

The partial differential $(\partial T/\partial P)_s$ can be evaluated as the derivative of the pressurevolume isentrope, Eq. (1.22)

$$\left(\frac{dT}{dP}\right)_s = \frac{\gamma_{PT} - 1}{\gamma_{PT}} \frac{T}{P}.$$
(2.16)

Substitution of the partial derivatives back into Eq. (2.14), we obtain

$$ds = c_p \frac{dT}{T} - c_p \frac{\gamma_{PT} - 1}{\gamma_{PT}} \frac{dP}{P}.$$
(2.17)

Integration of relation Eq. (2.17) between the zero state and the arbitrary state s(P,T) gives

$$\frac{\Delta s}{c_p} = \ln T + \frac{1 - \gamma_{PT}}{\gamma_{PT}} \ln P + C.$$
(2.18)

Rearranging terms, we arrive at

$$TP^{\frac{1-\gamma_{PT}}{\gamma_{PT}}} = e^{\frac{\Delta s}{c_p} + C}.$$
(2.19)

Again, in the isentropic case Δs vanishes and the right-hand side of Eq. (2.19) reduces to a constant, that is uniquely determined for each isentrope by the integration constant C. Therefore, Eq. (2.18) reduces to the assumed form the *PT*-isentrope in case of an isentropic process.

THREE

Behavior of the Isentropic Exponents

The isentropic relations for real gasses were formally introduced in the preceding chapters. In this chapter, the limits and overall behavior of the isentropic exponents will be explored.

After the initial derivation of the real exponents γ_{Pv} , γ_{Tv} , and γ_{PT} , Kouremenos and his co-authors engaged in similar investigations on the behavior of the exponents for different substances including dry steam, ammonia, and some refrigerants [2, 32]. In this respect, their work had mostly been of semi-empirical nature rather than a rigorous analytical investigation.

Having demonstrated the generalized application of the isentropic relations Eqs. (1.27-1.29) in Chapter 2, we will now focus on understanding the behavior of the isentropic exponents themselves. The present study will be a general investigation into the trends observed in the behavior of the real isentropic exponents. The Van der Waals equation of state is of particular interest for qualitative analysis, owing to the mathematically simple modification to the ideal gas law to incorporate fundamental molecular interactions. With the intent of a general investigation, the Van der Waals will be expressed in reduced form, which allows comparison of the results for different substances according to the principle of corresponding states.

3.1 Van der Waals Isentropic Exponents

Expressing the isentropic exponents for a Van der Waals substance is indeed very straightforward and is mostly an exercise in algebraic manipulations. Each of the terms in the definitions of the isentropic functions are evaluated by the Van der Waals equation. The results of this procedure are summarized in Table 3.1. A summary of the Van der Waals equation is provided in Chapter 11 on numerical simulation of real gases, along with the Soave-Redlich-Kwong and Peng-Robinson equations of state.

Note that the Van der Waals relations for the isentropic exponents in Table 3.1 can be verified independently, as they are associated according to the relation between the exponents Eq. (1.34). The combination of any two expressions will result in the third exponent.

Pv-plane		
$\gamma_{Tv}(P_r, v_r) = 1 + \frac{R}{c_v} \frac{3v_r}{3v_r - 1}$		
$\gamma_{Pv}(P_r, v_r) = \frac{c_p}{c_v} \frac{3v_r^{3}(P_r + 3/v_r^{2}) - 6(3v_r - 1)}{v_r^{2}(P_r + 3/v_r^{2})(3v_r - 1) - 3(3v_r - 1)}$		
$\gamma_{PT}(P_r, v_r) = \frac{1}{1 - \frac{R}{c_p} \frac{v_r^3(P_r + 3/v_r^2) - 3v_r}{v_r^3(P_r + 3/v_r^2) - 2(3v_r - 1)}}$		
Tv-plane		
$\gamma_{Tv}(T_r, v_r) = 1 + \frac{R}{c_v} \frac{3v_r}{3v_r - 1}$		
$\gamma_{Pv}(T_r, v_r) = \frac{c_p}{c_v} \frac{24v_r^{\ 3}T_r - 6(3v_r - 1)^2}{8v_r^{\ 2}T_r(3v_r - 1) - 3(3v_r - 1)^2}$		
$\gamma_{PT}(T_r, v_r) = \frac{1}{1 - \frac{R}{c_p} \frac{8v_r^3 T_r - 3v_r (3v_r - 1)}{8v_r^3 T_r - 2(3v_r - 1)^2}}$		

Table 3.1: Isentropic exponents for a Van der Waals substance in reduced form, explicit in temperature and volume, and pressure and volume.

Although the reduced Van der Waals equation in principle does not require any information to characterize the substance, this is no longer true if we wish to evaluate the isentropic exponents due to their dependency on the specific heat capacities c_v and c_p . To close the problem, the isochoric and isobaric heat capacities need to be quantified. The isochoric heat capacity will be assumed constant between states and to be solely a function of the molecular structure of the substance according to the equipartition theorem [34, 42], also known as the polytropic gas model [26, 39, 43]. Under this assumption, the isochoric heat capacity is expressed as

$$c_v = \frac{f}{2}R,\tag{3.1}$$

where f is the molecular degrees-of-freedom. The minimum d.o.f of a single molecule is 3 – one along each dimension for translation through three-dimensional space. More complex molecular structures have additional other types of internal motions such as molecular vibrations or rotations, adding to the total molecular degree-of-freedom. The dependency of the *d.o.f* of a molecule to the number of molecules N is presented in Table 3.2.

The specific heat capacities are related by Eq. (3.2) by definition [34]. Under the assumption of a constant value of the isochoric heat capacity, the variation of the isobaric heat capacity is entirely determined by the equation of state according to

Table 3.2: Relation between the molecular degrees-of-freedom and molecular size according to the equipartition theorem.

monatomic	N = 1	f = 3
diatomic	N = 2	f = 5
linear polyatomic	N > 2	f = 3N

$$c_p = c_v + T \left(\frac{\partial v}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_v. \tag{3.2}$$

Before we continue with the real gas analysis, let us reason about the limiting values of Eq. (3.2) in the ideal case. In this case, Eq. (3.2) reduces to $c_p - c_v = R$. As the isochoric specific heat capacity c_v is only a function of the molecular degree of freedom under the polytropic gas assumption, the same hold for the isobaric heat capacity c_p . In the ideal gas limit we have

$$c_v = \frac{f}{2}R, \quad c_p = \left(1 + \frac{f}{2}\right)R, \text{ and } \gamma = 1 + \frac{2}{f}.$$
 (3.3)

Referring to the specific heat ratio in relation to the molecular degree of freedom Table 3.2, the ideal adiabatic coefficient γ can be demonstrated to attain a maximum value of 1.6 for a monatomic gas, and approaches the value of 1 as the size of the molecule increases [33, 34]. Although this is not the general case for the real isentropic exponents, the same limit is satisfied in the ideal limit.

We will now continue with the real gas analysis using the Van der Waals equation of state. The relation between the specific heats Eq. (3.2) can be expressed as [44]

$$c_p = c_v + \frac{R}{1 - \frac{(3v_r - 1)^2}{4T_r v_r^3}}.$$
(3.4)

Due to the dependency of the specific heat capacities on the molecular composition, the analysis of behavior of the real isentropic exponents will explore two molecular species representing two limiting cases regarding molecular size. A light diatomic molecule will be considered, for which $c_v = 2.5R$, and a much heavier molecule for which $c_v = 50R$.

Although the isobaric specific heat capacity is no longer solely a function of the molecular size as in the ideal case, the limits of c_p in the non-ideal case may be explored in a similar way. With an increase of the molecular size, the term c_v in the expression for c_p above becomes increasingly more dominant, in the limiting case where $c_p \rightarrow c_v$ for a infinitely large molecule. The variation of the isobaric heat capacity on the isochoric heat capacity, therefore, becomes less pronounced as the molecular size increases, in the limit where c_p also becomes constant.

3.2 Physical Limits of the Isentropic Exponents

Physical limits bind the domain of the isentropic functions, forming a natural condition for validity of the isentropic gas model. Exploring these limits provides an intuitive way to start the investigation of the behavior of the isentropic relations, for which an equation of state does not yet have to be specified.

Two limits can be identified in the positive pressure-volume plane, consisting off the ideal gas limit as $v_r >> 1$ and the incompressible liquid model as $v_r << 1$. These two conditions are to be satisfied as boundary condition for the generalized isentropic substance model. The ideal gas limit is attained as either the temperature goes to infinity or the pressure of the system tends to zero [33, 34]. The incompressible limit for a Van der Waals substance is attained as the reduced volume as v_r tends to 1/3, corresponding to the limit where the size of the system becomes equal to molecular volume denoted as coefficient b in the Van der Waals equation. The area to the left of $v_r = 1/3$ is therefore unphysical and excluded from further discussion.

When the temperature tends to infinity, the behavior of any gas has been proven to approach ideal gas behavior under any circumstance [34]. The original authors also demonstrated that the real isentropic exponents tend to the value of $\gamma = c_p/c_v$ at increasingly higher temperatures, but did not explicitly demonstrated the equivalence between the two [1].

Inversely, one might of the resemblance with the ideal gas case to be a mathematical requirement, since the derivation of the real gas isentropic relations started out by the assumption of the ideal formulation. In fact, under the ideal analysis, the exponents γ_{Pv} , γ_{Tv} , and γ_{PT} together form different terms of Mayer's relation for an ideal gas [33, 34]

ideal gas limit

$$\gamma_{Pv} = \frac{c_p}{c_v}, \quad \gamma_{Tv} = \frac{c_v + R}{c_v}, \quad \text{and} \quad \gamma_{PT} = \frac{c_p}{c_p - R}.$$
(3.5)



Figure 3.1: Compression of an incompressible liquid

Conversely, the incompressible substance model must be satisfied for liquid states. The values for the isentropic exponents for an incompressible fluid can be obtained by letting the reduced volume $v_r \rightarrow 1/3$ in the Van der Waals expressions of the isentropic exponents. The incompressible limit can be explored heuristically, by considering a liquid brought under pressure in a piston arrangement Figure 3.1a. For an incompressible substance, the isentropic pressure-volume relationship reduces to an isochoric process for which $\gamma_{Pv} \rightarrow \infty$, Figure 3.1b. Upon isentropic compression of an incompressible fluid, the internal energy, and therefore the temperature, should remain unchanged. From here follows that the temperature is completely independent of changes in either pressure or volume for an incompressible substance, Figure 3.1c. Accordingly, the exponents γ_{Tv} and γ_{PT} tend to infinity and one in the incompressible limit, respectively. The incompressible limit can be summarized as

$$\gamma_{Pv} = \infty, \quad \gamma_{Tv} = \infty, \quad \text{and} \quad \gamma_{PT} = 1.$$
 (3.6) *incompressible limit*

Between the two volumetric limits, the two-phase region predicted by the Van der Waals equation imposes another boundary of the domain of the isentropic functions. The specific heat capacities are undefined in the coexistence region, thus neither are the exponents γ_{Pv} , γ_{Tv} , and γ_{PT} . From here we can conclude that the applicability of the generalized isentropic model is limited to stable single phase substances, as is also the case of the ideal isentropic model.

We conclude our discussion on the limits of the isentropic exponents by the limit imposed by the thermodynamic singularity at the critical point. This limit may be explored by setting $T_r = 1$ in the Van der Waals expressions for the isentropic exponents and by letting $v_r \rightarrow 1$. At the critical point, the isentropic exponents assume indeterminate forms, the exponent γ_{Tv} being the only exception which assumes a value of $1 + 3R/2c_v$. The limits of the isentropic exponents are summarized in Table 3.3.

	$\begin{array}{c} critical \ limit\\ v_r=1 \end{array}$	$\begin{array}{c} ideal \ gas \ limit \\ v_r \rightarrow \infty \end{array}$
$\gamma_{Pv} o \infty$	$\gamma_{Pv} = \infty$	$\gamma_{Pv} = \frac{c_p}{c_v}$
$\gamma_{Tv} o \infty$	$\gamma_{Tv} = 1 + \frac{3R}{2c_v}$	$\gamma_{Tv} = \frac{c_v + R}{c_v}$
$\gamma_{PT} \rightarrow 1$	$\gamma_{PT} = \infty$	$\gamma_{PT} = \frac{c_p}{c_p - R}$

Table 3.3: Isentropic limits in the pressure-volume diagram

3.3 Contours of the Isentropic Exponents

Now that the boundaries of the domain of the isentropic functions have been identified, their general behavior between those limits can be studied using the Van der Waals equation of state. We will turn to contour plots of the isentropic exponents which provide a graphical way to interpret their behavior, with it also raising the question of what lines of constant γ_{Pv} , γ_{Tv} , and γ_{PT} physically represent. To answer this underlying thought, observe that in the definition of the isentropic exponents Eqs. (1.30–1.32) all three exponents are composed of two physically different terms; either an explicit or implicit formulation of the specific heat ratio and a term involving compressibility of the state. The isentropic exponents may, therefore, be viewed as "compressibility corrected heat capacity ratios" where the derivative term is corrected according to its gas behavior and its density. The isentropic exponent γ_{Pv} , for example, includes the derivative term $(\partial P/\partial v)_T$ which for a given pressure is "corrected" for its location in the Pv-diagram as the compressibility of low-density gasses is naturally higher than liquids which have a much higher density.



Figure 3.2: Contours of γ_{Tv} of a Van der Waals substance

The contours of γ_{Tv} in Figure 3.2a and 3.2b consist of logarithmically spaced vertical lines, which is not surprising given the fact that the reduced volume is the only variable in the polytropic Van der Waals model for γ_{Tv} (see Table 3.1). The volumetric limit bounds the left-hand side at $v_r = 1/3$ for which γ_{Tv} goes to infinity, causing the logarithmic spacing of the contours towards this limit. At the right-hand side of the domain, the value of γ_{Tv} tends to the ideal gas limit and approaches $1 + R/c_v$ in both cases. By definition, γ_{Tv} is always positive as none of the terms in the analytical expression Eq. (1.31) can attain a negative sign. The derivative term $(\partial P/\partial T)_v$, or the pressure change by heating of a closed volume, must be positive from the condition of mechanical stability [34]. From here γ_{Tv} can be reasoned to be bound by the domain:

$$\infty > \gamma_{Tv} \ge 1 + \frac{R}{c_v}.$$
(3.7) domain γ_T

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The contour levels plotted for the light molecule $c_v = 2.5R$ and the heavy molecule $c_v = 50R$ in Figure 3.2 are of the same order of magnitude. Although the plots of both substances possess the same general features, due to the reduced variation of the isobaric heat capacity for large molecules, as was reasoned in section 3.1, the variation of γ_{Tv} has become more gradual, and its features are "squeezed" towards the incompressible limit. This trend will also be observed in the contour plots of γ_{Pv} and γ_{Tv} as we shall now see.



Figure 3.3: Contours of γ_{Pv} of a Van der Waals substance

Contours of the isentropic exponent γ_{Pv} are displayed in Figure 3.3a and 3.3b, bound by the same limits as γ_{Tv} . Because the value of γ_{Pv} tends to infinity as the reduced volume $v_r \rightarrow 1/3$, a logarithmic spacing of the contour lines toward this limit is again observed. The latter is more pronounced for the larger molecules than the smaller molecules, due to the reduced variations between the specific heats c_p and c_v for larger molecules.

Similar to γ_{Tv} the isentropic exponent γ_{Pv} can be reasoned to be restricted to positive values only, as solely the derivative term $(\partial P/\partial v)_T$ in the definition of γ_{Pv} can change sign. The sign change predicted by the Van der Waals equation can be seen graphically by looking at the isotherms plotted in Figure 3.4.



