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Homogeneous ignition for a three-step chain-branching reaction model

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Abstract Spatially homogeneous thermal explosions governed by a three-step chain-branching kinetic model are described in the asymptotic limit of large activation energy for a range of chain-branching cross-over temperatures. The model consists of a sequence of chain-initiation, chain-branching and chain-termination steps. Temperature-sensitive Arrhenius kinetics is employed for the initiation and branching steps, while the termination step has a temperature-independent rate. Marked distinctions in structure arise as the magnitude of the chain-branching cross-over temperature is increased relative to the initial system temperature. Attention is focused on the regime where the chain-branching cross-over temperature is close to the initial system temperature. Results are also obtained for the fast and slow explosion limits where the two temperatures are not close.

Keywords Branched-chain kinetics · Cross-over temperature · Thermal explosion

1 Introduction

Ignition of a spatially homogeneous exothermic chemical mixture is characterized by a marked rise in the rate of temperature growth. Temporal evolution of any subsequent thermal explosion, as well as the structure of the ignition phase, depend strongly on the chemical kinetics. Examples that have received considerable attention include one-step thermal decomposition models, and multi-step chain-branching reaction schemes.

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For a one-step process with Arrhenius kinetics at large activation energies, Kassoy [1, 2] gave a complete asymptotic description, from initiation to completion, of a spatially homogeneous thermal explosion. After an initial induction period, in which the variations in temperature and fuel concentration are small, thermal runaway takes place over a much shorter time scale. Significant changes in the temperature, together with a major depletion of the fuel concentration, occur exponentially fast. In many practical gaseous systems, however, one-step models do not provide a good representation of the actual kinetics. Nor do these schemes possess a critical initial temperature that defines the explosion limit delineating a distinct boundary between fast and slow reactions, which is a property of many gaseous systems [3, Chapter 2, Sect. 8].

Gaseous reactions often proceed through a sequence of chain initiation, chain-branching (production), and chain-termination steps [4, Sect. 2.3.4]. Examples include oxidation of hydrogen and the combustion of gaseous hydrocarbons. In most cases, the role of chain-initiation reactions is to decompose the fuel to produce a small initial quantity of chain carriers (free radicals or atoms). The chain carrier production rate and further decomposition of fuel is then accelerated by the chain-branching mechanism. Termination reactions, where most of the heat of reaction is released, deplete the carrier concentration and lead to the final limiting adiabatic temperature $T'_{\rm ad}$. In practice there may be many initiation reactions, but simplified descriptions assume that all of the chain initiation processes can be combined into a single one-step global reaction. Similarly, the chain-branching and termination reactions are represented, respectively, by one-step processes. A detailed description of the particular chain-branching model employed in the present paper is given in [5]. To describe thermal explosions for such overall three-step schemes, it is convenient to introduce an initiation cross-over temperature T'_i at which the rates for the initiation and termination steps are equal, and a branching cross-over temperature T'_b at which the branching and termination rates are equal. For ease of discussion, we assume that T'_i is greater than either $T'_{\rm ad}$ or T'_b, although the relative magnitudes of $T'_{\rm ad}$ and T'_b are varied. Reaction rates for the initiation and branching steps are governed by Arrhenius kinetics in which the inverse (dimensionless) activation energies are small. Using ϵ_i and ϵ_b to denote these inverse energies, it is the limit $\epsilon_i < \epsilon_b \ll 1$ that is considered here.

If the chain-branching temperature is significantly lower than the initial system temperature $T'_{\rm in}$, the small quantity of chain carriers produced in the initiation reaction multiplies rapidly in the chain-branching step, and is then depleted during the relatively slow termination stage. Specifically, the chain-induction period is much shorter than the termination step. When T'_b is significantly greater than the initial temperature, the chain-branching reaction does not lead to a rapid growth in the radical concentration, and the chain-induction period is substantially longer than the termination stage. When T'_b and $T'_{\rm in}$ are relatively close, the structure of the explosion becomes very sensitive to the precise ordering of the temperature difference with respect to the magnitude of the small parameter. Obviously, the branching temperature plays a critical role in the description of chain-branched reactions. In particular, it defines the second explosion limit between rapid and slow explosions for H_2–O_2 reactions [3]. Moreover, it has recently been shown to define a detonability limit in propagating detonations [5, 6]. The present paper examines the influence of the magnitude of the branching temperature on the overall structure of spatially homogeneous thermal explosions for a three-step chain-branching reaction model.

Gray and Yang [7] provided an early discussion concerning the significance of a chain-branching step in the evolution of thermal explosions. Subsequently, Kapila [8] gave a complete asymptotic description of thermal explosions at high activation energies for a two-step chain-branching scheme. The initiation reaction was replaced by the assumption that a small amount of the chain carrier was already present, and criticality occurred when the carrier was consumed by a sufficiently rapid chain-termination reaction. In the model used here, which includes a chain-initiation step, the explosion is always supercritical. Sen and Law [9] have also examined the Kapila two-step model for larger initial carrier concentrations, and a more recent analysis has been given by Bonilla et al. [10]. A complete description of homogeneous thermal explosions for a five-step mechanism, including dissociation and recombination effects, has been presented by Birkan and Kassoy [11] in the limit of large activation energies. The three-step chain-branching process employed

by these authors is similar to the present model, but they include quadratic reactions for the initiation and termination steps, and they permit the termination rate to have a weak temperature-dependence. Their analysis corresponds to a limit in which the chain-branching cross-over temperature is just above the initial system temperature. Del Alamo and Williams [12] have also considered the homogeneous problem for a three-step model, under the assumptions that the initiation reaction is of zero order, and that none of the three reactions is thermoneutral. However, their analysis only treats the induction phase of the explosion.

An outline of the chain-branching reaction scheme is given in Sect. 2. Results for cases when the chain-branching cross-over temperature is close to the initial system temperature are examined in Sects. 3 and 4. In Sects. 5–7, the broad details of the solutions relevant to the cases $T'_b = T'_{\rm in}$, $T'_b < T'_{\rm in}$, and $T'_b > T'_{\rm in}$ are presented. Sect. 8 provides a tabular summary of results for all the cases examined.

2 Reaction scheme

A three-step reaction scheme is adopted in which the initiation stage generates an intermediate radical Y (chain carrier) from the fuel F. Production of the radical Y is then enhanced through the chain-branching step, and the process is terminated when the intermediate is fully consumed through production of the final product P. As in [5], suitable forms for the reaction rates are:

$$\begin{aligned}
&\text{Chain-initiation:} \quad (F \to Y) && k'_i = c'_i \exp(-\theta'_i/T'),\\
&\text{Chain-branching:} \quad (F + Y \to 2Y) && k'_b = c'_b \exp(-\theta'_b/T'),\\
&\text{Chain-termination:} \quad (Y \to P) && k'_e = \text{ constant.}
\end{aligned} \tag{2.1}$$

Initiation and the chain-branching rates are assumed to have Arrhenius form with constant pre-exponential factors c'_i and c'_b. In ((2.1)), T' is the mixture temperature, and θ'_i and θ'_b are the activation temperatures. The termination rate is often only weakly dependent on temperature, and here it is taken to be constant.

Appropriate non-dimensional variables are defined by using $1/k'_e$ as the basic time scale, and the initial temperature $T'_{\rm in}$ as the basic temperature scale. Consequently, the dimensionless dependent and independent variables are

$$T = T'/T'_{\rm in} \quad \text{and} \quad t = k'_e t', \tag{2.2}$$

so that

$$T = 1 \quad \text{at} \quad t = 0. \tag{2.3}$$

Dimensionless inverse activation temperatures (or equivalently inverse activation energies) are given by

$$\epsilon \equiv \epsilon_b = \frac{T'_{\rm in}}{\theta'_b}, \quad \epsilon_i = \frac{T'_{\rm in}}{\theta'_i} = \frac{\epsilon}{m}. \tag{2.4}$$

It is assumed that the inverse activation energies are small and ordered so that

$$\epsilon_i < \epsilon_b \ll 1. \tag{2.5}$$

Equivalently, $m = O(1) > 1$. Corresponding dimensionless reaction rates are

$$k_i = \frac{k'_i}{k'_e}, \quad k_b = \frac{k'_b}{k'_e}, \quad k_e = \frac{k'_e}{k'_e} = 1. \tag{2.6}$$

From (2.1) the rates can be re-expressed in the form

$$k_i = \exp\left\{\frac{m}{\epsilon}\left(\frac{1}{T_i} - \frac{1}{T}\right)\right\}, \quad k_b = \exp\left\{\frac{1}{\epsilon}\left(\frac{1}{T_b} - \frac{1}{T}\right)\right\}, \tag{2.7}$$

where T_i is the cross-over temperature at which the initiation and termination rates become equal, while T_b is the cross-over temperature at which the branching and termination rates are equal. Using (2.1) these

temperatures can be related to the pre-exponential factors, the activation temperatures, and the termination rate. For ease of discussion, T_i is taken to be larger than the limiting adiabatic temperature (see (2.15) below.)

Based on (2.1) the relevant dimensionless production rates are

$$r_i = fk_i, \quad r_b = \rho f y k_b = f y k_b \quad \text{and} \quad r_e = y k_e = y, \tag{2.8}$$

where ρ ($\equiv 1$) is the dimensionless mixture density, f is the fuel mass fraction, and y is the radical mass fraction. The overall rate laws are then

$$\frac{\mathrm{d}f}{\mathrm{d}t} = -r_i - r_b, \quad \frac{\mathrm{d}y}{\mathrm{d}t} = r_i + r_b - r_e \tag{2.9}$$

with

$$f = 1 \quad \text{and} \quad y = 0 \quad \text{at} \quad t = 0. \tag{2.10}$$

If Q is the available (dimensionless) formation energy, then the chemical energy

$$q = Q(1 - f - y), \tag{2.11}$$

where heat absorption associated with any endothermic contributions from the chain-initiation and chain-branching steps is neglected [5]. For spatially homogeneous problems the specific internal energy

$$e = \frac{T}{\gamma - 1} - q = \text{ constant}, \tag{2.12}$$

where γ is an effective specific-heat ratio. Use of (2.11) and (2.12) enables the energy equation to be written as

$$T = 1 + \beta(1 - f - y). \tag{2.13}$$

Here

$$\beta = (\gamma - 1)Q = O(1) \tag{2.14}$$

is an effective heat release parameter. From (2.13), it follows that the limiting adiabatic temperature ($y \to 0$, $f \to 0$) is

$$T = T_{\mathrm{ad}} = 1 + \beta. \tag{2.15}$$

From (2.8) and (2.13) it is easily established that

$$\frac{\mathrm{d}T}{\mathrm{d}t} = \beta y > 0, \tag{2.16}$$

so that temperature increases monotonically throughout the reaction.

3 Thermal explosions: $1 - T_b = O(\epsilon) > 0$

When the chain-branching cross-over temperature is close to the initial system temperature, the evolution is sensitive to the precise magnitude of $1 - T_b$. Three distinguished limits are needed to capture the dynamics. These limits are described in Sects. 3–5.

