Resolving the Entropy Minimum Paradox of the Chapman-Jouguet Theory of Detonation

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27 April 2025

Abstract

Detonation waves and their properties have been a source of interest for physicists for over 150 years. In 1899, David Chapman constructed a theoretical model of one-dimensional detonation waves, which would later be independently developed by Émile Jouguet in 1905. The simple one-dimensional theory, known as the Chapman-Jouguet (CJ) theory of detonation, was massively successful in its predictions. However, in 1935, R.L. Scorah published a paper that acknowledged the success of CJ theory, but argued that the CJ solution represented an entropy minimum, which would violate the second law of thermodynamics given the adiabatic and spontaneous nature of detonation waves. Later theoretical approaches, such as the Zeldovich, von Neumann, and Döring (ZND) model of the 1940s and Wood-Kirkwood theory of the 1950s proved to be successful models of more sophisticated systems, but researchers using these methods would seemingly abandon the idea of using maximum entropy arguments in favor of numerical solutions to combined hydrodynamics and chemical rate equations. These early numerical methods formed the foundation for modern-day simulation of explosives using state-of-the-art hydrodynamic codes. In this paper, we show that Scorah made a mistake in his thermodynamic analysis by inadvertently allowing heat to transfer between the system and the surroundings. We have devised an iterative approach that avoids Scorah's mistake, and implement it in the context of an illustrative example that extends the parameter space to include a chemical reaction coordinate, showing that maximization of entropy does indeed connect initial and final state variables. Thus it is unnecessary to develop equations of state for matter under high pressures and temperatures for the purposes of numerical integration across the detonation wave, saving computational resources directed towards understanding detonation, whether applied to workplace safety, conventional explosives, or astronomical events, such as supernovae.

Acknowledgments

I would like to thank Professor David Dunlap for his immense support in this project and in my development as a physics student. I would also like to thank the Rayburn Reaching Up fund for their support.

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Chapter 1

The Study of Detonation

1.1 Introduction

The study of detonation waves and their propagation through fluids has long been of interest to physicists and chemists. A detonation wave is described as a shock wave that is self-sustained through an exothermic chemical reaction and is initiated by the compressive heating of an unstable mixture. During the early years of detonation theory's development, detonation waves were relevant for their applications to quickly developing weaponry and for describing hazards observed in industrial settings, tragically seen in the Great Mills Disaster in Minneapolis, MN, in 1878, where an ignition of flour dust in the Washburn A flour mill caused it to explode. Among the first measurements of detonation waves, and indeed the most important, came from French scientists M. Berthelot and P. Vieille of L'École Polytechnique in 1883 [1]. Berthelot and Vieille measured the detonation velocities of various explosive gas mixtures, and in the same year, two other Frenchmen, E. Mallard and H. Le Châtlier would be the first to argue that detonation waves are initiated by an adiabatic compression, raising the temperature of the explosive mixture enough to initiate a chemical reaction [7]. These findings would inspire researchers to investigate the theory of detonations, trying to predict the velocity of a detonation wave. In 1899, D. L. Chapman was successful in creating such a model for one-dimensional detonation waves in a gas mixture, which would be independently formulated by E. Jouguet in 1905. Both Chapman and Jouguet used fluid mechanics arguments of continuity, energy conservation, and momentum conservation to connect the initial and final states of a gas before and after the passing of a detonation wave in order to predict the velocity and the final pressure and density. This solution, known as the Chapman-Jouguet, or CJ, solution, proved massively successful in its predictions, coming within 2% of measured values for different gas mixtures [4]. The only weak point of the theory was that it relied on an assumption, made my Chapman, that a detonation wave will travel at the minimum possible velocity that obeys all of the conservation conditions. Jouguet strengthened the theory by determining the same velocity through a condition on the local sound speed in the final state. In 1935, R.L. Scorah published a paper that acknowledged the great success of the CJ theory and attempted to determine the velocity through maximization of entropy. In his analysis, Scorah found that the CJ solution represents a minimum in entropy of the final state. Detonation waves are spontaneous and adiabatic, and

Scorah's analysis suggested that the CJ solution violates the second law of thermodynamics [3]. This apparent violation is called the *entropy minimum paradox*. The implications of Scorah's findings would cause later researchers to abandon the use of maximum entropy as a method of determining the final state, instead opting for numerical methods.

1.2 The Chapman-Jouguet Theory of Detonation

The Chapman-Jouguet theory of detonation describes a stationary detonation wave traveling in an ideal gas mixture in one dimension.

