THERMODYNAMIC THEORY OF NON-IDEAL DETONATION AND FAILURE

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In a previous publication a novel theory of steady detonation has been sketched out and applied graphically to one-dimensional cases of normal (Chapman-Jouguet) and so-called eigenvalue detonation. In this paper the one-dimensional theory is put on a firmer footing by showing mathematically that the entropy of effective reaction, that is the entropy created in the detonation zone between the shock front and the back surface has a maximum, subject to the conservation of mass, momentum and energy, when the detonation velocity has its steady value. The variational theory is extended further to unconfined two-dimensional non-ideal detonation, where it is proposed that the global entropy of effective reaction created in the subsonic detonation driving zone is a maximum in the steady state with respect to the detonation velocity and the shape of the detonation front, subject to the conservation conditions, the reaction rate laws and the sonic condition at the back surface of the zone. The theory is supported by an approximate model calculation. Some results from a more sophisticated treatment introducing intrinsic non-orthogonal streamline coordinates which is being developed are presented.

INTRODUCTION

The author has previously published a novel theory of steady detonation applied to one-dimensional cases of normal Chapman-Jouguet (CJ) and so-called eigenvalue detonation. The leading idea is that the entropy of effective reaction, that is the entropy created in the detonation zone between the shock front and the back surface (a sonic locus), has a maximum, subject to the conservation of mass, momentum and energy, when the detonation velocity has its steady value.[1] This entropy of effective reaction (EoER) is to be distinguished from the total entropy change which is well-known to have a minimum value at the steady state along the Rankine-Hugoniot.

Since the theory was only sketched out graphically in the previous publication, the first section is devoted to a mathematical demonstration that in the case of one-dimensional CJ detonation, the principle of maximum entropy of reaction leads to Chapman's well-known minimum detonation velocity condition at the steady state, and in the so-called eigenvalue detonation cases which have been investigated it leads to the same results as the Zeldovich-Neumann-Döring (ZND) theory.

The much more controversial and interesting extension of the theory to two-dimensional detonation is illustrated with a simple model for a cylindrical charge (rate stick), whichmakes various approximations. It is shown that as the curvature of the detonation front is increased, subject to the global conservation of axial momentum (the mass and the energy being conserved locally) the global entropy of effective reaction (GEoER) increases to a maximum value. This is interpreted as corresponding to a thermodynamically stable steady state, with a well-defined detonation velocity, and leads to a familiar type of diameter effect curve. The model uses the simplest rate law, and unfortunately it has not yet proved possible to extend it to pressure-dependent kinetics. It is therefore not surprising that the maximum does not disappear as the diameter is reduced, which it would be natural to interpret as corresponding to detonation failure.

To carry out more accurate and sophisticated variational calculations of the GEoER, it is easiest to follow the streamlines and take the difference between the specific entropy at the back of the detonation driving zone and that at the detonation front, and adding the differences together. For this reason a theory based on streamlines is the most attractive. Unfortunately it turns out that in the two-dimensional case with axial symmetry the so-called natural streamline coordinates, namely the distance to a point along a streamline and the normal at that point, in terms of which the reactive flow equations assume their simplest form, are not suitable. It is necessary to introduce intrinsic streamline coordinates which are not orthogonal. This considerably complicates the mathematics, but has some surprising benefits, among which the direct connection between the metric tensor coefficients and the deflection angle χ at any point is the most useful and unexpected. This approach is sketched in the third section, and some preliminary results for the distribution of pressure, temperature, particle velocity and extent of reaction are presented, together with an example of the shape of the detonation zone and the streamlines; this is pleasingly similar to some computational simulation results of Gamezo and Oran[2].

