ON DETONATIONS AND FLAMES

INGO MÜLLER [a*]

ABSTRACT. Detonations and flames, -just like shocks -, are steep and rapid transitions between two equilibria which represent regular singularities. The nature of the singular points is more difficult to identify than for shock waves, because of more variable-fields. After a review of the Chapman-Jouguet theory the fields of velocity, pressure, temperature, entropy and entropy production are calculated for two detonations with Mach number 7. Problems with flames in viscous gases are briefly discussed.

Dedicated to Professor Giuseppe Grioli
on the occasion of his 100th birthday

1. Introduction

Detonations and flames are both phenomena characterized by a precarious balance between the inflow of fuel, heat conduction, and chemical reaction. Mathematically they connect two different equilibria like a shock wave, but -unlike a shock- the upstream equilibrium in the fuel is a metastable one, i.e. the fuel needs to be ignited before the reaction can occur. In the present work the reaction from the fuel F to the reaction product P is represented roughly by the stoichiometric equation $F \rightarrow P$, and both constituents are supposed to be ideal gases. Once the detonation or flame has started, it may be maintained in a stationary state provided that the inflow of fuel is exactly balanced by the reaction rate. The continued ignition is made possible by preheating of the fuel through forward heat conduction, see Fig. 1. The figure offers a schematic view; it is taken from [1].

The governing equations are the conservation laws of mass, momentum and energy, and the equation of balance of mass of the fuel. These equations must be supplemented by constitutive equations for the diffusion flux, the deviatoric stress, the heat flux and the reaction rate. Here we adopt their classical forms: the laws of Fick, Fourier and Navier-Stokes. The precarious nature of the phenomena is represented by a dimensionless detonation parameter – or flame parameter – which must be just right to balance mass inflow, heat conduction and reaction rate.

The basis for the characterization of the initial and final equilibria is the Chapman-Jouguet theory (e.g. see [2] and [3]), which corresponds to the Rankine-Hugoniot theory for shock waves, except that the former is richer, because of the heat of reaction. According to the Chapman-Jouguet theory detonations are supersonic, while flames are subsonic. And, generally, there are two of both. For detonations we have calculated the entropy growth and the entropy productions density. The latter has been decomposed into three

contributions representing the three dissipative mechanisms, viz. thermal conduction and diffusion, viscous friction, and chemical reaction. It is instructive to confirm that the thermal conduction and diffusion precede the chemical reaction . This is essential in order to maintain the ignition of the fuel.

Since detonations and flames are characterized by steep gradients of the thermodynamic fields, it might be suspected that extended thermodynamics is needed. At least, maybe, the inertia of the diffusive motion may have to be taken into account. However, the complexity of the resulting equations has so far made it impossible to find solutions for the extended theory.

In a previous paper [4] flames have been considered for non-viscous but heat conducting gases. That may be an artificial case physically, but it did allow us to calculate the profiles of the thermodynamic fields and to establish differences between ordinary and extended thermodynamics. Nothing like this can be done for detonations, because viscosity is essential for those. If one ignores viscosity in detonations, the possible values of the heats of reaction must be restricted in a most unrealistic manner.

All of the open questions in this area qualify this research as work in progress. It must be hoped that answers can be found in the future.

2. Chapman-Jouguet theory

A flame or a detonation as stationary, one-dimensional phenomena are somewhat like a shock wave in the sense that steep gradients occur in the thermodynamic fields, like velocity, temperature and pressure. They differ from shock waves, of course, in the sense that they propagate into a chemically metastable gas, the fuel, which needs to be heated, before it can react. Inside the reaction zone, – cf. Fig 1 the heat of reaction is set free and that is the main feature which affects the final state of stable equilibrium behind flames or detonations.

Important equations which relate the initial and final states are the conservation laws of mass, momentum, and energy of the mixture consisting of the fuel and the reaction product. They read

$$\frac{\mathrm{d}\rho v}{\mathrm{d}x} = 0, \quad \frac{\mathrm{d}\left(\rho v^2 + p - \tau_{xx}\right)}{\mathrm{d}x} = 0, \quad \frac{\mathrm{d}\left(\rho\left(h + \frac{1}{2}v^2\right)v + q - \tau_{xx}v\right)}{\mathrm{d}x} = 0. \quad (1)$$

ρ, v and p are density, velocity and pressure of the mixture, and h is its specific enthalpy. q is the heat flux and τ_{xx} is the normal component of the deviatoric stress in the x-direction. The latter two quantities vanish far in front of the reaction zone and far behind it. Thus integration between the initial and the final states provides the final state of pressure and density in terms of the initial state.

$$\frac{p_f}{p_i} - 1 = \gamma M_i^2 \left(1 - \frac{\rho_i}{\rho_f}\right), \quad \frac{p_f}{p_i}\frac{\rho_i}{\rho_f} - 1 - Q = \frac{\gamma - 1}{2\gamma}\left(\frac{\rho_i}{\rho_f} - 1\right)\left(\frac{p_f}{p_i} - 1\right) \quad (2)$$