Figure 3.4: Van der Waals isotherms and spinodal line

The derivative $(\partial P/\partial v)_T$ is negative for any stable single phase substance by the requirement of mechanical stability [33, 34]. Due to the minus sign in the definition of γ_{Pv} , the exponent γ_{Pv} , Eq. (1.30) is always positive. Moreover, the region where the partial derivative $(\partial P/\partial v)_T$ is predicted to change sign by the Van der Waals equation is enclosed by the two-phase region. The conditions of mechanical and thermal stability in the two-phase region are replaced by the requirement of equal chemical potential between the phases. The line where $(\partial P/\partial v)_T$ is zero – or alternatively, where γ_{Pv} is zero – denotes the line of ultimate stability of a single phase substance. Equating the exponent γ_{Pv} in Table 3.1 to zero we find the analytical expression of the dashed line in Figure 3.4, better known as the Van der Waals spinodal [45, 46] expressed as:

$$P_r = \frac{3v_r - 2}{v_r^3}, \text{ and } T_r = \frac{(3v_r - 1)^2}{4v_r^3}.$$
 (for $\gamma_{Pv} = 0$) (3.8)

This feature of
$$\gamma_{Pv}$$
 is of course not reserved for the Van der Waals substances only.
The spinodal line of any equation of state that predicts phase transitions can be obtained
by equating the exponent γ_{Pv} to zero.

From the above discussion follows that the γ_{Pv} spans the entire domain of positive rational numbers from zero to infinity:

domain γ_{Pv}

Van der Waals spinodals

$$\infty > \gamma_{Pv} \ge 0. \tag{3.9}$$

Values between zero the ideal limit c_p/c_v are observed in a narrow band along the spinodal line on the vapor side, which perhaps might be the result of the over prediction of the Van der Waals equation in this region.



Figure 3.5: Contours of γ_{PT} of a Van der Waals substance

We conclude this section on the behavior of the isentropic exponents by looking at the contours of γ_{PT} in Figure 3.5a and 3.5b. The contours of γ_{PT} look distinctly different from those of γ_{Pv} and γ_{Tv} , mostly due to absence of a limit towards infinity in the incompressible limit.

The limit of γ_{PT} to one in the incompressible case has another effect, shown in Figure 3.5b. As the isobaric heat capacity tend to the isochoric heat capacity for increasingly larger molecules $c_p \rightarrow c_v$, the ideal gas limit also tend to one. As a result, the variation of γ_{PT} becomes ever more uniform throughout the *Pv*-plane fro high molecular weight substances. Only the metastable states around the spinodal lines show slight changes in γ_{Tv} .

Lastly, note that the partial derivative $(\partial v/\partial T)_P$ in the definition of γ_{PT} must be positive for any single phase substance by the condition of thermal stability [34]. Furthermore, as neither P nor c_p can be negative, it follows that γ_{PT} is always positive, and cannot attain values smaller than one:

$$\infty > \gamma_{PT} \ge 1.$$
 (3.10) domain γ_{PT}

The limit where γ_{PT} is equal to 1 will be demonstrated to have special significance in Chapter 5, denoting the state of maximum density of a substance.

The trend of reduced variation of the isentropic exponents for high molecular weight substances was generally observed in this section. What does this say about the behavioral differences between high and low molecular weight species? From a mathematical point of view, a region where the isentropic exponents show only small variations can be reasoned to have isentropes with only small variations in their shape. Turning to the isentropic relations Eqs. (1.27), (1.28), and (1.29) of Chapter 1, a reduced variation of the isentropic exponents between adjacent isentropes implies that the isentropic state change is less dependent on the initial state.

Although this argument is certainly true from a mathematical point of view, the reality is more complicated. Recall from our previous discussion on the isentropic limits, that high values of γ_{Pv} and γ_{Tv} are associated with reduced compressibility moving towards liquid states. As the "sqeezing" of the contours towards the incompressible limit is a featured shared by both γ_{Pv} and γ_{Tv} , the former implies that high molecular weight substances in a supercritical state retain their gaseous compressibility longer than lower molecular weight species. The use of the term "gaseous compressibility" in this context is relative, however, as high molecular weight substances already exhibit reduced compressibility owing to higher densities in the gaseous phase.
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PART II

REAL PROPERTY RELATIONS

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In Part II of this work, the relation between the real isentropic gas model and other thermodynamic properties is explored and tested for consistency. Moreover, by relating the isentropic model to other thermodynamic properties, the model will be put into a broader perspective from which new insights will arise. In this process, we will also derive thermodynamic properties and derivatives in terms of the real isentropic exponents which may provide an alternative approach in calculating thermodynamic quantities in nonideal compressible gas flow simulations. The development of these relations will be the aim of Chapters 4 and 5. These relations will then be used in the final two chapters of this Part where the isentropic compression work of a real gasses is derived, and the ideal gas entropy change is extended to real gases.

FOUR

Real Specific Heat Functions and Compressibility

When we take a closer look at the definitions of the exponents of the generalized isentropic gas model Eqs. (1.27–1.32), we may recognize a multivariate dependency on both mechanical and thermal properties. In this regard, one might wonder how the isentropic gas model is related to other thermodynamic properties and concepts. This feeling furthermore emphasized by the notion that the ideal gas adiabatic coefficient $\gamma = c_p/c_v$ makes a frequent reappearance in – seemingly different – thermodynamic concepts.

In this chapter, we will explore the connection between the real isentropic gas model and the specific heat relations. Given the fact that the specific heat capacities of an ideal gas can be elegantly related to the universal gas constant, one might suspect a similar relation to hold for substances in general, involving the real adiabatic coefficients γ_{Pv} , γ_{Tv} , and γ_{PT} . The specific heats of an ideal gas are related by [33, 34]

$$c_p - c_v = R. \tag{4.1}$$

The specific heats can in turn be expressed as a function of the adiabatic coefficient and the universal gas constant

$$c_p = \frac{\gamma}{\gamma - 1} R$$
, and $c_v = \frac{R}{\gamma - 1}$. (4.2)

Demonstrating how Eq. (4.1) and Eq. (4.2) are related to the real isentropic exponents for calorically imperfect gases will be the purpose of this chapter. But first, we may elaborate on how the above expressions relate to gas compressibility.

Under the equipartition theorem, each molecular degree of freedom is demonstrated to contribute to the total internal energy of the molecule in equal parts [34, 42]. For a substance in thermal equilibrium, the macroscopic temperature of the gas is related to the average kinetic energy of its microscopic particles by the Boltzmann constant k_b , providing a physical relation between the energy and absolute temperature scales. The same holds true for the universal gas constant R, which may be thought of as a special case of the Boltzmann constant on a per mole basis by multiplication with Avogadro's number as

$$k_b = \frac{R}{N_A}.$$
(4.3)

In a more traditional sense, the universal gas constant was initially derived as the common limiting value as the pressure tends to zero, summarized as



Figure 4.1: Universal gas constant as limiting value for $P \rightarrow 0$.

$$\lim_{P \to 0} \frac{Pv}{T} = R,$$
(4.4a)

$$\lim_{P \to 0} Z = 1. \tag{4.4b}$$

The limits in Eq. (4.4) are displayed graphically in Figure 4.1, written as ZR = Pv/T. It is from here that we may start to appreciate the true implication of the term ZR – a term which will make a frequent appearance throughout this work. Whereas the compressibility factor is mostly defined as the ratio between the real and ideal volume of a gas, capturing the departure of mechanical behavior of a gas from the ideal case, the term ZR may be regarded as the departure of thermal behavior from the ideal case

$$\lim_{R \to 0} ZR = R. \tag{4.5}$$

4.1 Specific Heat Relation for Calorically Imperfect Gases

We will now turn to the relation between the specific heats to generalize this function for calorically imperfect gases. Considering the preceding discussion, we might already be able to guess that such a relation can be expressed solely in terms of the compressibility factor, universal gas constant and temperature. Developing this relationship will be the aim of this section.

Recall the relation between the specific heat capacities, defined as

$$c_p - c_v = T \left(\frac{\partial v}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_v.$$
(4.6)

The compressibility factor Z is introduced into the derivative terms. As the compressibility factor itself has a multivariate dependency on P, v, and T, the chain rule will give us addition derivatives in Z and T

$$\left(\frac{\partial v}{\partial T}\right)_{P} = \frac{ZR}{P} + \frac{RT}{P} \left(\frac{\partial Z}{\partial T}\right)_{P}, \qquad (4.7a)$$

$$\left(\frac{\partial P}{\partial T}\right)_{v} = \frac{ZR}{v} + \frac{RT}{v} \left(\frac{\partial Z}{\partial T}\right)_{v}.$$
(4.7b)

Substitution of expressions Eq. (4.7a) and Eq. (4.7b) in to the original relation yields

$$c_p - c_v = T \left[\frac{ZR}{P} + \frac{RT}{P} \left(\frac{\partial Z}{\partial T} \right)_P \right] \left[\frac{ZR}{v} + \frac{RT}{v} \left(\frac{\partial Z}{\partial T} \right)_v \right].$$
(4.8)

Rearranging terms, and further reduction of variables by again introducing the compressibility factor Z = Pv/RT, the relation between the specific heat capacities can be expressed solely in terms of the combination of thermal properties Z, R, and T.

specific heat relation

$$c_p - c_v = \frac{R}{Z} \left[Z + T \left(\frac{\partial Z}{\partial T} \right)_P \right] \left[Z + T \left(\frac{\partial Z}{\partial T} \right)_v \right]$$
(4.9)

It can be readily shown that the specific heat relation for an calorically perfect gas is a special case of Eq. (4.9), for which Z = 1 and constant. The latter implies the derivatives involving the compressibility factor reduce to zero, for which can be seen that Eq. (4.9) reduces to $c_p - c_v = R$ in the ideal gas case.

4.2 Real Specific Heat Functions

Using the same methodology, the specific heat capacities may be related to the isentropic exponents and the gas compressibility as for and ideal gas. Developing the real counterparts of the ideal specific heat functions will be the purpose of this section.

An expression for c_p can be derived with a similar manipulation as was done previously for the relation between the specific heats. Starting from the definition of the isentropic exponent γ_{PT} Eq. (1.32), the derivative term $(\partial v/\partial T)_P$ can be evaluated using the compressibility factor written as v = ZRT/P. Elimination of the derivative using Eq. (4.7a) yields

$$\gamma_{PT} = \frac{1}{1 - \frac{R}{c_p} \left[Z + T \left(\frac{\partial Z}{\partial T} \right)_P \right]}.$$
(4.10)

Rearranging in terms of c_p , the following expression is found for the isobaric heat capacity as a function of the compressibility factor, temperature and the ideal gas constant as

$$c_{p} = \frac{\gamma_{PT}}{\gamma_{PT} - 1} R \left[Z + T \left(\frac{\partial Z}{\partial T} \right)_{P} \right].$$
(4.11) isobaric heat function

It can be shown that the equation for the isobaric heat capacity Eq. (4.11) is equivalent to the ideal gas form, as the gas compressibility factor is equal to one and constant for an ideal gas, reducing any derivative in Z to zero. Moreover, as γ_{PT} is just c_p/c_v in the ideal gas case, the above relation indeed reduces to the ideal form.

Similarly, the isochoric heat capacity can be expressed in terms of the gas compressibility by elimination of the derivative $(\partial P/\partial T)_v$ in the definition of γ_{Tv} by Eq. (4.7b) resulting in

$$\gamma_{Tv} = 1 + \frac{R}{c_v} \left[Z + T \left(\frac{\partial Z}{\partial T} \right)_v \right]. \tag{4.12}$$

Rearranging in terms of c_v the following relation is obtained:

$$c_{v} = \frac{R}{\gamma_{Tv} - 1} \left[Z + T \left(\frac{\partial Z}{\partial T} \right)_{v} \right].$$
(4.13) *isochoric heat function*

Using the same arguments as before, it is clear that under the ideal gas assumption Eq. (4.13) reduces to the ideal gas case Eq. (4.2).

This leaves one exponent being unused. Looking at the definition of γ_{Pv} in Eq. (1.30) the ratio of the specific heats is instantly recognized. Using the previous relations for the specific heat capacity c_v and c_p , the equivalence between γ_{Pv} and the ratio of specific heats is further emphasized. Let γ_{Pv} be expressed in terms of the other exponents (1.34)

$$\gamma_{Pv} = (\gamma_{Tv} - 1) \left(\frac{\gamma_{PT}}{\gamma_{PT} - 1} \right). \tag{4.14}$$

Substitution of the expressions for γ_{PT} (4.10) and γ_{Tv} (4.12) and rearranging terms the expression for the adiabatic exponent γ_{Pv} yields

$$\gamma_{Pv} = \frac{c_p}{c_v} \left[\frac{Z + T \left(\frac{\partial Z}{\partial T} \right)_v}{Z + T \left(\frac{\partial Z}{\partial T} \right)_P} \right], \tag{4.15}$$

where the adiabatic coefficient simply reduces to c_p/c_v under the ideal gas assumption. Alternatively, the following expression is found for the ratio of the specific heats:

$$\frac{c_p}{c_v} = \gamma_{Pv} \left[\frac{Z + T\left(\frac{\partial Z}{\partial T}\right)_P}{Z + T\left(\frac{\partial Z}{\partial T}\right)_v} \right].$$
(4.16) heat ratio function

FIVE

Other Thermodynamic Properties and Derivatives

In the previous chapter we demonstrated the relation between the real isentropic exponents and the specific heat functions, thereby reaffirming our suspicions of a broader connection to other thermodynamic quantities. Continuing this line of reasoning, the generalized isentropic gas model will be brought in relation to a variety of other thermodynamic properties in this chapter. In doing so, we will fully resolve the derivatives between thermodynamic properties, whose general applicability can provide a more usable and direct way to obtain derivatives in non-ideal compressible gas flows simulations. The derivatives will be derived in this chapter, and are listed in Appendix A.3 for convenience.

5.1 Derivatives of Mechanical Properties

The real isentropic exponents were dubbed "compressibility corrected specific heat ratios" in Chapter 3. Indeed, the similarity between the isentropic exponents and the specific heat ratio c_p/c_v in the ideal case has been demonstrated on several occasions, ultimately leading to the development of the specific heat functions for calorically imperfect gases in the previous chapter. The latter part of this interpretation, the relation between the isentropic exponents and compressibility coefficients, will be outlined in this section.

In recent work by Baltadjiev on "An Investigation of Real Gas Effects in Supercritical CO_2 compressors" in 2012 [35, 36], the relation between the isentropic exponents and the compressibility coefficients has been demonstrated by incorporating them into their definitions. In the current discussion, however, we will aim to relate some of the special features of the compressibility coefficients to the value of the isentropic exponents.

Let the volume of a single phase substance be a function of natural variables, those of temperature and pressure v = v(T, P). The change in specific volume becomes

$$dv = \left(\frac{\partial v}{\partial T}\right)_P dT + \left(\frac{\partial v}{\partial P}\right)_T dP.$$
(5.1)

The two thermodynamic properties related to the partial derivatives appearing in Eq. (5.1) are the thermal expansion coefficient β and the isothermal compressibility κ commonly expressed as

$$\beta = \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_P, \quad \text{and} \quad \kappa = -\frac{1}{v} \left(\frac{\partial v}{\partial P} \right)_T.$$
(5.2)

We will first consider the the thermal expansion coefficient β . The thermal expansion coefficients describes the volume change of a substance caused by heating at constant pressure. The case where β is equal to zero refers to a special state, designated the *state* of maximum density. A notable example is the state of maximum density of water at a temperature of around 4°C at atmospheric pressure [47].

As the definitions of the isentropic exponents are exact a state, the thermal expansion coefficient β can be related to the isentropic exponent γ_{PT} in Eq. (1.32) as [35, 36]

$$\beta = \frac{\gamma_{PT} - 1}{\gamma_{PT}} \frac{c_p}{Pv}, \quad \text{or} \quad \beta = \frac{\gamma_{PT} - 1}{\gamma_{PT}} \frac{c_p}{ZRT}.$$
(5.3)

The condition of maximum density, may thus be related to the value of γ_{PT} being equal to one. This limit was demonstrated to be the lower bound of the domain of γ_{PT} in Chapter 3. As "gaseous" equations of state do not accurately predict liquid densities, this feature of water was not captured by the Van der Waals equation in Chapter 3. For a calculation, one must resort to a liquid equation of state such as the Tait equation to evaluate γ_{PT} for liquid states [48, 49].

