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THE DESCRIPTION OF HOMOGENEOUS BRANCHED-CHAIN EXPLOSIONS WITH SLOW RADICAL RECOMBINATION BY SELF-ADJUSTING TIME SCALES*

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Abstract. A nonlinear multiscale technique is used to describe the time history of a spatially homogeneous chain-branching/chain-breaking explosion when chain branching is much faster than chain breaking. We select a two-step chemistry model that closely reproduces the ignition characteristics of hydrogen-oxygen systems above the second explosion limit. The resulting combustion history exhibits an induction period with small radical concentrations, followed by a short period of rapid radical growth and a long period of slow radical recombination. The solution can be described by using the ratio of the rate of chain breaking to that of chain branching as an asymptotically small parameter. The problem is formulated by identifying a linear combination of the original variables that evolves with the slow time of radical recombination, and by allowing the fast time to depend on this slowly varying unknown. The associated solution procedure is nonstandard in that it exhibits different solvability conditions for the slow time evolution in the induction and recombination periods. The method proposed emerges as a natural alternative to activation-energy asymptotics for the analysis of branched-chain explosions at high temperatures.

Key words. self-adjusting scales, jump phenomena, multiple scale methods

AMS subject classifications. 34E15, 80A32

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1. Introduction.

A distinctive characteristic of combustion processes is the self-accelerating nature of their associated chemical reactions. This characteristic feature arises in some cases, e.g., thermal explosions, because of the temperature sensitivity of the reaction-rate constant through a large activation energy. In chain-branching processes [9], however, the accelerating factor is the autocatalytic character of the chain-branching reactions. They produce an intermediate species at a rate proportional to the concentration thereof (or, alternatively, to the concentration of another intermediate species if multiple radicals are involved). Chain-branching explosions are observed for instance in hydrogen-oxygen mixtures when the initial temperature is above the so-called crossover temperature [6].

These branched-chain explosions are typical examples within a category of problems generally termed jump phenomena, which commonly arise in combustion [4] and also in other unrelated fields [8]. They are characterized by large amplitude dynamic responses to small amplitude disturbances, and typically involve different time scales: as in chain-branching explosions, the system may change slowly during long time intervals which are separated by fast transition layers of large amplitude variation. This underlying multilayer structure makes it difficult to find a uniformly valid description of particular jump phenomena. Among efforts to overcome this difficulty, we may

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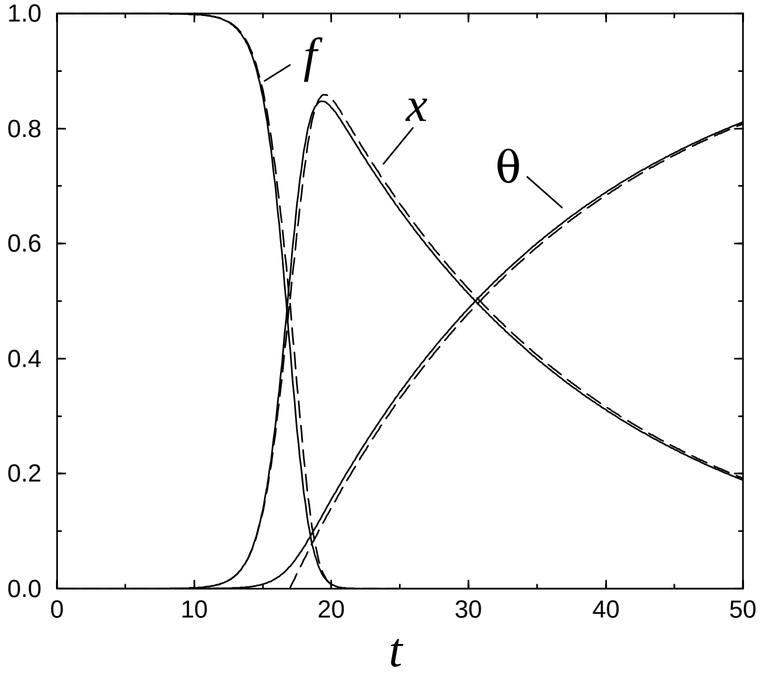

FIG. 1. *Time evolution of* x*,* f*, and* θ *for* $\epsilon = 0.05$*,* $\nu = 10^{-7}$*,* $\beta = 6$*, and* $q = 1$ *as obtained from integration of* (2.1)–(2.3) *(solid lines) and from the leading-order asymptotic representation given in* (3.3) *and* (3.57)–(3.60) *(dashed lines).*

cite the general treatment of jump phenomena by Reiss [8], which provides uniformly valid approximations.

One of the simplest combustion problems that one may consider is the time evolution of a spatially homogeneous mixture at constant pressure. This basic configuration helps in elucidating many important aspects of ignition dynamics. For instance, Kapila analyzed a homogeneous system with chain-branching chemistry whose evolution depends on the competition of branching and recombination processes [3]. A successful explosion, which is triggered in [3] by an initial small amount of radicals, only occurs when branching reactions are faster than recombination ones. A hot enviroment favors the onset of an explosion because branching reaction-rate constants normally increase with temperature while recombination reaction-rate constants do not. Then a chain-branching explosion may occur at temperatures higher than the critical *crossover temperature* (at which the rates of branching and recombination are equal for a given pressure). The associated explosion history typically exhibits a long induction period because either the amount of radicals is initially very low or the initiation reactions which generate radicals are very slow. This induction period ends with a rapid radical-growth stage in which all the reactants are consumed as the radicals reach their peak concentrations. The sudden jump in radical concentration is then followed by a long period of chain termination. In it, the radical concentration decays slowly toward its zero equilibrium value. This characteristic behavior can be seen in Figure 1, in which x, f, and θ, respectively, represent dimensionless measures (defined below) of the radical, fuel and temperature profiles.

Matched asymptotic expansions [3] can be employed to describe the structure of a branched-chain explosion by using the ratio β of the activation temperature of the branching reaction to the initial temperature as an asymptotically large parameter. As noticed in [3], only a fraction of the total heat is released during the branching period of a branched-chain explosion. The associated temperature increase becomes very small when the initial temperature is increased far above the crossover value. Together with the dependence of β on the reciprocal of the initial temperature, this fact limits the accuracy of large-activation-energy analyses in systems far from crossover. The resulting regime of slow radical recombination requires a choice of small parameter different from β^{-1} for its asymptotic description. A natural choice is the ratio ϵ of the characteristic chemical time of radical branching to that of radical recombination. The method of matched asymptotic expansions can be used to describe asymptotically a branched-chain explosion in the limit $\epsilon \to 0$, although we need an additional straining of the time coordinate for a more accurate description when the initial radical mass fraction is very small. For completion, this analysis is presented in an appendix.

The main body of the paper is devoted to studying the explosion history by means of a nonlinear multiscale technique based on the disparity of the two relevant chemical times. The resulting method is nonstandard in that the "fast" nonlinear time scale is allowed to depend on one of the unknowns, which in principle is "slowly-varying." The long induction period before the explosion has two results: (i) the solvability condition associated to the slow unknown changes during the fast stage of radical growth, and (ii) the nonlinear time scale changes character from fast to slow after the radicals peak and slowly recombine. This latter change of character suggests the name *self-adjusting* time scale used in the title. The objective of the paper is therefore twofold: to describe analytically Kapila's branched-chain explosion [3] in the limit of slow radical recombination, and to explain how to use multiscale methods to develop a new analytical tool potentially applicable to other chain-branching problems.

The paper is organized as follows. The governing equations for the homogeneous chain-branching/chain-breaking explosion problem are presented in section 2. In section 3, a detailed description of the proposed multiscale method is given. Section 4 contains some concluding remarks. For completeness, two appendices are added. Appendix A shows how matched asymptotic expansions can also be used to describe the proposed chain-branching/chain-breaking problem, whereas Appendix B contains the calculation of the first correction to the leading-order solution given in section 3. Further corrections can be straightforwardly found by following the procedure explained in this appendix up to the desired order.

2. Formulation.

Typical combustion processes involve a large number of elementary chemical reactions and intermediate species. As a consequence, some of the resulting phenomena cannot be explained by modeling the chemistry by means of a single irreversible step with an Arrhenius rate. In an effort to clarify the roles of the different chemical processes involved, previous investigators have employed different chemistry models. Thus Zeldovich [11] and Liñán [7] developed a two-step model which includes the separate effects of chain branching and chain breaking. This two-step mechanism suffices to explain the structure of premixed flames [2], in which molecular diffusion provides the radicals necessary to attack the fuel. On the other hand, when diffusionless combustion is considered [10], and also in studies of homogeneous explosions [3, 4], the initial formation of radicals is essential. This can be incorporated in the model by either assuming an arbitrarily small initial radical concentration [3], or by appending a separate initiation step to the chemistry description [10]. In this study, we follow the former approach, addressing Kapila's problem [3] in the limit of slow radical recombination.

The two-step mechanism considered [3] includes the branching reaction

$$\mathrm{F} + \mathrm{X} \overset{\mathrm{B}}{\rightarrow} 2\mathrm{X},$$

and the recombination reaction

$$\mathrm{X} \overset{\mathrm{R}}{\rightarrow} \mathrm{P}.$$

Here F, X, and P represent the reactant, radical, and product of the chemistry description. The reaction-rate constant of the first reaction is an increasing function of the temperature, T, given by $k_{\mathrm{B}} = \rho^{-1} A_{\mathrm{B}} \exp(-T_{\mathrm{B}}/T)$, where the prefactor A_{B} and the activation temperature T_{B} are constants. The dependence of k_{B} on the reciprocal density ρ^{-1} (which amounts to a linear dependence on the temperature for the constant-pressure system considered below) is introduced to simplify the writing of the kinetic rate equations. As in [3], the reaction-rate constant of the recombination reaction, k_{R}, does not depend on temperature. All the heat is generated through the recombination reaction, and we denote by Q the amount of heat released per unit mass of radicals consumed.

