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INITIATION OF FREE-RADICAL POLYMERIZATION WAVES*

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Abstract. Frontal polymerization is a process of converting a monomer into a polymer by means of a self-propagating thermal reaction wave. We study initiation of polymerization waves by a high temperature heat source. A five species reaction model is considered with a focus on the evolution of two of these species and the temperature of the mixture. The temperature is tracked from the inert heating to the transition stage. Through an asymptotic analysis, the first correction to the temperature in transition is found as the solution to an integral equation. Two parameters govern the qualitative behavior of the solution to the integral equation. Depending on the magnitude of these parameters, the solution exhibits either bounded or unbounded behavior indicating the onset or inhibition of propagation of a polymerization wave.

Key words. frontal polymerization, integral equation, initiation

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1. Introduction.

Frontal polymerization is the process of converting a monomer into a polymer by means of a self-propagating high temperature reaction wave. The chemical process involves two species: a monomer and an initiator, which is needed to start the growth of polymer chains. In a typical experiment, the species are placed into a test tube, and the temperature at the end of the tube is increased by applying a heat source. The increase in temperature induces decomposition of the initiator, which produces active radicals, and the highly exothermic propagation process begins. The resulting heat release promotes initiator decomposition ahead of the front, and a self-sustained reaction wave travels through the mixture leaving polymer in its wake.

Experimental and theoretical studies of frontal polymerization began in the 1970s (see references 1–4 in [5]). In [5] and [6], a mathematical model for the five species reaction is presented, and traveling wave solutions are sought. In these theoretical examinations of the process, the focus has been on the propagation of the thermal front and its velocity, the spatial profiles of the species involved, the degree of conversion of monomer, and the final temperature of the mixture. Initiation of a polymerization front is presumed. From experimental work, however, it is found that initiation of the front does not always occur. It is desirable to determine the dependence of initiation on the amount of reactants at the onset of the experiment, the initial temperature, the heat control imposed at the end of the test tube, and the properties of the initiator.

The purpose of this paper is to examine the initiation process necessary for propagation. In this respect, the current study is similar to ignition considerations in solid phase combustion problems. Unlike the combustion problem with a single reactant, the frontal polymerization process involves several chemical reaction steps with different reaction rates and activation energies. However, the reaction mechanism in both types of problem is assumed to be Arrhenius, and, upon nondimensionalization of the kinetic equations governing frontal polymerization, we can obtain a system of partial

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differential equations of a form similar to those arising in solid phase combustion. For this reason, the techniques applied in the current analysis are similar to those employed in [1, 2, 3, 4] in the examination of ignition of a combustible half-space. Lasseigne and Olmstead [4] consider the effects of reactant consumption, and they derive an integral equation governing the temperature at the ignition site. In this paper, we show that the mechanism governing initiation of the polymerization front gives rise to a similar two parameter integral equation governing the temperature in the transitional heating stage. In fact, under certain limiting conditions, the integral equation in [4] for a first order Arrhenius reaction appears as a special case of the integral equation presented in the current work. An asymptotic analysis of this integral equation is given, and numerical results are presented.

2. The mathematical model. The typical experiment in free radical frontal polymerization involves placing a mixture of initiator and monomer into a test tube. Assuming that the cross-sectional area of the tube is small relative to its length, we can model the tube as a thin semi-infinite channel $\hat{x} \geq 0$. A boundary condition on the heat flux will be prescribed at the end ($\hat{x} = 0$). The evolution of the reactants and the temperature can then be tracked. A mathematical model for a five species reaction is derived in [5] and [6], and the following system of equations governing the kinetics at time $\hat{t}$ in dimensional coordinates is given:

