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Title: Reactive Thermal Waves in Energetic Materials

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Reactive Thermal Waves in Energetic Materials

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The propagation of reactive thermal waves is important for the problems of 1) *energetic material cookoff*, 2) *detonation in heterogeneous explosives*, and 3) *self-propagating high temperature synthesis* (SHS). In this paper I compute reactive thermal waves in 1D, 2D, and 3D, assuming an Arrhenius reaction rate in conjunction with various depletion laws. The usual intuition, that conductive processes are relatively slow, is invalid for high energy, state-sensitive reactive systems. Instead, theory predicts that this class of wave can propagate exceedingly fast. This result helps to explain estimates for detonating heterogeneous explosives, which indicate that thermal waves must spread from hot spots at detonation-like speeds in order to achieve experimentally observed reaction zone thicknesses. I also compute the interaction of thermal waves emanating from multiple hot spots in close proximity. Finally, I discuss the applicability of the ideal theory to the real problems in which reactive thermal waves arise.

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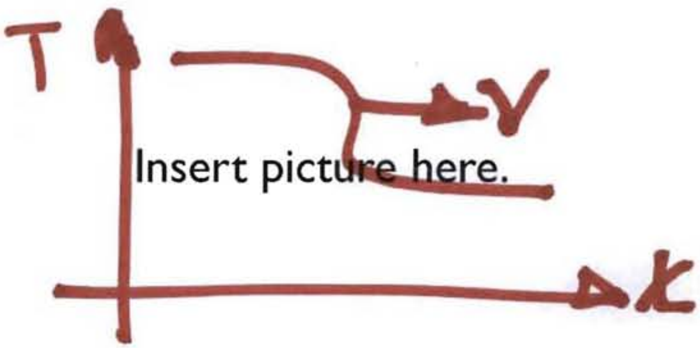
Problem

- Examine reactive thermal waves (RTWs) admitted by heat equation with Arrhenius heat addition. Seek structure, propagation speed.



- Generally, assume an arbitrary mass-fraction-based reaction progress function (RPF). Here, assume that reaction is first order.
- Assume constant density, constant specific heat.
- Nominally, idea is to extend classical pre-ignition cookoff modeling methods to post-ignition cookoff response.
- Actually, convective burning generates a rather different response. Tangential interest to cookoff, but other apps are more relevant.
- Question: Are there applicable cookoff scenarios or related problems that we haven't thought of yet? (Help)

Selected Applications

1. Self-Propagating High-Temperature Synthesis (SHS)

   Behavior is complex, involving heat *and* mass diffusion between constituent materials. Wave speeds depend on the size distributions and morphologies of constituents, plus their thermal properties. Contamination may also play a role.

2. Cookoff of High Explosives

   In this regime, HE product gases are 1000X less dense than solid reactants. Thus, reactive waves in these systems are convective in nature. Because of the volume increase they are also pressure-building, and far from purely thermal entities.

3. Strand Burning

   Nominally get a laminar burn wave, although convective burning (also called erratic burning) may occur. Substantial reaction product motion occurs because of the low product density. Again, the wave is not purely thermal in nature.

4. Detonation of Heterogeneous Explosives

   Shocked reactants are a supercritical fluid. Reactant and product densities are of the same order, such that little material motion is introduced. Waves are almost ideally thermal, although they propagate within an expanding flow.

Estimate of RTW Speed in a Detonation

- Residence time of a fluid element in the reaction zone is Δ/a, where Δ = reaction zone thickness, a = sound speed.
- Argue that time to complete reaction is also r/V, where r is the size of large particles, and V is the RTW speed.
- Further argue that for a heterogeneous reaction zone, Δ = O[r]. Equating the two times, find that V = O[a].
- Moreover in the detonation reaction zone, a = O[D], where D is the detonation speed. Thus, V = O[D].
- *Menikoff & Sewell*: Estimated RTW speeds are too fast for inert diffusion. Hot spots must propagate by another mech.
- I note that if a quasi-steady RTW is very thin, like a shock wave, then the RTW could travel as fast as the sound speed in the products. Then it would be fast enough.

