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Solution of the Riemann problem of classical gasdynamics

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Abstract

The mere structure of the linearly degenerate characteristic field of the equations of gasdynamics provides the natural frame to build the exact Riemann solver for any gas satisfying the condition $e_{vvv}(s, v) \neq 0$, which guarantees the genuine nonlinearity of the acoustic modes. Differently from single equation methods rooted in the γ-law ideal gas assumption, the new approach is based on the system of two nonlinear equations imposing the equality of pressure and of velocity, assuming as unknowns the two values of the specific volume, or temperature, on the two sides of the contact discontinuity. Newton iterative method is used. The resulting exact solver is implemented for van der Waals gas, including the treatment of nonpolytropic behavior with molecular vibrations at thermal equilibrium, as well as for Martin–Hou gas, as an example of the general applicability of the proposed approach. The correctness of the new Riemann solver is demonstrated by comparisons with other numerical techniques.

Keywords: Riemann problem; van der Waals gas; Nonpolytropic gas; Martin–Hou gas model; Classical gasdynamics

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1. Introduction

The Riemann problem for the ideal gas does not admit a solution expressible in closed form. This has led several authors to develop iterative solution schemes to determine the different waves issuing from an initial discontinuity in the flow field variables. Two methods were first proposed by Godunov, one based on a fixed-point scheme [1] and the other based on a higher order Newton iteration, with a tangent parabola instead of a straight line [2]. Chorin [3] improved the first Godunov's method to circumvent some difficulties and computational inefficiencies caused by strong rarefaction waves. A rather different approach was pursued by Smoller [4] leading to a compact implicit equation that can be solved by a secant method.

Among the numerous subsequent works, the paper by Gottlieb and Groth [5] has become the classical reference in the field in that it presents the most efficient solver and contains an exhaustive comparative review of several implemented algorithms. Essentially, all these solvers are formulated for an ideal gas with

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a constant specific heat ratio, called also ideal γ-law gas, for which the Riemann problem is reduced to a single equation for the pressure or another unknown. A complete and detailed description of the solution of the Riemann problem for this kind of gas is given by Godlewski and Raviart [6, Chapter II, Section 3].

These Riemann solvers have been extended to deal with gases endowed with more general thermodynamic properties, designated commonly as nonideal or real gases. For instance, Letellier and Forestier have generalized Smoller method to the van der Waals gas [7]. In the particular case of zero attractive interaction, indicated as "covolume gas", Pike has proposed an approximated Riemann solver for the efficient numerical solution of gasdynamic equations [8]. Other similar Riemann solvers for real gases are described in the monograph of Toro [9]. All these works rely on the hypothesis of a constant specific heat at constant volume, an assumption often stated by attaching the attribute *polytropic* to the gas, as will be done throughout this paper. In the field of solvers for nonpolytropic ideal gases, the pioneering work of Colella and Glaz [10] must be mentioned. Riemann solvers suitable for simulating the propagation of shock waves inside compressible liquids have been proposed recently by Ivings et al. [11].

All these Riemann solvers for fluids different from the γ-law, i.e., polytropic ideal gas are formulated in terms of a single equation for the pressure unknown. This is particularly convenient for the purpose of obtaining an approximate or even an exact Riemann solver to be used eventually in the numerical integration of the Euler equations by means of a Godunov-type method.

The aim of the present paper is to devise a new approach for solving the Riemann problem associated with gases endowed with thermodynamic equations of state more general than the γ-law ideal gas. It will be shown that this objective is easily achieved by formulating the Riemann problem in its most natural form: the equality of the velocity value *and* of the pressure value across the contact discontinuity. The two-equation Riemann solver will be developed here specifically for the van der Waals gas with polytropic or nonpolytropic behavior, adopting as unknowns the two values of the specific volume, or of the temperature, on each side of the contact discontinuity. For both van der Waals models Hugoniot's condition $e_{vvv}(s,v) \neq 0$, with e, s and v denoting specific energy, entropy and volume, is fulfilled in the single-phase regions, except under very special situations. As well known, this condition guarantees that the characteristic fields associated with the acoustic eigenvalues are genuinely nonlinear, and therefore identifies gas behaviour which is usually put under the banner of *classical gasdynamics*. This property, also referred to as convexity of the Euler equation system, is lost in a limited region near the saturation curve for vapors with a conveniently high molecular weight. The loss of genuine nonlinearity results in "exotic" wave structures, such as rarefaction shock waves, compression fans and composite or mixed waves, which are the hallmark of the so-called *nonclassical gasdynamics* [12].

The Riemann solver developed here requires only that condition $e_{vvv}(s,v) \neq 0$ is satisfied. As a consequence, it is not limited to the van der Waals gas and is applicable also to gases with more general equations of state, such as Martin–Hou gas model [13], with the restriction of remaining in the realm of classical gasdynamics and provided that the uniqueness of the solution to the Riemann problem can be assured by Smith's strong condition $e_v(P,v) > 0$ [14].

The paper is structured as follows. Section 2 describes the mathematical properties of the Euler equations written for the variables, specific volume, velocity, and specific entropy. We define the concept of linear degeneracy and describe the necessary condition for genuine nonlinearity of the acoustic wave fields, introducing also the fundamental derivative of gasdynamics. The section ends with a brief account of the possibility for the polytropic van der Waals gas of manifesting a nonclassical behavior. In Section 3, a detailed description of the proposed Riemann solver is given, arranged in the following four steps: (i) the formulation of the Riemann problem as a system of two equations for the two specific volumes at either side of the contact discontinuity, as well as the description of the associated Newton iterative method of solution; (ii) the solution of the rarefaction wave; (iii) the solution of the shock wave; (iv) the tests performed in order to check the correctness of the proposed algorithm. Section 4 is a simple replica of the same four steps for the nonpolytropic case where a different parametrization by temperature allows explicit expressions of the thermodynamic relations within the solution algorithm. Section 5 contains the application to the Martin–Hou gas model. Section 6 is devoted to some concluding remarks. In the appendix, the thermodynamic definition of polytropic and nonpolytropic van der Waals gas, including the respective expressions for the speed of sound, is reported.

2. Eigenstructure of Euler equations

Let us consider the Riemann problem for the Euler equations of gasdynamics governing the motion of a compressible fluid of zero viscosity and zero thermal conductivity. To make the solution of rarefaction waves most simple, it is convenient to use the specific volume v, the velocity u, and the specific entropy s as unknowns, see, e.g. [15]. In this representation, the quasilinear form of the hyperbolic system of the Euler equations in one dimension is

$$\begin{cases} \dfrac{\partial v}{\partial t} + u\dfrac{\partial v}{\partial x} - v\dfrac{\partial u}{\partial x} = 0, \\ \dfrac{\partial u}{\partial t} + u\dfrac{\partial u}{\partial x} + v\left(\dfrac{\partial P}{\partial v}\right)_s\dfrac{\partial v}{\partial x} + v\left(\dfrac{\partial P}{\partial s}\right)_v\dfrac{\partial s}{\partial x} = 0, \\ \dfrac{\partial s}{\partial t} + u\dfrac{\partial s}{\partial x} = 0, \end{cases} \tag{2.1}$$

where $P = P(s, v)$ represents an equation of state of the fluid. By introducing the definitions

$$\boldsymbol{w} = \begin{pmatrix} v \\ u \\ s \end{pmatrix} \quad \text{and} \quad \boldsymbol{A}(\boldsymbol{w}) = \begin{pmatrix} u & -v & 0 \\ v\left(\frac{\partial P}{\partial v}\right)_s & u & v\left(\frac{\partial P}{\partial s}\right)_v \\ 0 & 0 & u \end{pmatrix}, \tag{2.2}$$

the nonlinear hyperbolic system can be written compactly

$$\frac{\partial \boldsymbol{w}}{\partial t} + \boldsymbol{A}(\boldsymbol{w})\frac{\partial \boldsymbol{w}}{\partial x} = 0. \tag{2.3}$$

The eigenvalues of matrix $\boldsymbol{A}(\boldsymbol{w})$ are, written in increasing order,

$$\lambda_1(\boldsymbol{w}) = u - c(s, v), \quad \lambda_2(\boldsymbol{w}) = u, \quad \lambda_3(\boldsymbol{w}) = u + c(s, v), \tag{2.4}$$

where the speed of sound of the gas

$$c(s, v) = \sqrt{-v^2\frac{\partial P(s, v)}{\partial v}} = \sqrt{\frac{\partial P(s, \rho)}{\partial \rho}} \tag{2.5}$$

has been introduced, [1] thanks to the inequality $\frac{\partial P(s,v)}{\partial v} = -e_{vv}(s, v) < 0$, which holds by virtue of thermodynamic stability. The associated right eigenvectors are $\boldsymbol{r}_1(\boldsymbol{w}) = (v, c(s, v), 0)^{\mathrm{T}}$, $\boldsymbol{r}_2(\boldsymbol{w}) = ((\frac{\partial P}{\partial s})_v, 0, (\frac{\partial P}{\partial v})_s)^{\mathrm{T}}$ and $\boldsymbol{r}_3(\boldsymbol{w}) = (v, -c(s, v), 0)^{\mathrm{T}}$. The gradients of the eigenvalues are easily evaluated as $\boldsymbol{\nabla}\lambda_1(\boldsymbol{w}) = (-(\frac{\partial c}{\partial v})_s, 1, -(\frac{\partial c}{\partial s})_v)^{\mathrm{T}}$, $\boldsymbol{\nabla}\lambda_2(\boldsymbol{w}) = (0, 1, 0)^{\mathrm{T}}$ and $\boldsymbol{\nabla}\lambda_3(\boldsymbol{w}) = ((\frac{\partial c}{\partial v})_s, 1, (\frac{\partial c}{\partial s})_v)^{\mathrm{T}}$, where $\boldsymbol{\nabla} = (\partial_v, \partial_u, \partial_s)$.

It is immediately verified that

$$\boldsymbol{r}_2(\boldsymbol{w}) \cdot \boldsymbol{\nabla}\lambda_2(\boldsymbol{w}) = 0 \tag{2.6}$$

for any $\boldsymbol{w}$ in the domain of definition of the variables v, u and s, so that the intermediate eigenvalue λ_2 is *linearly degenerate*.

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[1] With a slight notational abuse, the same symbol is used to indicate mathematically different functions which correspond to the same physical quantity expressed in terms of different variables.

