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# Admissible shock waves and shock-induced phase transitions in a van der Waals fluid

Nanrong Zhao,<sup>1,a)</sup> Andrea Mentrelli,<sup>2,b)</sup> Tommaso Ruggeri,<sup>2,c)</sup> and Masaru Sugiyama<sup>3,d)</sup>

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A complete classification of shock waves in a van der Waals fluid is undertaken. This is in order to gain a theoretical understanding of those shock-related phenomena as observed in real fluids which cannot be accounted for by the ideal gas model. These relate to admissibility of rarefaction shock waves, shock-splitting phenomena, and shock-induced phase transitions. The crucial role played by the nature of the gaseous state before the shock (the unperturbed state), and how it affects the features of the shock wave are elucidated. A full description is given of the characteristics of shock waves propagating in a van der Waals fluid. The strength of these shock waves may range from weak to strong. The study is carried out by means of the theory of hyperbolic systems supported by numerical calculations. © 2011 American Institute of Physics. [doi:10.1063/1.3622772]

## I. INTRODUCTION

The ideal gas model has played a pivotal role in the study of shock wave phenomena. Many important and interesting features of shock waves have been obtained, thereby (see, for example, Refs. 1 and 2).

Real gases (fluids) are, evidently, not exactly described by the ideal gas model. There are always deviations from the ideal gas model in the behaviour of a real fluid, in particular with regard to shock wave phenomena. Thus, shock waves in real fluids exhibit richer behavior than that predicted by the ideal gas model. The model of a real fluid is usually prescribed by the thermal and caloric equations of state which show explicitly the differences from the ideal gas model.<sup>2</sup> This is exemplified, in particular, by the van der Waals equations of state.

Shock waves in real fluids have been the subject of many theoretical and experimental studies in past decades (see e.g., Ref. 3) starting from the pioneering work by Bethe.<sup>4</sup> In particular, shock waves in real fluids named Bethe-Zel'dovich-Thompson (BZT) fluids,<sup>4–6</sup> the definition of which will be given later, have attracted much interest of researchers in various fields. One example of the BZT fluid is the van der Waals fluid consisting of complex molecules. The crucial importance of real-fluid effects on shock waves is found in several practical applications, such as in mechanical engineering systems.<sup>7</sup> Typical phenomena related to shock waves in real fluids are propagation of rarefaction shock waves, shock splitting phenomena, and shock-induced phase transitions.

*Rarefaction* shock waves (also called *negative* shock waves) are shock waves of which the density in an unperturbed state ahead of the shock wave is larger than that of the perturbed state following the passage of the shock wave.<sup>6,8–12</sup>

Propagation of a rarefaction shock wave is impossible in the ideal gas model, where only (and all) the *compressive shock waves* can exist and be stable. Thus, in the terminology of the theory of hyperbolic systems, only compressive shocks are *admissible* in ideal gases. In real fluids, however, the situation is more complicated. Compressive shocks, as well as rarefaction shocks, may be either admissible or inadmissible depending both on the strength of the shock and on the characteristics of the unperturbed state.

*Shock splitting phenomena* are strictly connected to the above-mentioned dependence of the shock admissibility on the shock strength. We observe in this case the decomposition of an unstable shock wave into a combination of shock and rarefaction waves as the strength of the shock increases under certain conditions.<sup>13–15</sup> Rarefactive fronts and shock splitting phenomena in a van der Waals fluid have also been investigated via dynamical simulations.<sup>16</sup>

Finally, *shock-induced phase transition* is a dynamic phase transition accompanied by a shock wave (*phase boundary*) whose unperturbed and perturbed states are in different phases.<sup>17–22</sup> This phenomenon, which occurs only in real fluids, has been thoroughly investigated experimentally (see, for example, the *liquefaction shock wave* studied by Meier<sup>23</sup>). Several review articles are available on these topics; among others, it is worth mentioning Refs. 23–28. See also Refs. 17, 29–32 for the general theoretical Riemann problem in a van der Waals fluid.

Despite the remarkable success so far in theoretical studies of real-fluid effects, a comprehensive study embracing all the above-mentioned phenomena within a unified theoretical framework is, in our opinion, still missing.

Here, undertake a complete classification of shock waves, the strength of which ranges from weak to strong, when the unperturbed state is taken in the gas phase. We

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investigate how the choice of the unperturbed state affects the admissibility of compressive/rarefaction shock waves and the possibility of obtaining phase transitions induced by shock waves. In order to model the gas/liquid coexistence phase, the van der Waals equations of state are suitably modified according to the Maxwell construction.<sup>33</sup>

It will be shown, in detail, that it is possible to identify a set of regions in the  $\rho$ - $p$  (density-pressure) plane such that in each of these regions, the unperturbed states in the gas phase lead to shock waves with similar admissibility features. In particular, there exist regions such that: (i) all and only the compressive shocks are admissible and no phase transition is allowed, just as in an ideal gas; (ii) all the rarefaction shocks are inadmissible and the compressive ones may be admissible or inadmissible, depending on the strength of the shock; (iii) all the compressive shocks are admissible and the rarefaction ones may be admissible or inadmissible, depending on the strength of the shock; (iv) both compressive and rarefaction shocks may be admissible or inadmissible, depending on the strength of the shock. Moreover, for each of the last three scenarios, gas/liquid and gas/coexistence shock-induced phase transitions may occur.

The paper is organized as follows: Sections II–IV are preparatory. In Sec. II, the van der Waals model is reviewed along with salient aspects of thermodynamic stability and phase transitions. In Sec. III, an outline of hyperbolic systems of conservation laws is provided, while in Sec. IV, the basic concepts on shock waves and the related Rankine-Hugoniot (RH) conditions are summarized. These conditions, in the case of the van der Waals fluids, are also shown explicitly.

In Sec. V, the theoretical basis for the study of the admissibility of shock waves is recalled. It is shown that the Euler equations, together with the van der Waals equations of state, involves *locally linearly degenerate* (or *locally exceptional*) waves which are responsible, from a mathematical point of view, for most of the phenomena observed in real gases. The Liu condition,<sup>34,35</sup> which replaces the Lax condition<sup>36</sup> as a selection rule for the study of the shock admissibility when locally linearly degenerate waves are involved, is discussed and applied to the fastest non-characteristic shock wave which, without any loss of generality, is representative of all the non-characteristic shocks in a van der Waals fluid.

The detailed analysis of the van der Waals fluid is developed in Sec. VI. The theoretical results are presented along with numerical calculations coming from the solution of the given hyperbolic system of equations. In this context, the numerical approach plays a two-fold role: it supports the theoretical results and it completes the theory in all those cases where inadmissible shocks are expected and the shock profiles are not directly predictable by means of the theory.

Finally, in Sec. VII, a summary of the main results is given, along with conclusions that may be drawn in the light of the results obtained.

## II. THE VAN DER WAALS MODEL

In this section, characteristic features of the van der Waals fluids, which are necessary in the following analysis, are briefly summarized.

The van der Waals fluid is characterized by the caloric and thermal equations of state based on a modification of the ideal gas law. This modification involves the introduction of two material-dependent parameters,  $a$  and  $b$ , representing, respectively, a measure for the attraction between the constituent particles and the effective volume of each particle. These equations of state are the following:

$$e = c_v T - a\rho \quad (1)$$

and

$$p = R \frac{T\rho}{1 - b\rho} - a\rho^2, \quad (2)$$

where  $e$  is the specific internal energy,  $c_v$  is the specific heat at fixed volume,  $T$  is the absolute temperature,  $\rho$  is the mass density,  $p$  is the pressure, and  $R$  is the specific gas constant ( $R = k_B/m$ , being  $k_B$  the Boltzmann constant and  $m$  the mass of a particle). Throughout the present paper,  $c_v$  is assumed to be constant, that is, only polytropic fluids are studied. We define a dimensionless material-dependent quantity,  $\delta$ , as follows:

$$\delta \equiv R/c_v, \quad (3)$$

being  $0 < \delta \leq 2/3$ , with  $\delta = 2/3$  for a monatomic fluid. Equation (1) may thus be rewritten as

$$e = \frac{R}{\delta} T - a\rho. \quad (4)$$

By means of the Gibbs relation and making use of Eqs. (2) and (4), we obtain the specific entropy  $S$  of the van der Waals fluid

$$S = R \ln \left( K T^{1/\delta} \frac{1 - b\rho}{\rho} \right), \quad (5)$$

where  $K$  is a constant.

Furthermore, combining Eqs. (2) and (5), one can derive the expression of the sound velocity

$$c = \sqrt{(\partial p / \partial \rho)_S}, \quad (6)$$

as follows:

$$c = \sqrt{(1 + \delta) \frac{p + a\rho^2}{\rho(1 - b\rho)} - 2a\rho}. \quad (7)$$

It is convenient to introduce the dimensionless (or reduced) variables  $\hat{\rho}$ ,  $\hat{p}$ , and  $\hat{T}$  defined as follows:

$$\hat{\rho} = \rho/\rho_{cr}, \quad \hat{p} = p/p_{cr}, \quad \hat{T} = T/T_{cr},$$

where

$$\rho_{cr} = \frac{1}{3b}, \quad p_{cr} = \frac{a}{27b^2}, \quad T_{cr} = \frac{8a}{27Rb}$$

are the *critical values* of density, pressure, and temperature, respectively. The state  $(\rho_{cr}, p_{cr}, T_{cr})$  is called the *critical*



point. The introduction of the reduced variables allows us to write the equations of state in a form independent of the material constants  $a$  and  $b$  (*law of the corresponding states*). In addition to the reduced variables defined above, it is useful to introduce also the following dimensionless quantities:

$$\hat{e} = (\rho_{cr}/p_{cr})e, \quad \hat{c} = \sqrt{\rho_{cr}/p_{cr}} c, \quad \hat{S} = (T_{cr}\rho_{cr}/p_{cr})S.$$

In terms of the reduced variables, the caloric and thermal equations of state take the form

$$\hat{e} = \frac{8}{3\delta}\hat{T} - 3\hat{\rho}, \quad \hat{p} = \frac{8\hat{T}\hat{\rho}}{3 - \hat{\rho}} - 3\hat{\rho}^2, \quad (8)$$

and the dimensionless sound velocity,  $\hat{c}$ , and specific entropy,  $\hat{S}$ , appear as

$$\hat{c} = \sqrt{(1 + \delta) \frac{3(\hat{\rho} + 3\hat{\rho}^2)}{\hat{\rho}(3 - \hat{\rho})} - 6\hat{\rho}}, \quad (9a)$$

$$\hat{S} = \frac{8}{3} \ln \left( \hat{K} \hat{T}^{1/\delta} \frac{3 - \hat{\rho}}{\hat{\rho}} \right), \quad (9b)$$

where  $\hat{K}$  is a constant proportional to  $K$ .

As is well known, the thermodynamic stability requires that  $(\partial p / \partial \rho)_T > 0$  (or, in terms of the reduced variables,  $(\partial \hat{p} / \partial \hat{\rho})_{\hat{T}} > 0$ ); this means that there is a region in the reduced state space, where the van der Waals fluid described by the equations of state (8) is not thermodynamically stable. This region (dark shaded region, marked as gas/liquid coexistence (COE) region, in Fig. 1) is bounded by the so-called *spinodal curve*,  $S$ , which is the locus of the states in the  $\hat{\rho} - \hat{p}$  plane such that  $(\partial \hat{p} / \partial \hat{\rho})_{\hat{T}} = 0$ . From Eq. (8), it is easily seen that the spinodal curve,  $S$ , is given by

$$\hat{p} = \hat{\rho}^2(3 - 2\hat{\rho}). \quad (10)$$

Another important curve in the  $\hat{\rho} - \hat{p}$  plane is the so-called *coexistence curve*,  $C$  (also shown in Fig. 1), below which, according to the van der Waals model, the gas and liquid phases may coexist in the so-called *coexistence state*. For any temperature  $\hat{T} < 1$  ( $T < T_{cr}$ ), there are a *vaporization point* and a *liquefaction point*, with densities  $\hat{\rho}_G \equiv \hat{\rho}_G(\hat{T})$

and  $\hat{\rho}_L \equiv \hat{\rho}_L(\hat{T})$ , respectively, belonging to the same isotherm, between which the fluid may undergo a gas/liquid phase transition at constant pressure,  $\hat{p}_{coe} \equiv \hat{p}_{coe}(\hat{T})$ . It is worth recalling here that, in the context of the van der Waals model, the gas phase region is conveniently assumed to be bounded in the  $\hat{\rho} - \hat{p}$  plane by the coexistence curve (below the critical point) and by the critical isotherm  $\hat{T} = 1$  (above the critical point).

Recalling that the chemical potential,  $\mu$ , defined as  $\mu = e - TS + p/\rho$  must be constant on an isothermal phase transition process with a common pressure  $\hat{p}_{coe}$ , after some algebra, one can write down

$$3(\hat{\rho}_G - \hat{\rho}_L)(6 - \hat{\rho}_G - \hat{\rho}_L) + (3 - \hat{\rho}_G)(3 - \hat{\rho}_L)(\hat{\rho}_G + \hat{\rho}_L) \times \ln \left( \frac{\hat{\rho}_L(3 - \hat{\rho}_G)}{\hat{\rho}_G(3 - \hat{\rho}_L)} \right) = 0, \quad (11)$$

which implicitly define the coexistence curve  $C$  and give the quantities  $\hat{\rho}_G$  and  $\hat{\rho}_L$  in terms of  $\hat{p}_{coe}$ .