Based on the starting temperature $T = 1$, it is appropriate to re-write the rate constants in the form

$$k_i = k_{i0} \exp\left\{\frac{m}{\epsilon}\left(1 - \frac{1}{T}\right)\right\}, \quad k_b = k_{b0} \exp\left\{\frac{1}{\epsilon}\left(1 - \frac{1}{T}\right)\right\}, \tag{3.1}$$

where

$$k_{i0} = \exp\left\{-\frac{m}{\epsilon}\left(1 - \frac{1}{T_i}\right)\right\}, \quad k_{b0} = \exp\left\{-\frac{1}{\epsilon}\left(1 - \frac{1}{T_b}\right)\right\}. \tag{3.2}$$

Since $T_i - 1 = O(1) > 0$, k_{i0} is exponentially small. However, for the limit

$$1 - T_b = O(\epsilon) > 0 \tag{3.3}$$

being considered here, $k_{b0} = O(1)$. Consistent with this limit it is useful to set

$$T_b^{-1} = 1 + \epsilon T_{b1}, \tag{3.4}$$

which gives

$$k_{b0} = \exp(T_{b1}) = 1 + A, \quad \text{where} \quad A = O(1) > 0. \tag{3.5}$$

3.1 Initiation stage

From (3.1)–(3.4) and (2.8)–(2.9), it is apparent that all changes are initially exponentially small with respect to the activation parameter ϵ. This is the characteristic feature that defines the initiation stage. Appropriate asymptotic expansions are:

$$f = 1 - k_{i0}\hat{f}_1(t;\epsilon) - k_{i0}^2\hat{f}_2(t;\epsilon) - \cdots, \quad y = k_{i0}\hat{y}_1(t;\epsilon) + k_{i0}^2\hat{y}_2(t;\epsilon) + \cdots,$$
$$T = 1 + k_{i0}\hat{T}_1(t;\epsilon) + k_{i0}^2\hat{T}_2(t;\epsilon) + \cdots. \tag{3.6}$$

Note that, although the $\hat{f}_j$, etc., may include terms that are algebraically small in ϵ, they do not include terms that are exponentially small in ϵ. Substitution in (2.9) gives

$$\frac{\mathrm{d}\hat{f}_1}{\mathrm{d}t} = 1 + (1+A)\hat{y}_1, \quad \frac{\mathrm{d}\hat{y}_1}{\mathrm{d}t} = 1 + A\hat{y}_1, \tag{3.7}$$

and, from the energy equation (2.13),

$$\hat{T}_1 = \beta(\hat{f}_1 - \hat{y}_1). \tag{3.8}$$

It follows that, with $\hat{f}_1 = \hat{y}_1 = 0$ at $t = 0$,

$$\hat{y}_1 = \frac{1}{A}\left(\mathrm{e}^{At} - 1\right), \quad \hat{f}_1 = \frac{1+A}{A^2}\left(\mathrm{e}^{At} - 1\right) - \frac{t}{A}, \tag{3.9}$$

and

$$\hat{T}_1 = \beta\left\{\frac{1}{A^2}\left(\mathrm{e}^{At} - 1\right) - \frac{t}{A}\right\}. \tag{3.10}$$

The second-order term $\hat{y}_2$ satisfies

$$\frac{\mathrm{d}\hat{y}_2}{\mathrm{d}t} - A\hat{y}_2 = \frac{m}{\epsilon}\hat{T}_1 - \hat{f}_1 + (1+A)\hat{y}_1\left(\frac{\hat{T}_1}{\epsilon} - \hat{f}_1\right), \tag{3.11}$$

and the solution can be expressed in the form

$$\hat{y}_2 = \sum_{n=0}^{2} B_n(t; A, \beta, \epsilon)\mathrm{e}^{nAt}, \tag{3.12}$$

where the coefficients B_n are listed in Appendix A. Similarly,

$$\hat{f}_2 = \hat{y}_2 + \int_0^t \hat{y}_2(\hat{t})\,\mathrm{d}\hat{t} \quad \text{and} \quad \hat{T}_2 = \beta\int_0^t \hat{y}_2(\hat{t})\,\mathrm{d}\hat{t}. \tag{3.13}$$

If necessary, explicit expressions for $\hat{f}_2$ and $\hat{T}_2$ can be deduced.

Of particular importance is the asymptotic behavior of y as $t \to \infty$. From (3.9) and (3.12), it can be shown that

$$y \sim k_{i0}\left(\frac{1}{A}\mathrm{e}^{At} + \cdots\right) + k_{i0}^2\left\{\frac{1+A}{A^4}\left(\frac{\beta}{\epsilon} - 1 - A\right) + \cdots\right\}\mathrm{e}^{2At} + \cdots . \tag{3.14}$$

Inspection of this result, and the corresponding expressions for f and T, indicates that y does not remain exponentially small as t increases, and that the expansion (3.6) fails when

$$k_{i0}\mathrm{e}^{At} = O(\epsilon). \tag{3.15}$$

This signals the end of the initiation stage, which is characterized by the time scale

$$t_{\mathrm{ig}} = \epsilon^{-1}t_{\mathrm{ig}-1}(\epsilon) = \frac{1}{A}\log\frac{\epsilon}{k_{i0}} = \frac{m}{A\epsilon}\left(1 - \frac{1}{T_i}\right) - \frac{1}{A}\log\frac{1}{\epsilon}, \tag{3.16}$$

and leads to the onset of the induction stage described below.

3.2 Induction stage

Examination of (3.14) and (3.16) suggests that a suitable time scale for the the induction stage can be defined by

$$t = t_{\mathrm{ig}} + \tilde{t}, \quad \text{where} \quad \tilde{t} = O(1). \tag{3.17}$$

Over this period, it is useful to view $\tilde{t}$ as a dependent variable and to define a new independent variable by setting

$$T^{-1} = 1 - \epsilon u. \tag{3.18}$$

Because of the Arrhenius factor in the rate laws, employing u as the independent variable simplifies the algebra, and avoids possible disordering in subsequent asymptotic expansions. Note that (2.16) implies that u increases monotonically through the overall reaction process. In view of (3.17) and (3.18), (3.9)–(3.14) can be used to show that as $t \to t_{\mathrm{ig}}$,

$$\begin{aligned} y &\sim \epsilon\left[\frac{A}{\beta}u + \frac{1+A}{2\beta}u^2 + \cdots\right] + \epsilon^2\left[\left\{\frac{A}{\beta} - \frac{(1+A)^2}{2\beta^2}\right\}u^2 + \cdots\right] + O(\epsilon^3u^3), \\ f &\sim 1 - \epsilon\left[\frac{1+A}{\beta}u + \frac{1+A}{2\beta}u^2 + \cdots\right] + \epsilon^2\left[\left\{-\frac{1+A}{2\beta} + \frac{(1+A)^2}{2\beta^2}\right\}u^2 + \cdots\right] + O(\epsilon^3u^3), \end{aligned} \tag{3.19}$$

and

$$A\tilde{t} \sim \log\frac{A^2u}{\beta} - \frac{1+A}{2A}u + \cdots + \epsilon\left[\left\{1 + \frac{(1+A)^2}{2A\beta}\right\}u + \cdots\right] + O(\epsilon^2u^2). \tag{3.20}$$

These relations represent matching conditions, as $u \to 0$, for the induction solution.

Suitable expansions for the induction solution are

$$\begin{aligned} t - t_{\mathrm{ig}} = \ \tilde{t}(u;\epsilon) \ &= \tilde{t}_0(u) + \epsilon\tilde{t}_1(u) + \cdots, \\ y = \epsilon\tilde{y}(u;\epsilon) &= \epsilon\tilde{y}_1(u) + \epsilon^2\tilde{y}_2(u) + \cdots, \\ 1 - f = \epsilon\tilde{f}(u;\epsilon) &= \epsilon\tilde{f}_1(u) + \epsilon^2\tilde{f}_2(u) + \cdots. \end{aligned} \tag{3.21}$$

Over this stage, perturbations in temperature and mass fractions are all $O(\epsilon)$. Neglecting exponentially small terms, the governing equations become

$$\frac{\mathrm{d}\tilde{y}}{\mathrm{d}u} = \frac{(1-\epsilon\tilde{f})(1+A)e^u - 1}{\beta(1-\epsilon u)^2}, \quad \frac{\mathrm{d}\tilde{t}}{\mathrm{d}u} = \frac{1}{\beta\tilde{y}(1-\epsilon u)^2}, \tag{3.22}$$

and

$$\tilde{f} = \tilde{y} + \frac{u}{\beta(1-\epsilon u)}. \tag{3.23}$$

Using the expansion (3.21), and matching with (3.19) and (3.20), gives

$$\beta\tilde{y}_1 = (1+A)(\mathrm{e}^u - 1) - u, \quad \tilde{f}_1 = \tilde{y}_1 + \beta^{-1}u = \beta^{-1}(1+A)(\mathrm{e}^u - 1), \tag{3.24}$$

and

$$\tilde{t}_0 = \beta^{-1}\int_0^u \left\{\frac{1}{\tilde{y}_1(\bar{u})} - \frac{\beta}{A\bar{u}}\right\}\mathrm{d}\bar{u} + A^{-1}\log(A^2u/\beta). \tag{3.25}$$

Similarly, for the second-order terms,

$$\begin{aligned}\beta^2\tilde{y}_2 &= -(1+A)^2\left(\frac{1}{2}\mathrm{e}^{2u} - \mathrm{e}^u + \frac{1}{2}\right) + 2\beta(1+A)[(u-1)\mathrm{e}^u + 1] - \beta u^2,\\ \tilde{f}_2 &= \tilde{y}_2 + \beta^{-1}u^2,\end{aligned} \tag{3.26}$$

and

$$\tilde{t}_1 = \beta^{-1}\int_0^u \left\{\frac{2\bar{u}}{\tilde{y}_1(\bar{u})} - \frac{\tilde{y}_2(\bar{u})}{\tilde{y}_1^2(\bar{u})}\right\}\mathrm{d}\bar{u}. \tag{3.27}$$

Continuing the expansion to third order yields

$$\begin{aligned}\beta^3\tilde{y}_3 = {}& \frac{1}{6}(1+A)^3\mathrm{e}^{3u} - 2\beta(1+A)^2u\mathrm{e}^{2u} + (1+A)^2\left\{2\beta - \frac{1}{2}(1+A)\right\}\mathrm{e}^{2u}\\ &+ 3\beta^2(1+A)u^2\mathrm{e}^u + \beta(1+A)\{2(1+A) - 6\beta\}u\mathrm{e}^u\\ &+ (1+A)\left\{\frac{1}{2}(1+A)^2 - 4\beta(1+A) + 6\beta^2\right\}\mathrm{e}^u\\ &- \beta^2u^3 - \frac{1}{6}(1+A)^3 + 2\beta(1+A)^2 - 6\beta^2(1+A),\\ \tilde{f}_3 = {}& \tilde{y}_3 + u^3/\beta,\end{aligned} \tag{3.28}$$

and

$$\tilde{t}_2 = \beta^{-1}\int_0^u \tilde{R}_2(\bar{u})\,\mathrm{d}\bar{u}. \tag{3.29}$$