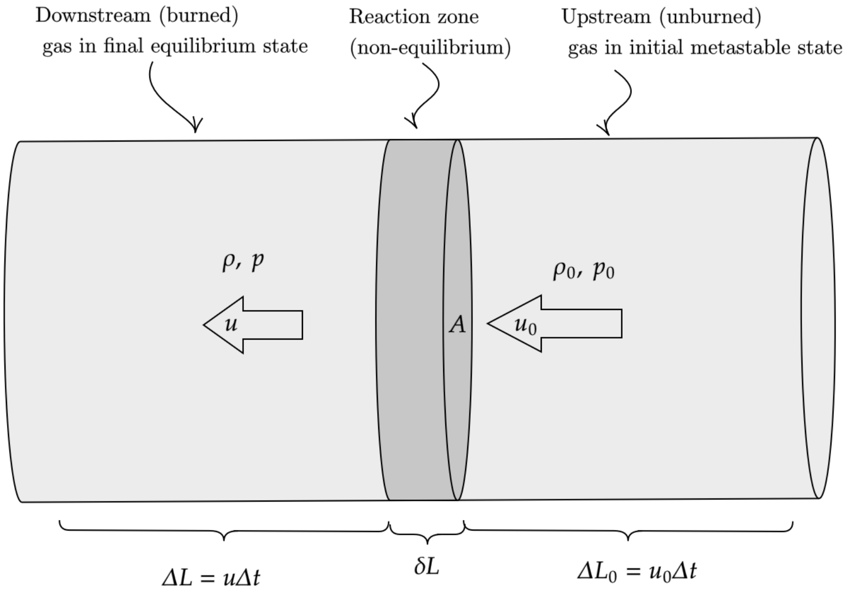

Figure 1.1: A sketch of a one-dimensional detonation wave shows a finite reaction zone propagating through a fluid at a constant velocity u_0. The detonation wave is sustained through a chemical reaction, with the reactants in front and the products behind. In the traveling frame of reference, the unburned reactants flow in and the burned products flow out.

A diagram is shown in Figure 1.1. The propagating shock wave is followed by a non-equilibrium region in which the chemical reaction takes place. This finite layer propagates through the mixture at a velocity u_0. The CJ theory treats this as a fluid flow problem, viewing the problem from the traveling frame. This type of analysis works to connect the initial and final equilibrium states. This requires that ones looks sufficiently far away from the non-equilibrium reaction zone, both in front and behind.

In the traveling frame of reference, the unreacted mixture of chemicals in a metastable state upstream approaches the shock front at velocity u_0 and has a pressure p_0 and density ρ_0. The reacted mixture downstream retreats from the front at a velocity u and a pressure p

and density ρ. The difference $u_0 - u$ is the speed of the *post-shock wind*, as observed by the stationary frame of reference. For a stationary wave in one-dimension, one can consider the change of state of a parcel of gas (the system) of an initial length $\Delta L_0 = u_0 \Delta t$ upstream, undergoing compression as it passes through the reaction zone, and taking on a new length $\Delta L = u\Delta t$, now downstream. By taking the time interval Δt to be arbitrarily long, we are assured that initial and final states are sufficiently far away from the detonation zone as to be unperturbed, and thus in thermodynamic equilibrium. Furthermore, since the thermal diffusion propagates as $\sqrt{\Delta t}$, in the limit where Δt is large, any heat diffusion through the boundaries in a time Δt will be negligible as compared with the size of the system. This illustrates why, in one dimension, this process can always be considered adiabatic. Applying mass continuity, the mass Δm entering the reaction zone in time Δt is equal to the mass exiting the reaction zone in time Δt,

$$\Delta m = \rho(u\Delta t A) = \rho_0(u_0 \Delta t A). \tag{1.1}$$

Here A is the cross-sectional area of the reaction zone, which is taken to be infinite in the one-dimensional case. The product $u\Delta t A$ is the flow volume. Canceling $A\Delta t$ on both sides gives the continuity equation

$$u\rho = u_0\rho_0. \tag{1.2}$$

Applying the impulse-momentum theorem to the mass as it crosses the reaction zone,

$$\Delta m(u - u_0) = F\Delta t, \tag{1.3}$$

and substituting Eq.(1.1) for Δm and $A(p_0 - p)$ for the (constant) force F, gives

$$\rho u^2 - \rho_0 u_0^2 = p_0 - p, \tag{1.4}$$

where we have again divided by $A\Delta t$ on both sides. The final relation in constructing the CJ model expresses conservation of energy for an adiabatic process. For simplicity, it was assumed that the chemical reactions that sustain a detonation wave are exothermic reactions that release some fixed amount of heat per kilogram $\bar{Q}$. For an ideal gas, the internal energy density is given by $\frac{p}{\rho(\gamma-1)}$, where γ is the adiabatic exponent. The work-energy theorem provides a relation between the change in kinetic energy of the flow plus the change in internal energy of the gas to the work done on the gas by the two constant forces, $p_0 A \Delta L_0$ upstream and $-pA\Delta L$ downstream,

$$\begin{aligned}(\frac{1}{2}(\rho A u \Delta t)u^2) + (\rho A u \Delta t)\frac{p}{\rho(\gamma-1)}) - (\frac{1}{2}(\rho_0 A u_0 \Delta t)u_0^2) + (\rho_0 A u_0 \Delta t)\frac{p_0}{\rho_0(\gamma-1)} + (\rho_0 A u_0 \Delta t)\bar{Q}) \\ = \Delta L_0 p_0 A - \Delta L p A. \end{aligned} \tag{1.5}$$