A straightforward manipulation of the kinetic rate equations for a constant-pressure homogeneous system, similar to that presented in [3], leads to the dimensionless problem

$$\frac{dx}{dt} = \exp\left[\frac{\beta\theta}{1+\theta}\right] x\, f - \epsilon\, x, \tag{2.1}$$

$$\frac{df}{dt} = -\exp\left[\frac{\beta\theta}{1+\theta}\right] x\, f, \tag{2.2}$$

$$\frac{d\theta}{dt} = q\, \epsilon\, x, \tag{2.3}$$

to be solved with the initial conditions

$$x(0) = \nu, \quad f(0) = 1, \quad \theta(0) = 0. \tag{2.4}$$

In this formulation, the mass fractions of radical and fuel, Y_{X} and Y_{F}, are scaled with the initial fuel mass fraction Y_{F_i} according to $x = (W_{\mathrm{F}}/W_{\mathrm{X}})(Y_{\mathrm{X}}/Y_{\mathrm{F}_i})$ and $f = Y_{\mathrm{F}}/Y_{\mathrm{F}_i}$, where W_{F} and W_{X} denote the molecular weights of the fuel and the radical, respectively. The variable $\theta = (T - T_i)/T_i$ measures the temperature increment with respect to the initial temperature T_i. The dimensionless time t is scaled with the characteristic branching time $(B_{\mathrm{B}} e^{-\beta} Y_{\mathrm{F}_i}/W_{\mathrm{F}})^{-1}$, where $\beta = T_{\mathrm{B}}/T_i$ is the nondimensional activation energy of the branching reaction. As can be seen, with this choice for the time scale, the chemical-time ratio $\epsilon = k_{\mathrm{R}}\,(B_{\mathrm{B}} e^{-\beta} Y_{\mathrm{F}_i}/W_{\mathrm{F}})^{-1}$ emerges as a factor affecting the recombination term in (2.1) and (2.3). The parameter $q = (W_{\mathrm{X}}/W_{\mathrm{F}})[Q/(c_p T_i)]$ represents a nondimensional heat release, assumed to be of order unity in the following development. The small initial radical mass fraction Y_{X_i} has been nondimensionalized to give $\nu = (W_{\mathrm{F}}/W_{\mathrm{X}})(Y_{\mathrm{X}_i}/Y_{\mathrm{F}_i}) \ll 1$.

Realistic values of the parameters ϵ and β can be obtained for different chain-branching/chain-breaking systems from their corresponding rate-limiting steps. For instance, in H_2-O_2 combustion, these rate-limiting steps are $H + O_2 \xrightarrow{1} OH + O$ (branching) and $H + O_2 + M \xrightarrow{2} HO_2 + M$ (recombination), where M represents a third body with concentration (M). Updated values of the associated reaction-rate constants can be found for instance in [1], yielding

$$\epsilon = \frac{k_2[\mathrm{M}]}{k_1} = 23.4\, pT_i^{-1.72} \exp\left(\frac{8582}{T_i}\right) \tag{2.5}$$

and

$$\beta = \frac{8620}{T_i}\,. \tag{2.6}$$

Here the units of temperature, T_i, and pressure, p, are kelvins and atmospheres, respectively. For a given pressure the condition $\epsilon = 1$ determines the so-called crossover temperature, T_c (for example, $T_c \simeq 985$ K at $p = 1$ atm), which defines the second explosion limit of H_2-O_2 mixtures [6]. Below this temperature, i.e., for $\epsilon > 1$, recombination of radicals dominates over radical branching and a branched-chain explosion cannot develop. Temperatures far above crossover, the limit considered here, correspond to small values of ϵ and to only relatively large values of β. To further illustrate this limit, we can use (2.5) and (2.6) to give at atmospheric pressure $\epsilon \simeq 2.5 \times 10^{-2}$ and $\beta \simeq 5.75$ at $T_i = 1500$ K and $\epsilon \simeq 3.6 \times 10^{-3}$ and $\beta \simeq 4.31$ at $T_i = 2000$ K.

3. The nonlinear multiscale method.

In what follows, we investigate homogeneous explosions for the two-step model chemistry defined previously at temperatures sufficiently above crossover. In view of the above considerations, this behavior corresponds to the solution of (2.1)–(2.4) in the asymptotic limit

$$\epsilon \ll 1. \tag{3.1}$$

In realistic applications, ν and β^{-1} are also small quantities but their scalings in terms of ϵ need not be specified at this point. The analysis will reveal in particular that β needs to be at least of order $1/[q\epsilon \ln(\epsilon^{-1})] \gg 1$ for the temperature sensitivity of the branching reaction to have a nonnegligible effect. A method of nonlinear multiple scales will be employed here to describe the solution. An alternative solution method, based on a combination of matched asymptotic expansions and strained coordinates, is presented in Appendix A.

3.1. Preliminary considerations.

Linear combinations of (2.1)–(2.3) lead to

$$\frac{d}{dt}[\theta + q(x+f)] = 0, \tag{3.2}$$

an equation that can be readily integrated subject to (2.4) to give

$$\theta = q[1 + \nu - (x+f)]. \tag{3.3}$$

This expression, which replaces (2.3) in the following analysis, reveals in particular that θ reaches a maximum value $\theta = q(1+\nu)$ as radicals and fuel are depleted. On the other hand, by adding (2.1) and (2.2) it is easy to see that the sum $x+f$ that appears in (3.3) varies only slowly in time, and would be conserved in the absence of radical recombination, i.e., if $\epsilon = 0$. The use of combined variables of this type is always convenient in combustion problems with multiple chemical scales. For instance, by introducing in this case the alternative variable

$$y = x + f \tag{3.4}$$

we can isolate the effect of radical branching. The problem reduces then to that of integrating

$$\frac{dx}{dt} = \exp\left[\frac{\beta\theta}{1+\theta}\right] x\,(y-x) - \epsilon\,x, \tag{3.5}$$

$$\frac{dy}{dt} = -\epsilon x, \tag{3.6}$$

with initial conditions

$$x(0) = \nu, \qquad y(0) = 1 + \nu, \tag{3.7}$$

and with θ given by

$$\theta = q[1 + \nu - y] \tag{3.8}$$

as follows from (3.3).

As explained above there are two chemical times (whose ratio is ϵ) entering the system (3.5)–(3.6). The small initial value of the radical mass fraction (measured through the small parameter $\nu \ll 1$) introduces a nonnegligible delay of the branched-chain explosion and, therefore, a new significant time. This can be seen by neglecting the effect of recombination in (3.5)–(3.8). Substituting the resulting constant values $y = 1 + \nu$ and $\theta = 0$ into (3.5) gives a mass fraction of radicals

$$x = \frac{1+\nu}{1 + \frac{1}{\nu}\, e^{-(1+\nu)t}}\,, \tag{3.9}$$

which reaches $x \simeq 1/2$ at $t = t_o = \ln \nu^{-1}/(1+\nu) \gg 1$. The induction time t_o will be slightly modified in the presence of recombination, as shown below.

3.2. The perturbation scheme. Incorporating the times of radical branching and radical recombination leads to the following selection of time scales (see, for instance, [5] for other applications of nonlinear multiscale methods)

$$\eta = \frac{\varphi(\tau)}{\epsilon}, \qquad \tau = \epsilon t. \tag{3.10}$$

The choice for the slowly varying function $\varphi(\tau)$ can be anticipated at this stage by using (3.10) to rewrite (3.5)–(3.6) in the approximate form corresponding to $\epsilon = 0$,

$$\frac{d\varphi}{d\tau}\frac{\partial x}{\partial \eta} = \exp\left[\frac{\beta\theta}{1+\theta}\right] (y-x)\,x, \tag{3.11}$$

$$\frac{d\varphi}{d\tau}\frac{\partial y}{\partial \eta} = 0. \tag{3.12}$$

The second of these two equations reflects the slow variation of y: the unknown y (and therefore the function θ through the dependence exhibited in (3.8)) is a function of the slow time scale τ to leading order. To obtain a leading-order equation for the radical evolution free from slowly-evolving coefficients, one needs to eliminate the slowly varying functions y and θ from (3.11). This can be achieved by defining a modified radical concentration ξ according to

$$x = y\,\xi, \tag{3.13}$$

and selecting φ so that the equation for ξ has constant coeficients. The result is the system of equations:

$$\frac{\partial \xi}{\partial \eta} = \xi\,(1-\xi),$$
$$\frac{d\varphi}{d\tau} = y\,\exp\left[\frac{\beta\theta}{1+\theta}\right],$$

whose solutions adequately capture the jump of ξ from $\nu \ll 1$ to 1 at $\eta \sim \ln(\nu^{-1}) \gg 1$.

The above considerations can be summarized in the following perturbation scheme for the solution of (3.5) and (3.8) in terms of the functions $\xi = x/y$, y, and θ:

$$\xi(\eta,\tau;\epsilon) = \xi^{(0)}(\eta,\tau) + \epsilon\,\xi^{(1)}(\eta,\tau) + o(\epsilon), \tag{3.14}$$
$$y(\eta,\tau;\epsilon) = y^{(0)}(\eta,\tau) + \epsilon\,y^{(1)}(\eta,\tau) + o(\epsilon), \tag{3.15}$$
$$\theta(\eta,\tau;\epsilon) = \theta^{(0)}(\eta,\tau) + \epsilon\,\theta^{(1)}(\eta,\tau) + o(\epsilon), \tag{3.16}$$

where the two time scales η and τ are defined as

$$\frac{d\eta}{d\tau} = \frac{y\exp\left[\frac{\beta\theta}{1+\theta}\right]}{\epsilon}\,, \quad \tau = \epsilon\,t, \tag{3.17}$$

with $\eta(0) = 0$ selected here as the initial value for the fast time scale. Clearly, because of its dependence on y and θ, the nonlinear fast time, η, must also be expressed as an asymptotic expansion in powers of ϵ.