Moreover, we assume that the coexistence state is homogeneous in phase composition, with no slip between the phases. Taking into account the additivity of the specific volume, one can obtain the following basic equations for a coexistence state. First, the caloric and thermal equations of state are given by

$$e_{coe} = \frac{R}{\delta} T - a \left( \rho_G + \rho_L - \frac{\rho_G \rho_L}{\rho} \right) \quad (12)$$

and

$$p_{coe} = R \frac{T \rho_G}{1 - b \rho_G} - a \rho_G^2 = R \frac{T \rho_L}{1 - b \rho_L} - a \rho_L^2. \quad (13)$$

Second, the specific entropy  $S_{coe}$  turns out to be

$$S_{coe} = (1 - \alpha)S_G + \alpha S_L,$$

where  $\alpha$  is the volume fraction of the liquid phase, expressed by

$$\alpha = \frac{\rho_L(\rho - \rho_G)}{\rho(\rho_L - \rho_G)},$$

and  $S_G$  and  $S_L$  are given by

$$S_G = R \ln \left( K T^{1/\delta} \frac{1 - b \rho_G}{\rho_G} \right),$$

$$S_L = R \ln \left( K T^{1/\delta} \frac{1 - b \rho_L}{\rho_L} \right).$$

Third, the sound velocity for a homogeneous coexistence state, defined as<sup>37</sup>

$$c_{coe} = \sqrt{\left( \frac{\partial p_{coe}}{\partial \rho} \right)_{S_{coe}}},$$

is proved to take the form of (see for example, Refs. 37 and 38)

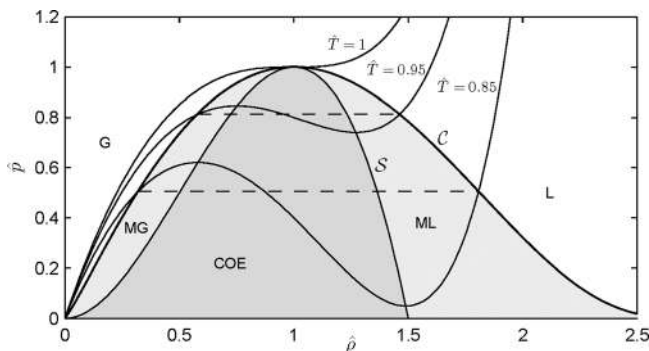


FIG. 1. Spinodal ( $S$ ) and coexistence ( $C$ ) curves in the  $\hat{\rho} - \hat{p}$  plane, along with three different isotherms ( $\hat{T} = 0.85, 0.95, 1$ ). The dashed lines represent the isotherms when phase transition is taken into account. (G: gas phase, L: liquid phase, MG: metastable gas phase, ML: metastable liquid phase, and COE: gas/liquid coexistence phase).

$$c_{coe} = \frac{\frac{dp_{coe}}{dT}}{\rho \sqrt{\frac{dS_G}{dT} - \frac{(\rho - \rho_G)d^2 p_{coe}}{\rho \rho_G dT^2} + \frac{1}{\rho_G^2} \frac{dp_{coe}}{dT} \frac{d\rho_G}{dT}}}}.$$

It must be emphasized that quantities  $\rho_G$  and  $\rho_L$  are functions only of  $T$  (through  $p_{coe}$ , see Eq. (11)), so is  $S_G$ . Therefore, based on this expression, the sound velocity in a coexistence state can be evaluated directly in terms of the thermodynamic quantities  $\rho$  and  $T$ .

For the sake of completeness, the reduced forms of the relations above are summarized as follows:

$$\hat{e}_{coe} = \frac{8}{3\delta} \hat{T} - 3 \left( \hat{\rho}_G + \hat{\rho}_L - \frac{\hat{\rho}_G \hat{\rho}_L}{\hat{\rho}} \right), \quad (14a)$$

$$\hat{p}_{coe} = \frac{8\hat{T}\hat{\rho}_G}{3 - \hat{\rho}_G} - 3\hat{\rho}_G^2 = \frac{8\hat{T}\hat{\rho}_L}{3 - \hat{\rho}_L} - 3\hat{\rho}_L^2, \quad (14b)$$

$$\hat{c}_{coe} = \frac{\frac{d\hat{p}_{coe}}{d\hat{T}}}{\hat{\rho} \sqrt{\frac{d\hat{S}_G}{d\hat{T}} - \frac{(\hat{\rho} - \hat{\rho}_G)d^2 \hat{p}_{coe}}{\hat{\rho} \hat{\rho}_G d\hat{T}^2} + \frac{1}{\hat{\rho}_G^2} \frac{d\hat{p}_{coe}}{d\hat{T}} \frac{d\hat{\rho}_G}{d\hat{T}}}}, \quad (14c)$$

$$\hat{S}_{coe} = (1 - \alpha)\hat{S}_G + \alpha\hat{S}_L, \quad (14d)$$

with

$$\hat{S}_G = \frac{8}{3} \ln \left( \hat{K} \hat{T}^{1/\delta} \frac{3 - \hat{\rho}_G}{\hat{\rho}_G} \right),$$

$$\hat{S}_L = \frac{8}{3} \ln \left( \hat{K} \hat{T}^{1/\delta} \frac{3 - \hat{\rho}_L}{\hat{\rho}_L} \right).$$

Finally, a comment is added here, concerning the metastable states and coexistence states of the van der Waals model. In the region below the spinodal curve (dark shaded region in Fig. 1), only coexistence states are physically meaningful, since these are the only thermodynamically stable ones. On the contrary, in the region between the coexistence and spinodal curves (light shaded region), both *metastable states* (metastable gas or metastable liquid states, respectively, denoted by MG and ML in Fig. 1) and coexistence states are physically meaningful. In other words, in the COE region, the dashed isotherms shown in Fig. 1 are the only acceptable ones, but in the MG and ML region, both the continuous and the dashed isotherms are acceptable. It should be noted, however, that although a metastable gas or liquid state is stable with respect to small fluctuations of thermodynamic quantities, such a state is *unstable* with respect to *large* fluctuations. A metastable state eventually changes to a corresponding coexistence state. In dynamical processes far from equilibrium such as shock-induced phase transitions under consideration, many kinds of fluctuations may inevitably appear. Therefore, it seems to be natural to assume that *only coexistence states occur when the perturbed state falls in the region between the coexistence and the spinodal curves*. Thus, in the following, we shall adopt this assumption. And we shall call the union of COE, MG, and ML regions *coexistence region* and denote it as G/L region.

### III. OUTLINE OF HYPERBOLIC SYSTEMS OF CONSERVATION LAWS

Let us consider a one-space-dimension problem. A quasi-linear first order system of  $N$  differential equations

$$\mathbf{A}^0(\mathbf{u}) \partial_t \mathbf{u} + \mathbf{A}(\mathbf{u}) \partial_x \mathbf{u} = 0 \quad (15)$$

( $\partial_t = \partial/\partial t$ ;  $\partial_x = \partial/\partial x$ ;  $\mathbf{u} \equiv \mathbf{u}(x, t) \in \mathbb{R}^N$ ;  $\mathbf{A}^0, \mathbf{A} \in \mathbb{R}^{N \times N}$ ) is hyperbolic in the time direction if  $\det(\mathbf{A}^0) \neq 0$ , and  $(\mathbf{A} - \lambda \mathbf{A}^0)\mathbf{r} = 0$  admits real eigenvalues,  $\lambda^{(k)}(\mathbf{u})$ , and a set of linearly independent right eigenvectors,  $\mathbf{r}^{(k)}(\mathbf{u})$ , ( $k = 1, \dots, N$ ).

The eigenvalues  $\lambda^{(k)}$  are called *characteristic velocities* and the system (15) is *symmetric* if  $\mathbf{A}^0$  and  $\mathbf{A}$  are symmetric matrices and  $\mathbf{A}^0$  is positive definite. It is easily seen, from linear algebra, that every symmetric system is hyperbolic.

The one-dimensional conservation laws of mass, momentum, and total energy for a perfect fluid (i.e., a fluid with zero viscosity and zero thermal conductivity; Euler equations) are written as

$$\partial_t \mathbf{u} + \partial_x \mathbf{F}(\mathbf{u}) = 0, \quad (16a)$$

$$\mathbf{u} \equiv \begin{pmatrix} \rho \\ \rho v \\ E \end{pmatrix}, \quad \mathbf{F} \equiv \begin{pmatrix} \rho v \\ \rho v^2 + p \\ (E + p)v \end{pmatrix}, \quad (16b)$$

where  $v$  is the velocity and  $E$  is the total energy ( $E = \rho e + \rho v^2/2$ ).

The system (16) is a particular case of quasi-linear first order systems, since it is obtained from Eq. (15) by setting  $N = 3$ ,  $\mathbf{A}^0 = \mathbf{I}$ ,  $\mathbf{A} = \partial \mathbf{F} / \partial \mathbf{u}$ .

In physical applications, like fluid-dynamics of perfect gases, every solution of Eq. (16) satisfies also a supplementary law

$$\partial_t h^0(\mathbf{u}) + \partial_x h(\mathbf{u}) = \Sigma \leq 0,$$

which has a physical interpretation: it represents the balance of entropy, provided that

$$h^0 = -\rho S, \quad h = -\rho S v,$$

while  $-\Sigma$  is the entropy production that, in the case of an Euler fluid, is zero for classical solutions and non-negative for weak solutions, in particular for shocks.

It was proven<sup>39,40</sup> that, if  $h^0(\mathbf{u})$  is a convex function, there exists a privileged set of field variables (the *main field*,  $\mathbf{u}'$ ) such that the original system becomes symmetric. Thus, the convexity of  $h^0$  (i.e., the concavity of  $\rho S$ ) guarantees the hyperbolicity of the system.

In the case of a van der Waals fluid, the convexity of  $h^0$  is guaranteed provided that  $(\partial p / \partial \rho)_T > 0$ , while the hyperbolicity requires  $(\partial p / \partial \rho)_S > 0$ . The former condition coincides with the well-known condition of thermodynamic stability, already mentioned in Sec. II, while the latter condition comes from imposing that all the eigenvalues of the system (16)

$$\lambda^{(1)} = v - c, \quad \lambda^{(2)} = v, \quad \lambda^{(3)} = v + c \quad (17)$$

are real, being  $c$  the sound velocity defined in Eq. (6).

From the following well-known thermodynamic relation (see e.g., Ref. 41),

$$\left(\frac{\partial p}{\partial \rho}\right)_s = \left(\frac{\partial p}{\partial \rho}\right)_T + \frac{T}{c_v \rho^2} \left[\left(\frac{\partial p}{\partial T}\right)_\rho\right]^2,$$

we obtain

$$\left(\frac{\partial p}{\partial \rho}\right)_s \geq \left(\frac{\partial p}{\partial \rho}\right)_T,$$

which is in agreement with the result according to which every symmetric system is hyperbolic.

If we adopted the caloric and thermal equations of state given in Eq. (8), we would have a region of non-hyperbolicity bounded, in the  $\hat{\rho} - \hat{p}$  plane, by the curve

$$\hat{p} = \frac{\hat{\rho}^2(3 - 3\delta - 2\hat{\rho})}{1 + \delta}. \quad (18)$$

It is easily seen, comparing Eqs. (18) and (10), that – in agreement with the above results – this region is a subset of the region delimited by the curve  $\mathcal{S}$  for any meaningful value of  $\delta$ . Since the modification of the van der Waals equations of state by means of the Maxwell construction described in Sec. II – which we are considering in this paper – allows to avoid the physically unstable region delimited by the curve  $\mathcal{S}$ , it also automatically allows to avoid any loss of hyperbolicity, therefore, the curve given by Eq. (18) is not even highlighted in Fig. 1 because it is not meaningful to the present analysis.

#### IV. SHOCK WAVES AND RANKINE-HUGONIOT CONDITIONS

A *shock wave* (or, in short, a *shock*) is a weak solution of the hyperbolic system (15), i.e., it is a solution which has a discontinuity localized on the so-called *shock front*. The shock front, propagating with velocity  $s$ , divides the space into two subspaces, in each of which the solution is smooth. Denoting as *unperturbed state*,  $\mathbf{u}_0$ , the state before the shock and as *perturbed state*,  $\mathbf{u}_1$ , the state after the shock (i.e., the states, respectively, ahead and behind the propagating front), it is well-known that a shock wave must satisfy the RH conditions (see, for example, Ref. 36)

$$-s[\mathbf{u}] + [\mathbf{F}] = 0, \quad (19)$$

where  $[\varphi(\mathbf{u})] = \varphi_1 - \varphi_0$  represents the discontinuity (jump) of the generic quantity  $\varphi$  across the propagating shock front, being  $\varphi_1 \equiv \varphi(\mathbf{u}_1)$  and  $\varphi_0 \equiv \varphi(\mathbf{u}_0)$  the quantity  $\varphi$  evaluated, respectively, in the perturbed and unperturbed states.

Taking into account Eq. (16b), the above conditions (19) may be written as follows:

$$\begin{aligned} -s[\rho] + [\rho v] &= 0, \\ -s[\rho v] + [\rho v^2 + p] &= 0, \\ -s[\rho e + \rho v^2/2] + [(\rho e + \rho v^2/2 + p)v] &= 0. \end{aligned}$$

The RH conditions admit a one-parameter family of solutions; letting  $\xi$  be the parameter, the perturbed state,  $\mathbf{u}_1$ , that

can be connected to a given unperturbed state,  $\mathbf{u}_0$ , through a shock front, and the velocity  $s$  of propagation of the front itself may be written as

$$\mathbf{u}_1 \equiv \mathbf{u}_1(\mathbf{u}_0, \xi), \quad s \equiv s(\mathbf{u}_0, \xi). \quad (20)$$

The set of all the perturbed states  $\mathbf{u}_1$  satisfying Eq. (19) for a given unperturbed state  $\mathbf{u}_0$  is called the *Hugoniot locus* for the point  $\mathbf{u}_0$  and is denoted as  $\mathcal{H}(\mathbf{u}_0)$ .

In the wide literature concerning shock waves in fluids, the shock velocity,  $s$ , is often replaced by the Mach number of the unperturbed state (*unperturbed Mach number*),  $M_0 = (s - v_0)/c_0$ , where  $c_0$  is the sound velocity (Eq. (7)) in the unperturbed state.