These equations are called the Hugoniot conditions. γ is the ratio of specific heats c_p and c_v at constant pressure and volume[1]. Throughout the paper we take $\gamma = \frac{4}{3}$ which is

---

[1]We assume for simplicity that both constituents -the fuel and the reaction product- are ideal gases with the same molar mass M and the same specific heats.
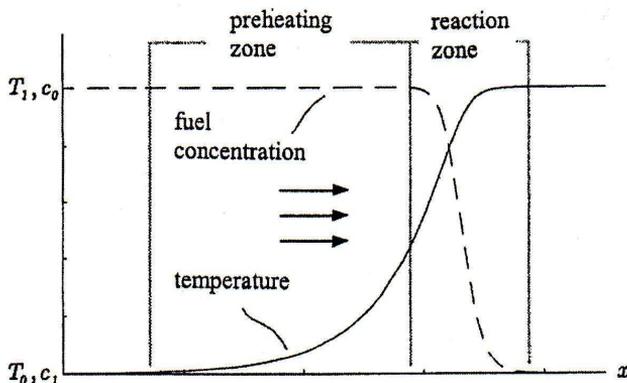
Figure 1. Schematic view of the fields of temperature and the field of fuel concentration for a flame or a detonation propagating in the x-direction. The situation is stationary in the frame which moves with the constant velocity of the reaction zone.

appropriate for ideal gases with molecules of three atoms or more. M_i is the initial Mach number, and Q - the dimensionless heat of reaction - is defined by

$$Q = -\frac{h_P^{ref} - h_F^{ref}}{c_P^{T_i}}, \qquad (3)$$

where h_P^{ref} and h_F^{ref} refer to some reference state common for both gases, the fuel F and the reaction product P.

The simplicity of the Hugoniot conditions permits a graphical construction of the final pressure and density in a $\left(\frac{p}{p_i}, \frac{\rho_i}{\rho}\right)$-diagram, the so-called Chapman-Jouguet diagram, cf. Fig. 2. The plot shows

- two straight lines which represent the linear equation $(2)_1$ -the momentum balance- for two Mach numbers. These lines are called the Raleigh lines. The steep one corresponds to $M_i > 1$, while the flat one corresponds to $M_i < 1$.
- several hyperbolae, so-called Hugoniot curves, which represent the energy balance $(2)_2$ for different non-negative values of Q. The Hugoniot curve through point A has the parameter $Q = 0$.

Obviously the point $\left(\frac{p}{p_i}, \frac{\rho_i}{\rho}\right) = (1, 1)$ represents the starting point far in front of a flame or a detonation. The final point $\left(\frac{p_f}{p_i}, \frac{\rho_i}{\rho_f}\right)$ must lie on the appropriate Raleigh line *and* on the appropriate Hugoniot curve.

For a given value of Q, i.e. a given Hugoniot curve, the value of the Mach number of the incoming flow generally determines a Raleigh line which intersects the Hugoniot curve in two points. There are two possibilities:
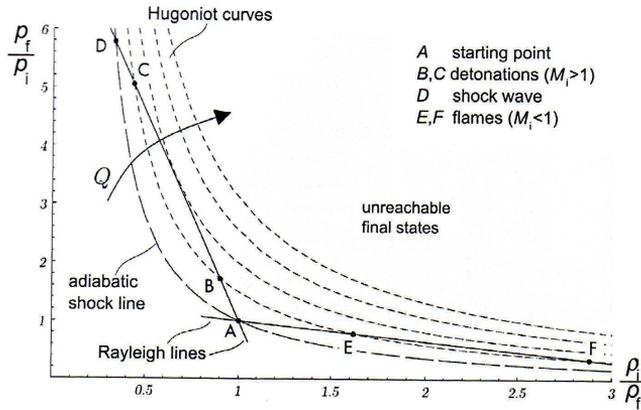
Figure 2. Chapman-Jouguet diagram.

- If the incoming flow is supersonic, i.e. $M_i > 1$, we speak of a detonation. The density grows and the velocity decreases. In Fig. 2 two possible end states are denoted by B and C. Note that, as Q tends to zero, the point B eventually coincides with the initial state A, and the point C approaches point D on the hyperbola with $Q = 0$. This state characterizes the Rankine-Hugoniot solution behind a shock wave in a gas. A shock wave is thus seen as the limiting case of a detonation when no chemistry is involved.
- If the incoming flow is subsonic, we speak of a flame. In this case the density of the gas decreases and the velocity increases. The points E and F characterize possible end-states behind the flame. For $Q = 0$ the Raleigh line intersects the Rankine-Hugoniot hyperbola in a point G not shown in the figure. That point corresponds to a rarefaction shock which cannot occur in nature, because it involves a decrease of entropy.

