News from the Chapman-Jouguet detonation front: A Velocity-Entropy Invariance theorem

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1. INTRODUCTION

The Chapman-Jouguet (CJ) model describes the detonation wave front as a fully reactive, planar and compressive discontinuity with a constant velocity supersonic relative to the initial state and sonic relative to the final burnt state. The CJ state and velocity can thus be calculated from the Rankine-Hugoniot (RH) relations, an equation of state for the detonation products, and the Gibbs chemical equilibrium constraints.

However, the detonation reaction zones of homogeneous explosives have a 3D cellular structure and are highly sensitive to losses. More broadly, fundamental studies of detonation today focus less on the CJ model than on identifying and modeling reaction and loss processes. These include cellular structure [1], high-pressure chemical kinetics [2, 3], adiabatic or non-adiabatic losses [4], turbulent mixing [5, 6], and, in rich explosives, carbon condensation [7]. They determine conditions for the existence of detonation, with debated combined contributions, and usually prevent the CJ equilibrium from being reached. Their prediction requires 3D modeling or numerical simulation with realistic chemical kinetics, which is beyond the physical capacity of the RH relations. Therefore, the CJ model is only an ideal limit useful to calibrate equations of state for detonation products at chemical equilibrium and to provide reference velocities and reaction-end states at no cost.

With these caveats in mind, the limited purpose of this work is to present two unnoticed properties of this staple of detonation modeling that are valid for explosives whose fresh and burnt states are single-phase inviscid fluids at thermal, mechanical and chemical equilibria. They may be useful to improve modeling and interpretation of experiments, i.e., to discuss whether the CJ equilibrium model can represent experimental or numerical data, not to indicate which assumptions would be incorrect, and perhaps to illustrate a more general property of horizons in hyperbolic systems.

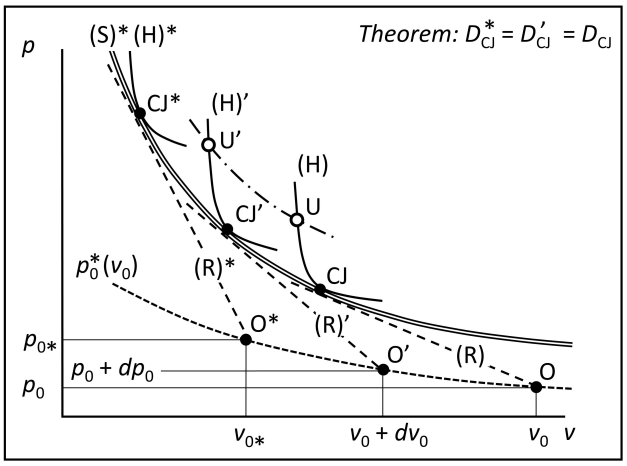

FIG. 1. An isentrope of detonation products (S)* is the common envelope of Hugoniot curves (H)*, (H)' and (H) and Rayleigh-Michelson (RM) lines (R)*, (R)' and (R) if their poles O*, O' and O lie on a particular $p_0^*(v_0)$ line through a reference initial state O*(p_{0*}, v_{0*}). The slopes of these RM lines, e.g., $-(D_{CJ}/v_0)^2$ for (R), increase with increasing initial volume v_0, but the invariance theorem ensures they have the same CJ velocity D^*_{CJ}.

Consider a series of experiments on a homogeneous explosive with the same uniform chemical composition, each conducted at different pairs of uniform initial pressures p_0 and temperatures T_0. The first property is that the CJ detonation velocity D_{CJ} and the CJ specific entropy s_{CJ} are invariant under the same dependence of T_0 on p_0, i.e., different pairs (p_0, T_0) that produce the same value of D_{CJ} produce different CJ states on the same isentrope (Fig. 1). The second derives from the first, and is a set of additional CJ relations, e.g., to calculate the CJ state – including the adiabatic exponent and the isentrope – only from the value of D_{CJ}, without information about the equation of state for the detonation products. Conversely, D_{CJ} can be obtained from any one of the CJ-state variables.

A broader description is given in [8].

