Joint Summer School on Fuel Cell and Hydrogen Technology
August 21-25, 2011, Viterbo, Italy

Primer

"Hydrogen Detonation"

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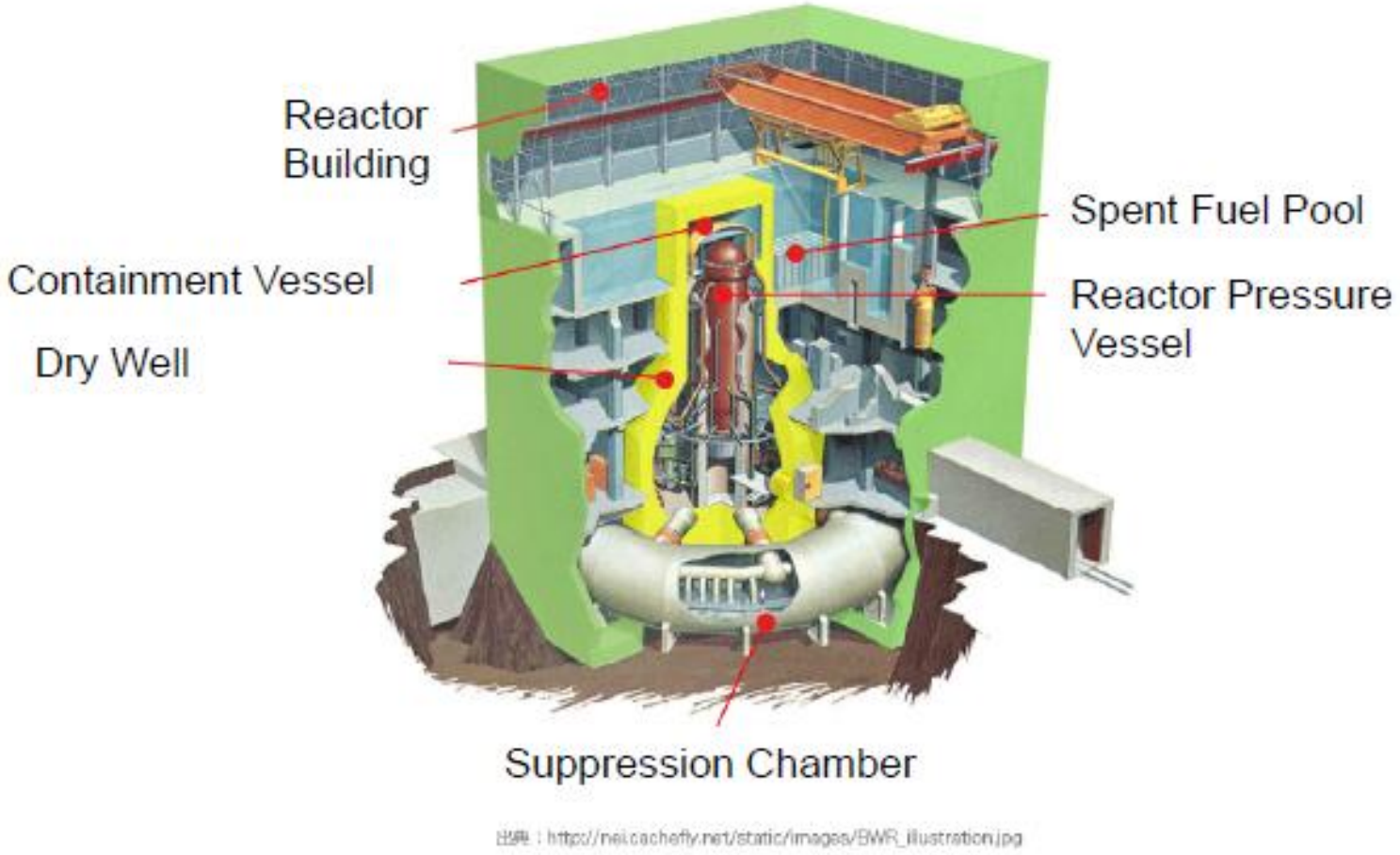
Hydrogen explosion in nuclear power plants a major concern



出典：http://nei.cacheflv.net/static/images/BWR_illustration.jpg

Detonation?

Fukushima nuclear power plant post hydrogen explosion, 2011

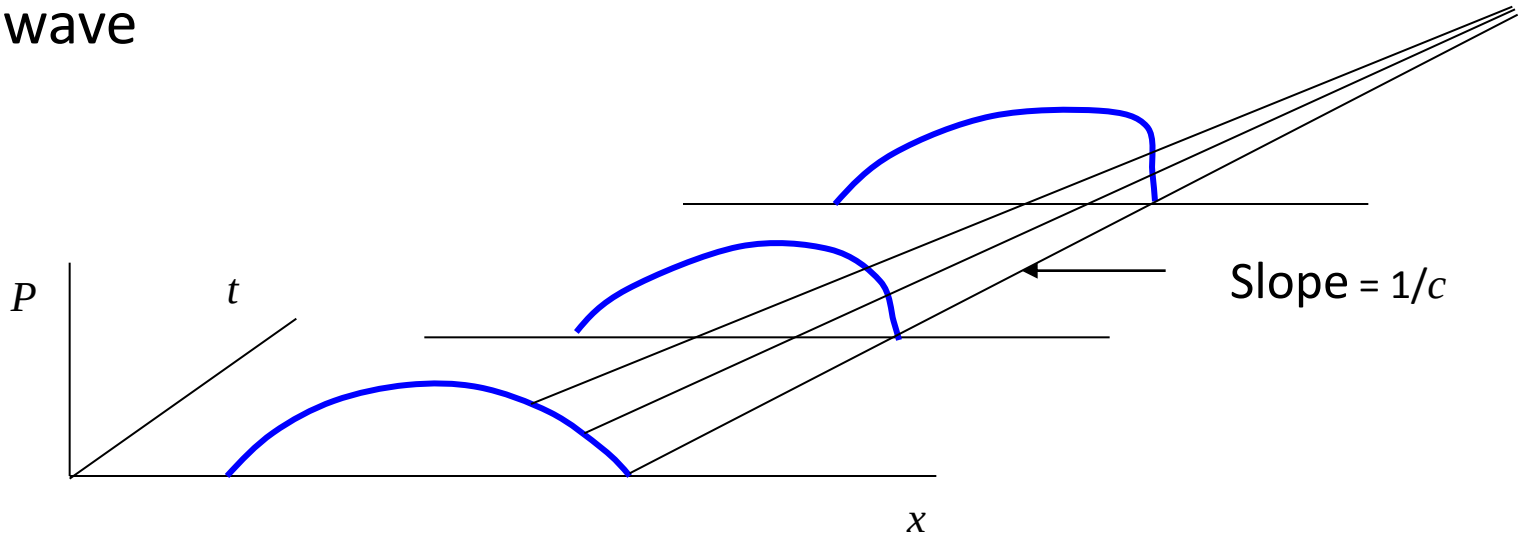
Content

- Shock waves
- One-dimension detonation theory
- Real detonations
- Deflagration-to-detonation transition
- Flame acceleration

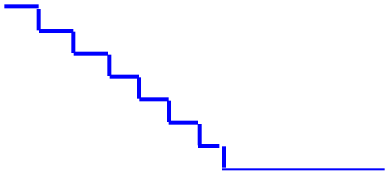
Shock waves

Formation of a Shock Waves

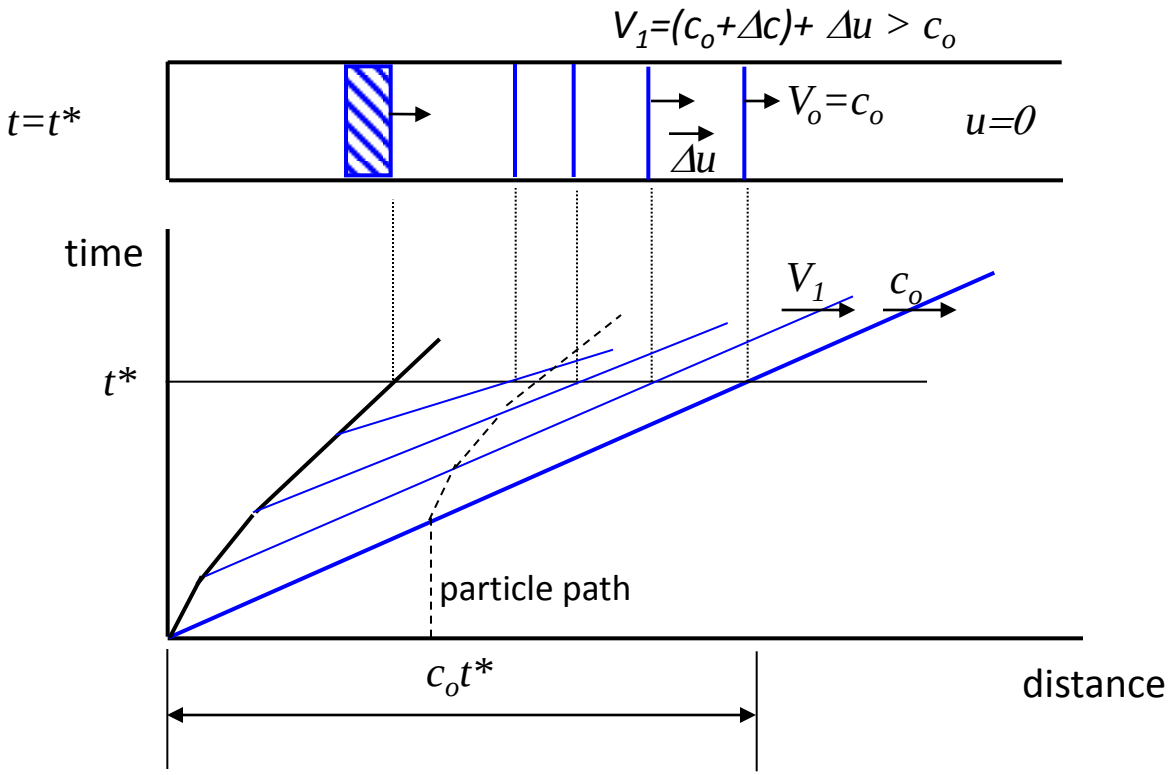
Compression waves of finite amplitude always steepen to form a shock wave



Compression wave can be generated by a series of infinitesimally small steps in piston velocity



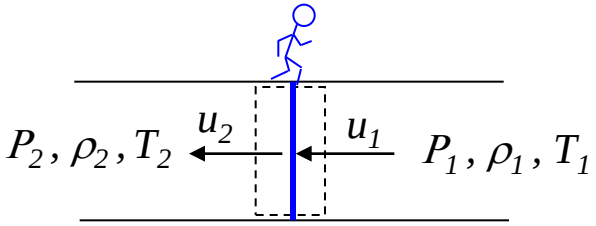
Formation of a Shock Waves



Since Δc and $\Delta u > 0$ the second wave moves faster than the first wave, eventually the two merge forming a stronger wave

As the waves merge the pressure and temperature rise becomes large and the compression can no longer be considered isentropic → this finite amplitude wave is called a **shock wave**.

Steady Control Volume Approach



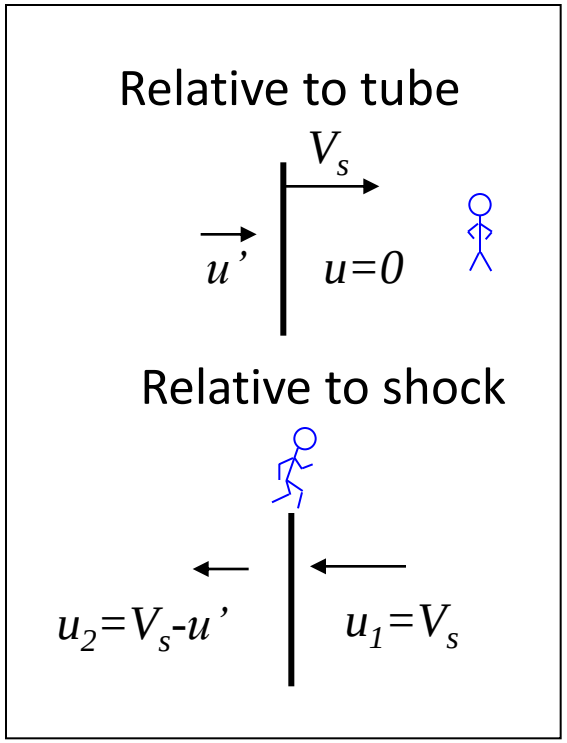
Mass: $$\rho_1 u_1 = \rho_2 u_2 \qquad (1)$$

Momentum: $$P_2 - P_1 = \rho_1 u_1 (u_1 - u_2) \qquad (2)$$

Energy: $$\frac{u_1^2}{2} + h_1 = \frac{u_2^2}{2} + h_2$$

For perfect gas: $$h = c_p T \qquad P = \rho R T$$

$$\frac{u_1^2}{2} + c_{p_1} T_1 = \frac{u_2^2}{2} + c_{p_2} T_2 \qquad (3)$$



Note the stagnation temperature does not change across a shock wave

Combine (1) and (2) to get the Rayleigh equation

$$P_2 - P_1 = (\rho_1 u_1)^2 \left(\frac{1}{\rho_1} - \frac{1}{\rho_2} \right)$$

Note: u_1 is the shock velocity and $\rho_1 u_1$ is the mass flux through the shock wave

$$V_s = \sqrt{\frac{P_1}{\rho_1} \frac{\left(P_2 / P_1 - 1 \right)}{\left(1 - \rho_1 / \rho_2 \right)}}$$

For V_s to be real:

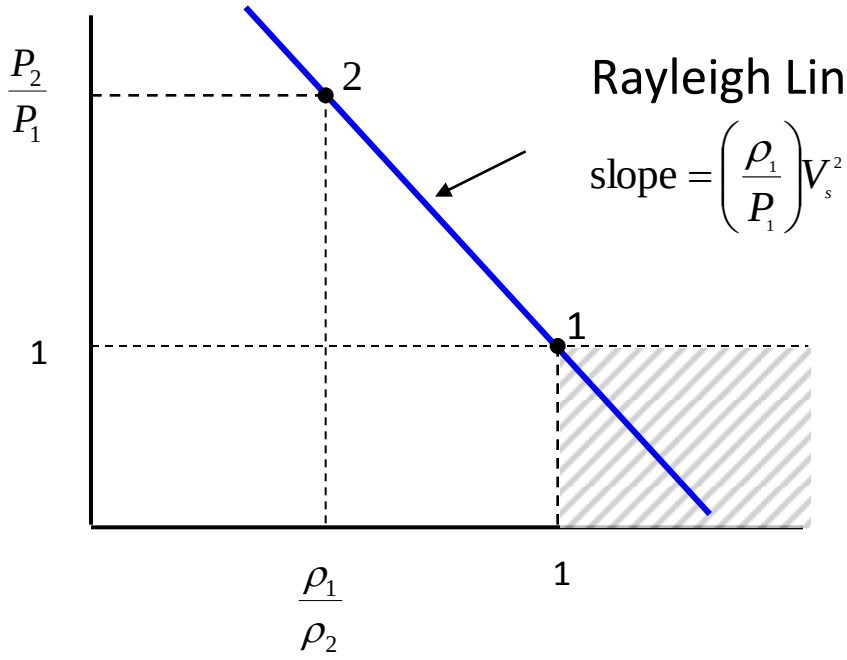
$$P_2 / P_1 > 1 \ , \ \rho_1 / \rho_2 < 1 \quad \text{compression shock}$$

$$P_2 / P_1 < 1 \ , \ \rho_1 / \rho_2 > 1 \quad \text{expansion shock}$$

Rearranging the Rayleigh Equation gives:

$$\frac{P_2}{P_1} = -\left(\frac{\rho_1 V_s^2}{P_1}\right)\frac{\rho_1}{\rho_2} + \left(1 + \frac{\rho_1 V_s^2}{P_1}\right)$$

This expression represents a straight line on a plot of $\frac{P_2}{P_1}$ vs $\frac{\rho_1}{\rho_2}$



Expansion shock
(not possible 2nd Law)

$$P_2/P_1 < 1 \;,\; \rho_1/\rho_2 > 1$$

Combining (2) and (3) yields the Rankine-Hugoniot equation that represents the locus of all possible downstream states:

$$h_2 - h_1 = \frac{1}{2}(P_2 - P_1)\left(\frac{1}{\rho_1} + \frac{1}{\rho_2}\right)$$

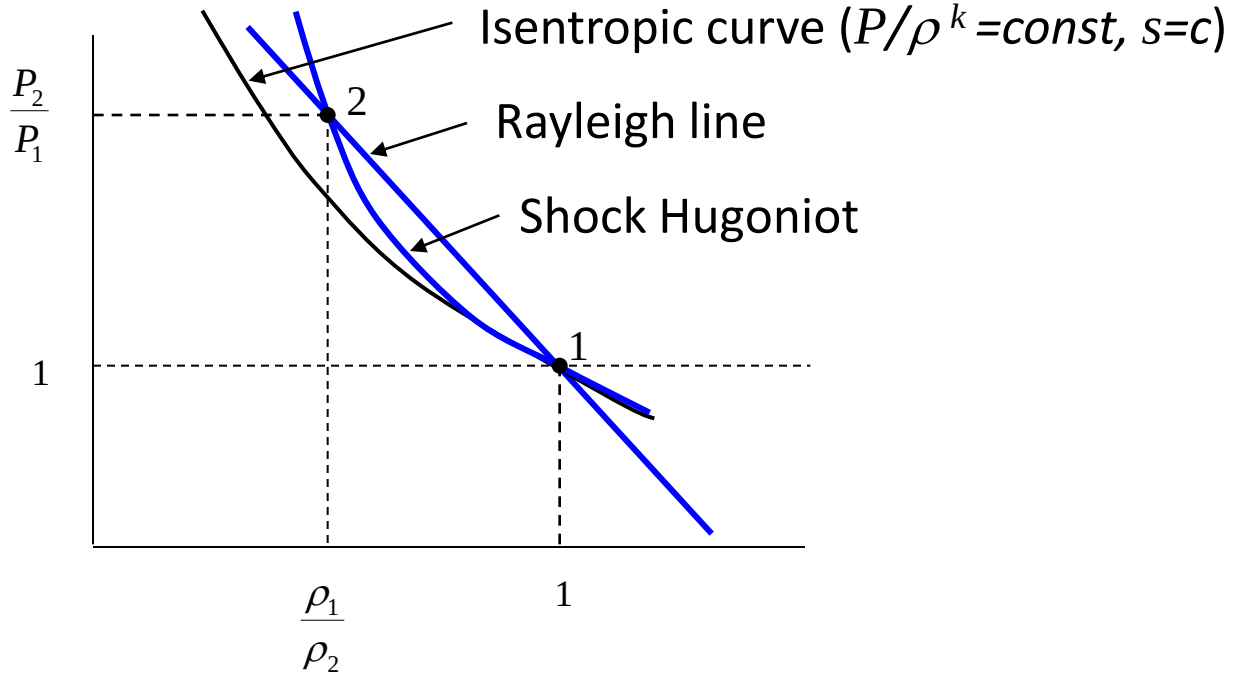
For perfect gas: $h = c_p T = \frac{kR}{k-1}T = \frac{kP}{\rho(k-1)}$

$\times \frac{\rho_1}{P_1}$ $\qquad \left(\frac{k_2}{k_2 - 1}\right)\frac{P_2}{\rho_2} - \left(\frac{k_1}{k_1 - 1}\right)\frac{P_1}{\rho_1} = \frac{1}{2}(P_2 - P_1)\left(\frac{1}{\rho_1} + \frac{1}{\rho_2}\right)$

If it is assumed that there is no change in the specific heat ($k_1 = k_2 = k$):

$$\left(\frac{2k}{k-1}\right)\left(\frac{P_2}{P_1}\frac{\rho_1}{\rho_2} - 1\right) = \left(\frac{P_2}{P_1} - 1\right)\left(1 + \frac{\rho_1}{\rho_2}\right) \longrightarrow \frac{P_2}{P_1} = \frac{\frac{k+1}{k-1} - \left(\frac{\rho_1}{\rho_2}\right)}{\frac{k+1}{k-1}\left(\frac{\rho_1}{\rho_2}\right) - 1}$$

The shock state must lie both on Rayleigh line and Hugoniot curve



Shock compression results in higher pressures than isentropic compression at the expense of increased entropy and reduced stagnation pressure.