The pressures, densities and temperatures in the final points B, C, E, and F can easily be calculated from (2) by solving a quadratic equation. We obtain

$$
\begin{aligned}
\frac{\rho_i}{\rho_f} &= \frac{1}{M_i^2 (\gamma + 1)} \left(1 + \gamma M_i^2 \pm \sqrt{(M_i^2 - 1)^2 - 2 (\gamma + 1) M_i^2 Q} \right) \\
\frac{p_f}{p_i} &= \frac{1}{(\gamma + 1)} \left(1 + \gamma M_i^2 \mp \gamma \sqrt{(M_i^2 - 1)^2 - 2 (\gamma + 1) M_i^2 Q} \right) \qquad (4) \\
\frac{T_f}{T_i} &= \frac{p_f}{p_i} \frac{\rho_i}{\rho_f}.
\end{aligned}
$$

With reference to the Chapman-Jouguet diagram we note that for a detonation the lower sign corresponds to point C, while the upper one refers to point B. For a flame the lower sign corresponds to point E and the upper one to point F.

Note that the permissible values of Q the heat of reaction is limited, because the radicand in (4) must be positive. Therefore we must have

$$Q \leq \frac{1}{2\left(\gamma + 1\right)} \frac{\left(M_i^2 - 1\right)^2}{M_i^2} \tag{5}$$

Thus for both $M_i = 7$ and $M_i = \frac{1}{7}$ we must have $Q \leq 10.0758$ which leaves ample room for the choice of heats of reaction.

For later reference I list some coordinates of the points A through F in the Chapman-Jouguet diagram, all calculated from (4).

Thus for a detonation with $M_i = 7$, and $Q = 8$ we have

$$\left.\frac{\rho_i}{\rho_f}\right|_C = \left.\frac{v_f}{v_i}\right|_C = 0.389619 \quad \left.\frac{p_f}{p_i}\right|_C = 40.9781 \quad \left.\frac{T_f}{T_i}\right|_C = 15.9269$$

$$\tag{6}$$

$$\left.\frac{\rho_i}{\rho_f}\right|_B = \left.\frac{v_f}{v_i}\right|_B = 0.77073 \quad \left.\frac{p_f}{p_i}\right|_B = 15.979 \quad \left.\frac{T_f}{T_i}\right|_B = 12.3155.$$

For a flame with $M_i = \frac{1}{7}$ and $Q = 8$ we have

$$\left.\frac{\rho_i}{\rho_f}\right|_E = \left.\frac{v_f}{v_i}\right|_E = 12.2342 \quad \left.\frac{p_f}{p_i}\right|_E = 0.694307 \quad \left.\frac{T_f}{T_i}\right|_E = 8.4943$$

$$\tag{7}$$

$$\left.\frac{\rho_i}{\rho_f}\right|_F = \left.\frac{v_f}{v_i}\right|_F = 30.9086 \quad \left.\frac{p_f}{p_i}\right|_F = 0.186159 \quad \left.\frac{T_f}{T_i}\right|_F = 5.75393.$$

The case of shock waves results from (4) by setting $Q = 0$. Thus for a compressive shock with $M_i = 7$ we obtain

$$\left.\frac{\rho_i}{\rho_f}\right|_D = \left.\frac{v_f}{v_i}\right|_D = 0.16035 \quad \left.\frac{p_f}{p_i}\right|_D = 55.8571 \quad \left.\frac{T_f}{T_i}\right|_D = 8.95668. \tag{8}$$

And for the (hypothetical) rarefaction shock for $M_i =$ for a shock, with $Q = 0$, we have

$$\left.\frac{\rho_i}{\rho_f}\right|_G = \left.\frac{v_f}{v_i}\right|_G = 42.1429 \quad \left.\frac{p_f}{p_i}\right|_G = -0.119534 \quad \left.\frac{T_f}{T_i}\right|_G = -5.03748. \tag{9}$$

The latter results, those with negative values for p_f and T_f reveal another precarious point for flames, – in addition to entropic decrease. Indeed, neither the Hugoniot curves nor the Raleigh lines are positive for all values of $M_i < 1$ and $Q \geq 0$, and their points of intersection may well lie below the abscissa of Fig. 2. Concerning the rarefaction shock this is of no concern, since such shocks are excluded anyway by the entropy condition mentioned above. However, even point F for flames may have negative values of p_f and T_f; this does not happen for the values given in (6), but for a somewhat smaller value of Q, namely $Q = 3$, it does happen. Obviously in that case point F cannot occur.

3. Equations for the structure of a flame and a detonation

Between the initial and the final state we are looking at a mixture of fuel and reaction product so that an additional field is needed for the characterization of the gas, namely

the fuel concentration d. Also, as long as both fuel and reaction product coexist, there will be diffusion and chemical reaction, and we need a diffusion flux J and a chemical production density τ. These quantities are related through the momentum balance of the fuel constituent which reads in the present stationary and one-dimensional situation

$$\frac{\mathrm{d}\rho_F v_F}{\mathrm{d}x} = \tau \quad \text{or, by} \quad d = \frac{\rho_F}{\rho} \quad \text{and} \quad \rho_F v_F = \rho dv + J : \quad \frac{\mathrm{d}\left(\rho dv + J\right)}{\mathrm{d}x} = \tau. \quad (10)$$

Thus the full set of balance equations is given by

$$\begin{cases} \frac{\mathrm{d}\rho v}{\mathrm{d}x} = 0, \quad \frac{\mathrm{d}\left(\rho v^2 + p - \tau_{xx}\right)}{\mathrm{d}x} = 0, \\[2ex] \frac{\mathrm{d}\left(\rho\left(h + \frac{1}{2}v^2\right)v + q - \tau_{xx}v\right)}{\mathrm{d}x} = 0, \quad \frac{\mathrm{d}(\rho dv + J)}{\mathrm{d}x} = \tau \end{cases} \quad (11)$$

Given that both constituents F and P are assumed to be ideal gases with the same molar mass M and the same specific heats c_p and c_v we have

$$p = \rho \frac{R}{M}T \quad \text{and} \quad h = \sum_{\alpha=F}^{P} \frac{\rho_\alpha}{\rho} h_\alpha, \quad h_\alpha = h_\alpha^{ref} + c_p\left(T - T_{ref}\right). \quad (12)$$

R is the ideal gas constant.