Insertion of (3.14)–(3.17) into (3.5)–(3.8) yields the following hierarchy of problems in increasing powers of ϵ:

$$\frac{\partial \xi^{(0)}}{\partial \eta} = (1-\xi^{(0)})\,\xi^{(0)}, \tag{3.18}$$

$$\frac{\partial y^{(0)}}{\partial \eta} = 0, \tag{3.19}$$

$$\theta^{(0)} = q(1+\nu-y^{(0)}), \tag{3.20}$$

$$\xi^{(0)}(0,0) = \frac{\nu}{1+\nu}\,, \qquad y^{(0)}(0,0) = 1+\nu, \tag{3.21}$$

$$\frac{\partial \xi^{(1)}}{\partial \eta} + (2\xi^{(0)}-1)\,\xi^{(1)} = -\frac{(1-\xi^{(0)})\,\xi^{(0)} + \frac{\partial \xi^{(0)}}{\partial \tau}}{y^{(0)}\exp\left[\frac{\beta\theta^{(0)}}{1+\theta^{(0)}}\right]}, \tag{3.22}$$

$$\frac{\partial y^{(1)}}{\partial \eta} = -\frac{\xi^{(0)}y^{(0)} + \frac{\partial y^{(0)}}{\partial \tau}}{y^{(0)}\exp\left[\frac{\beta\theta^{(0)}}{1+\theta^{(0)}}\right]}, \tag{3.23}$$

$$\theta^{(1)} = -qy^{(1)}, \tag{3.24}$$

$$\xi^{(1)}(0,0) = 0\,, \qquad y^{(1)}(0,0) = 0, \tag{3.25}$$

and so on. In these equations each $\xi^{(j)}$, $y^{(j)}$, and $\theta^{(j)}$ may change its order depending on the value of η and τ (obviously this is the case for $\xi^{(0)}$ which changes from $\sim \nu \ll 1$ to 1 as η increases), but we demand that the relative orders are kept, i.e.,

$$\frac{\xi^{(1)}}{\xi^{(0)}} = O(1), \qquad \frac{y^{(1)}}{y^{(0)}} = O(1), \tag{3.26}$$

uniformly in η and τ as $\epsilon \to 0+$.

We shall now show that the solution is obtained to leading-order by sequentially solving the hierarchy (3.18)–(3.25).

3.3. Solvability conditions. The solution of (3.18)–(3.21) is

$$\xi^{(0)}(\eta, \tau) = \frac{1}{1 + \exp[\eta_0(\tau) - \eta]}\,, \tag{3.27}$$

$$y^{(0)} = y^{(0)}(\tau), \quad \theta^{(0)} = q[1 + \nu - y^{(0)}(\tau)], \tag{3.28}$$

where $y^{(0)}(\tau)$ and $\eta_o(\tau)$ are as yet unknown slowly varying functions which must be determined now from the solvability conditions for (3.22)–(3.23). Equations (3.21) imply that $y^{(0)}(\tau)$ and $\eta_o(\tau)$ satisfy the initial conditions

$$\eta_o(0) = \ln \nu^{-1}, \quad y^{(0)}(0) = 1 + \nu. \tag{3.29}$$

To derive the first solvability condition, it is convenient to rewrite (3.22) as

$$\frac{\partial}{\partial \eta}\left(\frac{\xi^{(1)}}{\xi^{(0)}(1 - \xi^{(0)})}\right) = \frac{\frac{d\eta_o}{d\tau} - 1}{y^{(0)} \exp\left[\frac{\beta\theta^{(0)}}{1+\theta^{(0)}}\right]}. \tag{3.30}$$

This representation clearly reveals that $\xi^{(1)}(\eta, \tau)$ remains bounded as $\eta \to +\infty$ if

$$\frac{d\eta_o}{d\tau} = 1\,. \tag{3.31}$$

Together with (3.29), this yields

$$\eta_o(\tau) = \tau + \ln \nu^{-1}\,. \tag{3.32}$$

Guided the the previous discussion given below (3.8), we can guess at this point that the function η_o physically represents the time delay associated to the induction period. The effect of recombination, which enters in (3.32) through the additional term τ, causes a further delay in the chain-branching growth.

On the other hand, the solution of (3.23) is

$$y^{(1)}(\eta, \tau) = b(\tau) - \frac{\eta \frac{dy^{(0)}}{d\tau} + \ln\left(1 + e^{\eta - \eta_o(\tau)}\right) y^{(0)}}{y^{(0)} \exp\left[\frac{\beta\theta^{(0)}}{1+\theta^{(0)}}\right]}\,, \tag{3.33}$$

with $b(0) = \ln(1+\nu)$ due to the initial condition (3.25). Boundness of $y^{(1)}$ as $\eta \to +\infty$ provides the solvability condition for $y^{(0)}$. An unexpected behavior arises however associated to the large value of the induction time $\eta_o \sim \ln \nu^{-1} \gg 1$. Thus, in the limit $\eta \to +\infty$, the logarithmic term in (3.33) becomes singular only for $(\eta - \eta_o) \gg 1$, but remains bounded otherwise. Therefore, the solvability condition leads to two different equations for $y^{(0)}$, namely,

$$\frac{dy^{(0)}}{d\tau} = 0, \quad \text{if } (\eta - \eta_o) \le 0 \quad \text{or} \quad (\eta - \eta_o) = O(1), \tag{3.34}$$

and

$$\frac{dy^{(0)}}{d\tau} + y^{(0)} = 0, \quad \text{if} \quad (\eta - \eta_o) \to +\infty. \tag{3.35}$$

This dual behavior is rather novel, and not typical of perturbation methods. Its origin lies in the relatively large value of the induction time associated to the small radical mass fraction that exists at $t = 0$.

Since (3.34) and (3.35) have both been derived from (3.33), there always exists a certain arbitrariness defining the value of $(\eta - \eta_o)$ which selects the governing equation for $y^{(0)}$. Clearly, this critical value of $\eta(\tau) - \eta_o(\tau)$ is associated with a value of $\tau = \tau_o$. In the following discussion, we choose τ_o as the solution of $\eta(\tau) - \eta_o(\tau) = 0$, which implies that $\eta - \eta_o = 0$ is chosen as the critical value for selecting the governing equation for $y^{(0)}$. Equation (3.34) holds if $\tau < \tau_o$ or, equivalently, if $\eta < \eta_o$, whereas (3.35) holds if $\tau > \tau_o$ or, equivalently, if $\eta > \eta_o$. The function $y^{(0)}$ should be continuous at τ_o. With this choice, the solutions of (3.34) and (3.35) are

$$\begin{aligned} y^{(0)}(\tau) &= 1 + \nu \qquad &&\text{if} \qquad \tau \le \tau_o, \\ y^{(0)}(\tau) &= (1 + \nu)\, e^{-(\tau - \tau_o)} \qquad &&\text{if} \qquad \tau > \tau_o\,. \end{aligned} \tag{3.36}$$

The parameter τ_o is the smallest positive solution of $\eta(\tau) = \eta_o(\tau)$ (recall that $d(\eta - \eta_o)/d\tau = (1 + \nu - \epsilon)/\epsilon > 0$ at $\tau = 0$). Introducing now (3.36) into (3.20), we obtain

$$\begin{aligned} \theta^{(0)}(\tau) &= 0 \qquad &&\text{if} \qquad \tau \le \tau_o, \\ \theta^{(0)}(\tau) &= q\,(1 + \nu)\,(1 - e^{-(\tau - \tau_o)}) \qquad &&\text{if} \qquad \tau > \tau_o\,, \end{aligned} \tag{3.37}$$

for the leading-order temperature increment. Equations (3.36) and (3.37) clearly reveal how the selection for the solvability condition used here effectively amounts to a self-consistent *patching* at the induction time τ_o ($t_o = \tau_o/\epsilon$) of two approximations for $y^{(0)}$. In the induction period corresponding to $\tau < \tau_o$, the effect of radical recombinations is neglected, and the functions y and θ do not depart from their initial values. At $\tau = \tau_o$, the recombination reaction is switched on, causing the function y to decay exponentially for $\tau > \tau_o$ on the slow time scale $\epsilon\,(t - t_o)$, while the temperature increases towards its maximum value $q(1 + \nu)$. Our procedure may be extended to higher orders (see Appendix B) if we keep the following criterion (consistent with the previous discussion) to determine the induction time τ_o.

CRITERION. *Let* $\tau_o = \epsilon\, t_o$ *be selected so that*

$$\eta(\tau_o; \epsilon) = \eta_o(\tau_o)\,, \tag{3.38}$$

where $\eta(\tau; \epsilon)$ *is obtained by inserting* $y(\tau; \epsilon)$ *in* (3.17). *Solvability conditions of the perturbation scheme require the solutions of the hierarchy of problems to be bounded in the limits*

$$\eta \to +\infty, \quad \eta_o \to +\infty, \quad \text{with} \quad (\eta - \eta_o) \le 0 \quad \text{if} \quad \tau < \tau_o, \tag{3.39}$$

$$(\eta - \eta_o) \to +\infty \quad \text{if} \quad \tau > \tau_o. \tag{3.40}$$

At each order, the solutions of the hierarchy should be continuous at $\tau = \tau_o$.

At the present time it is not clear whether it is possible to devise a self-consistent *matching* of approximations such as (3.36) at $\tau = \tau_o$. A related question is whether such matching would yield more precise approximations than our patching.