THERMODYNAMICS OF ONE-DIMENSIONAL DETONATION

In this Section it will be shown that the entropy of reaction is a maximum at the Chapman-Jouget state where the Rayleigh line on a PV-diagram is tangent to the equilibrium Rankine-Hugoniot curve, corresponding to the minimum possible detonation velocity. The specific entropy of reaction (EoR) is defined as the difference between the specific entropy S_B for the reacted explosive products in chemical equilibrium (extents of reaction variables $\lambda=\lambda_e$, the equilibrium composition vector) at a state B on the product Rankine-Hugoniot, and that for unreacted explosive at a state F on the shock front ($\boldsymbol{\lambda}=\mathbf{0}$),

$$\Delta_R S = S_B - S_F \;. \tag{1}$$

It follows that for an infinitesimal change at the CJ state we must have

$$d\Delta_{\mathrm{R}} S = dS_B - dS_F = 0 \tag{2}$$

and

$$d^2 \Delta_R S \le 0 \;. \tag{3}$$

To prove this we start from the fact that, due to the conservation of mass, momentum and enery, both F & B lie on Rankine-Hugoniot (RH) curves on the PV-plane associated with the initial state 0, which have the general equation

$$RH \equiv \Delta U + \overline{P} \Delta V = 0, \tag{4}$$

where

$$\Delta U = U - U_0, \quad \overline{P} = \left(P + P_0\right)/2, \quad \Delta V = V - V_0. \tag{5}$$

The RH equation for the unreacted explosive through the initial state 0 and a state F on the shock front ($\lambda=0$) is therefore

$$RH_F \equiv U_F - U_0 + \tfrac{1}{2}\left(P_F + P_0\right)\left(V_F - V_0\right) = 0, \tag{6}$$

and that for the reacted explosive products at a state B is

$$RH_B \equiv U_B - U_0 + \tfrac{1}{2}\left(P_B + P_0\right)\left(V_B - V_0\right) = 0. \tag{7}$$

The states F and B are connected by the reactive RH as λ changes, and by the Rayleigh line (RL) through the initial state

$$RL_{FB} \equiv \frac{\Delta P_F}{\Delta V_F} - \frac{\Delta P_B}{\Delta V_B} = 0. \tag{8}$$

These three relations can be taken to express collectively the conservation of mass, linear momentum and energy during the steady detonation process. However, they do not determine the steady detonation state and in particular the steady detonation velocity. It is the claim of the current approach that the fourth condition follows from a heuristic application of classical thermodynamics.

To demonstrate this we begin by considering an infinitesimal change in a RH relation

$$d(RH) \equiv dU + \overline{P}dV + \tfrac{1}{2}\Delta V dP = 0, \tag{9}$$

where by thermodynamics

$$dU = TdS - PdV + \Delta_r \mathbf{G}.d\lambda, \tag{10}$$

where $\mathbf{\Delta_r G}$ is the specific Gibbs free energy of reaction vector, so by substitution we have

$$TdS = \tfrac{1}{2}(\Delta P dV - \Delta V dP) - \Delta_r \mathbf{G}.d\lambda. \tag{11}$$

Hence, since $\boldsymbol{\lambda_F = 0}$,

$$\begin{aligned} dS_F &= (\Delta P_F dV_F - \Delta V_F dP_F)/T_F \\ &= \left(\frac{\Delta P_F}{\Delta V_F} - \frac{dP_F}{dV_F}\right)\frac{\Delta V_F}{2T_F} dV_F \end{aligned}, \tag{12}$$

$$\begin{aligned} dS_B &= \tfrac{1}{2}(\Delta P_B dV_B - \Delta V_B dP_B)/T_B - (\Delta_r \mathbf{G}/T_B).d\lambda \\ &= \left(\frac{\Delta P_B}{\Delta V_B} - \frac{dP_B}{dV_B}\right)\frac{\Delta V_B}{2T_B} dV_B - (\Delta_r \mathbf{G}/T_B).d\lambda \end{aligned}. \tag{13}$$

Let us write the Rayleigh line condition in the form

$$\Delta P_F \Delta V_B - \Delta P_B \Delta V_F = 0, \tag{14}$$

so for the infinitesimal change we have

$$\Delta P_F dV_B - \Delta V_F dP_B + \Delta V_B dP_F - \Delta P_B dV_F = 0, \tag{15}$$

or

$$\left(\frac{\Delta P_B}{\Delta V_B} - \frac{dP_B}{dV_B}\right)\Delta V_F dV_B = \left(\frac{\Delta P_F}{\Delta V_F} - \frac{dP_F}{dV_F}\right)\Delta V_B dV_F. \tag{16}$$