Here we have assumed, for simplicity, that γ is the same for the products and the reactants. Substituting $\Delta L = u\Delta t$ and $\Delta L_0 = u_0 \Delta t$ and canceling $A\Delta t$ gives the standard Bernoulli equation,

$$(\frac{1}{2}\rho u^3 + \frac{1}{\gamma - 1}pu) - (\frac{1}{2}\rho_0 u_0^3 + \frac{1}{\gamma - 1}p_0 u_0 + \rho_0 u_0 \bar{Q}) = p_0 u_0 - pu. \tag{1.6}$$

In what follows, it is convenient to express our variables as dimensionless quantities, namely: the relative density,

$$x := \frac{\rho_0}{\rho}; \tag{1.7}$$

the relative pressure,

$$y := \frac{p}{p_0}; \tag{1.8}$$

the relative temperature, which for an ideal gas is

$$t := \frac{T}{T_0} = xy; \tag{1.9}$$

the dimensionless speed of the detonation wave,

$$\eta := \sqrt{\frac{\rho_0}{p_0}}u_0; \tag{1.10}$$

and the dimensionless heat of reaction,

$$q := \frac{\bar{Q}\rho_0}{p_0}. \tag{1.11}$$

Combining Eq.(1.2) and Eq.(1.4) to eliminate u gives the well-known *Rayleigh line*,

$$y = 1 - \eta^2(x - 1) := y_{_R}, \tag{1.12}$$

a relation between the pressure and volume of the final states with a slope proportional to the square of the velocity, which we will subsequently refer to with a subscript R.
Combining Eq.(1.2) and Eq.(1.6) gives the dimensionless form of the Bernoulli equation,

$$\frac{\gamma}{\gamma - 1}(t - 1) - q = -(x - 1) + \frac{\eta^2}{2}(x - 1)^2, \tag{1.13}$$

where here we have put the internal energy of the gas on the left and the change in flow kinetic energy on the right, together with the constant-pressure work performed by the surroundings while pushing the parcel of gas through the detonation wave. Substituting the ideal gas law $t = xy$ and using Eq.(1.12) to write $\eta^2 = \frac{y-1}{1-x}$, one can express the constraint for energy conservation independent of the velocity of the detonation wave,

$$y = \frac{2q + \frac{\gamma+1}{\gamma-1} - x}{\frac{\gamma+1}{\gamma-1}x - 1} := y_{_H}. \tag{1.14}$$

This relation between final state pressure and volume is known as the *Hugoniot*, which we will subsequently refer to with a subscript H.

The final state of the system is determined by the intersection of the Rayleigh line and the Hugoniot for a given value of η, shown in Figure 1.2.

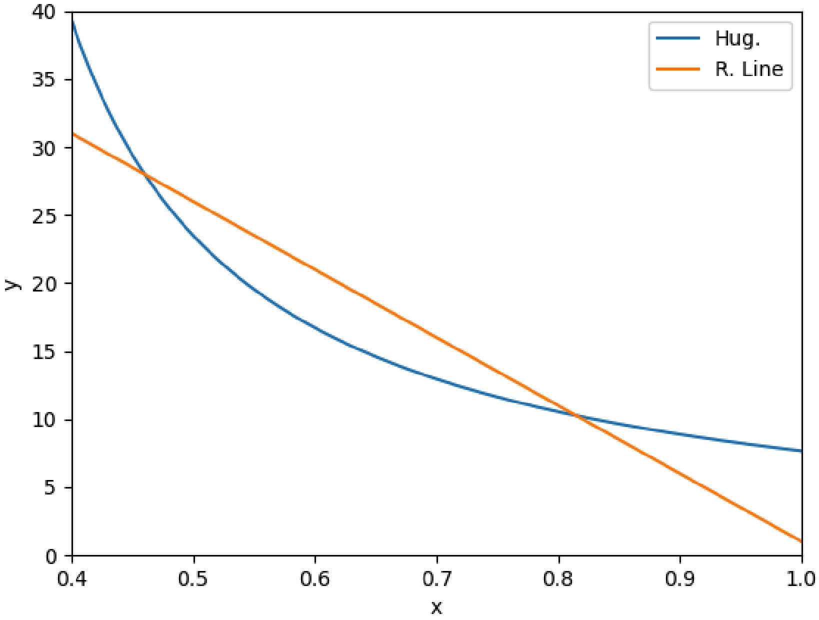

Figure 1.2: Rayleigh line (orange) and Hugoniot (blue) intersections. Here we use $\gamma = \frac{5}{3}$ for a monoatomic gas, $q = 10$, and $\eta = 7$. In general, the Rayleigh line will intersect the Hugoniot at two points.