Similarly, the isothermal compressibility coefficient κ may be related to the isentropic exponent γ_{Pv} by elimination of the derivative $(\partial v/\partial P)_T$ by Eq. (1.30). Although this leads to a very trivial result in case of gases, a more special form is obtained if we consider liquid states. Instead of the isothermal compressibility coefficient κ , we introduce the adiabatic bulk modulus K for liquids [50], defined as

$$K = -v \left(\frac{dP}{dv}\right)_T.$$
(5.4)

The bulk modulus is a measure of the incompressibility – or "spring constant" – of liquids, and defines the speed of sound in liquids according to the Newton-Laplace equation [50–52]. Comparing the Newton-Laplace equation with the general speed of sound equation Eq. (8.3), which will be formally introduced in Chapter 8, we obtain the following relation between the liquid bulk modulus and the isentropic exponent γ_{Pv} :

$$c = \sqrt{\frac{K}{\rho}}, \quad \text{where} \quad K = \gamma_{Pv} P.$$
 (5.5)

Newton-Laplace equation

From classical thermodynamics, the adiabatic bulk modulus of ideal gases can be readily derived as $K = \gamma P$ [51, 52]. The relation between the bulk modulus and the isentropic exponent γ_{Pv} presented in (5.5) can therefore be concluded to be the general from of this relation.

Values of the bulk modulus K between gaseous and liquid states differ by several orders of magnitude (kPa~MPa for gases, GPa for liquids [51, 52]). In the former case, the order of magnitude is completely determined by the pressure of the gas. In the latter case, the derivative $(\partial P/\partial v)_T$ becomes large due substance incompressibility, the order of magnitude of K for liquids is a combination of liquid incompressibility and the exerted pressure. The Newton-Laplace equation and the ideal gas relation for the speed of sound are therefore two limiting cases of the general speed of sound relation Eq. (8.3) in Chapter 8.

5.2 Derivatives of Internal Energy and Enthalpy

Another fundamental set of thermodynamic derivatives is formed by derivatives in internal energy and enthalpy, which will conclude this our investigation between the real isentropic model and other thermodynamic properties. In this process, we will ultimately derive of the Joule coefficient μ_J and Joule-Thomson coefficient μ_{JT} [33, 34] in terms of the isentropic exponents. Although the Joule coefficient – defined as the derivative of temperature with respect to volume at constant internal energy – has limited practical significance, it is included in this section for sake of completeness. The derivatives developed in this process are listed in Appendix A.3.

Let the enthalpy of a system be describe in terms of temperature and pressure h = h(T, P). For an isenthalpic process, the change in enthalpy can be written as

$$dh = \left(\frac{\partial h}{\partial T}\right)_P dT + \left(\frac{\partial h}{\partial P}\right)_T dP.$$
(5.6)

The partial derivatives in Eq. (5.6) can be expressed as

$$\left(\frac{\partial h}{\partial T}\right)_P = c_p, \quad \text{and} \quad \left(\frac{\partial h}{\partial P}\right)_T = -T\left(\frac{\partial v}{\partial T}\right)_P + v.$$
 (5.7)

Furthermore, the partial derivative $(\partial T/\partial P)_h$ defined as the Joule-Thomson coefficient can be expressed in terms of the partial derivatives in Eq. (5.7) using the triple product (App. A.1). Combining the two partial derivatives we find:

$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_h = \frac{1}{c_p} \left[T \left(\frac{\partial v}{\partial T}\right)_P - v \right].$$
(5.8)

Eliminating the partial derivative $(\partial v/\partial T)_P$ by the isentropic exponent γ_{PT} , the Joule-Thomson coefficient μ_{JT} can be expressed as:

$$\mu_{JT} = \frac{T}{P} \frac{\gamma_{PT} - 1}{\gamma_{PT}} - \frac{v}{c_p}, \quad \text{or} \quad \left[\mu_{JT} = \frac{T}{P} \left[\frac{\gamma_{PT} - 1}{\gamma_{PT}} - \frac{ZR}{c_p} \right].$$
(5.9)

The Joule-Thomson effect describes the temperature change of substances when undergoing an adiabatic throttling process. Since this effect is absent in ideal gases, its occurrence can be completely attributed to molecular kinetics in real gases [33, 34]. Moreover, as real gas effects are included into the isentropic gas model, the slope of the isenthalpic curve described by the Joule-Thomson coefficient can, therefore, be related to conditions related to the value of the isentropic exponent γ_{PT} .

It can be verified that Eq. (5.9) reduces to zero in the ideal case for which the isentropic exponent γ_{PT} reduces to the ratio of the specific heats. By equating μ_{JT} to zero, one can relate the properties of the Joule-Thomson coefficient explicitly to the value of γ_{PT} . Moreover, given the relation between the isentropic exponent γ_{PT} and the specific heat capacity c_p Eq. (4.11), the sign of u_{JT} can be related to the value and sign of the derivative $(\partial Z/\partial T)_P$, see Table 5.1.

A similar reasoning can be performed for derivatives related to internal energy. We chose the natural variables temperature and internal energy to define the internal energy of a substance, e = e(T, v). For an iso-energetic process, we can write

$$de = \left(\frac{\partial e}{\partial T}\right)_v dT + \left(\frac{\partial e}{\partial v}\right)_T dv.$$
(5.10)

The partial derivatives in Eq. (5.10) expressed as

$$\left(\frac{\partial e}{\partial T}\right)_v = c_v, \quad \text{and} \quad \left(\frac{\partial e}{\partial v}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_v - P.$$
 (5.11)

Again, the third partial derivative $(\partial T/\partial v)_e$, known as Joule's coefficient, can be expressed as a function of the other derivatives using the triple product giving

$$\mu_J = \left(\frac{\partial T}{\partial v}\right)_e = -\frac{1}{c_v} \left[T\left(\frac{\partial P}{\partial T}\right)_v + P\right].$$
(5.12)

The partial derivative $(\partial P/\partial T)_v$ can be eliminated by the isentropic exponent γ_{Tv} to yield Eq. (5.13). Like for the Joule-Thomson coefficient, one could relate similar conditions of μ_J to the value of the isentropic exponent γ_{Tv} . However, this will not be shown here, as the Joule coefficient has limited practical importance.

$$\mu_J = \frac{T}{v}(1 - \gamma_{Tv}) - \frac{P}{c_v}, \quad \text{or} \quad \mu_J = \frac{T}{v} \left[(1 - \gamma_{Tv}) - \frac{ZR}{c_v} \right].$$
(5.13)

Table 5.1: Conditions relating the value of $(\gamma_{PT} - 1)/\gamma_{PT}$ and the derivative $(\partial Z/\partial T)_P$ to the sign of the Joule-Thomson coefficient.

cooling	$\mu_{JT} > 0$	$\frac{\gamma_{PT} - 1}{\gamma_{PT}} > \frac{ZR}{c_p}$	$\left(\frac{\partial Z}{\partial T}\right)_P < 0$
inversion	$\mu_{JT} = 0$	$\frac{\gamma_{PT} - 1}{\gamma_{PT}} = \frac{ZR}{c_p}$	$\left(\frac{\partial Z}{\partial T}\right)_P=0$
heating	$\mu_{JT} < 0$	$\frac{\gamma_{PT} - 1}{\gamma_{PT}} < \frac{ZR}{c_p}$	$\left(\frac{\partial Z}{\partial T}\right)_P > 0$

SIX

Isentropic Work

The isentropic work defines the theoretical path-of-least-energy of an compression or expansion process between two states, providing an absolute reference to which the operation of non-reversible processes can be compared. In this chapter, the isentropic compression and expansion of a real fluid will be derived and their implications discussed.

Starting from the definition of enthalpy, the change in enthalpy for an isentropic process becomes a function of vdP, depending only on the initial and final states 1 and 2 from

$$dh = T \not ds + v dP, \tag{6.1}$$

where ds = 0. The finite enthalpy difference Δh is obtained by integration of Eq. (6.1) between arbitrary states 1 and 2 expressed as

$$\Delta h = \int_{1}^{2} v dP. \tag{6.2}$$

The pressure-volume relationship along an isentrope is described by Eq. (1.27) which can be expressed as $Pv^{\gamma_{P_v}} = P_1v_1^{\gamma_{P_v}}$. Here the assumption of a locally constant value of the function γ_{P_v} is introduced. The validity of this assumption is bound to compressibility effects set by the thermodynamic region. Eliminating the volume in Eq. (6.2), the integral becomes explicit in pressure:

$$\Delta h = \int_{1}^{2} v_1 \left(\frac{P_1}{P}\right)^{\frac{1}{\gamma_{Pv}}} dP.$$
(6.3)

The change in enthalpy for an isentropic compression process becomes

$$W_{c_{21}} = h_2 - h_1 = v_1 P_1 \frac{\gamma_{Pv}}{\gamma_{Pv} - 1} \left[\left(\frac{P_2}{P_1} \right)^{\frac{\gamma_{Pv} - 1}{\gamma_{Pv}}} - 1 \right],$$
(6.4)

isentropic work process and for an isentropic expansion process we have

$$W_{t_{21}} = h_2 - h_1 = v_1 P_1 \frac{\gamma_{Pv}}{\gamma_{Pv} - 1} \left[1 - \left(\frac{P_2}{P_1}\right)^{\frac{1 - \gamma_{Pv}}{\gamma_{Pv}}} \right].$$
(6.5)

Eqs. (6.4) and (6.5) are plotted in Figure 6.1 in nondimensional form against the compression ratio $r = P_2/P_1$ for several values of γ_{Pv} . It was reasoned in Chapter 3

that values of γ_{Pv} for ideal gases are limited to $1.0 < \gamma_{Pv} < 1.6$, depending on the composition of the gas molecules. Values higher than $\gamma_{Pv} > 1.6$ can be obtained under a real gas analysis. Figure 6.1 demonstrates some interesting features of the above equations. The trend is observed that the nondimensional form of the isentropic work increases with γ_{Pv} , to the limit where the work W becomes linear in the compression ratio r as the exponent $(\gamma_{Pv} - 1)/\gamma_{Pv} \rightarrow 1$ for increasing values of γ_{Pv} . This limit corresponds to the compression of liquids for which γ_{Pv} becomes large. In fact, Eq. (6.4) can be shown to reduce to the familiar pump work equation for liquid states [53]

$$W_{pump} = v_1 \left(P_2 - P_1 \right). \tag{6.6}$$

From these considerations, one can conclude that the isentropic work equations Eqs. (6.4) and (6.5) are generally applicable to gases and fluids alike, of which the ideal gas form and the pump equations are two limiting cases. This notation is supported by observations made in the development of supercritical carbon dioxide (sCO₂) compressors, which are reported to exhibit "pump-like" behavior [54–57] (see App. B). This observation can be explained by looking at Eq. (6.4) as the exponent γ_{Pv} has a local maximum at the critical point, although not quite of the order of magnitude of liquids.

Looking at the nondimensionalized form of Figure 6.1, one might wonder what the benefits are of operating compressors in the critical region as the nondimensionalized specific work *increases* with γ_{Pv} . Although this is certainly the case in the nondimensional sense, this effect is essentially mitigated by the term Pv, which is far more dominant in determining the order of magnitude of the isentropic work.

As Pv = ZRT, it can be reasoned that the isentropic work relates more or less proportionally to temperature, which is particularly true for turbines operating at high temperatures. For compressors and pumps, it is the density which dominates the work requirement. Due to the inverse relation between specific volume and density, the isentropic compression work of a pump is much lower than that of a compressor operating between the same initial pressure and the same compression ratio, owing to the high density of the fluid. The same holds true for compressors operating in the dense gas regime which require less work input than traditional compressors due to the increased gas density, giving rise to the interest in supercritical Brayton cycles [8, 9, 16].



Figure 6.1: Isentropic compression work for several values of γ_{Pv} as a function of compression ratio r. Values for γ_{Pv} are limited to $1 < \gamma_{Pv} \leq 1.6$ for an ideal gas, values larger than $\gamma_{Pv} > 1.6$ can be obtained under real gas analysis.

SEVEN

Real Entropy Changes and Carnot's Theorem

The entropy change of non-ideal was briefly discussed in Chapter 2 used in developing the isentropic functions Eqs. (1.27–1.29) for the isentropic gas model. In this final chapter of Part II, we will briefly review the entropy change of real gases based on the specific heat relations developed in the beginning of this part. Having demonstrated that the ideal isentropic relations are in fact a subset of the generalized isentropic relations in Chapter 1, the entropy change of ideal gases can likewise be demonstrated to be a specific case of the generalized form. Afterwards, the entropy change of real gases will be used to demonstrate Carnot's theorem – a prerequisite for validity of the model.

The TdS-equations are obtained from rearranging the *First Law* and *Second Law* in terms of entropy:

$$Tds = du + pdv, \tag{7.1a}$$

$$Tds = dh - vdP. \tag{7.1b}$$

Under the assumption of constant values of the specific heats, Eq. (7.1a) and Eq. (7.1b) for ideal gases reduces to a very simple mathematical from:

$$s_2 - s_1 = c_v \ln \frac{T_2}{T_1} + R \ln \frac{P_2}{P_1},$$
 (7.2a)

$$s_2 - s_1 = c_p \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}.$$
 (7.2b)

Similarly to the ideal gas model, the isentropic exponents γ_{Pv} , γ_{Tv} , and γ_{PT} can be assumed to have locally constant values whose extend of validity is determined by its place in the thermodynamic domain. Under this assumption, the entropy relations used in developing the isentropic functions in Chapter 2, Eq. (2.12) and Eq. (2.18) can be expressed as:

$$s_2 - s_1 = c_v \ln \frac{T_2}{T_1} + c_v \left(\gamma_{Tv} - 1\right) \ln \frac{v_2}{v_1},\tag{7.3a}$$

$$s_2 - s_1 = c_p \ln \frac{T_2}{T_1} - c_p \frac{\gamma_{PT} - 1}{\gamma_{PT}} \ln \frac{P_2}{P_1}.$$
 (7.3b)

The entropy change of an ideal gas can be reasoned to be a specific case of the above relations, as the right-hand side term can be shown to reduce to the universal gas constant in the ideal limit:

$$c_v(\gamma_{Tv}-1) = R$$
, and $c_p \frac{\gamma_{PT}}{\gamma_{PT}-1} = R$. (ideal gas) (7.4)

This feature is demonstrated even more explicitly by introducing the specific heat relations developed in Chapter 4. The entropy changes according to relations Eq. (7.1) and Eq. (7.5) are equivalent, although Eq. (7.3) might be of a more usable from. One could also have obtained Eq. (7.5) by introducing the compressibility relation Pv = ZRT in the derivation of the entropy change in the ideal gas case

$$s_2 - s_1 = c_v \ln \frac{T_2}{T_1} + R \left[Z + T \left(\frac{\partial Z}{\partial T} \right)_v \right] \ln \frac{v_2}{v_1}, \tag{7.5a}$$

$$s_2 - s_1 = c_p \ln \frac{T_2}{T_1} - R \left[Z + T \left(\frac{\partial Z}{\partial T} \right)_P \right] \ln \frac{P_2}{P_1}.$$
 (7.5b)

7.1 Carnot's Theorem Reviewed

The Carnot heat engine was conceived as a theoretical framework to present the Carnot corollaries, stating that the efficiency of any reversible heat engine depends only on the temperature of the hot and cold reservoirs between which the heat engine communicates. The theorem developed by Carnot eventually lead to the development of the concept of entropy, therefore presents itself as a natural case to conclude our investigation of entropy changes of real gases. The TS-diagram of the Carnot process is presented in Figure 7.1. Carnot's theorem is centred around the maximum thermal efficiency, which, for any reversible heat engine is give by

$$\eta = 1 - \frac{T_c}{T_h}.\tag{7.6}$$

The thermal efficiency of a reversible heat engine is solely a function of the temperatures of the thermal reservoirs. This should of course be true regardless of the behavior of the working fluid. We will assume an idealized cycle where the isentropic exponents γ_{Pv} , γ_{Tv} and γ_{PT} are constant throughout the cycle. Applying the *First Law* to the system boundaries of the Carnot heat engine, the thermal efficiency can be expressed as

$$\eta = 1 - \frac{Q_c}{Q_h},\tag{7.7}$$

where the heat flow across the system boundary is equal to the change in entropy at constant temperature

$$dQ = Tds. (7.8)$$



Figure 7.1: Carnot Heat Engine

Process 1-2: Reversible adiabatic compression **Process 2-3:** Isothermal heat addition at T_h **Process 3-4:** Reversible adiabatic expansion **Process 4-1:** Isothermal heat rejection at T_c

The change in enthalpy at constant temperature may be evaluated using either Eq. (7.3a) or Eq. (7.3b). Elimination of ds in Eq. (7.8), the Carnot efficiency can be expressed as

$$\eta = 1 - \frac{c_v T_c \left(\gamma_{Tv} - 1\right) \ln \frac{v_1}{v_4}}{c_v T_h \left(\gamma_{Tv} - 1\right) \ln \frac{v_2}{v_3}}.$$
(7.9)

Under the assumption of constant values for the isochoric specific heat capacity c_v and the isometry capacity γ_{Tv} , the efficiency of the Carnot cycle becomes

$$\eta = 1 - \frac{T_c \ln \frac{v_1}{v_4}}{T_h \ln \frac{v_2}{v_3}}.$$
(7.10)

Using the isentropic temperature-volume relation, Eq. (1.28), the specific volumes in each state can be related to each other. It follows from here that in the volumetric ratio during the isothermal heat addition an rejection phases are equal

$$\frac{v_4}{v_3} = \frac{v_1}{v_2}, \quad \text{or} \quad \frac{v_1}{v_4} = \frac{v_2}{v_3}.$$
 (7.11)

Hence, the thermal efficiency of a real gas Carnot cycle reduces to:

$$\eta = 1 - \frac{T_c}{T_h}.$$
(7.12)

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PART III

REAL GAS DYNAMICS

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In Part III of this work, the generalized isentropic relations are used to describe non-ideal compressible gas flows under the assumption of locally constant values of the isentropic exponents. Starting with isentropic flows in Chapter 8, fundamental concepts in gas dynamics such as stagnation properties and choked flow conditions will be derived for real compressible gas flows for implementation in non-ideal compressible fluid dynamics (NICFD) codes. Moreover, the isentropic flow relations will retain their familiar form by our choice to adhere to the ideal gas notation of the isentropic relations in Chapter 1. The departure from ideal behavior will solely be determined by the value of the real exponents γ_{Pv} , γ_{Tv} , and γ_{PT} in the equations. In chapters 9 and 10, we will depart from isentropicity with an investigation of discontinuities in non-ideal gas flows.