Without loss of generality, due to the Galilean invariance, we shall assume from now on that  $v_0 = 0$  and we consider only the shock wave propagating in the positive  $x$ -direction. Moreover, as already pointed out, we restrict ourselves to the case in which the unperturbed state is in the gas phase, i.e.,  $\mathbf{u}_0 \in G$ .

In order to explicitly write down the solutions (20) of the RH conditions (19), we need to distinguish two cases:

- (i) the perturbed state,  $\mathbf{u}_1$ , is in the gas or liquid phase ( $G \rightarrow G$  and  $G \rightarrow L$  solutions of the Rankine-Hugoniot conditions);
- (ii) the perturbed state,  $\mathbf{u}_1$ , is in the gas/liquid coexistence phase ( $G \rightarrow G/L$  solution of the Rankine-Hugoniot conditions).

#### A. The $G \rightarrow G$ and $G \rightarrow L$ solutions to the Rankine-Hugoniot conditions

In this case, the equations of state to be considered are those given in Eqs. (2) and (4).

Given an unperturbed state,  $\mathbf{u}_0 \equiv (\rho_0, 0, \rho_0 e_0)^T$ , in the gas region, and taking as parameter the density of the perturbed state  $\mathbf{u}_1 \equiv (\rho_1, \rho_1 v_1, \rho_1 e_1 + \rho_1 v_1^2/2)^T$ , i.e., letting  $\xi \equiv \rho_1$ , the solution of the RH conditions, written in terms of dimensionless quantities, is the following:

$$\hat{v}_1 = \hat{c}_0 M_0 \frac{\hat{\rho}_1 - \hat{\rho}_0}{\hat{\rho}_1}, \quad (21)$$

$$\hat{p}_1 = \hat{p}_0 + \hat{c}_0^2 M_0^2 \frac{\hat{\rho}_0(\hat{\rho}_1 - \hat{\rho}_0)}{\hat{\rho}_1}, \quad (22)$$

where the unperturbed Mach number,  $M_0$ , is given by

$$M_0 = \frac{1}{\hat{c}_0} \sqrt{\frac{2\hat{\rho}_1}{\hat{\rho}_0(\hat{\rho}_1 - \hat{\rho}_0)} \left( \hat{p}_1 - \frac{\hat{\rho}_0 \hat{\rho}_1 (\hat{e}_1 - \hat{e}_0)}{\hat{\rho}_1 - \hat{\rho}_0} \right)}. \quad (23)$$

Taking into account Eq. (8),

$$\hat{e}_0 = \frac{(\hat{p}_0 + 3\hat{\rho}_0^2)(3 - \hat{\rho}_0)}{3\delta\hat{\rho}_0} - 3\hat{\rho}_0, \quad (24a)$$

$$\hat{e}_1 = \frac{(\hat{p}_1 + 3\hat{\rho}_1^2)(3 - \hat{\rho}_1)}{3\delta\hat{\rho}_1} - 3\hat{\rho}_1, \quad (24b)$$

and Eq. (23) may be written as

$$M_0 = \frac{1}{\hat{c}_0} \sqrt{6\hat{\rho}_1 \frac{\hat{\rho}_0(1+\delta) + \hat{\rho}_0\hat{\rho}_1(\hat{\rho}_1 + \hat{\rho}_0 + 3\delta - 3)}{\hat{\rho}_0(2\hat{\rho}_0(3 - \hat{\rho}_1) + 3\delta(\hat{\rho}_0 - \hat{\rho}_1))}}. \quad (25)$$

The dimensionless sound velocity in the unperturbed state is given, following Eq. (9a), by

$$\hat{c}_0 = \sqrt{(1+\delta) \frac{3(\hat{\rho}_0 + 3\hat{\rho}_0^2)}{\hat{\rho}_0(3 - \hat{\rho}_0)} - 6\hat{\rho}_0}.$$

As the entropy production must be non-negative, the entropy production rate,  $\eta$ , may be calculated as follows:

$$\eta = -s[\hat{h}^0] + [\hat{h}] = s[\rho S] - [\rho S v] = \rho_0(s - v_0)[S] \geq 0$$

which may be written as, in terms of dimensionless quantities ( $\hat{\eta} = T_{cr} \rho_{cr}^{1/2} P_{cr}^{-3/2} \eta$ ):

$$\hat{\eta} = \hat{\rho}_0 \hat{c}_0 M_0 [\hat{S}] \geq 0 \quad (26)$$

where

$$[\hat{S}] = \frac{8}{3} \ln \left( \left( \frac{\hat{T}_1}{\hat{T}_0} \right)^{1/\delta} \frac{(3 - \hat{\rho}_1)\hat{\rho}_0}{(3 - \hat{\rho}_0)\hat{\rho}_1} \right).$$

## B. The $G \rightarrow G/L$ solutions to the Rankine-Hugoniot conditions

In this case, the equations of state given in Eqs. (2) and (4) are still to be used in the unperturbed state,  $\mathbf{u}_0$ , but the equations of state given in Eqs. (13) and (12) must be considered for the perturbed state  $\mathbf{u}_1$ .

The dimensionless perturbed fluid velocity,  $\hat{v}_1$ , pressure,  $\hat{p}_1$ , and the unperturbed Mach number,  $M_0$ , are still given by Eqs. (21)–(23), respectively, but Eq. (25) is not valid anymore, since Eq. (24b) must be replaced by

$$\hat{e}_1 = \frac{(\hat{p}_1 + 3\hat{p}_G^2)(3 - \hat{p}_G)}{3\delta\hat{p}_G} - 3 \left( \hat{p}_G + \hat{p}_L - \frac{\hat{p}_G\hat{p}_L}{\hat{p}_1} \right), \quad (27)$$

obtained from Eq. (14a).

Thus, Eq. (25) has to be replaced by Eq. (23), Eq. (24a), and Eq. (27) that set up a system which must be solved by means of a suitable numerical method.

The dimensionless entropy production rate,  $\hat{\eta}$ , is calculated by means of Eq. (26) where  $[\hat{S}]$ , according to Eq. (14d), is given by

$$\begin{aligned} [\hat{S}] &= (1 - \alpha)\hat{S}_G + \alpha\hat{S}_L - \hat{S}_0 \\ &= \frac{8}{3} \ln \left[ \left( \frac{\hat{T}_1}{\hat{T}_0} \right)^{1/\delta} \left( \frac{3 - \hat{p}_G}{\hat{p}_G} \right)^{1-\alpha} \left( \frac{3 - \hat{p}_L}{\hat{p}_L} \right)^\alpha \frac{\hat{\rho}_0}{(3 - \hat{\rho}_0)} \right]. \end{aligned}$$

## V. THE ADMISSIBILITY OF SHOCK WAVES

According to the theory of hyperbolic systems, not every solution of the Rankine-Hugoniot conditions corresponds to a physically meaningful shock wave. Thus, we need a criterion to select which of the states  $\mathbf{u}_1 \in \mathcal{H}(\mathbf{u}_0)$  are perturbed

states that together with  $\mathbf{u}_0$  form *admissible* shocks. Admissible shocks propagate with no change in shape and, moreover, they are stable with respect to small perturbations of the unperturbed and perturbed states;<sup>42</sup> for this reason, admissible shocks are usually called also *stable shocks*.

In order to provide a selection rule to evaluate the admissibility of shocks, it is necessary to recall that in the theory of hyperbolic systems a wave associated to a characteristic velocity  $\lambda$  is called ( $\nabla \equiv \partial/\partial \mathbf{u}$ ): *genuinely non-linear*, if  $\nabla \lambda \cdot \mathbf{r} \neq 0 \ \forall \mathbf{u}$ ; *linearly degenerate* (or *exceptional*), if  $\nabla \lambda \cdot \mathbf{r} \equiv 0 \ \forall \mathbf{u}$ ; *locally linearly degenerate* (or *locally exceptional*), if  $\nabla \lambda \cdot \mathbf{r} = 0$  for some  $\mathbf{u}$ .

From now on, we shall call  $\lambda$  the  $k$ th characteristic velocity and  $\mathbf{r}$  the corresponding eigenvector, i.e.,  $\lambda \equiv \lambda^{(k)}$  and  $\mathbf{r} \equiv \mathbf{r}^{(k)}$ .

The issue of shock admissibility when genuinely non-linear and linearly degenerate waves are involved has been largely investigated; the hyperbolic system of conservation laws of mass, momentum, and energy for an ideal gas, for example, features only waves belonging to these two types and it has been deeply analyzed in the past decades (see, among the others, the book by Landau and Lifshitz<sup>1</sup>). On the contrary, the hyperbolic system of the van der Waals fluid features linearly degenerate and locally linearly degenerate waves. A comprehensive analysis of the shock admissibility in this kind of fluid has never been presented up to now, as far as the authors know.

## A. Lax and Liu conditions

The selection rule useful to study the admissibility of shocks depends on the type of the involved non-linear waves. Thus, it is necessary to discuss separately the cases of genuinely non-linear, linearly degenerate, and locally linearly degenerate waves.

When we deal with genuinely non-linear waves, the selection rule is given by the *Lax condition*, according to which a shock wave is admissible if there exists a characteristic velocity  $\lambda$  such that<sup>36</sup>

$$\lambda_0 < s < \lambda_1,$$

where  $\lambda_0 \equiv \lambda(\mathbf{u}_0)$  and  $\lambda_1 \equiv \lambda(\mathbf{u}_1)$ ; such a shock wave is called *k-shock* (being  $\lambda$  the  $k$ th eigenvalue of the system). The Lax condition turns out to be equivalent (at least for *weak shocks*) to the condition of entropy growth across the shock

$$\eta = -s[\hat{h}^0] + [\hat{h}] > 0.$$

On the other hand, when we deal with a linearly degenerate wave, admissible *k-shocks* are called *characteristic shocks* and they propagate with velocity  $s = \lambda_0 = \lambda_1$ . In this case, there is no entropy growth across the shock, i.e.,  $\eta = 0$ . A characteristic shock depends on as many parameters as the multiplicity of the eigenvalue  $\lambda$ ;<sup>43</sup> the system of equations of the Euler fluid in three space dimensions, for example, exhibits an eigenvalue of multiplicity three, and the *contact shock wave* associated to this eigenvalue is thus a characteristic shock depending on three parameters.



Finally, when the system features locally linearly degenerate waves, the selection rule is given by the *Liu condition*,<sup>34,35</sup> stating that a shock wave is admissible if

$$\begin{aligned} s &\geq s_*, \\ \forall s_* \in \{s_* : s_*(\mathbf{u}_* - \mathbf{u}_0) &= \mathbf{F}(\mathbf{u}_*) - \mathbf{F}(\mathbf{u}_0), \\ \mathbf{u}_* &\in \mathcal{H}(\mathbf{u}_0) \text{ between } \mathbf{u}_0 \text{ and } \mathbf{u}_1\}. \end{aligned}$$

This means that a shock is admissible if its velocity,  $s$ , is not smaller than the velocity of any other shock with the same unperturbed state  $\mathbf{u}_0$  and with perturbed state  $\mathbf{u}_*$  lying on the Hugoniot locus for  $\mathbf{u}_0$  between  $\mathbf{u}_0$  and  $\mathbf{u}_1$  (see Fig. 2). If the Liu condition is not satisfied, the shock is *unstable* or *inadmissible*. It is well-known that the Liu condition implies the Lax condition, and at least for moderate shock, the entropy growth, and therefore, the stable shocks satisfy the second law of the thermodynamics (see, e.g., Ref. 42). Conversely, the entropy growth is not sufficient to imply the Liu condition, and we need additional conditions.<sup>42,44</sup>

## B. Further analysis

Differentiating Eq. (19) with respect to the parameter  $\xi$  and taking into account (Eq. (20)) we get

$$\dot{s}(\mathbf{u}_1 - \mathbf{u}_0) = (\mathbf{A} - s\mathbf{I})\dot{\mathbf{u}}_1, \quad (28)$$

where  $\dot{\cdot} \equiv d/d\xi$ . Letting  $\mathbf{l}$  and  $\mathbf{r}$  be, respectively, the left and right normalized eigenvectors of  $\mathbf{A}$ , i.e.,

$$\begin{aligned} \mathbf{l}(\mathbf{A} - \lambda\mathbf{I}) &= 0, \\ (\mathbf{A} - \lambda\mathbf{I})\mathbf{r} &= 0, \\ \mathbf{l}^{(i)} \cdot \mathbf{r}^{(j)} &= \delta_{ij} \quad (i, j = 1, \dots, N), \end{aligned}$$

we may write, from Eq. (28),

$$\dot{s}\mathbf{l} \cdot [\mathbf{u}] = (\lambda - s)\mathbf{l} \cdot \dot{\mathbf{u}}_1. \quad (29)$$

From Eqs. (28) and (29), when  $[\mathbf{u}] \rightarrow 0$  we have

$$s \rightarrow \lambda_0, \quad \dot{\mathbf{u}}_1 \rightarrow \mathbf{r}_0, \quad (30)$$

with  $\mathbf{r}_0 \equiv \mathbf{r}(\mathbf{u}_0)$ ; then, for *weak shocks*,<sup>53</sup>

$$[\mathbf{u}] = (\xi - \xi_0)\mathbf{r}_0 + \mathcal{O}((\xi - \xi_0)^2)$$

and

$$\mathbf{l} \cdot [\mathbf{u}] = \xi - \xi_0 + \mathcal{O}((\xi - \xi_0)^2), \quad (31a)$$

TABLE I. Relation between the quantity  $(\lambda - s)$  and the quantity  $\dot{s}$  along the positive and negative branches of the Hugoniot locus.