There is ambiguity in this as there are two different intersections and thus two different possible solutions. Furthermore, there is no specified velocity η. Chapman noticed that this ambiguity is removed under the assumption that the detonation wave will travel at its lowest possible velocity [2], corresponding to the case in which the Rayleigh line is tangent to the Hugoniot. By simultaneously solving for the Rayleigh line and Hugoniot intersection and the equivalence of their derivatives, one can determine the final pressure $y_{_{CJ}}$, volume $x_{_{CJ}}$, and velocity $\eta_{_{CJ}}$:

$$x_{_{CJ}} = \frac{\gamma(1+\eta_{_{CJ}}^2)}{\eta_{_{CJ}}^2(1+\gamma)}, \tag{1.15}$$

and

$$y_{_{CJ}} = \frac{1+\eta_{_{CJ}}^2}{1+\gamma}, \tag{1.16}$$

where

$$\eta_{_{CJ}} = \sqrt{\gamma + q(\gamma^2-1) + \sqrt{q(\gamma^2-1)(q(\gamma^2-1)+2\gamma)}}. \tag{1.17}$$

Jouguet arrived at the same result through a stationarity argument. Jouguet argued that in order for a detonation wave to be stationary as it propagates through the fluid, the post-shock wind traveling at $u_0 - u$ in the lab frame, plus the local speed of sound c_s at the end of the reaction zone, must keep up with the detonation front traveling at speed u_0 [5],

$$(u_0 - u) + c_s = u_0, \tag{1.18}$$

yielding

$$c_s = u = u_0 x. \tag{1.19}$$

Only then will any long-wavelength Fourier components describing modulation in density in the tail end of the reaction zone keep up with the wave front. The Newton-Laplace expression for the speed of sound [10] for the adiabatic bulk modulus,

$$c_s = \sqrt{\frac{\gamma p}{\rho}}, \tag{1.20}$$

can be re-written in terms of dimensionless variables

$$c_s = \sqrt{\frac{p_0}{\rho_0}}\sqrt{\gamma x y}. \tag{1.21}$$

Substituting Eq.(1.21) into Eq.(1.19) and noting that $\eta = \sqrt{\frac{\rho_0}{p_0}} u_0$, gives

$$\eta = \sqrt{\gamma \frac{y}{x}}. \tag{1.22}$$

Using the Rayleigh line to substitute $\sqrt{\frac{y-1}{1-x}}$ for η in Eq.(1.22) and solving for y gives us the *sound speed curve*,

$$y = \frac{x}{x(1+\gamma) - \gamma} := y_{SS}, \tag{1.23}$$

which we will subsequently refer to with a subscript SS. The final state is determined by the intersection of the sound speed curve, y_{SS} and the Hugoniot, y_H.

If we plot the Hugoniot, the sound speed curve, and the Rayleigh line with slope η_{CJ}, we can see in Figure 1.3 that all three curves intersect at the same point, showing that Chapman's tangency solution is equivalent to Jouguet's sound-speed condition.

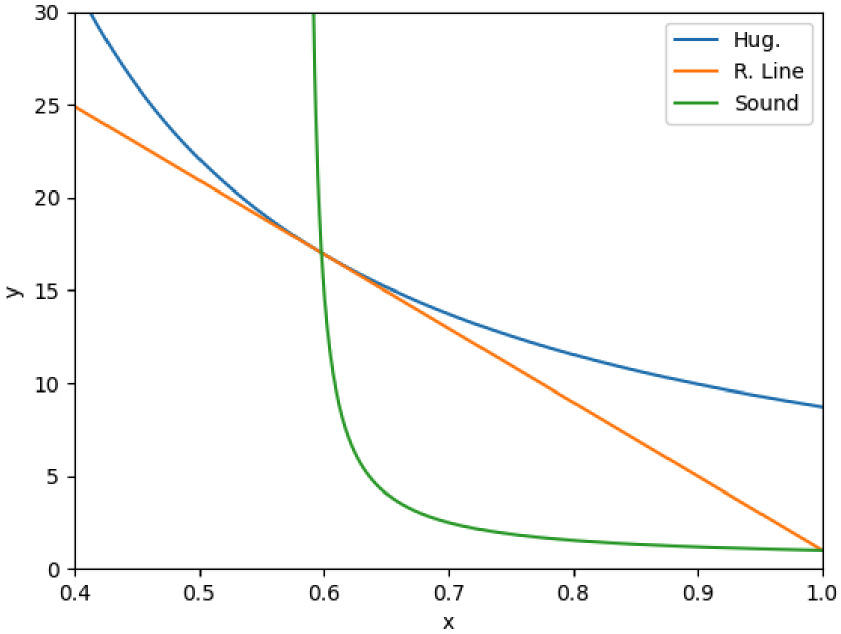

Figure 1.3: Plot showing the intersection of the Hugoniot (blue) and the sound speed curve (green). The Rayleigh line (orange) for at η_{CJ} is superimposed. We can clearly see that the intersection of all three curves occurs at the CJ tangency solution. Here we have $\gamma = \frac{5}{3}$ for a monoatomic gas and $q = 10$. The final state is determined at $x = 0.64$, $y = 14.93$, and $\eta = 6.23$.

