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Asymptotic analysis of premixed burning with large activation energy

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The structure and propagation rates of premixed flames are determined by singular perturbation in the limit where the activation temperature is large relative to other flow temperatures for several basic flows. Specifically, the simple kinetics of an exothermic first-order monomolecular decomposition under Arrhenius kinetics is studied for one-dimensional laminar flame propagation, spherically symmetric quasi-steady monopropellant droplet burning, and other simple geometries. Results elucidate Lewis-number effects, losses owing to fuel gasification processes, and conditions under which the thin-flame approximation is a limit of finite-rate Arrhenius kinetics.

1. Introduction

In his recent review of the state of theoretical understanding of laminar combustion problems, Williams (1971) points out that while singular perturbation techniques have been usefully exploited in the last decade, their full potential has yet to be realized. If one considers a typical gaseous flow undergoing exothermic burning, often the Schmidt and Lewis numbers are of order unity, so comparable flow times characterize transport of heat and mass by convection or diffusion. In such cases the principal dimensionless parameters for the gaseous phase of the flow are usually the first Damköhler number D_1 (the ratio of flow time to reaction time: the larger this parameter, the closer to chemical equilibrium); the second Damköhler number D_2 (the ratio of a heat of reaction to a static enthalpy: a measure of exothermicity); and the dimensionless Arrhenius activation temperature θ (non-dimensionalized against a suitable static temperature). In general, authors have not found it physically interesting to exploit D_2, and most existing singular perturbation studies in aerothermochemistry examine the (often singular) limits $D_1 \to 0$ (nearly frozen flow) and $D_1 \to \infty$ (near equilibrium). However, Williams notes that, particularly in premixed fuels, capitalizing upon large θ rather than D_1 is likely to be more illuminating of the cases of practical engineering interest. The previous tendency to exploit D_1 exclusively probably stems from its presence in the conservation laws, as normally written, in the role of a multiplicative factor, whereas θ occurs in the argument of an exponential function. No such case is worked out in the commonly cited texts on the method (Van Dyke 1964; Cole 1968). Indeed, the first solutions exploiting large θ in an exothermic flow retaining the three basic physical phenomena of convection, diffusion and reaction seem to be recent work examining one-dimensional flame propagation (Bush & Fendell 1970) and the structure of a planar steady detonation (Bush & Fendell 1971). Although the latter study is more difficult because the conservation of momentum must be carefully examined, the former study may be more worthy of further development because most controlled and uncontrolled burning processes are low speed and an isobaric model suffices to an excellent approximation.

This study seeks to respond to Williams's challenge for more useful perturbation studies by developing Bush & Fendell's (1970) work in the direction of more complex, though still simple, problems related to real phenomena. In particular, laminar flame propagation is reconstructed in § 2 because it is essential to following cases and because it reveals both *Lewis-number* and also *cold-boundary effects*. *Non-adiabatic effects* are then examined in § 3 by allowing for losses owing to gasification processes in one-dimensional burning. The spherically symmetric burning of a single uniform monopropellant droplet in an unbounded stagnant atmosphere is introduced in § 4 to permit evaluation of the *thin-flame model*. It must be emphasized that singular perturbation techniques (Fendell 1965) have shown how the thin-flame model of Burke & Schumann (1928) is the physically relevant limit for equilibrium irreversible burning in *initially unmixed* reactants under a Shvab–Zel'dovich formulation (Williams 1965). The question being raised here is under what conditions (if any) is the oft-used thin-flame model described by Adler & Spalding (1961) for *premixed reactants* a true limit of *finite-rate Arrhenius kinetics*. It is perhaps worth drawing an analogy between conventional and current thin-flame works with certain compressible-flow studies: one compressible-flow work might use the Rankine–Hugoniot relations to fit a shock of proper strength correctly in a region of diffusion-free flow (analogous to the Spalding–Adler work), and another might retain diffusion where appropriate and elucidate shock structure (analogous to the present work). Of particular relevance here is the use of the thin-flame model for monopropellant burning for no heat loss to the ambient fluid by Spalding & Jain (1959), and later with such heat loss by Jain (1963).

For all sections below, the simplest physically meaningful model of premixed chemical kinetics is adopted: an irreversible, direct, first-order, exothermic, monomolecular decomposition in the absence of inert species under an Arrhenius rate law, the largeness of the suitably non-dimensionalized activation temperature being exploited in the singular perturbation analysis undertaken.

2. Laminar flame propagation

The steady, plane, laminar, one-dimensional, isobaric burning of a combustible gas is examined in a co-ordinate system at rest with respect to the deflagration wave. A binary mixture with constant common heat capacity is studied in the absence of external forces, radiation, barodiffusion, thermodiffusion and inert gases.

In conventional notation, the non-dimensional two-point boundary-value problem describing the flow is (Williams 1965)

$$dY/d\xi = Le(Y-\epsilon), \tag{2.1}$$

$$d\tau/d\xi = \tau-\epsilon, \tag{2.2}$$

$$d\epsilon/d\xi = \Lambda(1-Y)\,\tau^{1+\delta}\exp\{-\beta(1-\tau)/(\alpha^{-1}+\tau)\}, \tag{2.3}$$

subject to

$$\epsilon,\ Y,\ \tau\rightarrow 0 \quad \text{as} \quad \xi\rightarrow-\infty, \tag{2.4}$$

$$\epsilon,\ Y,\ \tau\rightarrow 1 \quad \text{as} \quad \xi\rightarrow\infty. \tag{2.5}$$

If subscript 1 refers to the reactant R and 2 to the product P in a simple unimolecular reaction $R\rightarrow P$, then $Y_1 = 1-Y_2$ (the mass fractions sum to unity) and $\epsilon_1 = 1-\epsilon_2$ (the mass-flux fractions sum to unity). If subscript u refers to the unburned gas at the cold boundary ($\xi\rightarrow-\infty$) and b refers to the burned gas ($\xi\rightarrow\infty$), then

$$\epsilon = \frac{\epsilon_2-\epsilon_{2u}}{\epsilon_{2b}-\epsilon_{2u}},\quad Y = \frac{Y_2-Y_{2u}}{Y_{2b}-Y_{2u}},\quad \tau = \frac{T-T_u}{T_b-T_u},\quad \xi = \int_0^x \frac{mc_p}{\lambda}\,dx, \tag{2.6}$$

where λ is the thermal conductivity in Fourier's law, x is the Cartesian spatial co-ordinate and m is the mass flux (mass per cross-sectional area per time) of combustible mixture through the flame, the principal unknown. Under Fick's law with mass-transfer coefficient D, Y and ϵ are related by (2.1); provision for the presence of some product in the combustible upstream mixture is clearly included. The derivation permits the Lewis number $Le = \lambda/\rho c_p D$, where ρ is density, to be spatially varying but here it will be held fixed at order unity – usually a good approximation. The conservation of energy is given by (2.2), the conservation of product being given by (2.3). The expansion parameter will be $\beta = (T_a/T_b)$, where T_a is the activation temperature; $\alpha = (T_b-T_u)/T_u$. Since Λ contains m, i.e.