Branch of $\mathcal{H}(\mathbf{u}_0)$	$\dot{s} > 0$	$\dot{s} = 0$	$\dot{s} < 0$
Positive shocks ( $\xi > \xi_0$ )	$\lambda > s$	$\lambda = s$	$\lambda < s$
Negative shocks ( $\xi < \xi_0$ )	$\lambda < s$	$\lambda = s$	$\lambda > s$

$$\mathbf{l} \cdot \dot{\mathbf{u}}_1 = 1 + \mathcal{O}(\xi - \xi_0). \quad (31b)$$

Assuming that the quantities  $\mathbf{l} \cdot [\mathbf{u}]$  and  $\mathbf{l} \cdot \dot{\mathbf{u}}_1$ , which—as seen in Eq. (31)—are different from zero for weak shocks, do not vanish also for non-weak shocks, and denoting as *positive shocks*, the solution of the RH conditions with  $\xi > \xi_0$  (forming the *positive branch* of the Hugoniot locus  $\mathcal{H}(\mathbf{u}_0)$ ) and *negative shocks* those with  $\xi < \xi_0$  (forming the *negative branch* of  $\mathcal{H}(\mathbf{u}_0)$ ) and combining Eqs. (29) and (31), we obtain the results shown in Table I and sketched in Fig. 2(b).

Differentiating Eq. (28) and  $(\mathbf{A} - \lambda\mathbf{I})\mathbf{r} = 0$  with respect to  $\xi$ , we obtain, respectively,

$$-\dot{s}[\mathbf{u}] + (\dot{\mathbf{A}} - 2\dot{s}\mathbf{I})\dot{\mathbf{u}}_1 + (\mathbf{A} - s\mathbf{I})\ddot{\mathbf{u}}_1 = 0 \quad (32)$$

and

$$(\dot{\mathbf{A}} - \dot{\lambda}\mathbf{I})\mathbf{r} + (\mathbf{A} - \lambda\mathbf{I})\dot{\mathbf{r}} = 0. \quad (33)$$

Taking the limit  $[\mathbf{u}] \rightarrow 0$  of Eqs. (32) and (33) and then multiplying both by  $\mathbf{l}_0 = \mathbf{l}(\mathbf{u}_0)$ , we have the well-known result:<sup>36</sup>

$$\dot{s}_0 = \frac{1}{2}\dot{\lambda}_0. \quad (34)$$

If  $\dot{\lambda}_0 > 0$ , from Eq. (34), it is seen that  $\dot{s}_0 > 0$  and, taking into account the results shown in Table I, we get that positive shocks are admissible and negative ones are inadmissible. This is true at least for weak shocks ( $|\xi| \simeq \xi_0$ ) and it is certainly true also for strong shocks ( $|\xi| \gg \xi_0$ ) if  $s$  is an increasing function of the parameter  $\xi$ .

Analogously, if  $\dot{\lambda}_0, \dot{s}_0 < 0$  the opposite situation is verified: the negative shocks are admissible and the positive ones are inadmissible. This conclusion, which is always true for weak shocks, is true also for strong shocks if  $s$  is a decreasing function of  $\xi$ .

The case of the hyperbolic systems of the Euler equations of an ideal gas is a well-known example of a system with shocks whose velocity of propagation,  $s$ , is a strictly monotonous function of the parameter  $\xi$  so—except for the

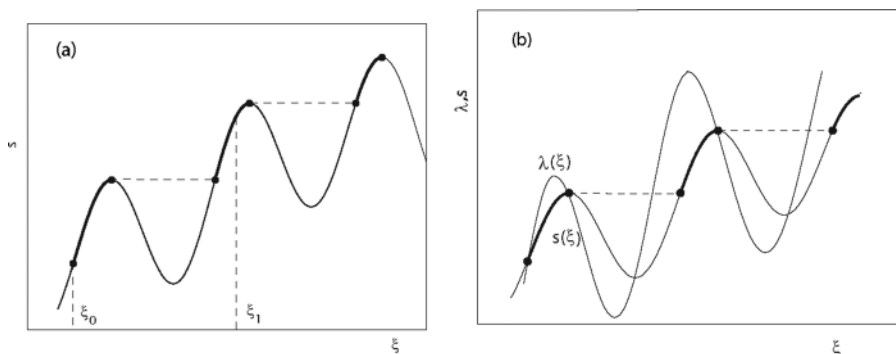


FIG. 2. Shock velocity  $s$  as a function of the shock parameter  $\xi$  and the range of the admissible shocks (bold curve).  $\lambda$  is the characteristic velocity.

characteristic shocks—there is an entire branch of  $\mathcal{H}(\mathbf{u}_0)$  which is admissible while the other branch is entirely inadmissible.

Since in fluid-dynamics a shock characterized by a density of the unperturbed state lower than the density of the perturbed state is usually called *compressive* shock, while in the opposite case a shock is called *rarefaction* (or *negative*) shock, it turns out that in an ideal gas all (and only) the compressive shocks are admissible.

If  $\dot{\lambda}_0 = \dot{s}_0 = 0$ , two situations are possible: if  $\xi_0$  corresponds to a minimum value of  $\lambda$ , then both positive and negative weak shocks are admissible; if  $\xi_0$  corresponds to a maximum value of  $\lambda$ , both positive and negative weak shocks are inadmissible.<sup>45</sup> This situation is encountered when dealing with locally linearly degenerate waves, in fact (see Eq. (30))

$$\dot{\lambda}_0 = (\nabla \lambda \cdot \dot{\mathbf{u}}_1)_0 = (\nabla \lambda \cdot \mathbf{r})_0,$$

so the condition  $\dot{\lambda}_0 = \dot{s}_0 = 0$  is verified when the unperturbed state belongs to the locus of states such that  $\nabla \lambda \cdot \mathbf{r} = 0$ , which exists only when the wave associated to the eigenvalue  $\lambda$  is locally linearly degenerate.

From the above discussion, it is clear that the *local exceptionality hypersurface*, defined as the locus of the states  $\mathbf{u}$  such that  $\nabla \lambda \cdot \mathbf{r} = 0$ , is crucial in the study of the shock admissibility when locally exceptional waves are involved.

In fact, aside from being the locus of the unperturbed states for which both positive and negative weak shocks are admissible or inadmissible, the local exceptionality hypersurface divides the space of the states into two subspaces: on one of these subspaces  $\dot{\lambda}_0 > 0$  and when the unperturbed state falls into this region, among the weak shocks, only the positive ones are admissible; on the other subspace, the opposite situation is verified: among the weak shocks, only the negative ones are admissible. We may choose the eigenvector  $\mathbf{r}$  such that  $\nabla \lambda \cdot \mathbf{r} > 0$  in the first case and  $\nabla \lambda \cdot \mathbf{r} < 0$  in the second case, for a reason that will become evident in Sec. V C.

From this discussion, it turns out that when locally linearly degenerate waves are involved, both compressive and rarefaction (i.e., positive and negative) shocks may be admissible, depending on where the unperturbed state is taken. This is exactly the case of the hyperbolic system of the van der Waals fluid described in Sec. II.

### C. The local exceptionality hypersurface for the van der Waals fluid

In order to calculate the local exceptionality hypersurface associated to the hyperbolic system of equations of the van der Waals fluid, we observe that if we perform the formal substitution

$$\partial_t \rightarrow -\lambda \delta, \quad \partial_x \rightarrow \delta, \quad (35)$$

where  $\delta$  is a differential operator (not to be confused with the constant  $\delta$  previously defined), we obtain from Eq. (15) that  $\delta \mathbf{u} \propto \mathbf{r}$ . Therefore,

$$\delta \lambda = \nabla \lambda \cdot \delta \mathbf{u} \propto \nabla \lambda \cdot \mathbf{r} = 0$$

and we conclude that the local exceptionality hypersurface is the locus of states such that  $\delta \lambda$  vanishes.

In the case of a van der Waals fluid, it is seen that locally linearly degenerate waves, with characteristic velocities  $\dot{\lambda}$ , are involved. It is thus possible to calculate the associated local exceptionality hypersurfaces, dividing the space of the states into two subspaces, over each of which  $\nabla \lambda \cdot \mathbf{r}$  does not vanish and never changes sign.

The wave associated to the eigenvalue  $\lambda^{(2)}$ , given in Eq. (17), is linearly degenerate while the waves associated to  $\lambda^{(1)}$  and  $\lambda^{(3)}$  are locally linearly degenerate. Focusing on the wave associated to  $\lambda \equiv \lambda^{(3)}$  (the study of  $\lambda^{(1)}$  is analogous), by applying Eq. (35) to the conservation laws of mass and entropy, and recalling the definition of the sound velocity given in Eq. (6), we obtain

$$\delta v = \frac{c}{\rho} \delta \rho, \quad \delta S = 0, \quad \delta c = \frac{(p_{\rho\rho})_S}{2c} \delta \rho.$$

Therefore, we get

$$\delta \lambda = \frac{\rho(p_{\rho\rho})_S + 2(p_\rho)_S}{2c\rho} \delta \rho, \quad (36)$$

and, as a result, the locus of the states such that  $\nabla \lambda \cdot \mathbf{r} = 0$ , which we shall call *local exceptionality curve*,  $\mathcal{L}_\delta$ , is given by

$$\rho(p_{\rho\rho})_S + 2(p_\rho)_S = 0$$

or taking into account the van der Waals thermal equation of state and switching to reduced variables

$$\hat{p} = \hat{\rho}^2 \left( \frac{2(3 - \hat{\rho})^2}{2 + 3\delta + \delta^2} - 3 \right). \quad (37)$$

The local exceptionality curve corresponds to what is commonly known in gasdynamic as *transition line* (see, for example, Ref. 46), i.e., the locus of thermodynamic states for which the *fundamental derivative*

$$\Gamma \equiv \frac{\tau^3}{2c^2} (p_{\tau\tau})_S = \frac{1}{2\rho c^2} \frac{\partial}{\partial \rho} \left[ \rho^2 (p_\rho)_S \right], \quad (38)$$

vanishes ( $\tau$  denotes here the specific volume, i.e.,  $\tau = 1/\rho$ ). In fact, comparing Eqs. (36) and (38), it is seen that

$$\frac{\delta \lambda}{\delta \rho} = \frac{c}{\rho} \Gamma.$$

Since the early Seventies, the curve  $\Gamma = 0$  has played a major role in the study of the so-called BZT fluid, i.e., those fluids in which *nonclassical phenomena* as rarefaction shock waves may come into play. The BZT fluids—which took this name after the works by Bethe, Zel’dovich, and Thompson<sup>4–6</sup>—are in fact those fluids for which a region with  $\Gamma < 0$  appears, in contrast to ideal gases and many real fluids for which  $\Gamma$  is always positive.

The choice of the eigenvectors pointed out in Sec. V B is made in order to let the sign of the quantity  $\nabla \lambda \cdot \mathbf{r}$  match

the sign of the fundamental derivative  $\Gamma$ ; the regions with  $\nabla\lambda \cdot \mathbf{r} > 0$  and  $\nabla\lambda \cdot \mathbf{r} < 0$  correspond, respectively, to the regions where  $\Gamma > 0$  (also known as *region of positive nonlinearity*) and  $\Gamma < 0$  (*region of negative nonlinearity*).

Since only the thermodynamic quantities  $\hat{\rho}$  and  $\hat{p}$  appear in Eq. (37), we can restrict ourselves to considering, instead of a surface in the state space, only the curve described by the above equation in the  $\hat{\rho} - \hat{p}$  plane.

The subscript in the notation we use for the local exceptionality curve,  $\mathcal{L}_\delta$ , points out the dependence of this curve on the parameter  $\delta$ , in contrast to what happens to the already defined  $\mathcal{S}$  and  $\mathcal{C}$  curves. This dependence is shown, for some values of the material constant  $\delta$ , in Fig. 3.

Since we are considering that below the coexistence curve only coexistence states are allowed (i.e., we are discarding metastable states), the  $\mathcal{L}_\delta$  curve is meaningful only outside the coexistence region. Making use of Eqs. (11) and (37), it is easily seen that the local exceptionality curve is meaningful only when  $0 < \delta < \delta_{BZT}$  with  $\delta_{BZT} \simeq 0.06$  since, as it may be appreciated from Fig. 3, as  $\delta \rightarrow \delta_{BZT}$  the region enclosed between the  $\mathcal{L}_\delta$  and  $\mathcal{C}$  curves vanishes.

As it will be discussed later,  $\delta_{BZT}$  is an important threshold value of the parameter  $\delta$ : only when  $\delta < \delta_{BZT}$ , a region of negative nonlinearity appears and nonclassical phenomena are possible. This happens, according to Eq. (3), when the specific heat,  $c_v$ , is *sufficiently* large.

## VI. ANALYSIS OF THE SHOCK ADMISSIBILITY AND SHOCK-INDUCED PHASE TRANSITIONS

In this section, first, we make theoretical considerations on the shock-related phenomena and show how the choice of the unperturbed states affects the features of the phenomena. Second, we show and discuss the typical numerical results in order to check the theoretical results and to investigate the wave profiles in the case of inadmissible shocks.

### A. Theoretical considerations

As pointed out in Sec. V, in the case of the hyperbolic system of the Euler equations (16) for an ideal gas, since the involved waves are genuinely non-linear, the study of the admissibility of non-characteristic shocks requires the Lax

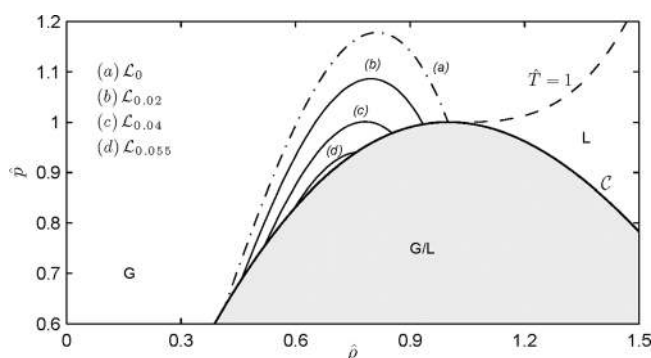


FIG. 3. Curves of local exceptionality ( $\mathcal{L}_\delta$  curves) for several values of the parameter  $\delta$  ( $\delta=0, 0.02, 0.04, 0.055$ ). The gas, liquid, and coexistence regions (respectively G, L, and G/L) are highlighted.

condition. The application of this selection rule gives results that may be easily summarized as follows:

1. Every compressive shock is admissible (*stable* shocks) and
2. Every rarefaction shock is inadmissible (*unstable* shocks).