Here,

$$\tilde{R}_2(u) = \frac{3u^2}{\tilde{y}_1(u)} - \frac{2u\tilde{y}_2(u) + \tilde{y}_3(u)}{\tilde{y}_1^2(u)} + \frac{\tilde{y}_2^2(u)}{\tilde{y}_1^3(u)}. \tag{3.30}$$

Of most interest is the asymptotic response of the solution as $u \to \infty$. For the local time scale $\tilde{t}$ the limiting behaviors are

$$\begin{aligned}\tilde{t}_0 &\sim \tilde{t}_{\mathrm{ig}0} - \frac{\mathrm{e}^{-u}}{1+A} + \cdots, \quad \tilde{t}_1 \sim \frac{u}{2\beta} + \tilde{t}_{\mathrm{ig}1} + \text{ exp. small},\\ \tilde{t}_2 &\sim \frac{1+A}{12\beta^2}\mathrm{e}^u + \frac{5+12\beta}{24\beta^2}u^2 - \frac{1+A}{12\beta^2}u + \tilde{t}_{\mathrm{ig}2} + \text{ exp. small},\end{aligned} \tag{3.31}$$

where

$$\begin{aligned}\tilde{t}_{\mathrm{ig}0} &= \frac{1}{A}\log\frac{A^2}{\beta} + \frac{1}{\beta}\int_0^1\left\{\frac{1}{\tilde{y}(u)} - \frac{\beta}{Au}\right\}\mathrm{d}u + \frac{1}{\beta}\int_1^\infty \frac{1}{\tilde{y}_1(u)}\mathrm{d}u,\\ \tilde{t}_{\mathrm{ig}1} &= \frac{1}{\beta}\int_0^\infty\left\{\frac{2u}{\tilde{y}_1(u)} - \frac{\tilde{y}_2(u)}{\tilde{y}_1^2(u)} - \frac{1}{2}\right\}\mathrm{d}u,\end{aligned} \tag{3.32}$$

and

$$\tilde{t}_{\mathrm{ig}2} = -\frac{1+A}{12\beta^2} + \frac{2(1+2\beta)}{\beta^2(1+A)} + \beta^{-1}\int_0^\infty \{\tilde{R}_2(u) - R_{2\infty}(u)\}\mathrm{d}u. \tag{3.33}$$

In (3.33) the function $R_{2\infty}(u)$ represents the asymptotic behavior of $R_2(u)$, neglecting terms of order $u^3\mathrm{e}^{-2u}$, and is defined by

$$R_{2\infty}(u) = \frac{1+A}{12\beta}\mathrm{e}^u + \frac{5+12\beta}{12\beta}u - \frac{1+A}{12\beta} + \frac{1+\beta}{\beta(1+A)}u^2\mathrm{e}^{-u} + \frac{2(1+\beta)}{1+A}u\mathrm{e}^{-u} - \frac{2\beta}{1+A}\mathrm{e}^{-u}. \tag{3.34}$$

Adopting (3.34), rather than the simpler result with an error term $O(u^2\mathrm{e}^{-u})$, is advantageous with respect to numerical evaluation of the integral in the expression for $\tilde{t}_{\mathrm{ig}2}$.

Corresponding results for the radical mass fraction are

$$\tilde{y}_1 \sim \frac{1+A}{\beta}\mathrm{e}^u + O(u), \quad \tilde{y}_2 \sim -\frac{(1+A)^2}{2\beta^2}\mathrm{e}^{2u} + O(u\mathrm{e}^u), \quad \tilde{y}_3 \sim \frac{(1+A)^3}{6\beta^3}\mathrm{e}^{3u} + O(u\mathrm{e}^{2u}) \tag{3.35}$$

with similar behaviors for $\tilde{f}_i$. Inspection of (3.35) indicates that the induction solution is no longer valid when

$$u = O\big(\log(1/\epsilon)\big). \tag{3.36}$$

The exponential growth associated with (3.35) implies that significant radical production will occur over the scale defined by (3.36). This growth period is discussed below.

3.3 Growth stage

From (3.21), (3.35) and (3.36), it appears that a new local structure is required when

$$u = \log(1/\epsilon) + \nu \tag{3.37}$$

with $\nu = O(1)$. On this scale the radical mass fraction undergoes $O(1)$ growth, while the magnitude of the temperature perturbation is $O\big(\epsilon\log(1/\epsilon)\big)$. Appropriate local expansions are

$$\begin{aligned} f &= F(\nu;\epsilon) = F_0(\nu) + \epsilon\log(1/\epsilon)F_{11}(\nu) + \epsilon F_{10}(\nu) + \cdots, \\ y &= Y(\nu;\epsilon) = Y_0(\nu) + \epsilon\log(1/\epsilon)Y_{11}(\nu) + \epsilon Y_{10}(\nu) + \cdots, \\ t - \hat{t}_{\mathrm{ig}}(\epsilon) &= \epsilon\hat{t}(\nu;\epsilon) = \epsilon\{\hat{t}_0(\nu) + \epsilon\log(1/\epsilon)\hat{t}_{11}(\nu) + \epsilon\hat{t}_{10}(\nu) + \cdots\}, \end{aligned} \tag{3.38}$$

where $\hat{t}_{\mathrm{ig}}(\epsilon)$ includes all constant terms that arise in the $\hat{t}_{ij}(\nu)$ as $\nu \to -\infty$. These factors follow from matching with the induction solution. Using (3.16) and (3.31)–(3.33) gives

$$\begin{aligned} \hat{t}_{\mathrm{ig}}(\epsilon) = \frac{1}{\epsilon}\,t_{\mathrm{ig}-1}(\epsilon) + \tilde{t}_{\mathrm{ig}0} + \epsilon\log(1/\epsilon)\frac{1}{2\beta} + \epsilon\tilde{t}_{\mathrm{ig}1} + \epsilon^2\log^2(1/\epsilon)\frac{5+12\beta}{24\beta^2} \\ - \epsilon^2\log(1/\epsilon)\frac{1+A}{12\beta^2} + \epsilon^2\tilde{t}_{\mathrm{ig}2} + \cdots. \end{aligned} \tag{3.39}$$

Corresponding asymptotic matching conditions for $\hat{t}_{ij}(\nu)$ and $Y_{ij}(\nu)$ as $\nu \to -\infty$ are listed in Appendix B.

Neglecting exponentially small terms, (3.22) is replaced by

$$\frac{\mathrm{d}Y}{\mathrm{d}\nu} = \frac{(1+A)F\mathrm{e}^\nu - \epsilon}{\beta[1-\epsilon\log(1/\epsilon) - \epsilon\nu]^2}, \quad \frac{\mathrm{d}\hat{t}}{\mathrm{d}\nu} = \frac{1}{\beta Y[1-\epsilon\log(1/\epsilon) - \epsilon\nu]^2}, \tag{3.40}$$

while (3.23) becomes

$$F = 1 - Y - \frac{1}{\beta}\left(\frac{\epsilon\log(1/\epsilon) + \epsilon\nu}{1-\epsilon\log(1/\epsilon) - \epsilon\nu}\right). \tag{3.41}$$

Substituting (3.38) in (3.40) and (3.41), and matching with (B.1) and (B.2) leads to

$$\begin{aligned} &Y_0 = 1 - \exp\{-\beta^{-1}(1+A)\mathrm{e}^{\nu}\}, \quad F_0 = 1 - Y_0 = \exp\{-\beta^{-1}(1+A)\mathrm{e}^{\nu}\}, \\ &\hat{t}_0 = \frac{1}{\beta}\int_{-\infty}^{\nu}\left\{Y_0^{-1}(\bar{\nu}) - \frac{\beta}{1+A}\mathrm{e}^{-\bar{\nu}} - \frac{1}{2}\right\}\,\mathrm{d}\bar{\nu} - \frac{1}{1+A}\mathrm{e}^{-\nu} + \frac{1}{2\beta}\nu. \end{aligned} \tag{3.42}$$

Terms $O\big(\epsilon\log(1/\epsilon)\big)$ in (3.38) are defined by

$$\begin{aligned} Y_{11} &= \frac{2(1+A)}{\beta}\exp\left\{\nu - \frac{1+A}{\beta}\mathrm{e}^{\nu}\right\} - \frac{1}{\beta}, \quad F_{11} = -Y_{11} - \frac{1}{\beta}, \\ \hat{t}_{11} &= \int_{-\infty}^{\nu}\left\{\frac{2}{\beta Y_0(\bar{\nu})} - \frac{Y_{11}(\bar{\nu})}{\beta Y_0^2(\bar{\nu})} - \frac{\mathrm{e}^{-2\bar{\nu}}}{(1+A)^2} - \frac{\mathrm{e}^{-\bar{\nu}}}{\beta(1+A)} - \frac{5+12\beta}{12\beta^2}\right\}\mathrm{d}\bar{\nu} \\ &\quad - \frac{\mathrm{e}^{-2\nu}}{2(1+A)^2} - \frac{\mathrm{e}^{-\nu}}{\beta(1+A)} + \frac{5+12\beta}{12\beta^2}\nu, \end{aligned} \tag{3.43}$$

and those $O(\epsilon)$ are

$$\begin{aligned} Y_{10} &= -\frac{1}{\beta}\nu + \frac{2(1+A)}{\beta}(\nu-1)\exp\left\{\nu - \frac{1+A}{\beta}\mathrm{e}^{\nu}\right\} - \frac{1+A}{\beta}\exp\left\{-\frac{1+A}{\beta}\mathrm{e}^{\nu}\right\}, \\ F_{10} &= -Y_{10} - \frac{1}{\beta}\nu, \\ \hat{t}_{10} &= \int_{-\infty}^{\nu}\left\{\frac{2\bar{\nu}}{\beta Y_0(\bar{\nu})} - \frac{Y_{10}(\bar{\nu})}{\beta Y_0^2(\bar{\nu})} - a_{10}(\bar{\nu})\right\}\mathrm{d}\bar{\nu} + b_{10}(\nu), \end{aligned} \tag{3.44}$$

where

$$\begin{aligned} a_{10} &= \frac{\nu\mathrm{e}^{-2\nu}}{(1+A)^2} + \frac{\mathrm{e}^{-2\nu}}{1+A} + \frac{\nu\mathrm{e}^{-\nu}}{\beta(1+A)} + \frac{2\mathrm{e}^{-\nu}}{1+A} + \frac{5+12\beta}{12\beta^2}\nu - \frac{1+A}{12\beta^2}, \\ b_{10} &= -\frac{\nu\mathrm{e}^{-2\nu}}{2(1+A)^2} - \frac{(3+2A)\mathrm{e}^{-2\nu}}{4(1+A)^2} - \frac{\nu\mathrm{e}^{-\nu}}{\beta(1+A)} - \frac{(2\beta+1)\mathrm{e}^{-\nu}}{\beta(1+A)} \\ &\quad + \frac{(5+12\beta)\nu^2}{24\beta^2} - \frac{(1+A)\nu}{12\beta^2}. \end{aligned} \tag{3.45}$$