It remains to relate the transport quantities J, τ_{xx} and q and the chemical production τ to the fields $d(x)$, $v(x)$, and $T(x)$. For the transport quantities we adopt the classical laws of Fick, Navier-Stokes and Fourier and set

$$J = -D\frac{\mathrm{d}d}{\mathrm{d}x}, \quad \tau_{xx} = \eta\frac{\mathrm{d}v}{\mathrm{d}x}, \quad q = -k\frac{\mathrm{d}T}{\mathrm{d}x} \quad (13)$$

D is the diffusion constant, η the viscosity and k the thermal conductivity.

The mass production density τ is less straightforward. We assume that, of course, it is negative and proportional to the fuel concentration d so that the reaction proceeds until no fuel is left. The metastable character of the fuel in front of the reaction zone is represented by the assumption that the factor of proportionality is given by

$$a\,exp\left(-\frac{E}{kT}\right), \quad \text{hence} \quad \tau = -a\,exp\left(-\frac{E}{kT}\right)d. \quad (14)$$

a is some positive rate factor, and E is called the activation energy needed to make the meta-stable fuel react. kT with k as the Boltzmann constant is a typical value for the kinetic energy of atoms at temperature T. Thus τ is negligible far in front of the reaction zone, because the temperature is small there, and it is zero behind the zone, because d vanishes when the fuel is burned up.

We introduce a dimensionless space variable $\hat{x} = \frac{c_p \rho v_i}{k} x$ and further dimensionless fields and parameters by

$$\hat{\rho} = \frac{\rho}{\rho_i}, \quad \hat{v} = \frac{v}{v_i}, \quad \hat{T} = \frac{T}{T_i}, \quad \hat{J} = \frac{J}{\rho_i v_i}$$

$$M_i = \frac{v_i}{\sqrt{\gamma \frac{R}{M} T_i}} \ (\text{Mach No.}), \ L = \frac{k}{\rho_i c_p D} \ (\text{Lewis No.}), \ W = \frac{k}{c_p \eta} \ (\text{Prandtl No.})$$

$$\tag{15}$$

$$Q = -\frac{h_P^{ref} - h_F^{ref}}{c_p T_i} \ (\text{heat of reaction}), \ \hat{E} = \frac{E}{k T_i} \ (\text{activation energy})$$

$$\mu = \frac{a}{\rho_i v_i} \frac{k}{c_p \rho_i v_i} \ (\text{detonation or flame parameter}).$$

The detonation or flame parameter might be considered as a dimensionless measure for the rate of reaction of the fuel once the activation has occurred. The parameter is composed of a product of two quotients: The first one represents the ratio between the reaction rate and the inflow of mass, and the second one is the ratio of thermal conductivity and the heat capacity of the inflowing mass. It must be realized that the dependence of the parameter on the inflow of mass is largely determined by the Mach number M_i, because we can write

$$\mu = \frac{\gamma - 1}{\gamma^2} \frac{1}{M_i^2} \frac{T_i}{p_i^2} a k \tag{16}$$

After a little calculation we obtain a set of ordinary differential equations of the form[2]:

Momentum balance $\quad\quad \gamma M_i^2 \frac{1}{W} v' = \gamma M_i^2 (v - 1) + \frac{T}{v} - 1$

Energy balance $\quad\quad T' = \frac{1}{\gamma} T - \frac{\gamma - 1}{2} M_i^2 v^2 + \left((\gamma - 1) M_i^2 + 1 - \frac{1}{\gamma} \right) +$
$\quad\quad\quad\quad\quad\quad\quad + Q (d + J - 1) - \left(\frac{\gamma - 1}{2} M_i^2 + 1 \right)$

$$\tag{17}$$

Fuel momentum balance $\quad J' = LJ - \mu d \, exp \left(-\frac{E}{T} \right)$

Fick's law $\quad\quad\quad\quad\quad d' = -LJ.$

This is a set of equations which Mathematica is well-equipped to solve provided that we supplement the equations with boundary conditions. With respect to those there are subtle points which are best explained for shock waves in a fluid without the possibility of chemical reactions.