The final state variables of x and y and the detonation velocity η are completely determined.

Both Chapman's and Jouguet's methods of determining the velocity of detonation waves proved to be effective and successful in modeling one-dimensional detonation waves by thermodynamically connecting the initial and final states. Later theoretical approaches, such as the aforementioned ZND model, [6], and the model of Wood and Kirkwood [9], would also be successful. However, these models involve numerically integrating chemical rate equations through the reaction zone, requiring an approximation of the hot, non-equilibrium state within the zone. The Chapman-Jouguet theory of detonation is an important and useful model in that it only relies on knowledge of the initial and final states in thermodynamic equilibrium.

Chapter 2

The Entropy Minimum Paradox

2.1 The Analysis of R.L. Scorah

Due to the spontaneous and adiabatic nature of detonation, Scorah was motivated to determine the velocity of the detonation wave by maximizing the entropy S of the final state of the system with respect to η [8]. Scorah began his analysis by combining the Bernoulli equation with the Hugoniot as an expression of energy conservation,

$$\frac{\gamma}{\gamma-1}(t-1)-q=-(x-1)+\frac{(\frac{y_H-1}{1-x})}{2}(x-1)^2, \tag{2.1}$$

by using the Rayleigh line to replace η^2 with $\frac{y_H-1}{1-x}$ on the right-hand side of Eq.(1.13). Adopting the notation of Lee [6], let $e=\frac{\gamma}{\gamma-1}t$ be a dimensionless quantity of internal energy, and where $t=xy_H(x)$. Differentiating Eq.(2.1) with respect to x gives

$$\frac{de}{dx}=\frac{1}{2}(1-x)\frac{dy_H}{dx}-\frac{1}{2}(1+y_H). \tag{2.2}$$

Scorah then used the second law of thermodynamics

$$de=xy_H ds-y_H dx, \tag{2.3}$$

or alternatively,

$$\frac{de}{dx}=xy_H\frac{ds}{dx}-y_H, \tag{2.4}$$

where s is the dimensionless entropy, to replace $\frac{de}{dx}$ on the left-hand side of Eq.(2.2), giving

$$xy_H\frac{ds}{dx}-y_H=\frac{1}{2}(1-x)\frac{dy_H}{dx}-\frac{1}{2}(1+y_H). \tag{2.5}$$

Rearranging terms gives an expression for the change in entropy along the Hugoniot,

$$\frac{ds}{dx}=[\frac{1-x}{2xy_H}][\frac{y_H-1}{1-x}+\frac{dy_H}{dx}]. \tag{2.6}$$

As shown by Lee [6], evaluating (2.16) at $x = x_{CJ}$ shows that $(\frac{ds}{dx})\Big|_{x=x_{CJ}} = 0$, corresponding to an entropy extremum. What Scorah showed is that the second derivative of entropy evaluated at $x = x_{CJ}$,

$$\frac{d^2s}{dx^2}\bigg|_{x=x_{CJ}} = [\frac{1-x}{2xy_H}][\frac{d^2y_H}{dx^2}] > 0, \tag{2.7}$$

is always positive because the curvature of the Hugoniot, $\frac{d^2y_H}{dx^2}$, is always positive, indicating that the extremum corresponds to an entropy minimum [8][6].

We can illustrate this point graphically by plotting the entropy for an ideal gas

$$s = \frac{1}{\gamma - 1}\ln(t) + \ln(x) \tag{2.8}$$

along the Hugoniot by substituting $t = xy_H(x)$. For the case of $\gamma = \frac{5}{3}$ and $q = 10$, Figure 2.1 shows an example plot where the entropy minimum occurs at $x = 0.64$, corresponding to the CJ solution shown in Figure 1.3 for the same values of γ and q.

