

A MODEL FOR POROUS-MEDIUM COMBUSTION

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SUMMARY

A model of time-dependent porous-medium combustion is presented. The model is of combustion in a three-dimensional porous medium. The typical situation envisaged is the combustion of a non-deforming porous solid medium through which a gas such as air passes. The model represents conservation of mass and energy for both the gas and solid species, whilst the fluid flow is governed by Darcy's law and the ideal-gas law. This model is highly complex and requires sophisticated computer analysis.

Consequently we derive a simplified model as a one-dimensional version of the equations, by a number of asymptotic considerations. Central to the analysis is the concept of the large-activation-energy limit. This limit is shown to have entirely different features from those which arise in conventional flame theory. This fact is a consequence of the two-stage reaction rate governing porous-medium combustion; the stages are first the diffusion of gas components between the gas mainstream and the reaction sites in the solid and secondly the conventional Arrhenius reaction. Thus the overall reaction rate is *not proportional* to the Arrhenius reaction rate, but is a *rational* function of it.

Because of this two-stage reaction rate, the limit $E \rightarrow \infty$ has a novel result not encountered in conventional flame theory. A critical switching temperature T_c , determined by $A = \exp(E/T_c)$, where A is the pre-exponential factor in the Arrhenius reaction term, arises naturally from the large-activation-energy analysis. For temperatures beneath T_c the reaction rate is negligible whereas for temperatures above T_c the reaction is controlled by the ability of the active gas components to diffuse into or out of the reaction sites in the solid. This rate of active gas-component diffusion has been shown experimentally to be proportional to a power (approximately the square) of the gas temperature. Thus, when switched on, the rate-limiting reaction rate grows algebraically with the temperature, in contrast to the explosive exponential growth of the Arrhenius term which governs the switching process.

1. Introduction

IN SECTIONS 2 and 3 of this paper we present a time-dependent, three-dimensional model of combustion in a porous medium consisting of gases flowing under small pressure gradients through non-deforming combustible materials. In sections 4 and 5 we examine solutions of the model equations which vary in one space direction only, and consider a combination of asymptotic limits under which the model equations simplify considerably. This paper shows that for two-stage reaction rates, the correct simple model, based on the large-activation-energy limit, is that of a process where

the heat production is switched on by a step function based on a threshold temperature T_c . The role of the Arrhenius reaction term is to initiate the reaction and to set a value for T_c ; note that the Arrhenius term does not appear in the reaction zone of the simplified model. The heat production may be switched off in the combustion zone, where the temperature is above T_c , by the exhaustion of either solid or gaseous reactants.

This type of porous-medium combustion has a number of applications. For example, the burning of coal (1), the smouldering of polyurethane (2), the use of catalytic converters as exhaust filters (3) and the burning of cigarettes (4) are all examples of porous-medium combustion. The governing equations represent the conservation of mass and thermal energy for both the solid and gas species, whilst the gas-velocity field and the pressure are determined by Darcy's law and by the ideal-gas law. However, because of the low viscosity of the fluid and/or the high porosity of the medium, pressure variations are negligible compared with temperature variations, and so we replace the ideal-gas law by Charles's law. The form of the reaction rate is more complicated than for flame theory (5), and involves the Arrhenius solid-temperature-dependent reaction rate in a nonlinear fashion as well as the effect of the localized diffusion (which we take as gas-temperature dependent) of gaseous products involved in the reaction. Our two-stage reaction rate is similar to Langmuir-Hinshelwood kinetics, see (6), and a description of these applied in coal combustion appears in (7).

Models describing combustion phenomena are often extremely complex, involving the equations governing the chemical kinetics coupled to those governing the fluid motion. The chemical kinetics involve changes in the amounts of substances involved in the chemical reactions and production of heat, whilst the fluid motion transports the gaseous substances and the heat. In seeking to gain an understanding of combustion, asymptotic analysis frequently plays an important role in elucidating the important features of the process. In particular, the large-activation-energy limit of Frank-Kamenetskii (8) has been fundamental in the development of an understanding of the chemistry of combustion. Recently Matkowsky and Sivashinsky (9) have employed more general asymptotic arguments, which revolve around the large-activation-energy limit, to demonstrate how the equations of fluid motion may be decoupled from the equations of flame theory (5), providing a rigorous justification for the use of diffusional-thermal models. In the second half of this paper we examine the equations governing one-dimensional porous-medium combustion and we consider the form of the equations in a particular set of asymptotic limits. Specifically we consider the limits of large activation energy E and small ratio of gas heat storage to solid heat storage.

The nature of the large-activation-energy limit for porous-medium combustion differs substantially from that in conventional flame theory. In the latter case (see (5, 9)) there are essentially two length scales in the

problem: the length of the pre-heat zone in which the temperature of the reactant is raised from its equilibrium level to a level at which chemical reaction is non-negligible, and the length of the reaction zone. Typically, the ratio of the length of the reaction zone to that of the pre-heat zone is small. Furthermore, the temperature variations within the reaction zone are taken to be small, relative to the temperature T^* (in the notation of (5)) beneath which the Arrhenius reaction rate is transcendently small and above which it is transcendently large.

The limit $E \rightarrow \infty$ in porous-medium combustion, however, provides three length scales essential to the problem. First we have the preheat-zone length scale on which the temperature of the solid reactant T_s is raised from its equilibrium level to a level T_c , at which the chemical reaction becomes significant. The temperature T_c (which is analogous to T^*) is determined by the magnitude of the pre-exponential factor in the Arrhenius term involved in the reaction rate, and is defined in equation (4.1). Next we have the length scale on which $T_s \sim T_c$, which is small relative to the first length scale. Thirdly we have the length scale on which T_s is greater than T_c by (at least) an $O(1)$ amount. This length scale is large relative to the second length scale. Note that in conventional flame theory the third region is absent, and attention is focused on the region where the temperature is close to the critical value T^* . Here the region $T_s \sim T_c$ is small, and of little consequence since the dominant heat processes occur in the third region where $T_s > T_c$. Now T_c is equivalent to the temperature T^* (see (5)) in the neighbourhood of which chemical reaction may be sustained in flame theory. Its role in the theory of porous-medium combustion, however, is completely different. In contrast to flame theory, chemical reaction *can* (and typically does) prevail in regions for which $T_s > T_c$ and $T_s \not\sim T_c$ as $E \rightarrow \infty$. This important fact is a consequence of the rate-limiting form of the reaction governing porous-medium combustion: asymptotically, the temperature T_c merely acts as a switch, below which the reaction is insignificant and above which the reaction is limited by the rate of diffusion of the gaseous products in the neighbourhood of the reaction sites. The temperature T_c is *not* an artificially imposed switching parameter, but arises naturally from analysis of the large-activation-energy limit.