The original authors behind the real isentropic exponents pursued a similar goal to derive gas dynamic relations for non-ideal compressible flows [31, 32, 58], though their investigations were more based on empiricism rather than analytical descriptions. More recently, Baltadijev also engaged in deriving relations for real gas flows, using an alternative notation [35, 36]. Nonetheless, his insights remain relevant for our present discussion.

EIGHT

One-Dimensional Real Isentropic Flow Relations

Classical compressible flow problems like steady constant cross-section duct flows, and accelerated nozzle and diffusers flows, can be approximately described as isentropic flows, which we are now able to review for real substances from the perspective of the generalized isentropic gas model. Starting with the fundamental speed of sound relation for real gases, this chapter will progressively expand the analytical description of real isentropic flows following with the derivation of real stagnation properties, and finally work towards critical conditions for real gas flows.

Section 8.1 on the speed of sound will be based on the original derivation by Kouremenos et al. [32, 58]. Although they did write on empirical stagnation properties, a formal derivation for analytical isentropic flow relations will be provided in this work. The stagnation properties of a real isentropic flow will be derived in section 8.2, based on the work of Baltadjiev which he derived in an alternative form [35, 36]. The last two sections will provide new insights on the characteristic speeds and critical flow conditions of real gas flows.

8.1 Speed of Sound in Real Gases

The speed of propagation of a sound wave in a non-ideal compressible gas flow is derived from the same fundamental mass and momentum conservation equations applied at the wavefront as for ideal gases, see Figure 8.1.



Figure 8.1: Propagation of sound through a substance [59]

conservation of mass

$$\begin{array}{ll} \mbox{conservation of mass} & \rho c = (\rho + d\rho)(c - du), \\ & du = c \frac{d\rho}{\rho}, \\ \mbox{conservation of momentum} & P + \rho cc = (P + dP) + \rho c(c - du), \\ & dP = \rho c \ du. \end{array}$$

Where the pressure disturbance may be assumed to be small, the second-order term $d\rho du$ appearing in the conservation equation can be neglected. The simplified mass conservation shows that du > 0 if $d\rho$ is positive, implying that the fluid behind the passing wavefront moves in the direction of the wave as shown in Figure 8.1. Eliminating du in the mass and momentum conservation equations yields the fundamental equation for the speed of sound in a gas [50, 59, 60] expressed as

$$c^2 = \frac{dP}{d\rho}.\tag{8.1}$$

The question remains at which constant property the derivative $dP/d\rho$ is to be evaluated. Pressure disturbances in the fluid are observed to cause small changes in temperature due to the compression and expansion effect of the passing disturbance [59]. This process is shown to behave approximately isentropic as the gas particles undergo near reversible and adiabatic compression and expansion. In fact, the entropy production across a sound wave can be demonstrated to be proportional to pressure according to $ds \propto dP^3$ [59]. Hence, the assumption of an isentropic sound wave is, therefore, reasonable for small pressure disturbances. Hence, the propagation velocity of a pressure disturbance in a medium becomes

$$c^2 = -v^2 \left(\frac{\partial P}{\partial v}\right)_s.$$
(8.2)

The partial derivative $(\partial P/\partial v)_s$ is simply the derivative of the pressure-volume isentrope Eq. (1.27). The speed of sound in a real compressible gas becomes [31, 32

$$c^2 = \gamma_{Pv} Pv$$
, or $c^2 = \gamma_{Pv} ZRT$. (8.3) speed of sound

And the Mach number of real gasses is expressed as

$$M = \frac{u}{\sqrt{\gamma_{Pv}Pv}}, \quad \text{or} \quad M = \frac{u}{\sqrt{\gamma_{Pv}ZRT}}.$$
 (8.4) Mach number

Due to the choice of notation, the speed of sound in Eq. (8.3) retains its familiar ideal gas from, where any real gas effects are incorporated into the term γ_{Pv} . Eq. (8.3) is, therefore, a general definition for the speed of sound in any single phase fluid as the definition of the real exponent γ_{Pv} is exact. This feature will be explicitly demonstrated in Chapter 12 where Eq. (8.3) is compared to the speed of sound of a Van der Waals gas in solving the Riemann problem. For now, we can already reason that Eq. (8.3) reduces to the ideal notation in the ideal gas case, for which γ_{Pv} simply reduces to the ratio of the specific heats. Moreover, as mentioned in Chapter 5, γ_{Pv} reduces the the liquid bulk modulus as $c_p \approx c_v$. In this case Eq. (8.3) takes the form of the Newton-Laplace equation for the speed of sound in liquids [50].

8.2 Real Stagnation Properties

Having established the analytical expression for the speed of sound in real gasses, the aim of this section is to derive dynamic properties of a steady adiabatic one-dimensional flow. Consider the constant cross-section stream tube in Figure 8.2. No matter is able to pass through the stream surface S, nor is there any exchange of heat or work across the stream tube surface by the requirement of the adiabatic condition.



Figure 8.2: Conservation equations along a constant cross-section adiabatic stream tube.

The mass, momentum, and energy conservation equations in integral form can be expressed as:

conservation of mass	$u_1\rho_1 = u_2\rho_2,$
conservation of momentum	$P_1 + \rho_1 {u_1}^2 = P_2 + \rho_2 {u_2}^2$
conservation of energy	$h_1 + \frac{u_1^2}{2} = h_2 + \frac{u_2^2}{2}.$

The concept of a stagnation state, or the total flow condition, provides a convenient reference state for a fluid in motion. The definition of the stagnation state of a fluid is the final state a fluid would attain if it was isentropically decelerated from the initial velocity u to rest. From this definition, it follows that the total enthalpy is constant throughout the isentropic flow field in absence of heat or work terms. The total enthalpy is defined as

$$h_0 = h_1 + \frac{u_1^2}{2} = h_2 + \frac{u_2^2}{2} = const.$$
 (8.5)

stagnation enthalpy In the traditional derivation of the stagnation state for ideal gases, one would proceed by relating the total temperature to the total enthalpy by the isobaric heat capacity c_p according to

$$dh = c_p dT. \tag{8.6}$$

Although the stagnation temperature will most certainly be constant for an isentropic flow, as would all stagnation properties, it is no longer possible to simply relate the stagnation temperature to the total enthalpy by the isobaric heat capacity Eq. (8.6). Another approach must be sought in order to derive stagnation properties for real gasses. Here we will diverge from the ideal derivation, resorting to the approach taken by Baltadjiev [35, 36].

Figure 8.3 provides a graphical definition of the stagnation enthalpy. The difference in energy between state 1 and state 0 may be thought of in two ways, either it being the difference in kinetic energy between the dynamic state 1 and the static state 0, or the isentropic compression work between two static states 1 and 2f. The former interpretation can be expressed as



Figure 8.3: Graphical interpretation of the stagnation enthalpy between static and dynamic states.

$$\Delta h = h_0 - h = \frac{u^2}{2}.$$
(8.7)

Elimination of the velocity u by the definition of the Mach number Eq. (8.4) the kinetic energy relation can be written as

$$\Delta h = \frac{M^2}{2} \gamma_{Pv} Pv. \tag{8.8}$$

Alternatively, the enthalpy difference between states 1 and 0 in Figure 8.3 can be interpreted as the isentropic compression work between P_1 to P_0 . We recall our result of Eq. (6.4) obtained in Chapter 6, repeated here for convenience

$$\Delta h = v_0 P_0 \frac{\gamma_{Pv}}{\gamma_{Pv} - 1} \left[\left(\frac{P_0}{P} \right)^{\frac{\gamma_{Pv} - 1}{\gamma_{Pv}}} - 1 \right].$$
(8.9)

Finally, as the two interpretation must yield the same energy difference between states 1 and 0, the stagnation pressure ratio for real gasses can be derived by equating the expressions Eqs. (8.8) and (8.9) for Δh .

$$\frac{P_0}{P} = \left[1 + \frac{\gamma_{Pv} - 1}{2}M^2\right]^{\frac{\gamma_{Pv}}{\gamma_{Pv} - 1}}.$$
(8.10) stagnation pressure

As γ_{Pv} reduces to the ratio of the specific heats in the ideal gas case, Eq. (8.10) is equivalent to its ideal gas counterpart. From the interpretation of an isentropic compression process between pressures P and P_0 , other stagnation properties of real gasses can now be derived using the real isentropic relations of Chapter 1. Here the assumption of locally constant values for the isentropic exponents between isentropic states is introduced. As the kinetic energy of the flow is usually much smaller than the static enthalpy of the flow – and therefore the isentropic state change is small – the assumption of constant exponents is justified (see App. B).

The stagnation temperature can be related to the stagnation pressure using the isentropic relation as a function of temperature and pressure, Eq. (1.29)

$$\frac{T_0}{T} = \left(\frac{P_0}{P}\right)^{\frac{\gamma_{PT}-1}{\gamma_{PT}}},\tag{8.11a}$$

$$= \left[1 + \frac{\gamma_{Pv} - 1}{2}M^2\right]^{\frac{\gamma_{Pv} - 1}{\gamma_{Pv} - 1}\frac{\gamma_{PT} - 1}{\gamma_{PT}}}.$$
(8.11b)

Using the relation between the isentropic exponents Eq. (1.34), the exponent can be rewritten as:

$$\frac{T_0}{T} = \left[1 + \frac{\gamma_{Pv} - 1}{2}M^2\right]^{\frac{\gamma_{Tv} - 1}{\gamma_{Pv} - 1}}.$$
(8.12)

Most notably about the stagnation temperature ratio is the addition of an exponent in the expression, whereas the ideal gas notation has none. Though, the reader is assured that as exponents $\gamma_{Tv} = \gamma_{Pv} = \gamma$ in the ideal case, the stagnation temperature relation is also equivalent to its ideal gas counterpart.

Likewise, the stagnation density can be expressed in terms of the stagnation pressure using Eq. (1.27)

$$\frac{\rho_0}{\rho} = \left(\frac{P_0}{P}\right)^{\frac{1}{\gamma_{Pv}}},\tag{8.13}$$

$$\frac{\rho_0}{\rho} = \left[1 + \frac{\gamma_{Pv} - 1}{2}M^2\right]^{\frac{1}{\gamma_{Pv} - 1}}.$$
(8.14)

Again, note that γ_{Pv} is equal to γ for ideal gasses reducing the formulation of the stagnation density to the ideal gas formulation.

In order to close the P-v-T relationship for real gasses, the stagnation compressibility may also be defined in terms of the other stagnation properties

$$\frac{Z_0}{Z} = \frac{P_0}{P} \frac{\rho}{\rho_0} \frac{T}{T_0}.$$
(8.15)

 $stagnation \\ density$

62

 $stagnation \\ temperature$

Substitution of the stagnation property ratios, the stagnation compressibility can be expressed as

$$\left| \frac{Z_0}{Z} = \left[1 + \frac{\gamma_{Pv} - 1}{2} M^2 \right]^{\frac{\gamma_{Pv} - \gamma_{Tv}}{\gamma_{Pv} - 1}}.$$
(8.16) stagnation compressibility

In the ideal case $\gamma_{Pv} = \gamma_{Tv}$ for which the stagnation compressibility ratio reduces to $Z_0/Z = 1$.

The inverse of the stagnation pressure ratio Eq. (8.10), stagnation density ratio Eq. (8.14), stagnation speed of sound Eq. (8.19) and critical area ratio Eq. (8.34) are plotted against the Mach number in Figure 8.4 for a range of values of the isentropic exponent γ_{Pv} . As was reasoned in Chapter 3, values for γ_{Pv} of polytropic ideal gas are limited between 1 and 1.6 depending on the molecular structure. Higher values for the isentropic exponent may be obtained for real gases as the fluid states moves towards the critical point.

An important feature demonstrated in Figure 8.4 is the reduced choked flow margin implied by the critical area ratio A^*/A for supersonic Mach numbers as γ_{Pv} increases. The critical area ratio A^*/A , which will be formally derived in section 8.4, suggests that real gas flows with exceedingly reduced compressibility have a greater tendency to become choked. This notion agrees with observations made in the operation and design of state-of-art ORC turbomachinery, where low values of the speed of sound and volumetric expansion cause the flow to become supersonic at modest pressure ratios [10, 25]. The dominant need of reducing the number of stages leads to acceptance of an efficiency penalty induced by loss mechanisms caused by strong shock waves in the nozzle and blade outlet regions [10, 21, 25, 61]. The occurrence of shock waves may therefore be explained by the combination of a reduced choking margin implied by the area ratio A^*/A and the unusual converging-diverging nozzle-blade configurations in ORC turbines [25, 61]. The reduced choking margin also implies a narrower operating envelope for turbomachinery dealing with non-ideal compressible gas flows [35, 36].

For the reason as why the choking margin is reduced, Figure 8.4 also hints at a possible explanation. The stagnation density ratio ρ/ρ_0 also increased with increasing values of the exponent γ_{Pv} , indicating that reduced compressibility in the region where high values of γ_{Pv} generally arise is the reason behind the reduced choking margin. As the density of the gas tends to that of a liquid and the compressibility of the flow decreases, ever smaller area ratios are required for the flow to become choked, in the limit where the area ratio is constant for an incompressible choked flow.

8.3 Real Characteristic Velocities

The Mach number defined in Eq. (8.4) may sometimes not be sufficient to describe the flow condition, as the Mach number is not directly proportional to the flow velocity [60]. The sound velocity itself is a variable that depends on the local flow state. This has lead to the development of several characteristic flow speeds that can be used to represent the overall properties of the flow.



Figure 8.4: Stagnation property ratios Eqs. (8.10), (8.14), (8.19), and critical area ratio Eq. (8.34) for several values of γ_{Pv} . For ideal gases, the value of γ_{Pv} is limited to $1 < \gamma_{Pv} \le 1.6$. Higher values may be encountered under a real gas analysis.