$$\Lambda = \rho B(T_b-T_u)^{1+\delta}\,\lambda\, e^{-\beta}/c_p m^2, \tag{2.7}$$

Λ plays the role of an eigenvalue; one seeks $\Lambda(\beta,\alpha,Le)$, where $\beta\gg 1$ and $\alpha, Le = O(1)$. In (2.7), B is the frequency factor, δ characterizes the pre-exponential thermal dependence of the specific rate constant (taken in the form of temperature above cold-boundary temperature for reasons discussed immediately below), and $\lambda\sim T$ for Λ to be constant (a physically reasonable convenience adopted here).

The temperature T_b of the burned gas is here the adiabatic flame temperature attained by exothermic burning of the combustible mixture without losses at the boundaries:

$$T_b = T_u + (h_1^0-h_2^0)\,(1-Y_{2u})/c_p, \tag{2.8}$$

where h_i^0 is the specific enthalpy of formation of species i at temperature T_u. Also $\delta > -1$ so that the right-hand side of (2.3) vanishes as $\xi\rightarrow-\infty$, where the left-hand side vanishes by boundedness. This requirement resolves the cold-boundary difficulty by demanding that the reaction rate vanish as $\tau\rightarrow 0$ so that, in the infinite time required to flow an infinite distance into the highly idealized model of the deflagration wave, the mixture will not have reacted.

The translationally invariant set is most conveniently treated in τ space:

$$dY/d\tau = Le(Y-\epsilon)/(\tau-\epsilon), \tag{2.9}$$

$$\frac{d\epsilon}{d\tau} = \frac{\Lambda(1-Y)\tau^{1+\delta}\exp[-\beta(1-\tau)/(\alpha^{-1}+\tau)]}{\tau-\epsilon}, \tag{2.10}$$

where

$$Y, \epsilon \to 0 \quad \text{as} \quad \tau \to 0, \tag{2.11}$$

$$Y, \epsilon \to 1 \quad \text{as} \quad \tau \to 1. \tag{2.12}$$

An exact integral for $Le = 1$ is $Y = \tau$.

For $\beta \gg 1$, with α^{-1}, Le, $\delta = O(1)$, the flow is divided into a relatively thin downstream region near $\tau = 1$ of intense reaction and a relatively thick upstream pre-heating zone in which an exponentially small amount of product is formed (Bush & Fendell 1970). Downstream, if $\bar{\tau} = \beta(1-\tau)$,

$$Y(\tau;\beta, Le, \alpha) = 1-\beta^{-1}Y_1(\bar{\tau}; Le, \alpha)-\beta^{-2}Y_2(\bar{\tau}; Le, \alpha)-\ldots, \tag{2.13}$$

$$\epsilon(\tau;\beta, Le, \alpha) = \epsilon_0(\bar{\tau}; Le, \alpha)+\beta^{-1}\epsilon_1(\bar{\tau}; Le, \alpha)+\ldots, \tag{2.14}$$

$$\Lambda(\beta; Le, \alpha) = \beta^2[\Lambda_0(Le, \alpha)+\beta^{-1}\Lambda_1(Le, \alpha)+\ldots]. \tag{2.15}$$

Substitution of (2.13)–(2.15) in (2.9) and (2.10) gives

$$dY_1/d\bar{\tau} = Le, \quad d\epsilon_0/d\bar{\tau} = -\Lambda_0 Y_1\{\exp[-\bar{\tau}/(\alpha^{-1}+1)]\}/(1-\epsilon_0); \tag{2.16}$$

$$\left.\begin{aligned} dY_2/d\tau &= Le(\bar{\tau}-Y_1)/(1-\epsilon_0),\\ \frac{d\epsilon_1}{d\bar{\tau}} &= -\frac{\Lambda_0 Y_1\exp[-\bar{\tau}/(\alpha^{-1}+1)]}{1-\epsilon_0}\left\{\frac{\Lambda_1}{\Lambda_0}+\frac{Y_2}{Y_1}-\frac{\bar{\tau}^2}{(\alpha^{-1}+1)^2}+\frac{\bar{\tau}+\epsilon_1}{1-\epsilon_0}-(1+\delta)\bar{\tau}\right\}.\end{aligned}\right\} \tag{2.17}$$

Upstream one adopts

$$Y(\tau;\beta, Le, \alpha) = \bar{Y}_0(\tau; Le, \alpha)+\beta^{-2}\bar{Y}_2(\tau; Le, \alpha)+\ldots, \tag{2.18}$$

$$\epsilon(\tau;\beta, Le, \alpha) = \beta^2\bar{\epsilon}_0(\tau;\beta, Le, \alpha), \tag{2.19}$$

where $\bar{\epsilon}_0(\tau;\beta\to\infty, Le, \alpha)\to 0$ exponentially rapidly. Substitution of (2.15), (2.18) and (2.19) in (2.9) and (2.10) yields

$$d\bar{Y}_0/d\tau = Le\bar{Y}_0/\tau, \quad d\bar{Y}_2 = Le\bar{Y}_2/\tau; \tag{2.20}$$

$$\bar{\epsilon}_0 = \Lambda_0\int_0^\tau [1-\bar{Y}_0(x)-\ldots]x^\delta\{\exp[-\beta(1-x)/(\alpha^{-1}+x)]\} \times\left\{1+\beta^{-1}\frac{\Lambda_1}{\Lambda_0}-\beta^{-2}\frac{\bar{Y}_2(x)}{1-\bar{Y}_0(x)}-\ldots\right\}dx, \tag{2.21}$$

where a formal first integral has been written in the light of (2.11), and $\delta > -1$ for the integral to exist.