4. Shock waves in a gas

If there is no chemical reaction, Q is zero in $(17)_2$ and the equations $(17)_{3,4}$ lose all meaning, since $d \equiv 1$ and $J \equiv 0$ hold. We may say that the activation energy is infinite

---

[2]The hats are dropped from the dimensionless fields for simplicity in notation. The prime denotes differentiation with respect to $\hat{x}$.

so that formally the equations $(17)_{3,4}$ are identically satisfied. The set of equations thus reduces to

$$v' = W \left[(v - 1) + \frac{1}{\gamma M_i^2} \left(\frac{T}{v} - 1 \right) \right] \equiv z_v(v,t)$$

(18)

$$T' = \frac{1}{\gamma} T - \frac{\gamma - 1}{2} M_i^2 v^2 + \left((\gamma - 1) M_i^2 + 1 - \frac{1}{\gamma} \right) - \left(\frac{\gamma - 1}{2} M_i^2 + 1 \right) \equiv z_T(v,t).$$

The right hand sides abbreviated by $z_v(v,T)$ and $z_T(v,T)$ obviously vanish before the shock and we are looking for solutions where they also vanish behind the shock, because we expect v' and T' to be very close to zero there.

In a (T, v)-diagram we have

$$\frac{\mathrm{d}T}{\mathrm{d}v} = \frac{z_T(v,T)}{z_v(v,T)},$$

(19)

so that both before and behind the shock we encounter singular points, see Fig. 3, where the graphs $z_v(v,T) = 0$ and $z_T(v,T) = 0$ are plotted for different Mach numbers M_i. The Prandtl number is chosen as 1 for simplicity. The graphs are both parabolae in a (T, v)-diagram and the points of intersection correspond to the state $(T, v) = (1, 1)$ – denoted by A in the Chapman-Jouguet diagram of Fig. 2 and to a state behind the shock which varies with M_i. For $M_i > 1$ the singular point behind the shock corresponds to point D in the Chapman-Jouguet diagram. The graph of the solution $T(v)$ which connects A to D must lie between the two parabolae of Fig. 3(Top), as indicated by the dashed line.

There are two complications: First of all, in a numerical solution of (18) it is important not to start with the boundary condition $(T, v) = (1, 1)$ *exactly* or with a pair (T, v) that corresponds to point D *exactly*, because that would give us the trivial constant solution. Rather we must start near the points A or D in order to find a non-trivial solution[3]. Given this constraint a second point comes up: We cannot hope to find the required solution by numerical integration from point A to D, because D is a saddle point from which the solution curves that pass near A veer away as indicated in Fig. 3(Top). Therefore, in order to obtain the desired shock solution numerically, we must start near D and integrate backwards toward A, because A is a nodal point and all solution curves that pass near A are squeezed together narrowly near D.

About saddles and nodes see the mathematical literature on ordinary differential equations, e.g. the book by Collatz [5]. The condition for node or saddle reads

$$\left(\frac{\partial z_v}{\partial v} \frac{\partial z_T}{\partial T} - \frac{\partial z_v}{\partial T} \frac{\partial z_T}{\partial v} \right) \Bigg|_{\text{at } A \text{ or } C} \begin{array}{c} \geq \\ \\ \leq \end{array} 0 \quad \begin{array}{c} \text{node} \\ \\ \text{saddle} \end{array}$$

(20)

In the present case the singular point A is a node for $M_i > 1$, while D behind the compressive shock – is a saddle. For $M_i < 1$ the role of the singular points is different; A is a saddle, while G behind the (hypothetical) rarefaction shock is a node. I believe that the first authors to call the attention to the relevance for shocks of that characterization of singularities were Gilbarg and Paolucci [6].

---

[3] Actually this makes sense physically, because a shock structure extends over the whole range of x and never reaches the sates A or D exactly.
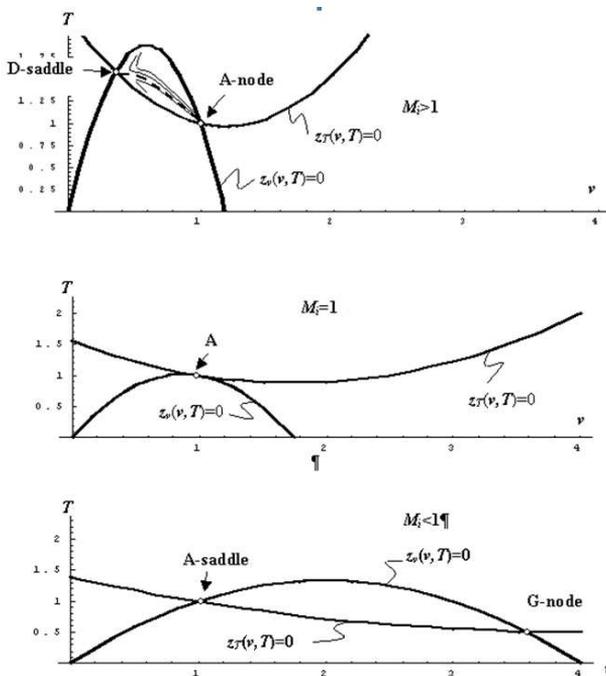
Figure 3. The graphs of $z_v\,(v, T) = 0$ and $z_T\,(v, T) = 0$ for three different Mach numbers
Top: $M_i > 1$. Point A is a nodal point, while D is a saddle
Center: At $M_i = 1$ points A and D change character
Bottom: $M_i < 1$. Point A is a saddle and G is a nodal point.