In order to make explicitly clear the asymptotic structure discussed above and used in section 4, we consider the simple model heat-equation problem

$$u_t = u_{xx} + f(u, \varepsilon) \quad \text{on } -1 < x < 1,$$

where

$$f(u, \varepsilon) = \frac{\lambda e^{u/\varepsilon}}{e^{u/\varepsilon} + e^{1/\varepsilon}} \quad \text{and} \quad u(-1) = 0 = u(1).$$

This problem has a forcing term $f(u, \varepsilon)$ analogous to the two-stage reaction-rate term that we take to typify porous-medium combustion (see

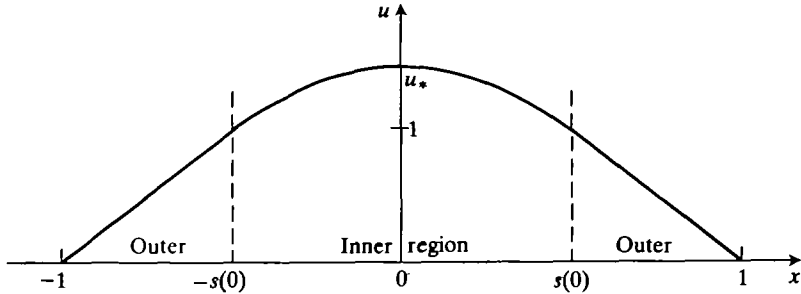


FIG. 1. The solution $u(x, \varepsilon)$ of the model problem, showing the outer region ($u < 1$), where u is almost linear, the inner region ($u > 1$), where u is almost quadratic, and the thin intermediate region where $u \sim 1$, the slope is continuous, and $s(\varepsilon) \rightarrow s(0)$ as $\varepsilon \rightarrow 0$

(2.9)). Note that it differs from the more familiar Arrhenius term of flame theory. The limit $\varepsilon \rightarrow 0$ is the large-activation-energy limit of chemical kinetics or combustion theory.

In the Appendix we shall solve the steady-state version of this problem explicitly, and investigate the dependence of the solution on the parameter ε . As Fig. 1 shows, the solution u has three asymptotic regions. In the outer region where $u < 1$ the reaction is essentially off (of size $O(e^{(u-1)/\varepsilon})$), and this region is similar to most outer regions in combustion analysis. In the inner region where $u > 1$ the reaction term balances the other terms in the equation at leading order, again as one would expect, except that here, because the reaction is two-stage and $e^{u/\varepsilon}$ dominates $e^{1/\varepsilon}$, we have $f(u, \varepsilon) = \lambda$ to leading order. Our exponential term increases more rapidly than any algebraic term as $\varepsilon \rightarrow 0$, and so the reaction rate is essentially that of the rate-limiting algebraic term which is a constant in this model problem. Although the Arrhenius term is dominant, only the algebraic rate-limiting term comes into the asymptotics of the inner layer.

The above inner layer is entirely new in porous-medium combustion asymptotics, and its presence reduces the usual inner layer to a passive intermediate layer. In this intermediate layer the Arrhenius term is of comparable size to the algebraic term, but growing dramatically as the reaction is being initiated. However, because of the small length scale of this region, the reaction term does not appear in the lowest zero-order asymptotic balance in the equation. That is, the growth of the Arrhenius term from being negligible to dominating all other source terms appears only in the smaller, asymptotically higher-order terms in the intermediate layer, a somewhat unusual situation in asymptotic theory. The inner and outer layers can be matched together across this layer without finding the solution in the layer, by imposing continuity of u and its first derivative across the layer.

For this reason we can replace the intermediate layer by a 'switch', a Heaviside step function dependent on a threshold temperature, as long as we insist that both the temperature and the temperature gradient are continuous at the switch to leading order. In a single-stage reaction-rate problem, as in flame theory, this intermediate layer would increase in length scale and become the inner layer; our inner layer would not appear, being a consequence of the second stage of the reaction.

In contrast to the use of a switch in flame theory in the early development of that subject, our use of a switch is mathematically consistent with the asymptotics as $\varepsilon \rightarrow 0$. Our use of a switch is also helpful in sorting out the different physical cases that usually arise. Thus we find in Norbury and Stuart (10) that, of the planar combustion waves propagating steadily in a normal direction, those that are switched on by the presence of combustible solid are stable, whereas those that are switched on by temperature thresholds are unstable.

Our main interest is in the existence and stability of slowly varying combustion waves (see Norbury and Stuart (10, 11)), not in their ignition or rapidly varying behaviour. We find that the large-activation-energy limit, where our two-stage reaction is approximated by the product of step functions (switches) and algebraic dependence on gas temperature, is an appropriate qualitative model. The simplified model which we derive in the second half of this paper involves four unknown quantities, the gas and solid temperatures, the product of oxygen concentration and gas temperature, and the solid heat capacity. The governing equations represent the conservation of mass for each of the individual gas and solid reactants and conservation of energy for each of the overall composite gas and solid phases. There are three important parameters in the simplified model: μ , the scaled driving velocity, λ , linearly related to the solid specific heat and a , which determines the ratio of the rate of oxygen consumption to that of the solid. The model is designed to investigate the dependence of quantities such as the maximum solid temperature, burning-zone length and speed of propagation of combustion wave on the key parameters μ , λ and a .

2. The basic model

In its essence a typical burning porous medium comprises a combustible solid (carbon, C) through which a gas carrying oxygen O_2 passes, the solid and the oxygen combining to produce carbon dioxide CO_2 , and heat. Usually the combustion leaves an ash skeleton of the solid matrix behind it. Thus we may represent the situation by



If we take the gas as (idealized) air, which is approximately 80 per cent nitrogen and 20 per cent oxygen, then, as a minimum requirement, we

formulate a model with two solid species, carbon and ash, and three gas species, carbon dioxide, oxygen and nitrogen. (In practice there is usually as much carbon monoxide produced as there is carbon dioxide. We also ignore the effect of water vapour.)

Although combustion typically comprises many hundreds of reactions, the work of (12), among others, demonstrates that simple models involving a limited number of reactions and reactants can be extremely effective in modelling combustion. The reason appears to be that determining the total amount of heat produced per unit of solid consumed is the basic requirement of a model; the detailed chemistry can then be considered as an extension (or iterative improvement) of the simplified model. Note, however, that different temperature profiles lead to different chains of reactions and hence different net heat outputs, so that the effectiveness of the assumption of an overall heat-supply rate depends on the assumption of the correct main chain reaction. In practice an experiment is designed to reproduce the actual reaction chain. Analysis, and computer simulation, tests the sensitivity of the model to the overall heat-supply rate.

The basic model equations are an extension to three dimensions of the model used by Lawson and Norbury and outlined in (13, 14). We define z to be directed parallel to the inlet gas velocity (typically also the direction of propagation of the combustion zone as shown in Fig. 2), and y, x to be normal coordinates to z . The unknown quantities are defined as follows:

- (i) γ_1 , the mass of unburnt material (carbon) and γ_2 , the mass of ash, per unit volume of space;
- (ii) α_1, α_2 and α_3 , the mass, respectively, of carbon dioxide, oxygen and nitrogen, per unit volume of space;
- (iii) T_s and T_g , the temperatures of the solid and the gas phases respectively;
- (iv) V_1 (or V_2 or V_3), the velocity of the composite gas in the x - (or respectively y - or z -) direction.