Integrating (2.16) using (2.12), and integrating (2.20) using (2.11) gives

$$Y_1 = Le\bar{\tau}, \quad \epsilon_0 = 1-\left\{2\Lambda_0 Le(\alpha^{-1}+1)^2\left[1-\left(1+\frac{\bar{\tau}}{\alpha^{-1}+1}\right)\exp\left(-\frac{\bar{\tau}}{\alpha^{-1}+1}\right)\right]\right\}^{\frac{1}{2}}; \tag{2.22}$$

$$\bar{Y}_0 = A\tau^{Le}, \tag{2.23}$$

where A is a constant of integration. Matching is effected through introduction of an intermediate variable

$$\tau_i = (1-\tau)/g(\beta), \quad \text{where} \quad 1 \gg g(\beta) \gg \beta^{-1} \quad \text{as} \quad \beta \to \infty; \tag{2.24}$$

as $\beta \to \infty$ with τ_i fixed, $\tau \to 1 - g\tau_i$ and $\bar{\tau} \to \beta g \tau_i \to \infty$. Since from (2.21), if $\delta > 0$, a uniformly valid asymptotic form for $\bar{\epsilon}_0$ is

$$\bar{\epsilon}_0 = \Lambda_0(1 - A\tau^{Le})\tau^{\delta}\left(\frac{\alpha^{-1}+\tau}{\alpha^{-1}+1}\right)\frac{\exp\left[-\beta(1-\tau)/(\alpha^{-1}+\tau)\right]}{\beta} + \ldots, \tag{2.25}$$

matching of Y and ϵ is effected to lowest order if

$$A = 1, \quad \Lambda_0 = 1/2Le(\alpha^{-1}+1)^2. \tag{2.26}$$

The special form of (2.26) for $Le = 1$ is attributed by Williams (1965) to Zel'dovich, Semenov and Frank-Kamenetski. It follows that, in view of (2.22), (2.26), and the boundary conditions

$$Y_2 = (1-Le)\,Le(\alpha^{-1}+1)^2\int_0^{\bar{\tau}/(\alpha^{-1}+1)} \frac{v\,dv}{[1-(v+1)\exp(-v)]^{\frac{1}{2}}},$$
$$\bar{Y}_2 = \beta\tau^{Le}. \tag{2.27}$$

Matching mass fractions gives

$$B = -(1-Le)\,Le(\alpha^{-1}+1)^2\int_0^{\infty}\left\{\frac{v}{[1-(1+v)\exp(-v)]^{\frac{1}{2}}} - v\right\}dv. \tag{2.28}$$

To obtain Λ_1, one may integrate (2.17) to obtain, by (2.12),

$$\epsilon_1 = -\frac{\Lambda_0 Le}{1-\epsilon_0(\bar{\tau})}\int_0^{\bar{\tau}} x\{\exp\left[-x/(\alpha^{-1}+1)\right]\}\left\{\frac{\Lambda_1}{\Lambda_0} + \frac{Y_2(x)}{Y_1(x)} - \frac{x^2}{(\alpha^{-1}+1)^2} + \frac{x}{1-\epsilon_0(x)} - (1+\delta)x\right\}dx, \tag{2.29}$$

and, in light of the lowest order matching, one may also require that $\epsilon_1(\bar{\tau} \to \infty) \to 0$. Hence,

$$\Lambda_1 = \frac{3(\alpha^{-1}+1)^{-1} + [1+\delta-I] - (1-Le)}{Le(\alpha^{-1}+1)}, \tag{2.30}$$

where
$$I = \lim_{p\to\infty}\int_0^p \{1 - [1-(1-x)\exp(-x)]^{\frac{1}{2}}\}\,dx = 1{\cdot}344\ldots. \tag{2.31}$$

In Bush & Fendell (1970) the excellent agreement (less than 10% error for $\beta \geqslant 3$) between the two-term expansion for Λ with $\delta = -1$ and numerical values obtained by von Kármán and co-workers for the special case $Le = 1$ is reported. In fact, the accuracy of the closed-form results is superior to that of any previously derived expression. The results for general Lewis number obtained here show that $m \sim (\lambda/c_p)\,Le^{\frac{1}{2}}$, so that increasing ρD does not always increase the velocity of flame propagation (cf. Williams 1965, p. 125).

Because a small parameter multiplies the most highly differentiated term in (2.9), the boundary-value problem posed by (2.9)–(2.12) might appear to be singular in the limit $Le \to \infty$, in which case conduction dominates diffusion.

Actually, however, an exact integral to the reduced equation which satisfies all the boundary conditions exists:

$$\epsilon = Y.$$

Thus, the eigenvalue given by letting $Le \to \infty$ in the result obtained for $Le = O(1)$ [given above in (2.15), (2.26) and (2.30)] would probably be valid:

$$\Lambda = \frac{\beta}{\alpha^{-1}+1} + \dots. \tag{2.32}$$

To confirm this and to obtain the first correction to (2.32), one writes for the downstream region

$$\epsilon(\tau;\,\beta,\,\delta,\,\alpha) = \epsilon_0(\bar{\tau};\,\delta,\,\alpha) + \beta^{-1}\epsilon_1(\bar{\tau};\,\delta,\,\alpha) + \dots, \tag{2.33}$$

$$\Lambda(\beta,\delta,\alpha) = \beta[\Lambda_0(\delta,\alpha) + \beta^{-1}\Lambda_1(\delta,\alpha) + \dots]. \tag{2.34}$$

For the upstream region

$$\epsilon(\tau;\,\beta,\,\delta,\,\alpha) = \beta\bar{\epsilon}_0(\tau;\,\beta,\,\alpha,\,\delta), \tag{2.35}$$

where $\bar{\epsilon}_0(\tau;\,\beta \to \infty,\,\alpha,\,\delta) \to 0$ exponentially. The governing differential equation and boundary conditions become

$$\frac{d\epsilon}{d\tau} = \frac{\Lambda\tau^{1+\delta}(1-\epsilon)\exp\left[-\beta(1-\tau)/(\alpha^{-1}+\tau)\right]}{\tau-\epsilon}, \tag{2.36}$$

$$\epsilon \to 0 \quad \text{as} \quad \tau \to 0, \quad \epsilon \to 1 \quad \text{as} \quad \tau \to 1. \tag{2.37}$$

Substituting the expansions into the governing equations, solving subject to the boundary conditions, and matching as above, one obtains

$$\epsilon_0 = \exp\left[-\bar{\tau}/(\alpha^{-1}+1)\right], \quad \Lambda_0 = (\alpha^{-1}+1)^{-1}; \tag{2.38}$$

$$\left.\begin{aligned} \epsilon_1 &= -\Lambda_0\int_0^{\bar{\tau}}\{\exp\left[-x/(\alpha^{-1}+1)\right]\}\left\{\frac{\Lambda_1}{\Lambda_0} - x(1+\delta) + \frac{x}{1-\epsilon_0(x)} - \frac{x^2}{(\alpha^{-1}+1)^2}\right\}dx,\\ \Lambda_1 &= \frac{2+(\alpha^{-1}+1)(1+\delta-\frac{1}{6}\pi^2)}{(\alpha^{-1}+1)}; \end{aligned}\right\} \tag{2.39}$$

$$\bar{\epsilon}_0 = \Lambda_0\int_0^{\tau} x^{\delta}\{\exp\left[-\beta(1-x)/(\alpha^{-1}+x)\right]\}\left[1+\beta^{-1}\frac{\Lambda_1}{\Lambda_0}+\dots\right]dx. \tag{2.40}$$

In obtaining (2.39) use is made of the known identity (Pierce & Foster 1956, p. 70, equation 526)

$$\int_0^1 \frac{\ln p}{1-p}\,dp = -\tfrac{1}{6}\pi^2. \tag{2.41}$$

The results confirm that, as $\beta \to \infty$, the flame propagates faster as the Lewis number increases. However, in most combustible gaseous mixtures not including hydrogen, the Lewis number remains of order unity.