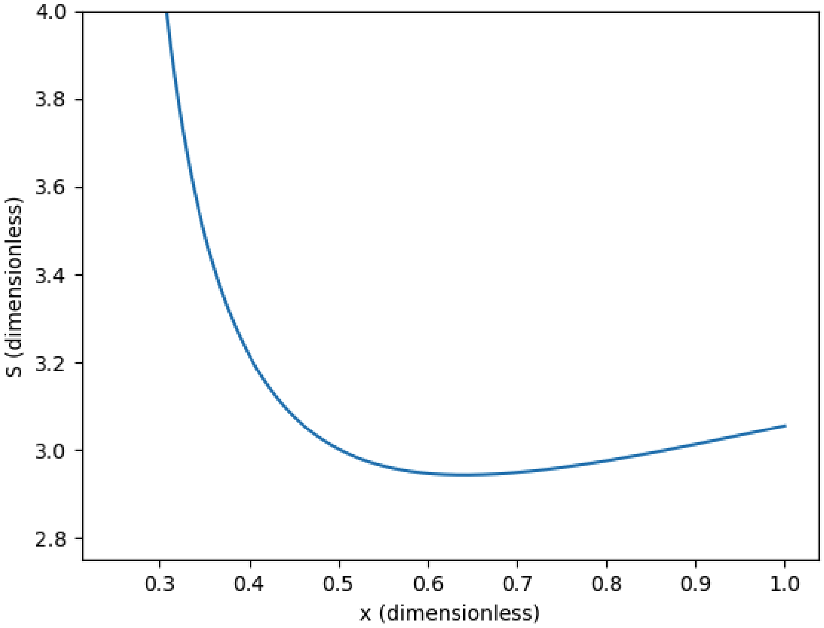

Figure 2.1: Entropy vs volume. Here we use $\gamma = \frac{5}{3}$ for a monoatomic gas and $q = 10$ just as in Fig. 1.3. We observe a minimum along the entropy curve at $x = 0.64$, exactly the same value of x determined by the CJ solution (see Figure 1.3).

This presents a dilemma, for detonations are observed to be spontaneous processes. Since heat exchange along the flow stream is negligible as $\Delta t \to \infty$, and heat exchanged laterally is negligible as $A \to \infty$, the detonation wave represents an adiabatic process in one dimension, as we have stated previously. Since $\Delta s > 0$ for a spontaneous and adiabatic process, Scorah's entropy minimum violates the second law of thermodynamics. To violate the second law of thermodynamics is obviously embarrassing, yet to this point nobody has been able to find a flaw in Scorah's argument.

2.2 Scorah's Mistake

The form of the Bernoulli equation as expressed in Eq.(1.13) puts all internal energy and the heat q released internally by the chemical reaction on the left-hand side, while the expression for the flow kinetic energy is on the right-hand side. We re-write Eq.(1.11) here for convenience

$$\frac{\gamma}{\gamma-1}(t-1) - q = -(x-1) + \frac{\eta^2}{2}(x-1)^2. \tag{2.9}$$

The Bernoilli equation expresses the exchange from thermal energy to flow energy, and vice-versa. In this manner, the thermodynamic system (internal energy) is not isolated from its surroundings (flow energy) as it needs to be in order to apply the maximum entropy principle. However, we are able to clearly observe a very important point; even though the flow kinetic energy has been combined with the constant-pressure P-V work on the right-hand side of Eq.(2.9), one can still interpret the right-hand side as P-V work,

$$w = -\int_1^x y_R(x)dx' = -\int_1^x (1-\eta^2(x'-1))dx' = -(x-1) + \frac{\eta^2}{2}(x-1)^2. \tag{2.10}$$

The right-hand side is no longer constant-pressure P-V work, but P-V work with pressure prescribed by the Rayleigh line. Integrating the Rayleigh line gives the flow kinetic energy on the right-hand side of Eq.(2.9); conversely, differentiating the right hand side of Eq.(2.9) gives back the pressure as determined by the Rayleigh line $y_R(x)$. This means that the Bernoulli equation can be interpreted as an expression of the first law of thermodynamics applied to the energy U of the thermal degrees of freedom, $\Delta U = Q + W$, with $Q = 0$, as it must be for an adiabatic process.

Scorah's mistake was to replace the Bernoulli equation by the Hugoniot as an expression of energy conservation, as we have remarked previously, by replacing η^2 with a function of x, $\frac{y_H-1}{1-x}$, as shown in Eq.(2.1). If we differentiate the right-hand side of Eq.(2.1) to determine the pressure of the final state,

$$y = -\frac{d}{dx}[(-(x-1) + \frac{1}{2}(x-1)^2\frac{y_H}{x-1})] = y_H - \frac{1}{2}(\frac{dy_H}{dx}(x-1) - (y_H-1)), \tag{2.11}$$

we see that the final state pressure $y \neq y_H$, due to a "correction term" $-\frac{1}{2}(\frac{dy_H}{dx}(x-1)-(y_H-1))$ on the right-hand side of Eq.(2.11), which ought not to be there. It should be noted that such a correction term will be present for any expression where the constant η is replaced by a function of x. This means that the right-hand side of Eq.(2.11) cannot be interpreted as P-V work alone, which can only mean that $Q \neq 0$. Thus, the process can no longer be considered adiabatic and there is no reason to expect that the entropy of the system will increase to a maximum.