Heat Equation with Heat Addition

- Heat equation with heat addition:

$$\frac{\partial T}{\partial t} = \kappa \left(\frac{\partial^2 T}{\partial x^2} + \frac{j}{x} \frac{\partial T}{\partial x} \right) + \frac{q}{c} \frac{\partial \chi}{\partial t}$$

$j = 0$: slab, $j = 1$: cylinder, $j = 2$: sphere

- Arrhenius heat addition with arbitrary RPF, denoted by g:

$$\frac{\partial \chi}{\partial t} = \mathrm{g}[\chi] Z \mathrm{e}^{-T^*/T}$$

- Consider a first-order reaction, $\mathrm{g}[\chi] = 1 - \chi$.
- *Goal*: Study universal structure, determine wave speed.
- *Strategy*: Make equations as universal as possible through nondimensionaliztion. Find the universal function for dimensionless speed with the aid of numerical calculations.

Dimensionless Temperature

- Define the dimensionless temperature ϕ:

$$\phi = \frac{T - T_0}{T_m - T_0}$$

- Max temperature T_m can be eliminated by the energy balance:

$$c\,(T_m - T_0) = q$$

- Dimensionless temperature can then be expressed as:

$$\phi = \frac{c\,(T - T_0)}{q}$$

- Next define the dimensionless parameters:

$$\tilde{T}_0 = \frac{T_0}{T^*}$$ Dimensionless Temperature

$$\tilde{q} = \frac{q}{c\,T^*}$$ Dimensionless Heat Release

High Activation Energy Approximation

- Because $T^{*}/T = \mathrm{O}[10]$, we can make Frank-Kamenetskii (F-K) high activation energy approximation. Do this is to eliminate one para-meter. (Simplifies the problem and aids in finding the wave speed.)
- Then exponent T^{*}/T can be expressed as:

$$\frac{T^*}{T} \approx \frac{1}{\tilde{T}_0} - \theta$$

where the θ is the F-K temperature given by

$$\theta = \frac{T^*}{T_0^2}(T - T_0) = \frac{\tilde{q}\,\phi}{\tilde{T}_0^2} \equiv \alpha\,\phi$$

- α is the only parameter in the problem. As we shall see, it is the heterogeneity parameter for a single hot spot. For values of $\alpha < 10$, behavior is homogeneous. For values of $\alpha > 10$, behavior is heterogeneous (i.e., it is dominated by RTWs).

Nondimensionalization

- Define reference time t_r and a reference length x_r. The dimensionless time and distance and are then

$$\tilde{x} = \frac{x}{x_r} \quad \text{and} \quad \tilde{t} = \frac{t}{t_r}$$

- The model equations then become

$$\frac{1}{t_r}\frac{\partial \chi}{\partial \tilde{t}} = Z\mathrm{g}[\chi]\mathrm{e}^{-1/\tilde{T}_0}\mathrm{e}^{\alpha\,\phi} \quad \text{and}$$

$$\frac{1}{t_r}\frac{\partial \phi}{\partial \tilde{t}} = \frac{\kappa}{x_r^2}\left(\frac{\partial^2 \phi}{\partial \tilde{x}^2} + \frac{j}{\tilde{x}}\frac{\partial \phi}{\partial \tilde{x}}\right) + \frac{1}{t_r}\frac{\partial \chi}{\partial \tilde{t}}$$

- Can eliminate all parameters except for α by choosing

$$t_r = \frac{\mathrm{e}^{1/\tilde{T}_0}}{Z} \qquad \text{and} \qquad x_r = \sqrt{\frac{\kappa}{Z}}\,\mathrm{e}^{1/(2\,\tilde{T}_0)}$$

Final Equations

- The dimensionless equations to be solved are

$$\frac{\partial \phi}{\partial \tilde{t}} = \frac{\partial^2 \phi}{\partial \tilde{x}^2} + \frac{j}{\tilde{x}} \frac{\partial \phi}{\partial \tilde{x}} + \frac{\partial \chi}{\partial \tilde{t}} \quad \text{and} \quad \frac{\partial \chi}{\partial \tilde{t}} = \mathrm{g}[\chi] \mathrm{e}^{\alpha\, \phi}$$