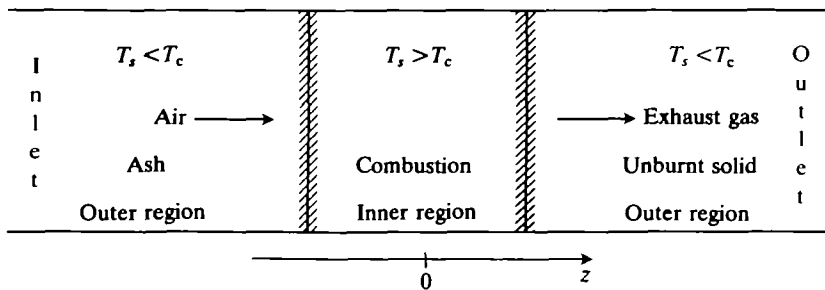


FIG. 2. A sketch of a porous medium with gas blown in the $z > 0$ direction supporting an inner combustion region where $T_s > T_c$: shown in hatch are the thin intermediate layers where $T_s \sim T_c$ (or $\gamma_1 \sim 0$) and the Arrhenius term is of the same magnitude as the gaseous diffusion term

Note that gas temperature, mass and velocity variables are not point evaluations of these quantities, but are continuum averages defined in terms of the energy and mass fluxes through the porous matrix. The solid temperature is a local average defined in terms of the volume density of the heat energy in the solid. (We could take α_1 as the mass of a carbon monoxide-carbon dioxide mixture.)

The fundamental physical properties involved in the model are conservation of energy and matter. Earlier models attempt to describe the energy balances by use of a single variable representing the average temperatures of the solid and the gas phases. However, experimental evidence shows that the temperature differences between the gas and the solid phases, and the heat transfer between the two phases, are significant, and so we treat the two temperatures separately.

The equations governing the concentration of the solid and gas species are simply mass-conservation laws. Since the solid is stationary the chemical reaction is the only effect of any importance, so that equation (2.1) follows. Since the gas is mobile, we require a convective flux-derivative to describe the conservation of gas mass, as shown in (2.2). Note that in (2.1) and (2.2) Q_k and q_k are reaction terms, to be defined later.

The processes governing the temperature of the solid medium are chemical reaction, heat storage, heat transfer between the solid medium and the gas mainstream, radiation and conduction. The effect of heat transfer is modelled by a linear heat-exchange term and the effects of radiation and conduction are combined to form a single nonlinear diffusion term. We take the radiation coefficient of the form $\beta_1 T^3$ since the usual radiation term proportional to T^4 occurs between elements of the solid in the porous medium that are near to each other and are separated by only small temperature differences. The resultant equation is (2.3) which represents conservation of heat energy in the solid phase of the medium. Note that the heat capacity σ_s depends on the composition of the solid phase, as shown in (2.7), and that DQ represents the heat source due to chemical reaction. Hence D is the (overall) heat of the reaction.

The processes governing the temperature dependence of the gas are somewhat different; we assume that the reaction takes place in the solid, or at least in a thin boundary layer in the neighbourhood of the solid-gas interface. Consequently there is no direct production of heat by chemical reaction in the gas phase (but note the effect of (2.8)). Furthermore, the effect of conduction is negligible compared with that of convection. Hence the two dominant processes involved in the conservation of energy in the gas phase are heat transfer and convection. Thus equation (2.4) follows. The effect of the reaction terms in (2.2) is to vary the composition of the gas. Hence σ_g changes, see (2.8), and the heat transfer between the reaction site and the convecting gas stream should allow for this. Note that a change of one degree Kelvin in the gas temperature corresponds, in terms of

energy, roughly, to a one hundred mile per hour velocity change of the air, so that the effect of mechanical energy is negligible.

Finally we turn to the equations governing the fluid motion. Since the air passing through the porous solid medium is a mixture of ideal gases, we take the ideal-gas law together with Darcy's law as the relevant constraints to determine the pressure variations and the movement of the gas. The porosities of the medium are typically greater than 0.5, so that over 50 per cent of the medium is occupied by gas. The resultant driving-pressure variations are small (of at most 10 per cent) and are negligible compared with the temperature variations (at least 300 per cent—300 to 1500 °K is typical). Thus we approximate the ideal-gas law by Charles's law, which states that the product of gas temperature and gas density for a given parcel of gas is constant, as stated in (2.5). (Note that the porosity ϕ is involved in the constant of proportionality in (2.5); because the later analysis focuses on the fluxes of mass and heat in one dimension this dependence on ϕ is not considered further.) Since Darcy's law states that the velocity field is proportional to the gradient of the pressure, taking its curl yields (2.6). (Note that if Darcy's law is not isotropic then we must scale the velocity components before taking the curl.)

The governing equations are now listed together:

$$\frac{\partial \gamma_k}{\partial t} = M_k Q_k, \quad k = 1, 2, \quad (2.1)$$

$$\frac{\partial \alpha_k}{\partial t} + \frac{\partial}{\partial x}(V_1 \alpha_k) + \frac{\partial}{\partial y}(V_2 \alpha_k) + \frac{\partial}{\partial z}(V_3 \alpha_k) = m_k q_k, \quad k = 1, 2 \text{ and } 3, \quad (2.2)$$

$$\begin{aligned} \sigma_s \frac{\partial T_s}{\partial t} = & \frac{\partial}{\partial x} \left\{ (\beta_1 T_s^3 + \beta_2) \frac{\partial T_s}{\partial x} \right\} + \frac{\partial}{\partial y} \left\{ (\beta_1 T_s^3 + \beta_2) \frac{\partial T_s}{\partial y} \right\} + \\ & + \frac{\partial}{\partial z} \left\{ (\beta_1 T_s^3 + \beta_2) \frac{\partial T_s}{\partial z} \right\} + h(T_g - T_s) + DQ, \end{aligned} \quad (2.3)$$

$$\sigma_g \left\{ \frac{\partial T_g}{\partial t} + V_1 \frac{\partial T_g}{\partial x} + V_2 \frac{\partial T_g}{\partial y} + V_3 \frac{\partial T_g}{\partial z} \right\} = h(T_s - T_g), \quad (2.4)$$

$$T_g \rho_g = T_g \left(\sum_{k=1}^3 \alpha_k \right) / \phi = \text{constant on air parcels}, \quad (2.5)$$

and

$$\frac{\partial V_3}{\partial y} - \frac{\partial V_2}{\partial z} = \frac{\partial V_3}{\partial x} - \frac{\partial V_1}{\partial z} = \frac{\partial V_2}{\partial x} - \frac{\partial V_1}{\partial y} = 0, \quad (2.6)$$

where only two of the expressions in (2.6) are independent. Here M_k and m_k are the molecular weights of the solid and gas species respectively; D , the heat of the reaction, is a positive constant since the reaction is exothermic. We define the heat capacities of the composite solid and gas

species, respectively, by

$$\sigma_s = \sum_{k=1}^2 c_{sk} \gamma_k \tag{2.7}$$

and

$$\sigma_g = \sum_{k=1}^3 c_{gk} \alpha_k. \tag{2.8}$$

Here c_{sk} and c_{gk} are the specific heats of the individual solid and gas components. The source terms Q , Q_k and q_k are all proportional to the reaction rate r . Specifically, $Q = r$, $Q_1 = -r$, $Q_2 = r$, $q_1 = r$, $q_2 = -r$ and $q_3 = 0$.

