# Detonation Structure for Chain-Branched Chemistry with Small Initiation Rate

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### 1 Introduction

Safety concerns associated with use of hydrogen as a fuel have led to renewed interest on chain-branching kinetics [1] and its effect on detonations. Short & Quirk [2] analyzed the stability of detonation waves for three step chain-branching kinetics. Liang & Bauwens [3] investigated three and four step schemes that approximate the chain-branching behavior of hydrogen-oxygen, and their effect on detonation structure. Extensive experimental work has been performed, such as for instance Pintgen et al. [4].

The most significant limitation of the single step model is that it unavoidably associates heat release with consumption of reactant in the induction zone perturbations. For chain-branching chemistry, both reactant consumption and chain-branching radical production are likewise small in the initiation zone. But in contrast with the single step model, heat release, now associated primarily with termination, is usually negligible, even when compared with the small concentration of the chain-branching radical. This key difference motivates the current work, an analysis in the slow initiation limit of the steady planar wave structure, for chain-branching chemistry. Previous analytical work included a high activation energy limit, plus eventually additional assumptions on the relative magnitudes of the various rates [5, 6, 7, 8]. In the current work, the small initiation rate assumption is explored by itself, assuming arbitrary activation energies. This assumption is typically quite accurate; thus the model below will often yield results indistinguishable from full integration.

### 2 Formulation: Rankine-Hugoniot Algebra

The detonation structure is described by the steady one-dimensional reactive, inviscid and non-conductive Euler's equations. The Rankine-Hugoniot formulation, made dimensionless scaling density and temperature by their preshock values, velocity by the preshock speed of sound, the heat release by the preshock speed of sound squared, and finally, pressure by  $\gamma$  times the preshock pressure, yields

$$\rho u = M_0, \quad M_0 u + p = M_0^2 + \frac{1}{\gamma}, \quad \frac{\gamma p}{(\gamma - 1)\rho} + \frac{u^2}{2} - q = \frac{1}{\gamma - 1} + \frac{M_0^2}{2} \tag{1}$$

in which  $\gamma p = \rho T$  and  $q = (1 - \lambda_1 - \lambda_2)Q$ . The chemical rate laws complete the formulation. Scaling the rate multipliers by the post-shock value of the termination rate multiplier, and length by  $c_0 u_N/k_{TN}$  (in which  $c_0 u_N$  is the dimensional value of the post-shock velocity),

$$\frac{u}{u_N}\frac{d\lambda_1}{dx} = -\lambda_1 k_I \exp \frac{-E_I}{T} - \rho \lambda_1 \lambda_2 k_B \exp \frac{-E_B}{T}, \\ \frac{u}{u_N}\frac{d\lambda_2}{dx} = \lambda_1 k_I \exp \frac{-E_I}{T} + \rho \lambda_1 \lambda_2 k_B \exp \frac{-E_B}{T} - \lambda_2$$
(2)

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in which  $k_T$  is a function of p and T. It is convenient to introduce  $T_I$  and  $T_B$ :  $k_I = \exp E_I/T_I$  and  $k_B = \exp E_B/T_B$ . At the shock, only reactants are present, but no chain-branching radicals, so  $\lambda_1 = 1$  and  $\lambda_2 = 0$ . Using the local Mach number M as the independent variable, the model is reduced to

$$\sqrt{T} = \frac{M(\gamma M_0^2 + 1)}{M_0(\gamma M^2 + 1)}, \ \rho = \frac{M_0^2(\gamma M^2 + 1)}{M^2(\gamma M_0^2 + 1)}, \ u = \frac{M^2(\gamma M_0^2 + 1)}{M_0(\gamma M^2 + 1)}, \ p = \frac{\gamma M_0^2 + 1}{\gamma(\gamma M^2 + 1)},$$
(3)

Introducing heat release,

$$\Delta = \Delta_N - \frac{q}{Q}, \quad \Delta_N = \frac{(M_0^2 - 1)^2}{2M_0^2(\gamma^2 - 1)Q}, \quad M^2 = \frac{\gamma M_0^2 + 1 \pm \sqrt{2M_0^2(\gamma^2 - 1)Q\Delta}}{\gamma M_0^2 + 1 \pm \gamma \sqrt{2M_0^2(\gamma^2 - 1)Q\Delta}}$$
(4)