In the case of the van der Waals fluid, locally linearly degenerate waves are involved; the admissibility of shocks is to be investigated by means of the Liu condition and the results of the application of this selection rule are not so straightforward as in the ideal gas case. As far as weak shocks are concerned, these results may still be easily summarized as follows:

1. Every compressive weak shock is admissible when the unperturbed state is taken in the region of the  $\hat{\rho} - \hat{p}$  plane where  $\nabla\lambda \cdot \mathbf{r} > 0$ , i.e., in the region of positive nonlinearity.
2. Every rarefaction weak shock is admissible when the unperturbed state is taken in the region of the  $\hat{\rho} - \hat{p}$  plane where  $\nabla\lambda \cdot \mathbf{r} < 0$ , i.e., in the region of negative nonlinearity.
3. Both compressive and rarefaction weak shocks are admissible (inadmissible) when the unperturbed state is taken on the curve of the  $\hat{\rho} - \hat{p}$  plane such that  $\nabla\lambda \cdot \mathbf{r} = 0$ , i.e., on the transition line, and  $\lambda \equiv \lambda(\xi)$  has a maximum (minimum) on this curve.

For non-weak shocks, a satisfactory classification requires a closer look at the features of the unperturbed state, as we shall see. Moreover, in the case of a van der Waals fluid, in contrast to the case of an ideal gas, the possibility of shock-induced phase transitions is to be considered.

It is thus interesting to analyze in greater detail how the admissibility of shocks and the possibility of shock-induced phase transitions are affected by the choice of the unperturbed state,  $\mathbf{u}_0$  (or, in terms of reduced variables,  $\hat{\mathbf{u}}_0$ ). In this analysis, we will assume that the unperturbed state is in the gas phase, i.e.,  $\hat{\mathbf{u}}_0$  is represented, in the  $\hat{\rho} - \hat{p}$  plane, by a state  $(\hat{\rho}_0, \hat{p}_0)$  in the region marked by G in Fig. 3. In agreement with the considerations expressed in Sec. II, we discard the possibility of shock-induced phase transition from gas phase to metastable phase, and we shall therefore be concerned with phase transitions from gas phase to coexistence phase ( $G \rightarrow G/L$  shocks) and from gas phase to liquid phase ( $G \rightarrow L$  shocks).

As already pointed out in Sec. V C, the local exceptionality curve depends on the parameter  $\delta$ , and only for  $\delta \leq \delta_{BZT} \simeq 0.06$ , this curve is meaningful from a physical point of view. Therefore, the two cases  $\delta \leq \delta_{BZT}$  and  $\delta > \delta_{BZT}$  have to be discussed separately.

#### 1. Case $\delta \leq \delta_{BZT}$ (BZT fluids)

When  $\delta \leq \delta_{BZT} \simeq 0.06$ , a region of negative nonlinearity ( $\Gamma < 0$  or, equivalently,  $\nabla\lambda \cdot \mathbf{r} < 0$ ) appears and non-classical shock phenomena may come into play: this corresponds to the case of so-called BZT fluids.

In this case, the gas region in the  $\hat{\rho} - \hat{p}$  plane may be subdivided into a set of non-overlapping regions (the union

of which completely covers the gas region), as it is shown—for  $\delta=0.01$ —in Fig. 4. It is essential to observe that the change of  $\delta$ , as far as  $\delta$  does not exceed  $\delta_{BZT}$ , leads to changes in size and shape of the regions that we are about to discuss, but does not alter the following qualitative analysis. Each of these regions (that we denote as **A**, **B**, **C**,  $\tilde{\mathbf{C}}$ , **D**, and **E**, assuming the region **B** as split up into the two subregions **B**<sub>1</sub> and **B**<sub>2</sub>, as seen in Fig. 4) contains states that, if taken as unperturbed states, lead to Hugoniot loci with similar features from the point of view of the shock admissibility. The gas region may be subdivided as follows:

- region  $\mathbf{A} \cup \mathbf{B} \cup \mathbf{C} \cup \tilde{\mathbf{C}}$ . This is the region where  $(\nabla \lambda \cdot \mathbf{r})_0 > 0$ . When the unperturbed state belongs to this region, compressive weak shocks are admissible and rarefaction weak shocks are inadmissible. A deeper analysis shows that:
  - region  $\mathbf{A} \cup \mathbf{B}$ . When the unperturbed state belongs to this region, the Hugoniot locus  $\mathcal{H}(\hat{\mathbf{u}}_0)$  does not go through the coexistence region nor the liquid region, so no shock-induced phase transition is possible. This region may be further subdivided as follows:
    - region **A**. When  $\hat{\mathbf{u}}_0 \in \mathbf{A}$ , all the compressive shocks are admissible and all the rarefaction shocks are inadmissible, i.e., the positive branch of  $\mathcal{H}(\hat{\mathbf{u}}_0)$  is entirely admissible and the negative branch is entirely inadmissible. In this case, the shock admissibility is *qualitatively* the same as in the ideal gas case, i.e., the Liu condition is equivalent to the Lax condition;
    - region **B**. When  $\hat{\mathbf{u}}_0 \in \mathbf{B}$ , the Hugoniot locus  $\mathcal{H}(\hat{\mathbf{u}}_0)$  crosses the local exceptionality curve. The Liu condition and the Lax condition are not equivalent. As a result, not all the compressive shocks are admissible but all the rarefaction shocks are inadmissible for the unperturbed states in **B**<sub>1</sub>, and not all the rarefaction shocks are admissible but all the compressive shocks are admissible for the unperturbed states in **B**<sub>2</sub>.
  - region **C**. When the unperturbed state belongs to this region, the Hugoniot locus  $\mathcal{H}(\hat{\mathbf{u}}_0)$  crosses the coexistence curve,  $\mathcal{C}$ , so phase transitions may be allowed. The Hugoniot locus may cross also the local exceptionality curve,  $\mathcal{L}_\delta$ , so inadmissible compressive shocks can be encountered.

- region  $\tilde{\mathbf{C}}$ . When the unperturbed state belongs to this region, admissible compressive strong shocks have the unusual property that, as the strength of the shock increases, the perturbed density decreases. This kind of shock, called *compressive upper shock*, and the properties of the region  $\tilde{\mathbf{C}}$  have been extensively analyzed elsewhere<sup>47</sup> and they will not be discussed here any further.
- region  $\mathbf{D} \cup \mathbf{E}$ . This is the region where  $(\nabla \lambda \cdot \mathbf{r})_0 < 0$ . When the unperturbed state belongs to this region, rarefaction weak shocks are admissible and compressive weak shocks are inadmissible. This region may be further subdivided as follows:
  - region **D**. When  $\hat{\mathbf{u}}_0 \in \mathbf{D}$  the Hugoniot locus  $\mathcal{H}(\hat{\mathbf{u}}_0)$  does not cross the coexistence region nor the liquid region, so no phase transition is allowed;
  - region **E**. When  $\hat{\mathbf{u}}_0 \in \mathbf{E}$  the Hugoniot locus  $\mathcal{H}(\hat{\mathbf{u}}_0)$  goes through the coexistence and liquid region, so phase transitions may be allowed.

It is worth noting that the curve of the  $\hat{p} - \hat{p}$  plane that separates regions **A** and **B**<sub>1</sub> is the locus  $\mathcal{L}_\delta^*$  of the states that, when taken as unperturbed states, lead to Hugoniot loci tangent to the local exceptionality curve.

For any fixed  $\delta$ , letting  $\hat{p}_{\mathcal{L}_\delta} \equiv \hat{p}_{\mathcal{L}_\delta}(\hat{p})$  the reduced pressure as a function of the reduced density on the local exceptionality curve  $\mathcal{L}_\delta$ , provided by Eq. (37), and  $\hat{p}_{\mathcal{H}} \equiv \hat{p}_{\mathcal{H}}(\hat{p}, \hat{\mathbf{u}}_0)$  the reduced pressure along the Hugoniot locus for  $\hat{\mathbf{u}}_0$ , provided by Eq. (22), the states  $\hat{\mathbf{u}}_0 \in \mathcal{L}_\delta^*$  are those that satisfy, for some  $\hat{p}$ , the following system of equations:

$$\begin{aligned} \hat{p}_{\mathcal{L}_\delta}(\hat{p}) &= \hat{p}_{\mathcal{H}}(\hat{p}, \hat{\mathbf{u}}_0), \\ \frac{\partial \hat{p}_{\mathcal{L}_\delta}(\hat{p})}{\partial \hat{p}} &= \frac{\partial \hat{p}_{\mathcal{H}}(\hat{p}, \hat{\mathbf{u}}_0)}{\partial \hat{p}}. \end{aligned}$$

Analogously, the curve separating regions **B** and **C** (and regions **D** and **E**) is the locus  $\mathcal{C}^*$  of the unperturbed states whose Hugoniot loci are tangent to the coexistence curve. Thus, the states  $\hat{\mathbf{u}}_0 \in \mathcal{C}^*$  are those that satisfy, for some  $\hat{p}$ , the conditions

$$\begin{aligned} \hat{p}_{\mathcal{C}}(\hat{p}) &= \hat{p}_{\mathcal{H}}(\hat{p}, \hat{\mathbf{u}}_0), \\ \frac{\partial \hat{p}_{\mathcal{C}}(\hat{p})}{\partial \hat{p}} &= \frac{\partial \hat{p}_{\mathcal{H}}(\hat{p}, \hat{\mathbf{u}}_0)}{\partial \hat{p}}, \end{aligned}$$

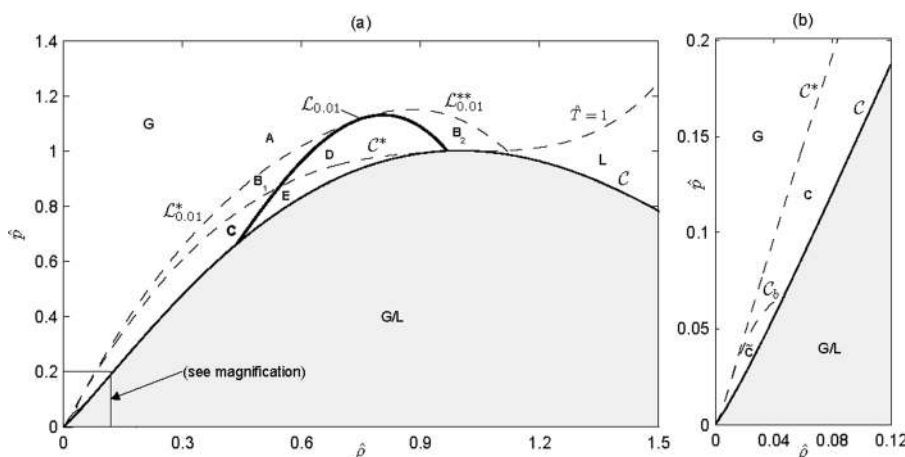


FIG. 4. (a) Regions of the  $\hat{p} - \hat{p}$  plane. Each region consists of states that, when taken as unperturbed states, lead to shocks with similar features as far as admissibility and phase-transition issues are concerned. (b) Magnification of the region enclosed in a box in part (a) of the figure. (The regions shown in this figure are obtained with  $\delta=0.01$ ).



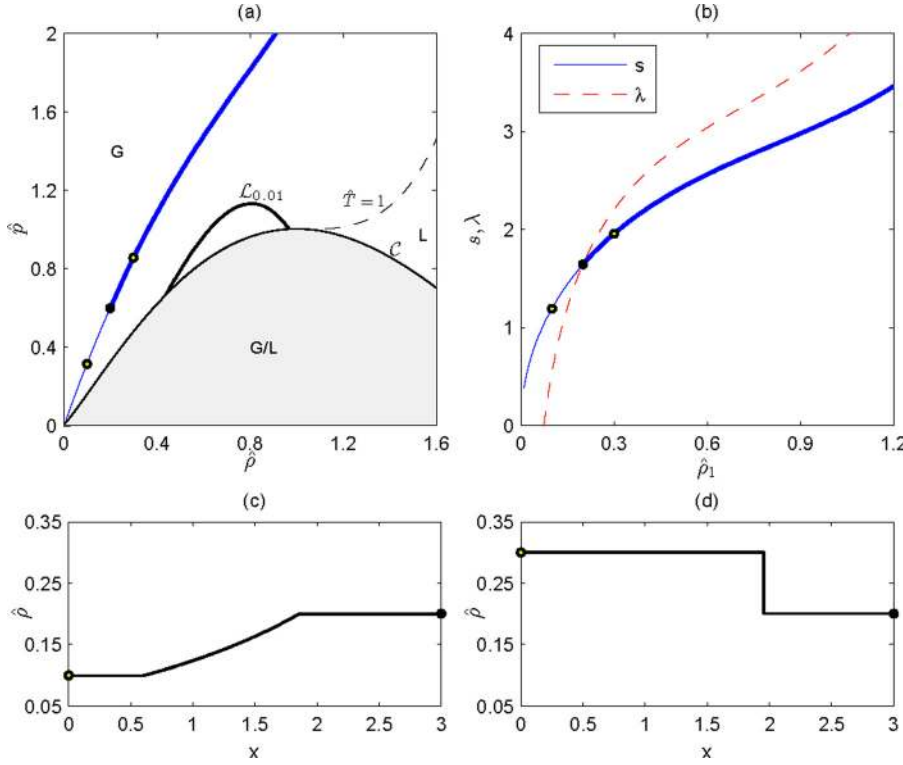


FIG. 5. (Color online) (a) Hugoniot locus  $\mathcal{H}(\hat{\mathbf{u}}_0)$  for an unperturbed state  $\hat{\mathbf{u}}_0 \in \mathbf{A}$  (thin/thick branches: inadmissible/admissible branches); (b)  $M_0$  and  $\lambda^*$  as functions of the parameter  $\xi \equiv \hat{\rho}_1$ ; (c) and (d): numerically calculated wave profiles related to the unperturbed state  $\hat{\mathbf{u}}_0$  (dark-faced dot) and perturbed states  $\hat{\mathbf{u}}_1$  (light-faced dots) highlighted on  $\mathcal{H}(\hat{\mathbf{u}}_0)$ .

where  $\hat{p}_C \equiv \hat{p}_C(\hat{\rho})$  is the reduced pressure as a function of the reduced density on the coexistence curve, obtained as explained in Sec. II.