We now derive the form of the reaction rate r . Because the reaction takes place in and/or near the solid, but is fuelled by the oxygen in the gas mainstream, the reaction is taken to be two-stage; the two stages are first the diffusion of active gas components between the gas mainstream and the reaction sites in or near the solid, and secondly the standard Arrhenius reaction. Glassman (following Langmuir and Hinshelwood, see also (7)) derives an expression for the overall reaction rate by relating the oxygen concentration in the reaction sites to the oxygen concentration in the gas mainstream. This is done by estimating the changes in oxygen concentration across the thin boundary layer in the neighbourhood of the solid reactant. The reaction rate is found to be

$$r = \frac{kb[\gamma_1][\alpha_2]}{k[\gamma_1] + b}. \tag{2.9}$$

Here $[\gamma_1]$ and $[\alpha_2]$ are the concentrations of carbon and oxygen respectively, given by $[\gamma_1] = \gamma_1/M_1$ and $[\alpha_2] = \alpha_2/m_2$. The quantity b is the rate of diffusion of the active rate-limiting gas component (which may be either CO_2 or O_2) and k is the Arrhenius reaction rate. Baker (15) has demonstrated experimentally that b is given, for $V^2 = V_1^2 + V_2^2 + V_3^2$, by

$$b = \eta(\phi)\sqrt{V} T_g^v, \tag{2.10}$$

where η is a constant proportional to ϕ and typically $v \sim 2.5$. This value for v is in strong disagreement with the value of 0.9 which is predicted by classical mass-transfer theory. The \sqrt{V} -dependence may be derived from standard arguments about diffusion behaviour across a viscous (or turbulent) boundary layer.

The Arrhenius reaction rate k is defined, as usual, by

$$k = A \exp(-E/RT_s), \tag{2.11}$$

where the constants A and E depend upon the materials involved in the combustion reaction. It is clear that the form of the overall reaction rate

(2.9) differs substantially from that which is found in most theories of homogeneous combustion, and we now discuss this.

When the solid temperature is below about 500 °K then the reaction rate r is similar to that of flame theory (and the Arrhenius-rate dependence on solid temperature (2.11) is determined experimentally); this corresponds to the ignition phase. When the solid temperature is about 1000 °K then the Arrhenius rate has increased (exponentially) from being negligible to being dominant. The reaction is now rate-limited by the ability of the active gas components to move from the gas mainstream to the reaction sites, which, depending on the many hundreds of reactions, occur in and between the gas mainstream and the solid interior. Oxygen is transported, often as carbon monoxide, through the gas boundary layer; the detailed structure at the solid–gas interface is complicated, and the penetration of oxygen into the (charred) solid interior (itself breaking up under the effects of temperature and the reactions) is often little understood. Our key assumption is to take this rate-limiting process as being gas-temperature dependent (see (2.10)).

In fact, on the micro-level, the temperature of the medium will be continuous as we pass from the gas into the solid; the interface will (usually) not be a sharp boundary. Our lumped reaction term (2.10) summarizes all these effects, and relates them essentially to the gas temperature, that is the energy density in the gas phase. The solid temperature represents the energy density in the solid phase, and the heat-transfer term relates the heat exchange between the solid and the gas phases in terms of these quantities. In section 4 we take the specific heats of oxygen and carbon dioxide as being equal (note that we could alternatively take the exhaust gas as a given CO–CO₂ mixture). This amounts to a convenient choice for the lumped heat-energy transfer term, and is consistent with both our assumptions that all the heat-energy release occurs in the solid and the large-activation-energy asymptotics (note that, in practice, we are dealing with a fraction of the 20 per cent of active gas components, and $E^{-1} \sim 0.1$).

Fortunately the increase in solid temperature from 500 to 1000 °K occurs in a thin (compared to the combustion zone) layer, and to leading order (as later analysis shows) we may ignore the details of this process and replace the layer by a solid-temperature-dependent switch. Thus the lumped reaction-rate term in the combustion zone covers, at the micro-level, intricate chemistry, geometry and fluid dynamics. The heat constant D gives the overall heat output per unit mass of solid consumed, and the two key constants in (2.10) (and those in (2.11)) can be estimated from calibration experiments. We view the main practical result of this work as showing that such a simple lumped reaction rate (together with the switch concept) is useful, both in estimating temperature and concentration profiles in the reaction zone and in classifying the stability properties of planar combustion waves.

3. The non-dimensionalization

We introduce the following non-dimensional variables denoted by overbars:

$$\begin{aligned}
 t &= t_0 \bar{t}, \quad z = z_0 \bar{z}, \quad y = y_0 \bar{y}, \quad x = x_0 \bar{x}, \quad \gamma_k = \Gamma_0 \bar{\gamma}_k, \\
 \alpha_k &= A_0 \bar{\alpha}_k, \quad T_g = T_0 \bar{T}_g, \quad T_s = T_0 \bar{T}_s, \quad V_1 = V_{10} \bar{V}_1, \quad V_2 = V_{20} \bar{V}_2, \\
 V_3 &= V_{30} \bar{V}_3, \quad \sigma_g = \Sigma_g \bar{\sigma}_g, \quad \sigma_s = \Sigma_s \bar{\sigma}_s, \quad r = R_0 \bar{r}.
 \end{aligned}$$

These scalings imply scalings for the activation-energy constants A and E , as discussed later. We first outline our choice of time scale t_0 , length scale z_0 and temperature scale T_0 , which leads to the key equation (3.3). The variables Γ_0 , Σ_g and Σ_s are determined by the nature of the combustible material and so they are fixed. The M_k and m_k are physical constants; D is the overall heat-supply rate, and is determined by the materials and the reaction chain. Our assumption of a value for D prejudices the correct chemistry—the value for D is usually taken from experiments; V_0 is determined by the inlet gas velocity under consideration, and for the typical combustion processes where V_0 is parallel to the z -axis in which we are interested it is natural to choose $V_{30} \sim 0.1$ to 1.0 ms^{-1} . Computational results suggest that if we choose $R_0 = \Gamma_0/10M_1$ then $\bar{r}_{\max} \sim 1$.

In general we set, for fixed R_0 , V_{30} , x_0 and y_0 ,

$$\begin{aligned}
 t_0 &= \Gamma_0/M_1 R_0, \quad z_0 = V_{30} \Gamma_0 \Sigma_g / M_1 R_0 \Sigma_s, \quad A_0 = m_2 \Gamma_0 \Sigma_g / M_1 \Sigma_s, \\
 V_{20} &= y_0 V_{30} / z_0, \quad V_{30} = x_0 V_{30} / z_0, \quad T_0 = \Gamma_0 D / M_1 \Sigma_s.
 \end{aligned}$$