The stagnation speed of sound corresponding to the stagnation state of the fluid is defined as

$$c_0^2 = \gamma_{Pv} \frac{P_0}{\rho_0}.$$
 (8.17)

The right-hand side of Eq. (8.17) can be expanded as

$$c_0^2 = \gamma_{Pv} \frac{P}{\rho} \frac{P_0/P}{\rho_0/\rho} = c^2 \frac{P_0/P}{\rho_0/\rho}.$$
(8.18)

Substitution of the stagnation property ratios P_0/P and ρ_0/ρ , Eqs. (8.10) and (8.14), the familiar expression is obtained for the stagnation speed of sound:

$$\frac{c_0^2}{c^2} = 1 + \frac{\gamma_{Pv} - 1}{2}M^2.$$
(8.19) stagnation speed of sound

In the process of deriving the stagnation properties in section 8.2, we have essentially transformed the isentropic relations in terms of the speed of sound. The reappearing bracketed term in the definition of the stagnation property ratios may be recognized as the dimensionless velocity ratio $(c_0/c)^2$. This equivalence is readily demonstrated by substitution of the definition of the speed of sound in any of the isentropic relations:

$$\frac{P_0}{P} = \left(\frac{c_0^2}{c^2}\right)^{\frac{\gamma_{P_v}}{\gamma_{P_v}-1}},$$
(8.20a)

$$\frac{T_0}{T} = \left(\frac{c_0^2}{c^2}\right)^{\frac{\gamma_T v - 1}{\gamma_{Pv} - 1}},$$
(8.20b)

$$\frac{\rho_0}{\rho} = \left(\frac{c_0^2}{c^2}\right)^{\frac{1}{\gamma_{P_v} - 1}},$$
(8.20c)

$$\frac{Z_0}{Z} = \left(\frac{c_0^2}{c^2}\right)^{\frac{\gamma_{Pv} - \gamma_{Tv}}{\gamma_{Pv} - 1}}.$$
(8.20d)

The critical speed of sound ratio is readily derived from Eq. (8.19) as the critical speed of sound $c = c^*$ for M = 1 [60]:

$$\frac{c_0^2}{c^{*2}} = \frac{\gamma_{Pv} + 1}{2}.$$
(8.21) critical speed of sound

Subsequently, the critical Mach number M^* can be derived using the critical speed of sound ratio. The critical Mach number provides a convenient dimensionless speed as it is directly related to the flow velocity itself [60]. The critical Mach number is defined as

$$M^{*2} = \left(\frac{u}{c^*}\right)^2. \tag{8.22}$$

Using the velocity relation u = Mc, Eq. (8.22) can be expanded as

$$M^{*2} = M^2 \left(\frac{c}{c^*}\right)^2.$$
 (8.23)

The speed of sound can be expressed in terms of the stagnation speed of sound by elimination of the speed of sound in Eq. (8.19), yielding

$$M^{*2} = \frac{M^2}{1 + \frac{\gamma_{Pv} - 1}{2}M^2} \left(\frac{c_0}{c^*}\right)^2.$$
 (8.24)

The critical Mach number can be directly related to the Mach number by substitution of Eq. (8.21):

critical Mach number ratio

$$M^{*2} = \frac{(\gamma_{Pv} + 1)M^2}{2 + (\gamma_{Pv} - 1)M^2}.$$
(8.25)

Inversely, the Mach number can be expressed explicitly in terms of the critical Mach number:

 $M^{2} = \frac{\frac{2}{\gamma_{Pv} + 1} M^{*2}}{1 - \frac{\gamma_{Pv} - 1}{\gamma_{Pv} + 1} M^{*2}}.$ (8.26)

From Eq. (8.25) the following special cases can be identified relating the Mach number and critical Mach number for real gasses [60]:

$$\begin{cases} M = 0 & \text{and} & M^* = 0, \\ M = 1 & \text{and} & M^* = 1, \\ M = \infty & \text{and} & M^* = \frac{\gamma_{Pv} - 1}{\gamma_{Pv} + 1}. \end{cases}$$
(8.27)

Lastly, using the previous relations, the stagnation speed of sound can be expressed in terms of the velocity like

$$\frac{u}{c_0} = \frac{u}{c^*} \frac{c^*}{c_0},\tag{8.28}$$

where $u/c^* = M^*$. Elimination of the ratio of the critical and stagnation speed of sound by Eq. (8.21) yields:

$$\frac{u}{c_0} = M^* \left[\frac{2}{\gamma_{Pv} + 1} \right]^{\frac{1}{2}}.$$
(8.29)

Alternatively, the ratio u/c_0 may be expressed in terms of the Mach number by substitution of Eq. (8.25) [60]:

 $number \ ratio$

critical Mach number ratio

stagnation sound velocity

$$\left| \frac{u}{c_0} = \left[\frac{M^2}{1 + \frac{\gamma_{Pv} - 1}{2} M^2} \right]^{\frac{1}{2}}.$$
(8.30) stagnation sound velocity

The alternative representations for the fluid velocity presented in this section are solely related to the real isentropic exponent γ_{Pv} and are equivalent to their ideal gas formulations for which γ_{Pv} reduces to the ratio of the specific heats.

8.4 Real Critical Properties

We conclude this chapter on real gas isentropic gas flows with the discussion of choked conditions. Knowing the physical conditions under which choking of the flow occurs is relevant to many practical engineering applications like the operation of turbomachinery and the design of flow devices such as gauges and valves [62] (see App. B).

The critical property ratios P^*/P_0 , T^*/T_0 , ρ^*/ρ_0 , and Z^*/Z_0 naturally follow from the different definitions of the stagnation properties by imposing critical flow conditions, and can be expressed as

$$\frac{P^*}{P_0} = \left[\frac{2}{\gamma_{Pv} + 1}\right]^{\frac{\gamma_{Pv}}{\gamma_{Pv} - 1}},$$
(8.31a)

$$\frac{T^*}{T_0} = \left[\frac{2}{\gamma_{Pv} + 1}\right]^{\frac{\gamma_{Tv} - 1}{\gamma_{Pv} - 1}},\tag{8.31b}$$
critical

(8.31c)

$$\frac{Z^*}{Z_0} = \left[\frac{2}{\gamma_{Pv}+1}\right]^{\frac{\gamma_{Pv}-\gamma_{Tv}}{\gamma_{Pv}-1}}.$$
(8.31d)

Using the critical property ratios, the critical area and mass ratio can be derived from the mass conservation equation. The critical area ratio can be written as

 $\frac{\rho^*}{\rho_0} = \left[\frac{2}{\gamma_{Pv}+1}\right]^{\frac{1}{\gamma_{Pv}-1}},$

$$\frac{A}{A^*} = \frac{\rho^*}{\rho} \frac{c^*}{u} = \frac{\rho^*}{\rho_0} \frac{\rho_0}{\rho} \frac{c^*}{c} \frac{c}{u}.$$
(8.32)

The term c^*/c is eliminated by substitution of the definition of the speed of sound Eq. (8.3). Under the assumption of a local constant value of the isentropic exponents, the term γ_{Pv} drops out of the equation. Gathering the remaining terms, the critical area ratio A/A^* can be expressed as

$$\frac{A}{A^*} = \left[\frac{\rho^*}{\rho_0}\frac{\rho_0}{\rho}\frac{P^*}{P_0}\frac{P_0}{P}\right]^{\frac{1}{2}}\frac{1}{M}.$$
(8.33)

Substitution of the stagnation property ratios and the critical ratios, the following relation is found for the critical area ratio

critical $area \ ratio$

$$\frac{A}{A^*} = \frac{1}{M} \left[\frac{2 + (\gamma_{Pv} - 1) M^2}{\gamma_{Pv} + 1} \right]^{\frac{\gamma_{Pv} + 1}{2(\gamma_{Pv} - 1)}}.$$
(8.34)

The formulation of the critical area ratio can be shown to be equivalent to the ideal gas formulation for which γ_{Pv} reduces to the ratio of specific heats.

The critical mass flow ratio is derived in a similar way as the critical area ratio from mass continuity. Starting with the definition of the mass flow rate of a one-dimensional flow, the mass flow rate can be expressed in terms of the flow area and the Mach number

$$\dot{m} = \rho A u = \rho_0 \frac{\rho}{\rho_0} A M c. \tag{8.35}$$

Using the isentropic pressure-volume relation and the speed of sound yields

$$\dot{m} = \rho_0 AM \sqrt{\gamma_{Pv} \frac{P}{\rho}} \left(\frac{P}{P_0}\right)^{\frac{1}{\gamma_{Pv}}}, \qquad (8.36a)$$

$$= AM \sqrt{\gamma_{Pv} \rho_0 P_0 \frac{P}{P_0} \frac{\rho_0}{\rho}} \left(\frac{P}{P_0}\right)^{\frac{1}{\gamma_{Pv}}}, \qquad (8.36b)$$

where $\rho_0/\rho = P/P_0^{-1/\gamma_{Pv}}$. Bringing all terms in P/P_0 into the same exponent, Eq. (8.36b) can be written as

$$\dot{m} = AM\sqrt{\gamma_{Pv}\rho_0 P_0} \left(\frac{P}{P_0}\right)^{\frac{1}{2\gamma_{Pv}}+1}.$$
(8.37)

Finally, by substitution of the stagnation pressure Eq. (8.9) and setting M = 1, we arrive at:

critical mass flow

$$\dot{m}^* = A^* \sqrt{\gamma_{Pv} \rho_0 P_0} \left(\frac{2}{\gamma_{Pv} + 1}\right)^{\frac{\gamma_{Pv} + 1}{2(\gamma_{Pv} - 1)}}.$$
(8.38)

NINE

Real Shock Waves

In the previous chapter, the classical isentropic flow description of ideal gases was extended to include real gas behavior. Shock waves present themselves as the logical step next to continue our discussion on real compressible gas dynamics. Shock waves are flow discontinuities usually accompanied by abrupt state changes, encountered in a wide variety of flow problems like detonation waves, supersonic flows past solid bodies and supersonic duct flows. Most significantly, the destruction of pressure across shock waves is an important loss mechanism in turbomachinery operation, especially in ORC turbines owing to high expansion across turbine stages [25, 61]. The prevention of shock wave occurrence, therefore, is an important aspect of turbomachinery design.

In this chapter we will attempt to relate thermodynamic properties across normal shock waves in real gases. It will appear that the mechanical properties of pressure and density may be readily related across the shock wave using the Rankine-Hugoniot conditions. Thermal properties however must be related by the introduction of an equation of state. But first, we will turn towards Prandtl-Meyer expansion waves. A wave phenomena which, due to its isentropic nature, may be described analytically using the isentropic relations for real gases introduced in the first part of this work.

9.1 Prandtl-Meyer Expansion Fans

Unlike irreversible normal or oblique shock waves, Prandtl-Meyer expansion waves can be described analytically as the flow may be treated as approximately isentropic [60, 63]. The analysis of expansion waves in real gas flows is therefore completely analogous to the ideal case starting from the notion that the stagnation properties are constant throughout the flow field due the assumption of an isentropic flow.

As the flow bends around corner O in Figure 9.1, the gas is to accelerate downwards if the downstream flow is to remain attached to the slope OB. The downward acceleration can only be achieved if the gas expands around the corner, therefore $P_2 < P_1$. An expansion of the fluid across a flow discontinuity would be accompanied by a decrease in its entropy, a requirement that is in violation with the *Second Law*. Consequently, the discontinuity is decomposed into a continuous field of weak Mach waves, across which the infinitesimal property changes of the flow are approximately isentropic [59, 60].



Figure 9.1: Prandtl-Meyer expansion fan

The Prandtl-Meyer analysis is based on the following assumptions [60]:

- *i*. Steady two-dimensional isentropic flow.
- *ii.* The streamlines in the pre-shock condition are parallel to *AO*, and the flow properties are homogeneous.
- iii. The streamlines in the post-shock condition are parallel to OB and the flow properties are homogeneous.
- iv. The flow properties are constant along each Mach line originating from the corner O.
- v. The isentropic exponents are constant across the expansion fan.

For sake of completeness, the complete derivation of the Prandtl-Meyer flow will be presented here, starting with the governing differential equation for the infinitesimal deflection $d\delta$ across a single Mach line. From the assumption of homogeneous flow properties in pre-shock and post-shock conditions, it follows that there can be no tangential pressure gradient along the Mach line. Hence, the tangential velocity component u_t in Figure 9.2 is constant. The tangential velocity component in pre-shock and post-shock condition can be written as

$$u_t = u\cos\alpha = (u + du)\cos(\alpha - d\delta),\tag{9.1}$$

where the trigonometric term in Eq. (9.1) can expanded as

$$\cos(\alpha - d\delta) = \cos\alpha \cos d\delta + \sin\alpha \sin d\delta = \cos\alpha + d\delta \sin\alpha.$$
(9.2)

For infinitesimal deflection angles $d\delta$, the identities $\cos d\delta \approx 1$ and $\sin d\delta \approx d\delta$. Combining equations Eqs. (9.1) and (9.2), and neglecting higer-order terms yields

$$\frac{du}{u} = -\tan\alpha d\delta. \tag{9.3}$$



Figure 9.2: Governing equations across a single Mach line with infinitesimal change in flow direction δ

The identity $\tan \alpha$ can be demonstrated to be equal to $1/\sqrt{M^2 - 1}$ from Mach-cone geometry [60]. Hence, Eq. (9.3) can be expressed as

$$d\delta = -\sqrt{M^2 - 1}\frac{du}{u}.\tag{9.4}$$

Eq. (9.4) is known as the governing differential equation for a Prandtl-Meyer expansion wave, which relates the infinitesimal deflection angle across a single Mach line of the expansion wave to the flow velocity.

From the notion of an isentropic flow, it follows that the stagnation properties are constant throughout the flow field. As such, the change in dynamic properties across the expansion fan are readily related by equating the expressions for the stagnation properties from section 8.2 between the pre- and post shock condition in Figure 9.1, summarized as

$$\frac{P_2}{P_1} = \left[\frac{1 + \frac{\gamma_{Pv} - 1}{2}M_1^2}{1 + \frac{\gamma_{Pv} - 1}{2}M_2^2}\right]^{\frac{\gamma_{Pv}}{\gamma_{Pv} - 1}},$$
(9.5a)

$$\frac{\rho_2}{\rho_1} = \left[\frac{1 + \frac{\gamma_{Pv} - 1}{2}M_1^2}{1 + \frac{\gamma_{Pv} - 1}{2}M_2^2}\right]^{\gamma_{Pv} - 1},\tag{9.5b}$$

expansion fan property ratios

$$\frac{T_2}{T_1} = \left[\frac{1 + \frac{\gamma_{Pv} - 1}{2} M_1^2}{1 + \frac{\gamma_{Pv} - 1}{2} M_2^2}\right]^{\frac{\gamma_{Tv} - 1}{\gamma_{Pv} - 1}},$$
(9.5c)

$$\frac{Z_2}{Z_1} = \left[\frac{1 + \frac{\gamma_{Pv} - 1}{2}M_1^2}{1 + \frac{\gamma_{Pv} - 1}{2}M_2^2}\right]^{\frac{\gamma_{Tv} - \gamma_{Pv}}{\gamma_{Pv} - 1}}.$$
(9.5d)

The real isentropic exponents γ_{Pv} , γ_{Tv} and γ_{PT} are assumed constant between the dynamic and static states. Using the property relations across the shock wave above and the governing differential for the Prandtl-Meyer expansion wave, it is possible to relate the terminal velocities across the shock wave from the notion that the stagnation speed of sound is constant everywhere written as

$$c_{01}{}^2 = c_{02}{}^2. (9.6)$$

The velocity is related to the stagnation speed of sound as a function of the Mach number by relation Eq. (8.30) in section 8.3. Substitution yields

$$u_1^2 \left[\frac{1 + \frac{\gamma_{Pv} - 1}{2} M_1^2}{M_1^2} \right] = u_2^2 \left[\frac{1 + \frac{\gamma_{Pv} - 1}{2} M_2^2}{M_2^2} \right], \tag{9.7}$$

hence the terminal velocity ratio becomes

terminal velocity ratio

$$\frac{u_2^2}{u_1^2} = \frac{M_2^2}{M_1^2} \left[\frac{1 + \frac{\gamma_{Pv} - 1}{2} M_1^2}{1 + \frac{\gamma_{Pv} - 1}{2} M_2^2} \right].$$
(9.8)

Alternatively, the velocities across the expansion fan can be related to the deflection angle using the differential form instead of the integral form of Eq. (9.8). Starting from the relation between the velocity and stagnation acoustic speed, Eq. (8.29), the velocity can be expressed as

$$u^{2} = \frac{c_{0}^{2}M^{2}}{1 + \frac{\gamma_{P_{v}} - 1}{2}M^{2}}.$$
(9.9)

Since c_0 is constant, the velocity can be related explicitly as a function of the Mach number of the flow by logarithmic differentiation of Eq. (9.9), yielding

$$\frac{du}{u} = \frac{1}{1 + \frac{\gamma_{Pv} - 1}{2}M^2} \frac{dM}{M}.$$
(9.10)

Replacing the differential du/u by the governing differential of a Prandtl-Meyer fan Eq. 9.4, the deflection angle can be related to the Mach number

$$d\delta = -\frac{\sqrt{M^2 - 1}}{1 + \frac{\gamma_{Pv} - 1}{2}M^2} \frac{dM}{M}.$$
(9.11)

Integration of Eq. (9.11) yields [60]

$$\delta = -\sqrt{\frac{\gamma_{Pv} + 1}{\gamma_{Pv} - 1}} \tan^{-1} \sqrt{\frac{\gamma_{Pv} - 1}{\gamma_{Pv} + 1}} \left(M^2 - 1\right) + \tan^{-1} \sqrt{M^2 - 1} + C.$$
(9.12)

The integration constant C is uniquely determined by the initial flow Mach number M_1 and the deflection angle δ_1 . In the special case where M_1 is unity and the initial flow deflection angle δ_1 is zero, the integration constant is zero. For this case, the symbol δ is replaced by the symbol ν for the Prandtl-Meyer function [60], commonly expressed as
$$\nu = -\sqrt{\frac{\gamma_{Pv} + 1}{\gamma_{Pv} - 1}} \tan^{-1} \sqrt{\frac{\gamma_{Pv} - 1}{\gamma_{Pv} + 1} (M^2 - 1)} + \tan^{-1} \sqrt{M^2 - 1}.$$
(9.13) *Prandtl-Meyer* function

The function of ν is plotted against a range of Mach numbers in Figure 9.3 for some values of the real isentropic exponent γ_{Pv} . The general trend is observed that the Prandtl-Meyer angle ν decreases for increasing value of γ_{Pv} . Figure 9.3 actually shows two general effects of the real gas exponent γ_{Pv} relating to molecular size of the substance and compressibility.