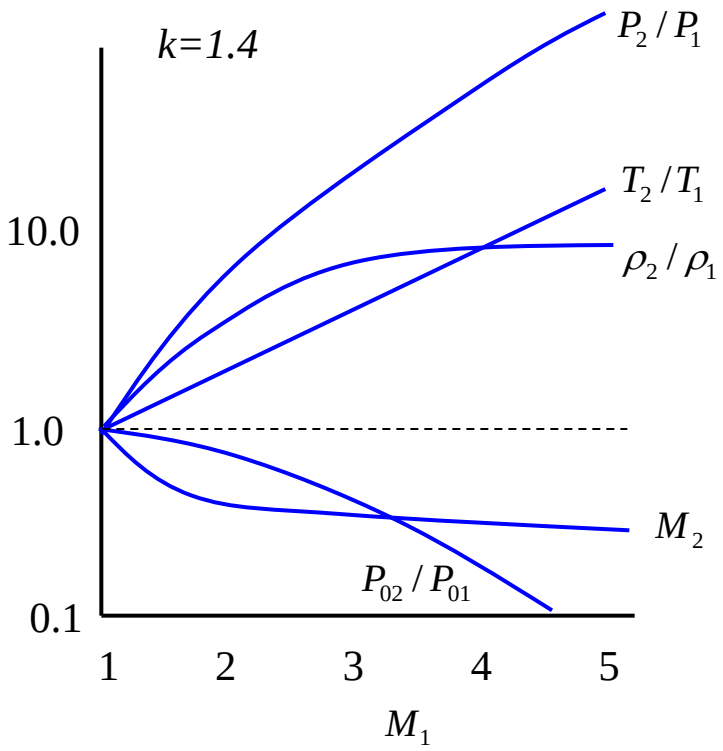
Shock jump relations in terms of the shock Mach number ($M_1 = V_s/c_o$) are typically tabulated for k=1.4

$$\frac{\rho_2}{\rho_1} = \frac{(k+1)M_1^2}{2+(k-1)M_1^2}$$

$$\frac{P_2}{P_1} = \frac{2kM_1^2-(k-1)}{(k+1)}$$

$$\frac{T_2}{T_1} = \frac{P_2}{P_1}\left(\frac{\rho_1}{\rho_2}\right)$$

$$M_2^2 = \frac{(k-1)M_1^2+2}{2kM_1^2+(k-1)}$$



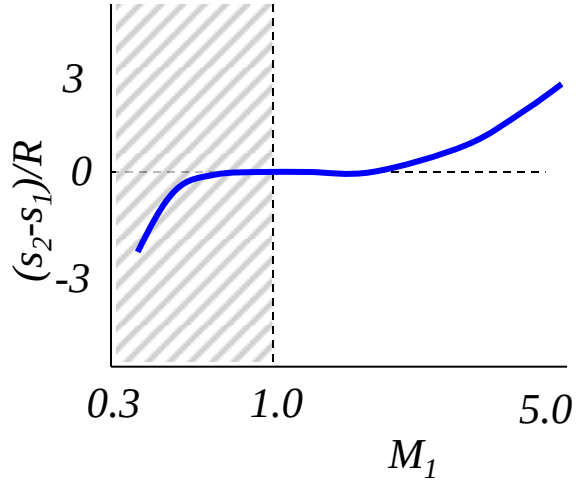
Since $1 < k < 2$ and $M_1 \geq 0$, it follows that $M_2 \leq 1$ → the flow down-stream of a normal shock is always subsonic relative to the shock

The entropy change across a shock wave is given by:

$$s_2 - s_1 = c_p \ln\left(\frac{T_2}{T_1}\right) - R\ln\left(\frac{P_2}{P_1}\right)$$

substituting the relations just developed provides:

$$\frac{s_2 - s_1}{R} = \ln\left\{\left[\frac{2k}{k+1}(M_1^2 - 1) + 1\right]^{\frac{1}{k-1}}\left[\frac{(k+1)M_1^2}{2 + (k-1)M_1^2}\right]^{\frac{-k}{k-1}}\right\}$$



Second Law requires that s_2-$s_1 \geq 0$, only satisfied for $M_1 \geq 0$

Entropy change across the shock wave is ($k_1=k_2=k$):

$$s_2 - s_1 = c_p \ln\left(\frac{T_2}{T_1}\right) - R\ln\left(\frac{P_2}{P_1}\right)$$

Substituting

$$\frac{s_2 - s_1}{R} = \ln\left\{\left(\frac{P_2}{P_1}\right)^{\frac{1}{k-1}}\left[\frac{\left(\frac{k+1}{k-1}\right)\frac{P_2}{P_1}+1}{\left(\frac{k+1}{k-1}\right)+\frac{P_2}{P_1}}\right]^{\frac{-k}{k-1}}\right\}$$

Second Law requires that s_2-$s_1 \geq 0$,
only satisfied if $P_2 \geq P_1$ → expansion shock ($P_2<P_1$) not possible

Can also derive an expression for the ratio of stagnation pressures

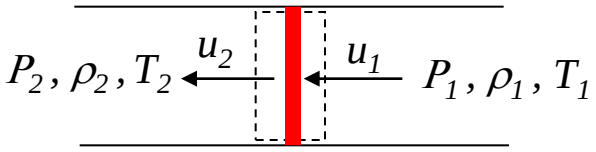
$$\frac{P_{02}}{P_{01}} = \exp\left[-\left(\frac{s_2 - s_1}{R}\right)\right]$$

Since $s_2 > s_1$ the stagnation pressure decreases across shock wave

1-D Detonation waves

1-D Combustion Wave Analysis

Steady-state combustion occurs within the control volume and equilibrium is achieved at state 2



$$\rho_1 u_1 = \rho_2 u_2$$

$$P_2 - P_1 = \rho_1 u_1 (u_1 - u_2)$$

$$\frac{u_1^2}{2} + h_1 = \frac{u_2^2}{2} + h_2$$

For perfect gas $P = \rho RT$ and $h = h_f^o + c_p (T - T^o)$ where $T^o = 0K$

Energy equation $\frac{u_1^2}{2} + c_{p_1} T_1 + q = \frac{u_2^2}{2} + c_{p_2} T_2$

where $q = h_{f_1}^o + h_{f_2}^o$
chemical energy per unit mass

Have 5 unkowns (P_2,ρ_2,T_2, u_2, u_1) and only 4 equations

Combining conservation of mass and momentum yields the Rayleigh eqn

$$\frac{P_2}{P_1} = -\left(\frac{\rho_1 u_1^2}{P_1}\right)\frac{\rho_1}{\rho_2} + \left(1 + \frac{\rho_1 u_1^2}{P_1}\right)$$

Combining conservation of momentum and energy yields the Hugoniot eqn

$$c_p T_2 - (c_p T_1 + q) = \frac{1}{2}(P_2 - P_1)\left(\frac{1}{\rho_1} + \frac{1}{\rho_2}\right)$$

$$\times \frac{\rho_1}{P_1} \qquad \left(\frac{k_2}{k_2 - 1}\right)\frac{P_2}{\rho_2} - \left(\frac{k_1}{k_1 - 1}\right)\frac{P_1}{\rho_1} - q = \frac{1}{2}(P_2 - P_1)\left(\frac{1}{\rho_1} + \frac{1}{\rho_2}\right)$$

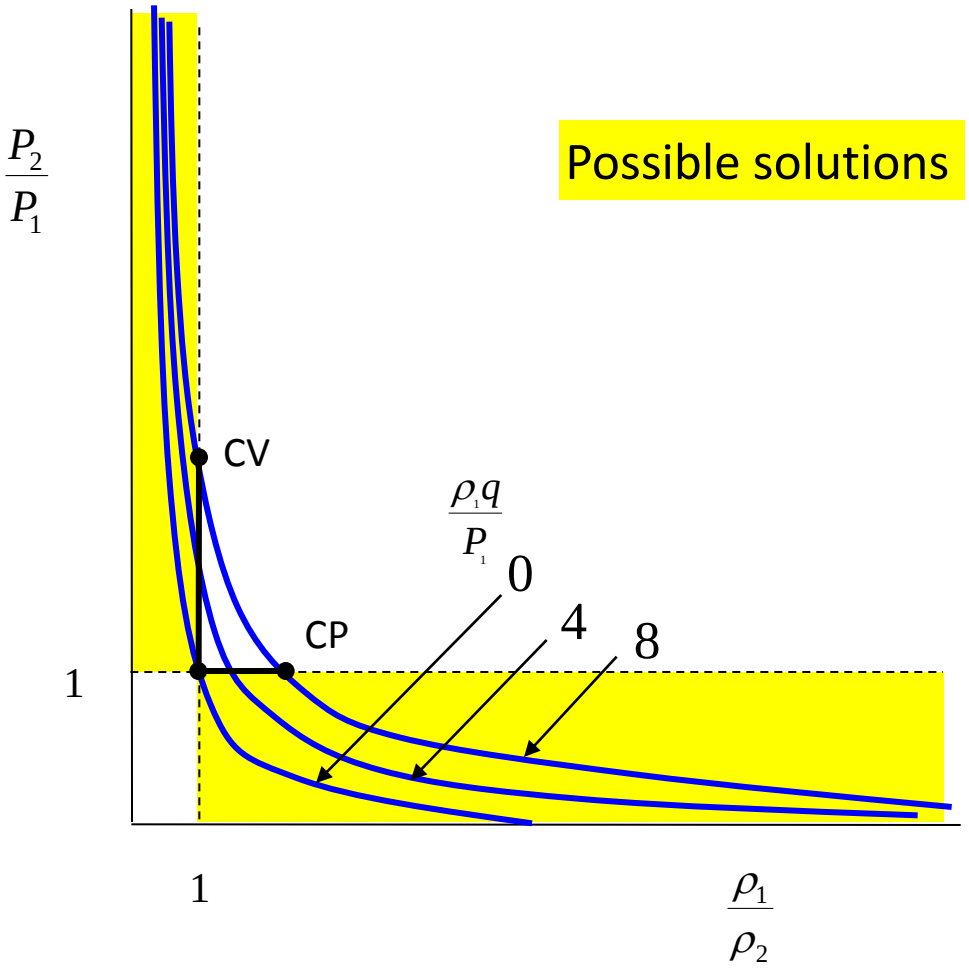
If it is assumed that there is no change in the specific heat ($k_1 = k_2 = k$):

$$\left(\frac{k}{k-1}\right)\left[\left(\frac{\rho_1}{\rho_2}\right)\left(\frac{P_2}{P_1}\right) - 1\right] - \frac{\rho_1 q}{P_1} = \frac{1}{2}\left(\frac{P_2}{P_1} - 1\right)\left(1 + \frac{\rho_1}{\rho_2}\right)$$

$q = 0$ gives the shock Hugoniot

where $$\frac{\rho_1 q}{P_1} = \frac{(k-1)q}{c_v T_1} = \frac{\text{chemical energy released}}{\text{initial sensible energy content}}$$

Hugoniot Curves for Combustion Waves



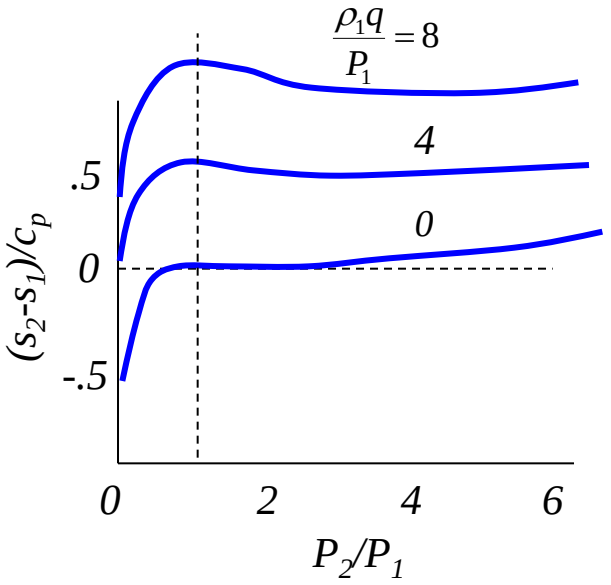
The Hugoniot equation gives all possible end states for given heat release q including constant volume and pressure process end states

Entropy Change Across Combustion Wave

$$\frac{s_2 - s_1}{c_p} = \ln\frac{T_2}{T_1} - \frac{R}{c_p}\ln\frac{P_2}{P_1}$$

$$= \ln\frac{T_2}{T_1} - \frac{(k-1)}{k}\ln\frac{P_2}{P_1}$$

$$= \ln\left[\left(\frac{P_2}{P_1}\right)^{1/k}\left(\frac{\rho_1}{\rho_2}\right)\right]$$



Second Law requires that $s_2\text{-}s_1 \geq 0$,

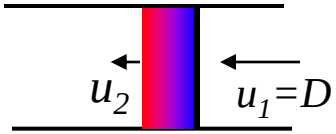
For $q = 0$ (shock wave) only satisfied for $P_2/P_1 \geq 1$, no expansion shocks

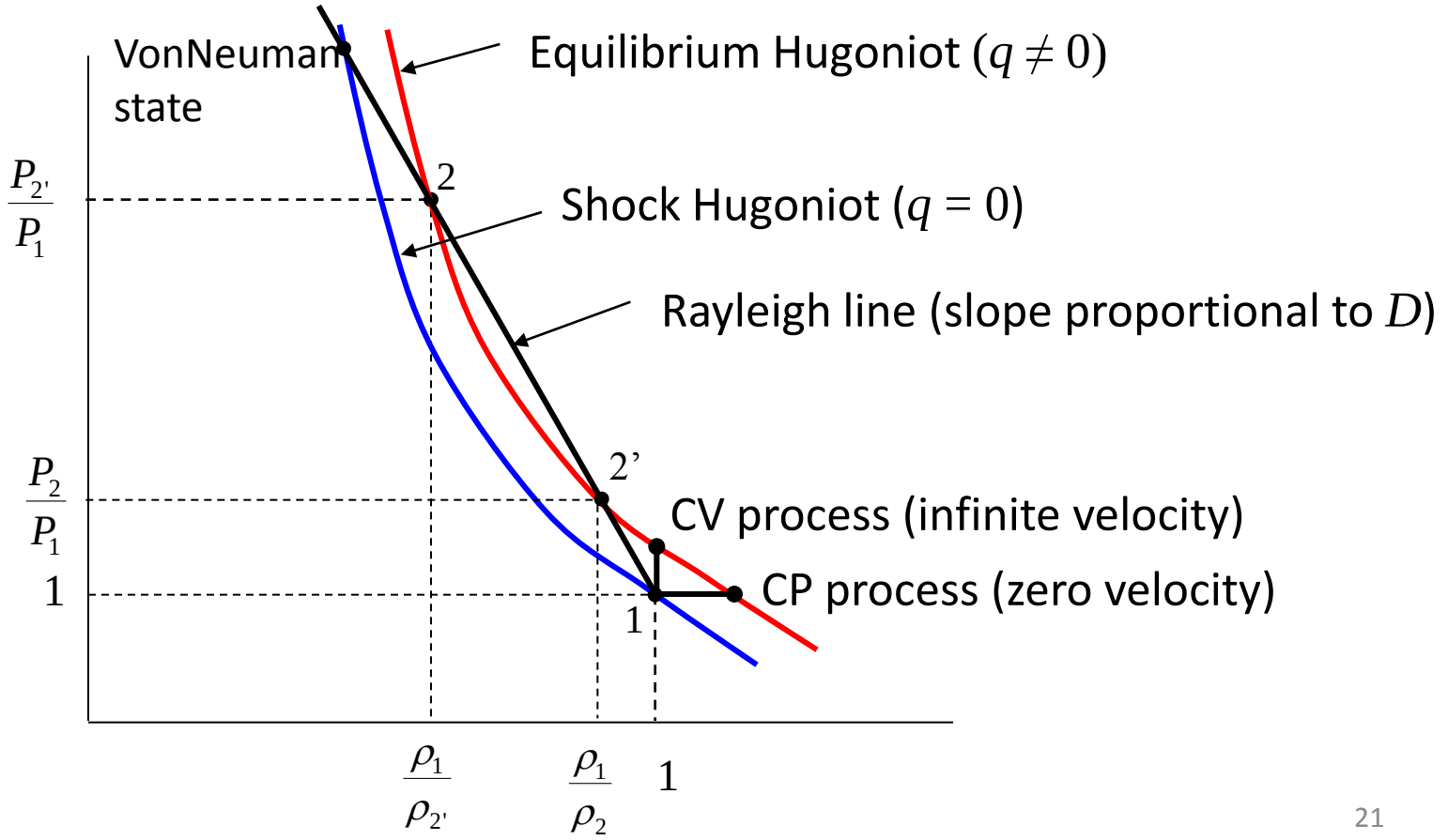
For $q > 0$ can have expansive and compressive combustion waves