Then, transforming equations (2.1) to (2.5) to the non-dimensional variables described above and dropping the bars, we obtain

$$\partial \gamma_k / \partial t = a_k r, \quad a_1 = -1, \quad a_2 = M_2 / M_1, \tag{3.1}$$

$$\frac{\Sigma_g}{\Sigma_s} \frac{\partial \alpha_k}{\partial t} + \frac{\partial}{\partial x} (V_1 \alpha_k) + \frac{\partial}{\partial y} (V_2 \alpha_k) + \frac{\partial}{\partial z} (V_3 \alpha_k) = b_k r, \tag{3.2}$$

where $b_1 = m_1/m_2$, $b_2 = -1$ and $b_3 = 0$,

$$\begin{aligned}
 \sigma_s \frac{\partial T_s}{\partial t} &= h \frac{\partial}{\partial x} \left\{ (d_1 T_s^3 + d_2) \frac{\partial T_s}{\partial x} \right\} + e \frac{\partial}{\partial y} \left\{ (d_1 T_s^3 + d_2) \frac{\partial T_s}{\partial y} \right\} + \\
 &+ \frac{\partial}{\partial z} \left\{ (d_1 T_s^3 + d_2) \frac{\partial T_s}{\partial z} \right\} + c(T_g - T_s) + r, \tag{3.3}
 \end{aligned}$$

$$\sigma_g \left\{ \frac{\Sigma_g}{\Sigma_s} \frac{\partial T_g}{\partial t} + V_1 \frac{\partial T_g}{\partial x} + V_2 \frac{\partial T_g}{\partial y} + V_3 \frac{\partial T_g}{\partial z} \right\} = c(T_s - T_g), \tag{3.4}$$

$$T_g \rho_g = T_g \left(\sum_{k=1}^3 \alpha_k \right) / \phi = \text{constant on air parcels}, \tag{3.5}$$

and

$$e \frac{\partial V_3}{\partial y} - \frac{\partial V_2}{\partial z} = h \frac{\partial V_3}{\partial x} - \frac{\partial V_1}{\partial z} = h \frac{\partial V_2}{\partial x} - e \frac{\partial V_1}{\partial y} = 0. \quad (3.6)$$

The parameters e , h , c , d_1 and d_2 are typically of order one (we can make $e = 1 = h$ by suitable choice of x_0 , y_0). Thus, inside the burning zone, where T_r is of order one (although not near one), the radiation term $d_1 T_r^3$ is significant. Outside the burning zone, where T_r is small, the term $d_1 T_r^3$ is negligible. The ratio $d_2/d_1 (c/d_1)$ determines the importance of solid heat conduction (heat transfer to the gas) compared with radiation in the burning zone.

The form of the reaction rate (2.9) is unchanged although the constants in (2.10) and (2.11) should now be reinterpreted in terms of the rescaled quantities. Henceforth A and E represent respectively the non-dimensionalized pre-exponential factor and the activation energy divided by R . For the moment we do not discuss appropriate boundary and initial conditions for these equations.

4. The large-activation-energy limit

In this section we seek an asymptotic expansion of the solution of equations (2.7) to (2.9) and (3.1) to (3.6) in the parameter regime $E \gg 1$, $\Sigma_g/\Sigma_s \ll 1$, $b_1 - 1 \ll 1$ and $c_{g1} - c_{g2} \ll 1$. (Note that the latter two conditions could be replaced by $\alpha_1 + \alpha_2 \ll \alpha_3$.) Combustion of carbonaceous material typically involves an activation energy $E \sim 10$, while the fact that gases are much less dense than solids implies that $\Sigma_g/\Sigma_s \sim 0.01$. Since the active gas components in air typically comprise about one fifth of the total amount of gas, and the exchange of CO_2 for O_2 involves a mass gain of about one third, the total errors in (4.4) and (4.5) are about five per cent, that is $O(E^{-1})$ at most. Hence our assumptions are consistent with the experimental values.

We exploit the magnitude of the activation energy to provide a simplification of the complicated reaction rate defined by equations (2.9) to (2.11). The pre-exponential factor A in equation (2.11) is large and so, following Kapila (16) (and see (5)), we write

$$A = \exp(E/T_c). \quad (4.1)$$

Thus, combining equations (2.11) and (4.1) gives us

$$k = \exp \left[\frac{E(T_s - T_c)}{T_s T_c} \right]. \quad (4.2)$$

Consequently, for $T_s - T_c$ not small, as $E \rightarrow \infty$, k is either transcendently large if $T_s > T_c$, or transcendently small if $T_s < T_c$. Our aim is to show that r takes the form (4.12) as $E \rightarrow \infty$. This involves showing that all variables are

continuous where the switch occurs, and that $\partial T_s/\partial z$ is continuous there but that $\partial^2 T_s/\partial z^2$ takes up the jump.

The outer (no combustion) and inner (combustion) regions

Here we assume that $|T_s - T_c| E \gg 1$, and that $k\gamma_1 \gg b$ (the inner region) or that $k\gamma_1 \ll b$ (the outer region—unless $\gamma_1 = 0$). We examine solutions with only one space dimension; that is, we assume that $V_2 = V_1 = 0$ and that all other unknowns depend upon z and t only. Further, we assume that the boundary conditions are compatible with this assumption. We seek expansions of the variables in the form

$$\begin{aligned} \sigma_s &= \sum_{i=0}^{\infty} \sigma_{si} E^{-i}, & \sigma_g &= \sum_{i=0}^{\infty} \sigma_{gi} E^{-i}, & \rho_g &= \sum_{i=0}^{\infty} \rho_{gi} E^{-i}, \\ \alpha_k &= \sum_{i=0}^{\infty} \alpha_{ki} E^{-i}, & T_g &= \sum_{i=0}^{\infty} w_i E^{-i}, & T_s &= \sum_{i=0}^{\infty} u_i E^{-i}, \\ V_3 &= \sum_{i=0}^{\infty} \tilde{V}_i E^{-i}, & r &= \sum_{i=0}^{\infty} r_i E^{-i}. \end{aligned}$$

Equation (3.2) gives, to lowest order in E^{-1} since $\Sigma_g/\Sigma_s \ll 1$,

$$\frac{\partial}{\partial z} (\tilde{V}_0 \alpha_{k0}) = b_k r_0, \quad k = 1, 2, 3. \tag{4.3}$$

Adding appropriate multiples of these equations gives us, to lowest order,

$$\frac{\partial}{\partial z} (\tilde{V}_0 \sigma_{g0}) = \sum_{k=1}^3 c_{gk} b_k r_0 = 0 \tag{4.4}$$

and

$$\frac{\partial}{\partial z} (\tilde{V}_0 \rho_{g0}) = \sum_{k=1}^3 b_k r_0 / \phi = 0, \tag{4.5}$$

since $b_2 = -1$ and $b_3 = 0$, and we have assumed that $b_1 - 1 \ll 1$ and $c_{g1} - c_{g2} \ll 1$. Integrating (4.4), writing $\mu = (\tilde{V}_0 \sigma_{g0})(-\infty) \equiv \tilde{V}_0 \sigma_{g0}$, and substituting into (3.4) yields, to lowest order in E^{-1} ,

$$\mu \frac{\partial w_0}{\partial z} = c(u_0 - w_0). \tag{4.6}$$

Here μ is proportional to the inlet-gas heat flux. Furthermore, on integrating (4.5), we have that the gas mass flux is constant in z to leading order. Using (3.5), we have, to lowest order in E^{-1} ,

$$w_0/\tilde{V}_0 = \text{constant in space.} \tag{4.7}$$

Thus we can eliminate \tilde{V}_0 by use of the inlet-gas conditions.