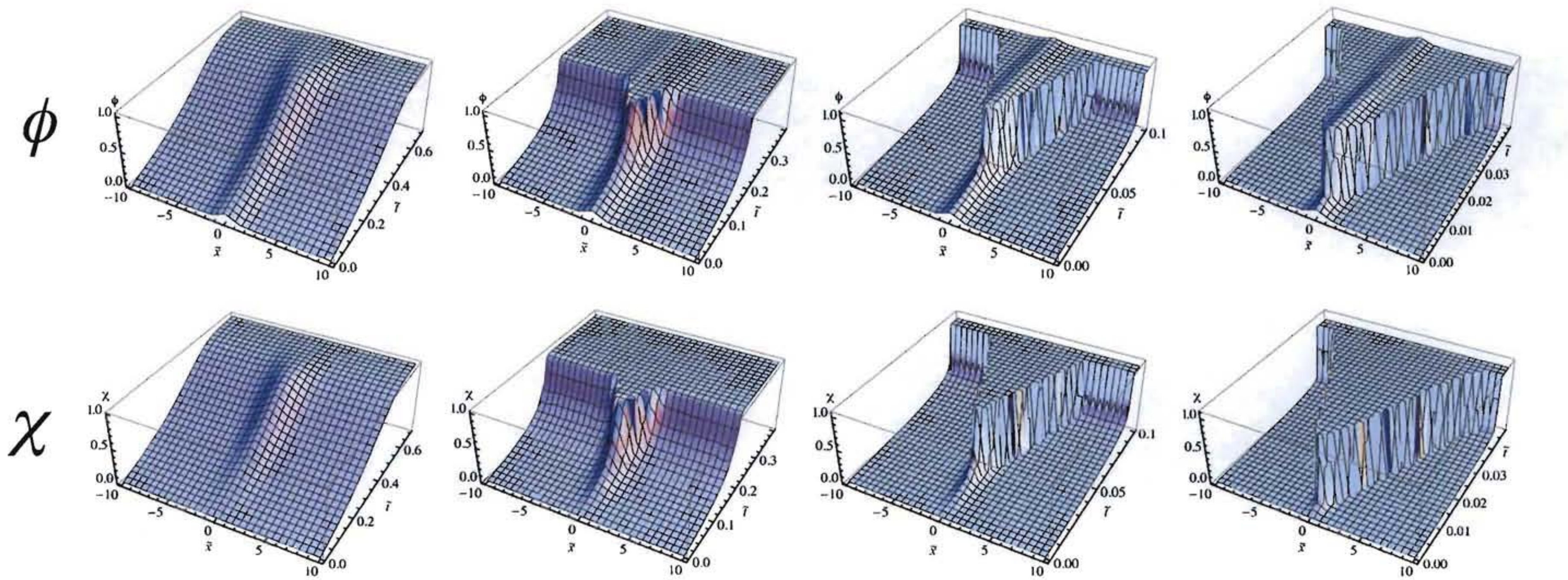
  subject to the initial and boundary conditions

$$\frac{\partial \phi}{\partial \tilde{x}}[0,t] = 0, \;\; \frac{\partial \phi}{\partial \tilde{x}}[\infty,t] = 0, \;\; \phi[\tilde{x},0] = \phi_{00}\, \mathrm{e}^{-(\tilde{x}/\sigma)^2}, \;\; \chi[\tilde{x},0] = 0$$

- Assume a Gaussian profile for the initiating hot spot. The form is noncritical. The only hard criterion is that the hot spot is super-critical. Heat release soon swamps the energy in the initial spot.
  - Can test for steady-travelling wave solutions by substituting the variable $\xi = \tilde{x} - \tilde{V}\, \tilde{t}$, where $\tilde{V}$ is the dimensionless wave speed.
- Substitution only works if $j = 0$. Thus, only plane waves are steady. Cylindrical, spherical waves become steady for large $\tilde{x}$.