- $P_2/P_1 > 1$, $\rho_1/\rho_2 < 1$ detonation waves
- $P_2/P_1 < 1$, $\rho_1/\rho_2 > 1$ deflagration waves

Classical 1-D Detonation Wave

Detonation process consists of shock compression followed by energy release, equilibrium achieved
at the end of the reaction zone



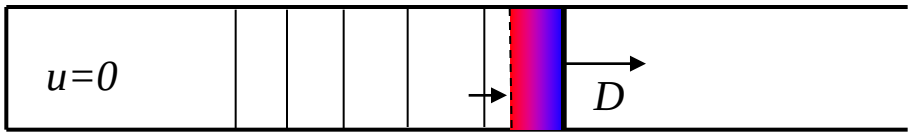


Classical 1-D detonation structure

The Rayleigh line intersects the Hugoniot curve at two points so there are two possible end states for a given detonation velocity:

Strong (overdriven) detonation wave (state 2):

- flow is subsonic relative to wave ($u_2 < c_2$)
- solution is unstable because expansion waves catch up to the front and weaken the lead shock wave

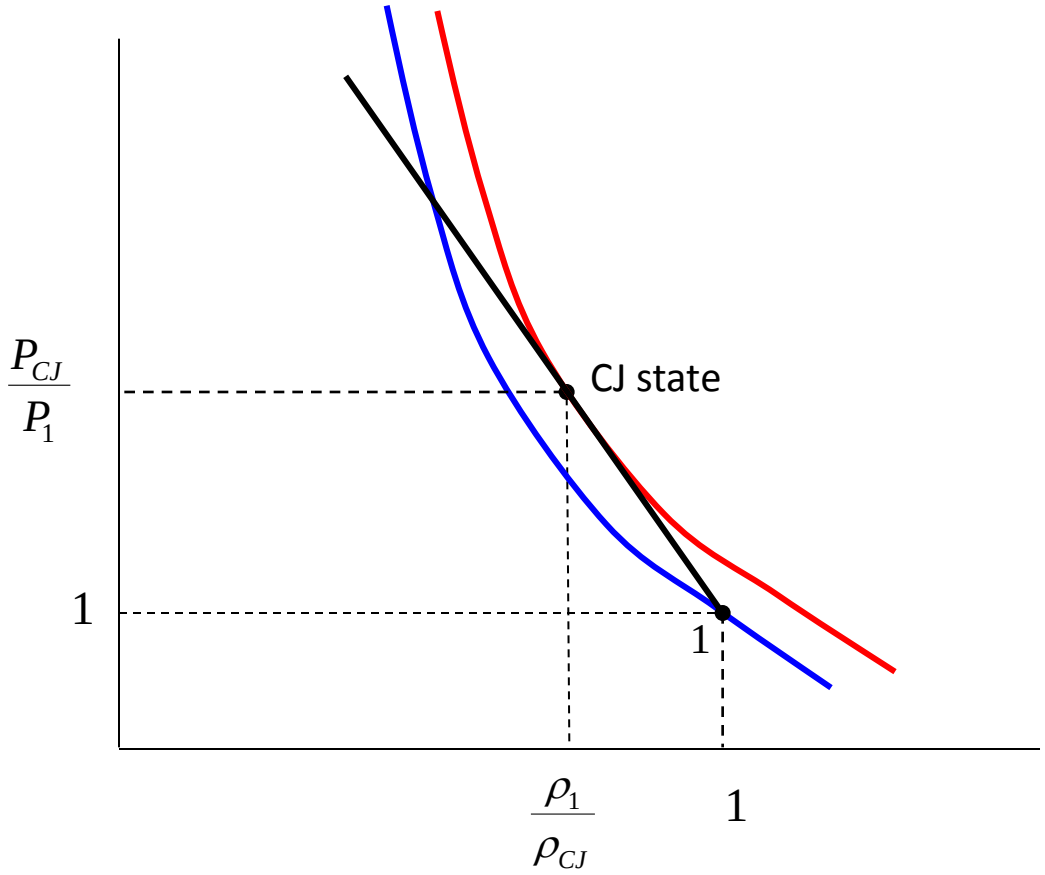


Weak detonation (state 2'):

- flow is supersonic relative to wave ($u_2 > c_2$)
- solution not possible because all of the energy is released at state 2, also entropy drops from state 2 to 2' violates 2nd Law

Classical 1-D detonation structure

Unique solution corresponds to the point where the Rayleigh Line is tangent to the Hugoniot curve, the Chapman-Jouget (CJ) state



CJ Detonation State

At the time of Chapman 1899 it was believed that energy release in a detonation occurred instantaneously, i.e., no reaction zone present

Chapman stated that since the Rayleigh line going through the CJ state represents the minimum velocity detonation it must be stable

This was supported by the fact that the measured detonation velocity agreed very well with the CJ theory, i.e, the measured detonation velocity depends on the energy released q and not the rate of chemical reaction.

The CJ state also represents the downstream state that has a minimum entropy rise across the wave.

Can use this to obtain jump relations across the detonation wave.

$$\frac{s_2 - s_1}{c_p} = \frac{1}{k}\ln\left(\frac{P_2}{P_1}\right) + \ln\left(\frac{\rho_1}{\rho_2}\right)$$

The minimum is determined as follows:

$$\frac{d\left(s/c_p\right)}{d\left(\rho_1/\rho_2\right)} = \frac{1}{k\left(P_2/P_1\right)}\frac{d\left(P_2/P_1\right)}{d\left(\rho_1/\rho_2\right)} + \frac{1}{\left(\rho_1/\rho_2\right)} = 0$$

Differentiating the Hugoniot equation to get $\frac{d\left(P_2/P_1\right)}{d\left(\rho_1/\rho_2\right)}$ yields:

$$\left.\frac{\rho_1}{\rho_2}\right|_{\min s} = \frac{k\left(P_2/P_1\right)}{\left(k+1\right)\left(P_2/P_1\right)-1}$$

From the Rayleigh equation and $\rho_1 u_1 = \rho_2 u_2$

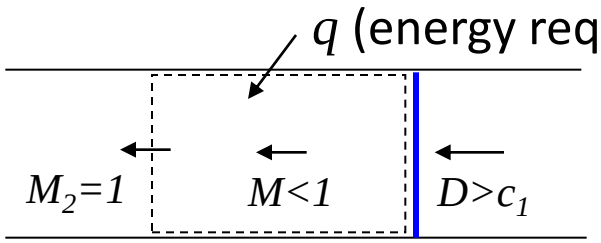
$$u_2^2 = \left(\frac{P_1 \rho_1}{\rho_2^2}\right)\frac{P_2/P_1 - 1}{1 - \rho_1/\rho_2}$$

$$M_2^2 = \frac{\rho_1/\rho_2}{k(P_2/P_1)}\left(\frac{P_2/P_1 - 1}{1 - \rho_1/\rho_2}\right)$$

Substituting $\left.\frac{\rho_1}{\rho_2}\right|_{\min s} = \frac{k(P_2/P_1)}{(k+1)(P_2/P_1) - 1}$ yields $M_2 = 1$

At the CJ state the flow is choked ($u_2 = c_2$) at the end of reaction zone
Rayleigh Line is tangent to isentrope as well as Hugoniot curve

Jouget (1917) pointed out that because of this disturbances from behind cannot enter the reaction zone and thus this is a stable solution



CJ Velocity

Solve for the density ratio by equating the pressure ratio in the Rayleigh and Hugoniot equations:

$$\frac{\rho_1}{\rho_2} = \frac{1}{k+1}\left(k + \frac{1}{M_1^2}\right) \pm \sqrt{\left(\frac{1}{M_1^2} - 1\right)^2 - \frac{\left(k^2-1\right)2\bar{q}}{M_1^2}} \qquad \text{where} \quad \bar{q} = \frac{q}{c_1^2}$$

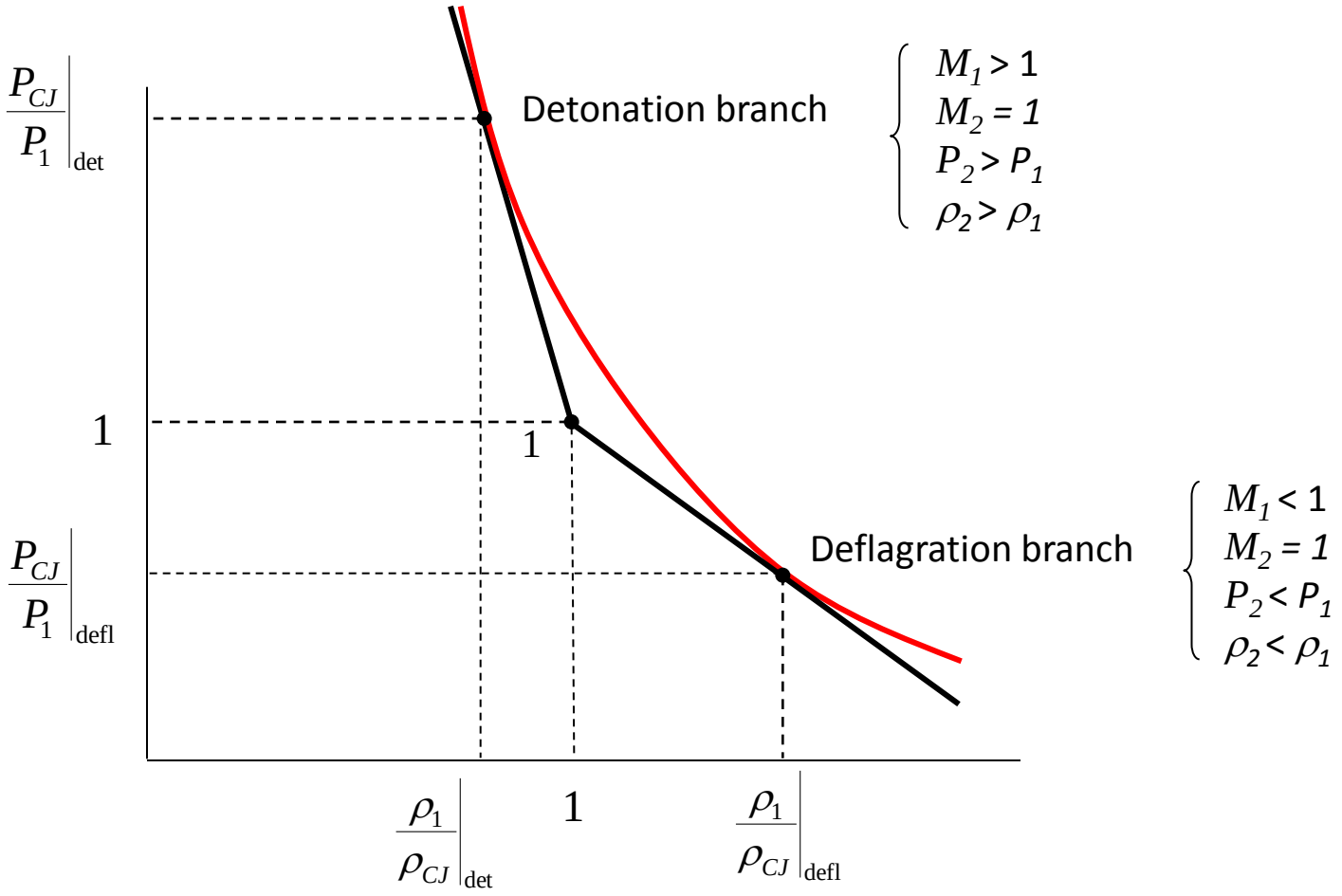
Note for a given front velocity M_1 there are two possible solutions:
(+) for weak solution and (–) for strong solution

Unique solution obtained when square root term is set to zero (CJ state)

$$\left(\frac{1}{M_{CJ}^2} - 1\right)^2 - \frac{\left(k^2-1\right)2\bar{q}}{M_{CJ}^2} = 0$$

$$\frac{1}{M_{CJ}^2} = \left(k^2-1\right)\bar{q}\left\{1 + \frac{1}{\left(k^2-1\right)\bar{q}} \pm \sqrt{1 + \frac{2}{\left(k^2-1\right)\bar{q}}}\right\}$$

Again there are two solutions, (+) for tangency at upper detonation branch and (-) for tangency at lower deflagration branch.



Approximate CJ state relations

Note, $M_{CJ} \approx 8, \bar{q} \approx 80$ so $(1/M_{CJ})^2 << 1$

$$\left(\frac{1}{M_{CJ}^2} - 1\right)^2 - \frac{(k^2-1)2\bar{q}}{M_{CJ}^2} = 1 - \frac{(k^2-1)2\bar{q}}{M_1^2} = 0$$

$$M_{CJ}^2 \approx (k^2-1)2\bar{q}$$

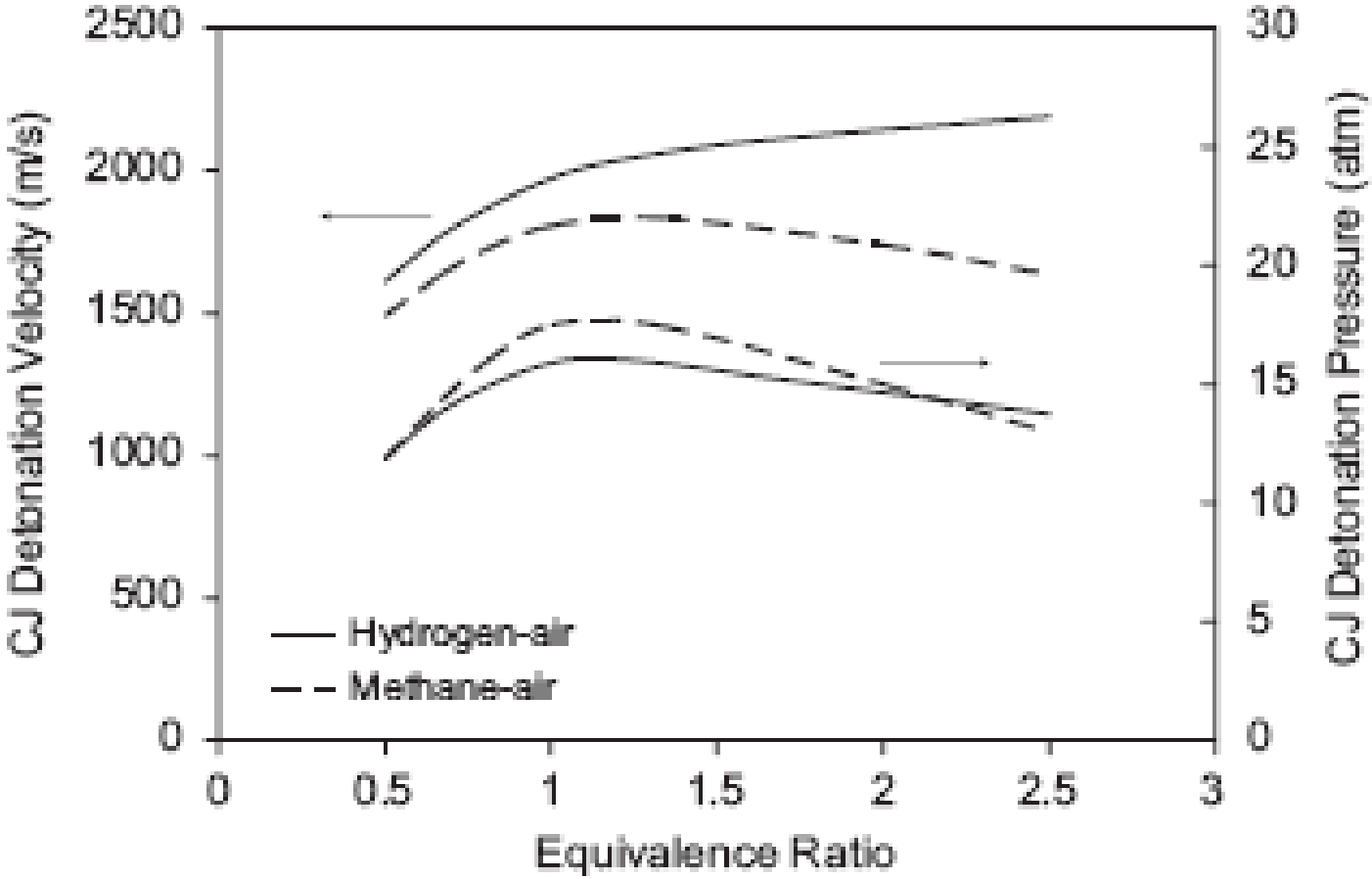
$$u_{CJ} \approx \sqrt{(k^2-1)2q} \approx 2000 m/s \quad (k=1.2, \bar{q}=80)$$

Therefore, the detonation velocity only depends on the specific energy q

For strong detonation $P_2/P_1 >> 1$,

$$\left.\frac{\rho_1}{\rho_2}\right|_{\min s} = \frac{\rho_1}{\rho_{CJ}} = \frac{k(P_2/P_1)}{(k+1)(P_2/P_1)-1} \rightarrow \frac{k}{k+1}$$