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To the memory of Dr Michael Cowperthwaite

2. BASIC RELATIONS

2.1. Thermodynamic functions and differentials

A single-phase inviscid fluid with composition invariant or at chemical equilibrium obeys equations of state with 2 independent thermodynamic variables, e.g., temperature T and pressure p. Indeed, the minimization of the Gibbs free energy defines an equilibrium composition as a function of T and p [9]. The specific volume $v(T,p)$ is also a convenient variable because it appears explicitly in the equations of hydrodynamics. Specific enthalpy h and entropy s are state functions essential in this work, and their differentials write

$$dh(s,p) = Tds + vdp, \tag{1}$$

$$dh(p,v) = \frac{G+1}{G}vdp + \frac{c^2}{G}\frac{dv}{v}, \tag{2}$$

$$Tds(p,v) = \frac{vdp}{G} + \frac{c^2}{G}\frac{dv}{v}, \tag{3}$$

$$c^2 = Gv\left.\frac{\partial h}{\partial v}\right)_p = -v^2\left.\frac{\partial p}{\partial v}\right)_s, \tag{4}$$

$$G = \frac{v}{\left.\frac{\partial h}{\partial p}\right)_v - v} = -\frac{v}{T}\left.\frac{\partial T}{\partial v}\right)_s, \tag{5}$$

where G and c are the Gruneisen coefficient and the sound speed. In gases, ideal or not, the adiabatic exponent γ conveniently defines c by

$$c^2 = \gamma pv, \quad \gamma = -\frac{v}{p}\left.\frac{\partial p}{\partial v}\right)_s > 0. \tag{6}$$

2.2. What the theorem brings to the CJ state

The Rankine-Hugoniot (RH) relations,

$$\rho_0 D = \rho(D-u), \tag{7}$$

$$p_0 + \rho_0 D^2 = p + \rho(D-u)^2, \tag{8}$$

$$h_0 + \frac{1}{2}D^2 = h + \frac{1}{2}(D-u)^2, \tag{9}$$

express the continuity of the mass, momentum and energy fluxes across a hydrodynamic discontinuity, with D the front velocity, u the material speed in a laboratory-fixed frame, and the initial state (ahead of the front, index 0) assumed at rest ($u_0 = 0$). Even completed with an $h(p,v)$ equation of state, they do not form a closed system since there are 4 equations for the 5 variables v, p, h, u and D, hence a 1-variable solution, given an initial state (p_0, v_0) and $h_0(p_0, v_0)$, e.g., with D,

$$p, v, h, u, T, s, c, \gamma, \Gamma, G, \ ... \equiv \eta(D; v_0, p_0). \tag{10}$$

The CJ condition $D_{\rm CJ} = u_{\rm CJ} + c_{\rm CJ}$ closes the system (2), (7)-(9), so the 1-variable solution (10) then gives the CJ velocity $D_{\rm CJ}$ and variables $\eta_{\rm CJ} = (p, v, h, u, T, s, c, \gamma, \Gamma, G, ...)_{\rm CJ}$ as functions of the initial state,

$$D_{\rm CJ} = D_{\rm CJ}(v_0, p_0), \quad \eta_{\rm CJ} = \eta_{\rm CJ}(v_0, p_0). \tag{11}$$

Simple $h(p,v)$ equations of state give explicit relations, e.g., for the "perfect" gas (i.e., the ideal gas with an invariant adiabatic exponent $\bar\gamma$), $\gamma_{\rm CJ} = \bar\gamma$ and

$$D_{\rm CJ} = \widetilde{D}_{\rm CJ}\left(\frac{1}{2} + \widetilde{M}_{0\rm CJ}^{-2} + \frac{1}{2}\sqrt{1 + 4\widetilde{M}_{0\rm CJ}^{-2}}\right)^{\frac{1}{2}}, \tag{12}$$

$$\widetilde{D}_{\rm CJ}^2 = 2\left(\bar\gamma^2 - 1\right)Q_0, \quad \widetilde{M}_{0\rm CJ} = \widetilde{D}_{\rm CJ}/c_0, \tag{13}$$

with $Q_0 = h_0(T_0, p_0) - h(T_0, p_0)$ the heat of reaction.

Accurate CJ properties require thermochemical computer programs, e.g., NASA's CEA [9], which include detailed chemical equilibria and thermodynamic properties at high temperatures and pressures.

Combining (6), the mass and momentum balances (7), (8), and the CJ condition $D_{\rm CJ} = u_{\rm CJ} + c_{\rm CJ}$, the hydrodynamic variables $y = (p, v, u, c, h)$ at CJ points have a well-known 2-variable exact representation as functions of $D_{\rm CJ}$ ***and*** $\gamma_{\rm CJ}$,

$$y_{\rm CJ} = y_{\rm CJ}(D_{\rm CJ}, \gamma_{\rm CJ}; v_0, p_0), \tag{14}$$

i.e.,

$$\frac{v_{\rm CJ}}{v_0} = \frac{c_{\rm CJ}}{D_{\rm CJ}} = \frac{\gamma_{\rm CJ}}{\gamma_{\rm CJ}+1}\left(1 + \frac{p_0 v_0}{D_{\rm CJ}^2}\right), \tag{15}$$

$$\frac{v_0 p_{\rm CJ}}{D_{\rm CJ}^2} = \frac{1 + \frac{p_0 v_0}{D_{\rm CJ}^2}}{\gamma_{\rm CJ}+1}, \quad \frac{u_{\rm CJ}}{D_{\rm CJ}} = \frac{1 - \gamma_{\rm CJ}\frac{p_0 v_0}{D_{\rm CJ}^2}}{\gamma_{\rm CJ}+1}. \tag{16}$$

The energy balance (9) rewritten as $(h - h_0)/D^2 = (1 - (v/v_0)^2)/2$ then gives $h_{\rm CJ}$. A 0-variable representation (11) is obtained from a complete set that includes an explicit equation of state and a detailed chemical equilibrium composition, hence the 2-variable representation (14) since it does not use these two constraints.