Firstly, as γ_{Pv} reduces to the ratio of the specific heats in the ideal gas limit, it was reasoned in Chapter 3 that the value of γ_{Pv} has a theoretical maximum of 1.6 for a monatomic gas and tends to one for increasingly larger molecules. According to Figure 9.3, larger deflection angles may be anticipated for increasingly larger molecules within the ideal gas domain.

Values for γ_{Pv} exceeding the ideal theoretical ideal limit of 1.6 may be anticipated in the dense gas region, as the density increases and the compressibility decreases. As the downward acceleration of the fluid is driven by expansion of the fluid, the trend shows that as γ_{Pv} increases – and hence the compressibility decreases – smaller deflection angles are encountered, tending to zero as $\gamma_{Pv} \to \infty$ for liquids.



Figure 9.3: Prandtl-Meyer angle as a function of the Mach number for several values of the the real exponent γ_{Pv} . For ideal gases, γ_{Pv} is limited to values between $1 < \gamma_{Pv} \le 1.6$. Higher values can be obtained for real gases.

9.2 Normal Shock Waves

Finally, we will turn to the problem of the change of thermodynamic properties across a normal shock wave. The normal shock waves represent flow discontinuities across which an abrupt change of thermodynamic state takes place. Because of the instantaneous change of thermodynamic properties across a normal shock wave, this process can no longer assumed to be isentropic. Kinetic energy is destroyed in the process leading to heating of the gas above the corresponding isentropic compression value, and, consequently, the entropy in the post shock condition increases [60].

The analysis of real normal shock waves is confined to the same assumptions as for an ideal gas:

- *i*. The flow is assumed to be inviscid.
- *ii.* The thickness of the flow structures that make up the wavefront is of the order of a few micrometers [59, 63]. The flow area is therefore assumed constant throughout the shock process, irrespective of the actual angle of the walls.
- *iii.* The shock wave is perpendicular to the flow by definition.
- iv. The flow process is adiabatic, and no external work or body forces are present.
- v. The isentropic exponents are assumed constant across the shock interface.

Figure 9.4 illustrates a control volume enclosing a normal shock wave. As the thermodynamic properties vary approximately discontinuously across the shock wave, the governing mass, momentum, and energy equations are presented in integral form.

As the mass and momentum conservation equations do not differentiate between ideal and real gasses, the Rankine-Hugonoit condition for relating pressure and density across normal shock waves remains nevertheless valid for real gas flows.



Figure 9.4: Change of thermodynamic state across a normal shock wave

 $u_1\rho_1 = u_2\rho_2,$

conservation of momentum
$$P_1 + \rho_1 u_1^2 = P_2 + \rho_2 V_2^2,$$
conservation of energy $h_1 + \frac{u_1^2}{2} = h_2 + \frac{u_2^2}{2}.$

By the definition of enthalpy, the energy equation may be rewritten in terms of the change of internal energy across the normal shock wave, leading to the classical Rankine-Hugoniot equation

$$e_2 - e_1 = \frac{1}{2} (p_1 - p_2) (v_1 - v_2).$$
 (9.14)

Under the assumption that the upstream conditions are known, one is able to relate the downstream enthalpy or internal energy to the pressure and density $h_2 = h_2(P_2, \rho_2)$ or $e_2 = e_2(P_2, \rho_2)$ using an equation of state, such that the Rankine-Hugoniot equation contains only thermodynamic quantities [58, 63].

Further rearranging the momentum equation, the pressure and density may be related explicitly across the shock wave as a function of the Mach number. The pressure ratio across a normal shock wave may be derived from the momentum equation, expressed as

$$P_1\left(1+\frac{\rho_1}{P_1}{u_1}^2\right) = P_2\left(1+\frac{\rho_2}{P_2}{u_2}^2\right).$$
(9.15)

The velocity terms may be eliminated using the definition of the Mach number and the speed of sound derived in the previous chapter

$$u = Mc = M\sqrt{\gamma_{Pv}\frac{P}{\rho}}.$$
(9.16)

Introducing Eq. (9.16) into the momentum equation, the pressure ratio across the normal shock wave may be related explicitly in terms of the pre-shock and post-shock Mach numbers [31, 58]:

$$\frac{P_2}{P_1} = \frac{1 + \gamma_{Pv1} M_1^2}{1 + \gamma_{Pv2} M_2^2}.$$
(9.17) normal shock pressure ratio

The isentropic exponent γ_{Pv} between the two states will not be equal in the general case. Depending on the strength of the shock wave and the thermodynamic region, the isentropic exponent may be held constant across the shock wave. This approximation holds for non-ideal gas flows whose thermodynamic state is far removed from the non-linear behavior of thermodynamic properties in the vicinity of the critical point.

The density across the shock wave may be related similarly as was the pressure ratio. The mass continuity equation may be expressed as:

$$\frac{\rho_2}{\rho_1} = \frac{M_1^2 P_1}{M_2^2 P_2}.$$
(9.18)

Elimination of the pressure ratio Eq. (9.17), we find an explicit function of the density ratio across the normal shock wave as a function of the Mach number.

normal shock density ratio

$$\frac{\rho_2}{\rho_1} = \frac{M_1^2}{M_2^2} \left[\frac{1 + \gamma_{Pv2} M_2^2}{1 + \gamma_{Pv1} M_1^2} \right].$$
(9.19)

In case of a perfect gas, the Rankine-Hugoniot conditions, derived from the fundamental conservation equations, can be closed by the proportional relationship between enthalpy and temperature by the isobaric specific heat capacity, thereby allowing to express the post-shock Mach number M_2 as an explicit function of M_1 . This is not the general case for real gases however. Are there perhaps different means of closing this problem?

A definitive answer to this question arises when taking the alternative approach of decomposition of the shock wave process into a sequence of processes, as presented in Figure 9.5. Instead of seeking to directly relate the pre-shock and post-shock conditions 1 and 2, we can instead define a series of thermodynamic processes whose net result is a change from state 1 to state 2:



Figure 9.5: Decomposition of a shock wave process

i.	Isentropic compression	$1 \longrightarrow 01$
ii.	Isenthalpic expansion	$01 \longrightarrow 02$
iii.	Isentropic expansion	$02 \longrightarrow 2$

Using the stagnation properties derived in the previous chapter, the decomposition of the shock tube process reduces the problem to an isenthalpic expansion process. The ratio of the speed of sound between the stagnation states 01 and 02 presents itself as a particularly useful quantity, as it forms a natural connection between mechanical and thermal properties

$$\left(\frac{c_{02}}{c_{01}}\right)^2 = \frac{Z_{02}T_{02}}{Z_{01}T_{01}} = \frac{P_{02}\rho_{01}}{P_{01}\rho_{02}}.$$
(9.20)

The stagnation pressure and density can be related by combining the stagnation properties and the Rankine-Hugoniot equations for pressure and density, summarized as

$$\frac{P_{02}}{P_{01}} = \left[\frac{1+\gamma_{Pv}M_1^2}{1+\gamma_{Pv}M_2^2}\right] \left[\frac{1+\frac{\gamma_{Pv}-1}{2}M_2^2}{1+\frac{\gamma_{Pv}-1}{2}M_1^2}\right]^{\frac{\gamma_{Pv}-1}{\gamma_{Pv}-1}},$$
(9.21a)

$$\frac{\rho_{02}}{\rho_{01}} = \frac{M_1^2}{M_2^2} \left[\frac{1 + \gamma_{Pv} M_2^2}{1 + \gamma_{Pv} M_1^2} \right] \left[\frac{1 + \frac{\gamma_{Pv} - 1}{2} M_2^2}{1 + \frac{\gamma_{Pv} - 1}{2} M_1^2} \right]^{\frac{1}{\gamma_{Pv} - 1}}.$$
(9.21b)

It becomes apparent that the difficulty lies in explicitly relating the stagnation compressibility factor ratio Z_{02}/Z_{01} across the shock wave. This feat is also demonstrated in Eq. (9.20), where the thermal property ratio $Z_{02}T_{02}/Z_{01}T_{01}$ is simply unity for a perfect gas. This allows the post-shock condition to be related the upstream condition under such condition by equating Eqs. (9.21a) and (9.21b).

TEN

Fundamental Derivative of Gas Dynamics

The preceding chapters covering this part on real gas dynamics sought to quantify nonideal compressible flow problems, whilst withholding from the qualification of real gas behavior. In fact, one can conclude that the formulation and structure of the isentropic flow relations presented in Chapter 8 – such as stagnation properties and choked flow conditions – are a consequence of conservation equations rather than the ideal gas model in their traditional derivation. The gas dynamic behavior of a substance in the onedimensional real isentropic flow relations is captured by the local values of the real exponents γ_{Pv} , γ_{Tv} and γ_{PT} . Moreover, the value of the exponents in the isentropic relations in Chapter 1 describe the local shape of the isentrope and how "ideal" or "non-ideal" the shape isentrope is. Hence, the kind of gas dynamic behavior exhibited by a substance may be attributed to the local shape of the isentropes, determined by the values of the real isentropic exponents. The exponents, and therefore the shape of the isentropes, are a function of the molecular structure and the thermodynamic region in question as outlined in Chapter 3. In this chapter we will review the implications of the real isentropic gas model on gas dynamic behavior.

This is a heuristic derivation of the thermodynamic quantity called the *fundamental* derivative of gas dynamics Γ , whose value is known to govern the compressible behavior of substances [37–41]. The fundamental derivative is defined as the change in the sound velocity with pressure or density at constant entropy [37, 38], written as

fundamental derivative

$$\Gamma = 1 - \frac{c}{v} \left(\frac{\partial c}{\partial v}\right)_s, \quad \text{or} \qquad \Gamma = 1 + \frac{c}{v} \left(\frac{\partial c}{\partial P}\right)_s.$$
 (10.1)

Conditions related to the value of the fundamental derivative suggest the occurrence of ideal gas behavior, and the departure from such behavior, of substances [37–39]. The conditions related to the fundamental derivative are summarized in Table 10.1.

Table 10.1: Conditions related to the sign and value of the fundamental derivative Γ and the behavior of compressible substances [39].

$\Gamma > 1$	$\left(\frac{\partial c}{\partial v}\right)_s < 0$	classical ideal behavior
$0 < \Gamma < 1$	$0 < \left(\frac{\partial c}{\partial v}\right)_s < \frac{c}{v}$	classical real behavior
$\Gamma < 0$	$\left(\frac{\partial c}{\partial v}\right)_s > \frac{c}{v}$	non-classical behavior

As the speed of sound itself is defined as the derivative of the pressure-volume isentrope Eq. (8.2), the fundamental derivative is essentially the second derivative – or curvature – of the isentrope in the P-v plane [37–40]

$$\Gamma = \frac{v^3}{2c^2} \left(\frac{\partial^2 P}{\partial v^2}\right)_s.$$
(10.2)

From this definition of the fundamental derivative follows the connection with the real isentropes introduced in Part I. The second derivative of the pressure-volume isentrope Eq. (1.27) using the the assumption of a local constant value of the isentropic exponent, can be expressed as

$$\left(\frac{\partial^2 P}{\partial v^2}\right)_s = \gamma_{Pv} \left(\gamma_{Pv} + 1\right) \frac{P}{v^2}.$$
(10.3)

It must be emphasized that Eq. (10.3) excludes the derivative of γ_{Pv} with respect to volume, due to the assumption of local constant values of the isentropic exponents.

Elimination of the second order derivative and the speed of sound in Eq. (10.2), the fundamental derivative becomes

$$\Gamma = \frac{\gamma_{Pv} + 1}{2}.$$
(10.4)

One can easily verify that the perfect gas case $\Gamma = (\gamma + 1)/2$ is a solution of Eq. (10.4), as the isentropic exponent γ_{Pv} reduces to the ratio of the specific heats in the ideal case. Furthermore, from Eq. (10.4), it can be reasoned that the existence of nonclassical behavior predicted by the fundamental derivative, can be attributed to the chain rule of the derivative of γ_{Pv} with respect to volume when treated as a variable, as γ_{Pv} cannot be negative. This feature has also been demonstrated by Thompson, who incorporated the derivative of the adiabatic coefficient in the formulation of Γ for ideal gases [38].

Moreover, as was stressed in Chapter 8, there is no reason why Eq. (10.4) should be only applicable for gases. If γ_{Pv} were to be evaluated for a liquid, using the Tait equation of state for example [48, 49], the value of Γ can be calculated for liquids [38, 63].

Table 10.2: The fundamental derivative evaluated for two common equation of state, satisfying two opposing limits, i.e. gas and liquid [63].

perfect gas	$(\gamma + 1)/2$
tait liquid	(K+1)/2

10.1 Fundamental Derivative and Isentropic Flows

In its relation to isentropic flows, the fundamental derivative governs is known to govern the relation between change in Mach number with change in velocity [38, 63]

$$\frac{du}{u} = \frac{dM/M}{1 + (\Gamma - 1)M^2}.$$
(10.5)

For $\Gamma \geq 1$, the Mach number increases monotonically with velocity. This condition is satisfied for most fluids, as $(\gamma+1)/2 \geq 1$ for ideal gases [63], see Table 10.2. Yet, there is no reason as to believe that Γ is greater than unity or even positive in the general case [63]. These conditions are referred to as *classical real behavior* and *non-classical behavior* in Table 10.1, respectively.