From what has been said we may now determine the shock structure $A \to D$ starting near point D at $x = 100$ (say) behind the shock, and ending near A at $x = 0$, in front of the shock. The boundary values are chosen as

$$T(100) = 8.95668, \quad v(100) = 0.16035$$

according to (8). The results are shown by dotted lines in Figs. 5, 6, 7 which represent the velocity, temperature and pressure respectively. The specific entropy and the entropy productions are also represented by dotted lines in Figs. 8, 9.

5. Detonations

A detonation is more complex than a shock, because it has four variable fields, viz. v, T and - in addition - d and J, the concentration and the diffusion flux of the fuel. The governing equations are given by (17) and we must choose all parameters other than γ, Q, and M_i which have already been chosen to be $\frac{4}{3}$, 8, and 7 respectively. Guided by physical intuition and by some experience with solving the equations we choose

$$W = 1, \quad E = 30, \quad L = 1. \tag{21}$$
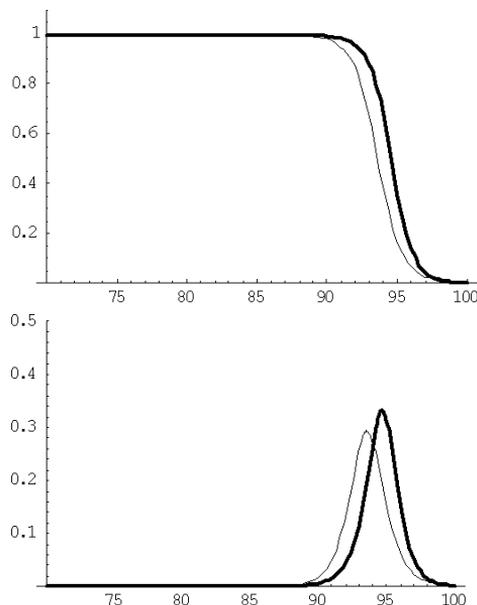
Figure 4. Fuel concetration (top) and diffusion flux (bottom) for the detonations
$A \to B$ (fat) and $A \to C$

The investigation of the singularities of the equations, and whether they are saddles, or nodes, or what not, is much more difficult for detonations than for shocks, because of the additional fields d and J, and I am helpless before that task. Therefore I let myself be motivated by the case of shocks and integrate backwards, starting the integration in the points B or C behind the detonation which are always supposed to correspond to $x = 100$. Indeed, this works.

The boundary values are chosen as

in point C : $v(100) = 0.389619, T(100) = 15.9269, d(100) = 0.001, J(100) = 0.001$

in point B : $v(100) = 0.77073, T(100) = 12.3155, d(100) = 0.001, J(100) = 0.001$.
$$(22)$$

The values for $v(100)$ and $T(100)$ are chosen in concordance with (6) and those for $d(100)$ and $J(100)$ reflect the expectation that the fuel concentration behind the detonations is very small and that no significant diffusion occurs there.

The integration is then straightforward except for one point: The determination of the detonation parameter μ. That parameter must be chosen so as to arrive at $x = 0$ with a value a little smaller than 1 as is appropriate for the initial state of the metastable fluid. The actual determination of μ is therefore a process of trial and error a shooting procedure – which involves many shots. Eventually one arrives at the graphs of Fig. 4 for $d(x)$ and $J(x)$ for the

detonation $A \to C$: $\mu = 14.3$ with $d(0) = 0.998939$
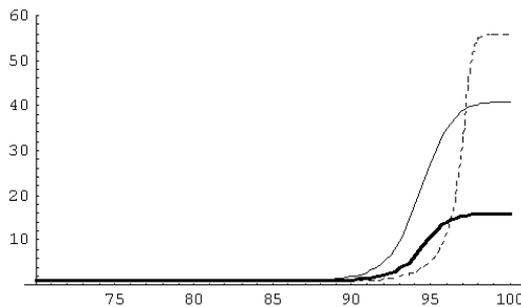detonation $A \to B$: $\mu = 33.5$ with $d(0) = 0.998337$.
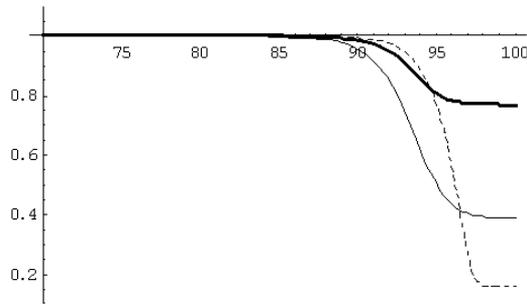
Figure 5. Velocity profile of shock (dotted) and detonations $A \to B$ (fat) and $A \to C$
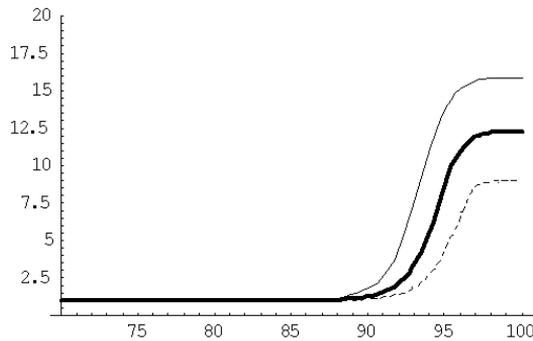
Figure 6. Temperature profile of shock (dotted), and detonations $A \to B$ (fat) and $A \to C$