The remedy of the problem is seemingly simple: if we would like to maximize the entropy, we must keep η constant in the P-V work term. Only in this case are we able to consider the internal degrees of freedom to be adiabatically decoupled from the surroundings. This means that one cannot search for a maximum entropy by varying η because any variation in η, be it along the Hugoniot, or otherwise, will allow heat to be exchanged with the surroundings. This does not mean we have to abandon maximum entropy, but it does mean that one must implement maximum entropy with a certain amount of caution with respect to variations in η.

2.3 Entropy Maximization Example

As we have just seen, as long as the Bernoulli equation is used as an expression for energy conservation with a constant η, we are able to apply maximum entropy to find thermodynamic variables. As an example, let us include a reaction progress variable, the *reaction coordinate*, denoted by λ, in our ideal gas model, which ranges between $\lambda = 0$ for all reactants to $\lambda = 1$ for all products. This parameter is included in other approaches, such as the ZND model [4], and brings in the chemical complexity of the process. We will show that we can determine the final state of the system by maximizing the entropy so long as we do not make the same mistake that Scorah made. To this end, consider a simple exothermic chemical reaction that converts species A to species B and releases some amount of heat per molecule q,

$$A \rightleftharpoons B + q. \tag{2.12}$$

Suppose that the total number of molecules is

$$N = N_A + N_B, \tag{2.13}$$

where N_A is the number of species A and N_B is the number of species B. The chemical coordinate allows us to relate N_A and N_B as the reaction progresses. For the simplest model, we assume that the number of degrees of freedom for vibrations and rotations are the same for both A and B. This ensures that γ stays the same in the initial and final states. In terms of the reaction coordinate, we write

$$N_A = N(1 - \lambda) \tag{2.14}$$

and

$$N_B = N\lambda. \tag{2.15}$$

The entropy of the final state of this new model is given by the same expression as Eq.(2.8),

$$s = \frac{1}{\gamma - 1} \ln(t) + \ln(x) - \lambda \ln(\lambda) - (1-\lambda)\ln(1-\lambda), \tag{2.16}$$

but with additional entropy of mixing terms as functions of λ. The reaction coordinate also appears in the Bernoulli equation,

$$\frac{\gamma}{\gamma - 1}(t-1) - q\lambda = -(x-1) + \frac{\eta^2}{2}(x-1)^2, \tag{2.17}$$

allowing us to express $t = t(x, \lambda)$ for a given value of η. The sound speed condition (CJ) gives,

$$x(\lambda) = \frac{(1+\gamma)\eta}{(1+\eta)\gamma}, \tag{2.18}$$

where now

$$\eta = \gamma + q\lambda(\gamma^2 - 1) + \sqrt{q\lambda(\gamma^2-1)(q\lambda(\gamma^2-1) + 2\gamma)}, \tag{2.19}$$

depends on λ. We can substitute $x(\lambda)$ into Eq.(2.17), but in order to avoid Scorah's mistake, we must be cautious to leave η as a constant parameter on the right-hand side. In this manner, the Bernoulli equation gives $t = t(\lambda; \eta)$, where η is a parameter. Substituting $t(\lambda; \eta)$ and $x(\lambda)$ into the entropy, Eq(2.16), we get $s = s(\lambda; \eta)$. To find the value of λ that maximizes the entropy, we proceed by an iterative method (the *iterative self-consistency method*).

We start by looking at the entropy as a function of λ for some initial guess of η, which we call η_0. We then find the value of λ at which the entropy curve reaches a maximum, and then used the value of λ at the maximum to update our value of η to a new guess, η_1, using Eq.(2.19), and the process is repeated. In doing this iterative process, we are ensuring that η appearing in the work term of the Bernoulli equation is always constant while maximizing the entropy. For any initial guess of η, this algorithm converges quickly and gives a maximum at $\lambda = \lambda_{eq}$. An example can be seen in Figure 2.3, where $q = 10$ and $\gamma = \frac{5}{3}$, for five different initial guesses of η shown in Figure 2.2.