Numerical Results for 1D Waves

$\alpha = 3$ $\alpha = 6$ $\alpha = 12$ $\alpha = 24$



Homogeneous | Homogeneous Transitional | Hetrogeneous Transitional | Heterogeneous

- We estimated that RTWs must be shock-like to propagate at exp-erimentally-deduced speeds. This is in fact the case.

1D Steady Wave Speed (1)

- The reference time and length

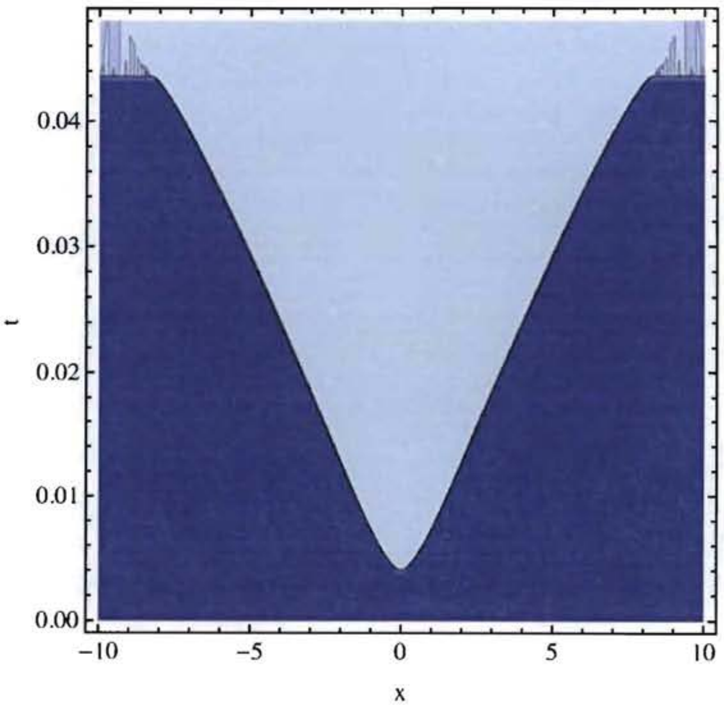
$$t_r = \frac{\mathrm{e}^{1/\tilde{T}_0}}{Z} \qquad \text{and} \qquad x_r = \sqrt{\frac{\kappa}{Z}}\,\mathrm{e}^{1/(2\,\tilde{T}_0)}$$

define a reference speed $v_r = \dfrac{x_r}{t_r} = \sqrt{\kappa\, Z}\,\mathrm{e}^{-1/(2\,\tilde{T}_0)}$

- The actual wave speed is $V = \tilde{V}[\alpha]\, v_r = \tilde{V}[\alpha]\sqrt{\kappa\, Z}\,\mathrm{e}^{-1/(2\,\tilde{T}_0)}$
- The dimensionless wave speed $\tilde{V}[\alpha]$ can depend only on α, because α is the only parameter in the problem.
- Because the problem evidently cannot be solved analytically, we must perform a series of numerical calculations to find $\tilde{V}[\alpha]$.
- The function $\tilde{V}[\alpha]$ depends on the reaction progress function, g. Here, we shall assume a first order reaction, for which $\mathrm{g} = 1 - \chi$.

1D Steady Wave Speed (2)