Figure 7. Pressure profile of shock (dotted), and detonations $A \to B$ (fat) and $A \to C$

The graphs for the velocity, temperature and pressure for the detonations are shown in Figs. 5, 6, 7 along with those of the shock $A \to D$. From the profiles of the velocity and the pressure we may conclude that a chemical reaction dampens the severity of a shock. The temperature, however, grows to higher values across both detonations than across a shock; this may be due to the heat of reaction associated with the burning of the fuel.

6. Discussion of the shooting parameter

We have considered the two detonations $A \to B$ and $A \to C$ for identical parameters γ, M_i, W, Q, L and E, and came to the conclusion that the parameter μ in (16) a combination of the reaction rate coefficient a and the Mach number , is determined by the shooting procedure. It might be more preferable for a physicist to fix all constitutive parameters γ, W, Q, L, E and a and use the Mach number M_i as the shooting parameter. In this manner it would be clear that the detonations in a mixture with fixed constitutive parameters can only propagate with fixed Mach numbers, while a shock may propagate for any $M_i > 1$.

7. Entropic quantities in shocks and detonations

It is possible and perhaps relevant to calculate the profiles for the specific entropy and for the entropy production density. For a shock the expression is very simple, since the only dissipative mechanisms are heat conduction and viscous friction. We have with s for the specific entropy and Σ for the entropy production density

$$\frac{1}{R/M}\left(s - s_i\right) = \frac{1}{\gamma - 1}\ln T + \ln v, \text{ and } \frac{k\Sigma}{\left(c_p\rho_i v_i\right)^2} = \frac{1}{W}\left(\gamma - 1\right)\frac{1}{T}v'^2 + \frac{1}{T^2}T'^2 \quad (23)$$

and those are plotted in Figs. 8,9 for $M_i = 7$ as dashed lines.

For detonations the entropy contains the entropy of mixing, and the entropy production contains terms due to diffusion and chemical reaction in addition to the terms due to heat conduction and friction. Thus the relevant expressions read

$$\begin{aligned}
\frac{1}{R/M}\left(s - s_i\right) &= \frac{1}{\gamma - 1}\ln T + \ln v - d\ln d - (1 - d)\ln(1 - d) + d_i\ln d_i + \\
&\quad + (1 - d_i)\ln(1 - d_i), \text{ and}
\end{aligned} \quad (24)$$

$$\begin{aligned}
\frac{k\Sigma}{\left(c_p\rho_i v_i\right)^2} &= \frac{1}{W}\left(\gamma - 1\right)\frac{1}{T}v'^2 + \frac{1}{T^2}T'^2 + \frac{1}{L}\frac{Q}{T^2}c'T' + \frac{1}{L}\left(\gamma - 1\right)\frac{1}{d\left(1 - d\right)}d^2 + \\
&\quad + \mu d^2 exp\left(-\frac{E}{T}\right)
\end{aligned} \quad (25)$$

The corresponding plots are shown in Figs. 8,9. The entropic effects of the weak and the strong detonations seem to differ only by little.

In Fig. 10 the contributions to the total entropy production are represented separately: The one due to the transport processes of diffusion and heat conduction, the one due to viscosity and the one due to the chemical reaction. All three of those add up to the total entropy production. Inspection shows that the viscous contribution is the least dissipative mechanism in the detonation.