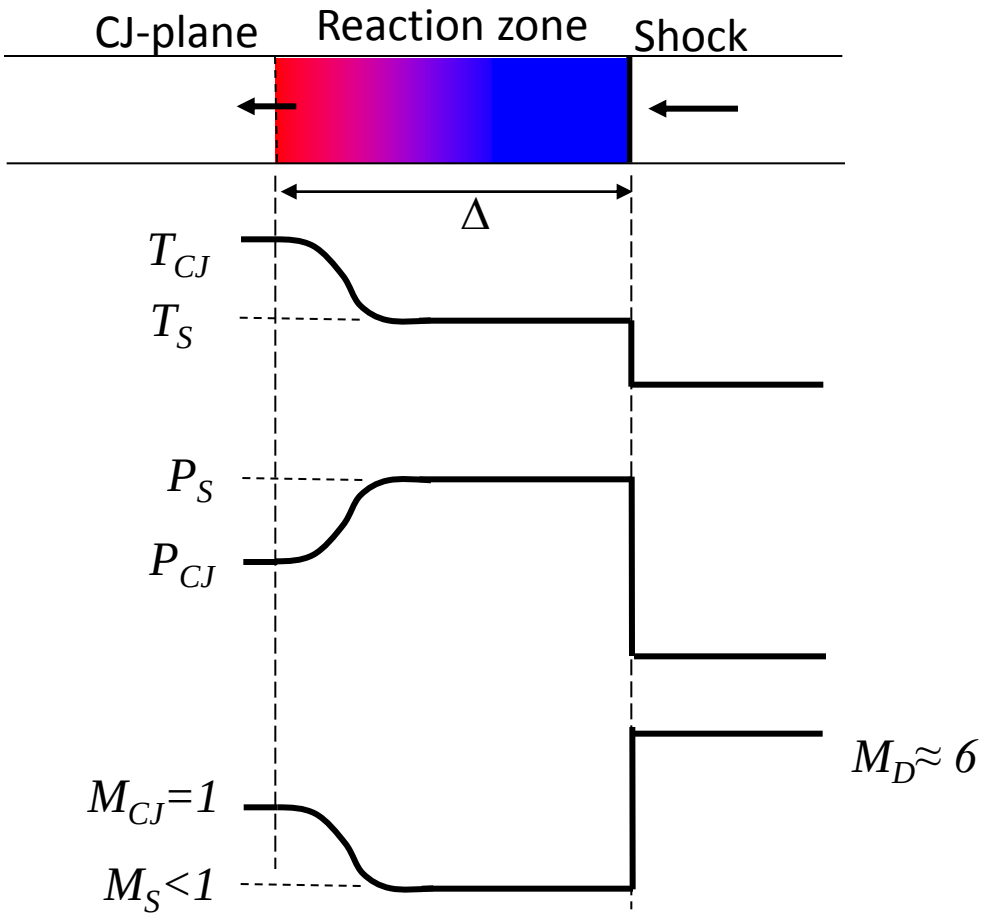
$$\frac{u_2}{u_{CJ}} = \frac{P_2}{\rho_1 u_{CJ}^2} \rightarrow \frac{1}{k+1}$$



Can calculate CJ detonation properties using chemical equilibrium codes such as STANJAN, GASEQ

ZND Detonation Model

1940's Zeldovich, vonNeuman and Doring independently developed the idea that a detonation wave consists of a shock wave followed by an inviscid reaction zone terminating at a sonic CJ plane (flow is steady)



Detonation Velocity Deficit

Experimentally measured detonation velocity is typically 1-3% below theoretical CJ value, the velocity deficit is inversely proportional to the initial pressure and the tube diameter

Zeldovich proposed that the deficit is due to momentum and heat losses within the reaction zone

$$\frac{d}{dx}(\rho u) = 0$$

$$\frac{d}{dx}\left(P + \rho u^2\right) = \frac{2\tau_w}{R}$$

$$\frac{d}{dx}\left(\rho u\left(h + \rho u^2\right)\right) + Q\frac{d\alpha}{dx} = -\frac{2q_c}{R} + D\frac{2\tau_w}{R}$$

friction factor ↓

τ_w: wall shear stress (= $f\rho u_\Delta^2$)

q_c: wall heat flux

α: reaction progress variable

Zeldovich theory predicts that velocity deficit should be proportional to the wall drag divided by the momentum flux: drag ~ Δ/R

Position of CJ Plane

Consider a simple reaction (R→P):

$h = h(P, \rho, \alpha)$ also $P = \rho RT$ *where* α *is the reaction progress*

$$dh = \left(\frac{\partial h}{\partial P}\right)_{\rho,\alpha} dP + \left(\frac{\partial h}{\partial \rho}\right)_{P,\alpha} d\rho + \left(\frac{\partial h}{\partial \alpha}\right)_{\rho,P} d\alpha$$

Combining with the conservation equations for diverging channel

$$\frac{1}{\rho} dP = \frac{\left(\frac{\partial h}{\partial \alpha}\right) d\alpha - \rho\left(\frac{\partial h}{\partial \rho}\right) d(\ln A)}{1 - \rho\left\{\left(\frac{\partial h}{\partial P}\right) + \frac{1}{u^2}\left(\frac{\partial h}{\partial \rho}\right)\right\}}$$

Can show that the denominator becomes zero when $u^2 = \left(\frac{dP}{d\rho}\right)_{s,\alpha}$

but $\left(\frac{dP}{d\rho}\right)_{s,\alpha} = c^2$, denominator equals zero when $u = c$ (CJ condition)

For the pressure gradient at the sonic plane ($u=c$) to be finite, the numerator must approach zero

Therefore, the CJ plane is located where

$$\left(\frac{\partial h}{\partial \alpha}\right) d\alpha = \rho \left(\frac{\partial h}{\partial \rho}\right) d \ln A$$

For a constant area duct $d(lnA)=0$ the CJ plane is located where $\frac{dh}{d\alpha} = 0$
this is the point where chemical equilibrium is reached

Note, theoretically equilibrium is approached asymptotically so it is difficult to identify the CJ plane

With flow divergence sonic plane reached before chemical equilibrium so energy deposited after choking is lost since it can't feed into the reaction
→ smaller q yields smaller D

Real detonation waves

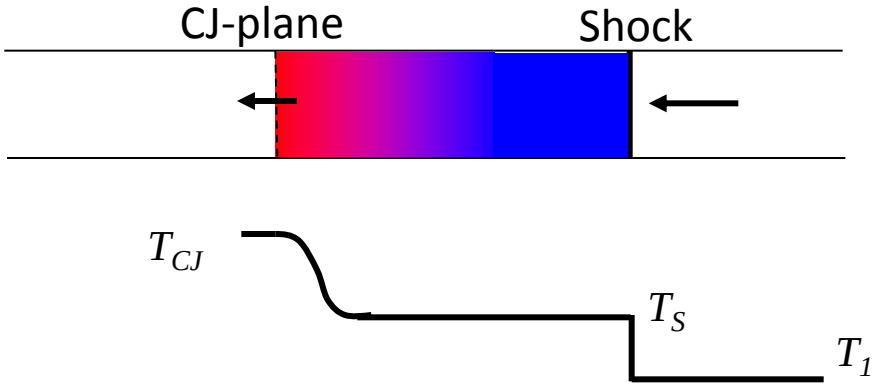
1-D Steady Detonation Wave Structure

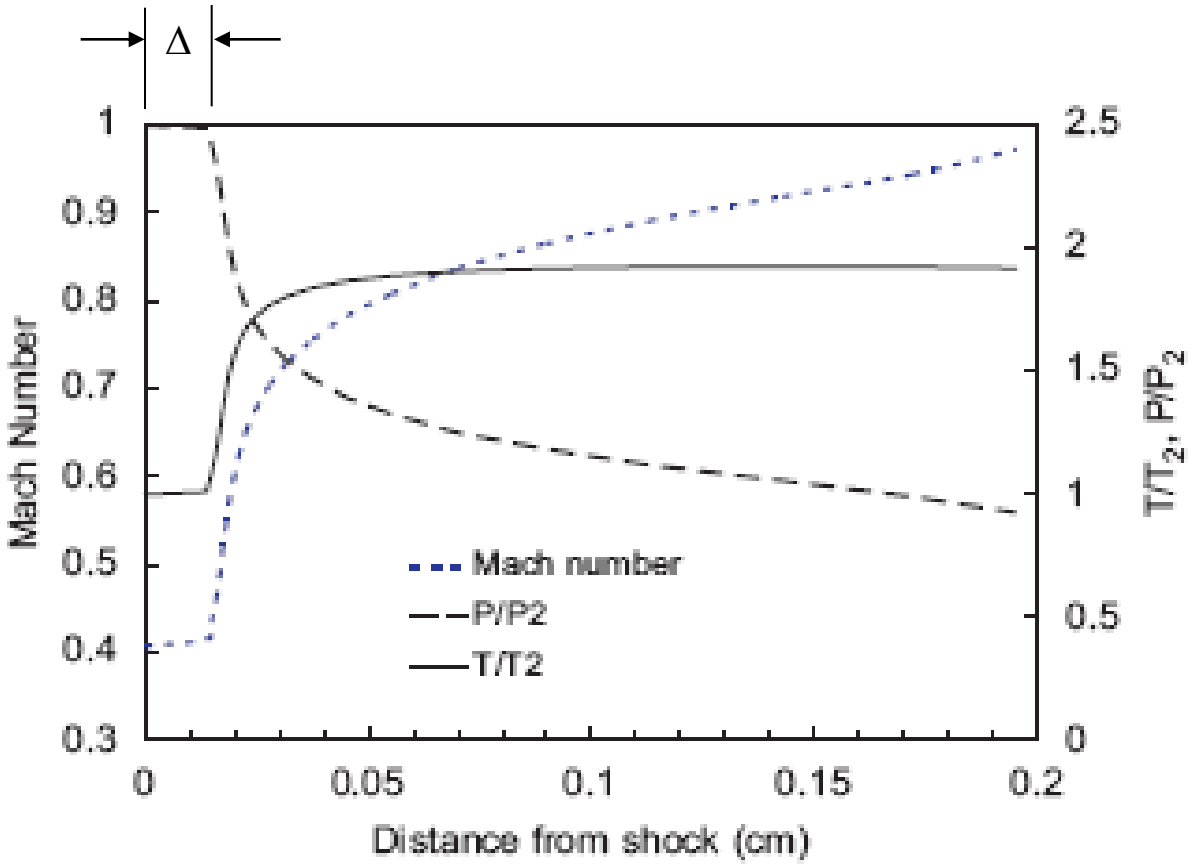
Hugoniot analysis assumes steady-state and predicts detonation velocity and change in properties from initial state to the equilibrium CJ state. No knowledge of the details of the chemistry is required

In order to model the reaction zone details an additional equation for the change in species with time is required:

$$\frac{d}{dt}(\rho\alpha) = -k\rho\alpha \exp\left(-\frac{E}{RT}\right) \qquad \alpha \text{ is the reactant mass fraction}$$

Knowing the post shock state can integrate the steady conservation and above equation get change in properties through the reaction zone



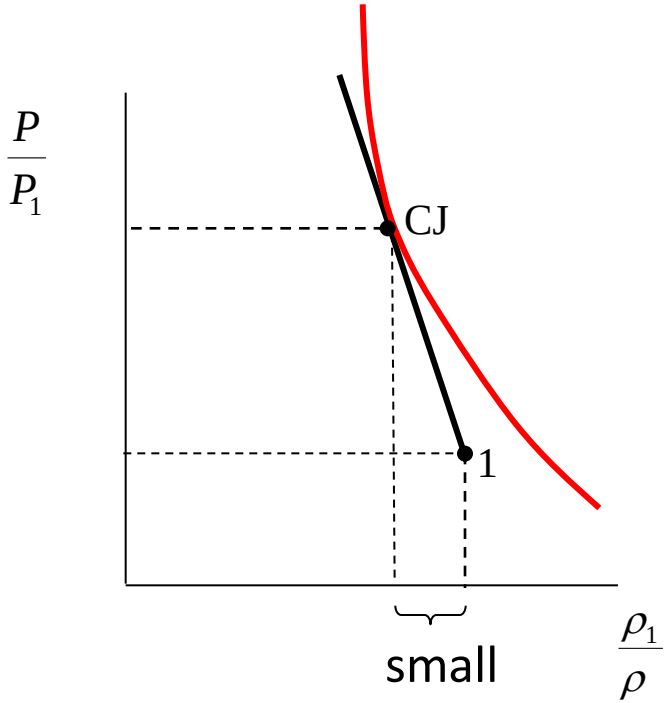


Since the post shock flow Mach number asymptotes to unity use point of maximum heat release (induction length) to define the detonation reaction zone length, Δ.

Steady Detonation Reaction Zone Length

Approximation: assume constant volume combustion in reaction zone, don't need to consider conservation of momentum. Solve the transient energy equation with reaction equation to get temperature vs time and get t_M corresponding to $dT/dt_{max} \rightarrow \Delta = u_{sh} t_M$

Validity of this approximation based on steepness of the Rayleigh Line



1-D Transient Detonation Wave

Erpenbeck (1960s) showed using perturbation theory that the steady ZND detonation wave structure is unstable to infinitesimal longitudinal perturbations

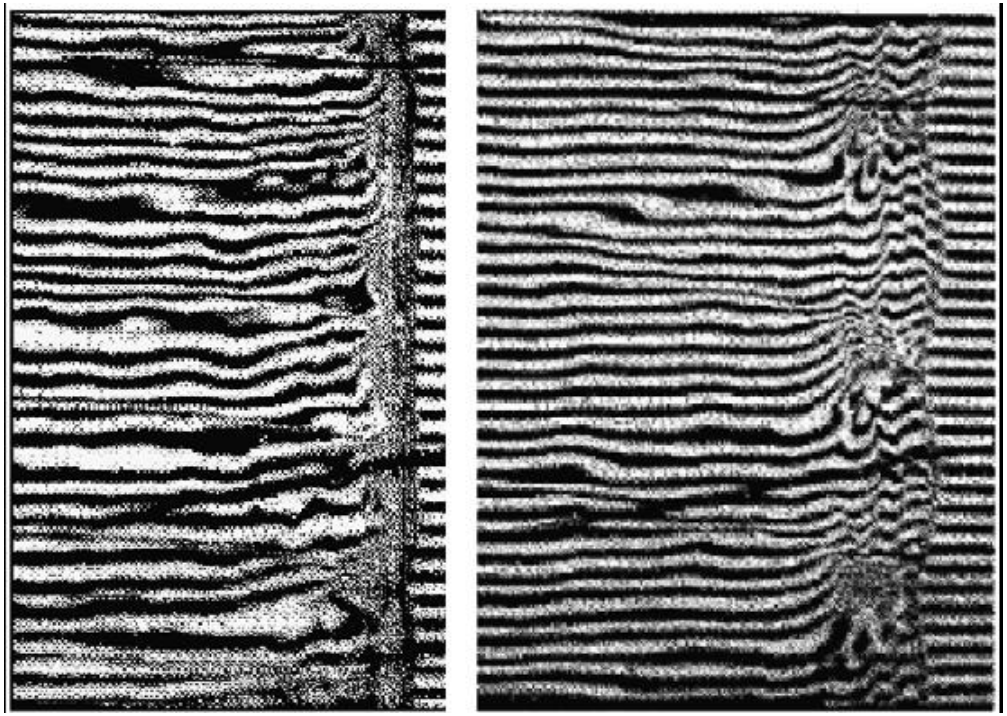
Later Ficket and Woods calculated the time-evolution of reaction zone using the transient equations and a simple one-step reaction

Parameters in the study were detonation overdrive ($f=D/D_{CJ}$) and the reduced activation energy, (E_a/RT_1). For the study Q/RT_1=50 and k=1.2

At time zero the piston is moved at a velocity greater than the CJ equilibrium flow velocity producing an overdriven detonation wave. A short time later the piston velocity is reduced to u_{CJ}

Multi-dimensional Detonation Wave Structure

White's (1961) interferograms showed that the detonation wave structure is transient and multi-dimensional.



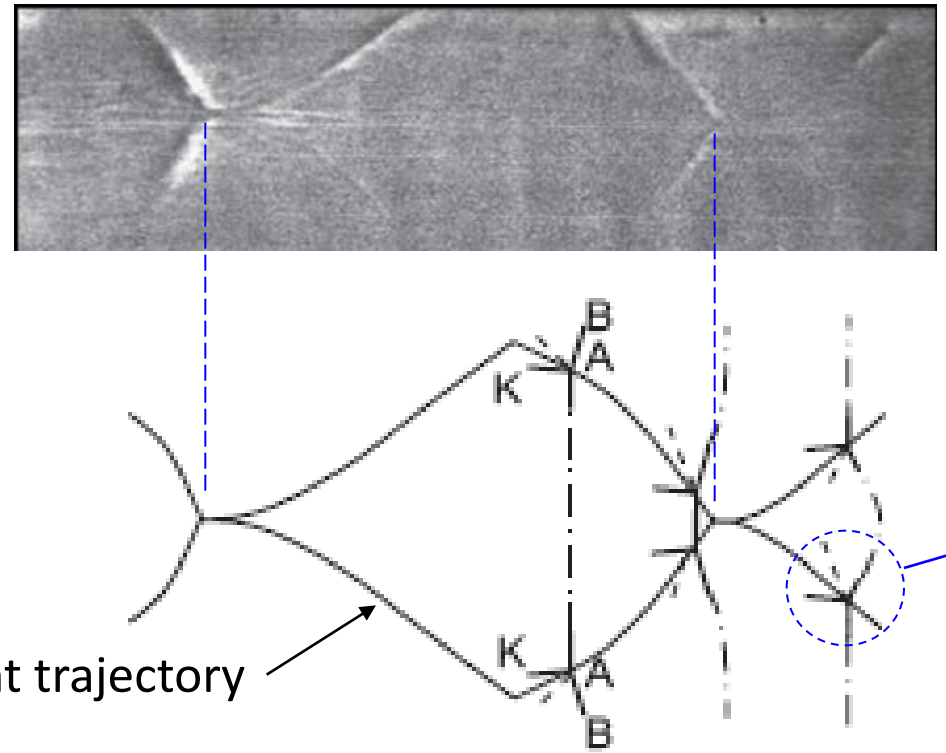
P_1= 0.075 atm P_1=0.04 atm

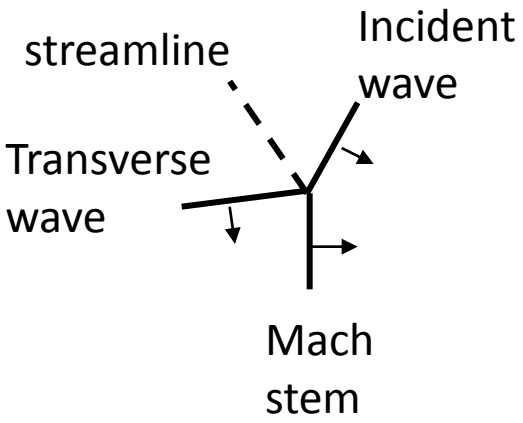
$2H_2+O_2+0.92Xe$

White DR. Turbulent structure of gaseous detonations. Phys Fluids 1961; 4(4)

Multi-dimensional Detonation Wave Structure

Denisov and Troshin (1961) used the soot foil technique to investigate t
detonation front structure