On the contrary, for the other two eigenvalues a direct calculation gives

$$\begin{aligned} \boldsymbol{r}_1(\boldsymbol{w}) \cdot \nabla\lambda_1(\boldsymbol{w}) &= -v\left(\frac{\partial c}{\partial v}\right)_s + c, \\ \boldsymbol{r}_3(\boldsymbol{w}) \cdot \nabla\lambda_3(\boldsymbol{w}) &= v\left(\frac{\partial c}{\partial v}\right)_s - c. \end{aligned} \tag{2.7}$$

The *genuinely nonlinear* character of the eigenvalues $\lambda_1(\boldsymbol{w})$ and $\lambda_3(\boldsymbol{w})$ depends on the vanishing of the quantity $v(\frac{\partial c}{\partial v})_s - c$, cf. [16]. The sign of this expression depends on that of the following derivative

$$\frac{\partial^2 P(s,v)}{\partial v^2} = -e_{vvv}(s,v), \tag{2.8}$$

since a direct calculation gives, cf. [6, pp. 44–45],

$$\frac{\partial^2 P(s,v)}{\partial v^2} = -\rho^2 \frac{\partial}{\partial \rho}\left(-\rho^2 \frac{\partial P(s,\rho)}{\partial \rho}\right) = \frac{2c}{v^3}\left(c - v\frac{\partial c(s,v)}{\partial v}\right). \tag{2.9}$$

The function

$$\mathscr{G}(s,v) \equiv \frac{v^3}{2c^2}\frac{\partial^2 P(s,v)}{\partial v^2} = \frac{1}{c}\frac{\partial[c(s,\rho)\rho]}{\partial \rho}, \tag{2.10}$$

was introduced by Thompson [17] and is called the *fundamental derivative* of gasdynamics. The curve of the plane v–P, where $\mathscr{G}(P,v) = 0$ represents the locus of loss of the genuine nonlinearity for the considered gas. Note that $\mathscr{G}(T,v) = \mathscr{G}(s(T,v),v)$ can be expressed in terms of $P(T,v)$ and $c_v(T,v)$ using the general relation (A.2.5) for the speed of sound $c(T,v)$ and from equation (78) of [15, p. 39] giving $(\partial^2 P/\partial v^2)_s$.

In the particular case of the polytropic van der Waals gas defined in Section A.1 of the appendix, the fundamental derivative is easily found to be

$$\mathscr{G}(P,v) \equiv \mathscr{G}(s(P,v),v) = \frac{(\delta+1)(\delta+2)\frac{P+a/v^2}{(v-b)^2} - \frac{6a}{v^4}}{2(\delta+1)\frac{P+a/v^2}{v(v-b)} - \frac{4a}{v^4}}. \tag{2.11}$$

As shown by Bethe [15], Zel'dovich [18], and Thompson [17], see also Cramer [19] and Argrow [20], for the polytropic van der Waals gas a finite region of negative $\mathscr{G}$ may exist in the vapor phase near the saturation curve, see Fig. 1. The critical point has coordinates $v_{\rm cr} = 3b, P_{\rm cr} = a/(27b^2)$ and the saturation curve has been determined by Maxwell's equal area rule.

The locus $\mathscr{G} = 0$, boundary between the classical and nonclassical regimes, is found by setting the numerator of (2.11) to zero and solving for the pressure P to find, cf. [21],

$$P_{\mathscr{G}=0}(v) = \frac{a}{v^2}\left[\frac{6}{(\delta+1)(\delta+2)}\left(1-\frac{b}{v}\right)^2 - 1\right]. \tag{2.12}$$

In the limit $\delta \to 0$, i.e., $c_v = R/\delta \to \infty$, and for δ small enough there is a locus $\mathscr{G} = 0$ which represents a curve in the plane v–P. This curve starts in a point on the saturation curve slightly to the right of the critical point. The curve $\mathscr{G} = 0$ and the saturation curve delimit a finite region of negative $\mathscr{G}$ in the vapor phase.

The area of this nonclassical region diminishes as δ increases, and for $\delta = \delta^\star = 1/16.66 = 0.06$ reduces to a single point on the saturation curve of coordinates $(1.4843\ v_{\rm cr}, 0.888\ P_{\rm cr})$, as given by Thompson and Lambrakis [22]. For $\delta > \delta^\star$, no anomalous behavior can be observed in the vapor phase. The nonclassical region for $\delta = 0.0125$ is shown in the same Fig. 1. Note that small values of the parameter δ are associated

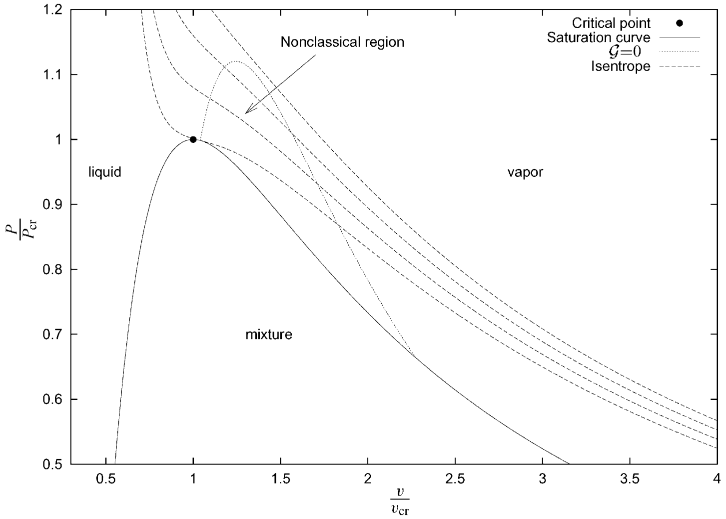

Fig. 1. Isentropes in the $v - P$ plane for the polytropic van der Waals gas with $\delta = 0.0125 < \delta^\star$. The "nonclassical" region is located between the locus $\mathscr{G} = 0$ and the saturation curve.

with a contribution to the specific heat by a large number of vibrational modes of the molecule, which are assumed here to be fully activated. In fact, the value of δ for a molecule of $N.A.$ atoms and with all its vibrational modes fully activated is given by

$$\delta = \begin{cases} \frac{1}{3N.A.-\frac{5}{2}} & \text{for linear molecules,} \\ \frac{1}{3(N.A.-1)} & \text{for nonlinear molecules.} \end{cases}$$

As a consequence the minimum number of atoms $N.A._{\rm min}$ required for making the nonclassical region accessible is $N.A._{\rm min} = \frac{5}{6} + \frac{1}{3\delta^\star}$ for linear molecules, and $N.A._{\rm min} = 1 + \frac{1}{3\delta^\star}$ for nonlinear molecules. For a description of the anomalous shock wave phenomena occurring in the nonclassical region, see [23].

In the forthcoming analysis of the Riemann problem, we are excluding states occurring inside the saturation curve and also gases allowing for nonclassical phenomena. In particular, for polytropic van der Waals gases with $\delta < \delta^\star$, we suppose that the Riemann problem does not involve states falling inside the region $\mathscr{G} < 0$.

3. Riemann problem for polytropic van der Waals gas

Let us now define the Riemann problem for the gasdynamic equations, associated with the two states $(v_{\rm l}, P_{\rm l}, u_{\rm l})$ and $(v_{\rm r}, P_{\rm r}, u_{\rm r})$, see, e.g. [4,14]. The Riemann problem of gasdynamics amounts to determine the system of the three waves issuing from the jump in the initial data. The system consists in a rarefaction or shock wave connecting the left state $(v_{\rm l}, P_{\rm l}, u_{\rm l})$ with a state on the left of the second wave which is always a contact discontinuity, and finally a rarefaction or shock wave connecting the state on the right of the contact discontinuity with the right state $(v_{\rm r}, P_{\rm r}, u_{\rm r})$, as depicted in Fig. 2.

3.1. Equation system for the Riemann problem

The peculiarity of the (intermediate) contact discontinuity is that both the velocity and pressure are constant across it while the other independent thermodynamic variable suffers a jump. In fact, the integral

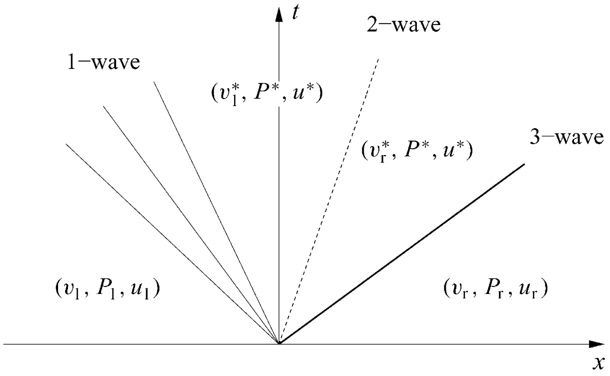

Fig. 2. Riemann problem for the Euler equations of gasdynamics.

curves of the linearly degenerate eigenvalue $\lambda_2(\boldsymbol{w})$ coincide with the Hugoniot loci and are obtained by solving the ODE system

$$\frac{\mathrm{d}\boldsymbol{w}}{\mathrm{d}\xi} = \alpha(\xi)\boldsymbol{r}_2(\boldsymbol{w}), \tag{3.1}$$

where α is an arbitrary function to fix the normalization. For the hyperbolic system of the Euler equations considered in Section 2, this system reads

$$\begin{cases} \dfrac{\mathrm{d}v}{\mathrm{d}\xi} = -\alpha(\xi)\dfrac{\partial P(s,v)}{\partial s}, \\ \dfrac{\mathrm{d}u}{\mathrm{d}\xi} = 0, \\ \dfrac{\mathrm{d}s}{\mathrm{d}\xi} = \alpha(\xi)\dfrac{\partial P(s,v)}{\partial v}. \end{cases} \tag{3.2}$$

Therefore, the variable u is constant along these curves. Moreover, taking the ratio of the first and the third equation we see that along the integral curves

$$\frac{\mathrm{d}v}{\mathrm{d}s} = -\frac{\partial P(s,v)}{\partial s}\bigg/\frac{\partial P(s,v)}{\partial v}. \tag{3.3}$$

The right-hand side is simply the derivative of the function $v = v(s)$ defined implicitly through the relation $P(s,v) =$ constant. Thus, also the variable P is constant along the integral curves. In conclusion, across the contact discontinuity $u = u^*$ and $P = P^*$, with u^* and P^* denoting the values of the constant velocity and pressure, as shown in Fig. 2.