The theorem (Sect. 3) does not use an equation of state explicitly, only implicitly, i.e., the general thermodynamic differentials (1)-(3). The consequence described in this abstract (Sect. 4) is a complement to the set (15)-(16), which yields an explicit 1-variable representation of the $y_{\rm CJ}$'s ***and*** $\gamma_{\rm CJ}$ as exact functions of $D_{\rm CJ}$,

$$y_{\rm CJ} = y_{\rm CJ}(D_{\rm CJ}; v_0, p_0), \ \gamma_{\rm CJ} = \gamma_{\rm CJ}(D_{\rm CJ}; v_0, p_0), \tag{17}$$

or, reciprocally, $D_{\rm CJ}$ as a function of any one of the CJ variable, for example, $D_{\rm CJ}(\gamma_{\rm CJ}; v_0, p_0)$. Other consequences are described in [8].

2.3. *Rankine-Hugoniot differentials*

The differentials of the RH relations (7)-(9, combined with that of the $h(p,v)$ equation of state (2), form the 3×3 linear system for dv, dp and dh

$$\frac{v_0 dp}{D^2}+\frac{dv}{v_0}=\frac{v_0 dp_0}{D^2}+(1-2z)\frac{dv_0}{v_0}+2z\frac{dD}{D}, \quad (18)$$

$$2\frac{dh}{D^2}-(2-z)\frac{v_0 dp}{D^2}-z\frac{dv}{v_0}= \ ...$$
$$... \ 2\frac{dh_0}{D^2}-(2-z)\frac{v_0 dp_0}{D^2}+z\frac{dv_0}{v_0}, \quad (19)$$

$$\frac{G}{1-z}\frac{dh}{D^2}-(G+1)\frac{v_0 dp}{D^2}-M^{-2}\frac{dv}{v_0}=0, \quad (20)$$

with M_0 and M the Mach numbers of the discontinuity relative to its initial and final states and z the dimensionless hydrodynamic variable defined by

$$M_0=\frac{D}{c_0}, \quad M=\frac{D-u}{c}, \quad z=1-\frac{v}{v_0}. \quad (21)$$

The differential ds of the specific entropy is obtained with $dh\,(s,p)$ (1) instead of $dh\,(p,v)$ (2),

$$\frac{Tds}{D^2}=z^2\frac{dD}{D}+\frac{dh_0}{D^2}+(1-z)\,z\frac{dv_0}{v_0}-(1-z)\frac{v_0 dp_0}{D^2}. \quad (22)$$

Therefore, consistently with (10), and using $dh_0(p_0,v_0)$ (2), the differentials ds, dv, dp and dh are linear combinations of dD, dv_0 and dp_0, for example,

$$\frac{Tds}{D^2}= \ z^2\frac{dD}{D}+a\frac{dv_0}{v_0}+b\frac{v_0 dp_0}{D^2}, \quad (23)$$

$$\frac{M^{-2}-1}{F/z}\frac{dv}{v_0}=-z^2\frac{dD}{D}+A\frac{dv_0}{v_0}+B\frac{v_0 dp_0}{D^2}, \quad (24)$$

where $$F=2-G\left(\frac{v_0}{v}-1\right), \quad (25)$$

$$a=z\,(1-z)+\frac{M_0^{-2}}{G_0}, \quad b=z+\frac{1}{G_0}, \quad (26)$$

$$A=\frac{z+\frac{2M_0^{-2}}{G_0}}{F}-a, \quad B=\frac{z+\frac{2}{G_0}}{F}-b. \quad (27)$$

The state functions c (4) and G (5) do not appear in $dh\,(s,p)$, so neither do M (21) and F 25) in ds.