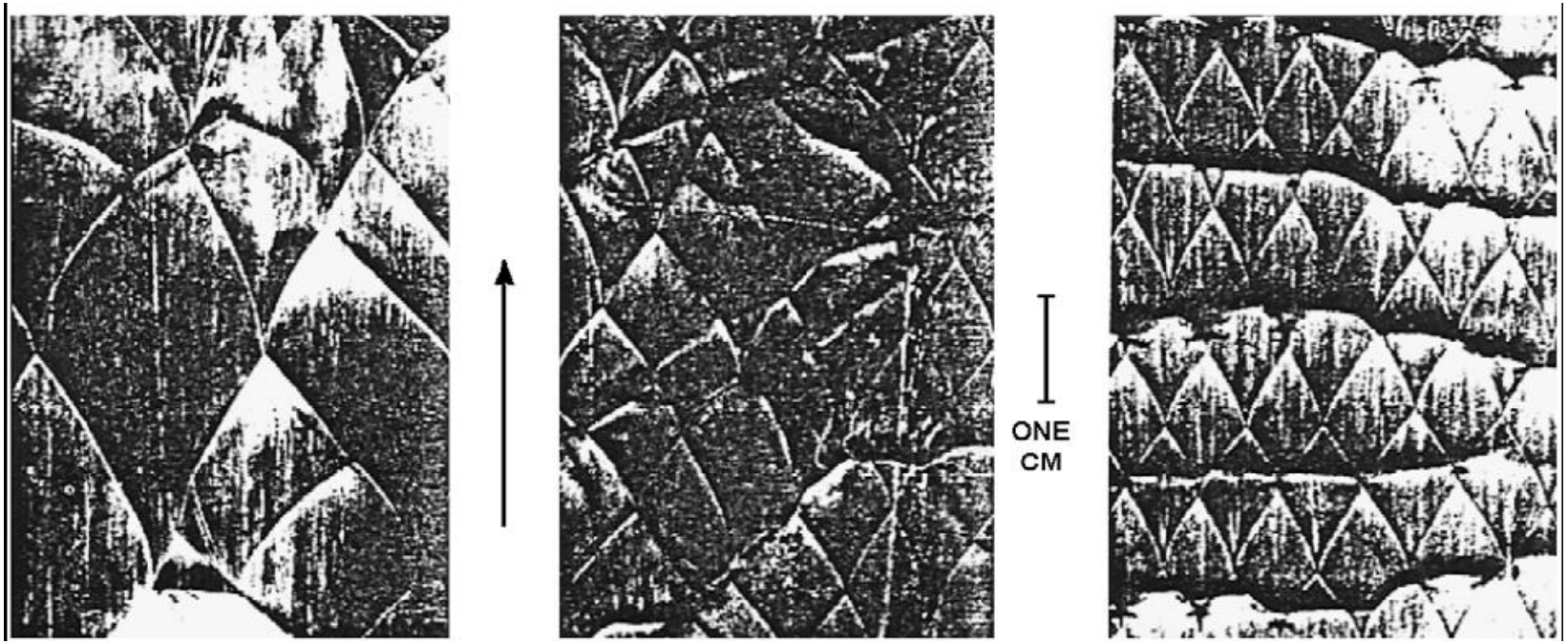




Based on converging and diverging lines observed on the imprint they described the structure of the detonation wave as two triple-point configurations ABK

Denisov YN, Troshin YK. On the mechanism of detonative combustion. Proc Combust Inst, 8, 1961

Detonation Front Triple-point Configuration



50% nitrogen dilution no dilution 40% argon dilution

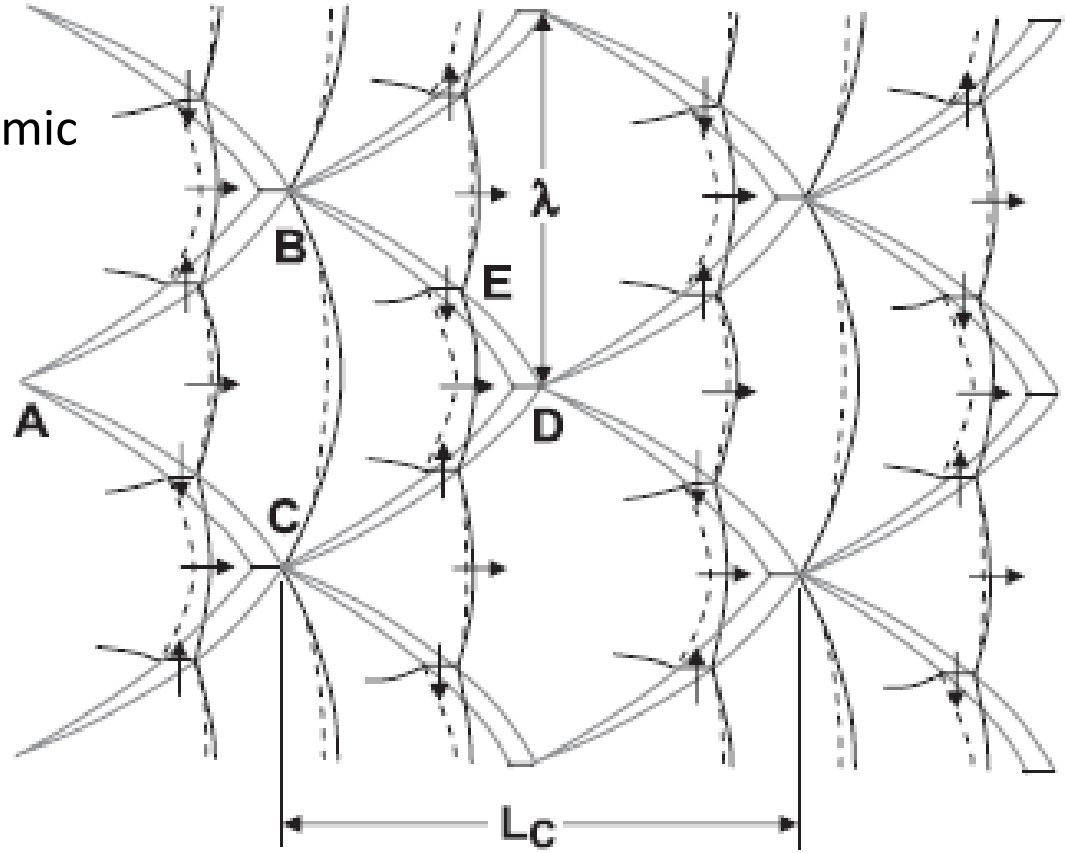
$H_2 + ½O_2$ at 0.2 atm

The higher the value E_a/RT_2, T_2 is the post shock temperature, the more irregular the cellular pattern. T_2 proportional to heat capacity of diluent

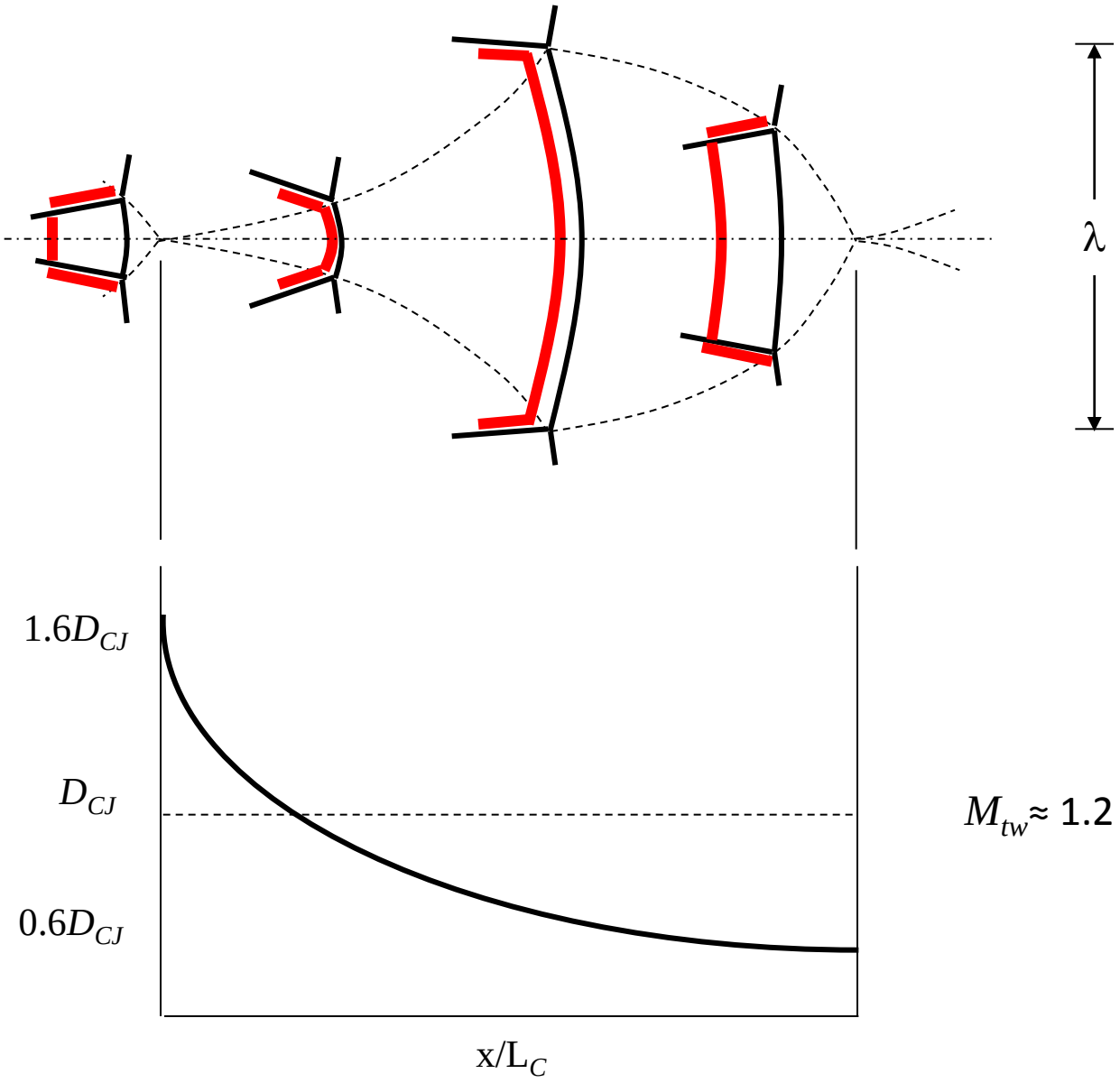
R.A. Strehlow, The nature of transverse waves in detonations, Astronautica Acta 14 ,1969

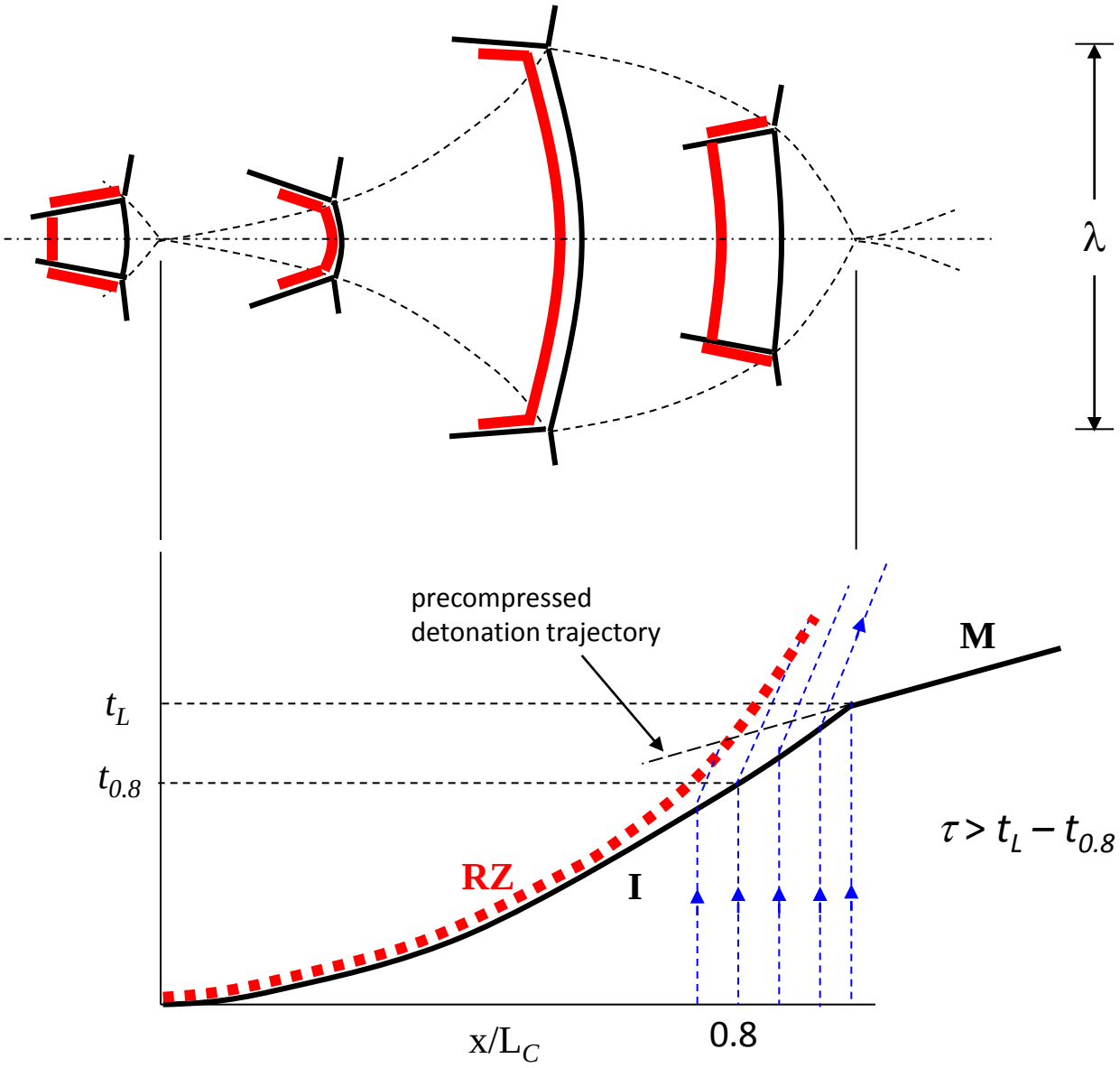
Detonation Cellular Structure

Start of exothermic reaction --------

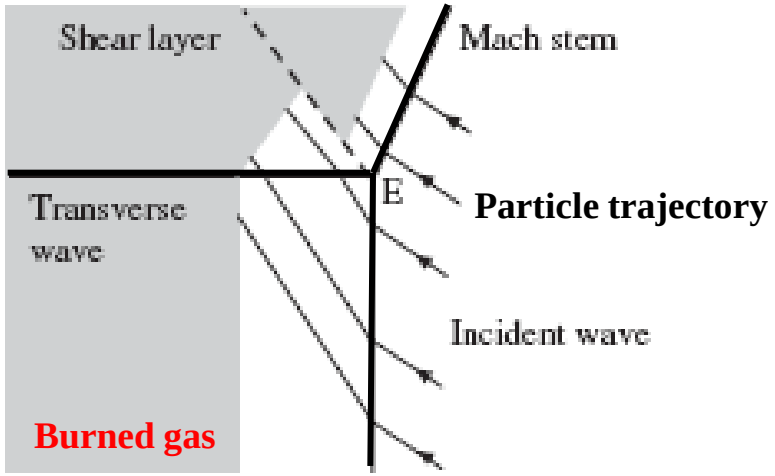


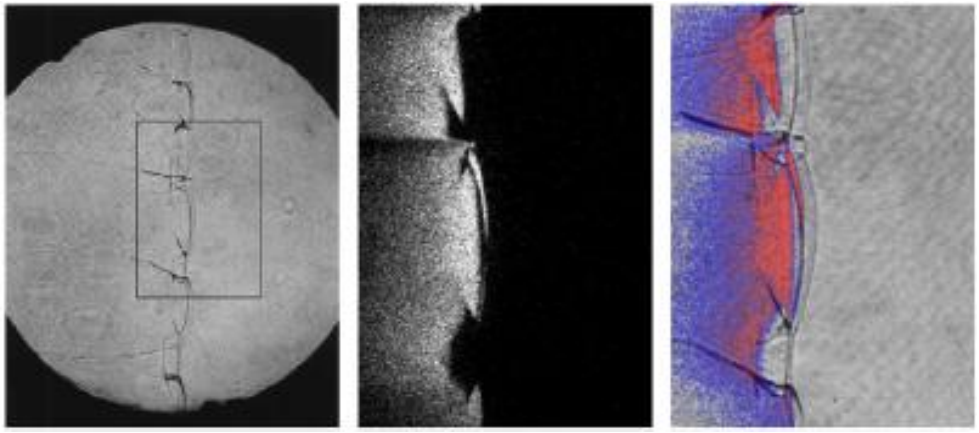
Detonation cell shock dynamics




λ
precompressed
detonation trajectory
M
t_L
$t_{0.8}$
$\tau > t_L - t_{0.8}$
RZ
I
x/L$_C$
0.8

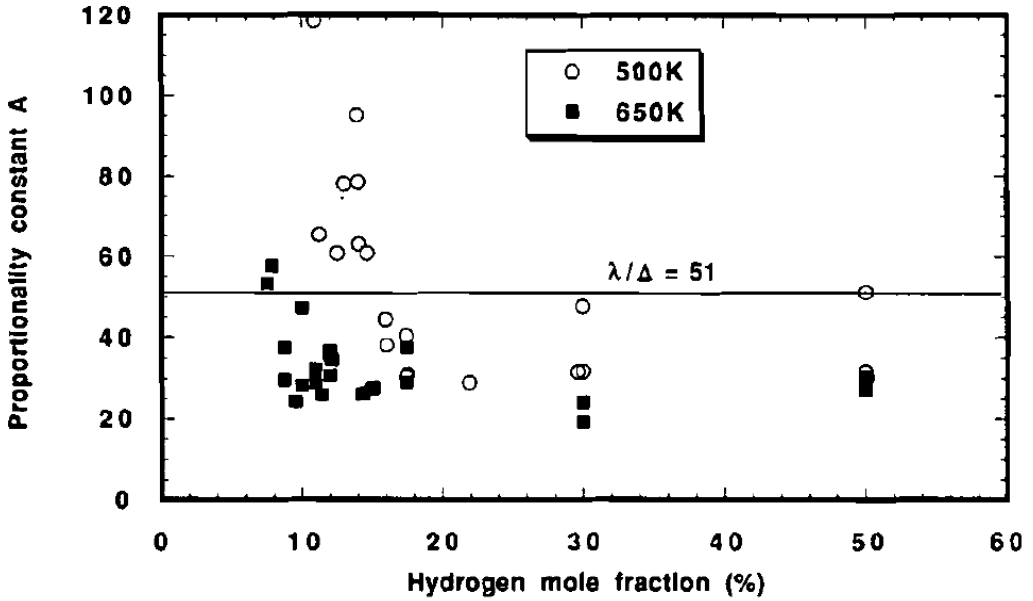
Multi-dimensional Reaction Zone





Austin JM, Pintgen F, Shepherd JE. Reaction zones in highly unstable detonations. Proc Combust Inst, 30, 2005