Although the above results give $t - \hat{t}_{\mathrm{ig}}$ correct to $O(\epsilon^2)$, it is necessary to extend the expansions for Y and F. After some algebra, these results can be written as

$$\begin{aligned} Y_{22} &= -\frac{1}{\beta} - \frac{2(1+A^2)}{\beta^2}\exp\left\{2\nu - \frac{(1+A)\mathrm{e}^{\nu}}{\beta}\right\} + \frac{3(1+A)}{\beta}\exp\left\{\nu - \frac{(1+A)\mathrm{e}^{\nu}}{\beta}\right\}, \\ Y_{21} &= -\frac{2\nu}{\beta} + \frac{6(1+A)}{\beta}\exp\left\{\nu - \frac{(1+A)\mathrm{e}^{\nu}}{\beta}\right\} + \left\{\frac{2(1+A)^2}{\beta^2} - \frac{6(1+A)}{\beta}\right\}\exp\left\{\nu - \frac{(1+A)\mathrm{e}^{\nu}}{\beta}\right\} \\ &\quad - \frac{4(1+A)^2(\nu-1)}{\beta^2}\exp\left\{2\nu - \frac{(1+A)\mathrm{e}^{\nu}}{\beta}\right\}, \end{aligned} \tag{3.46}$$

and

$$\begin{aligned} Y_{20} &= \left\{\frac{2(1+A)}{\beta} - \frac{(1+A)^2}{2\beta^2}\right\}\exp\left\{-\frac{(1+A)\mathrm{e}^{\nu}}{\beta}\right\} - \frac{\nu^2}{\beta} + c_{20}(\nu)\exp\left\{\nu - \frac{(1+A)\mathrm{e}^{\nu}}{\beta}\right\} \\ &\quad - \frac{2(1+A)^2(\nu-1)^2}{\beta^2}\exp\left\{2\nu - \frac{(1+A)\mathrm{e}^{\nu}}{\beta}\right\}, \end{aligned} \tag{3.47}$$

where

$$c_{20}(\nu) = \frac{3(1+A)\nu^2}{\beta} + \left\{\frac{2(1+A)^2}{\beta^2} - \frac{6(1+A)}{\beta}\right\}\nu + \frac{6(1+A)}{\beta} - \frac{2(1+A)^2}{\beta^2}. \tag{3.48}$$

In addition,

$$F_{22} = -Y_{22} - \frac{1}{\beta}, \quad F_{21} = -Y_{21} - \frac{2\nu}{\beta}, \quad \text{and} \quad F_{20} = -Y_{20} - \frac{\nu^2}{\beta}. \tag{3.49}$$

From these results it can be seen that F_0 and the higher-order perturbations F_{ij} become exponentially small as $\nu \to \infty$, so that the fuel is completely consumed in the growth stage; this depletion is accompanied by maximum production of the chain radical. The above solutions also indicate a significant enhancement in the thermal response as ν (or $\hat{t}$) increases, corresponding to the onset of the termination step. Appropriate local solutions are described below.

3.4 Termination stage

The above growth-zone analysis indicates that the fuel mass fraction F becomes exponentially small as $\nu \to \infty$. After neglecting these terms, results for the radical mass fraction (3.42)–(3.48) reduce to

$$Y_{00} \sim 1,\ Y_{11} \sim -\frac{1}{\beta},\ Y_{10} \sim -\frac{\nu}{\beta},\ Y_{22} \sim -\frac{1}{\beta},\ Y_{21} \sim -\frac{2\nu}{\beta} \text{ and } Y_{20} \sim -\frac{\nu^2}{\beta}. \tag{3.50}$$

Similarly for the time,

$$\hat{t}_0 \sim \frac{\nu}{\beta} + \hat{t}_{0\infty}, \quad \hat{t}_{11} \sim \frac{(1+2\beta)\nu}{\beta^2} + \hat{t}_{11\infty}, \quad \text{and} \quad \hat{t}_{10} \sim \frac{(1+2\beta)\nu^2}{2\beta^2} + \hat{t}_{10\infty}. \tag{3.51}$$

Here,

$$\hat{t}_{0\infty} = \int_{-\infty}^{0} \{r_0(\nu) - a_0(\nu)\}\, \mathrm{d}\nu + \int_{0}^{\infty} \left\{r_0(\nu) - \frac{1}{\beta}\right\}\, \mathrm{d}\nu - \frac{1}{1+A} \tag{3.52}$$

with

$$r_0 = \frac{1}{\beta} Y_0(\nu), \quad \text{and} \quad a_0 = \frac{\mathrm{e}^{-\nu}}{1+A} + \frac{1}{2\beta}. \tag{3.53}$$

Also,

$$\hat{t}_{11\infty} = \int_{-\infty}^{0} \{r_{11}(\nu) - a_{11}(\nu)\}\, \mathrm{d}\nu + \int_{0}^{\infty} \left\{r_{11}(\nu) - \frac{1+2\beta}{\beta^2}\right\}\, \mathrm{d}\nu - \frac{1}{2(1+A)^2} - \frac{1}{\beta(1+A)}, \tag{3.54}$$

where

$$r_{11} = \frac{2}{\beta Y_0(\nu)} - \frac{Y_{11}(\nu)}{\beta Y_0^2(\nu)}, \tag{3.55}$$

and

$$a_{11} = \frac{\mathrm{e}^{-2\nu}}{(1+A)^2} + \frac{\mathrm{e}^{-\nu}}{\beta(1+A)} + \frac{5+12\beta}{12\beta^2}. \tag{3.56}$$

Correspondingly,

$$\hat{t}_{10\infty} = \int_{-\infty}^{0} \{r_{10}(\nu) - a_{10}(\nu)\}\, \mathrm{d}\nu + \int_{0}^{\infty} \left\{r_{10}(\nu) - \frac{1+2\beta}{\beta^2}\nu\right\}\, \mathrm{d}\nu - \frac{11+10A}{4(1+A)^2} - \frac{1}{\beta(1+A)} \tag{3.57}$$

with

$$r_{10} = \frac{2\nu}{\beta Y_0(\nu)} - \frac{Y_{10}(\nu)}{\beta Y_0^2(\nu)}, \tag{3.58}$$

where $a_{10}(\nu)$ is defined in (3.45).

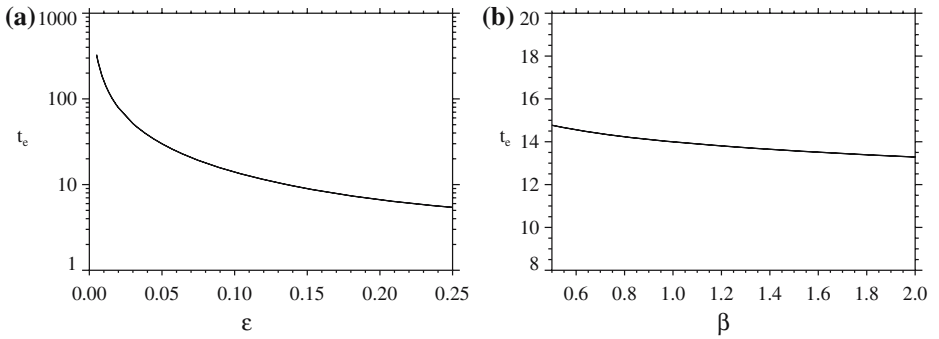

Fig. 1 (a) Variation of time scale for the onset of termination (**a**) with ϵ for $m = 2{\cdot}5$, $T_i = 3$, $\beta = 1$ and $A = O(1)$, with $A = 5$ (dashed line), $A = 1$ (solid line) and $A = 0{\cdot}25$ (dotted line); (**b**) with β, for $A = 1$, $\epsilon = 0{\cdot}1$, $m = 2{\cdot}5$ and for $T_i = 2$ (dashed line), $T_i = 3$ (solid line), $T_i = 5$ (dotted line)

Examination of these results suggests that the growth expansion (3.38) is no longer a valid description when $\nu = O(1/\epsilon)$. This signals the beginning of the termination step, wherein there is a marked reduction in the chain-carrier concentration. It is now appropriate to set

$$\nu = \frac{V}{\epsilon} - \log\frac{1}{\epsilon} \quad (\text{or } u = \epsilon^{-1}V). \tag{3.59}$$

Because f is exponentially small, matching conditions for this region as $V \to 0$ are

$$y \sim 1 - \frac{V}{\beta} - \frac{V^2}{\beta} + \cdots, \quad \text{and} \quad \tau = t - t_e \sim \frac{V}{\beta} + \frac{(2\beta+1)V^2}{2\beta^2} + \cdots, \tag{3.60}$$

where

$$t_e = \hat{t}_{ig}(\epsilon) - \epsilon\log(1/\epsilon)\frac{1}{\beta} + \epsilon\hat{t}_{0\infty} - \epsilon^2\log^2(1/\epsilon)\frac{2\beta+1}{2\beta^2} + \epsilon^2\log(1/\epsilon)\hat{t}_{11\infty} + \epsilon^2\hat{t}_{10\infty} + \cdots. \tag{3.61}$$

Figure 1a shows characteristic behaviors of the termination scale t_e as a function of ϵ for various values of the parameter A, with m, β, and T_i fixed. Figure 1b shows the variation of t_e as a function of β for various T_i with m, β, and ϵ fixed. Not surprisingly, the time scale for the onset of the termination reaction increases with decreasing ϵ, i.e., as the buildup of chain carriers in the initiation reaction becomes slower. Figure 1b shows that t_e has a relatively weak dependence on β for the range shown, but increases in value with increasing T_i, again due to the initiation reaction being slower. Note that the result defined by (3.61) is not uniformly valid as $A \to 0$ (see (3.16) and (3.32)). Necessary modifications to the theory are outlined briefly in Sect. 5.