The determinant of system (18)-(20) is M^2-1, and the right-hand side of (24) has to be set to zero for CJ discontinuities ($M=1$) so that dv, dp and dh are finite, hence the differentials of $s_{\rm CJ}(v_0,p_0)$ and $D_{\rm CJ}(v_0,p_0)$

$$T_{\rm CJ}\frac{ds_{\rm CJ}}{D_{\rm CJ}^2}=(A_{\rm CJ}+a_{\rm CJ})\frac{dv_0}{v_0}+(B_{\rm CJ}+b_{\rm CJ})\frac{v_0 dp_0}{D_{\rm CJ}^2}, \quad (28)$$

$$z_{\rm CJ}^2\frac{dD_{\rm CJ}}{D_{\rm CJ}}=A_{\rm CJ}\frac{dv_0}{v_0}+B_{\rm CJ}\frac{v_0 dp_0}{D^2}. \quad (29)$$

The CJ differentials (28) and (29) can be obtained directly from (18) and (19) by using $dh\,(s,p)$ (1), $dh_0(p_0,v_0)$ (2), $ds\,(p,v)$ (3), and the CJ condition $M=1$ in the form $c/v=D/v_0$ (7). In the acoustic sonic limit ($D\to c_0$, $v/v_0\to 1$, $z\to 0$, $F\to 2$), (22) and (28) reduce coherently to $dh_0\,(s_0,p_0)$ (1). This limit is irrelevant to this analysis.

At constant initial state (p_0,v_0), the differentials (23) and (24) of s and v give the partial derivatives along the same Hugoniot adiabatic curve (H) (Fig. 1), i.e., the relative variations induced by a change in the speed of a piston that would sustain the discontinuity (as $M<1<M_0$) from one experiment to another with the same initial state, e.g.,

$$\frac{v_0 T}{D^2}\left.\frac{\partial s}{\partial v}\right)_{p_0,v_0}=-\left(1-\frac{v}{v_0}\right)\frac{M^{-2}-1}{F}, \quad (30)$$

$$\frac{v_0}{D}\left.\frac{\partial D}{\partial v}\right)_{p_0,v_0}=-\left(1-\frac{v}{v_0}\right)^{-1}\frac{M^{-2}-1}{F}, \quad (31)$$

$$\frac{T}{D}\left.\frac{\partial s}{\partial D}\right)_{p_0,v_0}=\left(1-\frac{v}{v_0}\right)^2>0. \quad (32)$$

Subject to the constraint of a constant final-state variable, e.g., s or D, they give the relative variations induced by a change in the initial state from one experiment to another. The proof regards the self-sustained constraint $M=1$ as expressing the equivalence of the self-sustained detonation and the lower limit of the overdriven planar detonation.

3. PROOF

The physical premise is that final-state variations induced by initial-state variations, from one experiment to another, are finite, regardless of the constraint on that final state. Examples are the variations in the CJ state from one initial state to another or those of p and v along an isentrope (6). In contrast, variations at constant initial state, i.e., along the same Hugoniot, become infinite when approaching the CJ state ($M=1$), e.g., $\partial v/\partial D)_{v_0,p_0}$ (24), (31). That of entropy, $\partial s/\partial D)_{v_0,p_0}$, is unconditionally finite (23), (32).

It is convenient to distribute the initial states (v_0, p_0) on an arbitrary polar curve $p_0^*(v_0)$ through a reference point $\mathrm{O}^*(v_{0*}, p_{0*} = p_0^*(v_{0*}))$, (Fig. 1). Thus, final states subject to the same constraint lie on a (p-v) arc between a point U on a Hugoniot (H) with pole $\mathrm{O}(v_0, p_0 = p_0^*(v_0))$ and a point U' on another Hugoniot (H)' with pole O'$(v_0 + dv_0, p_0 + dp_0^*)$, both on $p_0^*(v_0)$.

The differentials of $s(D, v_0, p_0)$ (23) and $v(D, v_0, p_0)$ (24) reduce to differentials of $s^*(D, v_0) = s(D, v_0, p_0 = p_0^*(v_0))$ and $v^*(D, v_0) = v(D, v_0, p_0 = p_0^*(v_0))$. That gives the partial derivatives of v^*, s^* and D along final-state (p-v) arcs along which s^* or D is fixed

$$\frac{M^{-2}-1}{F/z}\left(\frac{\partial v^*}{\partial v_0}\right)_{s^*} = (A+a) + (B+b)\left(\frac{v_0}{D}\right)^2 \frac{dp_0^*}{dv_0}, \quad (33)$$

$$\frac{M^{-2}-1}{F/z}\left(\frac{\partial v^*}{\partial v_0}\right)_{D} = A + B\left(\frac{v_0}{D}\right)^2 \frac{dp_0^*}{dv_0}, \quad (34)$$

$$\frac{v_0 T}{D^2}\left(\frac{\partial s^*}{\partial v_0}\right)_{D} = -z^2 \frac{v_0}{D}\left(\frac{\partial D}{\partial v_0}\right)_{s^*} = a + b\left(\frac{v_0}{D}\right)^2 \frac{dp_0^*}{dv_0}, \quad (35)$$

$$\left(\frac{v_0}{D}\frac{\partial D}{\partial v_0}\right)_{s^*} = \frac{M^{-2}-1}{zF}\left(\left(\frac{\partial v^*}{\partial v_0}\right)_{D} - \left(\frac{\partial v^*}{\partial v_0}\right)_{s^*}\right). \quad (36)$$

