Semenov Theory on Thermal Explosion

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*Made with LaTeX.

1 Part 1. Introduction

This research project is devoted to the 'Semenov theory' on the thermal explosion of various substances (gases) at varying starting temperatures and concentrations for a time interval of maximum - 1 second. Semenov theory is the most basic form of the mentioned phenomena, mainly described by 2 Ordinary Differential Equations (from now on ODEs) with 3 constant parameters to be defined. All variables and parameters in the following formulas are defined as 'dimensionless' and do not have any physical units. All calculations involve basic academic version of "MATLAB" with no additional toolboxes.

2 Main ODEs and conditions

The following is a system of ODEs that describes the absolute dimensionless temperature θ and concentration ν. The constant parameters and their domains are $\alpha \in \{2.1, 2.2, ..., 3.0\}$, $\beta \in \pm\{0.01, 0.02, ..., 0.1\}$ and $\gamma \in \{0.01, 0.02, ..., 0.1\}$

$$\begin{cases} \gamma \frac{d\theta}{d\tau} = \nu e^{\frac{\theta}{1+\beta\theta}} - \alpha\theta \\ \frac{d\nu}{d\tau} = -\nu \frac{\theta}{1+\beta\theta} \end{cases} \tag{1}$$

with $\theta(\tau = 0) = \theta_0 = 1 = \nu_0 = \nu(\tau = 0)$ as initial values describing the reaction.

It is clearly seen that finding a precise algebraic solution to the given ODEs is quite problematic and might even be impossible to derive. Thus, a numerical solution must be implemented instead.
The solution will require solvers ode45 and ode15s. These solvers are based on different numerical analysis methods such as Dormand-Prince Method for ode45 and Numerical Differentiation formulas or Backward Differentiation Formula for ode15s.

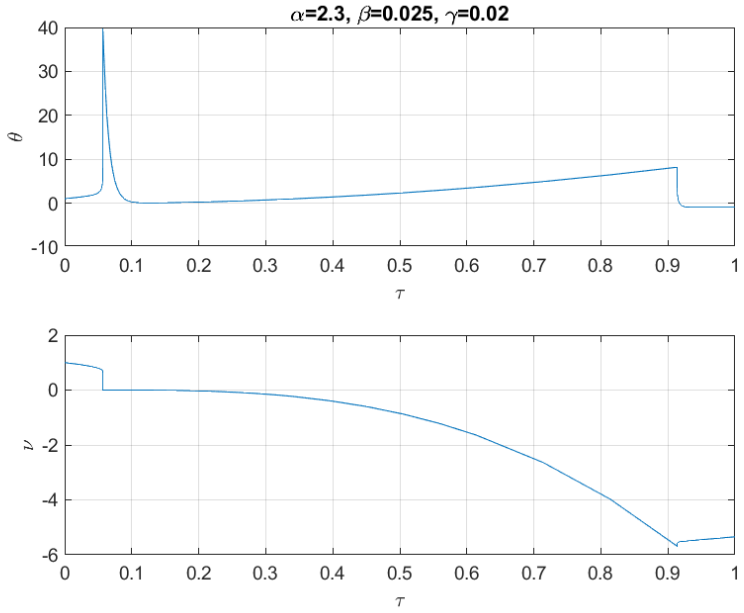


Figure 1: Solver ode15s derives an unstable graph for the given parameter values

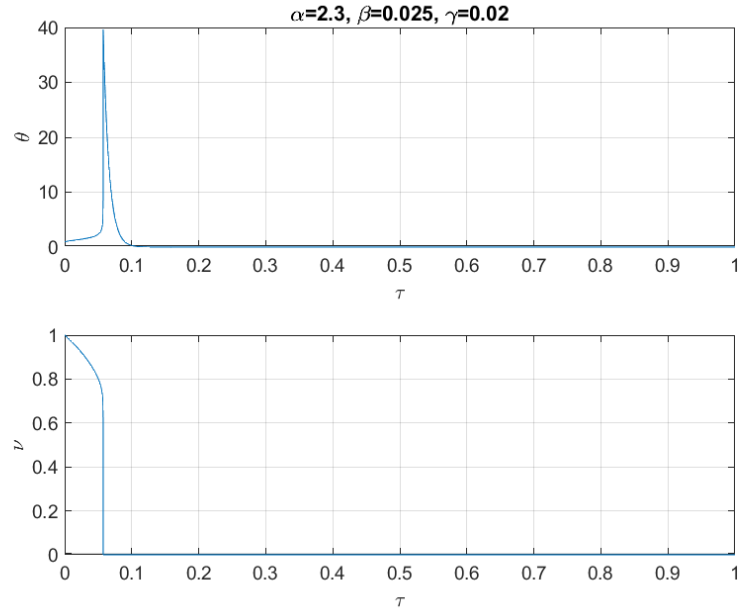


Figure 2: Solver ode45 derives in a more "non-stiff and smooth graph" for the same parameter values