Equation (3.3) simplifies to

$$\sigma_{s0} \frac{\partial u_0}{\partial t} = \frac{\partial}{\partial z} \left[\{d_1 u_0^3 + d_2\} \frac{\partial u_0}{\partial z} \right] + c(w_0 - u_0) + r_0. \quad (4.8)$$

By adding appropriate multiples of the solid-consumption equations (3.1) we obtain

$$a_2 \gamma_1 + \gamma_2 = \text{constant in time} = a_2. \quad (4.9)$$

Here we have used the (usual) initial conditions that no ash is present in the unburnt material, so that $\gamma_1 = 1$ and $\gamma_2 = 0$, to determine the constant of integration. Using equations (2.7) and (4.9) we may find a linear relationship between σ_s and γ_1 of the form

$$\sigma_s = \lambda \gamma_1 + \tau, \quad (4.10)$$

where $\lambda = c_{s1} - a_2 c_{s2}$ and $\tau = c_{s2} a_2$. Typically λ is positive so that the overall heat capacity of the solid σ_s decreases as solid is burned and ash is produced. (In (11, Theorem 4.1) it is proved that λ must be positive for sustained combustion.) The governing equation for σ_{s0} is

$$\frac{\partial \sigma_{s0}}{\partial t} = -\lambda r_0. \quad (4.11)$$

Examination of (2.9), which is scaled so that $b = O(1)$, in conjunction with (4.2), shows that, since $k \gg 1$ for $T_s > T_c$ (the inner region—unless $\gamma_1 \sim 0$) and $k \ll 1$ for $T_s < T_c$ (the outer region), r_0 has the form

$$r_0 = \begin{cases} b[\alpha_2] & \text{for } T_s > T_c \text{ and } k\gamma_2 \gg b, \\ 0 & \text{for } T_s < T_c \text{ or } k\gamma_1 \ll b. \end{cases}$$

Equations (4.6), (4.8), (4.11) form our basic model in these regions.

Thus, to complete our analysis as $E^{-1} \rightarrow 0$, we must solve the equations (3.1) to (3.6) in the intermediate regions where $T_s \sim T_c$ or where $k\gamma_1 \sim b$. Since γ_1 is necessarily bounded (because it is a monotonically decreasing function of time from equation (3.1)) the latter case can only arise for $T_s > T_c$, that is for $k \gg 1$ in the inner region, which is the combustion zone. We wish to show that it is not necessary to know the details of the solution in these intermediate layers. If we match the inner-layer solution to the outer-layer solution using continuity of all variables and continuity of the heat flux in the solid then we shall get the correct outer and inner solutions to leading order. Thus we justify the switch or step-function form for r_0 given in (4.12).

The intermediate regions

We first examine the case in which $T_s \sim T_c$. We seek expansions of the variables T_s , γ_k , α_k and V_1 in the form

$$\begin{aligned} T_s &= T_c + E^{-1} \tilde{T} + O(E^{-2}), & \gamma_k &= \tilde{\gamma}_k + O(E^{-1}), \\ \alpha_k &= \tilde{\alpha}_k + O(E^{-1}), & V_3 &= \tilde{V} + O(E^{-1}). \end{aligned}$$

From (4.2) we deduce that

$$k \sim \exp(\bar{T}/T_c^2) + O(E^{-1}),$$

and substituting this expression into (2.9) yields the leading-order behaviour $\bar{r} = O(1)$ for the reaction rate. We rescale the independent variables z and t by setting $\bar{z} = zE$ and $\bar{t} = tE$. This scaling of the spatial and temporal variables is consistent with a solution of equations (3.1) to (3.6) fairly close in form to a plane combustion wave propagating with $O(1)$ velocity. (If the wave velocity gets large the modelling assumptions will probably be violated.) Equation (3.3) yields, to lowest order,

$$\left(\sum_{k=1}^2 c_{s,k} \bar{\gamma}_k\right) \frac{\partial \bar{T}}{\partial \bar{t}} = E(d_1 T_c^3 + d_2) \frac{\partial^2 \bar{T}}{\partial \bar{z}^2} + c(T_g - T_c) + \bar{r}.$$

Taking the limit $E \rightarrow \infty$ then implies that $\partial \bar{T} / \partial \bar{z} = \text{constant}$ in z across this region. Hence, by matching $T_s = T_c + E^{-1} \bar{T} + O(E^{-2})$ across this region, we deduce that the outer variable $\partial u_0 / \partial z$ (since $\partial T_s / \partial z = \partial \bar{T} / \partial \bar{z} + O(E^{-1})$) is continuous across this region where $T_s \sim T_c$. (To solve in this layer we should take $\bar{z} = 0$ to be centred in, and move with, the layer.) With the same scalings, equation (3.2) yields to lowest order

$$\frac{\partial}{\partial \bar{z}} (\bar{V} \bar{\alpha}_k) = 0.$$

Thus $\bar{V} \bar{\alpha}_k = \text{constant}$ in space, and hence, by matching, the variable $\bar{V}_0 \alpha_{k0}$ is also continuous across the region where $T_s \sim T_c$. Finally we consider equation (3.1) which is the remaining equation involving the reaction rate r . We obtain

$$E \frac{\partial \bar{\gamma}_k}{\partial \bar{t}} = a_k \bar{r}.$$

Thus $\bar{\gamma}_k = \text{constant}$ across this region. Hence, by matching, γ_{k0} is continuous across the region where $T_s \sim T_c$. Equation (3.4) shows that T_g (and hence w_0) is continuous.

These results about the continuity of $\partial u_0 / \partial z$, $\bar{V}_0 \alpha_{k0}$ and γ_{k0} imply that the effect on the reaction rate r_0 of the region in which $T_s \sim T_c$ is merely to act as a switch between regimes in which the reaction rate is negligible and regimes in which it is dominated by the rate of active gas-component diffusion. No higher-order discontinuities are imposed. Thus r_0 has been demonstrated to have the form, where $\gamma_1 > 0$ as $E \rightarrow \infty$,

$$r_0 = \begin{cases} H(u_0 - T_c) b[\alpha_2] & \text{for } k\gamma_1 \gg 1, \\ 0 & \text{for } k\gamma_1 \ll 1. \end{cases}$$

Here $H(X)$ is the Heaviside step function defined by $H(X) = 0$ for $X \leq 0$ and $H(X) = 1$ for $X > 0$.

We now analyse equations (3.1) to (3.6) in an intermediate region where $k \gg 1$ and $k\gamma_1 = O(1)$; k , defined by (4.2), is transcendentally large in E ,

while $\gamma_1 \sim 0$ because nearly all the combustible solid is burnt up. The analysis of such a region is complicated because of the fact that γ_1 , the concentration of solid, always remains positive. However, for $k\gamma_1 \ll 1$ the reaction rate (2.9) becomes negligible so that, to $O(E^{-1})$, this inner region terminates when $k\gamma_1 = O(E^{-1})$. The result of a similar, but slightly more delicate argument to the one in the intermediate region examined above shows that

$$r_0 = H(\gamma_1)H(u_0 - T_c)b[\alpha_2]. \quad (4.12)$$

We outline the key arguments in deriving the expression (4.12). Before the region is reached in which $k\gamma_1 = O(1)$ a region occurs in which $\gamma_1 = O(E^{-1})$; thus we define $\gamma_1 = \bar{\gamma}E^{-1}$ in this region. The reaction rate, however, is of $O(1)$ and thus we set $t = \bar{t}E^{-1}$ to obtain, from (3.1),

$$\partial\bar{\gamma}/\partial\bar{t} = -b[\alpha_2] + \text{higher-order terms.}$$

As before we note that the solution is similar to a combustion wave propagating with an $O(1)$ velocity and so we suspect that the length scale on which $\gamma_1 = O(E^{-1})$ is $O(E^{-1})$. Employing this length scale it may be shown that in this region the variables V_3 , α_k , T_g , T_s and $\partial T_s/\partial z$ are constant to first order. Hence $\bar{\gamma}$ decreases linearly until it becomes zero.