The first equality in (35) can be directly obtained from (32) using the mathematical identity known as the triple product rule or Euler's chain rule

$$\left(\frac{\partial s^*}{\partial v_0}\right)_{D}\left(\frac{\partial v_0}{\partial D}\right)_{s^*}\left(\frac{\partial D}{\partial s^*}\right)_{v_0} = -1. \quad (37)$$

It shows that the partial derivatives, with respect to the initial state, of s^* at D fixed and of D at s^* fixed are proportional to each other. If one is zero, so is the other, since $\partial s^*/\partial D)_{v_0} \propto z^2$ is unconditionally finite (23), (32). The identity is valid for any $M \leqslant 1$ and any initial state. But it does not imply the equivalence of $ds = 0$ and $dD = 0$. In fact, relation (36) shows that it is only possible for final states continuously sonic ($M = 1$) – with $\partial v^*/\partial v_0)_D$ and $\partial v^*/\partial v_0)_{s^*}$ finite – which proves the theorem

$$\left(\frac{\partial s^*}{\partial v_0}\right)_{D}^{\mathrm{CJ}} = 0 \quad \Leftrightarrow \quad \left(\frac{\partial D}{\partial v_0}\right)_{s^*}^{\mathrm{CJ}} = 0, \quad (38)$$

$$\text{i.e.,} \quad ds_{\mathrm{CJ}} = 0 \quad \Leftrightarrow \quad dD_{\mathrm{CJ}} = 0. \quad (39)$$

Therefore, the same initial-state polar $p_0^*(v_0)$ produces final states with D_{CJ} and s_{CJ} constant. The relations (33) and (34), or (28) and (29), then give

$$-\left(\frac{v_0}{D_{\mathrm{CJ}}}\right)^2 \frac{dp_0^*}{dv_0} = \frac{A_{\mathrm{CJ}} + a_{\mathrm{CJ}}}{B_{\mathrm{CJ}} + b_{\mathrm{CJ}}} = \frac{A_{\mathrm{CJ}}}{B_{\mathrm{CJ}}}, \quad (40)$$

hence the additional constraint on the CJ state

$$A_{\mathrm{CJ}} b_{\mathrm{CJ}} - a_{\mathrm{CJ}} B_{\mathrm{CJ}} = 0, \quad (41)$$

or, with the notations in (21), (26) and (27),

$$G_0 z_{\mathrm{CJ}}^2 + 2 z_{\mathrm{CJ}} - \left(1 - M_{0\mathrm{CJ}}^{-2}\right) = 0. \quad (42)$$

The above proof by deduction demonstrates both the necessity and the uniqueness of the CJ condition for the theorem to hold. In fact, mathematics distinguishes between deduction and induction. It is correct to set the determinant of the system (28)-(29) to zero if $dD_{\mathrm{CJ}} = 0$ and $ds_{\mathrm{CJ}} = 0$ for the same $dp_0 \neq 0$ and the same $dv_0 \neq 0$, as the constraint (41) expresses it. But then there is no evidence that this is possible or that the theorem holds only for CJ states, hence the need for the above proof.

4. ADDITIONAL CJ PROPERTIES

The physical solution $z_{\mathrm{CJ}} > 0$ to the additional CJ constraint (42)

$$z_{\mathrm{CJ}} = \frac{\sqrt{1 + G_0\left(1 - M_{0\mathrm{CJ}}^{-2}\right)} - 1}{G_0}, \quad (43)$$

i.e.,

$$\gamma_{\mathrm{CJ}} = \frac{G_0 + 1 - \sqrt{1 + G_0\left(1 - M_{0\mathrm{CJ}}^{-2}\right)}}{\frac{p_0 v_0}{c_0^2} G_0 M_{0\mathrm{CJ}}^{-2} - 1 + \sqrt{1 + G_0\left(1 - M_{0\mathrm{CJ}}^{-2}\right)}}, \quad (44)$$

defines the one-variable (D_{CJ}) representation (17) of the CJ state and, reciprocally, the one-variable representation of D_{CJ} (Subsect. 2.2). The identity

$$G_0 = \frac{\alpha_0 c_0^2}{C_{p0}}, \ \alpha_0 = \frac{1}{v_0}\left(\frac{\partial v_0}{\partial T_0}\right)_{p_0}, \quad (45)$$

indicates that the necessary initial data are c_0, C_{p0}, and v_0 measured as a function of T_0 at constant p_0 so the coefficient of thermal expansion α_0 can be determined. For an ideal gas, c, C_p, α and γ are functions of T only, $G = \gamma - 1$ and $\alpha = 1/T$, hence,

$$\gamma_{\mathrm{CJ}} = \sqrt{\frac{\gamma_0}{1 - \frac{\gamma_0 - 1}{\gamma_0} M_{0\mathrm{CJ}}^{-2}}}, \quad \left(\frac{D_{\mathrm{CJ}}}{c_0}\right)^2 = \frac{1 - \gamma_0^{-1}}{1 - \frac{\gamma_0}{\gamma_{\mathrm{CJ}}^2}}. \quad (46)$$