3.4. Determination of $\boldsymbol{\eta}$ and $\boldsymbol{\tau_o}$ to leading order. We can now find the leading-order approximation for the fast time scale η by integrating (3.17) with the initial condition $\eta(0) = 0$ according to

$$\eta = \frac{1}{\epsilon} \int_0^\tau y^{(0)} \exp\left[\frac{\beta\theta^{(0)}}{1+\theta^{(0)}}\right] \mathrm{d}\tau. \tag{3.41}$$

The functions $y^{(0)}(\tau)$ and $\theta^{(0)}(\tau)$ are given in (3.36) and (3.37), respectively. The result corresponding to $\tau \le \tau_o$ is simply

$$\eta = \frac{(1+\nu)\tau}{\epsilon}. \tag{3.42}$$

Equating now (3.32) and (3.42) yields at leading order

$$\tau_o = \frac{\epsilon \ln \nu^{-1}}{1+\nu-\epsilon} \qquad \text{and} \qquad t_o = \frac{\tau_o}{\epsilon} = \frac{\ln \nu^{-1}}{1+\nu-\epsilon} \tag{3.43}$$

for the induction time. Integrating now (3.41) for $\tau > \tau_o$ and considering (3.38), we obtain

$$\eta(\tau) - \eta_o(\tau_o) = \frac{1}{\epsilon q} \int_0^{\theta^{(0)}(\tau)} \exp\left[\frac{\beta s}{1+s}\right] \mathrm{d}s, \tag{3.44}$$

where we have used $s = \theta^{(0)}(\tau)$ as an appropriate integration variable.

As can be seen from (3.27), the leading-order solution depends on the fast time scale through the function $\eta(\tau) - \eta_o(\tau)$. To write this function use must be made of (3.32), (3.42), and (3.44) to give

$$\eta(\tau) - \eta_o(\tau) = \frac{1}{\epsilon}(1+\nu-\epsilon)(\tau-\tau_o) \quad (\text{if} \quad \tau \le \tau_o) \tag{3.45}$$

and

$$\eta(\tau) - \eta_o(\tau) = \frac{\int_0^{q(1+\nu)(1-e^{-(\tau-\tau_o)})} \exp\left[\frac{\beta s}{1+s}\right] \mathrm{d}s}{\epsilon q} - (\tau - \tau_o) \quad (\text{if} \quad \tau > \tau_o). \tag{3.46}$$

The leading-order solution to the branched-chain explosion problem is therefore obtained by inserting (3.45) and (3.46) in the following expressions:

$$x \sim \frac{y^{(0)}}{1+\exp[-(\eta-\eta_o)]}, \tag{3.47}$$

$$y^{(0)} = (1+\nu)\left[H(\tau_o-\tau) + e^{-(\tau-\tau_o)}H(\tau-\tau_o)\right], \tag{3.48}$$

$$f \sim y^{(0)} - x, \tag{3.49}$$

$$\theta \sim q\,(1+\nu-y^{(0)}). \tag{3.50}$$

Here $H(\tau)$ is the Heaviside unit step function. More precise expressions for τ_o and $\eta - \eta_o$ may be obtained by inserting a two-term expansion of y in the corresponding formulas. These expressions are derived in Appendix B. Equations (3.45) and (3.46) show, in particular, how the scale $\eta-\eta_o$ changes as τ increases from the linear behavior shown in (3.45) to the more complicated dependence exhibited in (3.46).

Notice that $\eta-\eta_o$ vanishes again at a large time $\tau_1>\tau_o$ given approximately by

$$\tau_1 \sim \tau_o + \frac{1}{\epsilon q}\int_0^{q(1+\nu)} \exp\left[\frac{\beta s}{1+s}\right] \mathrm{d}s\,, \tag{3.51}$$

according to (3.46). After this time, the logarithmic term in (3.33) is no longer secular, and $y^{(0)}=(1+\nu)\,e^{-(\tau_1-\tau_o)}$ becomes again a constant. For $\tau>\tau_1$, we have

$$\eta-\eta_o = -\left[1-\frac{(1+\nu)\,e^{-(\tau_1-\tau_o)}}{\epsilon}\right](\tau-\tau_1). \tag{3.52}$$

To leading order the solution to the explosion problem is therefore

$$x \sim \frac{(1+\nu)\,e^{-(\tau_1-\tau_o)}}{1+\exp\left\{\left[1-\frac{1+\nu}{\epsilon}\,e^{-(\tau_1-\tau_o)}\right](\tau-\tau_1)\right\}}\,, \tag{3.53}$$

$$y \sim (1+\nu)\,e^{-(\tau_1-\tau_o)}, \tag{3.54}$$

for $\tau>\tau_1$. We see that the concentration of radicals tends to zero on the slow time scale τ and that an exponentially small fuel concentration $f\sim(1+\nu)\,e^{-(\tau_1-\tau_o)}$ remains unburnt. This result reflects the fact that $x=0$, $f=f_0$, $\theta=q\,(1+\nu-f_0)$ is a stationary solution of (2.1)–(2.3) for any constant f_0.

Thus we have devised a multiscale technique containing a nonlinear time scale which *adjusts* itself depending on the evolution of the unknowns y and θ. For this reason we use the term *self-adjusting time scales* when describing our method.

3.5. Additional approximations and explicit form of the radical and fuel mass fractions. Equations (3.43) and (3.45) to (3.50) can be further approximated to provide an explicit form of the leading-order solution at the stage $\tau_o<\tau<\tau_1$. To do this, let us investigate how the activation energy of the branching reaction appears in the solution.

As previously mentioned, the leading-order dependence of the solution on the fast time scale enters only through the exponential term in (3.27). Far from the induction time, as $\eta-\eta_o$ increases, this exponential term vanishes. More precisely, for values of $\eta-\eta_o$ of order $\ln\epsilon^{-1}$, the exponential term in (3.27) becomes a small quantity of order ϵ. As can be seen in (3.46), this range of values of η corresponds to very small temperature increments $\theta^{(0)}$ of order $q\epsilon\ln\epsilon^{-1}$ and to values of $\tau-\tau_o$ of order $\epsilon\ln\epsilon^{-1}\ll 1$. Therefore, in writing the leading-order solution for x and f one can simplify (3.46) to give

$$\eta(\tau)-\eta_o(\tau) = -(\tau-\tau_o) + \frac{\exp[\beta q(1+\nu)(\tau-\tau_o)]-1}{\beta q\epsilon}\,, \tag{3.55}$$

valid for $\tau>\tau_o$. Since $\tau-\tau_o$ is at most of order $\epsilon\ln\epsilon^{-1}$ for the fast time to be consequential, a further simplification applies when

$$\beta q\epsilon\ln\epsilon^{-1}\ll 1, \tag{3.56}$$

a case for which (3.55) reduces to the equation given in (3.45). In this limiting case, the self-adjustment of the fast time scale η does not affect the leading-order result.

With these simplifications in mind, we can now write

$$x = \frac{1+\nu}{1+e^{-(1+\nu-\epsilon)(t-t_o)}}, \tag{3.57}$$

$$f = \frac{(1+\nu)}{1+e^{(1+\nu-\epsilon)(t-t_o)}}, \tag{3.58}$$

for $t \leq t_o = \ln(\nu^{-1})/(1+\nu-\epsilon)$, and

$$x = \frac{(1+\nu)e^{-\epsilon(t-t_o)}}{1+\exp\left[\epsilon(t-t_o) - \frac{1}{B}\left(e^{B(1+\nu)(t-t_o)} - 1\right)\right]}, \tag{3.59}$$

$$f = \frac{(1+\nu)e^{-\epsilon(t-t_o)}}{1+\exp\left[-\epsilon(t-t_o) + \frac{1}{B}\left(e^{B(1+\nu)(t-t_o)} - 1\right)\right]}, \tag{3.60}$$

for $t > t_o$. In the above equations, we have introduced the rescaled activation energy $B = \beta q \epsilon$. As seen above, in the limit (3.56), that is, for values of $B \ll 1/\ln \epsilon^{-1}$ the above expressions (3.57)–(3.60) reduce to

$$x = \frac{(1+\nu)\{1+H(t-t_o)[e^{-\epsilon(t-t_o)} - 1]\}}{1+e^{-(1+\nu-\epsilon)(t-t_o)}}, \tag{3.61}$$

$$f = \frac{(1+\nu)\{1+H(t-t_o)[e^{-\epsilon(t-t_o)} - 1]\}}{1+e^{(1+\nu-\epsilon)(t-t_o)}}, \tag{3.62}$$

where $H(t-t_o)$ is the Heaviside step function.

3.6. Performance of the asymptotic description. In order to test the accuracy of the asymptotic description, we compare in Figure 1 the results of numerically integrating (2.1)–(2.4) with the profiles given in (3.3) and (3.57)–(3.60). We have selected parameter values such that the induction time $t_o = \ln(\nu^{-1})/(1+\nu-\epsilon) \simeq 16.97$ is of the order of the recombination time $\epsilon^{-1} = 20$. The activation energy is chosen sufficiently large for the small temperature variation which appears in the branching region to produce a nonnegligible change in the rate of chain branching ($\beta q \epsilon \ln(\epsilon^{-1}) \simeq 0.9$).

As can be seen, the fuel and radical profiles show excellent agreement everywhere. In particular, the asymptotic description reproduces accurately the peak value of the radical mass fraction and its associated time. Since the temperature is only a function of the slow time scale, its description reproduces directly the patching introduced at $t = t_o$. Thus the description for θ becomes very accurate away from this point, but large errors are necessarily seen in the vicinity of $t = t_o$.

As expected, better accuracy is obtained for smaller values of ϵ. The results corresponding to $\epsilon = 0.025$ are plotted in Figure 2. (The other parameters used there are as in Figure 1.) The profiles of x and f corresponding to (3.57)–(3.60) are practically indistinguishable from those numerically obtained at this level of accuracy of the asymptotic analysis. However the small differences in θ that appear near $t = t_o$ persist as a result of the patching associated to the solvability condition. Figure 2 is also used to test the accuracy of the simplified description (3.61) and (3.62) corresponding in the limit $\beta q \epsilon \ln(\epsilon^{-1}) \ll 1$. As can be seen, although the value of $\beta q \epsilon \ln(\epsilon^{-1}) \simeq 0.55$ is relatively small in this case, the temperature sensitivity of the branching reaction still has a noticeable effect that cannot be neglected.