Here the upper root corresponds to a supersonic branch (i.e. a weak detonation) while the lower root describes a deflagration preceded by a shock at the origin q = 0, where  $\Delta = \Delta_N$ . Indeed, initially, the upper root yields the preshock value  $M_0$ , while the negative root corresponds to the post-shock value. The wave ends when chemistry is complete, i.e. q = Q. Existence of a complete solution up to that point requires  $\Delta$  to be positive up to that point. The CJ wave corresponds to the limit case where  $\delta = 0$  at the CJ point, where q = Q.

Also,  $\Delta = \Delta_N - 1 + \lambda_1 + \lambda_2$ . Furthermore, introducing  $\kappa(M)$ :

$$\kappa = \frac{(\gamma - 1)(1 - \gamma M^2)}{1 - M^2} \frac{Q}{T_N}$$
(5)

T and q are related by

$$\frac{dT}{\kappa T_N} = \frac{dq}{Q} = -d\Delta = -d(\lambda_1 + \lambda_2) \tag{6}$$

#### 3 Small Initiation Rate

Introducing the symbols  $\epsilon$  and a, and the variable  $\theta$ ,

$$\epsilon = \exp\left(\frac{E_I}{T_I} - \frac{E_I}{T_N}\right), \ a = \rho_N \exp\left(\frac{E_B}{T_B} - \frac{E_B}{T_N}\right), \ \theta = \frac{E_B}{T_N} \left(1 - \frac{T_N}{T}\right)$$
(7)

initiation is taken to be slow in the sense that  $\epsilon \ll 1$ . The parameter a, of order unity, determines the location of the post-shock state on the explosion diagram. If a > 1, chain-branching is already stronger than termination. The Neumann point, is then in the explosion region. Using the notation in Eqs. (7), chemistry becomes

$$\frac{u}{u_N}\frac{d\lambda_1}{dx} = -\epsilon\lambda_1 \exp\frac{E_I\theta}{E_B} - a\frac{\rho}{\rho_N}\lambda_1\lambda_2 \exp\theta$$
(8)

$$\frac{u}{u_N}\frac{d\lambda_2}{dx} = \epsilon\lambda_1 \exp\frac{E_I\theta}{E_B} + a\frac{\rho}{\rho_N}\lambda_1\lambda_2 \exp\theta - \lambda_2 k_T \tag{9}$$

with

$$\frac{1}{\kappa T_N} \frac{dT}{dx} = -\frac{d(\lambda_1 + \lambda_2)}{dx} = k_T \frac{u_N}{u} \lambda_2 \tag{10}$$

 $\kappa_N$  is positive as long as the heat release or overdrive are high enough, provided that  $M_N^2 \ge 1/\gamma$  [9, 5]. For x = O(1), the solution only varies by order  $\epsilon$ . Using the notation  $\lambda_i = 1 + \epsilon \tilde{\lambda}_i + \epsilon^2 \lambda_i$  and  $\theta = \epsilon \phi$ ,

$$\frac{d\tilde{\lambda}_1}{dx} = -1 - a\tilde{\lambda}_2, \quad \frac{d\tilde{\lambda}_2}{dx} = 1 + (a - 1)\tilde{\lambda}_2, \quad \frac{d\phi}{dx} = \kappa_N \tilde{\lambda}_2 \tag{11}$$

Similar equations are obtained for  $O(\epsilon^2)$ . One can readily solve for both order  $\epsilon$  and  $\epsilon^2$ . The former is:

$$\tilde{\lambda}_2 = \frac{1}{a-1} \left[ \exp(a-1)x - 1 \right], \quad \tilde{\lambda}_1 = \frac{x}{a-1} - \frac{a}{(a-1)^2} \left[ \exp(a-1)x - 1 \right]$$
(12)

$$\phi = \frac{\kappa_N}{(a-1)^2} \left[ \exp(a-1)x - 1 - (a-1)x \right]$$
(13)

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## 4 Explosion region (a > 1)