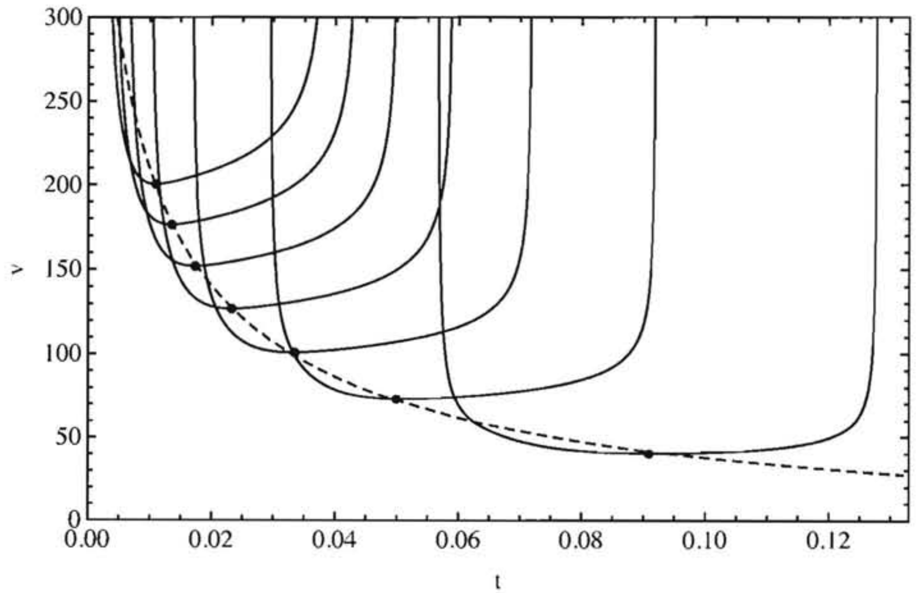
- There is a complication in finding $\tilde{V}[\alpha]$. The material ahead of the wave starts to cook off, which causes the wave to accelerate:



- We could get around this problem by assuming that the wave is quasi-steady. The main problem is that there is a calculated α, and a contradictory time-changing upstream value of α.

1D Steady Wave Speed (3)

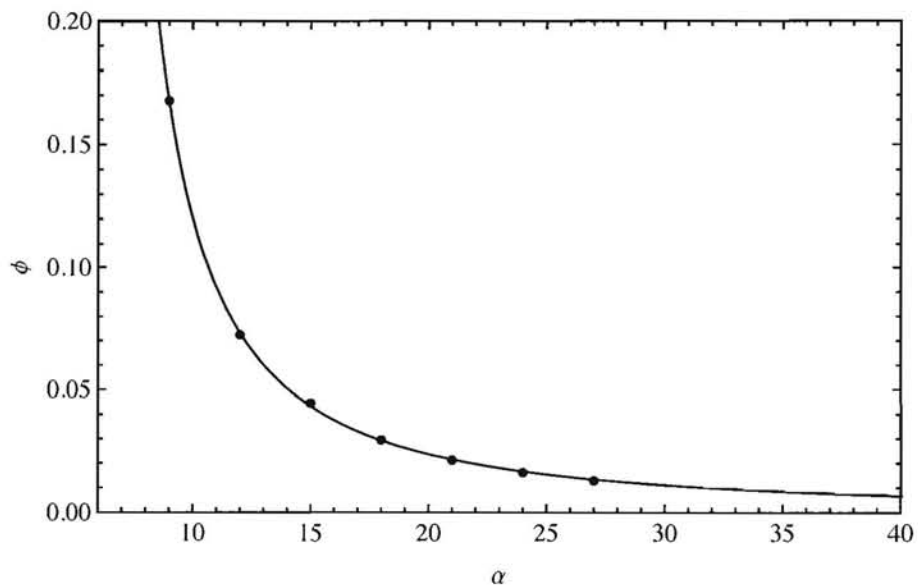
- The best way to address this problem is by extrapolation. Start by plotting speed curves for a series of computations:



- Choose the minimum of each curve because that is the point of zero acceleration. Non-steady effects will be minimal there.
- Pick off these points for further use.

1D Steady Wave Speed (4)