From (3.60) it follows that the limiting behavior of $y(\tau)$ can be determined directly as

$$y \sim 1 - \tau + \frac{1}{2}\tau^2 + \cdots, \tag{3.62}$$

and it should be observed that, to this order, the result is independent of ϵ. Neglecting exponentially small terms, with $\tau = t - t_e = O(1)$, the second of the rate equations (2.9) reduces simply to

$$\frac{\mathrm{d}y}{\mathrm{d}\tau} = -y, \tag{3.63}$$

and the appropriate solution consistent with (3.62) is

$$y = \mathrm{e}^{-\tau}. \tag{3.64}$$

Although the exponential form of the final decay of the intermediate radical is immediately apparent from (2.8) and (2.9), the determination of $t_e(\epsilon)$ requires knowledge of the initiation, induction and growth stage solutions discussed previously. Expressed in terms of V the solution (3.64) becomes

$$y = 1 - \frac{V}{\beta(1-V)}. \tag{3.65}$$

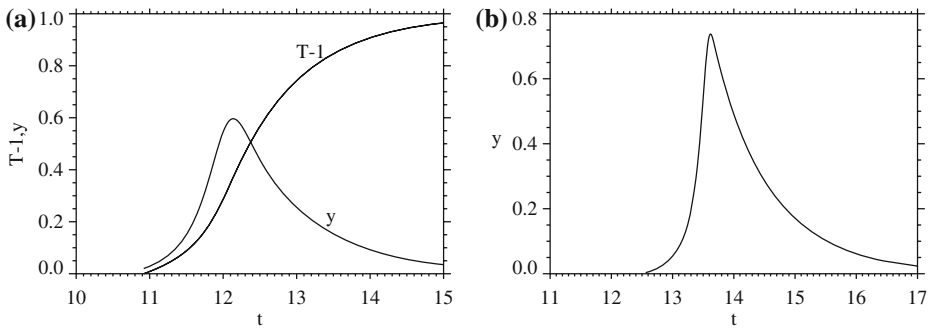

Fig. 2 (**a**) Comparison with exact (dashed lines) and asymptotic outer composite (solid lines) solutions for $A = O(1)$, for $T_b = 0{\cdot}925$, $T_i = 3$, $\beta = 1$, $\epsilon = 0{\cdot}125$ and $m = 2{\cdot}5$. (**b**) Comparison with exact (dashed lines) and asymptotic outer composite (solid lines) solutions for $A = O(1)$ for y for $T_b = 0{\cdot}96$, $T_i = 3$, $\beta = 1$, $\epsilon = 1/16$ and $m = 1{\cdot}5$

The corresponding result for the temperature is

$$T = \frac{1}{1-V} = 1 + \beta(1 - \mathrm{e}^{-\tau}). \tag{3.66}$$

3.5 Composite solutions and comparison with numerical results

Although changes are exponentially small within the initiation stage, this step provides important information concerning the initial behavior in the induction period. A composite solution for the growth and the termination stages can be obtained from the standard composite form

$$\chi = \chi_{\text{inner}} + \chi_{\text{outer}} - \text{inner}(\chi_{\text{outer}}), \tag{3.67}$$

where inner corresponds to the growth stage and outer to the termination stage. This composite solution is compared with an exact numerical solution in Fig. 2a for $\epsilon = 0{\cdot}125$ and $T_b = 0{\cdot}925$. As expected, the growth solution does not accurately incorporate the induction behavior, but there is good agreement between the asymptotic analysis and the numerical calculations for the growth and termination steps. A result for smaller values of ϵ and $1 - T_b$ is displayed in Figure 2b. Again, good agreement is obtained for the growth and termination phases.

4 Thermal explosions: $A = O(1/\epsilon)$

4.1 Initiation stage

The analysis in the preceding section was carried out for $A = O(1)$. Numerical values employed in the studies by Birkan and Kassoy [11] and Short and Quirk [5] suggest, however, that there are practical circumstances in which $A \gg 1$, and this case is considered here. The particular distinguished limit adopted is defined by

$$A = \frac{a}{\epsilon}, \quad \text{with} \quad a = O(1) \text{ and } > 0 \tag{4.1}$$

for which

$$1 - T_b = \epsilon \log(1/\epsilon) + O(\epsilon). \tag{4.2}$$

Although (3.9)–(3.13) were deduced by assuming $A = O(1)$, it can be shown that these results remain valid for $A = O(1/\epsilon)$ provided that $at < m(1 - 1/T_i)$, and the expansion (3.6) now fails when

$$k_{i0}\mathrm{e}^{At} = O(1), \tag{4.3}$$

thereby defining the chain-initiation time

$$t_{\rm ig} \sim \bar{t}_{\rm ig0} = \frac{m}{a}\left(1 - \frac{1}{T_i}\right) + \frac{\epsilon}{a}\log\frac{1}{\epsilon}. \tag{4.4}$$

In contrast with the initiation scale $t_{\rm ig0} = O(1/\epsilon)$ for $A = O(1)$, the initiation scale $\bar{t}_{\rm ig0}$ is $O(1)$ for $A = O(1/\epsilon)$. Subject to (4.1) the initiation and termination periods are of the same size. An appropriate time scale associated with the failure of expansion (3.6) can be defined by

$$t = \bar{t}_{\rm ig0} + \epsilon\bar{t}. \tag{4.5}$$

Again, it is convenient to regard $\bar{t}$ as a dependent variable and to use the perturbed inverse temperature u as the basic independent variable, see (3.18). As $u \to 0$, the matching conditions (3.19) and (3.20) are replaced by

$$\begin{aligned} y &\sim \frac{a}{\beta}u + \frac{(\beta-a)a}{2\beta^2}u^2 + \cdots + \epsilon\left\{\left(\frac{a}{\beta} + \frac{\beta-2a}{2\beta^2}\right)u^2 + \cdots\right\} + \epsilon^2\left(-\frac{u^2}{2\beta^2} + \cdots\right) + \cdots, \\ f &\sim 1 - \frac{a}{\beta}u - \cdots + \epsilon\left\{-\frac{u}{\beta} - \left(\frac{a}{\beta} + \frac{\beta-2a}{2\beta^2}\right)u^2 + \cdots\right\} + \epsilon^2\left\{\left(\frac{1}{2\beta^2} - \frac{1}{2\beta}\right)u^2 + \cdots\right\} + \cdots, \end{aligned} \tag{4.6}$$

and

$$a\bar{t} \sim \log\frac{a^2u}{\beta} - \frac{\beta-a}{2\beta}u^2 + \cdots + \epsilon\left\{\left(1 - \frac{\beta-a}{2\beta}\right)u + \cdots\right\} + \epsilon^2\left(\frac{u}{2a\beta} + \cdots\right) + \cdots. \tag{4.7}$$

4.2 Induction and growth stage

In contrast with $A = O(1)$, the limiting behaviors (4.6)–(4.7) indicate that there is already significant radical production, with $y = O(1)$ and $f = O(1)$, when the temperature change $T - 1 = O(\epsilon)$. The period when $u = O(1)$ corresponds to a combined induction and growth stage. Corresponding asymptotic expansions are

$$y = y_0(u) + \epsilon y_1(u) + \cdots, \quad f = f_0(u) + \epsilon f_1(u) + \cdots, \tag{4.8}$$

and

$$t = \bar{t}_{ig0} + \epsilon\bar{t}_1(u) + \cdots. \tag{4.9}$$

Neglecting exponentially small terms, the rate laws can be re-expressed in the form

$$\frac{{\rm d}y}{{\rm d}u} = \frac{(a+\epsilon){\rm e}^u f - \epsilon}{\beta(1-\epsilon u)^2}, \quad \frac{{\rm d}\bar{t}}{{\rm d}u} = \frac{1}{\beta y(1-\epsilon u)^2}, \tag{4.10}$$

and the energy equation (2.13) gives

$$f = 1 - y - \frac{1}{\beta}\frac{\epsilon u}{1-\epsilon u}. \tag{4.11}$$

Substituting expansions (4.8) and (4.9) in the rate law for y given in (4.10), together with (4.11), yields

$$\begin{aligned} &\beta{\rm d}y_0/{\rm d}u = a{\rm e}^u f_0, \beta{\rm d}y_1/{\rm d}u = a{\rm e}^u f_1 + (1+2au){\rm e}^u f_0 - 1, \\ &\beta{\rm d}y_2/{\rm d}u = a{\rm e}^u f_2 + (1+2au){\rm e}^u f_1 + (2u+3au^2){\rm e}^u f_0 - 2u \end{aligned} \tag{4.12}$$

with

$$f_0 = 1 - y_0, \quad f_1 = -y_1 - \frac{u}{\beta}, \quad \text{and} \quad f_2 = -y_2 - \frac{u^2}{\beta}. \tag{4.13}$$

Matching with (4.6) as $u \to 0$ leads to the solutions

$$\begin{aligned} y_0 &= 1 - \exp\left[\frac{a}{\beta}(1-\mathrm{e}^u)\right], \\ \beta y_1 &= (2a-1)\exp\left[\frac{a}{\beta}(1-\mathrm{e}^u)\right] + \{1+2a(u-1)\}\exp\left[\frac{a}{\beta}(1-\mathrm{e}^u)+u\right] - u, \end{aligned} \tag{4.14}$$

and

$$\beta y_2 = -u^2 + \exp\left[\frac{a}{\beta}(1-\mathrm{e}^u)\right]\sum_{n=0}^{2} C_n(u;a,\beta)\mathrm{e}^{nu}, \tag{4.15}$$

where the coefficients C_n are listed in Appendix A.

Using (4.13), the results (4.14) and (4.15) also define f_0, f_1 and f_2. Similarly, the $\bar{t}_n$ can then be found from the second of Eq. 4.10. Corresponding results are

$$\bar{t}_1 = \int_0^u \left\{\frac{1}{\beta y_0(\bar{u})} - \frac{1}{a\bar{u}}\right\} \mathrm{d}\bar{u} + \frac{1}{a}\log\frac{a^2 u}{\beta}, \tag{4.16}$$

and

$$\bar{t}_2 = \frac{1}{\beta}\int_0^u \left\{\frac{2\bar{u}}{y_0(\bar{u})} - \frac{y_1(\bar{u})}{y_0^2(\bar{u})}\right\} d\bar{u}. \tag{4.17}$$

As $u \to \infty$, it follows from (4.14) and (4.15) that, neglecting exponentially small terms,

$$y_0 \sim 1, \quad y_1 \sim -\frac{u}{\beta}, \quad \text{and} \quad y_2 \sim -\frac{u^2}{\beta}. \tag{4.18}$$

Similarly, from (4.16) and (4.17),

$$\bar{t}_1 \sim \frac{u}{\beta} + \bar{t}_{\mathrm{ig1}}, \quad \text{and} \quad \bar{t}_2 \sim \frac{1}{\beta}\left(1+\frac{1}{2\beta}\right)u^2 + \bar{t}_{\mathrm{ig2}}, \tag{4.19}$$

where

$$\bar{t}_{\mathrm{ig1}} = \int_0^1 \left\{\frac{1}{\beta y_0(\bar{u})} - \frac{1}{a\bar{u}}\right\} \mathrm{d}\bar{u} + \int_1^\infty \left\{\frac{1}{\beta y_0(\bar{u})} - \frac{1}{\beta}\right\} \mathrm{d}\bar{u} + \frac{1}{a}\log\frac{a^2}{\beta} - \frac{1}{\beta}, \tag{4.20}$$

and

$$\bar{t}_{\mathrm{ig2}} = \frac{1}{\beta}\int_0^\infty \left\{2\bar{u}\left(\frac{1}{y_0(\bar{u})} - 1\right) - \frac{y_1(\bar{u})}{y_0^2(\bar{u})} - \frac{\bar{u}}{\beta}\right\} \mathrm{d}\bar{u}. \tag{4.21}$$

From (4.13) and (4.18), it follows that for large u the fuel mass fraction f is exponentially small. Clearly, when $A = O(1/\epsilon)$, the peak production rate of the chain carriers is achieved in the present region with $u = O(1)$.