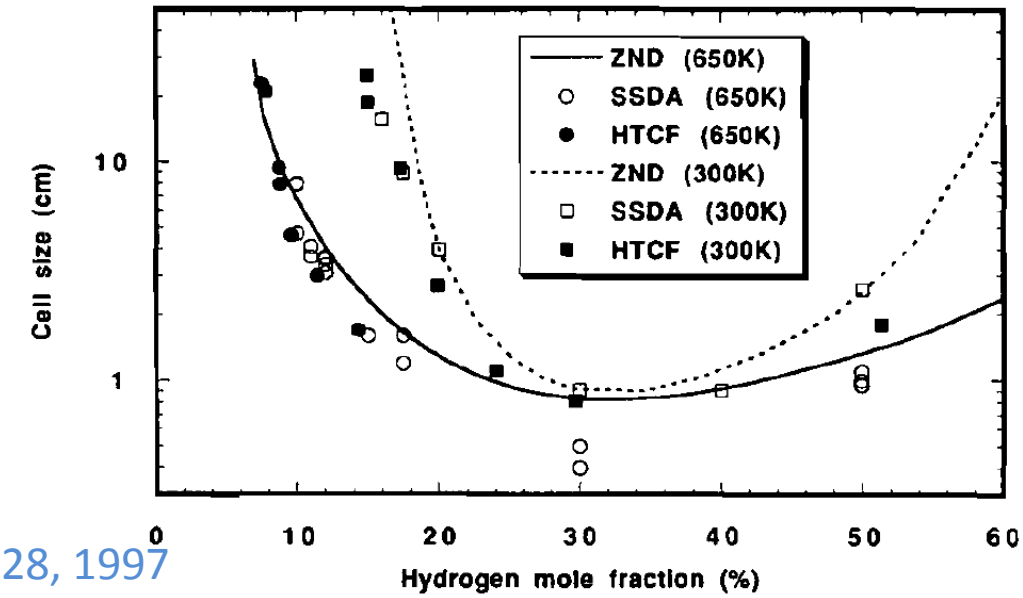
Measured and Predicted Detonation Cell Size (affect of temperature)



Detonation cell size represents the fundamental length-scale for a detonation wave

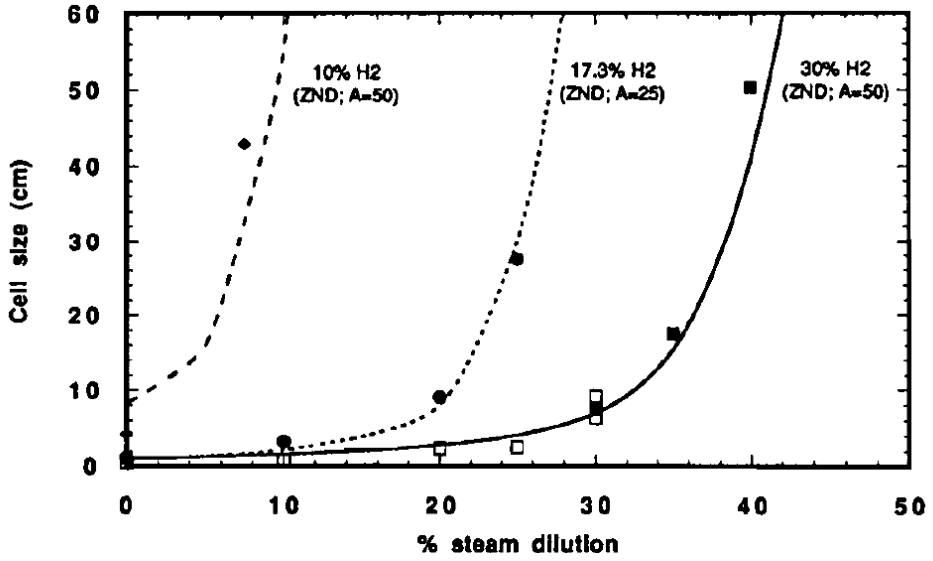
Hydrogen-air

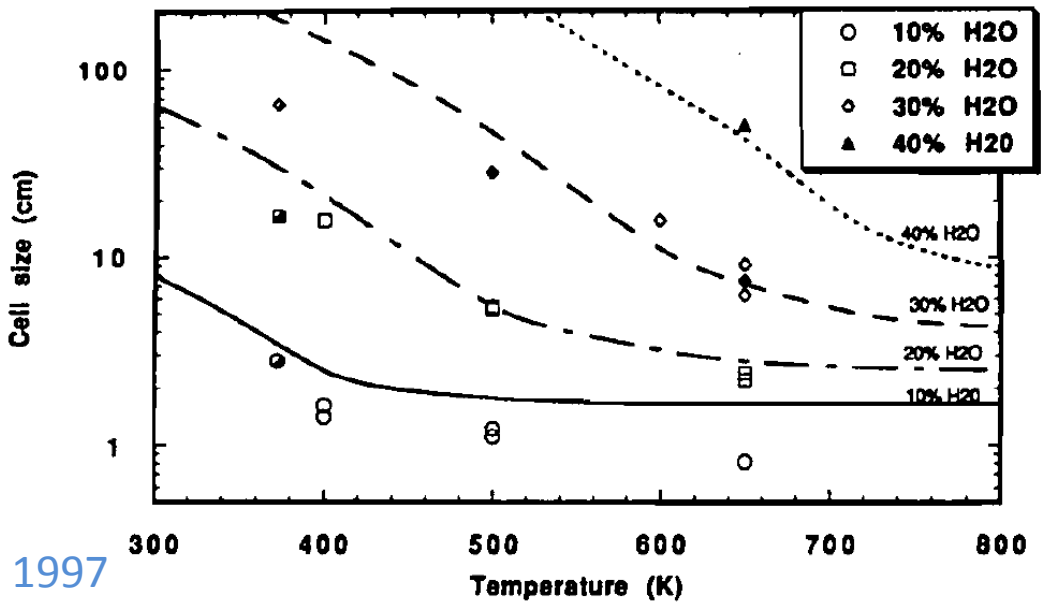
$\lambda = A\,\Delta_{ZND}$ $20 < A < 100$



Ciccarelli et al., Comb. Sci. and Tech., 128, 1997

Measured and Predicted Detonation Cell Size (affect of H2O)



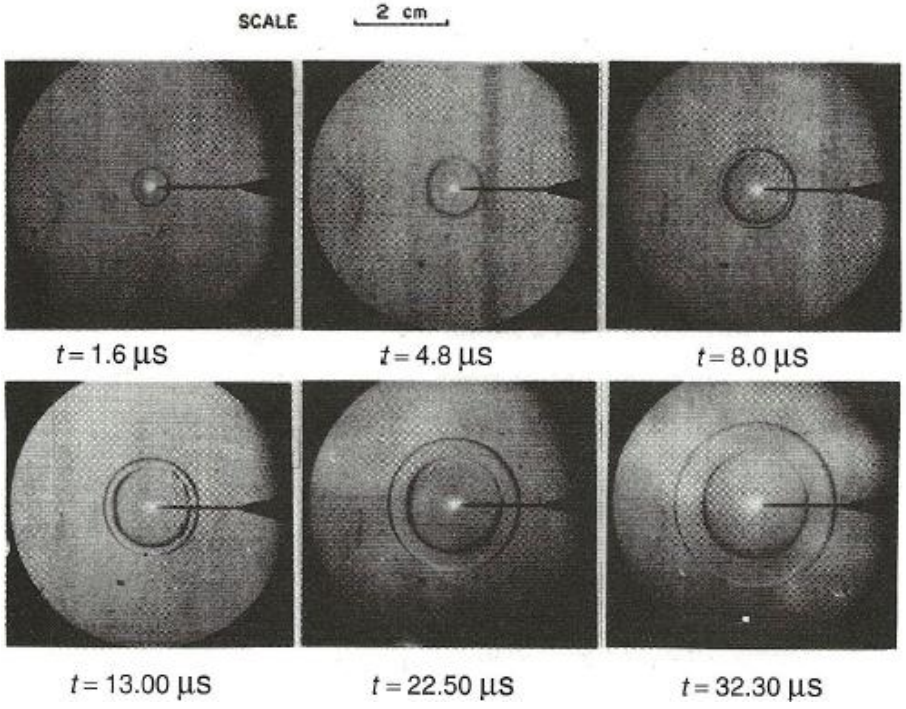


Ciccarelli et al., Comb. Sci. and Tech., 128, 1997

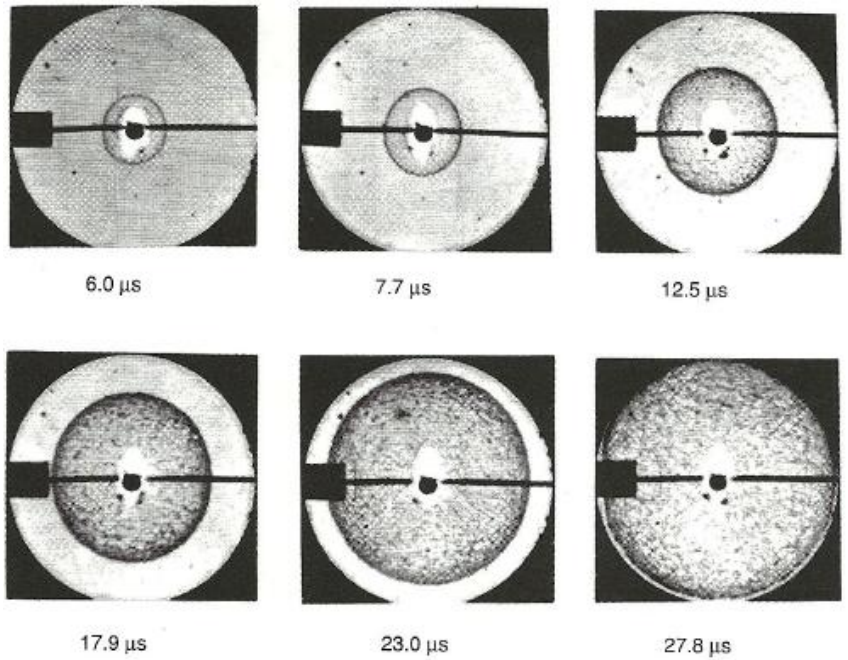
Detonation initiation

Direct initiation

A detonation can be initiated directly if sufficient energy is deposited at a point

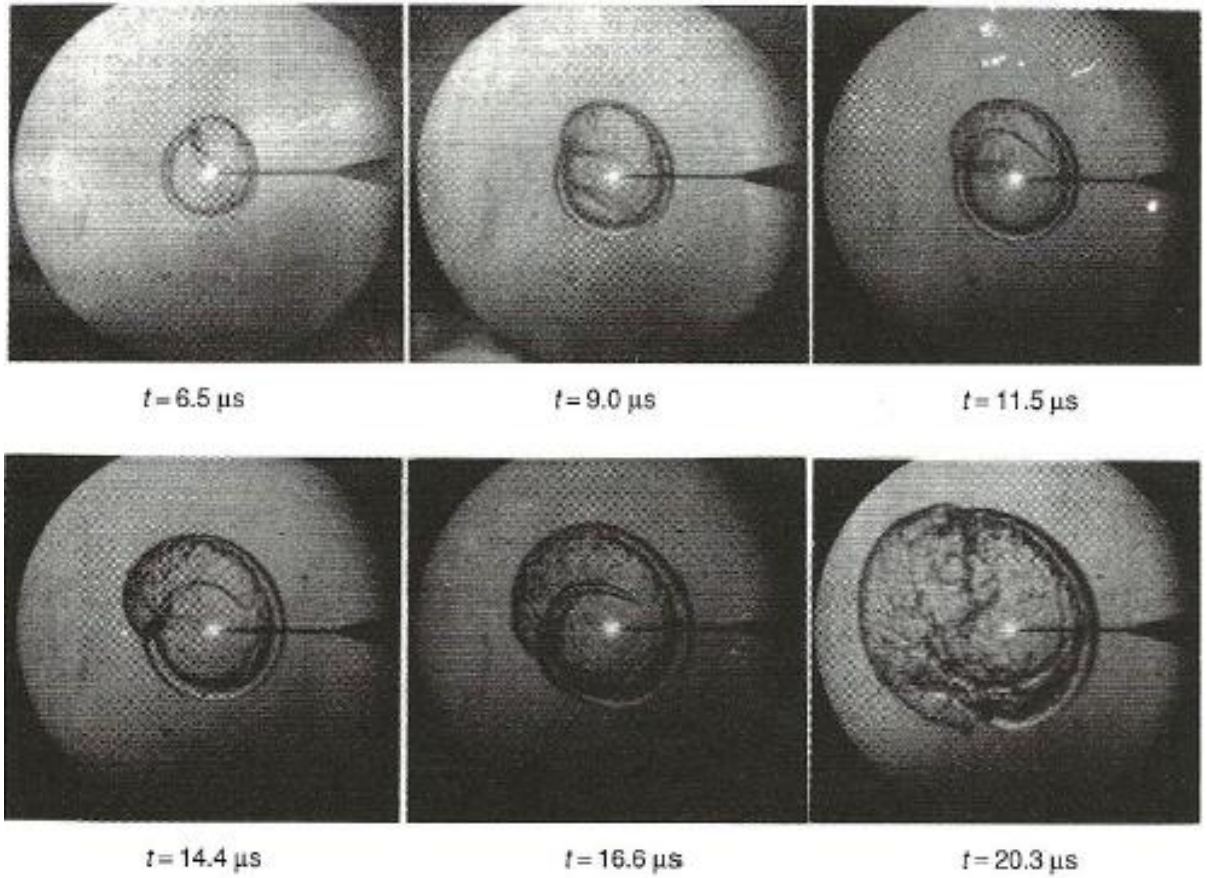


Subcritical



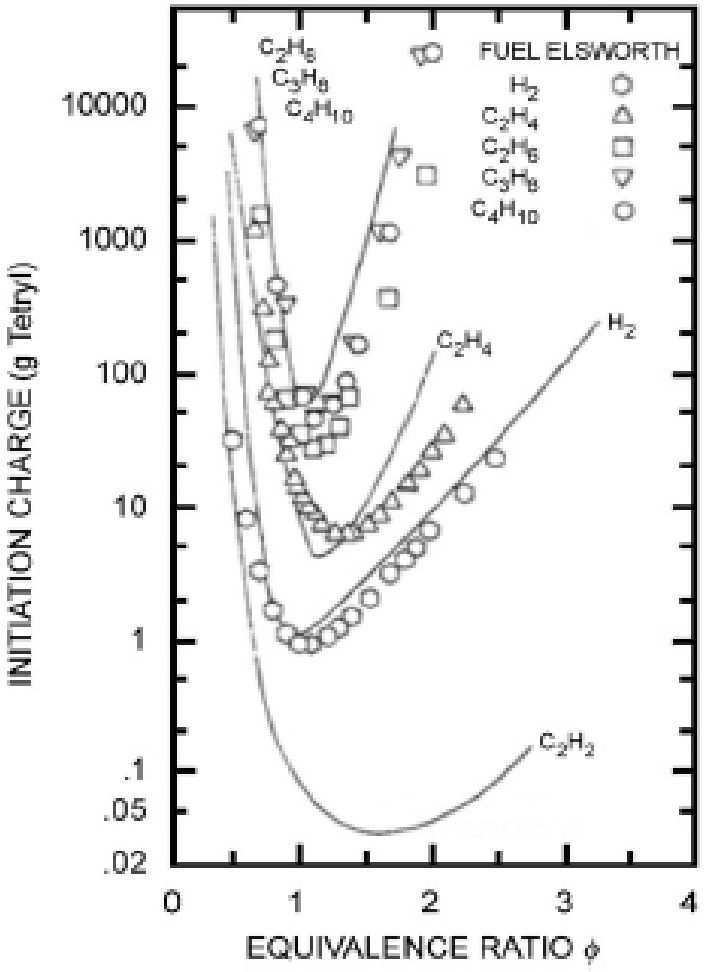
Supercritical

Critical initiation condition



Bach et al., 1969

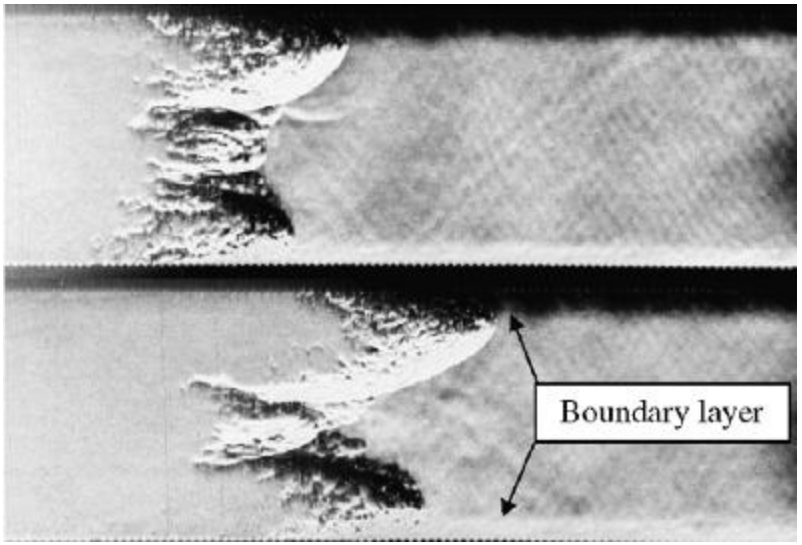
Critical Detonation Energy



$E_c \sim \lambda^3$

Lee JHS. Dynamic parameters of gaseous detonations. Ann Rev Fluid Mech , 16, 1984