For larger values of ϵ, the complete leading-order approximation (3.45) to (3.54) should be compared to the numerical solution of the combustion problem. In Figure 3(a), we have taken $\epsilon = 0.1$ to better appreciate the differences between approximation

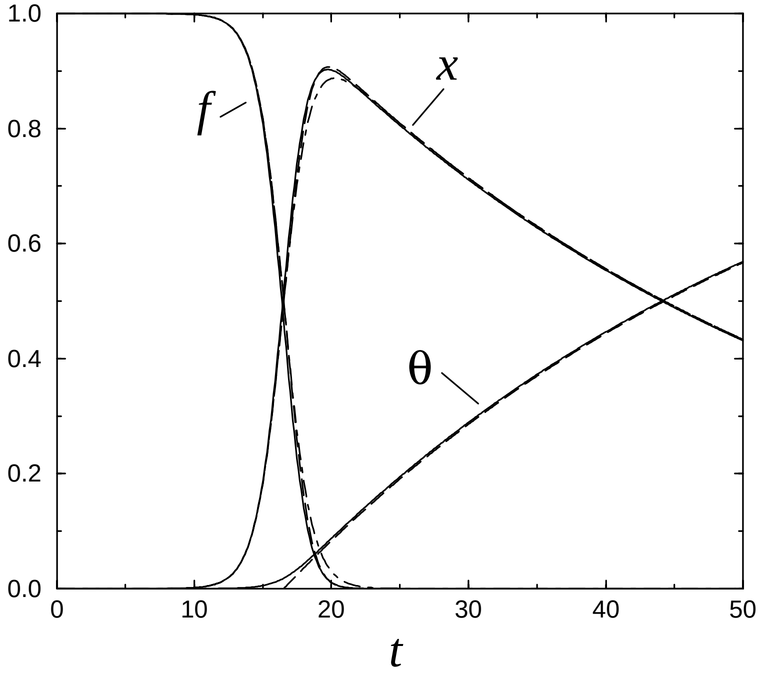

FIG. 2. *Time evolution of x, f, and θ for $\epsilon = 0.025$, $\nu = 10^{-7}$, $\beta = 6$, and $q = 1$ as obtained from integration of* (2.1)–(2.3) *(solid lines), from the leading-order asymptotic representation given in* (3.3) *and* (3.57)–(3.60) *(dashed lines), and from the simplified expressions given in* (3.61) *and* (3.62) *(dot-dashed lines).*

and numerical solution. Notice that the main error is the displacement of the induction time τ_o. A two-term approximation of the solution (as calculated in Appendix B) improves matters. See Figures 3(b) and (c): the induction time fits the numerical results better and so do the f and θ curves. Figure 3(c) shows the difference of leading-order and two-term approximations to the numerically computed x. We observe that the maximum discrepancies between these curves are about 0.07 (leading-order) and 0.04 (two-term). The relative differences are also comparable to 0.1 and 0.01, respectively.

4. Concluding remarks. A method of nonlinear multiple scales has been used to analyze Kapila's branched-chain explosion [3] in the asymptotic limit of slow radical recombination. The analysis uses the ratio ϵ of the branching time to the recombination time as an asymptotically small parameter. As in [3], the rescaled value of the initial radical mass fraction, ν, is assumed to be very small, which causes the resulting induction time (required for the radical mass fractions to reach values of order unity) to become a large quantity of order $\ln \nu^{-1}$. The presence of this long induction period for branched-chain explosion introduces difficulties in the asymptotic description. For instance, when matched asymptotic expansions are used, an additional Poincaré expansion must be incorporated to account for the effect of recombination acting in the induction period, which is seen to delay the chain-branching explosion by an amount

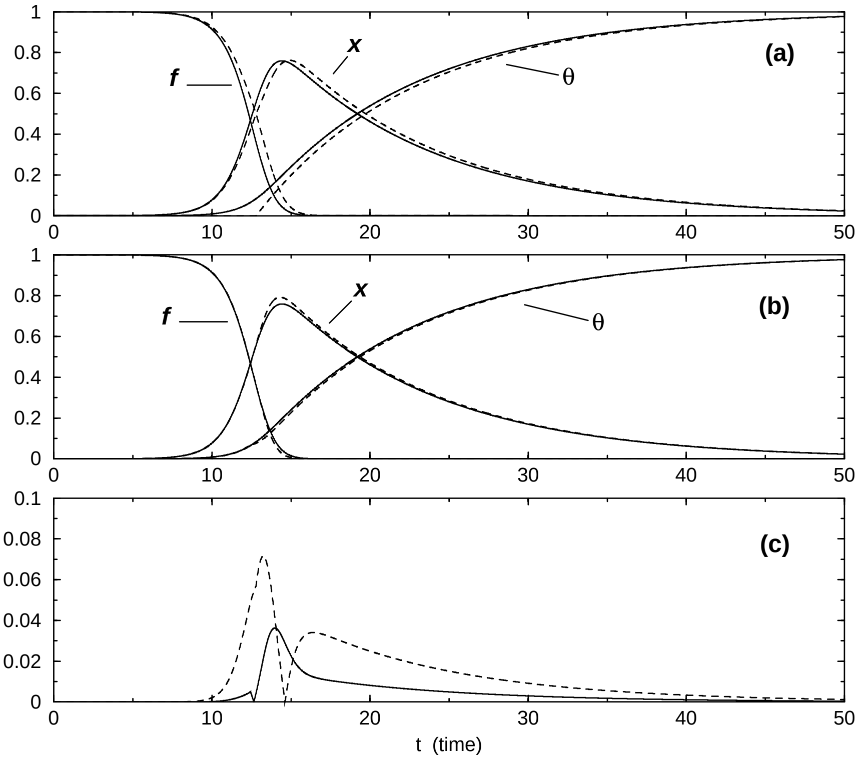

FIG. 3. (a) *Time evolution of* x*,* f*, and* θ *for* $\epsilon = 0.1$*,* $\nu = 10^{-5}$*,* $\beta = 5$*, and* $q = 1$ *as obtained from integration of* (2.1)–(2.3) *(solid lines) and from the leading-order asymptotic representation given by* (3.45) *to* (3.50) *(dashed lines). The time* $t_1 = \tau_1/\epsilon \approx 586$ *is outside the time axis in this figure.* (b) *Same as part* (a)*, but now we compare the numerical solution (solid lines) to the two-term approximation to* x*,* f*, and* θ *calculated in Appendix* B *(dashed lines).* (c) *Time evolution of the difference between the leading-order (dashed line) and the two-term expansion (solid line) of* x *and the numerical solution of* (2.1)–(2.3).

of order $\epsilon \ln \nu^{-1}$. This additional delay is automatically captured by the nonlinear multiple-scale method, which incorporates a fast time scale which changes size with the time of radical recombination. The problem is formulated in terms of the concentration of radicals x and of a linear combination of the original variables ($y = x + f$) which is not affected by branching. The smallness of the initial radical concentration gives rise to a long induction period and has the following consequences:

1. The scaled radical concentrations $\xi^{(i)}$, $i = 0, 1, \dots$, change scales as time evolves. For example, $\xi^{(0)}$ goes from $\nu \ll 1$ to 1 as time increases after the induction period.
2. This implies the need to consider different solvability conditions before and after the induction time (at which $\xi^{(0)} = 1/2$). The solvability conditions yield two different governing equations for the slow-time evolution of the solution.
3. We have introduced a natural criterion to define the induction time which allows us to calculate higher-order terms for the solutions to the explosion problem.

The method proposed is an adequate alternative to activation-energy asymptotics for the analysis of chain-branching explosions at temperatures sufficiently above the crossover value, when the temperature sensitivity of the branching reaction has only a secondary role. Although Kapila's problem is used as a simple model to illustrate the main features of the technique, applicability of the method to other chain-branching problems with slow heat-release rate can be anticipated. Alternative definitions for the variables y and ξ, and for the self-adjusting time scale η, should be incorporated in each case, but the essence of the resulting procedure would be that exposed above. Clearly it is also worth investigating other jump phenomena using self-adjusting time scales.

Appendix A. Solution in terms of matched asymptotic expansions. The solution to Kapila's problem in the limit $\epsilon \ll 1$ can also be computed in terms of matched asymptotic expansions. For simplicity in the presentation, we restrict our attention to the case $\beta = 0$, for which the radical and fuel profiles can be obtained by integrating

$$\frac{dx}{dt} = x\,f - \epsilon\,x, \tag{A.1}$$

$$\frac{df}{dt} = -x\,f, \tag{A.2}$$

to be solved with the initial conditions

$$x(0) = \nu, \quad f(0) = 1. \tag{A.3}$$

The temperature, which can be calculated from (3.3), does not enter in the solution for x and f. We shall see that (A.1)–(A.3) reproduces in fact the solution to the initial problem (2.1)–(2.4) in the limit (3.56).

The solution will be given below in terms of three different expansions. The first expansion describes the induction and branching periods, and will be seen to remain valid for t in the range $0 \le t < t_f$, with $t_f = \ln(\nu^{-1}\epsilon^{-1})/(1+\nu-\epsilon) \gg 1$. At $t \simeq t_f$ the fuel is depleted, and a new asymptotic expansion is needed to describe the solution for $t - t_f \sim O(1)$. In this fuel-depletion stage the mass fraction x will be seen to reach its peak value, given in the first approximation by $1 - \epsilon\ln(\epsilon^{-1})$. For $t - t_f \gg 1$, the solution, with $f = 0$, is only affected by recombination, yielding a radical mass fraction that decays with a characteristic rescaled time ϵ^{-1}.