3. Adiabatic vaporization and homogeneous combustion in a one-dimensional model

The effect of heat losses owing to the enthalpy required for gasification of a premixed fuel at its phase-transition temperature may readily be added to the model studied in § 2. The reduction in burning rate and the detailed flame structure is conveniently studied in a co-ordinate system fixed to the two-phase interface (say, $\xi = 0$) for the quasi-steady model adopted. Because no heat is expended in first raising the fuel to its vaporization temperature (for simplicity), this vaporization process is referred to as adiabatic in the combustion literature. Also, the non-gaseous fuel will be taken to be impervious to the gaseous product; both these restrictions could be easily relaxed. Of course, the need for tailoring the pre-exponential thermal dependence of the specific rate constant to resolve the cold-boundary difficulty has now been removed, and the formulation will reflect this alteration.

The non-dimensionalized two-point boundary-value problem may now be written as (Williams 1965)

$$dY/d\xi = Le(Y-\epsilon), \tag{3.1}$$

$$d\tau/d\xi = \tau-\epsilon, \tag{3.2}$$

$$d\epsilon/d\xi = \Lambda(1-Y)\exp[-\beta(1-\tau)/(Q+\tau)], \tag{3.3}$$

subject to

$$d\tau/d\xi = L, \quad \tau = L, \quad \epsilon = 0 \quad \text{at} \quad \xi = 0; \quad \tau = \epsilon = Y = 1 \quad \text{as} \quad \xi \to \infty. \tag{3.4}$$

The definitions are unaltered except as now noted. The mass fraction of product is Y and the mass-flux fraction of product is ϵ. The eigenvalue Λ, taken as constant, is

$$\Lambda = \frac{\lambda\rho BT^{\alpha_1}}{m^2 c_p}\exp(-\beta), \tag{3.5}$$

where α_1 characterizes the pre-exponential dependence of the specific rate constant. The temperature at the hot boundary is now

$$T_b = T_0 - \frac{L_v}{c_p} + \frac{h_1^0 - h_2^0}{c_p}, \tag{3.6}$$

where L_v is the specific heat of phase transition and T_0 is the temperature at the two-phase interface (given more exactly by the Clausius–Clapeyron equation, but taken here as known to an adequate approximation). The dimensionless vaporization heat $L = L_v/(h_1^0 - h_2^0)$. Also,

$$\tau = (1-L)\frac{T-T_0}{T_b - T_0} + L, \quad Q = (1-L)\frac{T_b}{T_b - T_0} - 1. \tag{3.7}$$

Since one expects $\tau(\xi \to \infty) > \tau(\xi = 0)$, one requires $L < 1$.

In τ space

$$dY/d\tau = Le(Y-\epsilon)/(\tau-\epsilon), \tag{3.8}$$

$$\frac{d\epsilon}{d\tau} = \frac{\Lambda(1-Y)\exp[-\beta(1-\tau)/(Q+\tau)]}{\tau-\epsilon}, \tag{3.9}$$

subject to

$$\epsilon = Y = 1 \quad \text{at} \quad \tau = 1; \quad \epsilon = 0, \quad dY/d\tau = Le\,Y/L \quad \text{at} \quad \tau = L. \tag{3.10}$$

Proceeding as before for $\beta \gg 1$, one defines downstream expansions with $[\bar{\tau} = \beta(1-\tau)]$

$$Y(\tau;\beta,Q,L,Le) = 1-\beta^{-1}Y_1(\bar{\tau};Q,L,Le)-\beta^{-2}Y_2(\bar{\tau};Q,L,Le)-\dots, \tag{3.11}$$

$$\epsilon(\tau;\beta,Q,L,Le) = \epsilon_0(\bar{\tau};Q,L,Le)+\beta^{-1}\epsilon_1(\bar{\tau};Q,L,Le)+\dots, \tag{3.12}$$

$$\Lambda(\beta,Q,L,Le) = \beta^2[\Lambda_1(Q,L,Le)+\beta^{-1}\Lambda_1(Q,L,Le)+\dots], \tag{3.13}$$

and upstream expansions

$$Y(\tau;\beta,Q,L,Le) = \bar{Y}_0(\tau;Q,L,Le)+\beta^{-2}\bar{Y}_2(\tau;Q,L,Le)+\ldots, \tag{3.14}$$

$$\epsilon(\tau;Q,\beta,L,Le) = \beta^2\bar{\epsilon}_0(\tau;\beta,Q,L,Le), \tag{3.15}$$

where $\epsilon_0(\tau;\beta\to\infty,Q,L,Le)\to 0$ exponentially.

Substituting the expansions in the boundary-value problem, collecting terms of the same order, solving subject to appropriate boundary conditions and matching yields to lowest order

$$\epsilon_0 = 1-\left[1-\left(1+\frac{\bar{\tau}}{Q+1}\right)\exp\left(-\frac{\bar{\tau}}{Q+1}\right)\right]^{\frac{1}{2}}, \quad Y_1 = Le\,\bar{\tau}, \quad \Lambda_0 = \frac{1}{2\,Le\,(Q+1)^2}; \tag{3.16}$$

$$\bar{Y}_0 = \tau^{Le}, \quad \bar{\epsilon}_0 = \Lambda_0\int_L^\tau \frac{(1-x^{Le})\exp\left[-\beta(1-x)/(Q+x)\right]}{x}dx+\ldots. \tag{3.17}$$

When comparing the lowest order eigenvalue from § 2 (no gasification loss),

$$m^2 \doteq \frac{2\lambda\rho B(T_b-T_u)^{1+\delta}\,Le[\exp(-T_a/T_b)]}{c_p(T_a/T_b)^2}\left(\frac{T_b}{T_b-T_u}\right)^2, \tag{3.18}$$

with that just derived (with gasification losses),

$$m^2 \doteq \frac{2\lambda\rho BT^{\alpha_1}Le[\exp(-T_a/T_b)]}{c_p(T_a/T_b)^2}\left(\frac{T_b}{T_b-T_0}\right)^2\left[1-\frac{L_v}{h_1^0-h_2^0}\right]^2, \tag{3.19}$$

one should recall the difference in the value of T_b attained [cf. (2.8) and (3.6)]. The decrease in the burning rate m owing to the vaporization process is greater for $\beta \gg 1$ than superficially appears. Much of the loss due to the vaporization may be simulated by diluting the premixed fuel with product in the geometry of § 2.