Let $u_{(l)}(v)$ and $P_{(l)}(v)$ indicate respectively the velocity and pressure of the one-parameter family of states which can be connected to the left state (v_l, P_l, u_l) of the Riemann problem, by either a rarefaction wave or a shock wave, depending on the value of v with respect to v_l. Similarly, let $u_{(r)}(v)$ and $P_{(r)}(v)$ denote similar functions of the one-parameter family of states which can be connected to the right state (v_r, P_r, u_r). In other words, let us define the two functions

$$u_{(l)}(v) \equiv \begin{cases} u_{(l)}^{\mathrm{RH}}(v) & \text{if } v < v_l \\ u_{(l)}^{\mathrm{rw}}(v) & \text{if } v > v_l \end{cases} \quad \text{and} \quad u_{(r)}(v) \equiv \begin{cases} u_{(r)}^{\mathrm{RH}}(v) & \text{if } v < v_r \\ u_{(r)}^{\mathrm{rw}}(v) & \text{if } v > v_r \end{cases} \tag{3.4}$$

and the two functions

$$P_{(\mathrm{l})}(v) \equiv \begin{cases} P^{\mathrm{RH}}_{(\mathrm{l})}(v) & \text{if } v < v_{\mathrm{l}} \\ P^{\mathrm{rw}}_{(\mathrm{l})}(v) & \text{if } v > v_{\mathrm{l}} \end{cases} \quad \text{and} \quad P_{(\mathrm{r})}(v) \equiv \begin{cases} P^{\mathrm{RH}}_{(\mathrm{r})}(v) & \text{if } v < v_{\mathrm{r}}, \\ P^{\mathrm{rw}}_{(\mathrm{r})}(v) & \text{if } v > v_{\mathrm{r}}, \end{cases} \tag{3.5}$$

where the superscripts rw and RH denote, respectively, the solution of the rarefaction wave and of the shock wave by Rankine–Hugoniot conditions, see below.

To solve the Riemann problem means to determine the two values v_{l}^* and v_{r}^* of the specific volume of the gas on each side of the contact discontinuity as well as the constant values P^* and u^* existing on either side. For notational simplicity, let us denote the two unknown densities by $v \equiv v_{\mathrm{l}}^*$ and $w \equiv v_{\mathrm{r}}^*$. The equality of the values of velocity and of pressure on either side of the contact discontinuity means that v and w are solution to the system of two equations

$$\begin{cases} u_{(\mathrm{l})}(v) = u_{(\mathrm{r})}(w), \\ P_{(\mathrm{l})}(v) = P_{(\mathrm{r})}(w), \end{cases} \quad \text{that is} \quad \begin{cases} \phi(v,w) = 0, \\ \psi(v,w) = 0, \end{cases} \tag{3.6}$$

with the obvious definitions

$$\begin{aligned} &\phi(v,w) \equiv u_{(\mathrm{l})}(v) - u_{(\mathrm{r})}(w), \\ &\psi(v,w) \equiv P_{(\mathrm{l})}(v) - P_{(\mathrm{r})}(w). \end{aligned} \tag{3.7}$$

Thus, the application of Newton iterative method for solving this system requires to evaluate the Jacobian matrix

$$J(v,w) \equiv \begin{pmatrix} \frac{\mathrm{d}u_{(\mathrm{l})}(v)}{\mathrm{d}v} & -\frac{\mathrm{d}u_{(\mathrm{r})}(w)}{\mathrm{d}w} \\ \frac{\mathrm{d}P_{(\mathrm{l})}(v)}{\mathrm{d}v} & -\frac{\mathrm{d}P_{(\mathrm{r})}(w)}{\mathrm{d}w} \end{pmatrix}. \tag{3.8}$$

The final element of the solution of the Riemann problem is provided by the values $u^* = u_{(\mathrm{l})}(v) = u_{(\mathrm{r})}(w)$ and $P^* = P_{(\mathrm{l})}(v) = P_{(\mathrm{r})}(w)$. Note that the use of the specific volumes as unknown variables stems from the adopted representation of the gasdynamic equations. Of course, different unknowns can be chosen to formulate the two-equation system of the Riemann problem. Anyhow, for the polytropic van der Waals gas the specific volume is found to be very convenient to obtain simple expressions, while for the nonpolytropic case the temperature will be revealed to be a more convenient choice. In this work the problem of finding the optimal parameterization that assures the highest computational efficiency of the solution algorithm is not addressed.

The existence and uniqueness of the solution of the Riemann problem of gasdynamics under appropriate conditions have been established by Liu [24] and by Smith [14]. In particular, the "strong" condition $\partial e(P,v)/\partial v > 0$, which is sufficient for existence and uniqueness of the solution for arbitrary initial data [14], is satisfied by the polytropic van der Waals gas, thanks to the form of the equation of state (A.1.8). Thus, the Newton iteration will converge to the correct solution of (3.6) provided the initial guess is chosen properly, a task which could be more difficult for strong waves.

3.2. Rarefaction waves

A rarefaction waves is a one-parameter family of states connecting a given state (v_i, u_i, s_i) of the fluid and satisfying the differential Euler equations (2.1) or (2.3). This kind of continuous solutions is obtained by determining the so-called *integral curves* of each genuinely nonlinear mode of the system, that is the curves tangent in any point to the vector field of the associated eigenvector. Considering simultaneously the rarefactions associated with the first or the third eigenvalue, denoted by $\lambda_{1|3}(\boldsymbol{w})$, the corresponding integral curves $\boldsymbol{w} = \boldsymbol{w}(\xi)$ are obtained by solving the ODE system

$$\frac{\mathrm{d}\boldsymbol{w}}{\mathrm{d}\xi} = \frac{\boldsymbol{r}_{1|3}(\boldsymbol{w})}{\boldsymbol{r}_{1|3}(\boldsymbol{w}) \cdot \boldsymbol{\nabla}\lambda_{1|3}(\boldsymbol{w})}, \tag{3.9}$$

under the condition $\lambda_{1|3}(\boldsymbol{w}(\xi)) = \xi$ and subject to the initial condition $\boldsymbol{w}(\xi_i) = \boldsymbol{w}_i = (v_i, u_i, s_i)$, with $\xi_i = \lambda_{1|3}(\boldsymbol{w}_i)$.

For the hyperbolic system of the Euler equations this system becomes

$$\begin{cases} \dfrac{\mathrm{d}v}{\mathrm{d}\xi} = \dfrac{v}{c(s,v) - v\dfrac{\partial c(s,v)}{\partial v}}, \\ \dfrac{\mathrm{d}u}{\mathrm{d}\xi} = \dfrac{\pm c(s,v)}{c(s,v) - v\dfrac{\partial c(s,v)}{\partial v}}, \\ \dfrac{\mathrm{d}s}{\mathrm{d}\xi} = 0. \end{cases} \tag{3.10}$$

The last equation has the immediate solution $s = \text{constant} = s_i$, so that we have to solve the system of two equations

$$\begin{cases} \dfrac{\mathrm{d}v}{\mathrm{d}\xi} = \dfrac{v}{c(s_i,v) - v\dfrac{\partial c(s_i,v)}{\partial v}}, \\ \dfrac{\mathrm{d}u}{\mathrm{d}\xi} = \dfrac{\pm c(s_i,v)}{c(s_i,v) - v\dfrac{\partial c(s_i,v)}{\partial v}} \end{cases} \tag{3.11}$$

with the initial conditions $v(\xi_i) = v_i$ and $u(\xi_i) = u_i$. The first equation for v is uncoupled from the second, is separable and is solved by a simple quadrature

$$\xi = \xi(v) = u_i \mp c(s_i, v_i) + \int_{v_i}^{v} \left[\frac{c(s_i, v')}{v'} - \frac{\partial c(s_i, v')}{\partial v} \right] \mathrm{d}v'. \tag{3.12}$$

The solution $v = v(\xi)$ so obtained can be substituted into the second equation of (3.11), yielding another separable equation for u, again solvable by simple quadrature

$$u = u(\xi) = u_i \pm \int_{\xi_i}^{\xi} \left[1 - \frac{v(\xi')}{c(s_i, v(\xi'))} \frac{\partial c(s_i, v(\xi'))}{\partial v} \right]^{-1} \mathrm{d}\xi'. \tag{3.13}$$

One can now eliminate the variable ξ by the change of variables $\xi \to v(\xi)$, and the solution for the velocity can be written as

$$u = u(v) = u_i \pm \int_{v_i}^{v} \frac{c(s_i, v')}{v'} \, \mathrm{d}v'. \tag{3.14}$$

Using the expression of the speed of sound (A.1.9) with $s = s_i$, the solution for the rarefaction wave issuing from the *initial* or *input* state $(i) \equiv (v_i, u_i, P_i)$ for the polytropic van der Waals gas is found to be given by

$$u_{(i)}^{\mathrm{rw}}(v) = u_i \pm \int_{v_i}^{v} \left[(\delta + 1)\left(P_i + \frac{a}{v_i^2} \right) \frac{(v_i - b)^{\delta+1}}{(v' - b)^{\delta+2}} - \frac{2a}{v'^3} \right]^{1/2} \mathrm{d}v' \tag{3.15}$$

whenever [2] $v > v_i$. By the equation of state (A.1.6), the pressure along the (isentropic) rarefaction wave is given by

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[2] In the particular case of the polytropic ideal gas, the integral of (3.15) can be evaluated analytically and gives $u_{(i)}^{\mathrm{rw}}(v) = u_i \mp \frac{2}{\delta}\sqrt{(\delta+1)P_i v_i}\left[\left(\frac{v_i}{v} \right)^{\delta/2} - 1 \right]$.

$$P^{\mathrm{rw}}_{(i)}(v) = \left(P_i + \frac{a}{v_i^2}\right)\left(\frac{v_i - b}{v - b}\right)^{\delta+1} - \frac{a}{v^2}. \tag{3.16}$$

The possibility of tackling a Riemann problem when the rarefaction wave requires a numerical integration was suggested by the work of Pons et al. [25] on the relativistic Riemann problem with non-zero tangential velocities. Note that the elements of the Jacobian (3.8) can be evaluated by means of explicit relations: the derivative $\mathrm{d}u^{\mathrm{rw}}_{(i)}(v)/\mathrm{d}v$ is the integrand of (3.15) while the derivative $\mathrm{d}P^{\mathrm{rw}}_{(i)}(v)/\mathrm{d}v$ from (3.16) is found to be simply the negative of the square of the previous derivative.