The solution in the initiation zone increases exponentially. On the other hand, the order unity formulation, obtained by setting  $\epsilon = 0$  in Eqs. (9), for leading order changes in both  $\lambda_1$  and  $\lambda_2$ , is

$$\frac{u}{u_N}\frac{d\lambda_1}{dx} = -a\frac{\rho}{\rho_N}\lambda_1\lambda_2\exp\theta, \quad \frac{u}{u_N}\frac{d\lambda_2}{dx} = a\frac{\rho}{\rho_N}\lambda_1\lambda_2\exp\theta - \lambda_2k_T \tag{14}$$

$$\theta = \frac{E_B}{T_N} \frac{(M^2 - M_N^2)(\gamma M M_N + 1)}{M^2 (\gamma M_N^2 + 1)^2}, \quad \frac{\rho}{\rho_N} = \frac{u_N}{u} = \frac{M_N^2 (\gamma M^2 + 1)}{M^2 (\gamma M_N^2 + 1)}$$
(15)

Chemistry becomes

$$\frac{d\lambda_1}{\lambda_1} = \frac{\rho}{\rho_N} \frac{a}{k_T} \exp\theta d\Delta = -a \left(\frac{\rho}{\rho_N}\right)^2 \lambda_2 \exp\theta dx \tag{16}$$

$$d\Delta = -k_T \frac{\rho}{\rho_N} \lambda_2 dx = -\frac{\rho}{\rho_N} (\Delta - \Delta_N + 1 - \lambda_1) dx \tag{17}$$

Both equations are integrated:

$$\lambda_1 = \exp \int_{\Delta_N}^{\Delta} \frac{\rho}{\rho_N} \frac{a}{k_T} \exp \theta d\Delta, \quad x - x^* = -\int_{\Delta^*}^{\Delta} \frac{\rho_N}{\rho} \frac{1}{\Delta - \Delta_N + 1 - \lambda_1} d\Delta \tag{18}$$

Close to  $\Delta_N$ ,  $\lambda_1 \to 1 + a(\Delta - \Delta_N)$ . So

$$x - x^* \to -\int^{\Delta} \frac{1}{(1 - a)(\Delta - \Delta_N)} d\Delta = \frac{1}{a - 1} \log(\Delta - \Delta_N)$$
(19)

The limit is singular. Thus the Neumann point cannot be used as the limit of integration. Instead, one defines  $M^* = 1/\sqrt{\gamma}$ , the point where temperature peaks (assuming overdrive is strong enough for a temperature peak to occur). In the initiation zone,

$$\lambda_1 + \lambda_2 = 1 + \epsilon \frac{1 - \exp(a - 1)x + x(a - 1)}{(a - 1)^2} + \epsilon^2 K \exp 2(a - 1)x$$
(20)

so that  $\Delta - \Delta_N$  is of order unity for x of order  $-\log \epsilon$  and the second order term remains small. Thus

$$\Delta - \Delta_N \to \epsilon \frac{-\exp(a-1)x}{(a-1)^2}, \quad x \to x^* = \frac{-\log\epsilon + \log[(a-1)^2(\Delta_N - \Delta)]}{a-1}$$
(21)

and for  $\Delta \to \Delta_N$ ,

$$x^* = \frac{1}{a-1} \log \left\{ \frac{(a-1)^2}{\epsilon} \lim_{\Delta \to \Delta_N} \left[ (\Delta_N - \Delta) \exp \int_{\Delta^*}^{\Delta} \frac{\rho_N}{\rho} \frac{a-1}{\Delta - \Delta_N + 1 - \lambda_1} d\Delta \right] \right\}$$
(22)

This determines the length of the initiation zone, which is of order  $-\log \epsilon$ .