4. Monopropellant droplet burning: thin-flame models

The quasi-steady, isobaric, radially symmetric burning of a pure monopropellant droplet uniformly at its vaporization temperature is examined for an unbounded stagnant ambient atmosphere of product gas. This is an obvious extension of the premixed burning with adiabatic vaporization discussed in § 2 in the direction of more complex phenomena.

The dimensionless two-point boundary-value problem describing this flow is (Williams 1965)

$$dY/dr = (\dot{m}/r^2)(Y-\epsilon), \tag{4.1}$$

$$\frac{d\tau}{dr} = \frac{\dot{m}}{Le\,r^2}\left(\tau-\tau_\infty+1-\epsilon+\frac{A}{\dot{m}}\right), \tag{4.2}$$

$$\frac{d\epsilon}{dr} = D_1\frac{r^2(1-Y)\exp(-\theta/\tau)}{\dot{m}}, \tag{4.3}$$

subject to

$$\epsilon = 0, \quad \tau = \tau_L, \quad d\tau/dr = L\dot{m}/Le \quad \text{at} \quad r = 1, \tag{4.4}$$

$$\epsilon = 1, \quad Y = 1, \quad \tau = \tau_\infty \quad \text{as} \quad r\to\infty. \tag{4.5}$$

Here Y is the mass fraction, and ϵ the mass-flux fraction, of product. The spherical radial co-ordinate r has been non-dimensionalized against the droplet radius a. The Lewis number $Le = \lambda/\rho c_p D$ will be taken (for convenience) as an order-unity constant, λ being the thermal conductivity, ρ the density of the binary mixture, c_p the constant heat capacity of both species and D the mass-transfer coefficient (taken for convenience to vary linearly with temperature). The burning rate $\dot{m}$ plays the role of an eigenvalue (v is the radial velocity component):

$$\dot{m} = (\rho v)_{r=a}/\rho_\infty(D_\infty/a), \tag{4.6}$$

where the numerator is evaluated at the droplet surface and the subscript infinity denotes evaluation at the ambient thermodynamic state. The dimensionless temperature τ is formed by non-dimensionalizing the physical temperature T against the specific heat of combustion $(h_1^0 - h_2^0)/c_p$, where h_i^0 is the enthalpy of formation of species i ($=1$ for reactant and 2 for product) at some reference thermodynamic state. The parameter θ (to be exploited in the perturbation expansion) is the ratio of the activation enthalpy $c_p T_a$ to the heat of combustion $h_1^0 - h_2^0$. The first Damköhler number, characterizing the ratio of a typical flow time to a reaction time, is

$$D_1 = a^2 \rho B T^{\alpha_1}/\rho_\infty D_\infty, \tag{4.7}$$

where B is the frequency factor and α_1 characterizes the pre-exponential thermal dependence of the specific rate constant; for simplicity, D_1 is taken as constant. The specific heat of vaporization L_v has been non-dimensionalized against the heat of combustion $h_1^0 - h_2^0$ to form L. Finally, the ambient temperature τ_∞ is readily shown to be given by

$$\tau_\infty = \tau_L + 1 - L + A/\dot{m}, \tag{4.8}$$

where A is the heat transfer to the ambient gas:

$$A = \lim_{r\to\infty} Le\, r^2(d\tau/dr). \tag{4.9}$$

Clearly $A > 0$ implies that heat is derived from the ambient gas and $A < 0$ implies heat is lost to the ambient gas. The case of no transfer to the ambient gas ($A = 0$) is often referred to as adiabatic burning in the combustion literature (although clearly heat derived from combustion is lost to the adiabatic vaporization process). Incidentally, under the non-dimensionalization adopted in this section, in this problem τ_∞ is the inverse of the second Damköhler number D_2 discussed in the introduction.

A rather limited number of numerical results have been reported for the boundary-value problem by Lorell & Wise (1955) and by Williams (1959), all for $A = 0$. In fact, the approximate analytic work described by Williams (1959) and by Spalding & Jain (1959) is also limited to adiabatic burning, believed to be the case holding in rocket engines [although Jain (1963) has reported some preliminary results for $A \neq 0$ based on an approximate procedure]. The work of Spalding & Jain is of particular interest because these authors assert that a solution to the governing boundary-value problem may be obtained by assuming that all burning occurs at an infinitesimally thin flame at a finite distance from the droplet; the temperature is continuous across the flame. Inside and outside this concentric spherical shell (thin flame) no burning occurs; inside, the flow is frozen and outside there is pure product. Their solution is completed by assuming that the dimensionless location of the thin flame is $r = \bar{\sigma}$, where

$$\bar{\sigma} = (\dot{m}/m)^{\frac{1}{2}} \tag{4.10}$$

and m is the burning rate for planar laminar flame propagation, derived in § 2. One goal of this section is to establish under what (if any) conditions such a model is a true limit of the boundary-value problem; physically, heat release from combustion will occur in a thin shell only for large activation energy, so examination of the case $\theta \gg 1$ seems profitable. However, unless D_1 is also large, it seems clear that nearly frozen flow is being examined; the precise criterion for $D_1(\theta)$ must therefore also be developed.

Previous singular perturbation analyses were indeed limited to the nearly frozen case $[D_1 \ll 1, \theta = O(1)]$, in which, to lowest order, combustion does not enter so heat drawn from the ambient gas must sustain the vaporization, and to the case of a thin spherical annulus contiguous to the droplet in which rapid decomposition occurred $[D_1 \gg 1, \theta = O(1)$, see Fendell 1969]. However, only those monopropellants with large activation energy are stable enough for practical use, so extending multiple-scaling techniques to such cases seems well motivated.