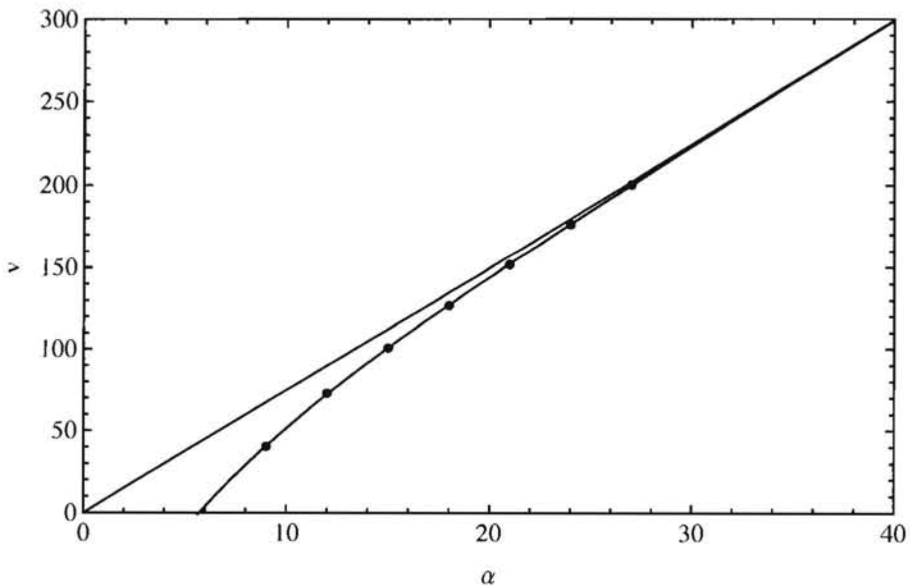
- Each speed point from the above plot is associated with an upstream value of $\phi = \phi_\infty$, which the model assumes to be zero.
- In reality ϕ_∞ is finite, but it decreases as α increases and reaction becomes more homogeneous:



- Calculations become more difficult as a is increased. $\alpha = 27$ was as high as I could compute. At this value, ϕ_∞ is 1%.

1D Steady Wave Speed (5)

- Plotting $\tilde{V}$ versus α, find that behavior seems to approach a straight line through the origin as $\phi_\infty \rightarrow 0$.
- A depends linearly on q, and q is required to produce a finite V. Thus, argue that $\tilde{V}[0] = 0$; i.e., line must pass through the origin.



- Fit the speed data to

$$\tilde{V}_{fit}[\alpha] = a\,\alpha - b\,e^{c\,\alpha}.$$

Find that V[a] is

$$\tilde{V}[\alpha] = 7.48\,\alpha,$$

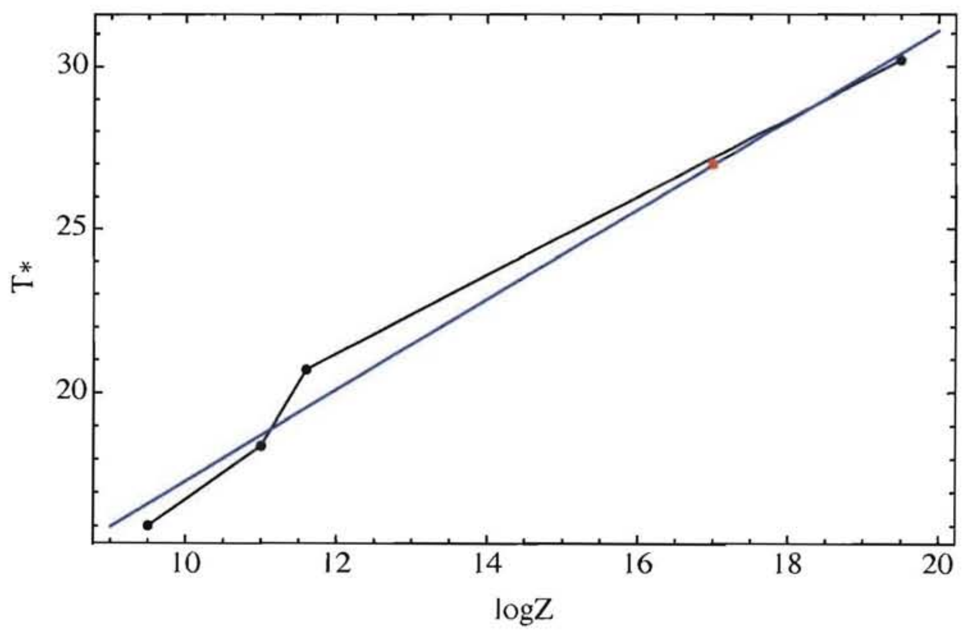
such that the complete formula is given by

$$V = \frac{7.48\,\tilde{q}\,\sqrt{\kappa\,Z}}{\tilde{T}_0^2\,e^{1/(2\,\tilde{T}_0)}}$$

- Argue that this formula is applicable to all well-defined quasi-steady RTWs.

