MULTIPLICITY OF SOLUTIONS OF A NONLINEAR BOUNDARY VALUE PROBLEM ARISING IN COMBUSTION THEORY.

by

Patrick Joseph Kelly

A thesis
presented to Massey University of Palmerston North
in fulfilment of the
thesis requirement for the degree of
Master of Science
in
Mathematics.

Palmerston North, New Zealand, 1991
Patrick Joseph Kelly.

Abstract

The problem of self-heating in spherical and spherically annular domains is addressed in this thesis. In particular, the Frank-Kamenetskii model is used to investigate the multiplicity of steady state solutions in these geometries. The differential equations describing this model depend crucially on a parameter, the "Frank-Kamenetskii" parameter; for spherical geometries it is known that: (a) a unique solution exists for sufficiently small parameter values, (b) there is a value of the parameter such that an infinite number of solutions exist. A convergent infinite series solution is developed for the problem in a spherical domain. The multiplicity of solutions when the problem is posed in spherically annular domains is then explored. It is shown, in contrast to (b), that multiple solutions exist for arbitrarily small parameter values and that no value of the parameter produces infinite multiplicity.

ACKNOWLEDGEMENTS.

To my supervisor Professor G.C. Wake....

Thanks Graeme for a wonderful year. Your guidance and patience were invaluable.

To Doctor Bruce van Brunt...

Thanks for your help in proof reading this thesis and for the discussions on series convergence.

To our computer consultant Richard Rayner, who was always available with cheerful efficient advice on matters computing. I have finished now so your weekends are your own and the equipment will work properly.

To my roomates, Daniel and Kim, who were always there with cheerful thoughts and helpful advice. Thanks for putting up with me. A special thanks to Daniel for putting up with my lousy chess playing, those stress relieving games were a godsend.

To Margaret and Graeme Murdoch with whom i boarded for four years while completing my studies. Thanks for everything.

DEDICATION.

I dedicate this thesis to those i love

My parents, Roxy and Brian,

My brothers and sisters,

Chris and Annette,

Jason,

Deborah,

Richard,

Rebecca.

My nephews

Daniel,

David.

Thanks for all the love and support you have given me over the years.

Yes i have finally finished and here it is...

CONTENTS

Chapter 1

Introduction

1.1 The theory of thermal ignition

The theory of thermal ignition addresses the question of what happens to a combustible substance when it is placed in a vessel, the walls of which are maintained at a prescribed temperature T_0 (usually constant). Under certain conditions, one observes a rapid rise in the temperature of the substance to a high value near the theoretical maximum temperature of explosion. Under other conditions, in contrast, only a small rise to a stationary level is observed. This small temperature rise remains constant until a large portion of the material has reacted. The conditions under which the transition occurs from one range to the other, for a small change in the external parameters, are termed the critical conditions of ignition.

When investigating the problem of thermal ignition, we consider the equation of heat conduction with continuously distributed sources of heat,

$$c\rho\frac{\partial T}{\partial t} = \nabla.(\lambda\nabla T)+q, \qquad (1.1)$$

where T is the temperature, c the heat capacity, ρ the density of the substance, λ the thermal conductivity, and q the density of the sources of heat, that is, the quantity of heat evolved as a result of chemical reactions in a unit volume per unit time.

Solving this equation under the boundary conditions involving a given temperature T_0 at the surface of the wall gives the temperature distribution in the vessel as a function of time. The nature of this dependence changes sharply at the critical conditions, where there is an abrupt transition from a small constant temperature rise to a large and rapid rise. Owing to the formidable mathematical difficulties involved in integrating the partial differential equation (1.1) one normally resorts to one of two approximations which are well known in the nonstationary and stationary theories of thermal explosion.

In the stationary theory, the spatial temperature is not taken into consideration; instead, a mean temperature is introduced and assumed to be equal at all points of the reaction vessel. This assumption is admittedly not valid in the conduction range where the temperature is by no means localised at the wall. This approach, however, does allow the temperature dependence on time to be examined; consequently, one can also determine the induction period, that is, the time within which an explosion occurs. Although the nonstationary theory is an integral part of the theory of thermal ignition, we will not deal with it any further. Instead, we will examine the stationary theory of thermal ignition in symmetrical regions.

In the stationary theory, only the temperature distribution over the vessel is considered and its change in time is not taken into account. The conditions under which the stationary temperature distribution becomes highly sensitive or even discontinuous due to changes in the external parameters are termed the critical conditions of ignition.