Adiabatic case ($A = 0$)

For the special case $A = 0$, one well-known integral of the boundary-value problem (4.1)–(4.5) is $Y = \tau - \tau_\infty + 1$ for $Le = 1$. [For $Le = 1$ and $A \neq 0$, the integral takes a far less tractable form: $Y = \tau - \tau_\infty + 1 + (A/\dot{m})\{1 - \exp(-\dot{m}/r)\}$.] No such integral can be given for general Le, and the problem is posed in τ space to make use of results presented in §§ 2 and 3:

$$\frac{dr}{d\tau} = \frac{Le\, r^2}{\dot{m}(\tau - \tau_\infty + 1 - \epsilon)}, \tag{4.11}$$

$$\frac{d\epsilon}{d\tau} = \frac{D_1 \exp(-\theta/\tau_\infty)\, Le\, r^4 (1-Y) \exp[-\theta(\tau_\infty - \tau)/\tau\tau_\infty]}{\dot{m}^2(\tau - \tau_\infty + 1 - \epsilon)}, \tag{4.12}$$

$$\frac{dY}{d\tau} = \frac{Le\,(Y-\epsilon)}{\tau - \tau_\infty + 1 - \epsilon}, \tag{4.13}$$

where (with $\tau_\infty = \tau_L + 1 - L$)

$$\epsilon = 0, \quad r = 1, \quad dY/d\tau = Le\, Y/L \quad \text{at} \quad \tau = \tau_L, \tag{4.14}$$

$$\epsilon = 1, \quad Y = 1, \quad r \to \infty \quad \text{at} \quad \tau = \tau_\infty. \tag{4.15}$$

For $\theta \gg 1$ [with Le, τ_∞, L, $\tau_L = O(1)$ and D_1 to be assigned] the flow is again divided into a relatively thin region of intense reaction near τ_∞ and a relatively thick preheating zone upstream. Also, if $\tau_\infty > \tau_L$, $1 > L$. Therefore, downstream one adopts as asymptotic expansions, if $\bar{\tau} = \theta(\tau_\infty - \tau)$,

$$Y(\tau; \theta, D_1, Le, L) = 1 - \theta^{-1} Y_1(\bar{\tau}; D_1, Le, L) - \theta^{-2} Y_2(\bar{\tau}; D_1, Le, L) - \ldots, \tag{4.16}$$

$$\epsilon(\tau; \theta, D_1, Le, L) = \epsilon_0(\bar{\tau}; D_1, Le, L) + \theta^{-1}\epsilon_1(\bar{\tau}; D_1, Le, L) + \ldots, \tag{4.17}$$

$$r(\tau; \theta, D_1, Le, L) = \bar{\alpha}(\theta) r_c(D_1, Le, L) + \sigma(\theta) r_1(\bar{\tau}; D_1, Le, L) + \sigma_1(\theta) r_2(\bar{\tau}; D_1, Le, L) + \ldots, \tag{4.18}$$

$$\Lambda(\theta, D_1, Le, L) = \theta^2\{\Lambda_0(D_1, Le, L) + \theta^{-1}\Lambda_1(D_1, Le, L) + \ldots\}, \tag{4.19}$$

where Λ plays the role of an eigenvalue because it contains $\dot{m}$:

$$\Lambda = D_1[\exp(-\theta/\tau_\infty)]\,\bar{\alpha}^4 r_c^4/\dot{m}^2. \tag{4.20}$$

It is required that $\bar{\alpha} \gg \sigma \gg \sigma_1$ but that $\bar{\alpha}(\theta) = O(1)$, as $\theta \to \infty$, if a thin flame is to lie a finite distance off the monopropellant droplet surface. Upstream one adopts

$$Y(\tau;\theta,D_1,Le,L) = \bar{Y}_0(\tau;D_1,Le,L) + \theta^{-2}\bar{Y}_2(\tau;D_1,Le,L) + \dots, \tag{4.21}$$

$$\epsilon(\tau;\theta,D_1,Le,L) = (\theta^2/\bar{\alpha}^4)\,\bar{\epsilon}_0(\tau;D_1,Le,L), \tag{4.22}$$

$$r(\tau;\theta,D_1,Le,L) = \bar{r}_0(\tau;D_1,Le,L) + \theta^{-1}\bar{r}_1(\tau;D_1,Le,L) + \dots. \tag{4.23}$$

Substitution of (4.16)–(4.20) in (4.11)–(4.15) gives to lowest order, if $\sigma = [D_1 \exp(-\theta/\tau_\infty)]^{-\frac{1}{2}}$,

$$\frac{dY_1}{d\bar{\tau}} = Le, \quad \frac{d\epsilon_0}{d\bar{\tau}} = -\frac{\Lambda_0 Le^2\,\bar{\tau}\exp(-\bar{\tau}/\tau_\infty^2)}{1-\epsilon_0}, \quad \frac{dr_1}{d\bar{\tau}} = -\frac{Le\,\Lambda_0^{\frac{1}{2}}}{1-\epsilon_0}. \tag{4.24}$$

The gradients in the downstream zone are so large that convection has become negligible relative to reaction and to diffusion, which is suitably represented solely by a second-derivative Cartesian-like form. The solution subject to (4.15) is

$$Y_1 = Le\,\bar{\tau}, \quad \epsilon_0 = 1 - \left\{2\Lambda_0 Le^2 \tau_\infty^4\left[1-\left(1+\frac{\bar{\tau}}{\tau_\infty^2}\right)\exp\left(-\frac{\bar{\tau}}{\tau_\infty^2}\right)\right]\right\}^{\frac{1}{2}}, \tag{4.25}$$

$$r_1 + C = -\frac{1}{2^{\frac{1}{2}}}\int_a^{\bar{\tau}/\tau_\infty^2} \frac{dx}{[1-(1+x)\exp(-x)]^{\frac{1}{2}}}, \tag{4.26}$$

where C and a are related by matching requirements. It may be readily confirmed that $\bar{r} \to \infty$ as $\bar{\tau} \to 0$, so the downstream expansion (4.18) satisfies the ambient-state boundary condition.

Since

$$\dot{m}^2 = \frac{D_1 \exp(-\theta/\tau_\infty)\,\bar{\alpha}^4 r_c^4}{\theta^2 \Lambda_0}\left\{1 - \theta^{-1}\frac{\Lambda_1}{\Lambda_0} - \dots\right\}, \tag{4.27}$$

substitution of (4.21)–(4.23) in (4.11)–(4.14) gives to lowest order

$$\frac{d\bar{Y}_0}{d\tau} = \frac{Le\,\bar{Y}_0}{\tau-\tau_\infty+1}, \quad \frac{d\bar{\epsilon}_0}{d\tau} \doteq \Lambda_0 \frac{Le\,(\bar{r}_0/r_c)^4\,[1-\bar{Y}_0]\exp[-\theta(\tau_\infty-\tau)/\tau\tau_\infty]}{\tau-\tau_\infty+1}, \tag{4.28}$$

$$\frac{d\bar{r}_0}{d\tau} = Le\,\Lambda_0^{\frac{1}{2}}\frac{(\bar{r}_0/r_c)^2}{\tau-\tau_\infty+1}, \tag{4.29}$$

if

$$\bar{\alpha} = \frac{\theta^{\frac{1}{2}}}{[D_1 \exp(-\theta/\tau_\infty)]^{\frac{1}{4}}} = \theta^{\frac{1}{2}}\sigma^{\frac{1}{2}} = O(1). \tag{4.30}$$