After solving the ODEs for 1 example with similar parameters, we can clearly see that ode45 is a slightly more suitable choice, as ode15s results in $\theta(\tau)$ and $\nu(\tau)$ graphs behaving unnaturally. This technical difference, however, can only be observed for certain parameters α, β and γ. For example, if one sets $\beta, \gamma = const.$, then for $\forall \alpha \in [2, 2.33)$ the following tendency of same graphs can be seen:

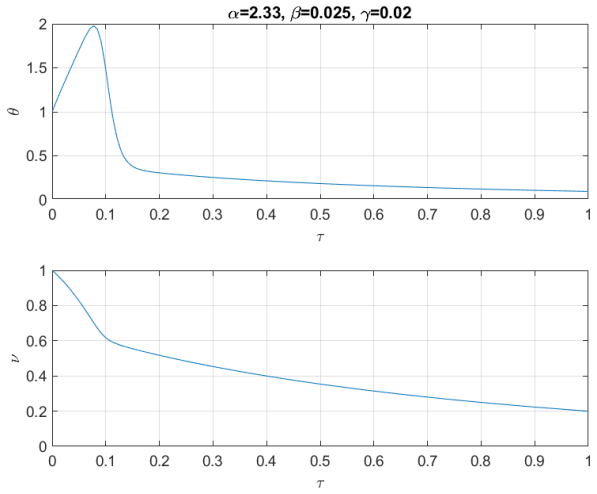


Figure 3: ode15s

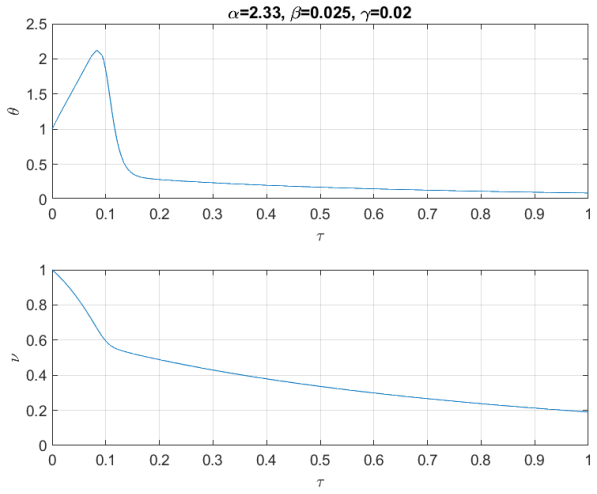
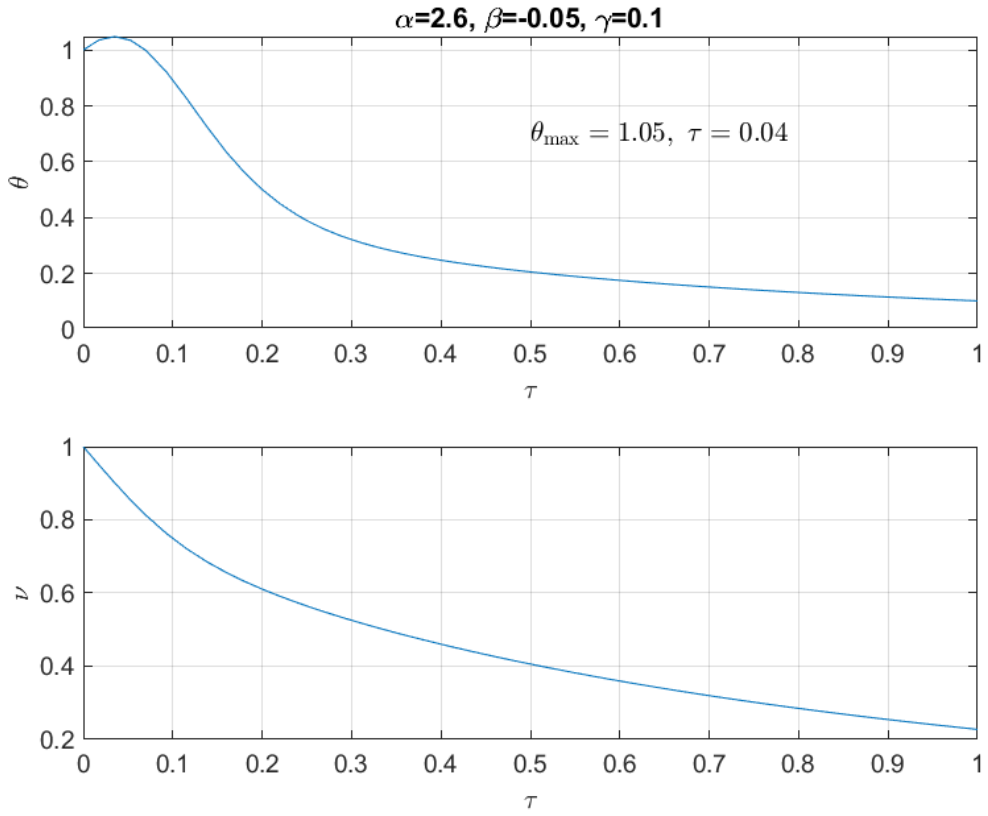