The stationary form of the heat conduction equation (1.1) is

$$\nabla . (\lambda \nabla T) + q = 0 . \tag{1.2}$$

In most cases, however, the temperature dependence of the heat conductivity is neglected and the above equation reduces to

$$\lambda\nabla^2 T + q = 0. \tag{1.3}$$

If the rate of reaction depends on the temperature in accordance with Arrhenius' Law then it can be represented by

$$Z = ze^{-E/RT} \tag{1.4}$$

where Z is the rate of reaction, T the absolute temperature, R the gas constant, and E and z are parameters characteristic of the given chemical reaction. The quantity E is termed the activation energy and represents the amount of energy required for a mole of the substance to react. The factor z depends on the pressure and composition of the substance, but not on the temperature in a first approximation. In this approximation one also assumes that the rate of reaction is independent of the loss of reactant. The density of the sources of heat can thus be expressed as

$$q = Qze^{-E/RT},$$

where Q is the thermal effect of the reaction per unit volume. Equations (1.3) can now be written in the form

$$\nabla^2 T + \frac{Q}{\lambda} ze^{-E/RT} = 0. \tag{1.5}$$

We can rewrite this equation in terms of a dimensionless temperature and spatial coordinate by taking

$$u = RT/E \tag{1.6}$$

as the dimensionless temperature and

$$\underset{\sim}{y} = \frac{1}{\ell}\underset{\sim}{x}$$

as the dimensionless spatial coordinates, where, $\underset{\sim}{x}$ are the dimensional spatial coordinates and ℓ is a typical length such as the radius or half-width of the vessel such that, on the surface $||\underset{\sim}{y}||=1$, the boundary condition is

$$u=u_0=RT_o/E.$$

In this way we have only the one dimensionless parameter

$$\gamma=QzR\ell^2/\lambda E$$

in the differential equation and a second dimensionless parameter

$$u_0=RT_0/E$$

in the boundary condition. The equation now has the form

$$\nabla^2_{\underset{\sim}{y}}u+\gamma e^{-1/u}=0. \tag{1.7}$$

If u is a solution to this equation and satisfies the boundary condition, then

$$u=f(\underset{\sim}{y},\gamma,u_0), \tag{1.8}$$

giving the temperature u as a function of $\underset{\sim}{y}$ with the two parameters γ and u_0. This represents the most general solution of the problem of thermal ignition in a purely conductive heat exchange. The condition under which a stationary temperature distribution is parametrically sensitive, that is, when a rapid rise in temperature occurs for a small change in the parameter γ, should be of the form

$$\gamma=g(u_0), \tag{1.9}$$

as neither the equation nor the boundary condition contain any parameters other than u_0 and γ. However, an empirical fact of great importance is that u_0 is small, i.e.

$$u_0 = RT_0/E << 1,$$

and so it is reasonable to look for the limiting form of (1.9) corresponding to $u_0 \to 0$. Moreover, if we consider $u_0 << 1$, we not only obtain more tractable results, but also specific features proper to combustion stand out more distinctly [13]. In examining this limiting case, we must keep in mind that we are considering a stationary temperature distribution below the explosion limit where the temperature rises are small.

Let $\upsilon = T - T_0$ where it is assumed that $\upsilon << T_0$: this is equivalent to $u_0 << 1$, a fact that will be established later. Now

$$e^{-E/RT} = e^{-E/R(\upsilon + T_0)} = e^{-E/RT_0 (1/(1+\frac{\upsilon}{T_0}))},$$

and since $\upsilon << T_0$, the quantity

$$\frac{1}{1+\frac{\upsilon}{T_0}},$$

can be estimated using a binomial series expansion and neglecting all terms of order $\left(\frac{\upsilon}{T_0}\right)^2$; thus,

$$e^{-E/RT} \approx e^{-E/RT_0 (1-\frac{\upsilon}{T_0})} = e^{-E/RT_0} e^{E\upsilon/RT_0^2}. \quad (1.10)$$

Using the above approximation, equation (1.5) can be written

$$\nabla^2 \upsilon + \frac{Q}{\lambda z} e^{-E/RT_0} e^{E\upsilon/RT_0^2} = 0, \tag{1.11}$$

subject to the boundary condition $\upsilon=0$ at the wall of the vessel.