4.3 Termination stage

Equations (4.18) and (4.19) indicate that the growth expansions (4.8)–(4.9) fail when $u = O(1/\epsilon)$. As in Sect. 3 with $A = O(1)$,

$$u = \frac{V}{\epsilon} \tag{4.22}$$

for which $T = O(1)$ and $t - \bar{t}_{\mathrm{ig0}} = O(1)$. Suitable local variables are

$$\tau = t - \bar{t}_{\mathrm{ig}} \quad \text{with} \quad T = T(\tau;\epsilon) \quad \text{and} \quad y = y(\tau;\epsilon). \tag{4.23}$$

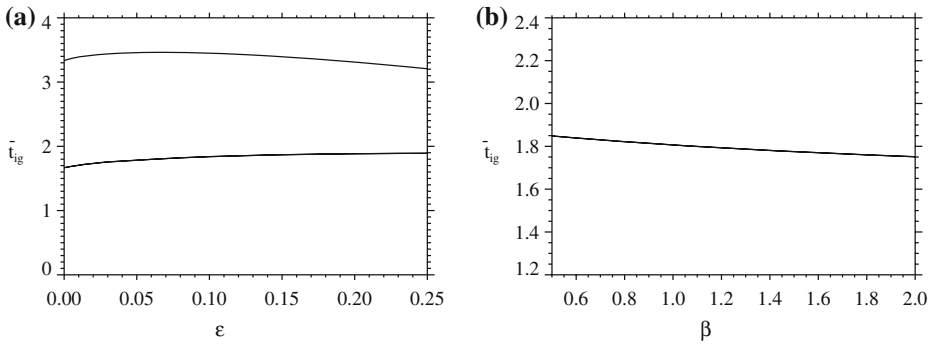

Fig. 3 (**a**) Ignition times $\bar{t}_{ig}$ as a function of ϵ for $a = O(1)$ with $m = 2{\cdot}5$, $T_i = 3$ and $\beta = 0{\cdot}6$ with $a = 2$ (dashed line), $a = 1$ (solid line), $a = 0{\cdot}75$ (dotted line) and $a = 0{\cdot}5$ (dot-dash line). (**b**) Ignition times $\bar{t}_{ig}$ as a function of β for $a = 1$, $\epsilon = 0{\cdot}1$ and $m = 2{\cdot}5$ for $T_i = 2$ (dashed line), $T_i = 3$ (soild line) and $T_i = 5$ (dotted line)

Here,

$$\bar{t}_{ig} = \bar{t}_{ig0} + \epsilon \bar{t}_{ig1} + \epsilon^2 \bar{t}_{ig2} + \cdots, \tag{4.24}$$

where the constants $\bar{t}_{igi}$ are defined in (4.4), (4.20) and (4.21).

Results for $\bar{t}_{ig}$ are displayed as a function of ϵ in Fig. 3a for various values of the parameter a. As shown in the figure and predicted by (4.4), $\bar{t}_{ig}$ decreases as a increases or as the chain-branching cross-over temperature becomes significantly lower than the initial system temperature. The dependence of $\bar{t}_{ig}$ on the heat release parameter is shown in Fig. 3b for a range of initiation cross-over temperatures T_i with $m = 2{\cdot}5$ and $\epsilon = 0{\cdot}1$. As can be seen from the figure, and consistent with (4.4), the growth time scale is only weakly dependent on the heat release when $\beta = O(1)$.

It can also be established from (4.18) and (4.19) that matching conditions as $\tau \to 0$ are

$$y \sim 1 - \tau + \frac{1}{2}\tau^2 + \cdots, \quad \text{and} \quad T \sim 1 + \beta\left(\tau + \frac{1}{2}\tau^2 + \cdots\right). \tag{4.25}$$

Because f is exponentially small, substitution in the rate laws and matching with (4.25) again leads to the results (3.64) and (3.66), although τ is now defined by (4.23) and (4.24), rather than by (3.60) and (3.61).

The current analysis requires

$$T_i > 1 + \beta. \tag{4.26}$$

If the above constraint does not apply but $T_i > 1$, there are minor modifications in the asymptotic ($t \to \infty$) exponential decays.

4.4 Composite solution

Although changes are exponentially small within the initiation stage, this step provides important information concerning the initial behavior in the induction period. For the limit (4.1) the induction and growth stages overlap (Sect. 4b). In addition, the solutions for the induction, growth and termination phases can be combined to yield a uniformly valid representation for $u \geq O(1)$. It has the standard composite form (3.67) and can be written

$$\begin{aligned} y_{\text{comp}} &= y_0(u) + \epsilon y_1(u) + \epsilon^2 y_2(u) - \beta^{-1} V^3 (1 - V)^{-1}, \\ f_{\text{comp}} &= f_0(u) + \epsilon f_1(u) + \epsilon^2 f_2(u), \\ t_{\text{comp}} &= \bar{t}_{ig0}(u) + \epsilon \bar{t}_1(u) + \epsilon^2 \bar{t}_2(u) + \log\left[\frac{\beta(1-V)}{\beta - (\beta+1)V}\right] \\ &\quad - \frac{V}{\beta} - \left(\frac{1}{\beta} + \frac{1}{2\beta^2}\right) V^2, \end{aligned} \tag{4.27}$$

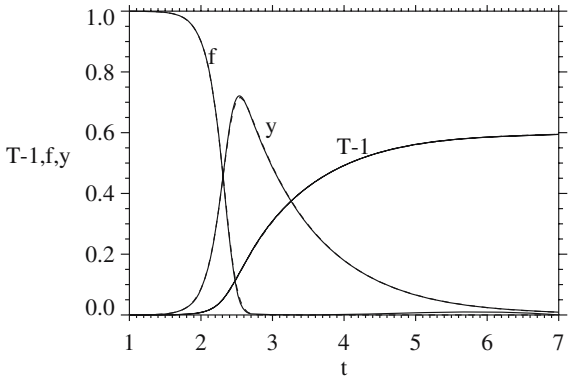

Fig. 4 Comparison with exact (dashed lines) and asymptotic (solid lines) solutions for $a = O(1)$, for $T_b = 0{\cdot}8$, $T_i = 3$, $\beta = 0{\cdot}6$, $\epsilon = 0{\cdot}125$ and $m = 2{\cdot}5$. The asymptotic and exact solutions overlay each other

and very simply

$$T_{\text{comp}} = \frac{1}{(1-V)}. \tag{4.28}$$

Comparison with an exact numerical solution is shown in Fig. 4. For this particular example $a = 0{\cdot}7986$. As can be seen, the agreement between exact and asymptotic solutions is excellent.

5 Thermal explosion with slow iniation: $T_b = 1$ ($A = 0$)

5.1 Initiation stage

The case $A = 0$, for which

$$T_b = 1 \quad \text{and} \quad k_{b0} = 1, \tag{5.1}$$

is used to characterize $T_b - 1 = o(\epsilon)$. As in the earlier analyses, perturbations from the initial state are exponentially small, but the duration of the initiation step is exponentially large with respect to ϵ. Only the leading-order terms are listed in the subsequent analysis. Higher-order terms can be obtained using the approaches followed in Sects. 3 and 4.

A suitable initial independent variable is

$$u = \epsilon^{-1} k_{i0} \hat{u}_0 \tag{5.2}$$

and corresponding leading-order results are

$$\begin{aligned} &T = 1 + k_{i0}\hat{u}_0 + O(k_{i0}^2), \quad y = k_{i0}(2\hat{u}_0/\beta)^{1/2} + O(\epsilon^{-1}k_{i0}^2), \\ &f = 1 - k_{i0}\left\{(2\hat{u}_0/\beta)^{1/2} + \hat{u}_0/\beta\right\} + O(\epsilon^{-1}k_{i0}^2), \quad t = (2\hat{u}_0/\beta)^{1/2} + O(\epsilon^{-1}k_{i0}^2). \end{aligned} \tag{5.3}$$

Examining the growth of the correction terms indicates that this solution fails when $\hat{u}_0 = O(\epsilon^{2/3}k_{i0}^{-2/3})$. Introducing a new independent variable $\hat{U}$ through

$$u = \epsilon^{-1/3} k_{i0}^{1/3} \hat{U}, \tag{5.4}$$

shows that there is a second layer of initiation in which changes are also exponentially weak. Suitable expansions are

$$\begin{aligned} &y = \epsilon^{1/3}k_{i0}^{2/3}\hat{Y}(\hat{U};\epsilon) + O(\epsilon^{1/3}k_{i0}), \quad f = 1 - \epsilon^{2/3}k_{i0}^{1/3}\hat{F}(\hat{U};\epsilon) + O(\epsilon^{1/3}k_{i0}^{2/3}), \\ &t = \epsilon^{1/3}k_{i0}^{-1/3}\hat{\tau}(\hat{U};\epsilon) + O(\epsilon^{-1/3}), \quad T = 1 + \epsilon^{2/3}k_{i0}^{1/3}\hat{U} + O(\epsilon^{4/3}k_{i0}^{2/3}). \end{aligned} \tag{5.5}$$

Neglecting exponentially small terms, the dominant approximations are

$$\beta\hat{\tau} = \int_0^{\hat{U}} \frac{\mathrm{d}\mu}{\hat{Y}(\mu;\epsilon)}, \quad \hat{F} = \hat{U}/\beta, \tag{5.6}$$

where $\hat{Y}(\hat{U};\epsilon)$ satisfies

$$\beta\hat{Y}\frac{\mathrm{d}\hat{Y}}{\mathrm{d}\hat{U}} = 1 + (1-\epsilon/\beta)\hat{U}\hat{Y}, \quad \text{with} \quad \hat{Y} \to 0 \text{ as } \hat{U} \to 0. \tag{5.7}$$

Note that as $\hat{U} \to \infty$,

$$\hat{\tau} \to \hat{\tau}_i = \beta^{-1}\int_0^{\infty} \frac{\mathrm{d}\mu}{\hat{Y}(\mu;\epsilon)}. \tag{5.8}$$

The higher-order exponentially small terms show that the expansion ceases to be uniformly valid when $\hat{U} = O(\epsilon^{1/3}k_{i0}^{-1/3})$ or $u = O(1)$.