Deflagration to detonation transition in a smooth tube



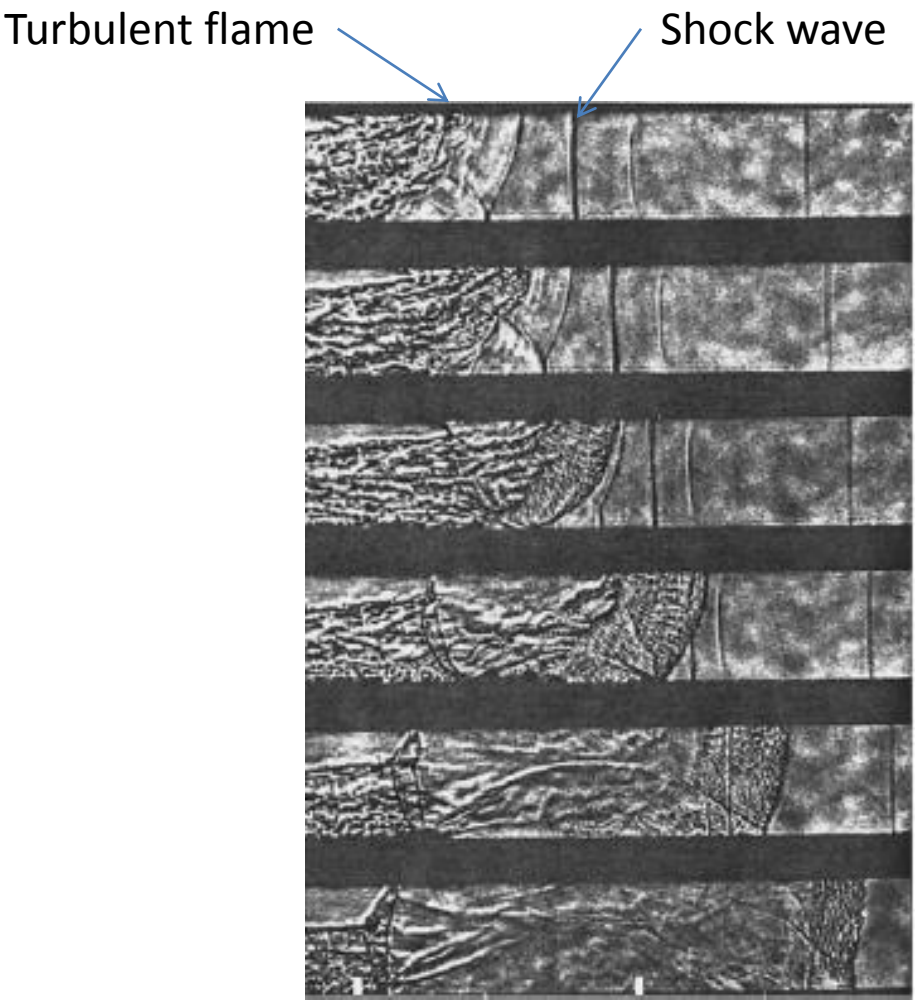
Normalized run-up distance:

$$\frac{X_S}{D} = \frac{\gamma}{C}\left[\frac{1}{\kappa}\ln\left(\gamma\frac{D}{h}\right) + K\right] \qquad \gamma = \left[\frac{a_p}{\eta(\sigma-1)^2 S_L}\left(\frac{\delta}{D}\right)^{1/3}\right]^{1/(2m+7/3)}$$

κ= 0.4, K= 5.5, C= 0.2, SL= laminar flame thickness, δ= flame thickness, σ= density ratio, a_p= speed sound η =2.1 and m=-.18 (empirical constants)

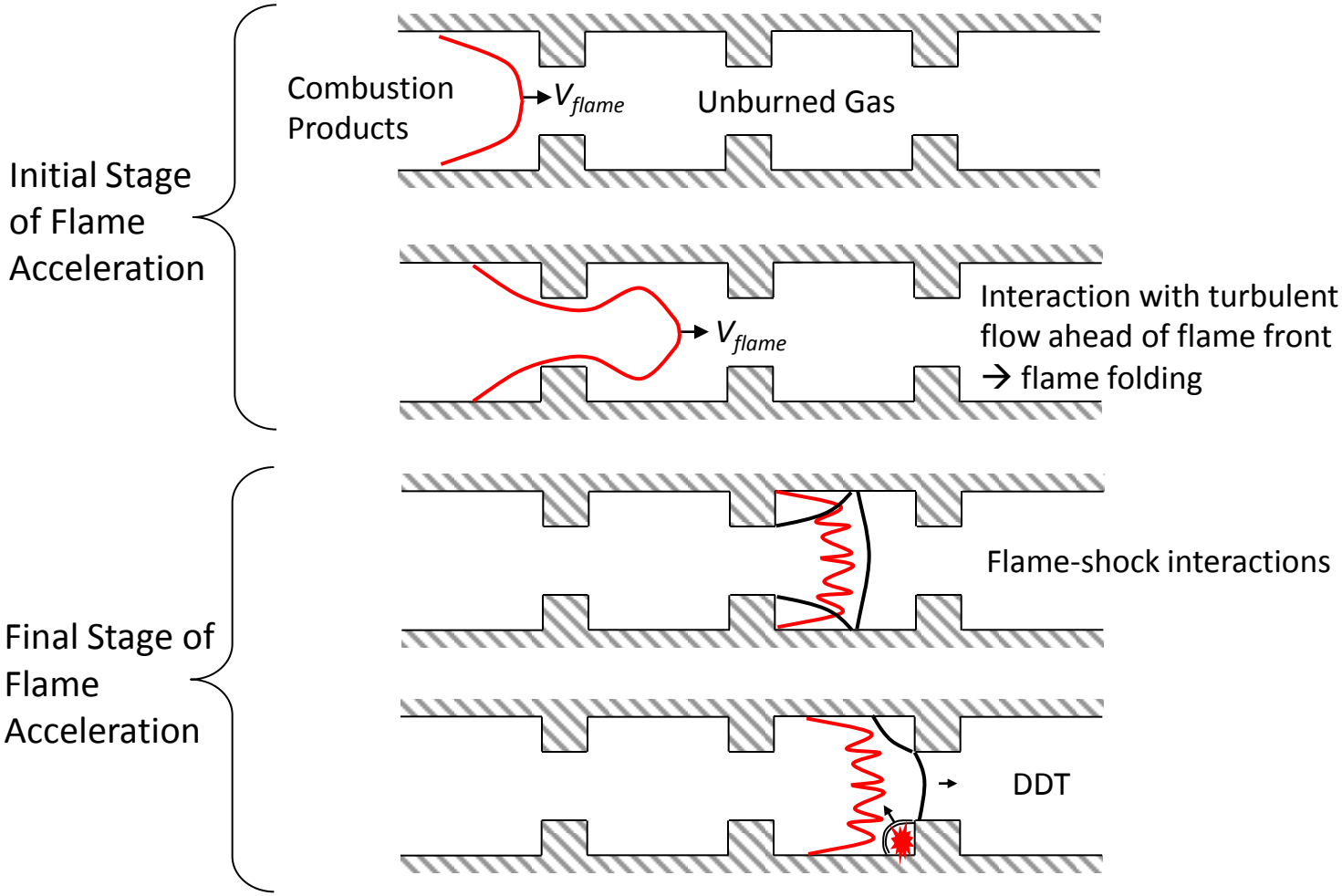
Kuznetsov M, Alekseev V, Matsukov I, Dorofeev S. DDT in a smooth tube filled with a hydrogen–oxygen mixture. Shock Waves 14(3), 2005;14(3)

Deflagration to detonation transition in a smooth tube

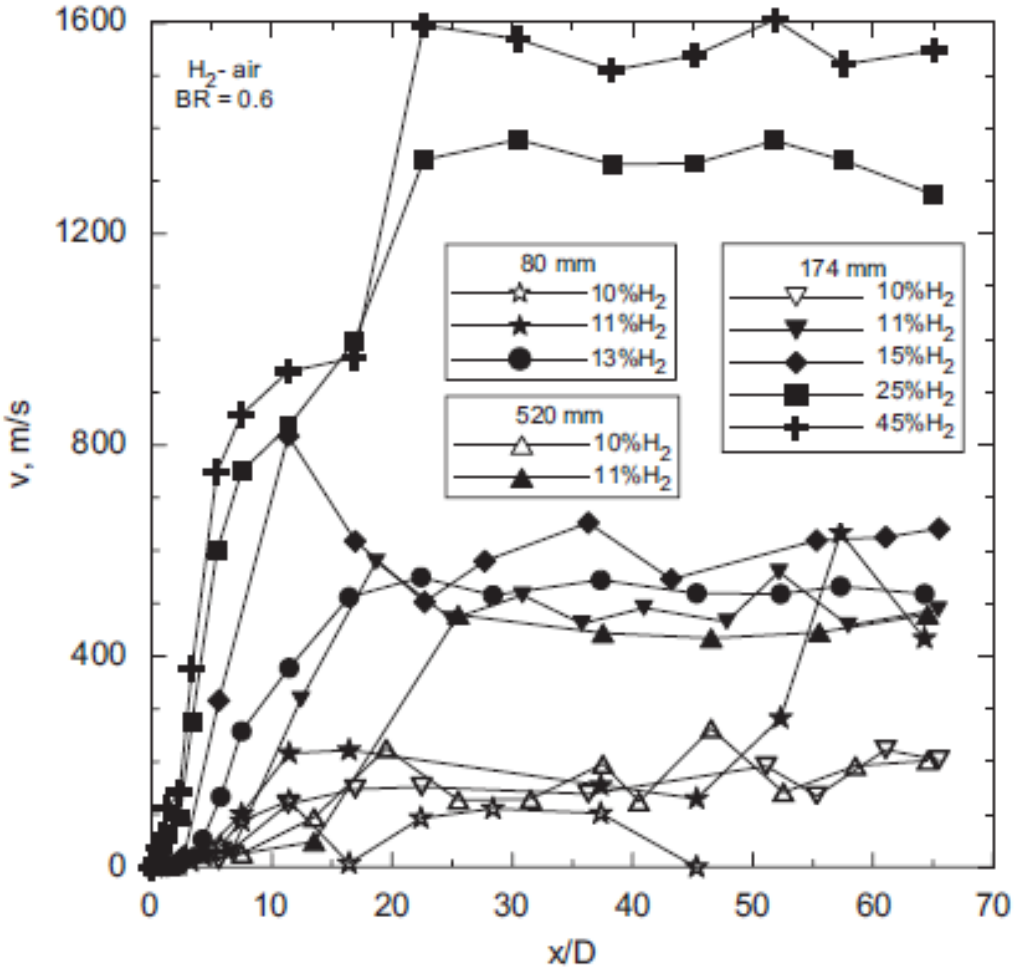


Urtiew PA, Oppenheim AK. Experimental observation of the transition to detonation in an explosive gas. Proc of Roy Soc A, 295, 1966.

Deflagration to detonation transition in a rough tube



Flame acceleration (BR=0.6)



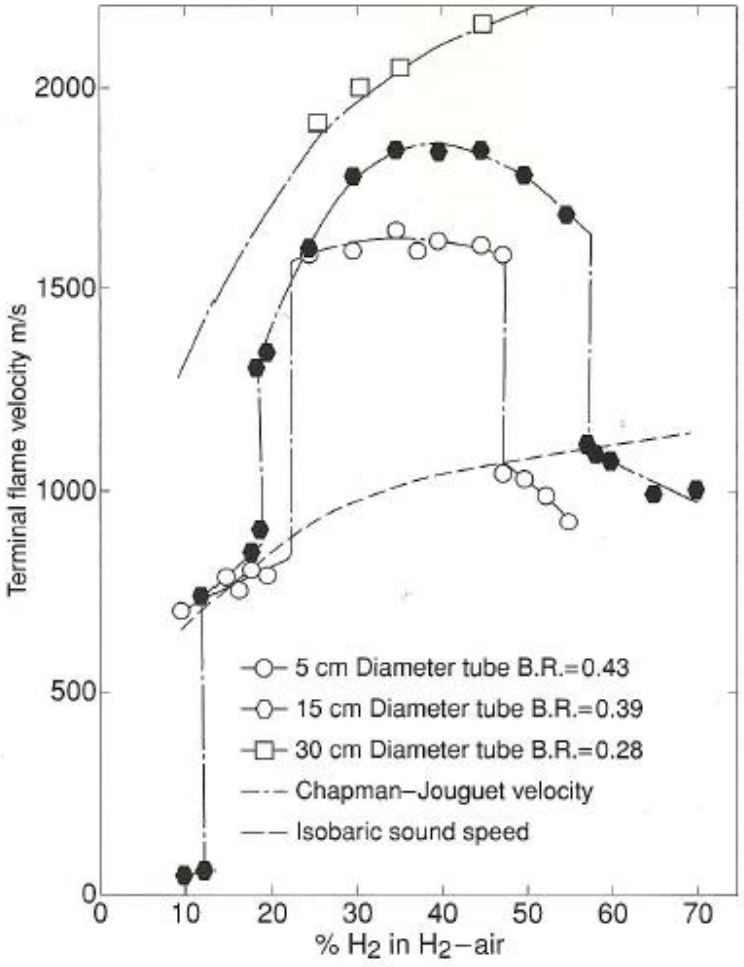
Detonation

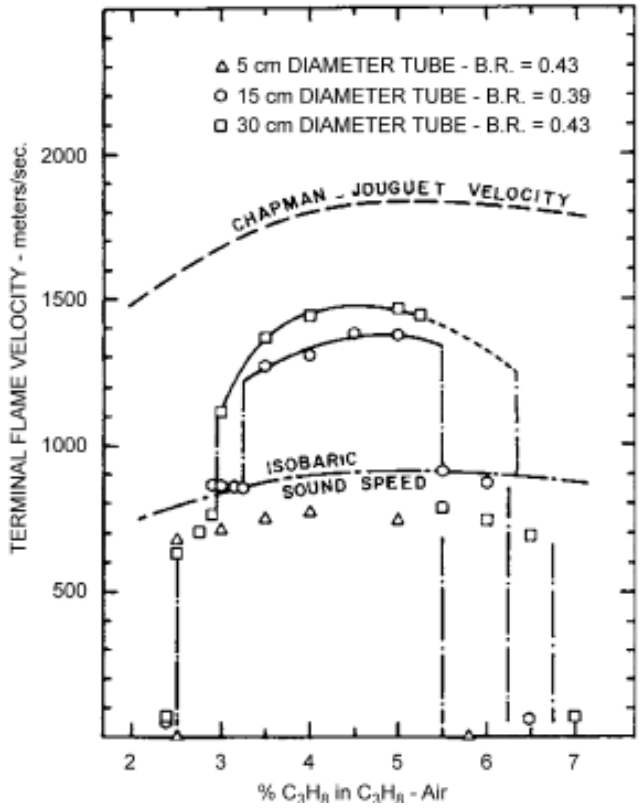
Fast flame

Slow flame

Kuznetsov et al., Effect of obstacle geometry on behavior of turbulent flames, Report No. FZKA-6328, Forschungszentrum Karlsruhe/Preprint No. IAE-6137/3 1999

Steady combustion propagation regimes

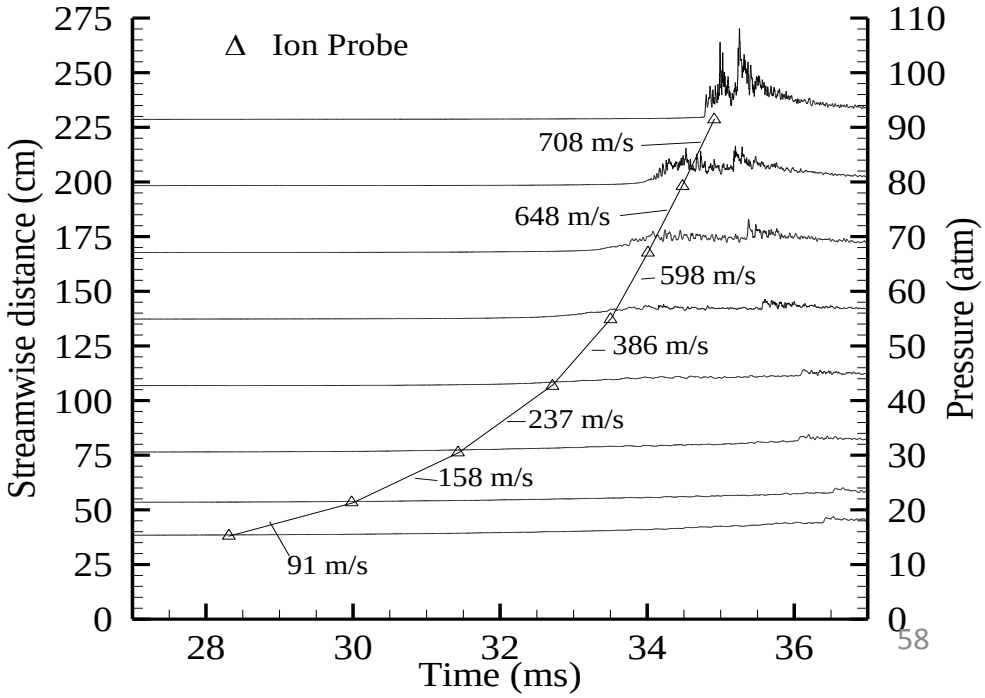




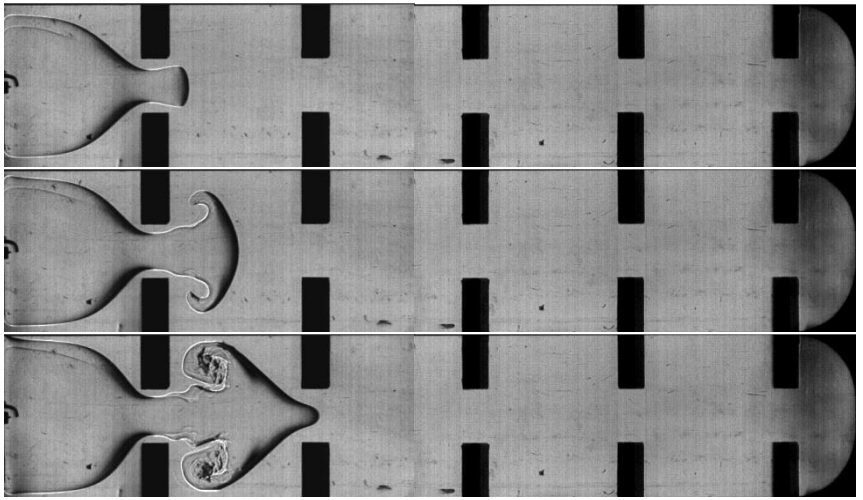
Detonation propagation limit:
$d > \lambda$