The second relation in (46) shows a large sensitivity of D_{CJ} to γ_{CJ}. The strong-shock limits ($M_{0\mathrm{CJ}}^{-2} \ll 1$) of γ_{CJ} and D_{CJ}^2 are $\sqrt{\gamma_0}$ and $\left(1 + \sqrt{\gamma_0}\right) v_0 p_{\mathrm{CJ}}$, respectively. Their acoustic limits ($M_{0\mathrm{CJ}} \sim 1$) are γ_0 and c_0^2. The typical values $\gamma_0 = 1.3$, $c_0 = 330$ m/s and $D_{\mathrm{CJ}} = 2000$ m/s give $\gamma_{\mathrm{CJ}} = 1.144$, $\sqrt{\gamma_0} = 1.140$, with relative error $100 \times \left(\gamma_{\mathrm{CJ}}/\sqrt{\gamma_0} - 1\right) = 0.316$ %.

5. RESULTS FOR IDEAL GASES

The invariance theorem and the additional CJ properties were investigated using the NASA's CEA computer program for ideal detonation products [9] to avoid uncertain interpretations induced by more complex equations of state.

The theorem was discussed based on $I = 5$ pairs $(p_0,\, T_0)$, with p_0 determined by dichotomy for given T_0 to produce the same CJ entropy $s_{\rm CJ}$. The third pair ($T_0 = 298.15$ K, $p_0 = 1$ bar) was chosen as the reference initial state (v_{0*}, p_{0*}). The joint invariance of the CJ velocity $D_{\rm CJ}$ was analyzed using the mean values $\bar{D}_{\rm CJ}$, the relative deviations $\Delta D_{\rm CJ}/\bar{D}_{\rm CJ}$ in percent and their absolute means $m_{D_{\rm CJ}}$, and the standard deviations $\sigma_{D_{\rm CJ}}$,

$$\bar{D}_{\rm CJ} = \frac{1}{I}\sum_{i=1}^{I=5} D_{{\rm CJ}i}\ ,\ \left(\frac{\Delta D_{\rm CJ}}{\bar{D}_{\rm CJ}}\right)_i = 100 \times \frac{D_{{\rm CJ}i} - \bar{D}_{\rm CJ}}{\bar{D}_{\rm CJ}},$$

$$m_{D_{\rm CJ}} = \frac{1}{I}\sum_{i=1}^{I=5}\left|\frac{\Delta D_{\rm CJ}}{\bar{D}_{\rm CJ}}\right|_i,\ \sigma_{D_{\rm CJ}} = \sqrt{\frac{1}{I}\sum_{i=1}^{I=5}\left(D_{{\rm CJ}i} - \bar{D}_{\rm CJ}\right)^2}.$$

Tables 1 show the numerical values of $s_{\rm CJ}$ and $D_{\rm CJ}$ for the four stoichiometric mixtures $CH_4 + 2\,O_2$, $C_3H_8 + 5\,O_2$, $CH_4 + 2$ Air and $H_2 + 0.5$ Air. All values of $m_{D_{\rm CJ}}$ and $\sigma_{D_{\rm CJ}}$ are very small, and those of $D_{\rm CJ}$ are close to the mean $\bar{D}_{\rm CJ}$ to $\mathcal{O}\,(0.1)$ % at most. Table 2 shows the initial data for calculating the theoretical CJ properties $r_{\rm CJ}$=($\gamma_{\rm CJ}$, $\rho_{\rm CJ}$, $p_{\rm CJ}$) of the stoichiometric mixture $C_3H_8 + 5\,O_2$ from its numerical CJ velocities $D_{\rm CJ}$ using (46), (15) and (16). The comparison with the numerical values in Table 3 shows small relative differences $\epsilon_r = 100 \times (1 - r_{\rm CJ}^{THEO}/r_{\rm CJ}^{NUM})$, at most $\mathcal{O}\,(1)$ %.