The expression of the rarefaction wave allows to detect the possibility of formation of vacuum in the solution of the Riemann problem. This situation occurs when the velocities u_{l} and u_{r} are such that the solution consisting of two rarefaction waves reaches a zero density at the contact dicontinuity, a condition which is expressed by $u^{\mathrm{rw}}_{(\mathrm{l})}(\infty) = u^{\mathrm{rw}}_{(\mathrm{r})}(\infty)$. Therefore, by (3.15) the condition for vacuum formation reads

$$u_{\mathrm{r}} - u_{\mathrm{l}} \geqslant \int_{v_{\mathrm{l}}}^{\infty} \frac{c(s_{\mathrm{l}}, v)}{v}\,\mathrm{d}v + \int_{v_{\mathrm{r}}}^{\infty} \frac{c(s_{\mathrm{r}}, v)}{v}\,\mathrm{d}v. \tag{3.17}$$

If this condition is satisfied, the solution of Riemann problem is characterized by the presence of a gap in the gas between the two rarefaction waves whose extremes move to the left and to the right with the respective velocity:

$$u^{\mathrm{vac}}_{\mathrm{l}} = u_{\mathrm{l}} + \int_{v_{\mathrm{l}}}^{\infty} \frac{c(s_{\mathrm{l}}, v)}{v}\,\mathrm{d}v \quad \text{and} \quad u^{\mathrm{vac}}_{\mathrm{r}} = u_{\mathrm{r}} - \int_{v_{\mathrm{r}}}^{\infty} \frac{c(s_{\mathrm{r}}, v)}{v}\,\mathrm{d}v, \tag{3.18}$$

while the pressure and the temperature of the gas vanish as $v \to \infty$.

3.3. Shock waves

Shock waves are piecewise constant discontinuous solutions, satisfying the entropy condition, that propagate at a velocity σ dependent on the states existing on the two sides of the jump. The conservation variables must respect the Rankine–Hugoniot jump conditions. By introducing the gas velocity U in the reference frame of the shock wave, namely, $U = u - \sigma$, the jump conditions between the two states (v_i, U_i, e_i) and (v, U, e) assume the form, cf. [6, p. 109],

$$\begin{cases} U_i/v_i = U/v, \\ U_i^2/v_i + P_i = U^2/v + P, \\ \left[\left(\frac{1}{2}U_i^2 + e_i\right)/v_i + P_i\right]U_i = \left[\left(\frac{1}{2}U^2 + e\right)/v + P\right]U, \end{cases} \tag{3.19}$$

under the equation of state $e = e(P, v)$. By indicating the mass flux through the discontinuity with $M = U/v$, the relations in (3.19) can be rearranged as follows

$$\begin{cases} e(P, v) - e(P_i, v_i) + \frac{1}{2}(P_i + P)(v - v_i) = 0, \\ M = \frac{u - u_i}{v - v_i}, \\ M^2 = -\frac{P - P_i}{v - v_i}. \end{cases} \tag{3.20}$$

The first relation is purely thermodynamical and is called *Hugoniot equation*. It defines the value of pressure P as a function of v for a given specific volume–pressure pair (v_i, P_i). The solution to the system (3.20) represents a one-parameter family of states satisfying the Rankine–Hugoniot jump relations and depends on the form of the equation of state $e = e(P, v)$.

Considering the polytropic van der Waals gas, the function $e(P, v)$ is easily obtained from the equation of state (A.1.8), namely, $e(P, v) = \frac{1}{\delta}(P + \frac{a}{v^2})(v - b) - \frac{a}{v}$. Using this relation in the first equation of (3.20) gives the solution of $P(v)$ in explicit form

$$P^{\mathrm{RH}}_{(i)}(v) = \frac{e_i - \frac{P_i}{2}(v - v_i) + a\left(1 - \frac{1}{\delta}\right)\frac{1}{v} + \frac{ab}{\delta v^2}}{\left(\frac{1}{2} + \frac{1}{\delta}\right)v - \left(\frac{v_i}{2} + \frac{b}{\delta}\right)}, \tag{3.21}$$

where $e_i \equiv e(P_i, v_i)$. In classical gasdynamics the entropy decreases monotonically with v along these curves, see, e.g. [6]. Consequently, the *admissible* discontinuities will be the compressive shocks for which the pressure increases and $v < v_i$. Furthermore, we should notice that on the Hugoniot locus just defined, the pressure can assume any value in the interval $[0, \infty[$, whilst the volume will be limited in a finite interval. In particular, the pressure will go to infinity when the specific volume reaches the value $v_{\min} = v_i/2 + b/\delta$.

Once the value of pressure $P^{\mathrm{RH}}_{(i)}(v)$ has been determined by relation (3.21), the other two equations of (3.20) allow one to express the velocity as

$$u = u_i - \operatorname{sign}(M)\sqrt{-(P - P_i)(v - v_i)}.$$

This equation is an implicit definition of the post-shock velocity u, since the sign of the mass flux through the shock M depends on u by virtue of relation $M = (u - u_i)/(v - v_i)$. The sign ambiguity can be solved by resorting to the knowledge of the wave the considered shock is associated with. Remembering that in classical gasdynamics an admissible shock is a compressive one, it can be shown that $M > 0$ for 1-wave and $M < 0$ for 3-wave. The value of the post-shock velocity is therefore

$$u^{\mathrm{RH}}_{(i)}(v) = u_i \mp \sqrt{-\left[P^{\mathrm{RH}}_{(i)}(v) - P_i\right](v - v_i)}, \tag{3.22}$$

where the two signs refer to the first and the third wave, respectively.

3.4. Numerical examples

The proposed Riemann solver has been implemented using an adaptive numerical quadrature to determine the velocity of the rarefaction wave with a relative accuracy $<10^{-9}$ and writing the Newton iterative method in incremental form, with a stop criterion when the sum of the relative errors of the two unknowns is $<10^{-7}$. The initial guess for v and w is taken to be the values v_{l} and v_{r} of the specific volume in the left and right states of the Riemann problem. In the particular case of the polytropic ideal gas this simple guess for the Newton method for the system has been verified to require only one iteration more than the optimal initial guess of Gottlieb and Groth [5] in solving the single nonlinear equation. However, the success obtained in all problems we have solved by no means guarantees that this initial guess leads to convergence in any case.

Three Riemann problems for the van der Waals gas have been solved with $\delta = 0.329$, thus excluding the occurrence of anomalous behavior. The corresponding initial data are collected in Table 1, in dimensionless form according to the definitions $\rho = \tilde{\rho}/\rho_{\mathrm{cr}}$, $v = \tilde{v}/v_{\mathrm{cr}}$, $P = \tilde{P}/P_{\mathrm{cr}}$ and $u = \tilde{u}/\sqrt{P_{\mathrm{cr}} v_{\mathrm{cr}}}$, where the tilde denotes dimensional quantities. Consistently, we assume $a = 3$ and $b = 1/3$. The solutions to these three problems consist, respectively, in two shock waves, a left rarefaction with a right shock, and two rarefaction waves, in addition to the contact discontinuity.

In Table 2, we report the values ρ^*_{l}, u^*, P^* and ρ^*_{r}, which represent the two intermediate states before and after the contact discontinuity, calculated by the proposed algorithm. The number of iterations is 4 or 5 to obtain these solutions with a relative accuracy $<10^{-7}$ (i.e., seven exact figures). The initial data and the solution in the plane v–P for the three Riemann problems above are represented in Fig. 3. The computed values ρ^*_{l}, u^*, P^* and ρ^*_{r} before and after the contact discontinuity are reported in Table 2.

Table 1
Definition of the Riemann problems used in the tests for polytropic van der Waals gas

	ρ_l	u_l	P_l	ρ_r	u_r	P_r
RP-1 (s-s)	0.4	1	1	0.8	−0.5	1
RP-2 (r-s)	0.5	0	1	0.125	0	0.75
RP-3 (r-r)	0.3	−1	0.75	0.4	0.5	0.75

Table 2
Solution of the Riemann problems for polytropic van der Waals

	ρ_l^*	u^*	P^*	ρ_r^*
RP-1 Present	0.63527	0.077503	1.91913	1.12721
RP-1 Ref. [21]	0.635254	0.077519	1.91903	1.12719
RP-2 Present	0.433416	0.22551	0.83405	0.135228
RP-2 Ref. [21]	0.433461	0.22555	0.83416	0.13524
RP-3 Present	0.189734	−0.207406	0.41809	0.247204
RP-3 Ref. [21]	0.189736	−0.207405	0.418096	0.247207

For comparison we report the solutions to the same three Riemann problems calculated by integrating the Euler equations by means of the approximate Riemann solver for nonideal gases described in [21]. The values occurring in the computed solution using a uniform grid of 2000 points are reported on the same Table 2. In the numerical solution there is a slight jump in velocity across the contact discontinuity and in the table the arithmetic average of the two values is reported. For instance, in problem RP-2 the numerical technique provides $u_\mathrm{l}^* = 0.225346$ and $u_\mathrm{r}^* = 0.225786$, and similarly for the other two Riemann problems. The comparison of the results calculated by the proposed Riemann solver with those provided by numerical integration of the conservation laws indicates that the new algorithm is correct.

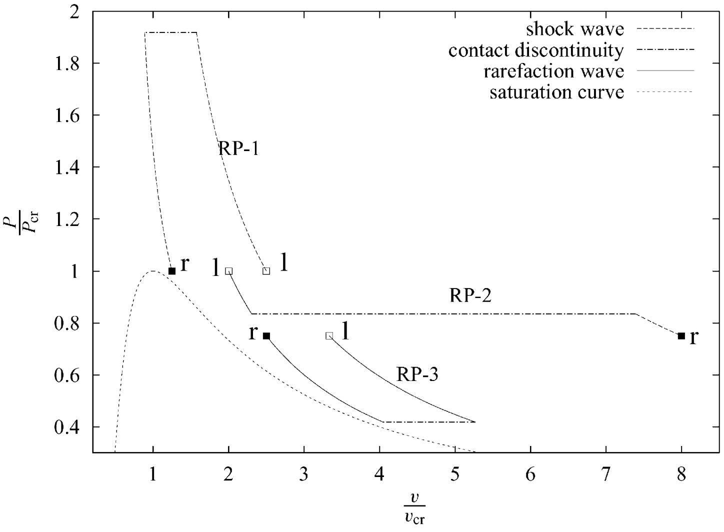

Fig. 3. Initial thermodynamic data and solutions of the Riemann problems of Table 2.