Let
$$\theta = E\upsilon/RT_0^2. \tag{1.12}$$

Transforming (1.11) into the dimensionless variables θ and $\underset{\sim}{y}$ we now have

$$\nabla^2_{\underset{\sim}{y}}\theta + \frac{QE}{\lambda RT_0^2} z\ell^2 e^{-E/RT_0} e^{\theta} = 0, \tag{1.13}$$

and the boundary condition at the surface $||\underset{\sim}{y}||=1$ is $\theta=0$. The differential equation and boundary condition now contain only the one dimensionless parameter

$$\delta = \frac{QE}{R\lambda T_0^2} z\ell^2 e^{-E/RT_0}, \tag{1.14}$$

which, in this approximation, characterises the properties of the substance and the vessel shape. The problem of thermal ignition can therefore be represented by the non-linear differential equation

$$\nabla^2_{\underset{\sim}{y}}\theta + \delta e^{\theta} = 0 \tag{1.15}$$

and the boundary condition at the surface of the vessel $\theta=0$, $||\underset{\sim}{y}|| = 1$. This approach was first developed by Frank-Kamenetskii [13] and the parameter δ is called the Frank-Kamenetskii parameter.

If θ is a solution to (1.15) representing a stationary distribution then

$$\theta = f(\underset{\sim}{y},\delta). \tag{1.16}$$

The critical condition of ignition depends solely on δ as neither the differential equation nor the boundary condition contain any parameters other than δ. Thus, there exists a

$$\delta = \text{constant} = \delta_{cr} \tag{1.17}$$

such that a stationary temperature distribution becomes impossible. If the conditions of any experiments give a value of δ less than the critical value δ_{cr} a stationary temperature distribution should establish itself; if not, an explosion or thermal runaway will occur (see figure 1.1).

The value of δ_{cr} depends crucially on the shape of the vessel, and the values are well known for simple geometric shapes. For a spherical vessel, $\delta_{cr}=3.3219$; for an infinitely long cylindrical vessel, $\delta_{cr}=2.00$; and for a vessel with two infinitely long parallel planar surfaces (the infinite slab), $\delta_{cr}=0.878$. These values calculated from the theory of thermal ignition are in close agreement with the experimental values obtained from substances whose kinetics are known [8].

From the solution (1.16), we can see that the maximum temperature rise below the explosion limit is given by

$$\upsilon_{max} = (T-T_0)_{max} = \frac{RT_0^2}{E} f(\underset{\sim}{0},\delta_{cr}), \tag{1.18}$$

where we have assumed that the vessel is symmetric, and consequently the hottest point is at $\underset{\sim}{y}=\underset{\sim}{0}$. Since $\upsilon \propto \frac{RT_0^2}{E}$, below the explosion limit $RT_0 << E$ and therefore $\upsilon << T_0$. Thus the assumption $\upsilon << T_0$ made in the derivation

Bifurcation Diagram.