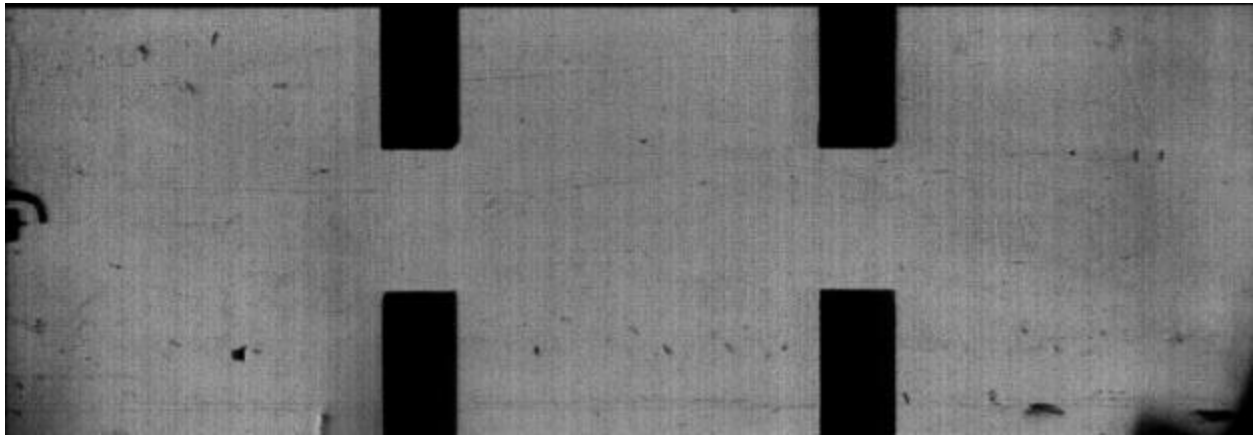
Lee JHS. Dynamic parameters of gaseous detonations. Ann Rev Fluid Mech , 16, 1984

Flame acceleration in obstacle laden channel



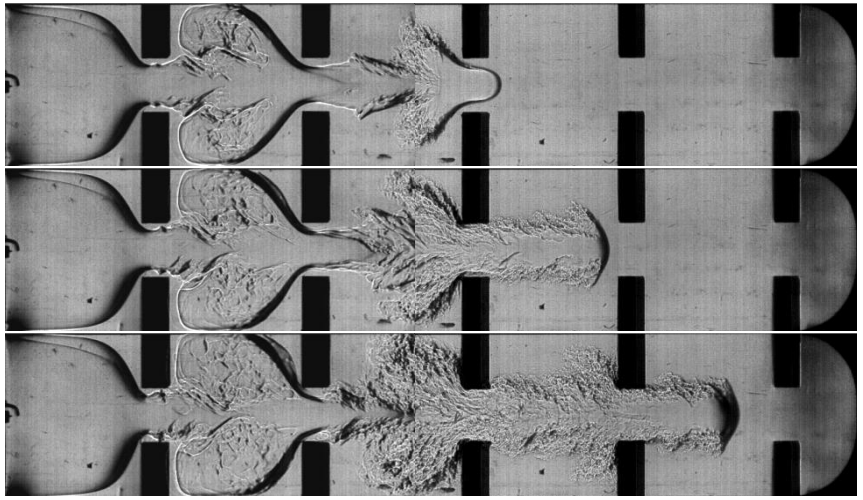
Flame acceleration, early stage

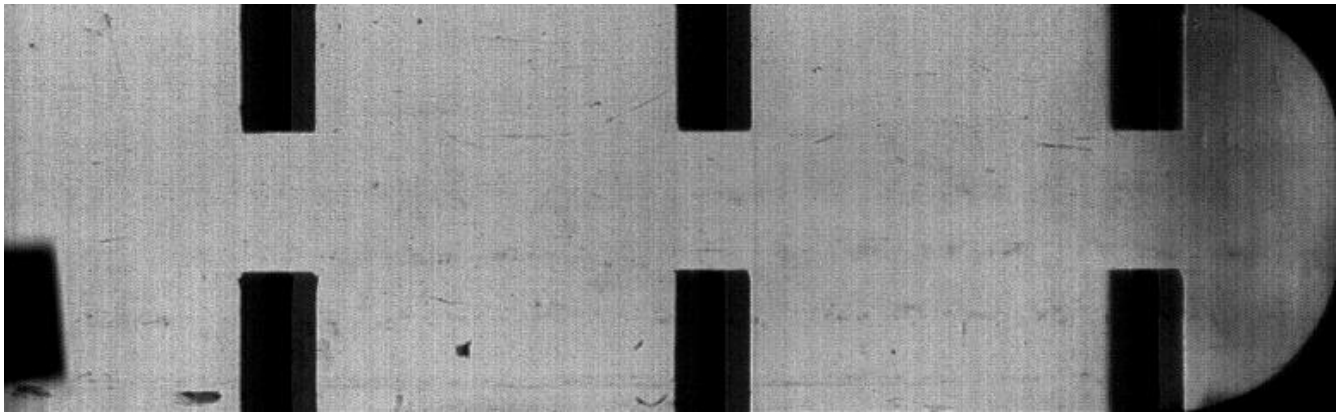




Johansen and Ciccarelli, Combustion and Flame, 2008

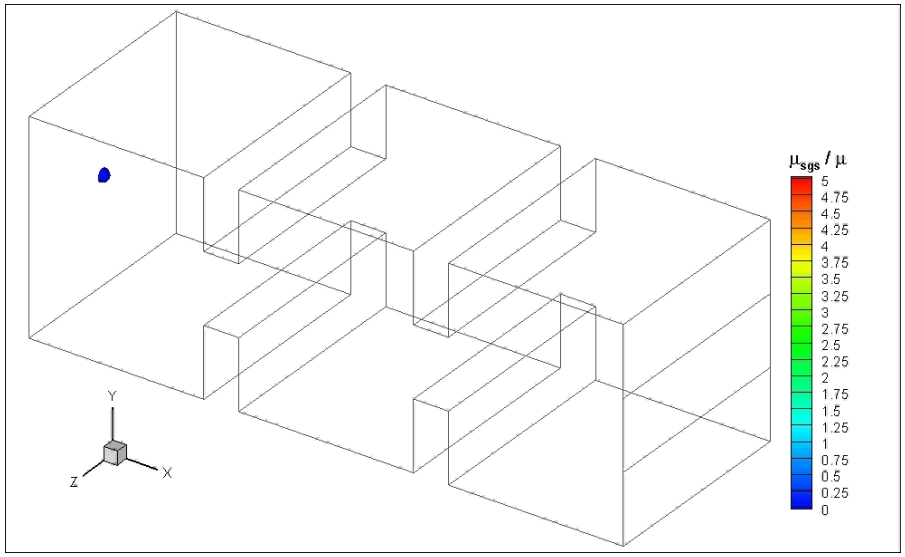
Flame acceleration, early stage

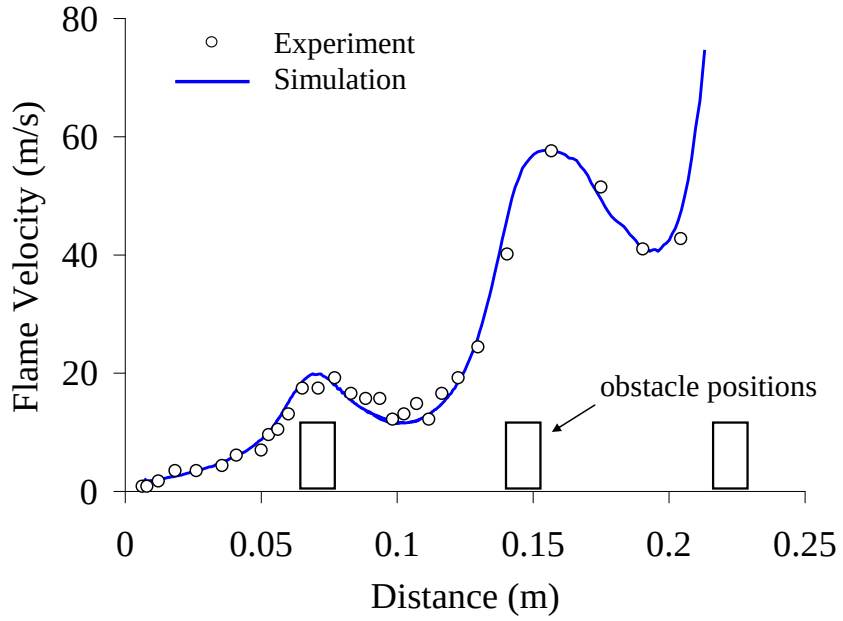




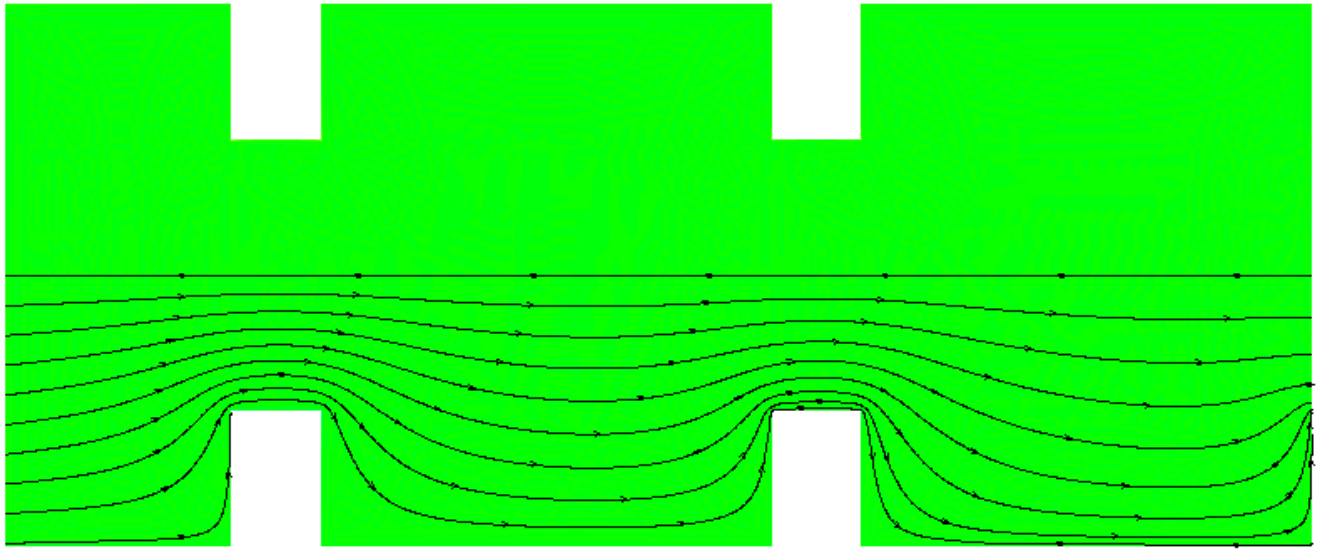
Johansen and Ciccarelli, Combustion and Flame, 2008

Flame acceleration (LES model w/ flame)

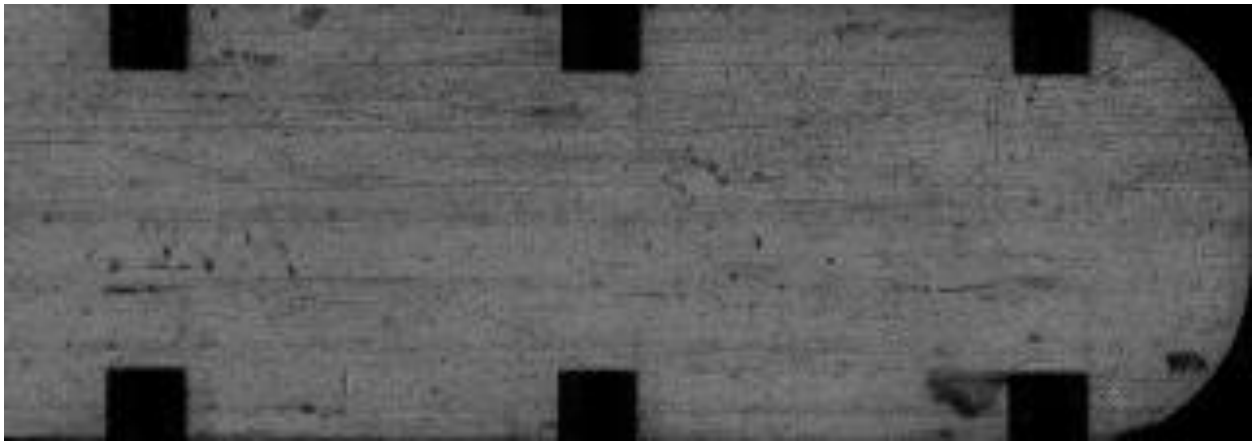




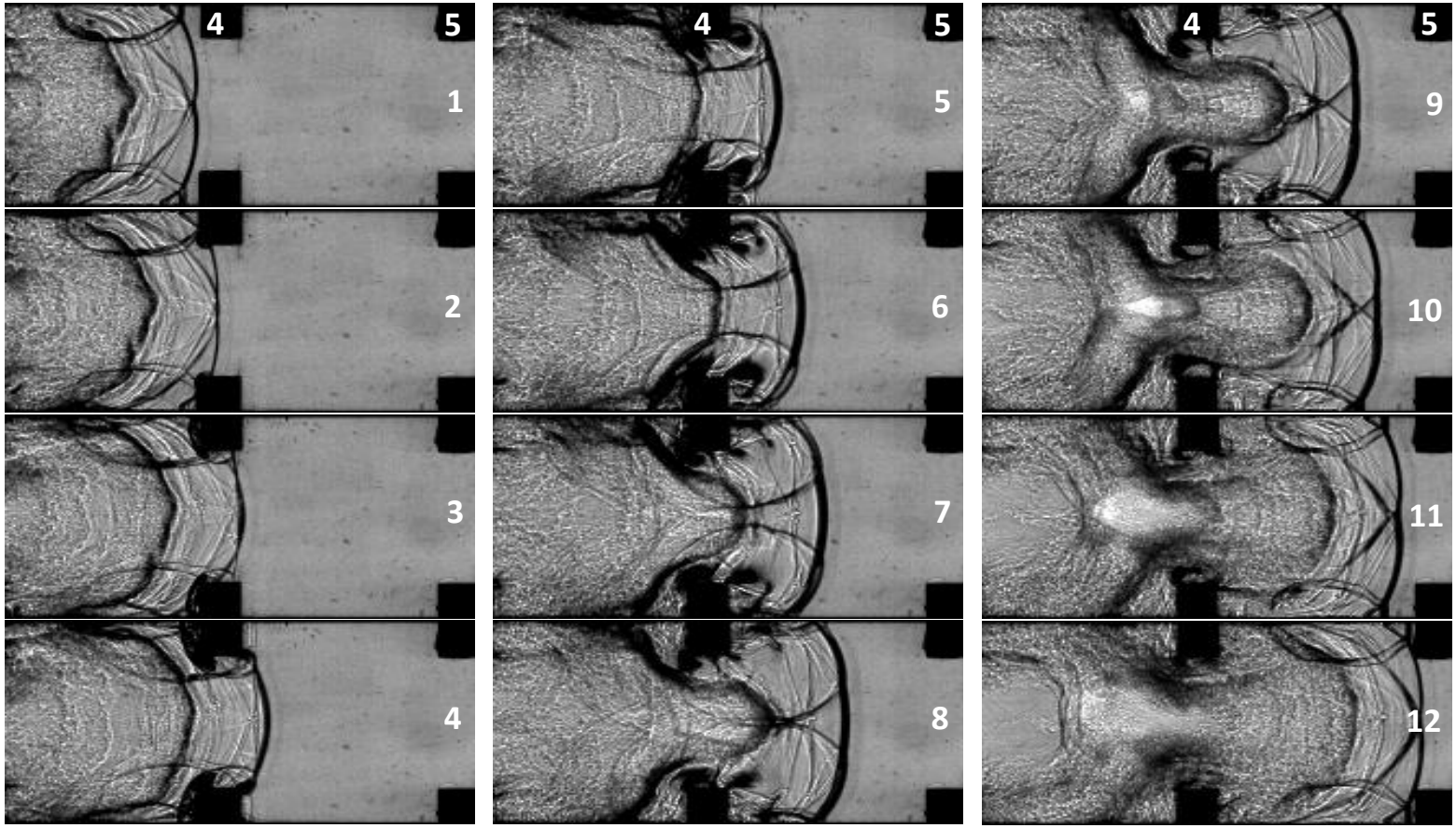
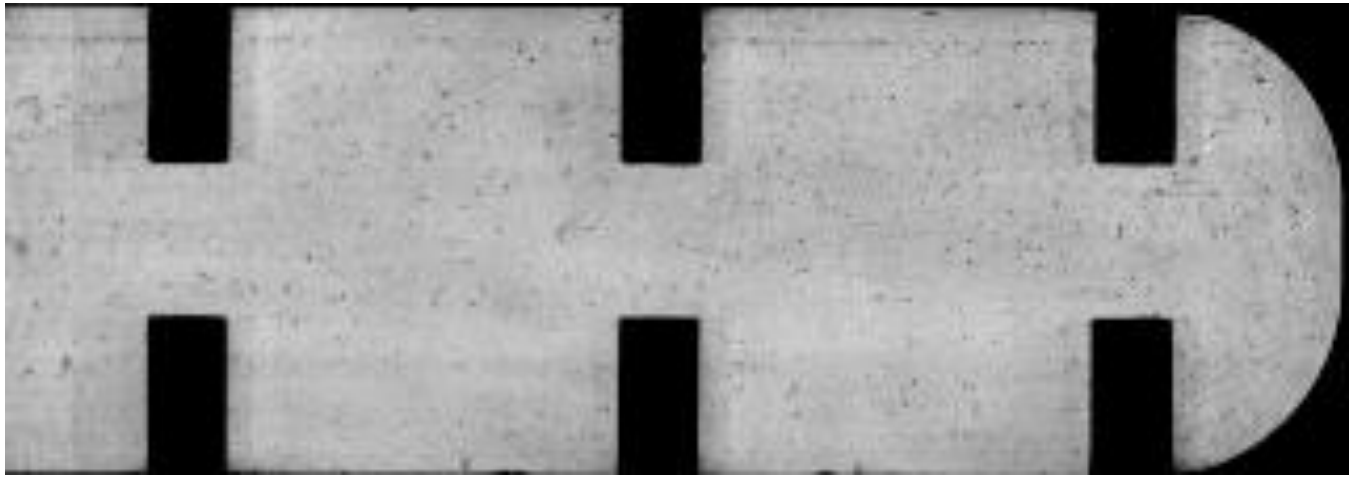
Shear layer development (LES model no flame)



Shock formation



Flame acceleration, late stage



Shock-flame interaction