A little bit trickier is the case of the curve  $\mathcal{L}_\delta^{**}$  separating the regions **A** and **B**<sub>2</sub>. The Hugoniot loci for the states belonging to the region **B**<sub>2</sub> have partially admissible negative branches, in contrast to the states of region **A** that have completely inadmissible negative branches of the Hugoniot loci. On the basis of the theory presented in Sec. V B, it may be shown that the curve  $\mathcal{L}_\delta^{**}$  is thus found as the locus of states  $\hat{\mathbf{u}}_0$  satisfying, for some  $\hat{\rho}$ , the following conditions:

$$s_{\mathcal{H}}(\hat{\rho}, \hat{\mathbf{u}}_0) = \lambda_{\mathcal{H}}(\hat{\rho}, \hat{\mathbf{u}}_0) = \lambda_0,$$

where  $s_{\mathcal{H}} \equiv s_{\mathcal{H}}(\hat{\rho}, \hat{\mathbf{u}}_0)$  and  $\lambda_{\mathcal{H}} \equiv \lambda_{\mathcal{H}}(\hat{\rho}, \hat{\mathbf{u}}_0)$  are, respectively, the shock velocity and the characteristic eigenvalue evaluated on the Hugoniot locus for  $\mathbf{u}_0$  and  $\lambda_0 \equiv \lambda_{\mathcal{H}}(\hat{\rho}_0, \hat{\mathbf{u}}_0)$ .

It is worth noting that the curve  $\mathcal{L}_\delta^{**}$  is the locus of the unperturbed states for which exactly one rarefaction shock wave is admissible. This curve was first obtained by Zamfirescu, Guardone, and Colonna<sup>11,12</sup> and, since the velocity of the unique admissible rarefaction shock obtainable for  $\hat{\mathbf{u}}_0 \in \mathcal{L}_\delta^{**}$  equals the sound velocity in both the unperturbed and perturbed states, this curve was named *double sonic locus* (DSL) by those authors (see also Ref. 48).

The details concerning the calculation of the curve  $\mathcal{C}_b$ , separating region **C** and region **C**<sub>tilde</sub>, are available, along with a discussion of the properties of the region **C**<sub>tilde</sub> in Ref. 47.

The curves  $\mathcal{L}_\delta^*$ ,  $\mathcal{C}^*$ ,  $\mathcal{L}_\delta^{**}$ , and  $\mathcal{C}_b$  are shown, for  $\delta = 0.01$ , in Fig. 4.

## 2. Case $\delta > \delta_{BZT}$ (non-BZT fluids)

In the second case to be discussed, i.e., when  $\delta > \delta_{BZT} \simeq 0.06$ , the local exceptionality curve,  $\mathcal{L}_\delta$ , is not

relevant, as seen in Sec. V C. This case corresponds to the case of *classical* (i.e., *non-BZT*) fluids, in which non-classical phenomena like rarefaction shocks do not come into play.

The regions **B**, **D**, and **E** previously discussed vanish as  $\delta \rightarrow \delta_{BZT}$  and it is seen that this case may still be described as the case of BZT fluids just letting  $\mathbf{B} \equiv \mathbf{D} \equiv \mathbf{E} \equiv \emptyset$  for  $\delta_{BZT} < \delta \leq \delta_{\mathcal{R}} \simeq 0.16$  or letting  $\mathbf{B} \equiv \mathbf{C} \equiv \mathbf{C}_{tilde} \equiv \mathbf{D} \equiv \mathbf{E} \equiv \emptyset$  for  $\delta > \delta_{\mathcal{R}}$ . That is, in the former case, phase-transition phenomena may still occur, even if the fluid is *classical* (in the sense of *non-BZT*). In the latter case, only the region **A** exists and therefore shock-induced phase transitions never occur.

The fluids exhibiting these two different behaviors are usually classified as *retrograde fluids* ( $\delta \leq \delta_{\mathcal{R}}$ ) and *regular fluids* ( $\delta > \delta_{\mathcal{R}}$ ). Retrograde fluids and their role in gas dynamics have been extensively studied in the past decades (see, for instance, Refs. 23 and 49) because of their capability of undergoing a phase transition as a consequence of an isoentropic process or an adiabatic shock compression.

## B. Numerical results

In order to check the results obtained by means of the theory of the hyperbolic systems previously discussed and to investigate the wave profiles in the case of inadmissible shocks, numerical calculations have been performed to solve the system (16) with the equations of state given in Sec. II in terms of adimensionalized quantities

$$\partial_t \hat{\mathbf{u}} + \partial_x \hat{\mathbf{F}}(\hat{\mathbf{u}}) = 0, \quad \hat{\mathbf{u}} \equiv \begin{pmatrix} \hat{\rho} \\ \hat{\rho} \hat{v} \\ \hat{E} \end{pmatrix}, \quad \hat{\mathbf{F}} \equiv \begin{pmatrix} \hat{\rho} \hat{v} \\ \hat{\rho} \hat{v}^2 + \hat{p} \\ (\hat{E} + \hat{p}) \hat{v} \end{pmatrix},$$

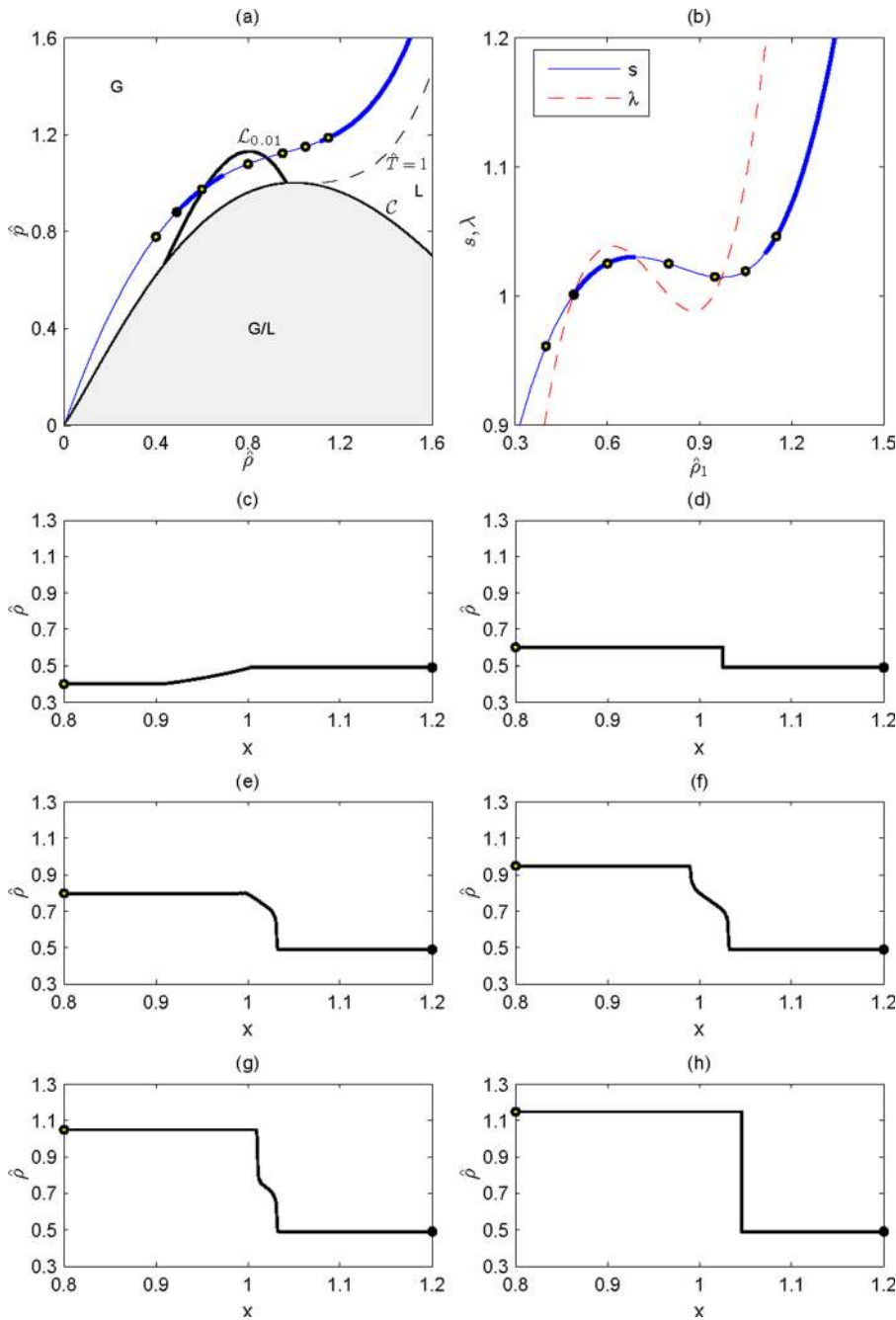


FIG. 6. (Color online) (a) Hugoniot locus  $\mathcal{H}(\hat{\mathbf{u}}_0)$  for an unperturbed state  $\hat{\mathbf{u}}_0 \in \mathbf{B}_1$  (thin/-thick branches: inadmissible/admissible branches); (b)  $M_0$  and  $\lambda^*$  as functions of the parameter  $\xi \equiv \hat{\rho}_1$ ; (c)–(h): numerically calculated wave profiles related to the unperturbed state  $\hat{\mathbf{u}}_0$  (dark-faced dot) and perturbed states  $\hat{\mathbf{u}}_1$  (light-faced dots) highlighted on  $\mathcal{H}(\hat{\mathbf{u}}_0)$ .

where  $\hat{x}$ ,  $\hat{t}$ , and  $\hat{v}$  are, respectively, dimensionless space, time, and velocity defined, after introducing a *characteristic length*,  $L$ , as

$$\hat{x} = \frac{x}{L}, \quad \hat{t} = \frac{t}{L\sqrt{\rho_{cr}/p_{cr}}}, \quad \hat{v} = \sqrt{\rho_{cr}/p_{cr}} v.$$

All the calculations have been carried out with a MATLAB/C++ general-purpose code, based on a central Runge-Kutta (CRK) scheme,<sup>50</sup> useful for the numerical solution of hyperbolic systems of balance and/or conservation laws elsewhere presented<sup>51</sup> and already used for the analysis of the interaction between shocks and acceleration waves in an ideal gas.<sup>52</sup>

The selection of the numerical results offered here includes six different set of results: for each of the five regions shown in Fig. 4, an unperturbed state  $\hat{\mathbf{u}}_0$  has been

selected and several perturbed states belonging to  $\mathcal{H}(\hat{\mathbf{u}}_0)$  have been chosen, with the aim of picking out interesting cases of admissible/inadmissible, compressive/rarefaction shocks. Finally, the last set of results concerns the case in which the unperturbed state  $\hat{\mathbf{u}}_0$  belongs to the local exceptionality curve,  $\mathcal{L}_\delta$ , leading to both admissible (or inadmissible) compressive, and rarefaction weak shocks, as discussed in Sec. V B. All the presented results are obtained, without any loss of generality, with  $\delta = 0.01$ .

Fig. 5 concerns the case of an unperturbed state  $\hat{\mathbf{u}}_0$  belonging to region A. The Hugoniot locus  $\mathcal{H}(\hat{\mathbf{u}}_0)$  is shown in Fig. 5(a); here, and in all the subsequent figures, the thin branch of the Hugoniot locus represents inadmissible shocks and the thick branch represents admissible shocks according to the Liu condition (see Sec. V A). We shall therefore call the thin and thick branches, respectively, *inadmissible* and