### 5 No explosion region (a < 1)

In the initiation zone  $\tilde{\lambda}_2$  now approaches the constant 1/(1-a), while  $\tilde{\lambda}_1$  and  $\phi$  change linearly with x:

$$\tilde{\lambda}_1 \to \frac{a}{(1-a)^2} - \frac{x}{1-a}, \quad \phi \to \frac{\kappa_N}{(a-1)^2} \left[ (1-a)x - 1 \right]$$
(23)

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It will take a length of  $O(1/\epsilon)$  until changes of oreder unity take place, hence the rescaling  $\chi = x\epsilon$ . This yields a solution in which  $\lambda_1$  now experiences order unity changes, but  $\lambda_2 = \epsilon \tilde{\lambda}_2$ .

$$\frac{u}{u_N}\frac{d\lambda_1}{d\chi} = -\lambda_1 \left( \exp\frac{E_I\theta}{E_B} - a\frac{\rho}{\rho_N}\tilde{\lambda}_2 \exp\theta \right), \quad \epsilon \frac{u}{u_N}\frac{d\tilde{\lambda}_2}{d\chi} = \lambda_1 \exp\frac{E_I\theta}{E_B} + \left( a\frac{\rho}{\rho_N}\lambda_1 \exp\theta - k_T \right)\tilde{\lambda}_2 \quad (24)$$

At leading order,  $\Delta = \Delta_N - 1 + \lambda_1$ . Thus one can use  $M^2(\Delta)$  and the relationships yielding  $\theta$  and  $\rho/\rho_N$ . The solution is

$$\tilde{\lambda}_2 = \frac{\lambda_1 \exp[E_I \theta / E_B]}{a(\rho/\rho_N)\lambda_1 \exp\theta - k_T}$$
(25)

$$\chi = \int_0^{\lambda_1} \left[ \frac{a}{k_T} \exp \theta - \frac{\rho_N}{\rho} \frac{1}{\lambda_1} \right] \exp \frac{-E_I \theta}{E_B} d\lambda_1 \tag{26}$$

This solution breaks down when  $\lambda_1 \to \lambda_1^*$  defined as the root of  $a\rho^*\lambda_1^* \exp \theta^* - \rho_N k_T^* = 0$  for

$$\chi \to \chi^* = \int_0^{\lambda_1^*} \left[ \frac{a}{k_T} \exp \theta - \frac{\rho_N}{\rho} \frac{1}{\lambda_1} \right] \exp \frac{-E_I \theta}{E_B} d\lambda_1 \tag{27}$$

where the slow raise in temperature finally results in chain-branching balancing the effect of termination. One can show that the scaling  $\eta = (x - x^*)\epsilon^{1/3}$  resolves the region close to the limit, with  $\lambda_1 = \lambda_1^* + \epsilon^{1/3} \hat{\lambda}_1$  and  $\lambda_2 = \epsilon^{2/3} \hat{\lambda}_2$ . A complete solution for that zone can then be obtained, using Airy functions. Beyond that zone, chain-branching has become stronger than termination and the solution follows the same formulation as in the explosion case. The length of the reaction zone remains dominated by the first region of order  $1/\epsilon$  and determined by the value of  $\chi^*$ .

### 6 Conclusion

The small initiation rate limit model yields the structure of the initiation zone, in both the explosion and no explosion cases. Closed form integral expressions were derived for both cases. In the explosion case, the initiation length equals  $-\log \epsilon$ , up to a correction of order unity; in the no-explosion case, the length is of order  $1/\epsilon$ . In the presentation, numerical results will be shown, including complete profiles, assuming  $k_T$  is constant.

#### References

- [1] N. N. Semenov, Chain Reactions, Goskhimizdat, Leningrad 1934. English translation, Oxford 1935.
- [2] M. Short J. & J. Quirk, J. Fluid Mech. 339 (1997) 89-119.
- [3] Z. Liang & L. Bauwens, Proc. Combust. Inst. 30 (2005) 1879–1887.
- [4] F. Pintgen, C. A. Eckett, J. M. Austin & J. E. Shepherd, Combust. Flame 133 (3) (2003) 211–229.
- [5] J. D. Buckmaster & G. S. S Ludford, Proc. Combust. Inst. 21 (1987) 1669–1676.
- [6] Birkan, M. & Kassoy, D.R., Combustion Science Technology 44 (5-6) (1986) 223–256.
- [7] Kapila, A.K., J. Eng. Mathematics 12 (1978) 221–235.
- [8] Del Alamo, G. & Williams, F. A., AIAA Journal 43 (12), (2005) 2599–2605.
- [9] Kassoy, D. R. & Clarke, J. F., J. Fluid Mech. 150 (1985) 235-280.