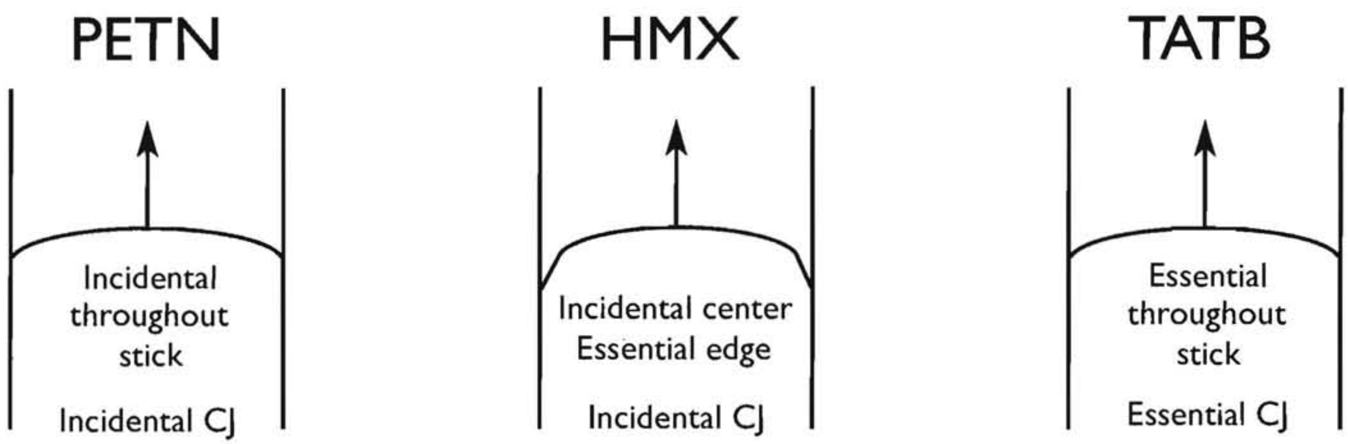
PBX 9502 Arrhenius Parameters

- For PBX 9502, published Arrhenius parameters give speeds between O[10] m/s and O[10^5] m/s (±2 orders of magnitude!).
- Can turn this around to constrain Arrhenius parameters. Use the fact that proposed sets tend follow a line in $\log Z$-T^* space:
- Constrain parameter values to the best-fit line. Find values that match the estimated sound speed in the 9502 reaction zone.



- A good "round number" set is $\log Z = 17$, $T^* = 27{,}000$ K. These parameters cannot be unreasonable, because they lie within the range of published values.

3 Classes of Heterogeneous Detonation



- Evidence that HMX is a transitional form:

  1) HMX has not been initiated in single crystal form (suggests essential heterogeneity, or nearly.

  2) PBX 9501 detonation follows Arrhenius kinetics according to Menikoff (suggests incidental heterogeneity).

  3) PBX 9501 reaction zone is shorter than the grain scale (suggests incidental heterogeneity).

  4) PBX 9404/9501 edge anomaly: suggests mixed behavior in a stick?

Conclusions

- Computed RTWs have a shock-like structure, and can be fast enough to agree with estimated RTW speeds in detonation reaction zones.
- Curved RTWs are unsteady, but approach steadiness as they grow.
- Deduced a parameter α that characterizes the reaction heterogeneity of a single hot spot.
- Found the speed formula for a plane steady RTW. It is propoartional to α, and depends exponentially on the upstream temperature.
- Computed wave speeds depend sensitively on Arrhenius parameters. Demonstrated that this quality can be used to constrain parameter sets.
- Find that, as expected, PBX 9501 CJ detonations are relatively homogenious; whereas, PBX 9502 CJ detonations are fully heterogeneous.
- Proposed three classes of heterogeneity in detonation waves: *fully incidental*, *incidental/essential mix*, and *fully essential*.
- Proposed that TATB anomalies, which have tacitly been attributed to chemistry, may be generic properties of fully essential behavior.