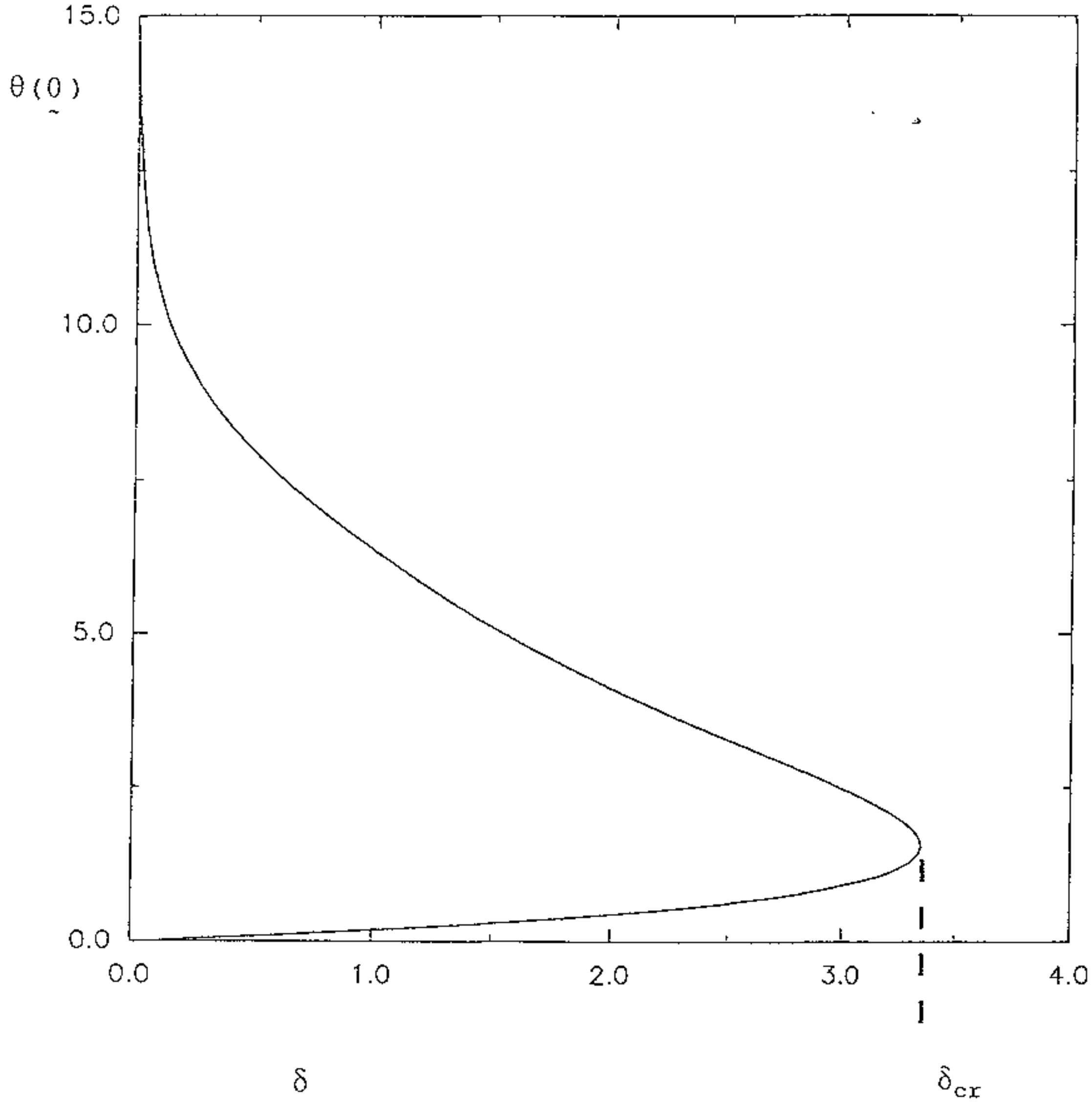

Figure 1.1

The critical value of the parameter δ.

of (1.10) is equivalent to $u_0 << 1$. If, however, RT_0 is not small compared to E then we do not get the characteristic picture of the combustion phenomena; instead, we are dealing with the theory of the nonisothermal course of a chemical reaction, a limiting form of which is considered in the theory of combustion and thermal ignition.

1.2 Formulating The Problem And Boundary Conditions.

Thus far we have considered only vessels whose walls were held at a fixed temperature equal to that of the surrounding medium. We now consider the case when heat released in the reaction warms the vessel walls and the surrounding medium, whose temperature typically changes if the heat exchange between the two mediums is not too rapid. Any steady-state theory of thermal explosion that includes this effect must begin with the complicated manner in which heat is exchanged between the reactive medium and the vessel walls. This problem is not addressed here but has been discussed by Borzykin and Marzhanov [9] and by Thomas [10]. The temperature distribution inside such a wall rapidly becomes quasistationary and the temperature on the inner surface of the wall is given by the Newtonian heat exchange equation [7],

$$\lambda \frac{\partial T}{\partial n} = -\alpha (T - T_0), \qquad (1.19)$$

where the heat flux on the left is calculated for the reacting substance next to the vessel surface ($\underset{\sim}{n}$ is a unit outward normal to the wall) and the heat flux on the right is calculated from the conditions of heat exchange between the wall and the surroundings. Here T_0 is the temperature of the surroundings far from the vessel surface, λ the heat conductivity, α the heat transfer coefficient depending on the nature of the heat transfer between the vessel and the surroundings and ℓ a measure of length. Equation (1.12) can be rearranged as

$$(T - T_0) = \frac{RT_0^2}{E}\theta.$$

Differentiating the above equation yields

$$\lambda\frac{\partial T}{\partial n} = \frac{1}{\ell}\frac{\lambda R T_0^2}{E}\frac{\partial \theta}{\partial n},$$