4. Riemann problem for nonpolytropic van der Waals gas

In this section we extend the analysis of the Riemann problem for the van der Waals gas to include the possibility of a nonconstant specific heat. More precisely, we elaborate upon the formulation of the Riemann problem for the particular case of the nonpolytropic van der Waals gas which includes the contribution to the internal energy of the molecular vibrations, according to the thermodynamic definition presented in Section A.2 of the appendix. In this case, due to the dependence on T of the specific heat c_v, the speed of sound $c = c(T, v)$ is expressed by explicit relation (A.2.6), instead of function $c = c(P, v)$ available only in the polytropic case. As a consequence in the solution of the rarefaction wave it is convenient to parametrize the integral curve by the temperature. We notice in passing that the parametrization by T was already employed by Beccantini [26] to derive an approximate two-shock Riemann solver for the nonpolytropic ideal gas.

According to the previous remark, the entire Riemann problem defined by left and right states (v_l, T_l, u_l) and (v_r, T_r, u_r) is formulated by taking as unknowns values T_l^* and T_r^* of the temperature on the two sides of the contact discontinuity; to simplify the notation, the two unknowns will be indicated by $T = T_l^*$ and $W = T_r^*$.

4.1. Equation system for the Riemann problem

The solution of the Riemann problem for the nonpolytropic van der Waals gas mimics that for the polytropic case considered in Section 3.1. We introduces the functions $u_{(l)}(T)$ and $P_{(l)}(T)$ which give, respectively, the velocity and pressure of the one-parameter family of states which can be connected to the left state (v_l, T_l, u_l) of the Riemann problem, by either a rarefaction wave or a shock wave, depending on the value of T with respect to T_l. Similarly, let $u_{(r)}(T)$ and $P_{(r)}(T)$ denote the functions of the one-parameter family of states which can be connected to the right state (v_r, T_r, u_r). These two pairs of functions are defined by

$$u_{(l)}(T) \equiv \begin{cases} u_{(l)}^{\mathrm{RH}}(T) & \text{if } T > T_l \\ u_{(l)}^{\mathrm{rw}}(T) & \text{if } T < T_l \end{cases} \quad \text{and} \quad u_{(r)}(T) \equiv \begin{cases} u_{(r)}^{\mathrm{RH}}(T) & \text{if } T > T_r \\ u_{(r)}^{\mathrm{rw}}(T) & \text{if } T < T_r \end{cases} \tag{4.1}$$

and

$$P_{(l)}(T) \equiv \begin{cases} P_{(l)}^{\mathrm{RH}}(T) & \text{if } T > T_l \\ P_{(l)}^{\mathrm{rw}}(T) & \text{if } T < T_l \end{cases} \quad \text{and} \quad P_{(r)}(T) \equiv \begin{cases} P_{(r)}^{\mathrm{RH}}(T) & \text{if } T > T_r, \\ P_{(r)}^{\mathrm{rw}}(T) & \text{if } T < T_r. \end{cases} \tag{4.2}$$

The equality of the values of velocity and of pressure on the two sides of the contact discontinuity means that T and W are the solution to the system of two equations

$$\begin{cases} u_{(l)}(T) = u_{(r)}(W), \\ P_{(l)}(T) = P_{(r)}(W). \end{cases} \tag{4.3}$$

The solution of this nonlinear system can be tackled by the same Newton method in incremental form described for the polytropic case in Section 3.1. The calculation of the present Jacobian matrix

$$J(T, W) \equiv \begin{pmatrix} \frac{\mathrm{d}u_{(l)}(T)}{\mathrm{d}T} & -\frac{\mathrm{d}u_{(r)}(W)}{\mathrm{d}W} \\ \frac{\mathrm{d}P_{(l)}(T)}{\mathrm{d}T} & -\frac{\mathrm{d}P_{(r)}(W)}{\mathrm{d}W} \end{pmatrix} \tag{4.4}$$

is however slightly more complicated. In fact, the evaluation of the derivatives with respect to temperature T and W requires the chain rule because function $P_{(i)}(T)$ is a composed function, $P_{(i)}(T) = P(T, v_{(i)}(T))$, with $v_{(i)}(T)$ representing the appropriate rarefaction or shock wave solution.

Concerning the existence and uniqueness of the solution to system (4.3) for the nonpolytropic gas, the sufficient condition $\partial e(P,v)/\partial v > 0$ for arbitrary initial data [14] is always satisfied, as can be shown from $e(P,v) = e(T(P,v),v)$ using the equation of states $e = e(T,v)$ given by (A.2.2) and $T = T(P,v)$.

Let us now study the rarefaction waves and the shock waves for this more general gas model, whose analytical expressions are necessary to solve the corresponding Riemann problem.

4.2. Rarefaction waves

The determination of the rarefaction wave for the nonpolytropic gas is made by evaluating the integral in (3.14) through the change of variable $v \to T$ along the integral curve and by exploiting the constancy of the entropy in the rarefaction wave. Letting $s = \text{constant} = s_i$ in relation (A.2.4) for the entropy, and then expressing s_i in terms of the values (T_i, v_i), the specific volume v of the one-parameter family of states of the rarefaction wave connected to the initial state (v_i, u_i, T_i) is given by the relation

$$\ln\frac{v-b}{v_i-b} = \ln\left(\frac{T_i}{T}\right)^{1/\delta} + \sum_{m=1}^{M_{\text{vib}}}\left\{\ln\frac{1-\mathrm{e}^{-T_m/T}}{1-\mathrm{e}^{-T_m/T_i}} + \frac{T_m/T}{1-\mathrm{e}^{T_m/T}} - \frac{T_m/T_i}{1-\mathrm{e}^{T_m/T_i}}\right\}. \tag{4.5}$$

This relation can be solved with respect to v and gives the following explicit function for $v_{(i)}^{\text{rw}}(T)$:

$$v_{(i)}^{\text{rw}}(T) = b + (v_i - b)\left(\frac{T_i}{T}\right)^{1/\delta}\prod_{m=1}^{M_{\text{vib}}}\frac{\exp\left(\frac{T_m/T}{1-\mathrm{e}^{T_m/T}}\right) - \exp\left(\frac{-T_m/T}{1-\mathrm{e}^{-T_m/T}}\right)}{\exp\left(\frac{T_m/T_i}{1-\mathrm{e}^{T_m/T_i}}\right) - \exp\left(\frac{-T_m/T_i}{1-\mathrm{e}^{-T_m/T_i}}\right)}. \tag{4.6}$$

This function is used in the integral of (3.14) with the speed of sound given by relation (A.2.6) expressed as a function only of T, namely, $c(T, v_{(i)}^{\text{rw}}(T))$, to give for any $T < T_i$

$$u_{(i)}^{\text{rw}}(T) = u_i \pm \int_{T_i}^{T}\frac{c(t, v_{(i)}^{\text{rw}}(t))}{v_{(i)}^{\text{rw}}(t)}\frac{\mathrm{d}v_{(i)}^{\text{rw}}(t)}{\mathrm{d}t}\,\mathrm{d}t, \tag{4.7}$$

where $c(T,v)$ is given by (A.2.6). The derivative under the integral is evaluated directly from (4.6) by differentiating the exponential functions and simplifying, to give

$$\frac{\mathrm{d}v_{(i)}^{\text{rw}}(T)}{\mathrm{d}T} = \left[v_{(i)}^{\text{rw}}(T) - b\right]\left\{-\frac{1}{\delta T} + \sum_{m=1}^{M_{\text{vib}}}\frac{\frac{\mathrm{d}}{\mathrm{d}T}\left(\frac{T_m/T}{1-\mathrm{e}^{T_m/T}}\right) + \mathrm{e}^{-T_m/T}\frac{\mathrm{d}}{\mathrm{d}T}\left(\frac{T_m/T}{1-\mathrm{e}^{-T_m/T}}\right)}{1-\mathrm{e}^{-T_m/T}}\right\}. \tag{4.8}$$

The pressure of the rarefaction family is similarly determined as a function of the T through the function $v_{(i)}^{\text{rw}}(T)$ by means of the equation of state for the pressure, namely, $P_{(i)}^{\text{rw}}(T) = P(T, v_{(i)}^{\text{rw}}(T))$, always with $T < T_i$.

4.3. Shock waves

To find the solution of the Rankine–Hugoniot jump conditions in the nonpolytropic case, the Hugoniot equation [i.e., the first equation of (3.20)] cannot be used directly in this form since the equation of state $e = e(P,v)$ is not available. Instead, relation (A.2.2) gives the function $e(T,v)$, so that the Hugoniot equation can be rewritten as follows

$$e(T,v) - e(T_i,v_i) + \frac{1}{2}[P(T_i,v_i) + P(T,v)](v - v_i) = 0. \tag{4.9}$$

By using the equation of state $P(T,v)=\frac{RT}{v-b}-\frac{a}{v^2}$ in this relation, we obtain

$$\frac{RT}{\delta}+\sum_{m=1}^{M_{\rm vib}}\frac{RT_m}{{\rm e}^{T_m/T}-1}+\frac{1}{2}\left(\frac{RT}{v-b}-\frac{a}{v^2}\right)(v-v_i)+\frac{1}{2}\left(\frac{RT_i}{v_i-b}-\frac{a}{v_i^2}\right)(v-v_i)-\frac{a}{v}-e_i=0, \tag{4.10}$$

where $e_i=e(T_i,v_i)$. This equation is of the form $f^{\rm RH}_{(i)}(T,v)=0$ and represents an implicit definition of the function $v=v^{\rm RH}_{(i)}(T)$, for $T>T_i$. For any $T>T_i$ the solution v can be determined by Newton iteration, using as initial guess the solution v_0 of Eq. (4.10) in the particular case $a=b=0$, namely,

$$\frac{1}{2}\left(\frac{T}{v_0}+\frac{T_i}{v_i}\right)(v_0-v_i)+\frac{T-T_i}{\delta}+\sum_{m=1}^{M_{\rm vib}}\left(\frac{T_m}{{\rm e}^{T_m/T}-1}-\frac{T_m}{{\rm e}^{T_m/T_i}-1}\right)=0.$$

This is a second-order equation for the dimensionless unknown $\nu\equiv v_0/v_i$ as follows:

$$\nu^2+2\beta(\tau)\nu-\tau=0,$$

where $\tau\equiv T/T_i$ and

$$\beta(\tau)\equiv\left(\frac{1}{2}+\frac{1}{\delta}\right)(\tau-1)+\sum_{m=1}^{M_{\rm vib}}\frac{T_m}{T_i}\left(\frac{1}{{\rm e}^{(T_m/T_i)/\tau}-1}-\frac{1}{{\rm e}^{T_m/T_i}-1}\right).$$

Thus, the value of v_0 is chosen to be the physically admissible solution of this equation, namely,

$$v_0=v_i\left[-\beta(\tau)+\sqrt{\beta(\tau)^2+\tau}\right].$$

During Newton iteration the tentative value of v is checked to ensure that it does not become less than the covolume b; in our implementation v is bounded from below by $1.01b$.