As $\bar{\gamma} \rightarrow 0$ we make a transition into a region in which γ_1 is transcendently small and $k\gamma_1 = O(1)$. Thus we rescale γ_1 , t and z accordingly by setting $\gamma_1 = \hat{\gamma}/\hat{k}$, $t = \hat{t}/\hat{k}$ and $z = \hat{z}/\hat{k}$. Here \hat{k} is obtained from (4.2) by taking $T_s = \hat{T}_s = \text{constant} > T_c$. We justify this assumption on T_s a posteriori. The resultant equation for $\hat{\gamma}$ is, from (3.1),

$$\frac{\partial\hat{\gamma}}{\partial\hat{t}} = -\frac{\hat{\gamma}b[\alpha_2]}{\hat{\gamma} + M_1 b}. \quad (4.13)$$

The reaction rate r becomes negligible when $\hat{\gamma}$ decreases to $O(E^{-1})$ for then $k\gamma_1 = O(E^{-1})$ and thus, from (2.9), $r = O(E^{-1})$. Solving (4.13) with b and α_2 held constant (which we may again justify a posteriori) shows that $\hat{\gamma}$ decreases to $O(E^{-1})$ on a time scale $\hat{t} = O(\ln E)$. Thus the appropriate time and length scales in the region in which γ_1 is transcendently small are $O(\ln E/\hat{k}) \ll 1$, which justifies the assumption that all other variables remain constant to lowest order. Consequently the effect of the non-uniformity which arises if $\gamma_1 \rightarrow 0$ is to switch off the reaction rate in the manner prescribed by (4.12). No higher-order discontinuities are introduced.

5. A simplified model

We now go on to produce a simplified model, which is analysed in (10, 11) for the existence and stability of travelling-wave solutions. The analysis in these papers enables us to find the qualitative properties of the travelling combustion-wave solutions and relate these properties to the types of switch at the end of the combustion zone. The qualitative

properties are broadly in agreement with earlier numerical calculations of the full model (13, 14).

Together with the reaction rate (4.12), equations (4.3), (4.6) to (4.8) and (4.11) determine the leading-order behaviour of equations (3.1) to (3.6) under the assumptions listed at the beginning of section 4. If we eliminate \bar{V}_0 between (4.3) and (4.7) and define a new variable to be $g = w_0\alpha_2$, the flux of oxygen, then we obtain

$$\partial g / \partial z = -ar_0/\mu, \tag{5.1}$$

where a is a constant. Equations (2.10) and (4.7) show that, in terms of the new variable g , the reaction rate r_0 may be written

$$r_0 = (\mu/a)^{1/2} H(\sigma_{s0} - \tau) H(u_0 - T_c) w_0^{\nu-1/2} g. \tag{5.2}$$

We now rescale equations (4.6), (4.8), (4.11) and (5.1), (5.2) to eliminate certain constants. We define, in order to rescale and for ease of notation,

$$\begin{aligned} \bar{\sigma} &= \sigma_{s0}, & \bar{u} &= u_0, & \bar{w} &= w_0, & \bar{u}_c &= T_c, & \bar{z} &= \sqrt{cz}/\sqrt{d_2}, \\ \bar{t} &= ct, & \bar{\mu} &= \mu/(cd_2)^{1/2}, & \bar{r} &= r_0/c. \end{aligned}$$

Substituting these rescaled variables into equations (4.6), (4.8), (4.11) and (5.1), (5.2) and dropping the bars yields

$$\partial \sigma / \partial t = -\lambda r, \tag{5.3}$$

$$\mu \partial w / \partial z = (u - w), \tag{5.4}$$

$$\sigma \frac{\partial u}{\partial t} = \frac{\partial}{\partial z} \left\{ (du^3 + 1) \frac{\partial u}{\partial z} \right\} + w - u + r \tag{5.5}$$

and

$$\partial g / \partial z = -ar/\mu. \tag{5.6}$$

Here a and d are positive constants. The reaction rate r is given by

$$r = H(\sigma - \tau) H(u - u_c) \mu^{1/2} g f(w). \tag{5.7}$$

In the case of porous-medium combustion we expect that $f(w) \approx w^{\nu-1/2}$, where typically $\nu - \frac{1}{2} \approx 2$.

If we assume that the gas temperature and gas flux are prescribed upstream and that the solid temperature is prescribed up- and downstream then the appropriate boundary conditions are

$$u(\pm\infty, t) = u_a, \tag{5.8}$$

$$w(-\infty, t) = u_a, \tag{5.9}$$

$$g(-\infty, t) = g_a. \tag{5.10}$$

Together with initial conditions on the variables σ , u , v and g , equations (5.3) to (5.10) form an initial boundary-value problem. The unknown

variables σ , u , w and g represent, respectively, the solid heat capacity, the solid temperature, the gas temperature and a quantity proportional to the product of oxygen concentration and gas temperature. These quantities arise naturally from the four conservation laws for solid and gas mass and energy. The effect of Charles's law, which governs the fluid motion, has been replaced by the dependence of the system of equations (5.3) to (5.10) on the parameter μ , proportional to the inlet-gas mass flux.

The problem contains eight parameters— a , d , μ , λ , u_c , u_a , τ , and a constant of proportionality in the function $f(w)$. The parameters of particular interest are a , μ and λ . The parameter a determines the rate of depletion of the variable g and represents the ratio of the rate of oxygen consumption to that of solid consumption. The parameter μ is proportional to the inlet-gas mass flux. The parameter λ relates the amount of combustible solid present to the heat content of the solid, and thus λ and a depend upon the nature of the solid being burned. From its definition λ is seen to be a linear function of c_{s1} , the specific heat of the combustible solid. The remaining parameters are all of $O(1)$ for our typical combustion process and we do not consider them as important in determining the mathematical structure of solutions of equations (5.3) to (5.10).

Finally we note that it is possible to simplify equation (5.5) by replacing the nonlinear radiation–diffusion term by an overall effective linear-conduction term. A further rescaling then renders the coefficient of such a term unity. We believe that equations (5.3) to (5.7) will form the essence of most macro-models of burning porous media where air is blown through the combustion zone. For small a the stable combustion waves are those whose combustion is terminated by exhaustion of solid, not by the lowering of the solid temperature (10).

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APPENDIX

In this section we solve the following ordinary-differential-equation boundary-value problem and explore the dependence of the solution on ϵ as $\epsilon \rightarrow 0$. Here λ and ϵ are strictly positive constants, and we are only interested in solutions which have $u > 1$ somewhere:

$$\frac{d^2u}{dx^2} = -\frac{\lambda e^{u/\epsilon}}{e^{u/\epsilon} + e^{1/\epsilon}} = \frac{-\lambda}{1 + e^{(1-u)/\epsilon}}, \quad 0 < x < 1,$$

where $du/dx = 0$ at $x = 0$ and $u = 0$ at $x = 1$.