5.2 Induction stage

As noted above, in the present limit the initiation time is exponentially large; see (5.5) and (5.8). After this initiation stage, perturbations are $O(\epsilon)$ and the solution adopts the standard induction structure. The leading approximation is

$$y = \epsilon(\mathrm{e}^u - 1 - u)/\beta + O(\mathrm{e}^2), \quad f = 1 - \epsilon(\mathrm{e}^u - 1)/\beta + O(\epsilon^2), \quad T = 1 + \epsilon u + O(\epsilon^2) \tag{5.9}$$

with

$$t - \hat{t}_{\mathrm{ig}}(\epsilon) = \int_0^u \left\{\frac{1}{\mathrm{e}^\mu - 1 - \mu} - \frac{2}{\mu^2} + \frac{2}{3\mu}\right\}\mathrm{d}\mu - \frac{2}{\mu} - \frac{2}{3}\log u + O(\epsilon), \tag{5.10}$$

and

$$\hat{t}_{\mathrm{ig}} = \epsilon^{1/3}k_{i0}^{-1/3}\hat{\tau}_i + O(\epsilon^{-2/3}). \tag{5.11}$$

As $u \to \infty$, it can be seen that

$$\begin{aligned} t \to t_g = \hat{t}_{\mathrm{ig}}(\epsilon) + t_{0g} = \hat{t}_{\mathrm{ig}}(\epsilon) &+ \int_0^1 \left\{\frac{1}{\mathrm{e}^u - 1 - u} - \frac{2}{u^2} + \frac{2}{3u}\right\}\mathrm{d}u \\ &+ \int_1^{\infty} \left\{\frac{1}{\mathrm{e}^u - 1 - u}\right\}\mathrm{d}u - 2 + O(\epsilon\log 1/\epsilon). \end{aligned} \tag{5.12}$$

5.3 Growth stage

As u increases, the induction solution (5.9) does not remain uniformly valid. Significant fuel depletion, accompanied by a marked growth in the chain-carrier concentration, occurs. A suitable new variable, equivalent to that found for $A = O(1)$, is again

$$u = \log(1/\epsilon) + v. \tag{5.13}$$

Straightforward calculations lead to

$$\begin{aligned} &y = 1 - \exp(-\mathrm{e}^v/\beta) + O(\epsilon\log(1/\epsilon)), \quad f = \exp(-\mathrm{e}^v/\beta) + O(\epsilon\log(1/\epsilon)), \\ &T = 1 + \epsilon\log(1/\epsilon) + \epsilon v + O(\epsilon^2\log(1/\epsilon)), \end{aligned} \tag{5.14}$$

and

$$t - \hat{\tau}_g = \epsilon \int_{-\infty}^{\nu} \left\{ \frac{1}{\beta y(\nu)} - \mathrm{e}^{-\nu} - \frac{1}{2\beta} \right\} \mathrm{d}\nu - \mathrm{e}^{-\nu} + \frac{\nu}{2\beta} + O(\epsilon^2 \log(1/\epsilon)). \tag{5.15}$$

In the limit $\nu \to \infty$, the basic approximations give

$$y \to 1, \quad f \to \text{exp. small}, \quad t \to \nu/\beta + \hat{\tau}_g + \epsilon\tau_{0\infty}, \tag{5.16}$$

where

$$\tau_{0\infty} = \int_{-\infty}^{0} \left\{ \frac{1}{\beta y(\nu)} - \mathrm{e}^{-\nu} - \frac{1}{2\beta} \right\} \mathrm{d}\nu + \int_{0}^{\infty} \frac{1}{\beta} \left(\frac{1}{y(\nu)} - 1 \right) \mathrm{d}\nu - 1. \tag{5.17}$$

5.4 Termination stage

The above growth expansions fail when $u = O(1/\epsilon)$. Setting

$$u = V/\epsilon, \tag{5.18}$$

and following the analysis given for the termination stage in Sect. 3.4, shows that the dominant structure still has the form

$$y = \mathrm{e}^{-\tau}, \quad T = 1 + \beta(1 - \mathrm{e}^{-\tau}), \quad \tau = t - t_e, \tag{5.19}$$

and

$$t_e = \hat{\tau}_g - \beta^{-1}\epsilon \log(1/\epsilon) + \epsilon\tau_{0\infty} + O(\epsilon^2 \log^2(1/\epsilon)). \tag{5.20}$$

6 Thermal explosion with rapid branching: $1 - T_b = O(1) > 0$

6.1 Initiation stage

When the branching temperature T_b is significantly below the initial temperature $T = 1$, the branching rate is exponentially fast, but for $T_i > 1$ the initiation rate is exponentially slow. Consequently, the initiation reaction will still produce only an exponentially small concentration of chain carriers. It remains useful to employ k_{b0} and k_{i0} as initial measures of the rates with

$$k_{b0} \gg 1 \gg k_{i0}. \tag{6.1}$$

In this limit it is straightforward to use time as the dependent variable. Subject to (6.1), the initial stage is now exponentially short with

$$t = \hat{s}/k_{b0}. \tag{6.2}$$

The initiation expansion has the form

$$y = a\hat{\Gamma}(\hat{s};\epsilon), \quad f = 1 - a\hat{\Phi}(\hat{s};\epsilon), T = 1 + (a/k_{b0})\hat{\Theta}(\hat{s};\epsilon), \tag{6.3}$$

where the amplitude

$$a = k_{i0}/k_{b0} \tag{6.4}$$

is exponentially small. It is not difficult to show that

$$\hat{\Gamma} = \mathrm{e}^{\hat{s}} - 1 + O(1/k_{b0}), \quad \hat{\Phi} = \mathrm{e}^{\hat{s}} - 1 + O(1/k_{b0}), \quad \hat{\Theta} = \beta(\mathrm{e}^{\hat{s}} - 1 - \hat{s}) + O(1/k_{b0}). \tag{6.5}$$

Continuation with the expansion indicates that difficulties arise when

$$\hat{s} = \log(1/a) = O(1/\epsilon). \tag{6.6}$$

6.2 Growth stage

Based on (6.6) and arguments given in Sect. 3, the exponential growth (6.5) associated with the initiation stage fails on the scale defined by (6.6) and a suitable new time scale is

$$\hat{s} = \log(1/a) + s \tag{6.7}$$

with

$$y = \Gamma(s) + O(1/k_{b0}), \quad f = \Phi(s) + O(1/k_{b0}), \quad T = 1 + O(1/k_{b0}). \tag{6.8}$$

Using this expansion gives

$$\Gamma(s) = \frac{1}{1+\mathrm{e}^{-s}}, \quad \Phi(s) = \frac{\mathrm{e}^{-s}}{1+\mathrm{e}^{-s}}. \tag{6.9}$$

6.3 Termination stage

Examination of higher-order terms in the growth solution indicates that (6.9) is no longer valid when s becomes exponentially large, specifically $s = O(k_{b0})$ or $\Delta t = O(1)$. A suitable new variable is

$$t - t_E = \sigma, \tag{6.10}$$

where

$$t_E = \frac{1}{\epsilon k_{b0}} \left(\frac{1}{T_b} - 1 + m \left(1 - \frac{1}{T_i} \right) \right). \tag{6.11}$$

Neglecting exponentially small terms, the solution again has the form defined by (3.64) and (3.66), i.e.,

$$y = \mathrm{e}^{-\sigma}, \quad T = 1 + \beta \left(1 - \mathrm{e}^{-\sigma} \right). \tag{6.12}$$

7 Slow thermal explosion: $T_b - 1 = O(1) > 0$

7.1 Initiation stage

When the branching temperature exceeds the initial temperature by $O(1)$, both the initiation rate k_{i0} and the branching rate k_{b0} are exponentially slow, see (3.3), and there is a long initiation period prior to the onset of significant fuel depletion. In this limit, $A \to -1$, and provided $T_i > T_b > 1$,

$$1 \gg k_{b0} \gg k_{i0}. \tag{7.1}$$

For ease of discussion it is, in fact, assumed that

$$T_i > T_b > 1 + \beta. \tag{7.2}$$

The initial expansion is now similar to that outlined in Sect. 3, but the error terms must be modified. In the present case,

$$u = k_{i0}\hat{u}_b/\epsilon, \tag{7.3}$$

and

$$\begin{gathered} y = k_{i0}\{\hat{y}(\hat{u}_b;\epsilon) + O(k_{b0}, k_{i0})\}, \quad f = 1 - k_{i0}\{\hat{f}(\hat{u}_b;\epsilon) + O(k_{b0}, k_{i0})\}, \\ t = \hat{t}(\hat{u}_b;\epsilon) + O(k_{b0}, k_{i0}), \; T = 1 + k_{i0}\hat{u}_b + O(k_{i0}^2). \end{gathered} \tag{7.4}$$

Again the terms $\hat{y}(\hat{u}_b;\epsilon)$, etc. retain all terms that are algebraically small in ϵ. The leading approximations are given by

$$\hat{y} + \log(1-\hat{y}) = -\hat{u}_b/\beta, \quad \hat{f} = \hat{y} + \hat{u}_b/\beta, \quad \hat{t} = -\log(1-\hat{y}). \tag{7.5}$$

7.2 Induction stage

Evaluation of higher-order exponentially small terms in the initiation expansion indicates that the solution (7.5) is no longer valid when $u = O(1)$ or $t = O(\epsilon/k_{i0})$. Local variables are

$$f = 1 - \epsilon f_{\rm in}(u;\epsilon), \quad y = k_{i0} y_{\rm in}(u;\epsilon), \quad t = \epsilon \tilde{t}_b / k_{i0}, \tag{7.6}$$

and the leading-order terms are

$$\begin{aligned} &y_{\rm in} = \mathrm{e}^{mu}(1 - \epsilon u/\beta + O(\epsilon^2)),\ f_{\rm in} = u/\beta + O(\epsilon), \\ &\tilde{t}_b = \frac{1 - \mathrm{e}^{-mu}}{m\beta} + \epsilon \frac{2\beta + 1}{(m\beta)^2}\{1 - (1 + mu)\mathrm{e}^{-mu}\} + O(\epsilon^2). \end{aligned} \tag{7.7}$$

Note that the radical mass fraction remains exponentially small.

7.3 Depletion stage

From (7.7), it can be seen that the induction structure fails when $u = O(1/\epsilon)$. On this scale, where there is a significant change in the fuel mass fraction and system temperature, it is found that there are exponentially fast changes in the radical concentration, and the relevant time scale must be modified in a similar manner. Setting

$$u = V/\epsilon, \tag{7.8}$$

and neglecting terms that remain exponentially small, gives

$$\begin{aligned} &f = 1 - \frac{V}{\beta(1 - V)},\ y = k_{i0}\left(1 - \frac{V}{\beta(1 - V)}\right)\mathrm{e}^{mV/\epsilon}, \\ &t = t_{\rm eg} - \left(\frac{\epsilon}{k_{i0}}\right)\frac{\mathrm{e}^{-mV/\epsilon}}{m(1 - V)(\beta - (1 + \beta)V)} \times \{1 + O(\epsilon)\}, \end{aligned} \tag{7.9}$$

where

$$t_{\rm eg} = \frac{\epsilon}{k_{i0}}\left(\frac{1}{m\beta} + \epsilon\frac{1 + 2\beta}{(m\beta)^2} + \cdots\right). \tag{7.10}$$

7.4 Relaxation stage

Equation (7.9) indicates that as $V \to \beta/(1 + \beta)$, which is the adiabatic limit with $T \to 1 + \beta$, the depletion solution requires modification. Introduction of

$$V = \beta/(1 + \beta) - \epsilon v \tag{7.11}$$

with

$$t = t_{\rm eg} + \frac{1}{k_{i0}}\exp\left\{-\frac{m\beta}{\epsilon(1 + \beta)}\right\}\xi, \tag{7.12}$$

leads to

$$\xi = \int_v^1 \frac{\mathrm{e}^{mw}}{w}\mathrm{d}w + c. \tag{7.13}$$

Here the upper limit of the integral has been inserted for convenience, and the constant c is associated with exponentially small terms in the ignition time $t_{\rm eg}$. In addition,

$$f = \epsilon\frac{(1 + \beta)^2}{\beta}v, y = \epsilon k_{i0}\frac{(1 + \beta)^2}{\beta}v\exp\left\{\frac{m\beta}{\epsilon(1 + \beta)} - mv\right\}. \tag{7.14}$$

For the case (7.2) it is apparent that y remains exponentially small through all stages of the reaction.