The amount of product formed in the upstream region is so small that the energy balance is between convection and diffusion, with no heat from reaction. It follows that

$$D_1 = O[\theta^2 \exp(\theta/\tau_\infty)] \to \infty \quad \text{as} \quad \theta \to \infty; \quad \sigma = O(\theta^{-1}). \tag{4.31}$$

If D_1 were much larger, the flame would go to the droplet surface, and heterogeneous effects might well enter; if D_1 were much smaller, the flame would move off to infinity and again the thin-flame model would be of dubious physical relevance.

$$\bar{Y}_0 = \bar{A}(\tau - \tau_\infty + 1)^{Le},$$

$$\bar{\epsilon}_0 \doteq \Lambda_0 Le \int_{\tau_L}^{\tau} \frac{1-\bar{A}[1+x-\tau_\infty]^{Le}}{1+x-\tau_\infty}\left[\frac{r_0(x)}{r_c}\right]^4 \exp\left[-\theta(\tau_\infty - x)/x\tau_\infty\right] dx, \quad (4.32)$$

$$\bar{r}_0 = \frac{1}{1+(\Lambda_0^{\frac{1}{2}} Le/r_c^2)\left[\ln L - \ln(\tau - \tau_\infty + 1)\right]}. \quad (4.33)$$

For matching of the upstream and downstream expansions one introduces an intermediate variable $\tau_i = (\tau_\infty - \tau)\phi(\theta)$ such that $\theta \gg \phi(\theta) \gg 1$ as $\theta \to \infty$. So for τ_i fixed, $\theta \to \infty$, the downstream variable $\bar{\tau} = [\theta/\phi(\theta)]\tau_i \to \infty$, and the upstream variable $\tau = \tau_\infty - [\phi(\theta)]^{-1}\tau_i \to \tau_\infty$. Since

$$\bar{\epsilon}_0 \sim \Lambda_0 Le\left(\frac{r}{r_c}\right)^4 \frac{1-\bar{A}(1+\tau-\tau_\infty)^{Le}}{1+\tau-\tau_\infty}\frac{\tau^2 \exp\left[-\theta(\tau_\infty - \tau)/\tau\tau_\infty\right]}{\theta} + \ldots, \quad (4.34)$$

for large θ as τ increases toward τ_∞, one may confirm that matching may be carried out provided that

$$\bar{A} = 1, \quad \Lambda_0 = \frac{1}{2Le^2\tau_\infty^4}, \quad \bar{\alpha} r_c = \tfrac{1}{2}\{1+[1+4\bar{\alpha}^2 Le\,\Lambda_0^{\frac{1}{2}} \ln L^{-1}]^{\frac{1}{2}}\}. \quad (4.35)$$

Since $L < 1$, $\bar{\alpha} r_c > 1$. The position $\bar{\alpha} r_c$ of the flame is independent of the Lewis number Le, but the burning rate $\dot{m}$ increases linearly with Le to lowest order. Matching also gives

$$C = 2^{-\frac{1}{2}}\left\{a - \int_a^\infty \left[\frac{1-[1-(1+x)\exp(-x)]^{\frac{1}{2}}}{[1-(1+x)\exp(-x)]^{\frac{1}{2}}}\right] dx\right\}, \quad (4.36)$$

so one may write

$$r_1 = -\frac{1}{2^{\frac{1}{2}}}\frac{\bar{\tau}}{\tau_\infty^2} + \frac{1}{2^{\frac{1}{2}}}\int_{\bar{\tau}/\tau_\infty^2}^{\infty} \frac{1-[1-(1+x)\exp(-x)]^{\frac{1}{2}}}{[1-(1+x)\exp(-x)]^{\frac{1}{2}}}\, dx. \quad (4.37)$$

If $\bar{\sigma} = \bar{\alpha} r_c$, then (4.10) holds precisely, as may be shown with the aid of (2.7), (2.8) with $Y_{2u} = 0$, (3.18), (4.6), (4.7), (4.27) and (4.35), provided that

$$Le = 1, \quad D/D_\infty = T/T_\infty, \quad 1+\delta = \alpha_1, \quad T_b \gg T_u, \quad 1 \gg L, \quad (4.38)$$

and provided that one associates T_∞ in (4.8) with T_b in (2.8). While there may be other conditions under which (4.10) holds precisely, this establishes at least one physically interesting set. Further, since, by (4.27) and (4.30), $\dot{m} = r_c^2 \Lambda_0^{-\frac{1}{2}} + \ldots$, the position of the thin flame for $Le = 1$ is given by

$$\bar{\sigma} \equiv \bar{\alpha} r_c = \tfrac{1}{2}\{1+[1+4m^{-1}\ln L^{-1}]^{\frac{1}{2}}\}, \quad (4.39)$$

the position given by thin-flame theory. Thus, thin-flame theory is a limit of finite-rate Arrhenius kinetics for monopropellant burning at least for the adiabatic case with the Lewis number unity, the limit being $\theta \gg 1$,

$$D_1 = O[\theta^2 \exp(\theta/\tau_\infty)] \gg 1.$$

The (dimensional) mass transfer from a monopropellant droplet

$$(M = 4\pi(\rho v)_{r=a} a^2)$$

is known to be linearly proportional to the droplet radius a for nearly frozen flow, with $D_1 \ll 1$ (Fendell 1969). From (4.6) and (4.27), $M \sim a^2$ for the intense burning associated with a thin flame.

Because the two-term expansion for the eigenvalue does appreciably extend the range of validity of the asymptotic result to smaller β in § 2, it is deemed worthwhile to examine Λ_1 in (4.27). Substituting (4.16)–(4.19) in (4.11)–(4.13), to next-to-lowest order one obtains, for $\sigma_1 = \sigma/\theta$,

$$\frac{dY_2}{d\bar{\tau}} = Le\frac{\bar{\tau}-Y_1}{1-\epsilon_0}, \quad \frac{dr_2}{d\bar{\tau}} = \frac{dr_1}{d\bar{\tau}}\left\{\frac{\Lambda_1}{2\Lambda_0}+\frac{\epsilon_1+\bar{\tau}}{1-\epsilon_0}+2\bar{\alpha}\frac{r_1}{r_c}\right\}, \tag{4.40}$$

$$\frac{d\epsilon_1}{d\bar{\tau}} = \frac{d\epsilon_0}{d\bar{\tau}}\left[\frac{\Lambda_1}{\Lambda_0}+\frac{Y_2}{Y_1}+\frac{4\bar{\alpha}r_1}{r_c}+\frac{\epsilon_1+\bar{\tau}}{1-\epsilon_0}-\frac{\bar{\tau}^2}{\tau_\infty^3}\right]. \tag{4.41}$$