To anticipate the asymptotic treatment needed to describe the induction and branching periods, one has to understand the nonnegligible effect of the last term in (A.1) (i.e., recombination of radicals) on the solution. If this term is neglected, an approximation apparently valid as long as $f \gg \epsilon$, we can readily solve (A.1) and (A.2) to give the radical profile given in (3.9). As can be seen, the resulting function x reaches values of order unity at times t of order $\ln(\nu^{-1}) \gg 1$. We conclude that, although the recombination terms is relatively small, it acts on the solution during a long period. Its cumulative effect introduces a delay, causing a shift of the branching location of order $\epsilon\ln(\nu^{-1})$ that becomes increasingly important for decreasing values of ν. For instance, in configurations with ν small enough for the induction time $\ln(\nu^{-1})$ to be comparable to the recombination time ϵ^{-1}, the time delay associated to radical recombination becomes of order unity. This nonnegligible effect cannot be captured unless appropriate straining of the independent variable t is permitted. Therefore, besides expanding x and f in powers of ϵ according to $x = x_0 + \epsilon x_1 + \epsilon^2 x_2 + \cdots$ and $f = f_0 + \epsilon f_1 + \epsilon^2 f_2 + \cdots$, a Poincaré expansion $\bar{t} = (1 + \epsilon a_1 + \epsilon^2 a_2 + \cdots)t$ must be introduced. The constants $a_1, a_2, \ldots$ must be chosen so as to preclude the appearance of singular terms in the resulting asymptotic expansions for x and f.

Substituting the previous expansions for x, f, and t into (A.1) and (A.2) and equating terms of like order yields

$$\frac{dx_0}{d\bar{t}} = x_0\, f_0, \tag{A.4}$$

$$\frac{df_0}{d\bar{t}} = -x_0\, f_0, \tag{A.5}$$

and

$$\frac{dx_1}{d\bar{t}} = x_0 f_1 + x_1 f_0 - a_1 x_0 f_0 - x_0, \tag{A.6}$$

$$\frac{df_1}{d\bar{t}} = -x_0 f_1 - x_1 f_0 + a_1 x_0 f_0, \tag{A.7}$$

to be integrated with initial conditions

$$x_0(0) = \nu, f_0(0) = 1, \tag{A.8}$$

$$x_1(0) = f_1(0) = 0. \tag{A.9}$$

Straightforward integration of the zeroth-order problem (A.4)–(A.5) with (A.8) gives

$$x_0 = \frac{(1+\nu)\nu e^{(1+\nu)\bar{t}}}{1+\nu e^{(1+\nu)\bar{t}}}, \tag{A.10}$$

$$f_0 = \frac{(1+\nu)}{1+\nu e^{(1+\nu)\bar{t}}}. \tag{A.11}$$

The profile given in (A.10) reveals that x remains very small for $0 < \bar{t} < \ln(\nu^{-1})/(1+\nu)$, as corresponds to the induction period. On the other hand, as can be concluded from (A.1), failure of the proposed solution can be expected to occur as f becomes of order ϵ. Observation of (A.11) reveals that this failure is associated with a time given in the first approximation by $\bar{t} = \ln(\nu^{-1}\epsilon^{-1})/(1+\nu)$.

The branching period, characterized by values of x and f of order unity, corresponds to $\bar{t}$ in the intermediate range $\ln(\nu^{-1})/(1+\nu) \lesssim \bar{t} \lesssim \ln(\nu^{-1}\epsilon^{-1})/(1+\nu)$. Using now (2.3) together with the above estimates yields $\theta \sim q\epsilon \ln(\epsilon^{-1})$ for the temperature increment at the end of the branching period. Since the branching reaction is frozen once fuel is depleted, one can safely neglect the temperature dependence of the branching reaction-rate constant if the condition $\beta\theta \ll 1$ is satisfied for $\bar{t} \lesssim \ln(\nu^{-1}\epsilon^{-1})/(1+\nu)$. We can then conclude that (A.1)–(A.3) is the limiting form of (2.1)–(2.4) in the asymptotic limit (3.56), a problem whose solution by the multiscale method is exhibited in (3.61) and (3.62).

Before proceeding with the analysis of the fuel-depletion stage, we extend the asymptotic description of the induction and branching regions to the following order, an analysis that provides in particular the value of a_1. To solve the first-order problem, we first add (A.6) and (A.7). We then integrate the resulting equation taking into account the initial conditions (A.9) to obtain

$$x_1 + f_1 = \ln(1+\nu) - \ln(1+\nu e^{(1+\nu)\bar{t}}), \tag{A.12}$$

which can now be used to rewrite (A.7) in the form

$$\frac{d}{d\bar{t}}\left(\frac{f_1}{x_0 f_0}\right) = a_1 + \frac{1}{x_0}\ln\left[\frac{1+\nu e^{(1+\nu)\bar{t}}}{1+\nu}\right]. \tag{A.13}$$

Integrating this last equation gives

$$\frac{f_1}{x_0 f_0} = \left(a_1 + \frac{1-\ln(1+\nu)}{1+\nu}\right)\bar{t} + \frac{1}{(1+\nu)^2}\left\{\int_0^{(1+\nu)\bar{t}} \ln(1+\nu e^s)\mathrm{d}s - \frac{1+\nu e^{(1+\nu)\bar{t}}}{\nu e^{(1+\nu)\bar{t}}}\ln\left[\frac{1+\nu e^{(1+\nu)\bar{t}}}{1+\nu}\right]\right\}. \tag{A.14}$$

The values of $\epsilon f_1/f_0$ must remain small everywhere in the induction and branching regions for the asymptotic expansion of f to hold. The terms in curly brackets satisfy this boundness condition everywhere, as the evaluation of (A.14) at $\bar{t} = \ln(\nu^{-1}\epsilon^{-1})$ shows. On the other hand, the first term on the right-hand side of (A.14) increases linearly with time, and becomes of order $\ln(\nu^{-1}\epsilon^{-1})$ at the end of the branching region. A singular behavior appears for values of ν such that $\epsilon\ln(\nu^{-1}\epsilon^{-1}) \gg 1$, unless the value

$$a_1 = -\frac{1-\ln(1+\nu)}{1+\nu} \tag{A.15}$$

is selected for the first term of the Poincaré expansion. With this choice for a_1, the first-order corrections to the radical and fuel mass fractions become

$$x_1 = -\frac{\nu e^{(1+\nu)\bar{t}}}{1+\nu e^{(1+\nu)\bar{t}}}\left\{\frac{\int_0^{(1+\nu)\bar{t}} \ln(1+\nu e^s)\mathrm{d}s}{1+\nu e^{(1+\nu)\bar{t}}} + \ln\left[\frac{1+\nu e^{(1+\nu)\bar{t}}}{1+\nu}\right]\right\} \tag{A.16}$$

and

$$f_1 = \frac{1}{1+\nu e^{(1+\nu)\bar{t}}}\left\{\frac{\nu e^{(1+\nu)\bar{t}}\int_0^{(1+\nu)\bar{t}} \ln(1+\nu e^s)\mathrm{d}s}{1+\nu e^{(1+\nu)\bar{t}}} - \ln\left[\frac{1+\nu e^{(1+\nu)\bar{t}}}{1+\nu}\right]\right\}. \tag{A.17}$$

Using now (A.10), (A.11), (A.14), (A.15), and (A.16) allows us to write

$$x = \frac{\nu e^{(1+\nu-\epsilon)t}}{1+\nu e^{(1+\nu-\epsilon)t}} \times \left\{1+\nu-\epsilon\left[\frac{\int_0^{(1+\nu-\epsilon)t}\ln(1+\nu e^s)\mathrm{d}s}{1+\nu e^{(1+\nu-\epsilon)t}} + \ln\left(\frac{1+\nu e^{(1+\nu-\epsilon)t}}{1+\nu}\right)\right]\right\} \tag{A.18}$$

and

$$f = \frac{1}{1+\nu e^{(1+\nu-\epsilon)t}}\left\{1+\nu+\epsilon \times \left[\frac{\nu e^{(1+\nu-\epsilon)t}\int_0^{(1+\nu-\epsilon)t}\ln(1+\nu e^s)\mathrm{d}s}{1+\nu e^{(1+\nu-\epsilon)t}} - \ln\left(\frac{1+\nu e^{(1+\nu-\epsilon)t}}{1+\nu}\right)\right]\right\}, \tag{A.19}$$

where the approximated form $(1+\nu)\bar{t} = (1+\nu-\epsilon)t$ has been employed. These expressions give the asymptotic solution in the induction and branching periods to order ϵ. Observation of (A.18) indicates that the first-order correction (A.16) becomes logarithmically large as the fuel-depletion time

$$t_f = \frac{\ln(\nu^{-1}\epsilon^{-1})}{1+\nu-\epsilon} \tag{A.20}$$

is approached, given a negative contribution to x of order $\epsilon \ln(\epsilon^{-1})$. This nonnegligible decrease, which is due to the effect of recombination, must be incorporated for a correct asymptotic description of the fuel-depletion stage.

At $t = t_f$, the fuel mass fraction becomes of order ϵ causing branching and recombination to be equally important in (A.1). Description of the fuel-depletion process necessitates the introduction of a translated time scale $t' = t - t_f$, and expansions of the form $x = 1 - \epsilon \ln(\epsilon^{-1}) + \epsilon X_1 + \cdots$ and $f = \epsilon F_1 + \cdots$. Introducing these rescaled variables into (A.2) yields the leading-order equation

$$\frac{dF_1}{dt'} = -F_1. \tag{A.21}$$

Its solution is

$$F_1 = e^{-t'}, \tag{A.22}$$

where the integration constant has been selected by matching the fuel profile to that given in (A.19). Using now this result in (A.1) yields

$$\frac{dX_1}{dt'} = e^{-t'} - 1. \tag{A.23}$$

This can be integrated to give

$$X_1 = -e^{-t'} - t', \tag{A.24}$$

a solution that exhibits both an exponential chain-branching behavior for $-t' \gg 1$ and slow recombination for $t' \gg 1$. It should be pointed out that at the order calculated here the solution of the fuel-depletion stage is contained in (A.18) and (A.19), i.e., introducing $t' = t - t_f$ in (A.18) and (A.19) gives in the first approximation $f = \epsilon e^{-t'}$ and $x = 1 - \epsilon \ln(\epsilon^{-1}) - \epsilon(e^{-t'} + t')$. Equations (A.18) and (A.19) are therefore a valid approximation for the solution also in the range $t - t_f \sim 1$.