Figure 4: ode45

3 Graph analysis

In this section, general behavior of the graphs will be described and subsequent statements made.

In the following example, random parameters were chosen. For the case of $\theta(\tau)$, we observe that after the start of ignition, the temperature function quickly reaches its maximum at $\tau = 0.04s$, and subsequently the gas cools down exponentially. As for the $\nu(\tau)$ graph, the maximum value is - obviously - at $\tau = 0s$, and concentration decreases exponentially as well.



In comparison with the illustrations on the last page, the difference in parameter α seems to "shift" the time of explosion at its peak from the start of reaction. In addition, $\frac{d\nu}{d\tau}(\tau \in [0, 0.1])$ seems to have much higher absolute value than that of the current graph.

Thus, some questions occur regarding the behavior of the functions. That is,

- What do these parameters describe in general?
- Why is there such a "fatal" boundary value for α?
- How accurate are these computational experiments compared to empirical data? Considering the intentionally oversimplified model of the reaction, how far are Semenov Theory assumptions from the currently leading most precise theory of Thermal Explosion?
- And last but not least, what are the industrial and engineering-related applications of this theory?

The answers are left open to the reader as a self-exercise.

4 Conclusion of Part 1

It turns out that Semenov Theory of Thermal Explosion is dependent only on starting absolute temperature of the system (gas) and its concentration. The author, seemingly, states that the 3 parameters that describe the reaction are dependent on system parameters such as activation energy, gas molecules properties and so on. If so, it is of high interest for me to research the possible reaction kinetics and the system properties further describing the behavior of Thermal Explosion.

Thank you, dear reader!

5 Part 2

In this paragraph, we will mostly answer to the questions from Part 1. Mainly, the physics behind parameters α, β and γ will be described. In addition, we will take a deeper glance at physics of the ODEs.

Firstly, Semenov Theory assumes the following first-order chemical reaction:

$$\mathrm{C} \xrightarrow{\mathrm{k(T)}} \mathrm{P} \tag{2}$$

Here, one defines C as concentration, P as product and k(T) as temperature dependent reaction rate with

$$k(T) = Ae^{-\frac{E_A}{RT}} \tag{3}$$

where E_A is the activation energy, R is the universal gas constant and A is the so-called "frequency constant". This relation is called Arrhenius equation. Let's now define the material balance (rate of reactant consumption) and energy balance in the system:

$$\frac{dC}{dT} = -k(T) \cdot C \tag{4}$$

$$\rho \cdot c_p \cdot V \cdot \frac{dT}{dt} = V \cdot Q \cdot (-\frac{dC}{dt}) - \sigma \cdot S \cdot (T - T_0) \tag{5}$$

The latter expression equates the general heat change rate (power) due to temperature change to heat released from chemical reaction and heat dissipation into the environment, where

· Q - heat released per mole of reactant
· c_p - specific isobaric heat capacity $[\frac{J}{(K \cdot kg)}]$
· σ - heat transfer coefficient $[\frac{W}{K \cdot m^2}]$
· S - surface area

Note that if heat generation overtakes heat loss, temperature can uncontrollably, and explosion might happen. This model shows that small changes in conditions (e.g., ambient temperature or reaction parameters) can trigger an explosion. It helps identify critical conditions for safe operation of reactors or storage systems (we have already seen this behavior in the previos part when α had a critical value ≈ 2.33).