and substituting this into (1.19) gives

$$\frac{1}{\ell}\frac{\lambda R T_0^2}{E}\frac{\partial \theta}{\partial n} = -\alpha\frac{R T_0^2}{E}\theta,$$

which in turn yields

$$\frac{\partial \theta}{\partial n} + \frac{\alpha\ell}{\lambda}\theta = 0.$$

The Biot number is defined as

$$Bi = \frac{\alpha\ell}{\lambda},$$

giving the so called arbitrary Biot number condition on the boundary

$$\frac{\partial \theta}{\partial n} + Bi\,\theta = 0. \qquad (1.20)$$

When $Bi \to \infty$ equation (1.20) becomes the Frank-Kamenetskii boundary condition $\theta=0$. When $Bi \to 0$ there is no heat exchange and an adiabatic thermal explosion occurs. Our problem can thus be stated

$$\nabla^2_{\underset{\sim}{y}}\theta + \delta e^{\theta} = 0 \qquad \text{in region,}$$

$$\frac{\partial\theta}{\partial n} + Bi\,\theta = 0 \qquad \text{on boundary.} \tag{1.21}$$

<u>The sphere.</u>

In the next chapter we consider a sphere of reactive material with radius R. Neglecting reactant consumption and using the Frank-Kamenetskii truncation along with the dimensionless variables θ and r, the dimensionless form of the radius, the governing system of equations is (1.21) where

$$\delta = \frac{QE}{R\lambda T_0^2} z\ell^2 e^{-E/RT_0}$$

is the Frank-Kamenetskii parameter. The symmetry of the reactive medium implies that there is no heat flux at the centre of the sphere therefore we have the condition

$$\left.\frac{d\theta}{dr}\right|_{r=0} = 0$$

It is known [2], that the non-linear heat conduction equation in a spherical region with sources depending on the temperature, admits only spherically symmetric solutions (provided the boundary conditions are also spherically symmetric). Thus for spherical geometries, system (1.21) is equivalent to

$$\frac{d^2\theta}{dr^2}+\frac{2}{r}\frac{d\theta}{dr}+\delta e^{\theta}=0, \quad 0<r\leq 1,$$

$$\frac{d\theta}{dr}(1)+Bi\theta(1)=0, \tag{1.22}$$

$$\frac{d\theta}{dr}(0)=0,$$

This is the Frank-Kamenetskii model for steady state thermal regimes in a spherical region, and it is known [1], to have a gross multiplicity of steady state solutions for an arbitrary Biot number. The analytic condition for infinite multiplicity is $\delta_\infty = 2e^{\frac{-2}{Bi}}$. In chapter two we find an infinite series solution to the system (1.22). We then generalise some results found in [1] to spheres in n dimensions. Finally, we apply the infinite series solution to n-dimensional spheres.

<u>The spherical annulus.</u>

In chapter 3 we consider spherically annular geometries. The problem consists of a sphere of inert material completely enclosed by a spherical annulus of reactive material. We define this problem by considering the inert core to have radius α' and the outer radius of the reactive sphere to be R. Neglecting reactant consumption, using the Frank-Kamenetskii truncation, and by choosing the dimensionless variables θ and r, the governing system of equations is

$$\frac{d^2\theta}{dr^2}+\frac{2}{r}\frac{d\theta}{dr}+\delta e^{\theta}=0, \quad \alpha<r\leq 1,$$

$$\frac{d\theta}{dr}(1) + Bi\theta(1) = 0,$$

where $\alpha = \alpha'/R$ and

$$\delta = \frac{QE}{R\lambda T_0^2} z\ell^2 e^{-E/RT_0}$$

is the Frank-Kamenetskii parameter.

In spherically annular geometries, heat transfer occurs at the inner surface. Dust explosions with laser optics give the linear boundary condition

$$\frac{d\theta}{dr}(\alpha) = A < 0,$$

where A is the heat flux at the inner surface of the reactive medium. Using phase plane analysis we investigate the multiplicity of steady state solutions. In spherical geometries it is known that:

(1) for δ small enough there is only one steady state solution;

(2) when $\delta = \delta_\infty = 2e^{\frac{-2}{Bi}}$ there is an infinite multiplicity of steady state solutions.

We show in chapters three and four the above results are not valid for spherically annular geometries . Specifically, we find, that for small values of δ there are two steady state solutions, and, although arbitrarily large multiplicity is obtainable given suitable values for α and A, we do not get infinite multiplicity.