The very small values of the larger deviations $\Delta D_{\rm CJ}/\bar{D}_{\rm CJ}$ at constant $s_{\rm CJ}$ are numerically and physically valid, and smaller than at constant p_0 or T_0. Their numerical significance was validated with a sensitivity analysis using variations at constant initial pressure or temperature and the numerical accuracy of CEA as a criterion. Similarly, the differences between the theoretical and the numerical values were shown not greater than those induced by the physical uncertainty in the initial thermochemical coefficients. Similar agreement was obtained for CH_4, C_2H_2, C_2H_4, C_2H_6, and H_2, e.g., $\epsilon_\gamma = -3.4$ % and $m_{D_{\rm CJ}} = 0.08$ % for $CH_4 + 2\,O_2$ at $T_0 = 298.15$ K and $p_0 = 1$ bar. For these ideal gases, numerical calculation thus supports the invariance theorem and its consequences for a wide range of initial condition [8].

TABLE 1. Joint invariances of the CJ entropy $s_{\rm CJ}$ and velocity $D_{\rm CJ}$: mean value $\bar{D}_{\rm CJ}$, relative deviation $\Delta D_{\rm CJ}/\bar{D}_{\rm CJ}$, mean relative deviation $m_{D_{\rm CJ}}$, corrected standard deviation $\sigma_{D_{\rm CJ}}$.

$CH_4 + 2\,O_2$		$m_{D_{\rm CJ}} = 0.08$ %		
$\bar{D}_{\rm CJ} = 2389.7$ m/s		$\sigma_{D_{\rm CJ}} = 2.21$ m/s		
T_0 (K)	p_0 (bar)	$s_{\rm CJ}$ (kJ/kg/K)	$D_{\rm CJ}$ (m/s)	$\frac{\Delta D_{\rm CJ}}{\bar{D}_{\rm CJ}}$ (%)
200.00	0.6284	*id.*	2392.9	0.13
250.00	0.8118	*id.*	2391.2	0.06
298.15*	1.0000*	12.6653*	2389.6	~ 0.00
350.00	1.2165	*id.*	2388.0	-0.07
400.00	1.4410	*id.*	2386.7	-0.12

$C_3H_8 + 5\,O_2$		$m_{D_{\rm CJ}} = 0.012$ %		
$\bar{D}_{\rm CJ} = 2356.7$ m/s		$\sigma_{D_{\rm CJ}} = 0.37$ m/s		
T_0 (K)	p_0 (bar)	$s_{\rm CJ}$ (kJ/kg/K)	$D_{\rm CJ}$ (m/s)	$\frac{\Delta D_{\rm CJ}}{\bar{D}_{\rm CJ}}$ (%)
200.00	0.6304	*id.*	2357.3	0.03
250.00	0.8127	*id.*	2356.7	~ 0.00
298.15*	1.0000*	11.9293*	2356.3	-0.01_5
350.00	1.2165	*id.*	2356.3	-0.01_5
400.00	1.4419	*id.*	2356.7	~ 0.00

$CH_4 + 2$ Air		$m_{D_{\rm CJ}} = 0.05$ %		
$\bar{D}_{\rm CJ} = 1799.9$ m/s		$\sigma_{D_{\rm CJ}} = 1.10$ m/s		
T_0 (K)	p_0 (bar)	$s_{\rm CJ}$ (kJ/kg/K)	$D_{\rm CJ}$ (m/s)	$\frac{\Delta D_{\rm CJ}}{\bar{D}_{\rm CJ}}$ (%)
200.00	0.6044	*id.*	1801.4	0.08
250.00	0.7968	*id.*	1800.7	0.05
298.15*	1.0000*	9.4218*	1799.9	~ 0.00
350.00	1.2401	*id.*	1799.1	-0.04
400.00	1.4949	*id.*	1798.3	-0.09

$H_2 + 0.5$ Air		$m_{D_{\rm CJ}} = 0.1$ %		
$\bar{D}_{\rm CJ} = 1964.7$ m/s		$\sigma_{D_{\rm CJ}} = 2.28$ m/s		
T_0 (K)	p_0 (bar)	$s_{\rm CJ}$ (kJ/kg/K)	$D_{\rm CJ}$ (m/s)	$\frac{\Delta D_{\rm CJ}}{\bar{D}_{\rm CJ}}$ (%)
200.00	0.6004	*id.*	1967.9	0.16
250.00	0.7941	*id.*	1966.4	0.08
298.15*	1.0000*	10.5927*	1964.8	~ 0.00
350.00	1.2444	*id.*	1963.1	-0.08
400.00	1.5042	*id.*	1961.5	-0.16

6. DISCUSSION AND CONCLUSIONS

These properties are not intended to replace thermochemical calculations with detailed equilibrium equations of state, e.g., [9]. This raises the question of the benefit over the standard method of measuring a pair of variables, for example, $p_{\rm CJ}$ and $D_{\rm CJ}$, to calibrate equations of state. Outside a possible formal academic

TABLE 2. Initial data for calculating the theoretical CJ state from the CJ velocity D_{CJ} for the stoichiometric mixture $C_3H_8 + 5\,O_2$ (Table 3, *THEO*).