Equation (A.22) indicates that for times $t' = t - t_f \gg 1$, the value of f becomes exponentially small, so that the solution for the radical concentration can be readily obtained from (A.1) to give $x = C \exp[-\epsilon(t - t_f)]$. The parameter C is an integration constant that must be calculated as an asymptotic expansion in ϵ by matching with the transition layer, to give in the first approximation

$$x = (1 - \epsilon \ln \epsilon^{-1}) e^{-\epsilon(t - t_f)}. \tag{A.25}$$

Summarizing now the above results, we see that, at the level of approximation used in deriving (3.61) and (3.62), the solution by matched asymptotic expansions can be written in the compact form

$$x = \frac{\nu e^{(1+\nu-\epsilon)t}}{1 + \nu e^{(1+\nu-\epsilon)t}} \left[1 + \nu - \epsilon \ln \left(\frac{1 + \nu e^{(1+\nu-\epsilon)t}}{1 + \nu} \right) \right], \quad f = \frac{1 + \nu}{1 + \nu e^{(1+\nu-\epsilon)t}} \tag{A.26}$$

for $t - t_f \lesssim 1$ and

$$x = (1 - \epsilon \ln \epsilon^{-1}) e^{-\epsilon(t - t_f)}, \quad f = 0 \tag{A.27}$$

for $t - t_f \gg 1$. The accuracy of these approximations is tested in Figure 4, where the results of numerical integrations of (A.1)–(A.3) are compared with (A.26) and (A.27),

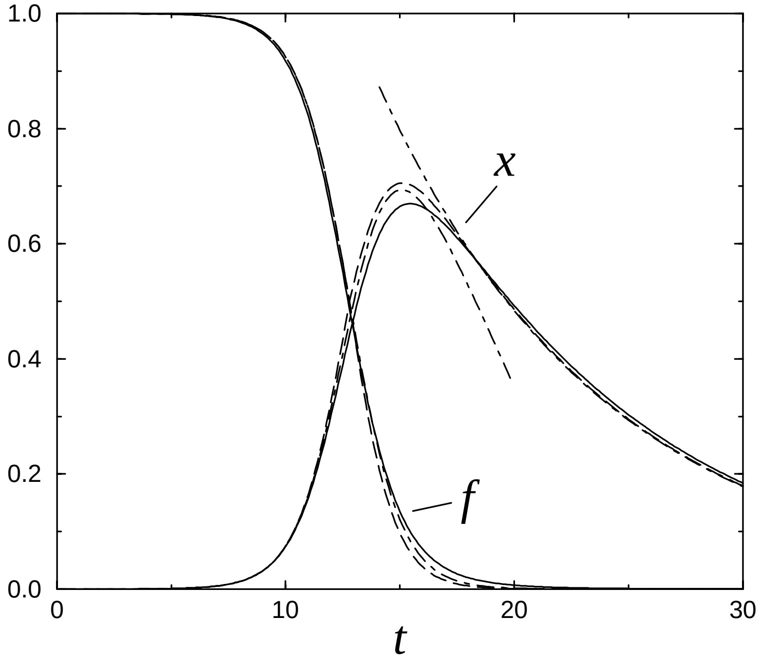

FIG. 4. *Time evolution of the fuel and radical mass fractions for* $\epsilon = 0.1$ *and* $\nu = 10^{-5}$ *as obtained from numerical integrations of* (A.1)–(A.3) *(solid lines), from the multiscale profiles* (3.61) *and* (3.62) *(dashed lines), and from the matched asymptotic expansions* (A.26) *and* (A.27) *(dot-dashed lines).*

and also with the profiles of the multiscale method exhibited in (3.61) and (3.62). A relatively large value $\epsilon = 0.1$ is chosen to make differences between the different approaches more noticeable. The choice for the initial radical mass fraction $\nu = 10^{-5}$ produces in this case an induction time comparable to the recombination time $\epsilon^{-1} = 10$, a case for which straining the time through the Poincaré expansion is a necessary addition to the asymptotics, as previously explained. In particular, the induction time defined in (3.43) is $t_o \simeq 12.79$, while the fuel-depletion time defined in (A.20) is $t_f \simeq 15.35$. The plot shows that the solution by matched asymptotic expansions and by multiscale methods have comparable accuracy everywhere.

Appendix B. Higher-order terms. Once (3.36) is inserted in (3.33), we obtain

$$y^{(1)} = b(\tau) - \ln\left(1 + e^{\eta-\eta_o}\right) \quad \text{if} \quad \tau < \tau_o, \tag{B.1}$$

$$y^{(1)} = b(\tau) - \exp\left[-\frac{\beta q(1+\nu)(1-e^{-\tau})}{1+q(1+\nu)(1-e^{-\tau})}\right] \ln\left(e^{-\eta} + e^{-\eta_o}\right) \quad \text{if} \quad \tau > \tau_o. \tag{B.2}$$

Continuity of $y^{(1)}$ at $\tau = \tau_o$, $\eta = \eta_o$, yields the condition

$$b(\tau_o-) = b(\tau_o+) + \tau_o + \ln \nu^{-1}. \tag{B.3}$$

Similarly, we can obtain $\xi^{(1)}$ by integrating (3.30) once (3.31) has been substituted. The result is

$$\xi^{(1)}(\eta,\tau) = a(\tau)\,\frac{\partial \xi^{(0)}}{\partial \eta}\,, \tag{B.4}$$

where $a(\tau)$ is a function to be determined.

$a(\tau)$ and $b(\tau)$ are determined from the solvability conditions for $\xi^{(2)}$ and $y^{(2)}$. The corresponding problem is

$$\begin{aligned}\frac{\partial \xi^{(2)}}{\partial \eta} + (2\xi^{(0)}-1)\,\xi^{(2)} &= -\frac{\frac{\partial \xi^{(1)}}{\partial \tau} + \xi^{(1)}\,(1-2\xi^{(0)})}{y^{(0)}\exp\left[\frac{\beta\theta^{(0)}}{1+\theta^{(0)}}\right]} - \xi^{(1)2} \\ &\quad + \frac{\frac{\partial \xi^{(0)}}{\partial \tau} + (1-\xi^{(0)})\,\xi^{(0)}}{y^{(0)}\exp\left[\frac{\beta\theta^{(0)}}{1+\theta^{(0)}}\right]}\left[\frac{y^{(1)}}{y^{(0)}} + \frac{\beta\theta^{(1)}}{(1+\theta^{(0)})^2}\right],\end{aligned} \tag{B.5}$$

$$\begin{aligned}\frac{\partial y^{(2)}}{\partial \eta} &= \left\{\frac{\beta\xi^{(0)}y^{(0)}\theta^{(1)}}{(1+\theta^{(0)})^2} - \xi^{(1)}y^{(0)} - \frac{\partial y^{(1)}}{\partial \tau} + \frac{dy^{(0)}}{d\tau}\left[\frac{y^{(1)}}{y^{(0)}} + \frac{\beta\theta^{(1)}}{(1+\theta^{(0)})^2}\right]\right\} \\ &\quad \times \frac{\exp\left[-\frac{\beta\theta^{(0)}}{1+\theta^{(0)}}\right]}{y^{(0)}}\,,\end{aligned} \tag{B.6}$$

$$\theta^{(2)} = -q\,y^{(2)}, \tag{B.7}$$

$$\xi^{(2)}(\;0\;,0) = 0\,, \qquad y^{(2)}(0,0) = 0. \tag{B.8}$$

Equation (B.5) may be rewritten as

$$\begin{aligned}\frac{\partial}{\partial \eta}\left(\frac{\xi^{(2)}}{\frac{\partial \xi^{(0)}}{\partial \eta}}\right) &= -\frac{y^{(1)}}{y^{(0)}}\left(1 - \frac{\beta q y^{(0)}}{(1+\theta^{(0)})^2}\right)\frac{\partial}{\partial \eta}\left(\frac{\xi^{(1)}}{\frac{\partial \xi^{(0)}}{\partial \eta}}\right) \\ &\quad - \frac{\xi^{(1)2}}{\frac{\partial \xi^{(0)}}{\partial \eta}} - \frac{\frac{\partial \xi^{(1)}}{\partial \tau} + (1-2\xi^{(0)})\,\xi^{(1)}}{y^{(0)}\exp\left[\frac{\beta\theta^{(0)}}{1+\theta^{(0)}}\right]\frac{\partial \xi^{(0)}}{\partial \eta}}\,.\end{aligned} \tag{B.9}$$

We now substitute (3.27), (3.36), and (B.4) in the right-hand side of this equation, thereby obtaining

$$\frac{\partial}{\partial \eta}\left(\frac{\xi^{(2)}}{\frac{\partial \xi^{(0)}}{\partial \eta}}\right) = -a^2\,\frac{\partial \xi^{(0)}}{\partial \eta} - \frac{\frac{da}{d\tau} + a\left(\frac{\partial}{\partial \eta} + \frac{\partial}{\partial \tau}\right)\ln\frac{\partial \xi^{(0)}}{\partial \eta}}{y^{(0)}\exp\left[\frac{\beta\theta^{(0)}}{1+\theta^{(0)}}\right]}\,. \tag{B.10}$$

Since $\xi^{(0)}$ is a function of $[\eta - \eta_o(\tau)]$ and $d\eta_o/d\tau = 1$, the term proportional to a in the previous expression is zero. Integration of (B.10) yields

$$\frac{\xi^{(2)}}{\frac{\partial \xi^{(0)}}{\partial \eta}} = c(\tau) - a^2\xi^{(0)} - \frac{\eta\,\exp\left[-\frac{\beta\theta^{(0)}}{1+\theta^{(0)}}\right]}{y^{(0)}}\,\frac{da}{d\tau}\,. \tag{B.11}$$

There is only one secular term in (B.11) and its cancellation yields

$$\frac{da}{d\tau} = 0 \Longrightarrow a \equiv 0 \Longrightarrow \xi^{(1)} \equiv 0 \tag{B.12}$$

once the initial condition (B.8) is considered. To obtain $b(\tau)$ and therefore completely determine $y^{(1)}$, we insert (B.12) in (B.6):

$$-\exp\left[\frac{\beta\theta^{(0)}}{1+\theta^{(0)}}\right]\,\frac{\partial y^{(2)}}{\partial\eta} = \frac{d}{d\tau}\left(\frac{y^{(1)}}{y^{(0)}}\right) + \frac{\beta q y^{(1)}\left(\xi^{(0)}+\frac{d\ln y^{(0)}}{d\tau}\right)}{(1+\theta^{(0)})^2}\,. \tag{B.13}$$

If $\tau < \tau_o$, the only secular term in the right-hand side of this expression is proportional to $db/d\tau$. Therefore we find

$$\frac{db}{d\tau} = 0 \Longrightarrow b \equiv \ln(1+\nu) \Longrightarrow y^{(1)} = -\ln\left(\frac{1+e^{\eta-\eta_o}}{1+\nu}\right) \tag{B.14}$$

for $\tau < \tau_o$.