In the downstream region, the spherical nature of the geometry and convection enter in forcing-function roles in next-to-lowest order. On solving (4.40) and (4.41) subject to (4.15), one has

$$Y_2 = Le\,(1-Le)\,\tau_\infty^4\int_0^{\bar{\tau}/\tau_\infty^2}\frac{x\,dx}{[1-(1+x)\exp{(-x)}]^{\frac{1}{2}}}, \tag{4.42}$$

$$\epsilon_1(\bar{\tau}) = [1-\epsilon_0(\bar{\tau})]^{-1}\int_0^{\bar{\tau}}\frac{d\epsilon_0(x)/dx}{[1-\epsilon_0(x)]^{-1}}\left[\frac{\Lambda_1}{\Lambda_0}+\frac{Y_2(x)}{Y_1(x)}+\frac{4\bar{\alpha}r_1(x)}{r_c}+\frac{x}{1-\epsilon_0(x)}-\frac{x^2}{\tau_\infty^3}\right]dx. \tag{4.43}$$

From the earlier matching one may anticipate that $\epsilon_1(\bar{\tau}\to\infty)\to 0$, so

$$\Lambda_1/2\Lambda_0 = 3\tau_\infty + 2^{\frac{1}{2}}(\bar{\alpha}/r_c)\,(2-I_1)+\tau_\infty^2(Le-1-I), \tag{4.44}$$

where, for convenience, it is recalled that $\tau_\infty = \tau_L + 1 - L, I = 1{\cdot}344\ldots$ [cf. (2.31)], $\bar{\alpha}$ is given by (4.30) and r_c by (4.35). Also,

$$I_1 = \int_0^\infty \{1-[1-(1+t)\exp{(-t)}]^{\frac{1}{2}}\}\{1-(1+t)\exp{(-t)}\}^{\frac{1}{2}}\,dt \doteq 0{\cdot}656. \tag{4.45}$$

For the adiabatic case, the thin-flame approximation has been imbedded in a systematic perturbation expansion which permits an evaluation of the error incurred, and which provides a means for reducing that error.

5. Concluding remarks

A widely appreciated lesson, further reinforced by the problems treated here, is that *ad hoc* approximations to the Arrhenius factor can yield misleading solutions. For example, the polynomial-type temperature-explicit approximation to Arrhenius kinetics yields a negative first-order correction to the laminar-flame-propagation eigenvalue (Jain & Kumar 1969); however, as noted earlier, the positive correction given here in (2.30) further improves the lowest order result (2.26) so that the two-term result (Bush & Fendell 1970) differs from the numerical solution for a Lewis number of unity by less than 10 % for β as small as three and by less than 1 % for $\beta \geqslant 10$. Further, the author's own *ad hoc* approximation to the Arrhenius factor for spherically symmetric monopropellant droplet decomposition (Fendell 1969) yielded ambiguous results with regard to the variation of the mass-transfer rate M with droplet radius for thin-flame intense-burning conditions. The current work gives $M \sim a^2$, and while early experimental work was itself ambiguous (Williams 1965), recent relevant experimental work tends to confirm this result.

For example, Rosser & Peskin (1966) found $M \sim a^2$ for a porous-sphere apparatus, although failure to preheat the liquid hydrazine fuel to nearly its vaporization temperature before injection to the sphere, and also the presence of ambient oxidant in even small amounts, cast some doubt on applicability of the analysis developed here to their experiment. Lawver (1966) also reports $M \sim a^2$ for hydrazine-droplet burning, although, again, whether sufficient precaution was taken to exclude oxidizing gases from the ambient environment is uncertain. Faeth, Karhan & Yanyecic (1968) also found $M \sim a^2$ for nitrate-ester droplets burning at higher pressures and $M \sim a$ for lower pressures; this is consistent with the present analytical results since the burning rate is expected to increase with the pressure. Of course, for pressures many times atmospheric the critical point for such monopropellants is approached, the adiabatic vaporization condition (4.4) becomes inaccurate, and the present quasi-steady combustion model is inappropriate. [More refined experimental results than burning rates have not been given, although Lawver reports a decomposition flame zone of the thickness of the droplet diameter; the current large-activation-energy solution does yield a flame that remains a finite distance off the droplet surface, in contrast to Williams's deductions (Williams 1965, pp. 235–238) for the Spalding–Jain analysis in which $M \sim a^2$ implies a thin gas-phase flame coincident with the droplet surface.] Nevertheless, enough experimental confirmation exists to state confidently that monopropellant droplet combustion is at least a two-parameter problem (involving D_1 and θ) in practice, and statements that $M \sim a^2$ at small activation energy and $M \sim a^{1 \cdot 1}$ at large activation energy (Williams 1965, p. 243) seem oversimplified. Also, while thin-flame and temperature-explicit models *may* happen to yield gross quantities like M over a wide range of parametric values for D_1 and θ, the generally unknown accuracy with which such models simulate Arrhenius kinetics and the generally unknown correspondence between Arrhenius parameters and parameters in these *ad hoc* models makes their use for calculation of flow details suspect. In fact, occasional inadequacy for even gross properties has been documented. With the increasing analytic tractability of Arrhenius models there seems less justification for increasingly refined numerical integration of *ad hoc* models (cf. Jain & Ramani 1969) that have never been adequately correlated with Arrhenius kinetics.

Large-activation-energy asymptotic expansions have now been indicated to be feasible for one-step reaction mechanisms, but they may be quite practical for some multiple-step mechanisms as well. Currently, multi-step chemistry in laminar flame propagation, such as (for example) would be needed to investigate cool-flame phenomena, is currently treated by numerical integration of an Arrhenius model or (as just noted) by approximate analytic treatment of simplified *ad hoc* models, such as ignition-temperature models (cf., for example, Korman 1970). The advantages of explicit parametric dependencies may be achievable for multi-step mechanisms by singular perturbation. Perhaps aerothermochemists may eventually regard large activation energy as an opportunity rather than a difficulty.

While the present work emphasizes fully developed flames, the possibilities of analytically treating gas-phase ignition deserve scrutiny. What seems to be missing from the existing literature is a complete, effectively time-dependent investigation of flame formation, from nearly frozen conditions to stable burning for a flow geometry of practical interest. Current analyses are restricted to early-time solution, and study flame evolution only until some arbitrary temperature, thermal gradient, or heat-balance criterion for incipient ignition is fulfilled.

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