Once the solution of the nonlinear equation $f^{\rm RH}_{(i)}(T,v)=0$ has been determined, the post-shock pressure is immediately given by $P^{\rm RH}_{(i)}(T)=P(T,v^{\rm RH}_{(i)}(T))$, and the post-shock velocity is calculated from

$$u^{\rm RH}_{(i)}(T)=u_i\mp\sqrt{-\left[P^{\rm RH}_{(i)}(T)-P_i\right]\left[v^{\rm RH}_{(i)}(T)-v_i\right]}, \tag{4.11}$$

always under the assumption $T>T_i$. It must be remembered that the shock solution here considered is based on the hypothesis that the gas behind the shock front is in a complete thermodynamic equilibrium. This assumption is to some an extent physically artificial in the presence of molecular vibrations since a finite relaxation time is needed before the vibrational energy reaches an equilibrium with the translational and rotational energy of the molecules, as explained in detail by Zel'dovich and Raizer [23, Chapter VII, Sections 6 and 7], see also Grossman and Cinnella [27]. Anyway, the effect of vibrational non equilibrium is confined to a relatively narrow layer behind the shock front, see, e.g. [10], so the proposed Riemann solver for the nonpolytropic gas should be physically significant at least as a first approximation and under this restriction.

It is worthwhile to note that the solver described so far can accommodate also the contribution to the internal energy from the rotational degrees of freedom, by simply including the corresponding terms in the expressions for $c_v(T)$ and $e(T,v)$. We have not considered this more general nonpolytropic case only to avoid an unnecessary complication in the description of the algorithm.

Coming to the evaluation of the derivatives of the elements of the Jacobian matrix (4.4), we have

$$\frac{{\rm d}P_{(i)}(T)}{{\rm d}T}=\left[\frac{\partial P(T,v)}{\partial T}+\frac{\partial P(T,v)}{\partial v}\frac{{\rm d}v_{(i)}(T)}{{\rm d}T}\right]\bigg|_{v_{(i)}(T)}, \tag{4.12}$$

where $P(T,v)=\frac{RT}{v-b}-\frac{a}{v^2}$ and where the derivative of $v_{(i)}(T)$ in the case of the rarefaction wave is given by (4.8), while in the case of the shock wave is given by the implicit function differentiation

$$\frac{\mathrm{d}v^{\mathrm{RH}}_{(i)}(T)}{\mathrm{d}T}=-\left.\frac{\partial f^{\mathrm{RH}}_{(i)}(T,v)}{\partial T}\right|_{v^{\mathrm{RH}}_{(i)}(T)}\Bigg/\left.\frac{\partial f^{\mathrm{RH}}_{(i)}(T,v)}{\partial v}\right|_{v^{\mathrm{RH}}_{(i)}(T)}. \tag{4.13}$$

In conclusion, it can be remarked that the nonpolytropic character of the gas increases the complexity of some explicit expressions with respect to its polytropic counterpart. From this viewpoint, we reiterate that the proposed Riemann solver has been developed without paying attention to the issue of which is the best parametrization for the computational efficiency.

4.4. Numerical examples

To verify the solution algorithm for the nonpolytropic van der Waals gas we have considered the two Riemann problems defined by the dimensionless values reported in Table 3.

The nonpolytropic van der Waals gas is assumed to be a diatomic gas so that $\delta=0.4$ and there is only one oscillatory mode with a vibrational temperature assumed to be $T_{m=1}=3T_{\mathrm{cr}}$, where $T_{\mathrm{cr}}=\frac{8a}{27b}$. Moreover, we take $a=3$ and $b=1/3$; with this choice the variables P and v in all the equations above become dimensionless and assume a unit value at the critical point, while the variable T is dimensionless but assumes the value $\frac{8}{3}$ at the critical point. The values of T and W chosen for starting Newton method are the two temperatures T_l and T_r in the left and right states of the considered Riemann problem.

In Table 4, we report the values ρ^*_l, T^*_l, u^*, P^*, T^*_r and ρ^*_r, in the two intermediate states before and after the contact discontinuity, obtained by means of the proposed algorithm.

These values are compared with those calculated by integrating Euler equations with the approximate Riemann solver for nonideal gases [21] using a uniform grid of 2000 points, which are given in the same Table 4. Since in the numerical solution there is a slight jump in velocity and in pressure across the contact discontinuity, the corresponding arithmetic average is reported in the table. The comparison with the results of the proposed Riemann solver indicates that the algorithm for the nonpolytropic gas is correct.

Table 3
Definition of the Riemann problems used in the tests for nonpolytropic van der Waals gas

	ρ_l	u_l	P_l	ρ_r	u_r	P_r
RP-4 (s-s)	1	1	1.5	$\frac{1}{0.594}$	−0.5	0.8957
RP-5 (r-r)	0.3	−1	0.75	0.4	0.5	0.75

Table 4
Solution of the Riemann problems for the nonpolytropic van der Waals

	ρ^*_l	T^*_l	u^*	P^*	T^*_r	ρ^*_r
RP-4 Present	1.239035	3.318938	0.583287	2.400107	3.463791	1.106865
RP-4 Ref. [21]	1.23904	3.31894	0.58329	2.40012	3.46379	1.10687
RP-5 Present	0.188664	2.639612	−0.2089145	0.424642	2.266568	0.245020
RP-5 Ref. [21]	0.188669	2.63963	−0.208915	0.42465	2.266568	0.245020

Table 5
Riemann problems used in the tests for gas CCl_4

	v_l (m^3/kg)	u_l (m/s)	T_l (K)	v_r (m^3/kg)	u_r (m/s)	T_r (K)
RP-6 (s-s)	$12. \times 10^{-3}$	200	450	5.0×10^{-3}	−100	850
RP-7 (r-r)	6.0×10^{-3}	−600	550	3.0×10^{-3}	600	750

Table 6
Comparison of results for gas CCl_4 with constant and nonconstant specific heat

	$\lvert\Delta v_l^*/v_l^*\rvert$ (%)	$\lvert\Delta u^*/u^*\rvert$ (%)	$\lvert\Delta P^*/P^*\rvert$ (%)	$\lvert\Delta v_r^*/v_r^*\rvert$ (%)
RP-6	8.4	1.39	0.59	0.41
RP-7	2.1	0.36	11.0	3.6

4.5. Nonpolytropic effects: carbon tetrachloride CCl_4

It is interesting to show the differences in the solution of the Riemann problem caused by a variable specific heat with respect to the constant polytropic case, a comparison that may be relevant for real gases applications. For this reason we briefly investigate the issue in connection with a definite gas model represented by the Carbon tetrachloride. The molecule CCl_4 has four different normal modes, characterized by the vibrational temperatures $T_1 = 314\,°\mathrm{C} = 587.15\,\mathrm{K}$, $T_2 = 452\,°\mathrm{C} = 725.15\,\mathrm{K}$, $T_3 = 659\,°\mathrm{C} = 932.15\,\mathrm{K}$ and $T_4 = 1120\,°\mathrm{C} = 1393.15\,\mathrm{K}$, with a degeneracy of 2, 3, 1 and 3, respectively [28]. The critical values are as follows: $T_{cr} = 556.3\,\mathrm{K}$, $P_{cr} = 4.516 \times 10^6$ Pa and $v_{cr} = 1.79211 \times 10^{-3}$ m^3/kg, so that the critical compressibility factor $Z_{cr} = P_{cr}v_{cr}/(RT_{cr}) = 0.26917$, since $R = R_{CCl_4} = 54.05$ J/(kg K).

Notice that, in accordance with the harmonic oscillation model, the value of δ for the nonpolytropic CCl_4 accounts only for the translational and rotational energy, i.e., $\delta = \frac{1}{3}$, whereas for the polytropic version of the same gas $\delta = \frac{1}{12}$, including the contribution from the fully excited 9 vibrational modes.

A couple of Riemann problems with the initial temperature jump encompassing the vibrational temperatures of the first two modes have been chosen to illustrate the size of the possible errors associated with the polytropic assumption. The dimensionless values consistent with the present formulation are related to their dimensional counterparts by: $v^{\mathrm{adim}} = 8Z_{cr}v/3v_{cr}$, $u^{\mathrm{adim}} = u\sqrt{8Z_{cr}/3P_{cr}v_{cr}}$, and $T^{\mathrm{adim}} = 8T/3T_{cr}$. The problems are defined in Table 5 and produce shock–shock and rarefaction–rarefaction solutions.

In Table 6 the difference $\Delta X = X^{\mathrm{nonpoly}} - X^{\mathrm{poly}}$ between values pertaining to solutions to the polytropic and nonpolytropic models are reported. The maximum size of the relative difference is around 10%. These results demonstrate that the nonpolytropic approximation for the specific heat is needed to guarantee an accurate solution when the number of excited vibrational modes is changing between the states of the Riemann problem.