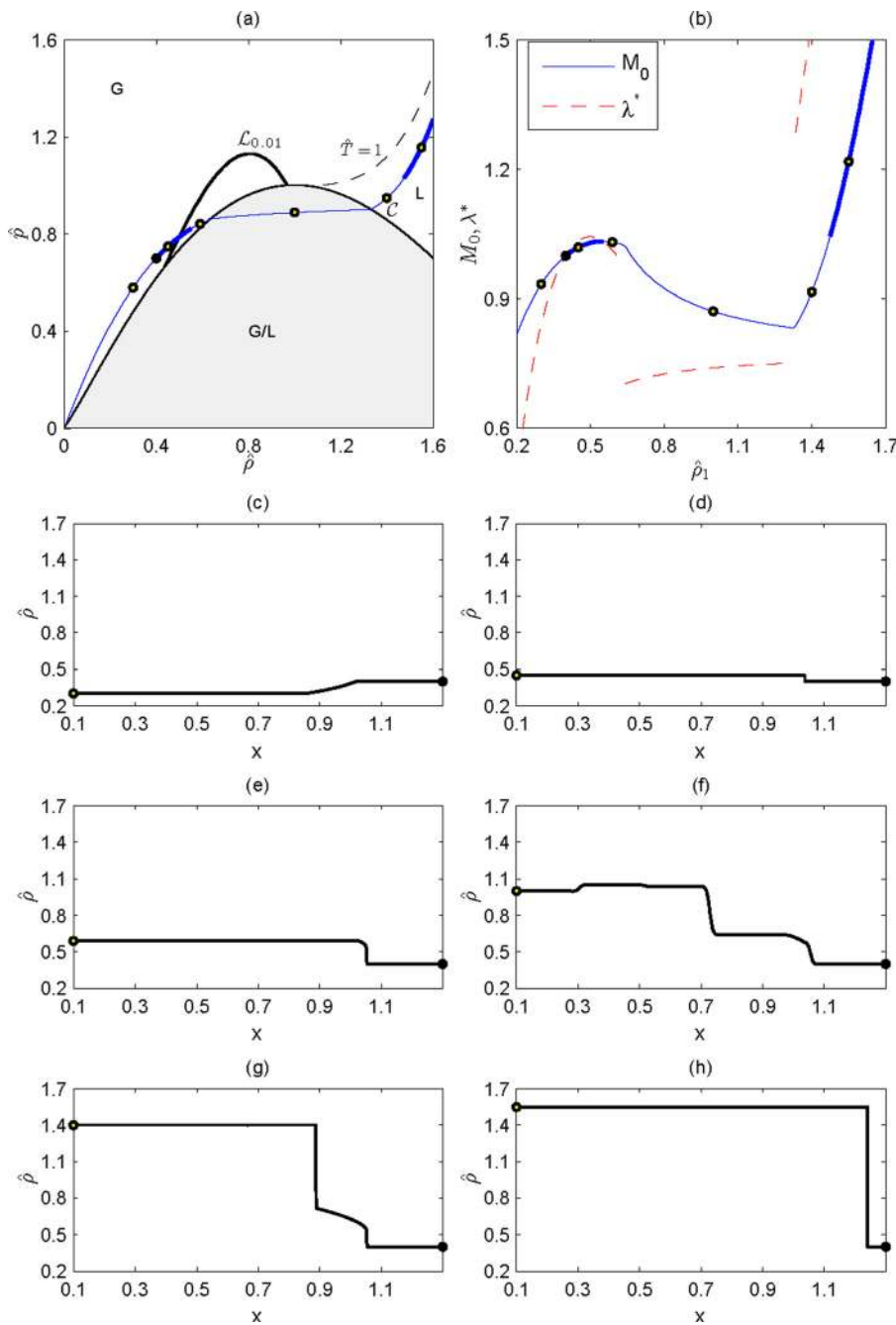


FIG. 7. (Color online) (a) Hugoniot locus  $\mathcal{H}(\hat{\mathbf{u}}_0)$  for an unperturbed state  $\hat{\mathbf{u}}_0 \in \mathbf{C}$  (thin/thick branches: inadmissible/admissible branches); (b)  $M_0$  and  $\lambda^*$  as functions of the parameter  $\xi \equiv \hat{\rho}_1$ ; (c)–(h): numerically calculated wave profiles related to the unperturbed state  $\hat{\mathbf{u}}_0$  (dark-faced dot) and perturbed states  $\hat{\mathbf{u}}_1$  (light-faced dots) highlighted on  $\mathcal{H}(\hat{\mathbf{u}}_0)$ .

*admissible branches*. In this figure, as well as in all the other figures, the dark-faced dot along  $\mathcal{H}(\hat{\mathbf{u}}_0)$  represents the chosen unperturbed state and the light-faced dots represent the perturbed states on  $\mathcal{H}(\hat{\mathbf{u}}_0)$  for which the wave profiles have been numerically calculated as the solution, at a given time  $t > 0$ , of the Riemann problem associated to the initial data

$$\hat{\mathbf{u}}(x, t = 0) = \begin{cases} \hat{\mathbf{u}}_1 & x < 0 \\ \hat{\mathbf{u}}_0 & x > 0 \end{cases} \quad \text{with } \hat{\mathbf{u}}_1 \in \mathcal{H}(\hat{\mathbf{u}}_0).$$

Since  $\hat{\mathbf{u}}_1$  belongs to the Hugoniot locus for  $\hat{\mathbf{u}}_0$ , the states  $\hat{\mathbf{u}}_1$  and  $\hat{\mathbf{u}}_0$  are connected through an (admissible or inadmissible) shock associated to the eigenvalue  $\lambda \equiv \lambda^{(3)}$ .

For the case of the unperturbed and perturbed states taken in region A, these profiles are shown in Figs. 5(c) and

5(d). The behavior of the unperturbed Mach number,  $M_0$ , and of a suitably adimensionalized characteristic velocity,  $\lambda^* = \lambda/c_0$ , as functions of the parameter  $\xi \equiv \hat{\rho}$  are shown in Fig. 5(b).<sup>54</sup> In this case, two perturbed states have been selected: one on the admissible branch and one on the inadmissible branch of the Hugoniot locus. As expected, the numerical results concerning the case of the inadmissible shock show the typical profile of a rarefaction wave, while in the other case the typical sharp profile of a stable shock is obtained.

In Fig. 6, the case of an unperturbed state  $\hat{\mathbf{u}}_0$  belonging to region B (in particular,  $\hat{\mathbf{u}}_0 \in \mathbf{B}_1$ ) is discussed. In this case, as expected, not the whole positive branch of the Hugoniot locus is admissible: this is clearly shown in Figs. 6(e)–6(g),

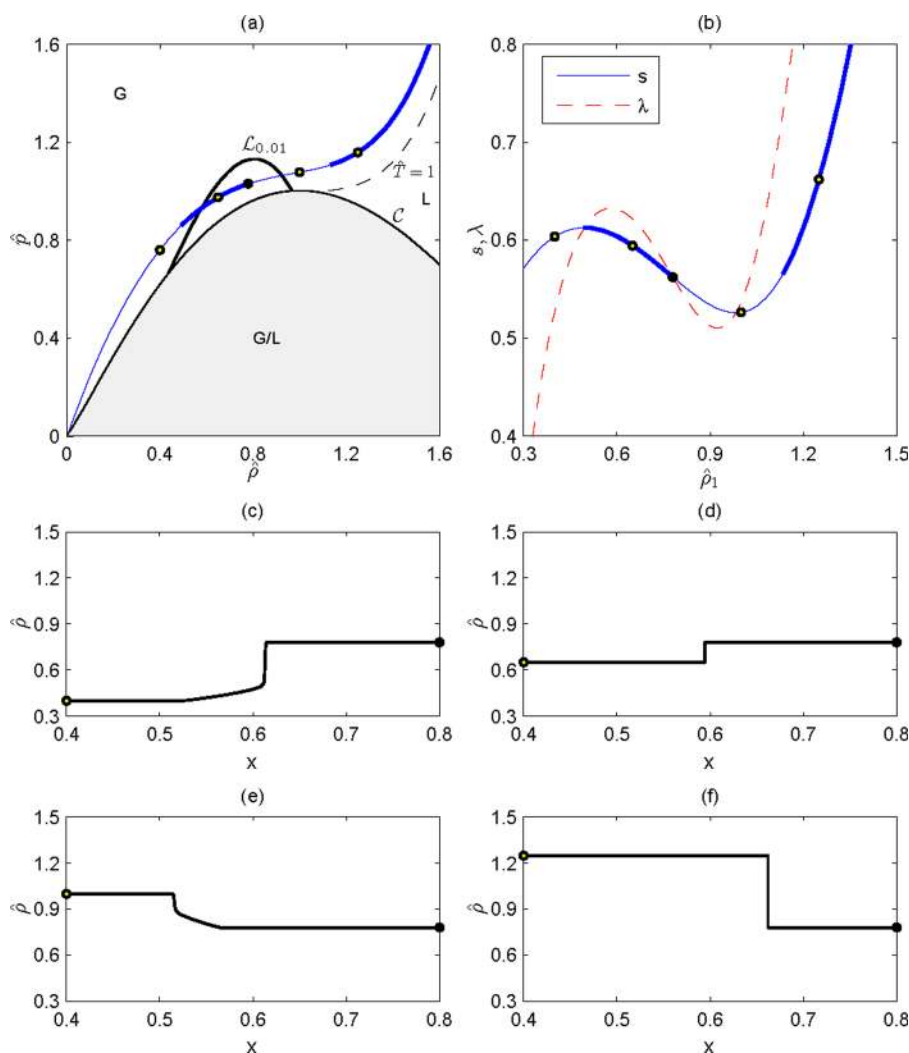


FIG. 8. (Color online) (a) Hugoniot locus  $\mathcal{H}(\hat{\mathbf{u}}_0)$  for an unperturbed state  $\hat{\mathbf{u}}_0 \in \mathbf{D}$  (thin/thick branches: inadmissible/admissible branches); (b)  $M_0$  and  $\lambda^*$  as functions of the parameter  $\xi \equiv \tilde{\rho}_1$ ; (c)–(f): numerically calculated wave profiles related to the unperturbed state  $\hat{\mathbf{u}}_0$  (dark-faced dot) and perturbed states  $\hat{\mathbf{u}}_1$  (light-faced dots) highlighted on  $\mathcal{H}(\hat{\mathbf{u}}_0)$ .

where the wave profiles for three inadmissible compression shocks are given. These profiles are interesting because, aside from confirming the inadmissibility of the shocks, they also show the so-called *shock splitting* phenomenon: the wave profiles numerically obtained as a solution of the Riemann problem are a composition of shocks, rarefaction waves and, possibly, constant states.

From Figs. 6(d)–6(h) it is also possible to appreciate that, in agreement with the theory, not all the compressive shocks are inadmissible: when the perturbed states are taken on the admissible branch of  $\mathcal{H}(\hat{\mathbf{u}}_0)$  (thick part of the Hugoniot locus in Fig. 6(a)), the numerically calculated wave profiles clearly show stable shocks. This set of results is completed by a rarefaction wave profile, shown in Fig. 6(c), obtained for an inadmissible rarefaction shock.

In contrast to what happens for regions A and B, when the unperturbed state  $\hat{\mathbf{u}}_0$  belongs to region C, the Hugoniot locus crosses the coexistence region. An example of such a case is shown in Fig. 7. Both gas/liquid and gas/coexistence shock-induced phase transitions (respectively,  $G \rightarrow L$  and  $G \rightarrow G/L$  shocks) may be allowed when  $\hat{\mathbf{u}}_0 \in \mathbf{C}$ . An example of a  $G \rightarrow L$  shock is presented in Fig. 7(h), while a stable shock with no phase transition (both the unperturbed and

perturbed state are in the gas phase) is shown in Fig. 7(d). The wave profile shown in Fig. 7(c) represents a rarefaction wave associated to an inadmissible rarefaction shock, while in Figs. 7(e)–7(g) shock-splitting phenomena associated to inadmissible compressive shocks are shown.

It is interesting to observe that, as already pointed out, shock-induced gas/liquid phase transitions are possible for non-weak shocks when the unperturbed state  $\hat{\mathbf{u}}_0$  belongs to region C. Nevertheless, the admissible branch of the Hugoniot locus  $\mathcal{H}(\hat{\mathbf{u}}_0)$  crosses the critical isotherm  $\hat{T} = 1$  (dashed curve in Fig. 7(a), which is conveniently regarded as the boundary between gas and liquid regions) when the parameter of the shock further increases, thus no phase transition occurs in the strong shock limit.<sup>55</sup> An explanation of such a behavior of real fluids may be found in the book by Landau and Lifshitz<sup>1</sup>, even if it is nowadays well-known (see Ref. 23) and the references cited therein) that the arguments by those authors are not always valid, since phase transitions induced by shock waves may exist in real fluids for *moderate shock*, i.e., not in the weak nor in the strong shock limits. (With this regard, an analysis of liquid/solid phase transitions induced by shock waves in a hard-sphere system may be found in Ref. 21).



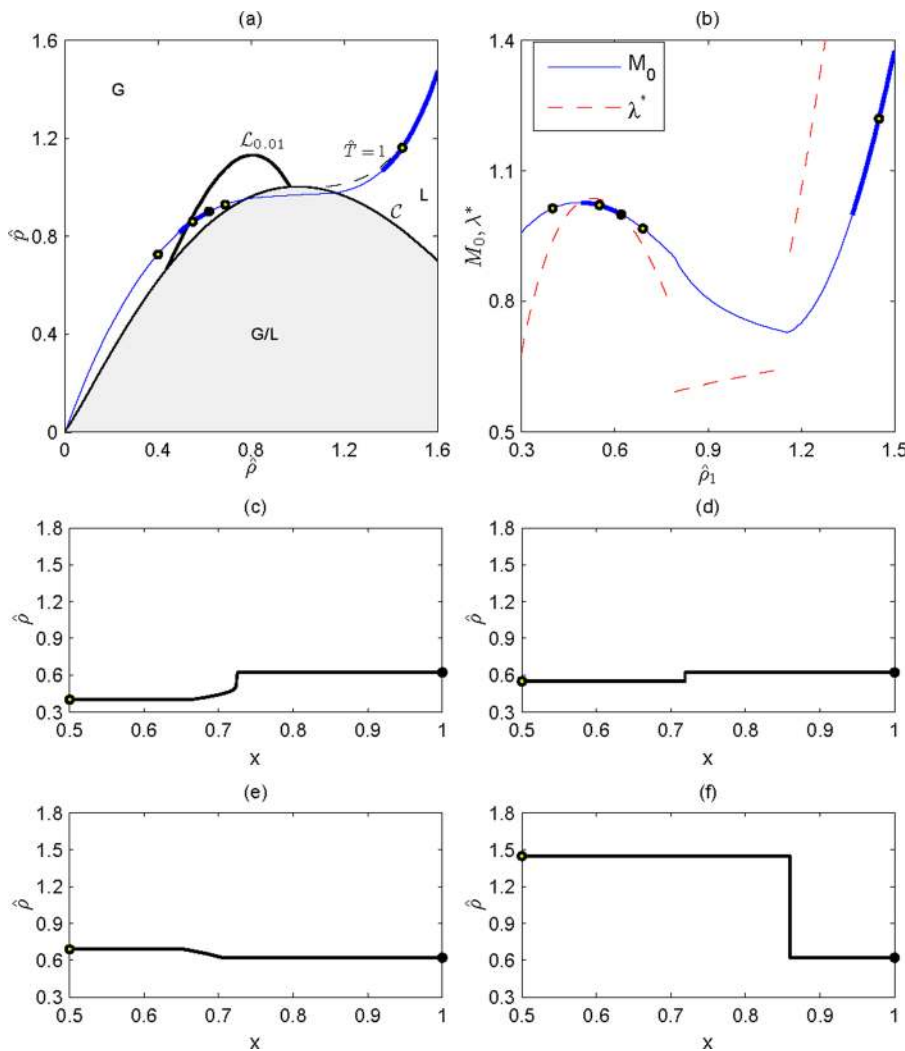


FIG. 9. (Color online) (a) Hugoniot locus  $\mathcal{H}(\hat{\mathbf{u}}_0)$  for an unperturbed state  $\mathbf{u}_0 \in \mathbf{E}$  (thin/thick branches: inadmissible/admissible branches); (b)  $M_0$  and  $\lambda^*$  as functions of the parameter  $\xi \equiv \hat{\rho}_1$ ; (c)–(f): numerically calculated wave profiles related to the unperturbed state  $\hat{\mathbf{u}}_0$  (dark-faced dot) and perturbed states  $\mathbf{u}_1$  (light-faced dots) highlighted on  $\mathcal{H}(\hat{\mathbf{u}}_0)$ .