We first note that $u(x, \epsilon)$ strictly decreases from its value $u_* = u(0, \epsilon) > 1$ at $x = 0$ through $u(x, \epsilon) = 1$ at $x = s(\epsilon)$ to $u(x, \epsilon) = 0$ at $x = 1$. Then the solution $u(x, \epsilon)$ of our problem is given implicitly by

$$F(u, u_*, \epsilon) = \int_u^{u_*} \frac{dv}{[\log \{1 + \exp((u_* - 1)/\epsilon)\} - \log \{1 + \exp((v - 1)/\epsilon)\}]^2} = (2\lambda\epsilon)^{1/2}x, \tag{A.1}$$

where u_* is related to ϵ , for fixed $\lambda > 0$, by

$$F(0, u_*, \epsilon) = (2\lambda\epsilon)^{1/2}. \tag{A.2}$$

(This solution is found by noting that a first integral of the differential equation is

$$\frac{1}{2} \left(\frac{du}{dx} \right)^2 = -\lambda\epsilon \log \left(1 + \exp \left(\frac{u - 1}{\epsilon} \right) \right) + \lambda\epsilon \log \left(1 + \exp \left(\frac{u_* - 1}{\epsilon} \right) \right),$$

where we use $du/dx = 0$ at $x = 0$ to evaluate the constant of integration.)

Having found the formula (A.1) for the solution, we now evaluate its behaviour as $\epsilon \rightarrow 0$. We are led directly to consider the three regions $u > 1$ (the inner layer), $u - 1 = O(\epsilon)$ (the intermediate layer), and $0 < u < 1$ (the outer layer) as $\epsilon \rightarrow 0$. We find that $u(x, \epsilon) \rightarrow u_0(x)$ as $\epsilon \rightarrow 0$ uniformly for $0 \leq x \leq 1$, where

$$u_0(x) = \begin{cases} 1 + \frac{1}{2}\lambda(s(0)^2 - x^2), & 0 \leq x \leq s(0), \\ (1 - x)/(1 - s(0)), & s(0) \leq x \leq 1, \end{cases} \tag{A.3}$$

and

$$1/\lambda = s(0)(1 - s(0)); \tag{A.4}$$

and that $s(\epsilon) \rightarrow s(0)$ as $\epsilon \rightarrow 0$.

Note that $u_0(x) = 1$ at $x = s(0)$, and that $du_0(x)/dx$ is continuous at $x = s(0)$ because of the condition on λ . Since both these conditions hold it is not necessary to examine the details of the solution $u(x, \epsilon)$ near $x = s(0)$ in order to determine $u_0(x)$ uniquely. The function $u_0(x)$ may be found by solving the formal limit problem as $\epsilon \rightarrow 0$ separately in both $x < s(0)$, $u > 1$ and $x > s(0)$, $u < 1$, and then matching for the free boundary $x = s(0)$ by using the continuity conditions on $u_0(x)$ and du_0/dx at $x = s(0)$.

To prove the above assertions we need to evaluate $F(u, u_*, \epsilon)$ for $\epsilon \rightarrow 0$ separately in $u > 1$ and $u < 1$. This is straightforward once we know that $u_* = u(0, \epsilon) \rightarrow 1 + \frac{1}{2}\lambda s(0)^2$ and $s(\epsilon) \rightarrow s(0)$ as $\epsilon \rightarrow 0$, where $s(0) \in (0, 1)$ satisfies (A.4). The latter condition on $s(\epsilon)$ follows from the identity $F(1, u_*, \epsilon) = (2\lambda\epsilon)^{\frac{1}{2}}s(\epsilon)$ when we know the behaviour of u_* as $\epsilon \rightarrow 0$. So the crucial step is to solve (A.2) for u_* as $\epsilon \rightarrow 0$ with λ given by (A.4).

If we write

$$w(x, \epsilon) = \log(1 + \exp[(u - 1)/\epsilon]), \quad w_0 = \log(1 + \exp(-1/\epsilon)),$$

$$w_* = \log(1 + \exp[(u_* - 1)/\epsilon]),$$

then (A.2) becomes

$$\int_{w_0}^{w_*} \frac{\sqrt{\epsilon} dw}{(1 - \exp(-w))(w_* - w)^{\frac{1}{2}}} = (2\lambda)^{\frac{1}{2}}. \tag{A.5}$$

We note that $u = 1$ corresponds to $w = \log 2$, while $u = u_* > 1$ corresponds to $w = w_* \sim (u_* - 1)/\epsilon \gg 1$, and $u = 0$ corresponds to $w = w_0 \sim \exp(-1/\epsilon) \ll 1$, as $\epsilon \rightarrow 0$. Hence the integrand in (A.5) has the three regions

- (i) $w \sim 0$, where the integrand is approximately $\sqrt{\epsilon}/w\sqrt{w_*}$: this is the outer layer of (A.1);
- (ii) $w = O(1)$, where the integrand is approximately $\sqrt{\epsilon}/\sqrt{w_*(1 - \exp(-w))}$: this is the intermediate layer of (A.1);
- (iii) $w \gg 1$, where the integrand is approximately $\sqrt{\epsilon}/\sqrt{(w_* - w)}$: this is the inner layer of (A.1).

Thus the integral in (A.5) may be uniformly approximated as $\epsilon \rightarrow 0$, and we obtain, for $w_1 = \epsilon^{-\frac{1}{2}}$,

$$\begin{aligned} (2\lambda)^{\frac{1}{2}} &= \epsilon(u_* - 1)^{-\frac{1}{2}} \int_{\exp(-1/\epsilon)}^{w_1} \frac{dw}{1 - \exp(-w)} + \int_{w_1}^{w_*} \frac{\sqrt{\epsilon} dw}{(w_* - w)^{\frac{1}{2}}} + O(\epsilon^{-\frac{1}{2}}) \\ &= \epsilon(u_* - 1)^{-\frac{1}{2}} \{ \log(\exp(w_1) - 1) - \log(\exp(\exp(-1/\epsilon)) - 1) \} \\ &\quad + 2\sqrt{\epsilon} (w_* - w_1)^{\frac{1}{2}} + O(\epsilon^{-\frac{1}{2}}) \\ &= \epsilon(u_* - 1)^{-\frac{1}{2}} \{ w_1 + 1/\epsilon \} + 2(u_* - 1 - \epsilon w_1)^{\frac{1}{2}} + O(\epsilon^{\frac{1}{2}}), \\ &= (u_* - 1)^{-\frac{1}{2}} + 2(u_* - 1)^{\frac{1}{2}} + O(\epsilon^{\frac{1}{2}}). \end{aligned}$$

Hence

$$u_* \rightarrow 1 + \frac{1}{2} \frac{s(0)}{1 - s(0)} \quad \text{as } \epsilon \rightarrow 0,$$

where $s(0)$ satisfies (A.4). Thus $F(1, u_*, \epsilon) = (2\lambda\epsilon)^{\frac{1}{2}}s(\epsilon)$ shows that $s(\epsilon) \rightarrow s(0)$ as $\epsilon \rightarrow 0$, and it is now straightforward to see that $u(x, \epsilon)$ satisfying (A.1) will tend to $u_0(x)$, given by (A.3), as $\epsilon \rightarrow 0$.