6 Finding the critical value of the first parameter

Now that we have determined the physics behind the 3 dimensionless parameters, let us determine α_{crit} using a simple iteration method. As a spoiler, we will learn to find it with the following precision:

$$\alpha_{crit} = 2.3294005 \tag{6}$$

Thus, we determine to find an upper boundary $\alpha_{crit} = \alpha_{upper}$ such that $\forall \alpha \geq \alpha_{crit}$ the reaction occurs in non-explosive regime and vice versa happens for values less than that. The simple algorithm to be implemented involves iterating through each order (number of decimal digits), within what incrementing by 1 is implemented. Afterwards, we can use at least two methods to analyze the reaction behavior. First, one can simply count the values of concentration near zero, we can see this effect in the following graph. Second, one can use the convention that explosive regime - by definition - results in peak temperature being close to $\frac{1}{\gamma}$. After implementing both methods (which are available in the GitHub repository provided in page 10), one can only find precise values until order 8.

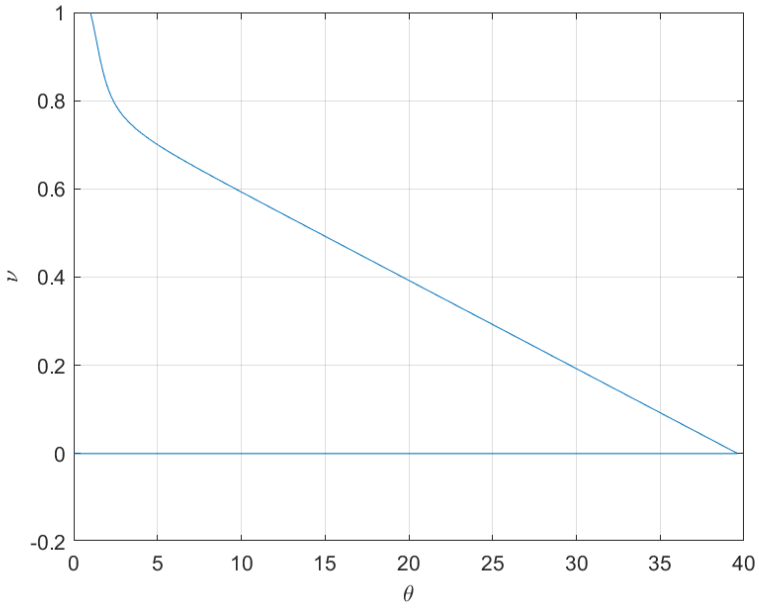


Figure 5: $\alpha = 2.3; \beta = 0.025; \gamma = 0.02$

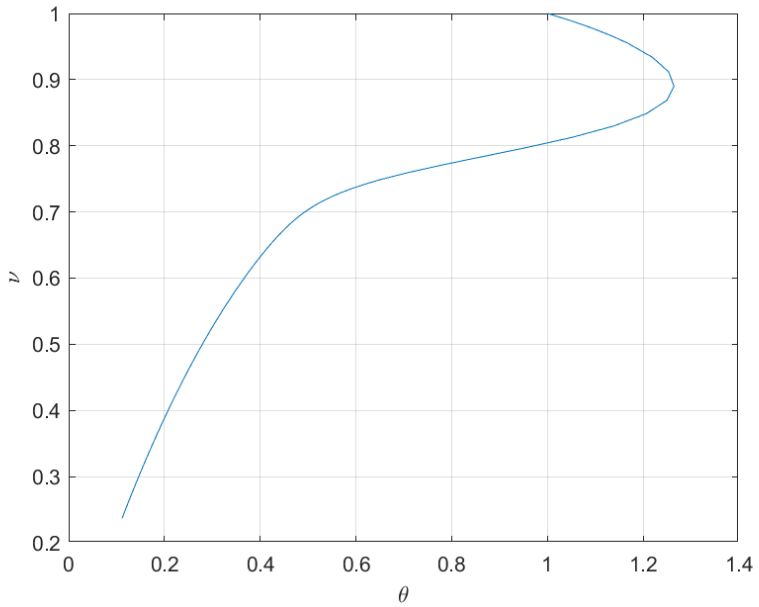


Figure 6: $\alpha = 2.4; \beta = 0.025; \gamma = 0.02$

After clearly seeing that we can choose $\alpha = 2.3$ and $\alpha = 2.4$ for boundary values, we just iterate through the above mentioned algorithm 10 times, to get α_{crit} as predefined at the beginning of this section.

7 Contents and literature

- Full MATLAB code used in calculations, both ode45 and ode15s versions can be found in this link
- All information in this work was taken from this wiki and thanks to Dr. Viatcheslav Bykov