Now let $\tau > \tau_o$. Equation (B.13) becomes

$$\begin{aligned} \exp\left[\frac{\beta\theta^{(0)}}{1+\theta^{(0)}}\right]\,\frac{\partial y^{(2)}}{\partial\eta} &= \frac{\beta q\left\{b-\exp\left[-\frac{\beta\theta^{(0)}}{1+\theta^{(0)}}\right]\,\ln\left(e^{-\eta}+e^{-\eta_o}\right)\right\}}{(1+e^{\eta-\eta_o})\,(1+\theta^{(0)})^2} \\ &\quad -\frac{1}{1+\nu}\frac{d}{d\tau}\left\{e^{\tau-\tau_o}b-\exp\left[\tau-\tau_o-\frac{\beta\theta^{(0)}}{1+\theta^{(0)}}\right]\,\ln\left(e^{-\eta}+e^{-\eta_o}\right)\right\}\,. \end{aligned} \tag{B.15}$$

Integration of this equation yields

$$\begin{aligned} y^{(2)} = -\frac{\eta\exp\left[-\frac{\beta\theta^{(0)}}{1+\theta^{(0)}}\right]}{1+\nu}\,\frac{d}{d\tau}\left\{e^{\tau-\tau_o}b+\eta_o\exp\left[\tau-\tau_o-\frac{\beta\theta^{(0)}}{1+\theta^{(0)}}\right]\right\} \\ +\,\text{nonsecular terms}\,. \end{aligned} \tag{B.16}$$

Elimination of secular terms yields

$$b(\tau) = \ln(1+\nu)\,e^{-(\tau-\tau_o)} - \eta_o(\tau)\,\exp\left[-\frac{\beta q(1+\nu)\,(1-e^{-(\tau-\tau_o)})}{1+q(1+\nu)(1-e^{-(\tau-\tau_o)})}\right], \tag{B.17}$$

for $\tau > \tau_o$. Here we have used the continuity condition (B.3) and $b(\tau_o-) = \ln(1+\nu)$, which yield $b(\tau_o+) = \ln(1+\nu) - \tau_o - \ln\nu^{-1}$. Equations (B.2), (B.14), and (B.17) provide the following expression for $y^{(1)}$:

$$\begin{aligned} y^{(1)} &= -\ln\left(\frac{1+e^{\eta-\eta_o}}{1+\nu}\right) \quad \text{if} \quad \tau<\tau_o, \\ y^{(1)} &= \ln(1+\nu)\,e^{-(\tau-\tau_o)} \\ &\quad -\exp\left[-\frac{\beta q(1+\nu)\,(1-e^{-(\tau-\tau_o)})}{1+q(1+\nu)(1-e^{-(\tau-\tau_o)})}\right]\,\ln\left(1+e^{\eta_o-\eta}\right) \quad \text{if} \quad \tau>\tau_o. \end{aligned} \tag{B.18}$$

With these equations we may obtain more precise approximations for τ_o and $(\eta-\eta_o)$. From (3.15), (3.17), (3.20), and (3.24), we find

$$\begin{aligned} \frac{d(\eta-\eta_o)}{d\tau} &= \exp\left[\frac{\beta q\,(1+\nu-y^{(0)})}{1+q\,(1+\nu-y^{(0)})}\right] \\ &\quad\times\left\{\frac{y^{(0)}}{\epsilon}+\left[1-\frac{\beta q y^{(0)}}{[1+q\,(1+\nu-y^{(0)})]^2}\right]\,y^{(1)}\right\}\,. \end{aligned} \tag{B.19}$$

Here we have used the two-term expansion $y \sim y^{(0)} + \epsilon\, y^{(1)}$. To find τ_o we should first solve this equation for $\tau < \tau_o$, and then impose that $\eta(\tau_o;\epsilon) = \eta_o(\tau_o)$ according to (3.38) in the criterion of section 3. From (3.36), (B.18), and (B.19), we obtain

$$\frac{\tau}{\epsilon} = \int_{\ln\nu}^{\eta-\eta_o} \frac{dh}{1+\nu-\epsilon+\epsilon\,[\beta q\,(1+\nu)-1]\,\ln\left(\frac{1+e^h}{1+\nu}\right)}\,. \tag{B.20}$$

Then (3.38) yields the following equation for $t_o = \tau_o/\epsilon$:

$$\frac{\tau_o}{\epsilon} = \int_{\ln\nu}^{0} \frac{dh}{1+\nu-\epsilon+\epsilon\,[\beta q\,(1+\nu)-1]\,\ln\left(\frac{1+e^h}{1+\nu}\right)}\,. \tag{B.21}$$

Insertion of (3.36), and (B.17) in (B.19) yields the following equation for $\eta - \eta_o$ when $\tau > \tau_o$:

$$\begin{aligned}\frac{d(\eta-\eta_o)}{d\tau} = {} & \left(\frac{1+\nu}{\epsilon} + \ln(1+\nu) - \frac{(1+\nu)\,\ln(1+\nu)q\beta\,e^{-(\tau-\tau_o)}}{[1+q\,(1+\nu)\,(1-e^{-(\tau-\tau_o)})]^2}\right) \\ & \times \exp\left[\tau_o - \tau + \frac{\beta q(1+\nu)\,(1-e^{-(\tau-\tau_o)})}{1+q(1+\nu)(1-e^{-(\tau-\tau_o)})}\right] - 1 \\ & + \left[\frac{(1+\nu)\,q\beta\,e^{-(\tau-\tau_o)}}{[1+q\,(1+\nu)\,(1-e^{-(\tau-\tau_o)})]^2} - 1\right]\,\ln\left(1+e^{\eta_o-\eta}\right),\end{aligned} \tag{B.22}$$

to be solved with the initial condition $\eta - \eta_o = 0$ for $\tau = \tau_o$. Notice that a two-term expansion for y has been used here. This equation is not separable and has to be integrated numerically. Once $\eta - \eta_o$ is known as a function of τ, we find the following two-term approximations for x and y:

$$x \sim \frac{y}{1+e^{\eta_o-\eta}}\,, \tag{B.23}$$

$$y \sim 1+\nu-\epsilon\,\ln\left(\frac{1+e^{\eta-\eta_o}}{1+\nu}\right) \quad \text{if} \quad \tau < \tau_o, \tag{B.24}$$

$$\begin{aligned} y \sim {} & [1+\nu+\epsilon\ln(1+\nu)]\;e^{-(\tau-\tau_o)} - \epsilon\,\exp\left[-\frac{\beta q(1+\nu)(1-e^{-(\tau-\tau_o)})}{1+q(1+\nu)(1-e^{-(\tau-\tau_o)})}\right] \\ & \times \ln\left(1+e^{\eta_o-\eta}\right) \quad \text{if} \quad \tau > \tau_o. \end{aligned} \tag{B.25}$$

We have depicted in Figure 3(b) the functions x, $f = y-x$, and $\theta = q\,(1+\nu-y)$ as given by (B.23)–(B.25), in which $\eta - \eta_o$ is given by (B.20)–(B.22). The improvement over the leading-order approximation is evident for this relative large value of $\epsilon = 0.1$. See Figure 3(c) where we have depicted the leading-order and two-term approximations to x for times $\tau < \tau_1$, as compared to the numerical solution of the original problem. It is interesting to compare the numerical values of the times τ_o and τ_1 at which $\eta = \eta_o$ as calculated from the leading-order (section 3) or the two-term approximations (this appendix). While the change in τ_o is small, τ_1 is drastically reduced by using the two-term approximation instead of the leading-order one. For $\epsilon = 0.1$, $t_o = \tau_o/\epsilon$ changes from 12.8 (leading-order) to 12.4 (two-term expansion), whereas $t_1 = \tau_1/\epsilon$ changes from 585.7 to 55.1. The latter reduction follows from (B.22): as $(\tau - \tau_o) \gg 1$, this equation approximately becomes

$$\frac{d(\eta-\eta_o)}{d\tau} = -1 - \ln\left(1+e^{-(\eta-\eta_o)}\right) \sim -1 - e^{-(\eta-\eta_o)}.$$

Its solution $(\eta - \eta_o) \sim \ln[K\, e^{-(\tau-\tau_o)} - 1]$ ($K > 1$ is an integration constant) tends to $-\infty$ as $(\tau - \tau_o)$ approaches $\ln K > 0$. Thus $(t_1 - t_o) \approx \ln K/\epsilon$ is a number of order $1/\epsilon$, and not of order ϵ^{-2} as suggested by the leading-order approximation.

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