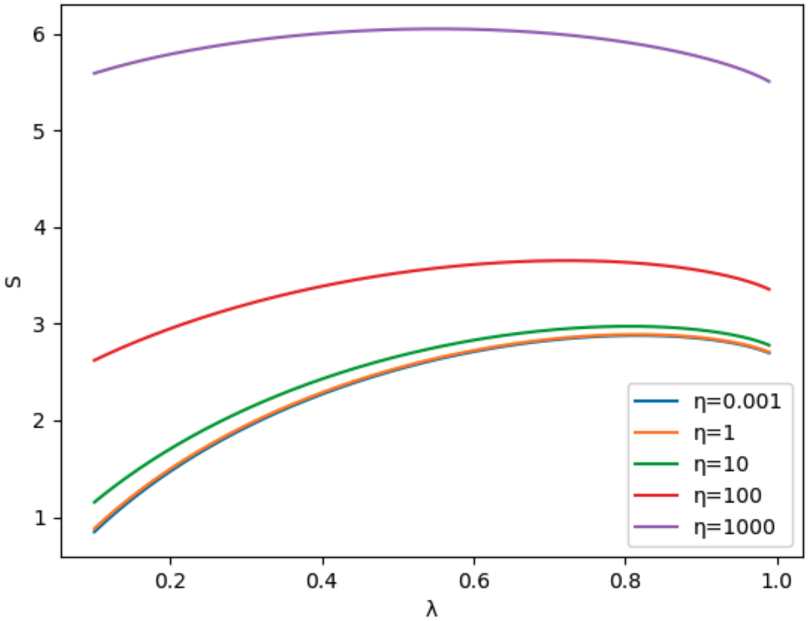

Figure 2.2: A. Entropy vs λ for different initial guesses of η. We can see that all have maxima at different values of λ. Here we use $q = 10$ and $\gamma = \frac{5}{3}$.

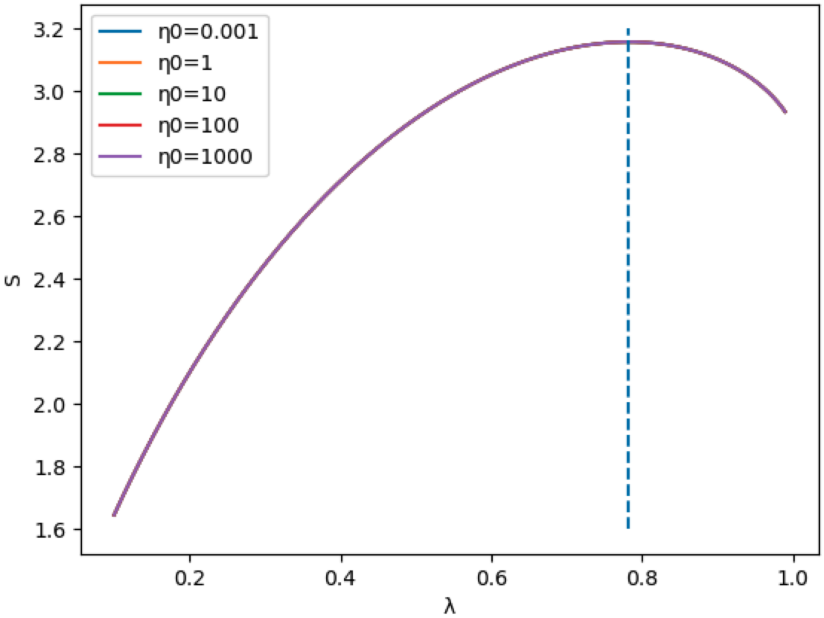

Figure 2.3: B. Entropy vs λ for all initial guesses after five iterations of the self-consistency method. All initial guesses converge to the same $\lambda_{eq} = 0.78$. Here we use $q = 10$ and $\gamma = \frac{5}{3}$.

To verify that this is the correct solution, we notice that our algorithm finds $\lambda_{eq} = 0.78$, from which we determine our value of $\eta = 5.6$ for these parameters. From Eq.(1.13) and Eq.(1.14), we find $x(\lambda_{eq}) = 0.64$ and $y(\lambda_{eq}) = 12.5$, giving a value of $t = xy = 8.0$. Plugging this value into the standard equilibrium expression for a two-state system,

$$\lambda = \frac{1}{e^{-\frac{q}{t}} + 1} = \frac{1}{e^{-10/8.0} + 1} = 0.78, \tag{2.20}$$

we obtain the same λ_{eq}. Thus, we are indeed able to connect the initial and final states through maximizing entropy.

2.4 Conclusions and Discussions

We find that Scorah made a mistake by searching for a value of η as a function of x, which implicitly allows for the flow of heat because the connection between the system and surroundings cannot be described as only consisting of work. The larger implication is that one is unable to search for a value of η by maximizing entropy, as Scorah attempted to do in 1935. One needs to rely on the fact that the velocity is determined as purely a condition for stationarity.

Scorah was not wrong to think that entropy maximization methods can be used to connect initial and final states. The mistake in his work was to use the Hugoniot as a way of constraining the system's energy; a mistake that has seemingly been overlooked by investigators for 90 years. As we have shown, the use of the Bernoulli equation iteratively allows one to connect initial and final detonation states by maximizing the entropy. This is significant in that it shows that numerically integrating through the reaction zone is not necessary. One problem that remains is determining why Scorah was not only unable to find an entropy maximum, but instead found specifically an entropy minimum in his analysis. While Scorah's mistake may only be a accident, understanding why his mistake leads to exactly a minimum in entropy at the CJ solution could be enlightening in further understanding this problem. .

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