Figure 11 presents a synoptic view of the plots of Fig. 10. We confirm that the dissipation due to the transport phenomena thermal conduction and diffusion precedes the chemical contribution to the dissipation, as was already indicated in the schematic view of Fig. 1.
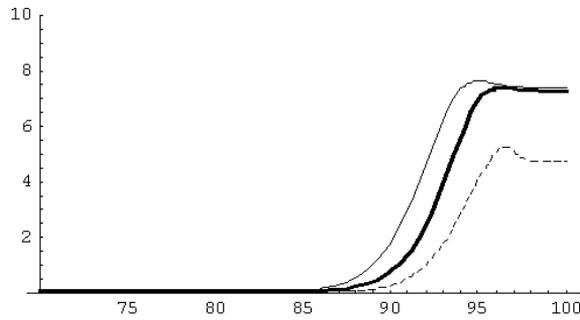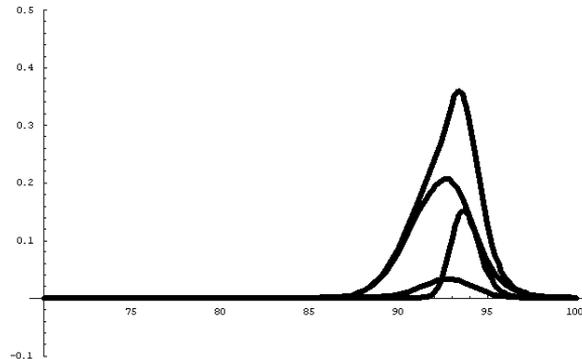
Figure 8. Entropy profile of shock (dotted), and detonations $A \rightarrow B$ (fat) and $A \rightarrow C$
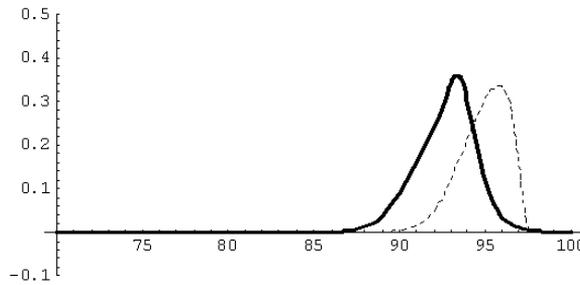
Figure 9. Entropy production of shock (dotted), and detonations $A \rightarrow B$ (fat) and $A \rightarrow C$. The latter two cannot be distinguished in the plot
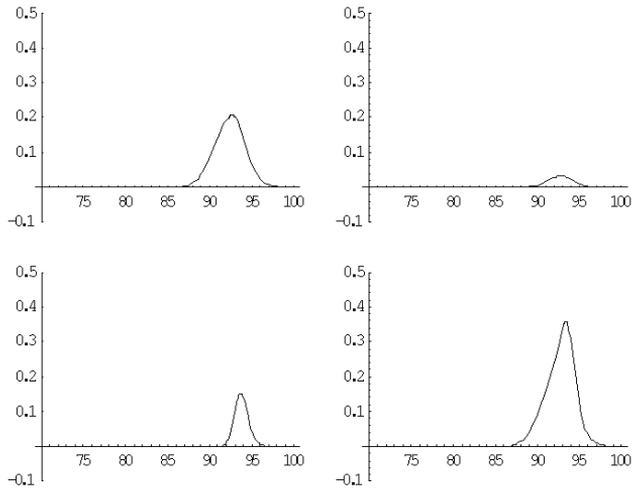
Figure 10. Contributions to the entropy production $A \rightarrow C$.
Top left: transport processes. Top right: viscosity.
Bottom left: chemistry. Bottom right: Total.

Figure 11. Synopsis of entropy productions due to different dissipative mechanisms. Cf. Fig. 10

8. Problems with flames

Nothing would be more satisfactory at this point than to proceed to subsonic flames now for the same material parameters but with $M_i = \frac{1}{7}$ (say) and possibly with a different parameter μ. Unfortunately we have not been able to find solutions leading from point A in Fig. 2 to points E and F, neither by forward nor by backward integration. We suspect that a complex and unknown – landscape of singularities in the (v, T, d, J)-space is responsible for the failure. Solutions may not be available by the shooting method.

What is possible, and indeed rather easy, is the special case when viscous friction is disregarded, i.e. when $\frac{1}{W}$ is set equal to zero. That assumption changes the character of the differential equations considerably; the temperature is then algebraically related to the velocity v and there are thus only three variable-fields, namely v, c, J. Müller [4] has calculated flame profiles in that case and Brini [7] has even successfully treated the case when both constituents, the fuel and the reaction product, have their own temperatures.

It must be said, however, that the neglect of viscosity in a gas without simultaneous neglect of heat conduction is quite unphysical in ideal gases, because viscosity and thermal conductivity have a fixed ratio. Therefore the case of an inviscid but heat conducting gas has nothing to recommend it, – except that it produces solutions of the desired shape.

Also the study of detonations provides strong evidence that viscosity is needed for smooth fields of velocity and temperature. Because, indeed, the required smoothness in the range between v_i and v_f places a strong lower bound on the heat of reaction which along with the upper bound (5) leaves Q only a very small range of possible values for all Mach numbers greater than 1. This constraint seems to make it imperative to take viscosity into account, because the lower bound is invalid in that case.

Clearly more study is needed, particularly about flames in viscous gases.

References

[1] M. Torrilhon, "Thermodynamische Berechnung der Ausbreitung von Flammen", *Bachelor thesis*, TU Berlin (1999).

[2] J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, "The Theory of Flame Propagation IV", *J. of Physical Chemistry* **57**, 403–414 (1953).

[3] F. Bartlmä, *F. Gasdynamik der Verbrennung* (Springer, Wien, 1975).

[4] I. Müller, "Flame structure in ordinary and extended thermodynamics", in *Asymptotic methods in nonlinear wave propagation*; T. Ruggeri, M. Sammartino, Eds. (World Scientific, Singapore 2007); pp. 144-153.

[5] L. Collatz, *Differentialgleichungen* (Teubner, Stuttgart 1981).

[6] D. Gilbarg and D. Paolucci, "The structure of shock waves in the continuum theory of fluids", *J. Ration Mech. Anal.* **2**, 617–642 (1953).

[7] F. Brini, "On the flame structure in multi-temperature mixture theory", *Ricerche Mat.* **58**, 63–76 (2009).

a   Technical University of Berlin
        Berlin, Germany

*   Email: ingo.mueller@alumni.tu-berlin.de