By substitution to eliminate dV_F it follows that the change in the EoR can be written

$$d\Delta_{\mathrm{R}}S = dS_B - dS_F$$
$$= \tfrac{1}{2}\left(\frac{\Delta P_B}{\Delta V_B} - \frac{dP_B}{dV_B}\right)\left(\frac{\Delta V_B^2}{T_B} - \frac{\Delta V_F^2}{T_F}\right)\frac{dV_B}{\Delta V_B} - \left(\frac{\Delta_r \mathbf{G}}{T_B}\right).d\lambda \quad .(17)$$

For chemical equilibrium $\mathbf{\Delta_r G = 0}$, so the last term vanishes, and since

$$\Delta V_F^2 > \Delta V_B^2, \quad \text{and} \quad T_F < T_B$$

$$\text{we have} \quad \frac{\Delta V_F^2}{T_F} > \frac{\Delta V_B^2}{T_B} \tag{18}$$

so the second factor in brackets is non-zero, and therefore if the EoR has an extremum it follows that the first factor vanishes, that is

$$\frac{\Delta P_B}{\Delta V_B} = \frac{dP_B}{dV_B}\,, \tag{19}$$

which is the usual CJ/ZND condition for the tangency of the Rayleigh line and the product RH at the steady 1D detonation state.

It remains to be shown that the EoR is a maximum at this state. From equatin (17) we have

$$\frac{d\Delta_{\mathrm{R}}S}{dV_B} = \left(\frac{\Delta P_B}{\Delta V_B} - \frac{dP_B}{dV_B}\right)\left(\frac{\Delta V_B^2}{T_B} - \frac{\Delta V_F^2}{T_F}\right)\frac{1}{2\Delta V_B} - \left(\frac{\Delta_r \mathbf{G}}{T_B}\right).\frac{d\lambda}{dV_B} \quad ,(20)$$

so differentiating along the product RH, and recalling that $\mathbf{\Delta_r G = 0}$ all along the equilibrium product RH,

$$\left(\frac{d^2\Delta_{\mathrm{R}}S}{dV_B{}^2}\right)_{CJ} = \left[\frac{d}{dV_B}\left(\frac{\Delta P_B}{\Delta V_B} - \frac{dP_B}{dV_B}\right)\right]_{CJ}\left(\frac{\Delta V_B^2}{T_B} - \frac{\Delta V_F^2}{T_F}\right)\frac{1}{2\Delta V_B} \quad ,(21)$$

where all other terms vanish on the product RH at the CJ point. By carrying out the differentiation we get

$$\left(\frac{d^2\Delta_{\mathrm{R}}S}{dV_B{}^2}\right)_{CJ} = \left\lfloor \frac{1}{\Delta V_B}\left(\frac{dP_B}{dV_B} - \frac{\Delta P_B}{\Delta V_B}\right) - \frac{d^2P_B}{dV_B{}^2}\right\rfloor_{CJ}\left(\frac{\Delta V_B^2}{T_B} - \frac{\Delta V_F^2}{T_F}\right)\frac{1}{2\Delta V_B}$$

$$= \left(\frac{d^2P_B}{dV_B{}^2}\right)_{CJ}\left(\frac{\Delta V_F^2}{T_F} - \frac{\Delta V_B^2}{T_B}\right)\frac{1}{2\Delta V_B} \qquad (22)$$

Now the slope of the product RH, dP_B/ dV_B , is negative, and is increasing, in particular at the CJ point, so

$$\left(\frac{d^2P_B}{dV_B{}^2}\right)_{CJ} > 0 \,, \qquad (23)$$

and by the inequality for the two quantities in the bracket, the second factor in the equation is also positive. The sign of the second derivative of the EoR at the CJ point is therefore determined by that of ΔV_B , which is always negative, thereby proving that the EoR has a maximum at the ZND/CJ state.

In the cases of eigenvalue detonation[3] , two of which have been discussed before in the context of the thermodynamic theory[1], the back of the detonation driving zone (DDZ) does not correspond to the end of reaction, and it is natural to refer to the entropy of effective reaction (EoER). In the case of reversible reactions, the back of the DDZ is a state of chemical equilibrium and is also the state of maximum EoER.