8 Concluding remarks

A spatially homogeneous thermal explosion for three-step chain-branching reaction kinetics has been investigated in the asymptotic limit of large activation energy. What distinguishes this work from previous studies is that a broad range of chain-branching crossover temperatures is considered. As illustrated in Tables 1–5, details of the evolutionary structure, including the ignition delay times and the temporal extents of the various stages of evolution, are found to be markedly sensitive to the departure of the crossover temperature T_b from the initial system temperature of unity. Although they contain other generalizations, recent studies of similar systems with a similar asymptotic approach have been confined to the range $1 - T_b = O(\epsilon)$, where ϵ is the dimensionless measure of the inverse activation energy. For example, Birkan and Kassoy [11], while staying within the narrow range of crossover temperatures, considered second-order initiation and chain branching, and included dissociation and recombination steps, in their comprehensive analysis of the full temporal history of spatially homogeneous explosions. Del Alamo and Williams [12] confined their asymptotic treatment of chain-branching to the induction stage, as they were primarily

Table 1 Structure for $1 - T_b = O(1) > 0$ (A is exponentially large); k_{b0} is exponentially large and k_{i0} exponentially small with respect to ϵ

Step	t	T	f	y
Initiation	$O(k_{b0}^{-1})$	$1 + O(k_{i0}/k_{b0})$	$1 - O(k_{i0}/k_{b0})$	$O(k_{i0}/k_{b0})$
Growth	$O\big((\epsilon k_{b0})^{-1}\big)$	$1 + O(k_{b0}^{-1})$	$O(1)$	$O(1)$
Termination	$t - t_E = O(1)$	$O(1)$	exp. small	$O(1)$
	$t_E = O\big((\epsilon k_{b0})^{-1}\big)$			

Table 2 Structure for $1 - T_b = \epsilon \log \epsilon + O(\epsilon)$ ($a = O(1)$ or $A = O(1/\epsilon)$); k_{i0} is exponentially small with respect to ϵ and k_{b0} is $O(1/\epsilon)$

Step	t	T	f	y
Initiation	$O(1)$	$1 + O(k_{i0})$	$1 - O(k_{i0})$	$O(k_{i0})$
Induction and growth	$t - \bar{t}_{\mathrm{ig}} = O(\epsilon)$ $\bar{t}_{\mathrm{ig}} = O(1)$	$1 + O(\epsilon)$	$O(1)$	$O(1)$
Termination	$t - \bar{t}_{\mathrm{ig}} = O(1)$	$O(1)$	exp. small	$O(1)$

Table 3 Structure for $1 - T_b = O(\epsilon) > 0$ ($A = O(1)$); k_{i0} is exponentially small and $k_{b0} = O(1)$ with respect to ϵ

Step	t	T	f	y
Initiation	$O(1)$	$1 + O(k_{i0})$	$1 - O(k_{i0})$	$O(k_{i0})$
Induction	$t - t_{\mathrm{ig}} = O(1)$ $t_{\mathrm{ig}} = O(1/\epsilon)$	$1 + O(\epsilon)$	$1 - O(\epsilon)$	$O(\epsilon)$
Growth	$t - \hat{t}_{\mathrm{ig}} = O(\epsilon)$	$1 + O(\epsilon \log(1/\epsilon))$	$O(1)$	$O(1)$
	$\hat{t}_{\mathrm{ig}} = t_{\mathrm{ig}} + O(1)$			
Termination	$t - \hat{t}_{\mathrm{ig}} = O(1)$	$O(1)$	exp. small	$O(1)$

Table 4 Structure for $T_b = 1$ ($A = 0$); k_{i0} is exponentially small with respect to ϵ while $k_{b0} = 1$

Step	t	T	f	y
Initiation 1	$O(1)$	$1 + O(k_{i0})$	$1 - O(k_{i0})$	$O(k_{i0})$
Initiation 2	$O\big((\epsilon/k_{i0})^{1/3}\big)$	$1 + O(\epsilon^{2/3}k_{i0}^{1/3})$	$1 - O(\epsilon^{2/3}k_{i0}^{1/3})$	$O(\epsilon^{1/3}k_{i0}^{2/3})$
Induction	$t - \hat{t}_{\rm ig} = O(1)$ $\hat{t}_{\rm ig} = O\big((\epsilon/k_{i0})^{1/3}\big)$	$1 + O(\epsilon)$	$1 - O(\epsilon)$	$O(\epsilon)$
Growth	$t - \hat{t}_g = O(\epsilon)$ $\hat{t}_g = \hat{t}_{\rm ig} + O(1)$	$1 + O(\epsilon \log(1/\epsilon))$	$O(1)$	$O(1)$
Termination	$t - t_e = O(1)$ $t_e = \hat{t}_g + O\big(\epsilon \log(1/\epsilon)\big)$	$O(1)$	exp. small	$O(1)$

Table 5 Structure for $T_b - 1 = O(1) > 0$ ($A \to -1$); k_{i0} and k_{b0} are exponentially small with respect to ϵ. Note that $T_i > T_b > 1 + \beta$

Step	t	T	f	y
Initiation	$O(1)$	$1 + O(k_{i0})$	$1 - O(k_{i0})$	$O(k_{i0})$
Induction	$O\big(\epsilon k_{i0}^{-1}\big)$	$1 + O(\epsilon)$	$1 - O(\epsilon)$	$O(k_{i0})$
Depletion	$t - t_{\rm eg} =$exp. small $t_{\rm eg} = O\big(\epsilon k_{i0}^{-1}\big)$	$1 + O(1)$	$O(1)$	exp. small
Relaxation	$t - t_{\rm eg} =$ exp. small	$1 + \beta - T = O(\epsilon)$	$O(\epsilon)$	exp. small

concerned with a determination of the ignition-delay times. They considered a marginally broader range of crossover temperatures, and allowed all three kinetic steps to be energetic. In both of these studies, the expressions for ignition delay times for the cases considered therein agree with ours.

The spatially homogeneous problem is only the first step in the study of how explosions occur. In any realistic configuration, spatial nonuniformities and the associated acoustic and diffusive transport will have an important role to play. Such problems for the chain-branching model are currently under investigation.

Appendix A. Constants for the second-order solutions

The coefficients B_n in the second-order solution (3.12) are

$$
\begin{aligned}
B_2 &= \frac{1+A}{A^4}\left(\frac{\beta}{\epsilon} - 1 - A\right),\\
B_1 &= -\frac{1+A}{2A^2}\left(\frac{\beta}{\epsilon} - 1\right)t^2 + \left[\frac{\beta}{A^2\epsilon}\left\{m - \frac{2(1+A)}{A}\right\} + \frac{(1+A)(2+A)}{A^3}\right]t\\
&\quad + \frac{\beta}{\epsilon A^3}\left(\frac{1+A}{A} - 2m\right) + \frac{A^2+A-1}{A^4},\\
B_0 &= \left[\frac{\beta}{\epsilon A^2}\left\{m - \frac{1+A}{A}\right\} + \frac{1}{A^3}\right]t + \frac{2\beta}{\epsilon A^3}\left\{m - \frac{1+A}{A}\right\} + \frac{2+A}{A^4}.
\end{aligned}
\tag{A.1}
$$

Similarly, the coefficients C_n in the second-order solution (4.15) are

$$
\begin{aligned}
C_0 &= 2(1-2a) - \frac{1}{2\beta}(1-2a)^2, \\
C_1 &= 6a - 2 + \frac{(1-2a)^2}{\beta} + 2\left\{1 - 3a + \frac{a(1-2a)}{\beta}\right\} u + 3au^2, \\
C_2 &= -\frac{1}{\beta}\left[\frac{1}{2}(1-2a)^2 + 2a(1-2a)u + 2a^2u^2\right].
\end{aligned}
\tag{A.2}
$$

Appendix B. Matching conditions for the growth solution when $A = O(1)$

The matching conditions for the growth solutions (3.38) when $A = O(1)$ (Sect. 3.3) are:

$$
\begin{aligned}
\hat{t}_0 &\sim -\frac{\mathrm{e}^{-\nu}}{1+A} + \frac{\nu}{2\beta} + \frac{(1+A)\mathrm{e}^{\nu}}{12\beta^2} + \cdots, \\
\hat{t}_{11} &\sim -\frac{\mathrm{e}^{-2\nu}}{2(1+A)^2} - \frac{\mathrm{e}^{-\nu}}{\beta(1+A)} + \frac{(5+12\beta)\nu}{12\beta^2} + o(1), \\
\hat{t}_{10} &\sim -\frac{\nu\mathrm{e}^{-2\nu}}{2(1+A)^2} - \frac{(3+2A)\mathrm{e}^{-2\nu}}{4(1+A)^2} - \frac{\nu\mathrm{e}^{-\nu}}{\beta(1+A)} - \frac{(2\beta+1)\mathrm{e}^{-\nu}}{\beta(1+A)} + \frac{(5+12\beta)\nu^2}{24\beta^2} - \frac{(1+A)\nu}{12\beta^2} + o(1).
\end{aligned}
\tag{B.1}
$$

Corresponding results for chain-carrier mass fractions are

$$
\begin{aligned}
Y_0 &\sim \frac{(1+A)\mathrm{e}^{\nu}}{\beta} - \frac{(1+A)^2\mathrm{e}^{2\nu}}{2\beta^2} + \cdots, \\
Y_{11} &\sim -\frac{1}{\beta} + \frac{2(1+A)\mathrm{e}^{\nu}}{\beta} + \cdots, \\
Y_{10} &\sim -\frac{\nu}{\beta} - \frac{1+A}{\beta} + \frac{2(1+A)\nu\mathrm{e}^{\nu}}{\beta} + \left\{\frac{(1+A)^2}{\beta^2} - \frac{2(1+A)}{\beta}\right\}\mathrm{e}^{\nu} + \cdots, \\
Y_{22} &\sim -\frac{1}{\beta} + \frac{3(1+A)\mathrm{e}^{\nu}}{\beta} + \cdots, \\
Y_{21} &\sim -\frac{2\nu}{\beta} + \frac{6(1+A)\nu\mathrm{e}^{\nu}}{\beta} + \left\{\frac{2(1+A)^2}{\beta^2} - \frac{6(1+A)}{\beta}\right\}\mathrm{e}^{\nu} + \cdots, \\
Y_{20} &\sim -\frac{\nu^2}{\beta} - \frac{(1+A)^2}{2\beta^2} + \frac{2(1+A)}{\beta} + \frac{3(1+A)\nu^2\mathrm{e}^{\nu}}{\beta} \\
&\quad + \left\{\frac{2(1+A)^2}{\beta^2} - \frac{6(1+A)}{\beta}\right\}\nu\mathrm{e}^{\nu} + \left\{\frac{(1+A)^3}{2\beta^3} - \frac{4(1+A)^2}{\beta^2} + \frac{6(1+A)}{\beta}\right\}\mathrm{e}^{\nu} + \cdots.
\end{aligned}
\tag{B.2}
$$

Related results for the F_{ij} are easily obtained from the algebraic relations (3.24), (3.26) and (3.28).

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