Let us further explore the implications of Eq. (10.5) for isentropic flows. Moreover, the form taken on by the fundamental derivative in Eq. (10.4) hints at yet another relation, namely that of the ratio between the stagnation speed of sound and critical speed of sound $(c_0/c^*)^2$ Eq. (8.21). To demonstrate this equivalence, we will first derive Eq. (10.5) from the momentum equation of a one-dimensional inviscid flow, or Bernoulli equation, where changes in elevation have been discarded

$$udu + vdP = 0. (10.6)$$

The definition of the fundamental derivative Eq. (10.1) can be rearranged in the following form [38]

$$vdP = \frac{cdc}{\Gamma - 1}.$$
(10.7)

Substitution of the term vdP in Eq. (10.6), the one-dimensional momentum equation for a frictionless flow can be expressed as

$$udu + \frac{cdc}{\Gamma - 1} = 0. \tag{10.8}$$

Subsequent elimination of the sound velocity by c = u/M, the momentum equation is expressed explicitly in terms of the flow velocity and the dimensionless quantities Mand Γ

$$udu = -\frac{\frac{u}{M} \frac{d}{M}}{\Gamma - 1}.$$
(10.9)

The derivative du/M in Eq. (10.9) can be expanded using the chain rule

$$d\frac{u}{M} = \frac{1}{M}du - \frac{u}{M^2}dM.$$
(10.10)

Substitution of Eq. (10.10) into Eq. (10.9) yields the following relation between the velocity and the Mach number [38]:

$$\frac{du}{u} = \frac{1}{1 + (\Gamma - 1)M^2} \frac{dM}{M}.$$
(10.11)

Eq. (10.11) may be recognized as the relation between the flow velocity and Mach number for Prandtl-Meyer expansion waves Eq. (9.10), obtained by logarithmic differentiation. The relation between Γ and the characteristic speed $(c_0/c^*)^2$ can be showed by performing the inverse of this process

$$\ln u = \ln M - \frac{1}{2}\ln(1 + (\Gamma - 1)M^2) + \ln C, \qquad (10.12)$$

where C is the constant of integration. The integration constant will be demonstrated to be the stagnation speed of sound c_0 for an isentropic flow. Combining terms yields

$$u^{2} = \frac{C^{2}M^{2}}{1 + (\Gamma - 1)M^{2}}.$$
(10.13)

The value of C can be determined by introducing a non-trivial combination of u and M. It his case, we let $u = c^*$ for M = 1. Solving for the integration constant, the relation between the fundamental derivative and the ratio $(c_0/c^*)^2$ of Eq. (8.21) for a real isentrope with constant exponent is demonstrated

$$C^{2} = c^{*2} \Gamma = c^{*2} \frac{\gamma_{Pv} + 1}{2} = c_{0}^{2}.$$
 (10.14)

Hence, we have proven the relation between the fundamental derivative and the ratio $(c_0/c^*)^2$ for real isentropes assuming a local constant value of the exponent γ_{Pv} :

$$\Gamma = \frac{c_0^2}{c^{*2}} = \frac{\gamma_{Pv} + 1}{2}.$$
(10.15)

Alternatively, Eq. (10.13) can be expressed as:

$$\frac{u}{c_0} = \left[\frac{M^2}{1 + (\Gamma - 1)M^2}\right]^{\frac{1}{2}}.$$
(10.16)

Eq. (10.16) is an alternative notation of the relation between the flow velocity and the stagnation speed of sound Eq. (8.30) in Chapter 8. Furthermore, Eq. (10.16) can be expressed as the ratio between the speed of sound and the stagnation speed of sound, Eq. (8.19):

$$\frac{c_0^2}{c^2} = 1 + (\Gamma - 1)M^2.$$
(10.17)

The stagnation properties and critical properties naturally follow from Eq. (10.17) for a non-ideal isentropic compressible flow.

Stagnation Properties	
$\frac{P_0}{P} = \left[1 + (\Gamma - 1)M^2\right]^{\frac{\gamma_{Pv}}{\gamma_{Pv} - 1}}$	
$\frac{T_0}{T} = \left[1 + (\Gamma - 1)M^2\right]^{\frac{\gamma_{Tv} - 1}{\gamma_{Pv} - 1}}$	
$\frac{\rho_0}{\rho} = \left[1 + (\Gamma - 1)M^2\right]^{\frac{1}{\gamma_{P_v} - 1}}$	
$\frac{Z_0}{Z} = \left[1 + (\Gamma - 1)M^2\right]^{\frac{\gamma_{Pv} - \gamma_{Tv}}{\gamma_{Pv} - 1}}$	
Critical Properties	
$\frac{P_0}{P^*} = \Gamma^{\frac{\gamma_{Pv}}{\gamma_{Pv}-1}}$	
$\frac{T_0}{T^*} = \Gamma^{\frac{\gamma_{Tv} - 1}{\gamma_{Pv} - 1}}$	
$\frac{\rho_0}{\rho^*} = \Gamma^{\frac{1}{\gamma_{P_v} - 1}}$	
$\frac{Z_0}{Z^*} = \Gamma^{\frac{\gamma_{Pv} - \gamma_{Tv}}{\gamma_{Pv} - 1}}$	

Table 10.3: Non-ideal is entropic compressible flow properties expressed in terms of the fundamental derivative Γ under the assumption of a local constant value of the isentropic exponents.

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PART IV

NUMERICAL SIMULATION OF REAL GAS FLOWS

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By condensing all unknowns that describe the isentropic behavior of substances into the variables γ_{Pv} , γ_{Tv} and γ_{PT} in Part I, an implicit form has been obtained which allowed for the evaluation of thermodynamic properties in Part II, and was used to describe non-ideal isentropic compressible flows in Part III. In the final part of this work, the real isentropic gas model will take on an explicit form by introducing equations of states, look-up tables, or a thermodynamic library to evaluate their terms for application of numerical simulations of non-ideal compressible flows.

Chapter 11 is written to serve as a reference for the numerical modeling of nonideal compressible fluid dynamics (NICFD). Several options for numerical schemes are discussed for the evaluation of the isentropic exponents. Additionally, an overview is provided of the Van der Waal, Soave-Redlich-Kwong, and Peng-Robinson equations of states for code implementation. In Chapter 12, the Van der Waals scheme is selected for the numerical simulation of a common shock tube problem for validation of the generalized isentropic gas model presented in this work.

ELEVEN

Explicit Numerical Schemes

In this chapter, the generalized isentropic gas model will be evaluated in a straightforward approach using equations of state explicit in pressure, volume and temperature. The Van der Waals (VdW), Soave-Redlich-Kwong (SRK), and Peng-Robinson (PR) equations of state will be treated in sections 11.1 through 11.3 to be used as a reference.

Where an equation of state is used explicit in pressure, volume, or temperature, a modular approach can be pursued where thermodynamic models that exhibit this property can be readily interchanged. The goal of such an approach is to fully resolve the P-v-T behavior of a substance and its derivatives and then use thermodynamic relations to obtain other properties rather than explicitly express thermodynamic quantities in terms of the equation of state of choice.

In Chapter 3 the "polytropic gas" model was introduced for gases whose isochoric specific heat capacity c_v is assumed constant [43] and a function of its molecular structure [34, 42]. Although the polytropic gas model does lead to inaccuracies approaching the critical point, their application is justifiable for qualitative studies, the initialization of simulations where non-ideal flow effects are of concern, and where high computational efficiency is required [26].

The polytropic gas model is no longer sufficient if a high degree of accuracy is desired. The isentropic properties may then be evaluated using multiparameter equations of state (MPEOS) like the Span-Wagner equation of state [64], or by use of thermodynamic libraries [65, 66], in the latter case at the cost of reduced computational efficiency. Alternatively, a look-up table (LuT) approach may be used as a compromise between high computational-speed and high accuracy [30, 67]. In such a scheme, the isentropic exponents may be pre-computed to speed up simulations. Other thermodynamic properties and stagnation properties can then be evaluated by the exact thermodynamic definition summarized in Table 11.1.

A hybrid scheme is also conceivable. In such a scheme, the P-v-T behavior in the simulation is captured by an equation of state of choice, and the true isochoric heat capacity c_v is provided in the form of a look-up table. The straightforward, yet significant improvement over the polytropic gas model of such a scheme by including the real change of the isochoric heat capacity could improve the accuracy the simulation at a minimal increase in computational costs. Moreover, the isochoric heat capacity makes for a readily tabulated property, as its relatively small variations require less consideration of meshing of different thermodynamic regions with regard to interpolation accuracy.

Table 11.1: Relevant equations of application to CFD code

Specific Heats		
$c_v = \frac{f}{2}R$		
$c_p = c_v + T \left(\frac{\partial v}{\partial T}\right)_T \left(\frac{\partial P}{\partial T}\right)_T$		
Isentropic Exponents		
$\gamma_{Pv} = -\frac{v}{P} \frac{c_p}{c_v} \left(\frac{\partial P}{\partial v}\right)_T$		
$\gamma_{Tv} = 1 + \frac{v}{c_v} \left(\frac{\partial P}{\partial T}\right)_v$		
$\gamma_{PT} = \frac{1}{1 - \frac{P}{c_p} \left(\frac{\partial v}{\partial T}\right)_P}$		
Speed of Sound		
$c = \sqrt{\gamma_{Pv} Pv}$		
Stagnation Properties		
$\frac{P_0}{P} = \left[1 + \frac{\gamma_{Pv} - 1}{2}M^2\right]^{\frac{\gamma_{Pv}}{\gamma_{Pv} - 1}}$		
$\frac{T_0}{T} = \left[1 + \frac{\gamma_{Pv} - 1}{2}M^2\right]^{\frac{\gamma_{Tv} - 1}{\gamma_{Pv} - 1}}$		
$\frac{\rho_0}{\rho} = \left[1 + \frac{\gamma_{Pv} - 1}{2}M^2\right]^{\frac{1}{\gamma_{Pv} - 1}}$		
Critical Mass Flux		
$\frac{M^*}{A^*} = \sqrt{\gamma_{Pv}\rho_0 P_0} \left(\frac{2}{\gamma_{Pv}+1}\right)^{\frac{\gamma_{Pv}+1}{\gamma_{Pv}-1}}$		

11.1 The Van der Waals Equation of State

The Van der Waals equation of state was the first, simplest and best-known equation of state to account for real gas effects [44]. Due to the statistical nature of thermodynamic properties, the Van der Waals equation served as the earliest connection between the macroscopic behavior of substances and the microscopic interaction of molecules. Although lacking in accuracy, the two-parameter extension of the ideal gas law to include real gas effects laid the foundation towards more complex and more accurate empirical equations of state such as the Redlich-Kwong and the Peng-Robinson equations of state also included in this discussion.

The convenience of the Van der Waals equation lies in the simplicity of the twoparameter approach to capturing the influence of fundamental molecular interactions on the overall behavior of the substance [44]. The two-parameter approach is based on two concepts related to molecular interactions. The first is the notion that molecules themselves have a finite volume, parameter b, that should be subtracted from the measurable volume occupied by a gas. Secondly, concerning intermolecular forces, it is reasoned that the collective force exerted by a molecule on a surface – i.e. the statistical definition of pressure – is reduced by intermolecular attraction forces that increase in density, parameter a [68, 69].

The Van der Waals equation is summarized in Table 11.2. When the P-v-T behavior at a state is fully resolved, the derivatives may be used to evaluate other thermodynamic quantities according to Table 11.1.

Van der Waals $P(T, v) = \frac{RT}{v - b} - \frac{a}{v^2}$ $e(T, v) = c_v T - \frac{a}{v}$
$P(T, v) = \frac{RT}{v - b} - \frac{a}{v^2}$ $e(T, v) = c_v T - \frac{a}{v}$
$e(T,v) = c_v T - \frac{a}{v}$
$s(T, v) = c_v \ln T + R \ln(v - b)$
where $a = \frac{27}{64} \frac{R^2 T_c^2}{P_c}$ and $b = \frac{1}{8} \frac{R T_c}{P_c}$
$\left(rac{\partial P}{\partial T} ight)_v = rac{R}{v-b}$
$\left(\frac{\partial P}{\partial v}\right)_T = -\frac{RT}{(v-b)^2} + \frac{2a}{v^3}$
$\left(\frac{\partial v}{\partial T}\right)_{P} = -\left(\frac{\partial P}{\partial T}\right)_{v} \left/ \left(\frac{\partial P}{\partial v}\right)_{T}\right.$

11.2 Soave-Redlich-Kwong Equation of State

Over the years many modifications were proposed to improve the Van der Waals equation. Some by the empirical fitting of data, others by capturing specific molecular interactions that persist in certain kinds of molecules such as hydrogen bonds or molecular bipolarity. Either way, most of the modifications addressed the attraction coefficient ain the original Van der Waals equation that incorporates these effects [28, 29].

One of the most successful modifications has been the Redlich-Kwong equation of state, that gave an empirical temperature dependency to the attraction term. The change of the attraction term was entirely empirical without any rigorous substantiation [70]. The Redlich-Kwong equation of state performs well for substances above the critical temperature but lacks the ability to predict phase-equilibria accurately even for single phase substances [29, 71].

G. Soave proposed an improvement on the temperature dependency of the attraction coefficient to better predict phase transitions. The improvement arose from solving the iso-fugacity for the vapor pressure at the vapor-liquid boundary [29, 71]. This modification is now known as the Soave-Redlich-Kwong equation of state and is summarized in Table 11.3.

11.3 Peng-Robinson Equation of State

The Soave-Redlich-Kwong equation rapidly established itself as an industry standard given the accuracy for its relative simplicity of use and its ability to predict vapor-liquid equilibria of mixtures with reasonable accuracy [28, 72], even though the SRK equation provided unsatisfactory results when it came to the prediction of the densities in the liquid phase and the critical region.

To resolve this issue, Peng and Robinson proposed a further modification of the SRK equation, based on semi-empirical arguments, to change the volumetric dependency of the attraction term to yield more realistic values for the critical compressibility factor [72]. The temperature dependence of the attraction term proposed by Soave was left intact due to its previous successful application to the Redlich-Kwong equation of state. The Peng-Robinson equation is summarized in Table 11.4.

The Peng-Robinson equation performs equally well or better as the Soave-Redlich-Kwong [29, 72]. Both have become industry standard due to their ease of use, and their ability to accurately describe temperature, pressure and phase compositions in binary and multicomponent systems. However, the success is limited by the calculation of liquid saturation densities, which are invariably overpredicted [28].

Soave-Redlich-Kwong		
$P(T, v) = \frac{RT}{v - b} - \frac{a\alpha^2(T)}{v(v + b)}$		
$e(T,v) = c_v T + \frac{a}{b} \left(\alpha^2(T) - 2\alpha(T)\alpha'(T) \right) \ln \frac{v}{v+b}$		
$s(T, v) = c_v \ln T + \frac{2a}{b} \alpha(T) \alpha'(T) \ln \frac{v+b}{v}$		
where $a = 0.42748 \frac{R^2 T_c^2}{P_c^2}$ and $b = 0.08664 \frac{RT_c}{P_c}$		
$\alpha = 1 + \kappa \left(1 - \sqrt{\frac{T}{T_c}} \right)$		
$\kappa = 0.480 + 1.574\omega - 0.176\omega^2$		
$\left(\frac{\partial P}{\partial T}\right)_v = \frac{R}{v-b} - \frac{2a\alpha(T)\alpha'(T)}{v(v+b)} \qquad \text{where} \alpha' = \frac{d\alpha}{dT}$		
$\left(\frac{\partial P}{\partial v}\right)_T = -\frac{RT}{(v-b)^2} + \frac{a\alpha^2(T)(2v-b)}{v^2(v+b)^2}$		
$\left(\frac{\partial v}{\partial T}\right)_{P} = -\left(\frac{\partial P}{\partial T}\right)_{v} \left/ \left(\frac{\partial P}{\partial v}\right)_{T}\right.$		

Table 11.3: Summary of the Soave-Redlich-Kwong Equation of State [71]

Peng-Robinson		
$P(T,v) = \frac{RT}{v-b} - \frac{a\alpha^2(T)}{v(v+b) + b(v-b)}$		
$e(T, v) = c_v T - \frac{a\alpha(T)(\kappa+1)}{b\sqrt{2}} \tanh^{-1} \frac{b\sqrt{2}}{v+b}$		
$s(T,v) = c_v \ln T + R \ln(v-b) - \frac{a\alpha(T)\kappa}{b\sqrt{2TT_c}} \tanh^{-1} \frac{b\sqrt{2}}{v+b}$		
where $a = 0.45724 \frac{R^2 T_c^2}{P_c^2}$ and $b = 0.0778 \frac{RT_c}{P_c}$		
$\alpha = 1 + \kappa \left(1 - \sqrt{\frac{T}{T_c}} \right)$		
$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2$		
$\left(\frac{\partial P}{\partial T}\right)_{v} = \frac{R}{v-b} - \frac{2a\alpha(T)\alpha'(T)}{v(v+b) + b(v-b)} \qquad \text{where} \alpha' = \frac{d\alpha}{dT}$		
$\left(\frac{\partial P}{\partial v}\right)_T = -\frac{RT}{(v-b)^2} + \frac{2a\alpha^2(v+b)}{[v(v+b)+b(v-b)]^2}$		
$\left(\frac{\partial v}{\partial T}\right)_{P} = -\left(\frac{\partial P}{\partial T}\right)_{v} \left/ \left(\frac{\partial P}{\partial v}\right)_{T}\right.$		

Table 11.4: Summary of the Peng-Robinson Equation of State [72]

TWELVE

The Riemann Problem

In this final chapter, the real isentropic gas model presented in this work is applied in solving the one-dimensional Euler equations for the Riemann problem [73] for a nonideal compressible flow. Doing so, we will combine the theoretical investigations of earlier parts with the numerical schemes of the previous chapter to demonstrate and validate the real isentropic gas model for NICFD codes [24, 26, 27]. The validation will lie in the affirmation that the general equation of the speed of sound Eq. (8.3), is capable of correctly calculating the sound velocity for non-ideal fluid flows for a selected equation of state. If this is true, any other concepts related to the isentropic exponents evaluated at a state is also exact, as discussed in Chapter 2.