SIMPLE MODEL FOR TWO-DIMENSIONAL DETONATION

The model for a cylindrical charge has the following features:

1. The shock front F is assumed hemispherical in shape.
2. The streamlines are assumed to be straight.
3. The equations of state of the explosive and the products are assumed to be polytropic with a single identical adiabatic gamma.
4. The reaction rate is described by a single extent of reaction variable λ, and is of order m=1/2 and independent of temperature and pressure.
5. The particle velocity is assumed linear in the root extent of reaction

$$\mu = 1 - \sqrt{1-\lambda} \,, \qquad (24)$$

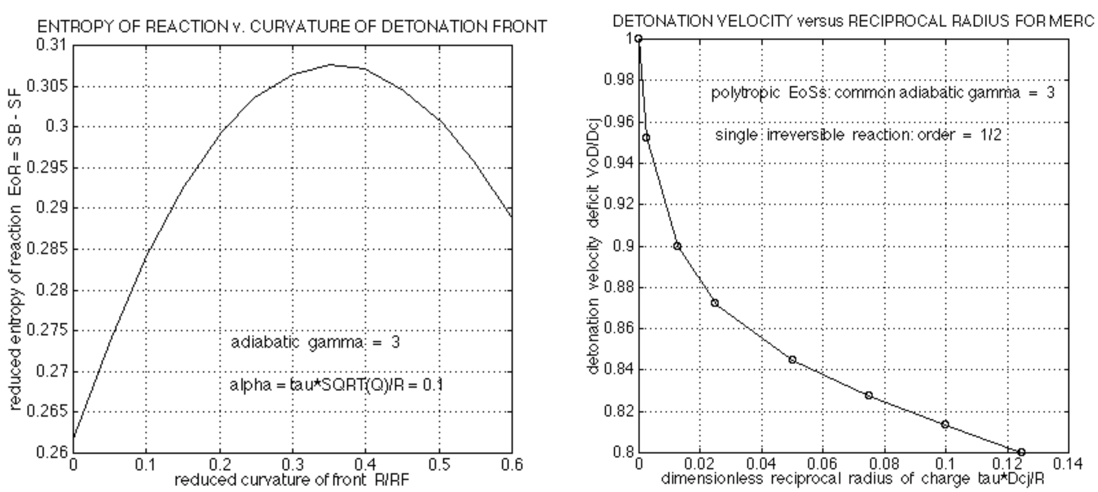
as in one-dimensional (1D) detonation, and on the axis in 2D detonation[4]. Apart from the jump conditions at F and the Bernoulli relation, the key equation is that for the particle speed gradient at the sonic locus B which defines the back of the DDZ, due originally to Devonshire[5] and exploited by Wood & Kirkwood[6] along the axis. It has the form

$$\sigma_B \dot{\lambda}_B = c_B \left(\frac{\partial \chi}{\partial n} + \frac{\sin \chi}{r} \right)_B , \tag{25}$$

where σ is the thermicity (or entropicity) coefficient, $\dot{\lambda}$ is the reaction rate, c the sound speed, χ the deflection angle of a streamline, n the normal to the streamline at the point in question, and r the radial coordinate from the axis to the point. This equation is solved for the extent of reaction λ_B at B along a set of streamlines, for a given charge radius R and shock front curvature κ_F ; the detonation velocity D is determined by the constraint that the global axial momentum is the same at B as at F. The GEoER is calculated and optimized with respect to the curvature κ_F. A typical result is shown in Figure 1, which plots the specific GEoER in units of the gas constant against the dimensionless reduced curvature $R\kappa_F$, and in Figure 2 which is a plot of the VoD for the maximum GEoER against a dimensionless reciprocal radius parameter

$$\alpha = \tau\sqrt{Q}/R \, , \tag{26}$$

where τ is the characteristic reaction time and Q is the heat of reaction.



FIGURES 1 & 2. PLOTS FOR A POLYTROPIC EXPLOSIVE WITH ORDER OF REACTION M=1/2 AND PRESSURE INDEX N=0, OF (1) THE GLOBAL ENTROPY OF EFFECTIVE REACTION (GEOER) AS A FUNCTION OF THE OF THE SHOCK FRONT CURVATURE FOR FIXED RADIUS R AND FIXED VOD, SHOWING A MAXIMUM; (2) THE VOD AS A FUNCTION OF RECIPROCAL RADIUS FOR GEOER OPTIMIZED WITH RESPECT TO THE CURVATURE OF THE SHOCK FRONT (IE. "SIZE EFFECT" PLOT)