		$C_3H_8 + 5\,O_2$ $W_0 = 34.015$ (g/mol)			
T_0 (K)	p_0 (bar)	γ_0	c_0 (m/s)	v_0 (m^3/kg)	D_{CJ} (m/s)
	0.2	*id.*	*id.*	2.4444	2306.7
200.	1	1.3286	254.9	0.4889	2377.6
	5	*id.*	*id.*	0.0978	2447.5
	0.2	*id.*	*id.*	3.6439	2284.6
298.15	1	1.2924	306.9	0.7288	2356.3
	5	*id.*	*id.*	0.1458	2427.6
	0.2	*id.*	*id.*	4.8887	2267.6
298.15	1	1.2563	350.5	0.9777	2340.1
	5	*id.*	*id.*	0.1956	2412.6

TABLE 3. Comparison of numerical (*NUM*) and theoretical (*THEO*) CJ properties (r_{CJ}) for the stoichiometric mixture $C_3H_8 + 5\,O_2$ (Table 2).

T_0	p_0	r_{CJ}	$C_3H_8 + 5\,O_2$		
(K)	(bar)		*NUM*	*THEO*	ϵ_r (%)
		γ_{CJ}	1.127	1.154	*-2.41*
	0.2	ρ_{CJ}/ρ_0	1.870	1.849	*1.14*
		p_{CJ}/p_0	51.635	50.966	*1.29*
		γ_{CJ}	1.136	1.154	*-1.60*
200.	1	ρ_{CJ}/ρ_0	1.865	1.850	*0.77*
		p_{CJ}/p_0	54.602	54.121	*0.88*
		γ_{CJ}	1.144	1.154	*-0.86*
	5	ρ_{CJ}/ρ_0	1.859	1.851	*0.43*
		p_{CJ}/p_0	57.612	57.325	*0.50*
		γ_{CJ}	1.125	1.139	*-1.23*
	0.2	ρ_{CJ}/ρ_0	1.863	1.852	*0.58*
		p_{CJ}/p_0	34.170	33.947	*0.65*
		γ_{CJ}	1.134	1.139	*-0.43*
298.15	1	ρ_{CJ}/ρ_0	1.857	1.854	*0.20*
		p_{CJ}/p_0	36.165	36.084	*0.23*
		γ_{CJ}	1.143	1.139	*0.34*
	5	ρ_{CJ}/ρ_0	1.852	1.855	*-0.16*
		p_{CJ}/p_0	38.204	38.273	*-0.18*
		γ_{CJ}	1.124	1.124^-	*-0.04*
	0.2	ρ_{CJ}/ρ_0	1.855	1.855	*-0.00*
		p_{CJ}/p_0	25.232	25.233	*-0.00*
		γ_{CJ}	1.133	1.123	*0.85*
400.	1	ρ_{CJ}/ρ_0	1.850	1.857	*-0.39*
		p_{CJ}/p_0	26.726	26.843	*-0.44*
		γ_{CJ}	1.142	1.123	*1.62*
	5	ρ_{CJ}/ρ_0	1.845	1.859	*-0.76*
		p_{CJ}/p_0	28.262	28.505	*-0.86*

contribution, the benefit is a semi-empirical criterion for discussing whether the measured pair represents the CJ equilibrium state and, therefore, the single-phase inviscid fluid hypothesis used in this work to define that state.

The proof of the theorem involves the 2-variable differentials (1)-(3) applied to the initial and final states, with constant initial composition. This excludes frozen final equilibria since T_{CJ}, p_{CJ} and, therefore, the final composition should vary with T_0 and p_0. Thus, the theorem holds only for CJ equilibrium detonations.

The physical premise is that no initial variation induces an infinite CJ-state variation. That is an analog in the thermodynamic plane to the transonic condition in the physical space [4],[10].

The Rankine-Hugoniot relations (7)-(9) link piecewise continuous solutions allowed by the Euler equations for inviscid fluids. The closed hyperbolic system these equations form with relevant equations of state requires data distributed on a non-characteristic, i.e., "non-sonic", surface to define a well-posed Cauchy problem. The CJ detonation is a characteristic surface. In fact, the CJ locus is the sound-like separatrix between the time-like Taylor-Zel'dovich-Döring expansion, where $u+c \leqslant D_{CJ}$, and the space-like Zel'dovich-von Neuman-Döring reaction zone, where $u+c \geqslant D_{CJ}$, i.e., an event horizon in the TZD expansion for an observer in the ZND reaction zone, and vice versa. The theorem indicates that using entropy helps obtain additional CJ properties without an equation of state, perhaps illustrating a more general property of horizons in hyperbolic systems.

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