It is worth mentioning that the discontinuities of the slope of the Hugoniot locus and of  $\lambda^*$  that may be appreciated in Figs. 7(a) and 7(b) (as well as in Figs. 9(a) and 9(b)), are due to the abrupt changes of the constitutive laws that take place on the  $\mathcal{C}$  curve.

In Fig. 8, the case of an unperturbed state lying in region **D** is presented. In agreement with the theory, this is the case in which both compressive and rarefaction shocks may be admissible or inadmissible. An example of each of these four possible cases is presented in Fig. 8, where the wave profiles obtained by means of the numerical calculations are in complete agreement with the expectations, as seen in Figs. 8(c)–8(f).

It is remarkable that, in contrast to what happens when the unperturbed state is taken in region **C** or in region **E**, when the unperturbed state belongs to region **A**, **B**, or **D**, no shock-induced phase transition may be allowed because the Hugoniot locus  $\mathcal{H}(\hat{\mathbf{u}}_0)$  never crosses the coexistence curve  $\mathcal{C}$  nor the critical isotherm  $\hat{T} = 1$  on the right (in the  $\hat{p}$ – $\hat{\rho}$  plane) of the critical point.<sup>56</sup>

The case analyzed in Fig. 9, concerning an unperturbed state belonging to region **E**, is similar to the previous one, except that the Hugoniot locus crosses, in this case, the coexistence curve. As a consequence, both  $G \rightarrow G/L$  and  $G \rightarrow L$

shocks may be allowed; an example of a gas/liquid shock-induced phase transition is given in Fig. 9(f). As it is seen in Fig. 9(a), the Hugoniot locus  $\mathcal{H}(\hat{\mathbf{u}}_0)$  crosses the critical isotherm  $\hat{T} = 1$  regarded, as explained in Sec. II, as the boundary between gas and liquid phases. This fact, which is not peculiar to the chosen state  $\hat{\mathbf{u}}_0$  but is, instead, common to all the unperturbed states belonging to region **C** and region **E**, means that—as already explained—no phase transition occurs in the strong shock limit.

In Figs. 10 and 11, two different cases of unperturbed states on the local exceptionality curve,  $\mathcal{L}_\delta$ , are finally shown. In the first of these two cases, all the shocks whose perturbed states are sufficiently close to the unperturbed state turn out to be inadmissible—as seen in Figs. 10(c) and 10(d)—and in the other case, the opposite situation is encountered, i.e., all the shocks whose perturbed states are sufficiently close to the unperturbed state are admissible (Figs. 11(c) and 11(d)). This is in complete agreement with the theoretical results explained in Sec. V B (see also Ref. 45).

## VII. CONCLUSIONS

Several outstanding phenomena related to shock propagation in real gases, including rarefaction shocks (also

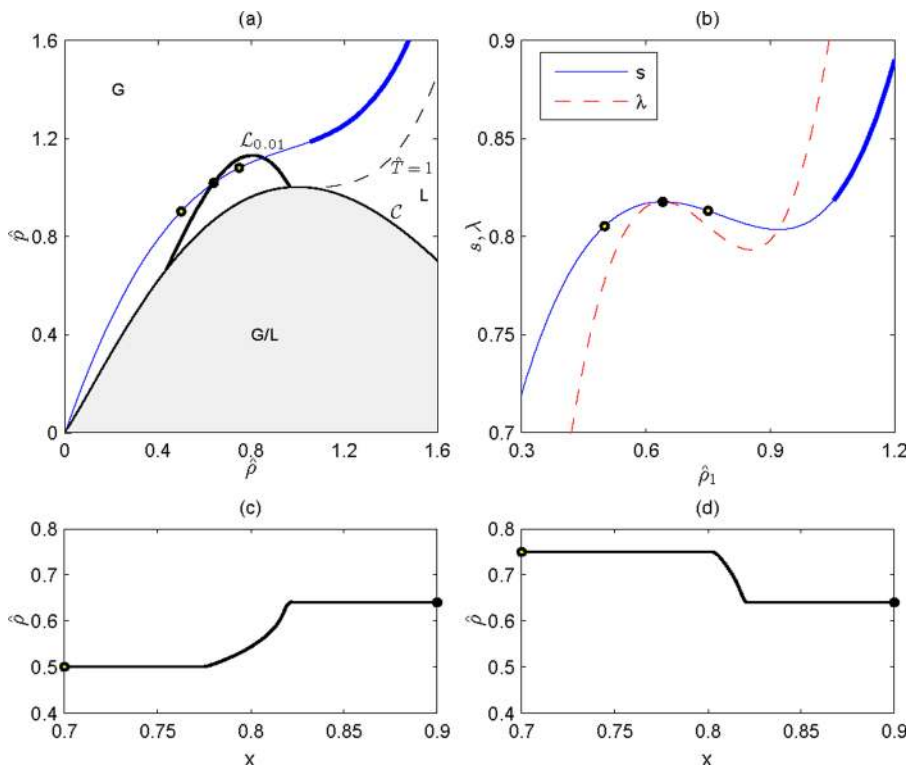


FIG. 10. (Color online) (a) Hugoniot locus  $\mathcal{H}(\hat{\mathbf{u}}_0)$  for an unperturbed state  $\hat{\mathbf{u}}_0 \in \mathcal{L}_{0,01}$  such that no weak shock is admissible (thin/thick branches: inadmissible/admissible branches); (b)  $M_0$  and  $\lambda^*$  as functions of the parameter  $\xi \equiv \hat{\rho}_1$ ; (c) and (d): numerically calculated wave profiles related to the unperturbed state  $\hat{\mathbf{u}}_0$  (dark-faced dot) and perturbed states  $\hat{\mathbf{u}}_1$  (light-faced dots) highlighted on  $\mathcal{H}(\hat{\mathbf{u}}_0)$ .

known as negative shocks), the so-called shock splitting phenomena, and shock-induced phase transitions are nowadays well-known and have been studied over the past decades by many authors, especially from the standpoint of theoretical gas dynamics, but a unified approach capable of giving account of all the above mentioned phenomena in the framework of the theory of hyperbolic system

was missing. This task has been accomplished by studying the features of shock propagation in a fluid modelled by means of the hyperbolic system of Euler equations with the van der Waals equations of state. This model, despite its simplicity, has turned out to be a suitable model capable of giving account of all the above-mentioned phenomena.

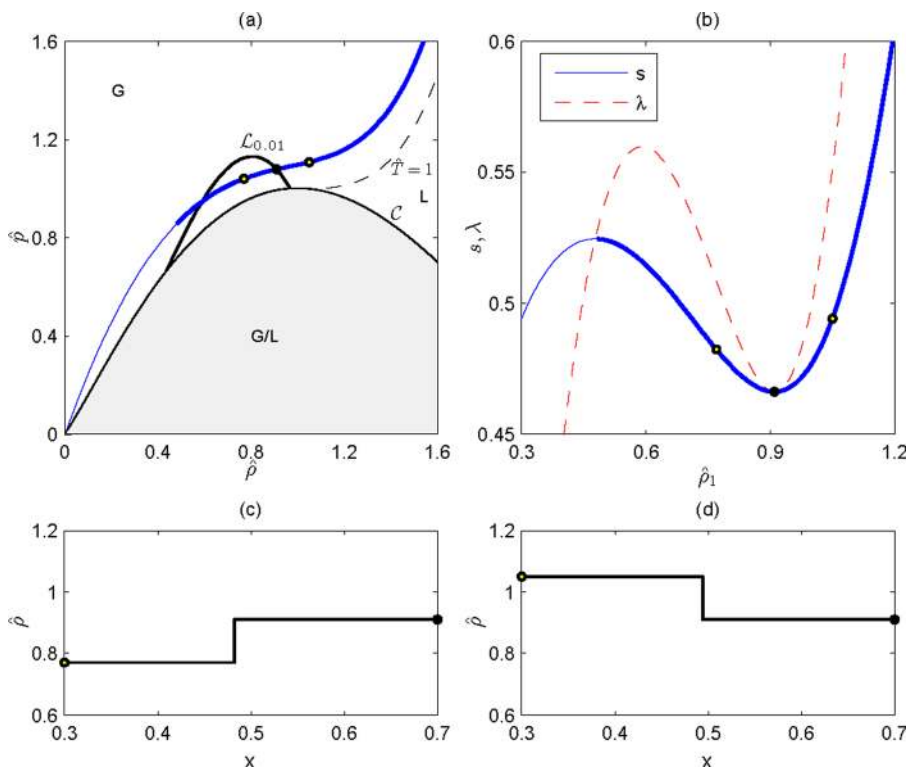


FIG. 11. (Color online) (a) Hugoniot locus  $\mathcal{H}(\hat{\mathbf{u}}_0)$  for an unperturbed state  $\hat{\mathbf{u}}_0 \in \mathcal{L}_{0,01}$  such that every weak shock is admissible (thin/thick branches: inadmissible/admissible branches); (b)  $M_0$  and  $\lambda^*$  as functions of the parameter  $\xi \equiv \hat{\rho}_1$ ; (c) and (d): wave profiles related to the unperturbed state  $\hat{\mathbf{u}}_0$  (dark-faced dot) and perturbed states  $\hat{\mathbf{u}}_1$  (light-faced dots) highlighted on  $\mathcal{H}(\hat{\mathbf{u}}_0)$ .

We have shown by means of the well-established theory of hyperbolic systems and by numerical calculations, how rarefaction shocks may propagate in the van der Waals fluid and how shock splitting phenomena—strictly related to the shock admissibility—take place in some circumstances. This target is accomplished by means of the understanding of the crucial role of the unperturbed state, i.e., the state before the shock wave. In particular, the gas region (in the  $\hat{p} - \hat{p}$  plane) has been subdivided into several regions, each of which contains states that, when taken as unperturbed states, lead to shock waves with similar features as far as shock admissibility is concerned. In particular, we have shown that, depending on where the unperturbed state is taken in the  $\hat{p} - \hat{p}$  plane, the following situations are possible: all and only the compressive shocks are admissible and no phase transition is allowed (i.e., the van der Waals fluid *qualitatively* behaves like an ideal gas as far as shock phenomena are concerned); all the compressive shocks are admissible and rarefaction ones may be admissible or inadmissible; all the rarefaction shocks are inadmissible and compressive ones may be admissible or inadmissible; both compressive and rarefaction shocks may be admissible or inadmissible.

Moreover, it was shown that—except for the first case—gas/coexistence and gas/liquid shock-induced phase transitions may occur for some unperturbed states.

All these results, obtained by applying the well-established theory of hyperbolic systems, have been confirmed by numerical calculations. The numerical approach was useful in testing the theoretical results and in obtaining the wave profiles in all those cases in which the shock is not stable and the wave profile is not directly provided by the theory, as in the cases in which shock-splitting phenomena occur.

## ACKNOWLEDGMENTS

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- <sup>53</sup>As usual in the literature of hyperbolic systems, we call *weak shock* a shock such that  $\xi \simeq \xi_0$  and *strong shock* a shock such that  $|\xi| \gg \xi_0$ , where  $\xi_0$  is the value of the parameter corresponding to the *null shock* ( $\mathbf{u}_1 \rightarrow \mathbf{u}_0$  when  $\xi \rightarrow \xi_0$ ). The *weak shock limit* and *strong shock limit* are obtained, respectively, when  $\xi \rightarrow \xi_0$  and  $|\xi| \rightarrow \infty$ .
- <sup>54</sup>Since, as explained in Sec. IV, we consider without any loss of generality  $v_0 = 0$ , the unperturbed Mach number is proportional to the shock velocity:  $M_0 = s/c_0$ . The quantities  $s$  and  $\lambda$  appearing in the selection rules given in Sec. V A are thus connected to the quantities  $M_0$  and  $\lambda^*$  through the same constant of proportionality.
- <sup>55</sup>This is easily seen considering that (see Eqs. (22) and (25)) the Hugoniot locus has the vertical asymptote  $\hat{p} = 3\hat{p}_0(\delta + 2)/(2\hat{p}_0 + 3\delta)$  which is, for any meaningful value of both  $\hat{p}_0$  and  $\delta$ , always *on the left*, in the  $\hat{p} - \hat{p}$  plane, of the asymptote  $\hat{p} = 3$  of the critical isotherm (see Eq. (8)<sub>2</sub>), thus guaranteeing that the states belonging to the Hugoniot locus are, at least in the strong shock limit, always in the gas phase.
- <sup>56</sup>This is proven considering that any Hugoniot locus  $\mathcal{H}(\hat{\mathbf{u}}_0)$  for  $\mathbf{u}_0 \in \{\mathbf{A}, \mathbf{B}, \mathbf{D}\}$  passes *above* the critical point, in the  $\hat{p} - \hat{p}$  plane, in accordance with the definition of the  $C^*$  curve. Since the (reduced) temperature is always increasing, along the Hugoniot locus, as the (reduced) density increases (see Eqs. (8) and (22)), it follows that the Hugoniot locus can never cross the critical isotherm *on the right* of the critical point.