ANALYTIC STREAMLINE APPROACH

The coordinates in terms of which the reactive flow equations are most tractable analytically are the length ℓ along a streamline from the front F to the point of interest, and the radial coordinate r_F of the streamline where it crosses F. The Stokes stream function Ψ is proportional to r_F^2 , and it is convenient to label the streamlines by the dimensionless "Stokes" coordinate $\psi = r_F/R$. The basic equation involving the coordinates (ψ, ℓ) is that for the line element ds

$$ds^2 = \left(d\ell + \eta d\psi\right)^2 + \left(\xi d\psi\right)^2 \tag{27}$$

where ξ & η are the metric tensor coefficients whose geometrical signifiance is illustrated in Figure 3; note that ℓ has also been reduced by R.

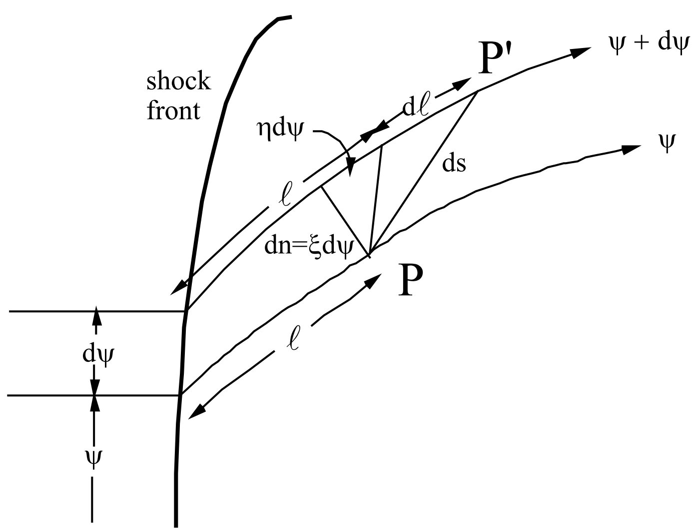
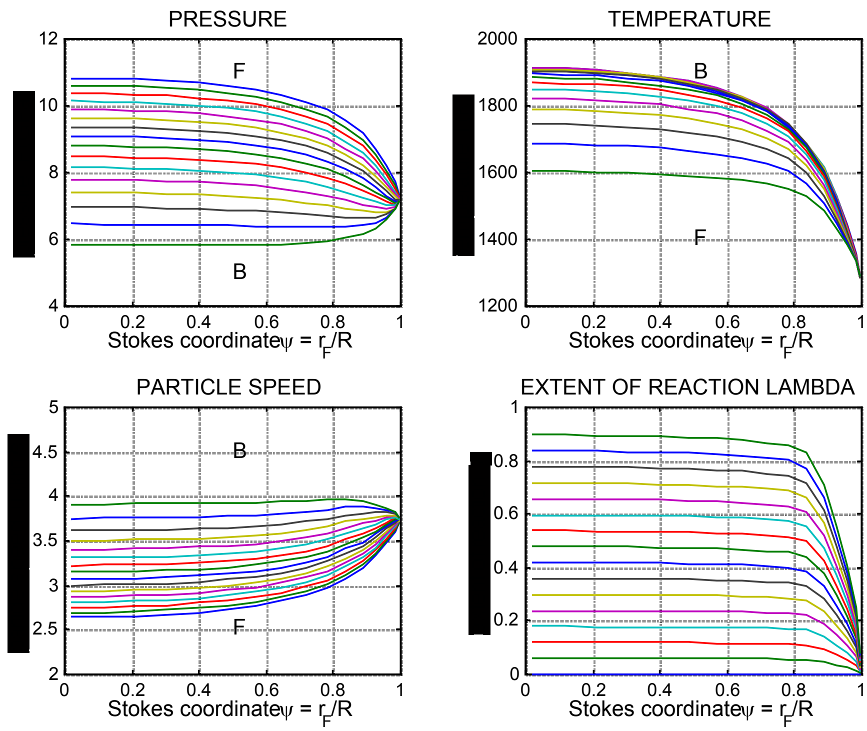