A standard shock tube problem has been selected for this exercise [74] whose initial conditions are based on the work of Rinaldi et al [23]. In this work, an exact scheme is presented for solving the Riemann problem for real gas flows. Moreover, the work conducted by Rinaldi concentrates on numerical simulations in the dense gas region for single phase substances. The real isentropic gas model is also confined to stable single phase substances since the specific heat capacities are undefined in the two-phase region, as outlined in Chapter 3.

Unlike Rinaldi's work, which relied on a thermodynamic library for the evaluation of gas properties [23, 65], fluid properties will be evaluated using the polytropic Van der Waals model of the previous chapter for a qualitative validation. The substance under investigation is Helium, with the initial conditions as presented in Table 12.1. The fluid is initially at rest.

	left	right	
temperature	$1.275 T_{r}$	$1.100 T_{r}$	K
	6.624	5.715	K
density	$1.400 \rho_{\rm r}$ 101.594	$0.400 \rho_{\rm r}$ 29.027	$ m kg/m^3$ $ m kg/m^3$
pressure	$5.648 P_r$	$1.029P_{r}$	kPa
	1285.530	234.294	kPa

Table 12.1: Initial conditions for the shock tube problem

The polytropic Van der Waals model has been implemented in both the exact solver and the numerical solver [23, 75]. The only difference between them is the way in which the speed of sound is defined across both solvers. For the exact solver, the explicit definition of the sound velocity of a Van der Waals gas had been implemented [39]

$$c^{2} = \left(1 + \frac{2}{f}\right) RT \left(\frac{v}{v-b}\right)^{2} - \frac{2a}{v}.$$
 (solver) (12.1)

The numerical solver, on the other hand, uses the general relation for the speed of sound repeated here for convenience:

$$c^2 = \gamma_{Pv} Pv. \qquad (simulation) \qquad (12.2)$$

The exponent γ_{Pv} is treated as a variable, whose value is re-evaluated for each control volume for every time step.

The AUSM flux splitting scheme is implemented in the numerical solver [73, 76, 77]. The grid stretches a length of one meter from (-0.5, 0.5), where the initial state discontinuity is placed at the origin. The grid is discretized in 500 equal intervals. The CFL number is set to 0.10, resulting in a time step of $\Delta t = 7.1684 \times 10^{-7}$ s [77]. The simulation is run for 2000 time steps.

The result of the numerical simulation is presented in Figure 12.1, and compared to the exact solution. The exact solution and the numerical simulation show to be in good agreement with each other. The fact that the locations of the expansion fan, contact discontinuity, and the shock discontinuity between the exact and numerical solver coincide implies that the definitions of the speed of sound given by Eqs. (12.1) and (12.2) are indeed equivalent. We have thereby demonstrated the validity of the real isentropic gas model.

We can perhaps demonstrate this equivalence even more explicitly. Namely, if the exact solution of the Riemann problem yields the same results if the definitions of the speed of sound Eqs. (12.1) and (12.2) were interchanged. In fact, let us derive Eq. (12.1) for a Van der Waals gas from the general definition of the speed of sound.

Substitution of the definition of γ_{Pv} Eq. (1.30) into the definition of the speed of sound yields

$$c^{2} = -v^{2} \frac{c_{p}}{c_{v}} \left(\frac{\partial P}{\partial v}\right)_{T}.$$
(12.3)

The isobaric heat capacity is related to the isochoric heat capacity according to

$$c_p = c_v + T \left(\frac{\partial v}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_v.$$
(12.4)

Eliminating c_p , and using the reciprocity between the partial derivatives, Eq. (12.3) can be expressed as



Figure 12.1: Solution of the Riemann problem for the initial conditions selected in Table 12.1 for Helium, modeled as a polytropic Van der Waals gas. The numerical simulation (-) shows good correspondence with the exact solution (-) provided by Rinaldi [23].

$$c^{2} = \frac{v^{2}}{c_{v}}T\left(\frac{\partial P}{\partial T}\right)_{v}^{2} - v^{2}\left(\frac{\partial P}{\partial v}\right)_{T}.$$
(12.5)

The partial derivatives $(\partial P/\partial T)_v$ and $(\partial P/\partial v)_T$ are evaluated for a Van der Waals gas (see Table 11.2). Elimination of the derivatives we can write

$$c^{2} = \frac{1}{c_{v}}RT\left(\frac{v}{v-b}\right)^{2} + \left[RT\left(\frac{v}{v-b}\right)^{2} - \frac{2a}{v}\right].$$
(12.6)

Finally, for a polytropic gas, the isochoric heat capacity is defined as $c_v = f/2R$. Rearranging of Eq. (12.6), we indeed find the explicit expression of the speed of sound for a Van der Waals gas:

$$c^{2} = \left(1 + \frac{2}{f}\right) RT \left(\frac{v}{v-b}\right)^{2} - \frac{2a}{v}.$$
(12.7)

This result perhaps might not be surprising. As any departure of gas dynamic behavior from ideal behavior is captured by the term γ_{Pv} , the validity of the model lies in the correctness of its definition. A definition which, apart from the assumed from the isentropes, Eqs. (1.27–1.29), had been based on nothing but exact differentials and Maxwell transformations. The previous outcome is, therefore, not just a confirmation of the generalized equation for the speed of sound, but more so a reaffirmation that our the assumed form of the isentropes in Chapter 1 was indeed correct.

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Conclusion

The generalized isentropic gas model has been successfully used to extend ideal compressible gas relations to real gas flows. The state functions of the real isentropic exponents can be adapted to take on the form of any equation of state, which determines the accuracy of their evaluation. Moreover, by adhering to the ideal gas notation of the isentropic relations, the real gas relation retain their familiar form, emphasizing the equivalence between the ideal gas relations and the general case. The applicability of the model to non-ideal fluid dynamics (NICFD) codes has been demonstrated and validated.

The isentropic gas model was found to satisfy all necessary physical requirements for application throughout the single phase domain ranging from liquid to gaseous states. Its limits were determined to satisfy physical constraints, reducing to the incompressible substance model at high densities and reducing to the ideal gas model at low densities and high temperature respectively. Between the volumetric limits, the model loses its validity within the two-phase region – except for metastable states up to the spinodal lines – as the specific heat capacities are undefined here and the requirements for thermodynamic stability are violated.

The model is reasoned to be exact at a state point. As a consequence, the isentropic model is thermodynamically consistent with other properties at a point and can thus be used to evaluate those properties. This has lead to new insights regarding the caloric behavior, compressibility coefficients, Joule-Thomson coefficient, and entropy relations of real fluids in the general case, all of which can be shown to reduce to the ideal case in the ideal limit.

When it comes to relating states, the ability to accurately relate isentropic states using the assumption of locally constant values of the real isentropic exponents depends on the thermodynamic region and the molecular complexity of the substance. The validity of the assumption improves moving away from the critical point as the influence of higher-order derivatives diminishes, in the limit where the isentropes with approximated exponents and isentropes with continuously varying exponents coincide for an ideal gas. Although the approximation deteriorates with increasing molecular complexity, this effect is partially counteracted by reduced variation of the isentropic exponents as the molecular weight increases. Though, the assumption of constant exponents is found to be acceptable for small isentropic changes such as stagnation properties and other isentropic flow properties.

Recommendations

This work was intended to be both an introduction and extension of the generalized isentropic gas model, following the theoretical nature of the investigation. The choice not to go in-depth on practical applications, therefore, has been a deliberate one, as is the nature of fundamental research. During this period, the following matters arose which certainly do have practical relevance.

- The implicit and analytical character of the generalized isentropic gas model makes it suitable for a modular implementation into computer codes, where any equation of state, thermodynamic library, or look-up table may be used for its evaluation. The modular approach, combined with the significantly reduced complexity of thermodynamic relations, like the generalized speed of sound equation, has much potential to reduce computational costs of non-ideal compressible fluid simulations.
- Use of the model in simulations also presents several options to make effective compromises between accuracy and computational costs. For this purpose, a hybrid scheme is proposed where an accurate semi-empirical equation of state may be combined with a look-up table for the isochoric heat capacity constructed by a thermodynamic library. In a more experimental scheme, one could also choose to tabulate two of the three isentropic exponents. If the pressure, volume, and temperature are known, other properties such as the speed of sound, and Joule-Thomson coefficient can be obtained in a straightforward approach.
- The assumption of locally constant values for the isentropic exponents γ_{Pv} , γ_{Tv} , and γ_{PT} has frequently been used throughout this work providing the necessary means to treat real substances as if it were ideal gases. To improve the accuracy this assumption, one might include derivatives of the real exponents into the functions relating states along an isentrope. Although this could be done analytically, this will likely be a most complex procedure due to the multivariate dependency of the isentropic exponent on state variables. Regarding NICFD simulations, perhaps a more useful extension would be to numerically linearize the exponents at a state point using a Taylor expansion to include the local variation of the exponents.
- The definition of the fundamental derivative in terms of the real exponent γ_{Pv} presented in Chapter 10 could be completed by introducing the derivative of the exponent with respect to volume. Including the derivative of the exponent may yield a general expression for the fundamental derivative, whose terms can be evaluated directly using any equation of state. Completing the expression may also yield interesting insights in the relation between the fundamental derivative and isentropic flows demonstrated in that chapter.

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APPENDIX A

Thermodynamic Identities

A.1 Exact Differentials

Exact differential:

$$dX = \left(\frac{\partial X}{\partial Y}\right)_Z dY + \left(\frac{\partial X}{\partial Z}\right)_Y dZ.$$
 (A.1)

Test for exactness:

$$\left(\frac{\partial X}{\partial Y}\right)_{Z} \left(\frac{\partial Y}{\partial Z}\right)_{X} \left(\frac{\partial Z}{\partial X}\right)_{Y} = -1.$$
(A.2)

A.2 Maxwell Relations

$$\begin{pmatrix} \frac{\partial P}{\partial s} \end{pmatrix}_{v} = -\left(\frac{\partial T}{\partial v}\right)_{s}, \qquad \left(\frac{\partial P}{\partial s}\right)_{T} = -\left(\frac{\partial T}{\partial v}\right)_{P}.$$

$$\begin{pmatrix} \frac{\partial s}{\partial v} \end{pmatrix}_{P} = \left(\frac{\partial P}{\partial T}\right)_{s}, \qquad \left(\frac{\partial s}{\partial v}\right)_{T} = \left(\frac{\partial P}{\partial T}\right)_{v}.$$
(A.3)

A.3 Derivatives

derivatives in internal energy	$\left(\frac{\partial e}{\partial T}\right)_v = c_v$	$\left(\frac{\partial e}{\partial P}\right)_v = c_v \left(\frac{\partial T}{\partial P}\right)_v$	$\left(\frac{\partial e}{\partial T}\right)_v = T \left(\frac{\partial P}{\partial T}\right)_v - P$	$\left(\frac{\partial T}{\partial v}\right)_e = \frac{T}{v}(1 - \gamma_{Tv}) - \frac{P}{c_v}$
derivatives in enthalpy	$\left(\frac{\partial h}{\partial T}\right)_P = c_P$	$\left(\frac{\partial h}{\partial v}\right)_{P} = c_{p} \left(\frac{\partial T}{\partial v}\right)_{P}$	$\left(\frac{\partial h}{\partial P}\right)_T = -T \left(\frac{\partial v}{\partial T}\right)_P + v$	$\left(\frac{\partial T}{\partial P}\right)_{h} = \frac{T}{P}\frac{\gamma_{PT}-1}{\gamma_{PT}} - \frac{v}{c_{p}}$
derivatives in entropy	$\left(\partial P \right) = \sum_{\alpha = 1}^{\infty} P$	$\left(\left. \frac{\partial v}{\partial v} \right)_s = -\frac{1}{1} P_v \frac{v}{v}$ $\left(\left. \partial T \right)_s = -\frac{1}{1} P_v \frac{v}{v}$	$\left(\begin{array}{c} \partial v \end{array} \right)_s = -\langle \gamma_{Tv} - 1 \rangle \frac{v}{v}$ $\left(\partial P \right)_s = \gamma_{PT} P$	$\left(\left. \overline{\partial T} \right)_s - \left. \gamma_{PT} - \overline{1} \right. \overline{T}$

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APPENDIX B

Supercritical CO₂ Compressor

In this section, the application of some of the real isentropic gas relations presented in this work are demonstrated for the thermodynamic analysis of a supercritical CO_2 compressor. The analytical expressions for the isentropic outlet state, stagnation properties, and critical area ratios are compared to values obtained by the conventional approach of using a thermodynamic library [66].

The supercritical CO_2 compressor of the SANDIA supercritical Brayton cycle test program has been selected for this exercise, as the operational status of this program is more advanced in its progress than any other such facility and is well documented. The compressor geometry and operating point are taken from the 2010 SANDIA report on the progress of the project [78].

The values of the isentropic exponents are calculated at the inlet state, and assumed to be constant throughout the compressor stage. When a greater degree of accuracy is required, one could define intermediate pressure levels where the isentropic exponents could be re-evaluated. The flow area A is calculated based on shroud and hub radii. Accordingly, the fluid velocity follows from the mass flow rate and the inlet density.

flow:	m	3.53	kg/s
	u	22.7	m/s
geometry:	A	255	mm^2
inlet:	P_1	7690	kPa
	T_1	305	Κ
	Z_1	0.219	—
	$ ho_1$	608.8	$\mathrm{kg/m^3}$
	c_1	215.2	m/s
	h_1	304.6	kJ/kg
	s_1	1.341	$\rm kJ/kgK$
outlet:	P_2	14000	kPa
exponents:	γ_{Pv}	3.668	_
	γ_{Tv}	1.345	-
	γ_{PT}	1.103	_

Table B.1: sCO₂ compressor operation condi-

tions.



Figure B.1: sCO_2 compressor T-s diagram

Outlet Isentropic State						
T_{2s}	Eq. (1.29)	322.6	Κ	err. 0.28 %		
	refprop	321.7	Κ			
ρ_{2s}	Eq. (1.27)	716.8	kg/m^3	orr 1 38 %		
	refprop	686.7	$\rm kg/m^3$	сл. 4.00 /0		
	Isentropic Work					
Δh_{s12}	Eq. (6.4)	9.663	kJ/kg	omm 1 95 07		
	refprop	9.484	kJ/kg	<i>ett.</i> 1.65 /0		
Inlet Stagnation Properties						
P_{01}	Eq. (8.10)	7874.1	kPa	0.00 (4		
	refprop	7874.1	kPa	<i>err.</i> 0.00 %		
T_{01}	Eq. (8.12)	305.6	К	0.00 (4		
	refprop	305.6	Κ	err. 0.00 %		
$ ho_{01}$	Eq. (8.14)	612.1	$\mathrm{kg/m^{3}}$	0.01.07		
·	refprop	612.2	kg/m^3	<i>err.</i> 0.01 %		
Z_{01}	Eq. (8.16)	0.222	_	0.00 14		
	refprop	0.222	_	<i>err</i> . 0.00 %		

Table B.2: Calculated quantities of the thermodynamic analysis of the SANDIA sCO₂ compressor compared to values obtained from REFPROP [66].

Unfortunately, the choked flow conditions cannot be verified by a thermodynamic library, nor is the critical mass flux of the SANDIA sCO_2 compressor documented in literature. Instead, we can calculate the area at which the flow is predicted to choke, and then check the corresponding critical mass flux to match the mass flux in Table B.1.

Table B.3: Chocked flow conditions of SANDIA sCO2 compressor.

A/A^*	Eq. (8.34)	4.56	_	
A^*		55.82	mm^2	
m^*	Eq. (8.38)	3.53	$\rm kg/s$	err.~0.00~%