5. An application to general equations of state: Martin–Hou gas model

As an example of the application of the two-equation Riemann solver to a gas with more complex equations of state we consider the Martin–Hou gas model. This model was first introduced by Martin and Hou [13] and improved subsequently by Martin et al. [29], and is defined by the following (compatible) equations of state for the pressure and the internal energy:

$$P(T,v) = \frac{RT}{v-b} + \sum_{i=2}^{5} \frac{Q_i(T)}{(v-b)^i}, \tag{5.1}$$

$$e(T,v) = e_0 + \int_{T_0}^{T} c_v(T',\infty)\,\mathrm{d}T' - \sum_{i=2}^{5} \frac{TQ_i'(T) - Q_i(T)}{(i-1)(v-b)^{i-1}}, \tag{5.2}$$

where the functions $Q_i(T)$ are given by

$$Q_i(T) = A_i + B_i T + C_i \exp(-kT/T_{\rm cr}), \quad k = 5.475. \tag{5.3}$$

The gas-dependent coefficients b, A_i, B_i, and C_i are obtained by applying the procedure given in [13] and their evaluation requires the knowledge of the critical point coordinates and of one state point along the vapor pressure curve. In [30] an approximate procedure to compute the Martin–Hou coefficients, which requires the specification of the critical point coordinates and the boiling temperature at 1 atm, is presented. Martin–Hou model, thanks to its 11 parameters, allows for a better representation of the thermodynamic behavior of real gases than van der Waals model, especially in the description of the isotherms. Martin–Hou equations of state are complicate enough to constitute a proper test for the general applicability of the proposed Riemann solver. We have considered the polytropic version of Martin–Hou model, for which $\int_{T_0}^{T} c_v(T',\infty)\,\mathrm{d}T' = c_v(T - T_0)$ as applied to hydrogen sulfide gas H_2S, whose Martin–Hou approximation is defined by the values reported in Table 7.

For the tests we have chosen the three Riemann problems given in dimensionless form in Table 8, which roughly represent a Martin–Hou counterpart of the initial data in Table 1 for the van der Waals gas.

Table 7
Coefficients for Martin–Hou model of hydrogen sulfide gas H_2S, with $c_v/R = 3.125$, $R = 243.955$ J/(kg K), $b = 0.679059 \times 10^{-3}$ m^3/kg, $P_{\rm cr} = 8.93990 \times 10^6$ Pa, $T_{\rm cr} = 373.2$ K and $v_{\rm cr} = 2.89226 \times 10^{-3}$ m^3/kg

i	A_i (Pa (kg/m^3)^i)	B_i ((Pa/K) (kg/m^3)^i)	C_i (Pa (kg/m^3)^i)
2	−493.624	0.412243	−7591.87
3	0.930361	-0.660362×10^{-3}	18.3012
4	-0.781845×10^{-3}	0	0
5	0	0.948924×10^{-9}	-7.34187×10^{-6}

Table 8
Dimensionless initial conditions of the Riemann problems for Martin–Hou model of H_2S

	$v_{\rm l}$	$u_{\rm l}$	$P_{\rm l}$	$v_{\rm r}$	$u_{\rm r}$	$P_{\rm r}$
RP-8 (s-s)	5	1	1	1.5	−0.5	1
RP-9 (s-r)	8	0	0.75	2	0	1
RP-10 (r-r)	2.5	−0.5	1.1	5/3	0	1.1

Table 9
Solution of the Riemann problems for Martin–Hou model of H_2S

	$v_{\rm l}^*$	u^*	P^*	$v_{\rm r}^*$
RP-8 Present	3.5106	3.6529×10^{-3}	1.6665	1.11194
RP-8 Ref. [21]	3.5107	3.663×10^{-3}	1.6664	1.11195
RP-9 Present	7.41829	−0.218675	0.832205	2.28579
RP-9 Ref. [21]	7.4184	−0.21868	0.83220	2.2858
RP-10 Present	2.89182	−0.220935	0.900629	1.912350
RP-10 Ref. [21]	2.8918	−0.22092	0.90062	1.91237

In Table 9 the solutions provided by the exact Riemann solver are compared with results obtained by means of the numerical integration of Euler equations. The agreement is completely satisfactory.

6. Conclusion

This work has described a new approach to determine the exact solution to Riemann problems for gases satisfying the condition $e_{vvv}(s,v) \neq 0$. In the proposed method, the two intermediate states are found by solving the system of two nonlinear equations which impose the equality of pressure and of velocity on the two sides of the contact discontinuity, the two values of another thermodynamic variable playing the rôle of unknowns. This procedure exploits the very nature of the characteristic field of the linearly degenerate eigenvalue of the Euler equations of gasdynamics. The method extends to gases with rather general thermodynamic properties the classical procedures for solving Riemann problems for the γ-law ideal gas by means of a single nonlinear equation for a single unknown.

For the particular case of the polytropic van der Waals gas, the unknowns of the system can be chosen to be the values of the specific volume on the two sides of the contact surface, while for the nonpolytropic case, with the effect of molecular vibrations at thermal equilibrium included, the value of the two temperatures represents the natural choice. In the latter situation, the Euler equations, and consequently the proposed analysis, are valid only under the assumption that all the thermodynamic degrees of freedom relax to the equilibrium instantaneously, which is often admittedly not the case for the vibrational degrees of freedom behind shock waves. The proposed approach is suitable also for more complex equations of state, provided the states remain inside the region of classical behavior. As an example of the general applicability of the new two-equation scheme, it has been used to solve three Riemann problems for Martin–Hou model of the hydrogen sulfide gas.

The results computed with the new method have been compared successfully with the numerical solutions of the shock tube problems calculated by means of the Godunov-type approximate Riemann solver for nonideal gases developed by Guardone and Vigevano [21]. From a computational viewpoint, no effort has been made to analyze and improve the efficiency of the new exact solver.

From a theoretical viewpoint, the existence and uniqueness of the solution to the Riemann problem of gasdynamics for arbitrarily large data is covered by Smith's analysis [14]; this theory guarantees that the sufficient condition is satisfied by van der Waals gas, irrespective of its polytropic or nonpolytropic character. On the other hand, the convergence of Newton method to the solution of the nonlinear system is guaranteed only if the contractivity of the iteration mapping can be demonstrated, and this requires a gas-dependent specific analysis.

Considering gases for which a nonclassical behavior is possible, as for instance a van der Waals gas of sufficiently high molecular weight within the "anomalous" region near the saturation curve, the proposed two-equation strategy should not face additional difficulties with respect to those of any single equation method. In this case, the left and right waves of the Riemann problem solution include the possibility of rarefactive shocks, compressive fans and the formation also of hybrid and composite waves. Following the comprehensive study of Müller and Voss [31], and the analysis about the conditions for producing single-phase rarefaction shock wave in a shock tube experiment developed by Fergason et al. [32], the modifications necessary to extend the proposed approach to include Riemann problems involving the nonclassical region may be envisaged.

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Appendix A. Thermodynamics of van der Waals gas

In this section, we introduce the thermodynamic properties of the van der Waals gas. This physical model was proposed by Johannes Diderik van der Waals in his doctoral dissertation [33] of 1873 investigating the behaviour of a fluid when both the liquid and the gas phases are present. At the microscopic level the system considered in this study consisted in colliding atoms or molecules which are interacting in pair through weak attractive forces at a large distance and strong repulsive forces at a short distance.

We will consider two physical models compatible with the equation of state for the pressure originally introduced by van der Waals. These models differs in the form of the second equation of state for the energy which is necessary to make the description of the thermodynamic properties of the fluid mathematically complete. More precisely, we first consider the *polytropic* van der Waals gas, which is characterized by a constant specific heat (at fixed volume) and then we generalize this physical model to a *nonpolytropic* van der Waals gas, in which the gradual contribution of the energy of the molecular oscillations to the internal energy of the gas is included according to the quantum mechanical statistical treatment.

A.1. Polytropic van der Waals gas

Instead of providing the aforesaid two equations of state defining the polytropic van der Waals gas, we prefer to state the fundamental thermodynamic relation embodying all its thermodynamic properties in a single mathematical expression. This choice follows the principles of thermodynamics, as described, for instance, by Callen [34]. The fundamental relation gives the extensive variable energy or entropy of a thermodynamic system as a function of only the other extensive variables defining the equilibrium states of the system. More precisely, for a single component fluid the fundamental relation can be written as the specific energy e or specific entropy s as a function of the pair of variables s–v or e–v, respectively, where v denotes the specific volume and the attribute "specific" means, as usual, per unit mass.

For the sake of completeness, we give here both fundamental relations, which are the inverse of each other, and provide two alternative and but completely equivalent description of the same thermodynamic system. The polytropic van der Waals gas is defined by either of the two fundamental thermodynamic relations:

$$s = s(e, v) = R \ln \left[\left(\frac{e + \frac{a}{v}}{e_0 + \frac{a}{v_0}} \right)^{1/\delta} \frac{v - b}{v_0 - b} \right] + s_0, \tag{A.1.1}$$

$$e = e(s, v) = -\frac{a}{v} + \left(e_0 + \frac{a}{v_0} \right) \left(\frac{v_0 - b}{v - b} \right)^{\delta} \exp[\delta(s - s_0)/R], \tag{A.1.2}$$

where $R = \mathscr{R}/W$ is the constant associated with the considered gas of molecular weight W, with $\mathscr{R} = 8.314\,\mathrm{J/(mol\ K)}$ denoting the universal gas constant. In the expressions above, a and b are the dimensional constants of the van der Waals gas while the dimensionless parameter $\delta = R/c_v$, with c_v being the specific heat at constant volume. The other quantities e_0, v_0 and s_0 appearing in relations (A.1.1) and (A.1.2) are the values of specific energy, volume and entropy in a reference state of the gas.