FIGURE 3. DIAGRAMMATIC SECTION SHOWING TWO NEIGHBOURING STREAMLINES WITH STOKES' COORDINATES ψ AND $\psi + d\psi$ PASSING THROUGH POINTS P AND P' RESPECTIVELY, A DISTANCE dS APART. THE INFINITESIMAL NORMAL dn AT P IS EQUAL TO $\xi d\psi$, AND $\eta d\psi$ IS THE SEGMENT INDICATED BY AN ARROW ON THE NEIGHBOURING STREAMLINE. THE INFINITESIMAL LENGTH OF ARC $d\ell$ BETWEEN P AND P' IS ALSO SHOWN, AND HENCE PYTHAGORAS THEOREM APPLIED TO THE SMALL RIGHT-ANGLED TRIANGLE WITH DIAGONAL ds AND SIDES $\xi d\psi$ AND $d\ell + \eta d\psi$ LEADS TO (27).

The mathematical details involved in the use of this approach will be published elsewhere, but it seems appropriate to present some of its first fruits. Figures 4 show plots of the pressure (GPa), temperature (K), particle speed (km/s) and extent of reaction calculated for parameter values corresponding to some experimental results for an ANFO explosive. However, the underlying equation of state is the simple polytropic one, the temperature has been adjusted to agree with ideal detonation code values, and the GEoER has not been maximized. Nevertheless the plots show what can be achieved with

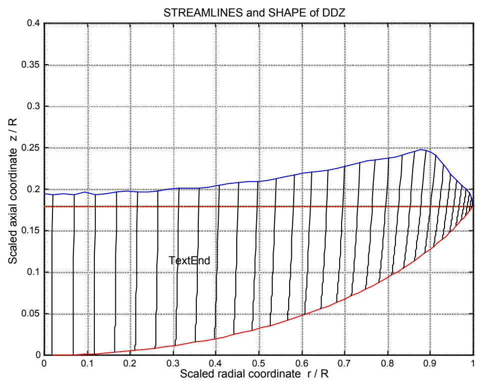


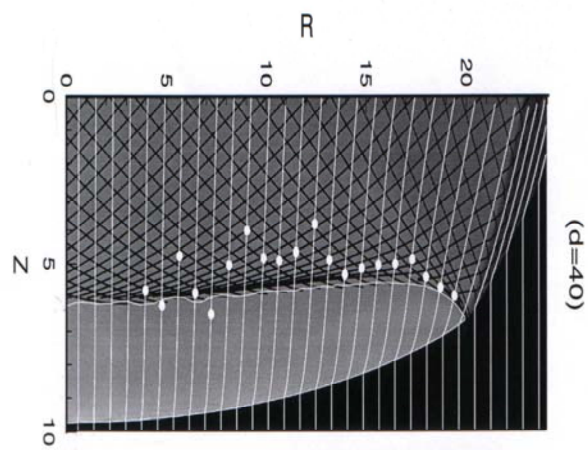
FIGURES 4. PLOTS OF THE DISTRIBUTION OF FOUR KEY PROPERTIES ALONG STREAMLINES LABELLED BY THE STOKES' RADIAL COORDINATE $\psi = r_F/R$ FROM THE SHOCK FRONT F TO THE BACK B (SONIC LOCUS) OF THE DETONATION ZONE CALCULATED FOR A CYLINDER OF AN ANFO EMULSION EXPLOSIVE OF DENSITY 1.25 G/CC, DIAMETER 5 CM WITH VOD 5.2 KM/S USING THE AUTHOR'S MEDEA PROGRAM..

an essentially analytic approach based on the streamlines. Figure 5 shows a plot of the streamlines and shape of the DDZ in a similar case, to be compared with a computer simulation study by Gamezo and Oran[2] shown in Figure 6.

CONCLUSION

It is planned to apply the streamline approach sketched in the last section to the more accurate and thorough exploration of the maximum global entropy of effective reaction theory of steady non-ideal detonation. The feature of greatest interest is undoubtedly the possible explanation of failure in the linear diameter effect cases of solid explosives such as PBX 9502.





FIGURES 5 & 6. THE PLOT ON THE LEFT-HAND SIDE IS FROM THE AUTHOR'S MEDEA PROGRAM FOR SIMILAR DIMENSIONLESS PARAMETER VALUES AS THE FIGURE ON THE RIGHT-HAND SIDE TAKEN FROM THE PAPER BY GAMEZO AND ORAN[2].

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