By introducing the constant $K_0 = (e_0 + \frac{a}{v_0})(v_0 - b)^{\delta} \exp(-\delta s_0/R)$, the fundamental relations above assume a simpler form:

$$s(e, v) = R \ln \left[K_0^{-1/\delta} \left(e + \frac{a}{v} \right)^{1/\delta} (v - b) \right], \tag{A.1.3}$$

$$e(s, v) = K_0 \frac{\exp(\delta s/R)}{(v - b)^{\delta}} - \frac{a}{v}. \tag{A.1.4}$$

The equations of state of the polytropic van der Waals gas are easily obtained from relation (A.1.4)

$$T = e_s(s,v) = \frac{K_0\delta}{R}\,\frac{\exp(\delta s/R)}{(v-b)^{\delta}}, \tag{A.1.5}$$

$$P = -e_v(s,v) = K_0\delta\,\frac{\exp(\delta s/R)}{(v-b)^{\delta+1}} - \frac{a}{v^2}. \tag{A.1.6}$$

The elimination of variable s in favor of e using relation (A.1.4) gives an alternative expression of the equations of state:

$$T = \frac{\delta}{R}\left(e + \frac{a}{v}\right), \tag{A.1.7}$$

$$P = \delta\,\frac{e + \frac{a}{v}}{v-b} - \frac{a}{v^2}. \tag{A.1.8}$$

For solving the Riemann problem, the expression of the speed of sound for the polytropic van der Waals gas is required. A direct calculation gives

$$c(s,v) \equiv \sqrt{-v^2\frac{\partial P(s,v)}{\partial v}} = \left[K_0\delta(\delta+1)\,\frac{\exp(\delta s/R)v^2}{(v-b)^{\delta+2}} - \frac{2a}{v}\right]^{1/2}. \tag{A.1.9}$$

By eliminating the variable s in favor of P with the aid of the equation of state (A.1.6), we obtain

$$c(P,v) = \left[(\delta+1)\,\frac{Pv^2 + a}{v-b} - \frac{2a}{v}\right]^{1/2}. \tag{A.1.10}$$

A.2. Nonpolytropic van der Waals gas

A polytropic gas is such that its specific heat at constant volume is constant. This condition is satisfied by mono atomic gases, whose particles contribute individually to the internal energy only by means of the kinetic energy associated with their translational motion. For molecular gases, the internal energy of the gas receives further contributions from the individual energy of each particle: these contributions are associated with the rotation and the vibrations of the molecule, as well as with the excitation of the electrons of the outer orbitals. This last contribution, present also in atomic gases but meaningful only at very high temperatures, will not be considered in the model of nonpolytropic van der Waals gas. Moreover, the model does not appeal to the coupling effect between rotational and vibrational degrees of freedom, neither to the anharmonicity effect of vibrations, see, e.g. [23, p. 183]. Similarly, excluded from the model of the gas is the possibility of molecular dissociation.

The inclusion of the effect of the rotational energy of the molecules in the physical model of the gas is made difficult due to the basically quantum mechanical character of the rotation of the molecules. In principle, due to the discrete character of the quantum mechanical states of allowed rotations, at a sufficiently low temperature the rotations are forbidden (frozen) and the rotational degrees of freedom are as if completely absent. The value of temperature for which the molecular rotations become accessible and therefore can contribute to the internal energy of the gas is typically around 100 K, depending on the particular molecule. Thus, for the range of temperatures of interested here, i.e., for $T > 300$ K, we can assume that the molecular rotations are active well beyond their quantum threshold and contribute to the energy in a purely classical fashion. In this range of temperatures it is necessary to distinguish two different possibilities of rotation, according to whether the molecule of the gas is *linear* or *nonlinear*. In the first case only rotations around two axis are to be considered, while in the second case rotations around the three spatial directions are involved. Correspondingly, by virtue of the equipartition principle the contribution to the internal energy of the molecular gas due to rotational kinetic energy will be R for linear molecules and $3R/2$ for nonlinear molecules. Once summed up with the contribution due to the translational kinetic energy, we will have a value of $5R/2$ for linear molecules and of $3R$ for nonlinear molecules. These two values will correspond to the following values for the parameter $\delta = R/c_v$: $\delta = 2/5$ for linear molecules and $\delta = 1/3$ for nonlinear molecules.

The inclusion of the kinetic energy of rotation according to the classical approximation does not break the polytropic character of the molecular gas. The model of a nonpolytropic gas considered here for the purpose of obtaining more a general Riemann problem is based on including the energy contribution associated with the oscillations (called also vibrations) of the molecules. As well know, any molecule with a number *N.A.* of atoms has a number of normal modes equal to $M_{\text{vib}} = 3\ N.A. - 5$, if the molecule is linear, and to $M_{\text{vib}} = 3\ N.A. - 6$, if the molecule is nonlinear. Each normal mode has a characteristic frequency of oscillation (some modes may have the same frequency, in which case they are said *degenerate*) and has both a kinetic and a potential energy. In compliance with a quantum mechanical treatment of the molecular vibrations, since the energy levels of the quantum oscillator are discrete, the contribution of molecular oscillations to the internal energy of the gas follows a gradual switching mechanism similar to that of the rotations, although at temperatures of the order of 1000 K, cf. [23, p. 489] and [28, p. 37]. Since closed expressions for the energy of the molecular vibrations are available, they can be used to extend the mathematical model of the van der Waals gas beyond the polytropic regime.

The specific heat at constant volume of the considered physical model of the gas is therefore

$$c_v(T) \equiv \frac{\partial e(T,v)}{\partial T} = \frac{R}{\delta} + R\sum_{m=1}^{M_{\text{vib}}} \left(\frac{T_m}{T}\right)^2 \frac{\exp(T_m/T)}{[\exp(T_m/T) - 1]^2}, \tag{A.2.1}$$

where T_m denotes the so-called vibrational temperature of the mth normal mode of the molecule. This value is related to the angular frequency ω_m of oscillation of the normal mode by $T_m = \hbar\omega_m/k$, with $\hbar$ denoting Planck constant and k Boltzmann constant. In the summation of (A.2.1) one could take into account the possibility of degenerate vibrational modes with an identical vibrational temperature by summing only on the different temperatures and introducing the corresponding multiplicity factors, but we content ourselves with the expression above, for simplicity.

Coming to the fundamental thermodynamic relation for the nonpolytropic van der Waals gas, in contrast with the polytropic case this relation cannot be written in closed form. On the other hand, the specific heat defined by (A.2.1) is a function only of the temperature, and this allows an immediate evaluation of the two functions $e = e(T, v)$ and $s = s(T, v)$. The relation for the specific energy of the nonpolytropic van der Waals gas is given by

$$e(T,v) = e_0 + \int_{T_0}^{T} c_v(T')dT' - \frac{a}{v} = e_0 - \frac{a}{v} + \frac{RT}{\delta} + \sum_{m=1}^{M_{\text{vib}}} \frac{RT_m}{\exp(T_m/T) - 1}, \tag{A.2.2}$$

where the contribution dependent on the temperature is simply the integral of the $c_v(T)$ expression given by (A.2.1). The specific entropy of the nonpolytropic van der Waals gas is given by

$$s(T,v) = s_0 + R\ln\frac{v-b}{v_0-b} + \int_{T_0}^{T} \frac{c_v(T')}{T'}\,\mathrm{d}T'. \tag{A.2.3}$$

The two equations (A.2.2) and (A.2.3) can be regarded as a *parametric* representation of the fundamental relation of the considered gas model.

Using the expression (A.2.1) for $c_v(T)$ we have the specific entropy of the nonpolytropic van der Waals in the form

$$s(T,v) = s_0 + R\ln\frac{v-b}{v_0-b} + R\int_{T_0}^{T}\left[\frac{1}{\delta} + \sum_{m=1}^{M_{\mathrm{vib}}}\left(\frac{T_m}{T'}\right)^2 \frac{\mathrm{e}^{T_m/T'}}{(\mathrm{e}^{T_m/T'}-1)^2}\right]\frac{\mathrm{d}T'}{T'}.$$

A direct integration, using the indefinite integral $\int \ln x\,\mathrm{d}x = x\ln x - x$, leads to the following explicit expression

$$s(T,v) = s_0 + R\ln\frac{v-b}{v_0-b} + R\ln\left(\frac{T}{T_0}\right)^{1/\delta} + R\sum_{m=1}^{M_{\mathrm{vib}}}\left\{\ln\frac{1-\mathrm{e}^{-T_m/T_0}}{1-\mathrm{e}^{-T_m/T}} + \frac{T_m/T}{\mathrm{e}^{T_m/T}-1} - \frac{T_m/T_0}{\mathrm{e}^{T_m/T_0}-1}\right\}.$$

By choosing the value of s_0 such that $s_0 = R\sum_{m=1}^{M_{\mathrm{vib}}}\frac{T_m/T_0}{\mathrm{e}^{T_m/T_0}-1}$, the relation for the specific entropy of the nonpolytropic van der Waals gas simplifies to

$$\frac{s(T,v)}{R} = \ln\frac{v-b}{v_0-b} + \ln\left(\frac{T}{T_0}\right)^{1/\delta} + \sum_{m=1}^{M_{\mathrm{vib}}}\left\{\ln\frac{1-\mathrm{e}^{-T_m/T_0}}{1-\mathrm{e}^{-T_m/T}} + \frac{T_m/T}{\mathrm{e}^{T_m/T}-1}\right\}. \tag{A.2.4}$$

For a more general gas with a specific heat dependent also on volume, namely, $c_v = c_v(T,v)$, a parametric representation of the fundamental relation is still possible and can be obtained by means of the "unified approach" of [28, p. 143]. This leads to the following defining relations

$$e(T,v) = e_0 + \int_{v_0}^{v}\left[T\frac{\partial P(T,v')}{\partial T} - P(T,v')\right]\mathrm{d}v' + \int_{T_0}^{T} c_v(T',\infty)\,\mathrm{d}T',$$

$$s(T,v) = s_0 + \int_{v_0}^{v}\frac{\partial P(T,v')}{\partial T}\,\mathrm{d}v' + \int_{T_0}^{T}\frac{c_v(T',\infty)}{T'}\,\mathrm{d}T',$$

whose evaluation requires to know the *single variable* function $c_v = c_v(T,\infty)$ in addition to the equation of state $P = P(T,v)$.

The speed of sound of a gas can be expressed as a function of the two variables T and v via the function $c_v(T,v)$ and the derivatives of $P = P(T,v)$ by the following relation

$$c(T,v) = v\left[\frac{T}{c_v(T,v)}\left(\frac{\partial P(T,v)}{\partial T}\right)^2 - \frac{\partial P(T,v)}{\partial v}\right]^{1/2}, \tag{A.2.5}$$

which can be obtained by a straightforward calculation.

Considering the equation of state $P(T,v) = \frac{RT}{v-b} - \frac{a}{v^2}$ and specific heat relation (A.2.1), a direct calculation gives immediately the speed of sound of the nonpolytropic van der Waals gas

$$c(T,v) = \left\{\left[1 + \frac{R}{c_v(T)}\right]\frac{RTv^2}{(v-b)^2} - \frac{2a}{v}\right\}^{1/2}. \tag{A.2.6}$$

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