$$\frac{dI}{d\hat{t}} = -k_d I, \tag{2.1}$$

$$\frac{dR}{d\hat{t}} = 2fk_d I - k_i RM - k_e RR_p, \tag{2.2}$$

$$\frac{dM}{d\hat{t}} = -k_i RM - k_p MR_p, \tag{2.3}$$

$$\frac{dR_p}{d\hat{t}} = k_i RM - k_e RR_p - 2k_t R_p^2, \tag{2.4}$$

$$\frac{dP}{d\hat{t}} = k_e RR_p + k_t R_p^2. \tag{2.5}$$

The five species are the initiator, free radicals, monomer, polymer radicals, and the final polymer, denoted by I, R, M, R_p, and P, respectively. The parameter f appearing in the second equation is the ratio of primary radicals in the polymer to the primary radicals formed by the initiator. In practice, its value is taken to be $1/2$ (see [5]). The quantities, written above as k with a subscript, are assumed to have an Arrhenius dependence on the temperature T of the system. Thus, they can be expressed as

$$k_\alpha(T) = k_\alpha^0 \exp\left(\frac{-E_\alpha}{R_g T}\right) \quad \text{for} \quad \alpha = d, i, p, e, t.$$

Here, k_α^0 is the frequency factor, E_α is the activation energy for the corresponding reaction, and R_g is the universal gas constant. The subscripts correspond to the five reaction steps—initiator decomposition d, polymer chain initiation i, chain propagation p, free radical termination e, and polymer radical termination t.

To formulate the heat balance in the system, we note that the decomposition step is slightly endothermic but that each of the four subsequent reactions is exothermic. However, the most significant heat release occurs in the propagation step [9]. Thus, only this contribution to the net energy of the system will be considered here. Letting

$T(\hat{t}, \hat{x})$ denote the temperature of the mixture at time $\hat{t}$ and at the point $\hat{x}$, $\kappa > 0$ the thermal diffusivity of the mixture, and $q > 0$ the increase in temperature induced per unit reacted monomer, we can write the following reaction diffusion equation governing the temperature:

$$\frac{\partial T}{\partial \hat{t}} = \kappa \frac{\partial^2 T}{\partial \hat{x}^2} - q \frac{\partial M}{\partial \hat{t}}. \tag{2.6}$$

Equations (2.1)–(2.6), together with appropriate initial and boundary conditions, completely describe the state of the mixture. Because we are interested in initiation of a polymerization front, we will consider a reduced system obtained by imposing the quasi-steady-state assumption (QSSA) [6], reducing the number of unknowns as in [5] and [6], and considering only the evolution of the initiator, the monomer, and the temperature. The QSSA states that the level of free and polymer radicals in the mixture is nearly constant. Hence, we set $(d/d\hat{t})(R + R_p) = 0$. In addition, we make the following simplifying assumptions as justified in [6]:

$$k_i = k_p,\ k_e = k_t, \quad \text{and} \quad R_p \gg R.$$

Summing (2.2) and (2.4) and making the aforementioned assumptions yields

$$R + R_p \approx \sqrt{\frac{2fk_d}{k_t}}\sqrt{I}.$$

Then (2.3) becomes

$$\frac{dM}{d\hat{t}} = -k_p \sqrt{\frac{2fk_d}{k_t}} M\sqrt{I}.$$

Noting that the coefficient in front of M in the above equation is an Arrhenius exponential motivates the following convenient notation for the effective reaction rate:

$$k_{eff} = k_p\sqrt{\frac{2fk_d}{k_t}}, \quad k^0_{eff} = k^0_p\sqrt{\frac{2fk^0_d}{k^0_t}}, \quad \text{and} \quad E_{eff} = \frac{1}{2}(E_d - E_t) + E_p.$$

The initial amounts of monomer and initiator present are known and will be denoted by M_0 and I_0. Similarly, the initial temperature of the system is given as T_0. In the current work, we will assume that the boundary condition on the temperature at $\hat{x} = 0$ will be a Neumann condition. That is, the heat flux is prescribed as

$$\frac{\partial T}{\partial \hat{x}} = -\hat{h}(\hat{t}) \quad \text{for} \quad \hat{x} = 0,\ \hat{t} > 0.$$

Further, we assume that $\hat{h}(\hat{t}) > 0$ for all $\hat{t}$. This restriction implies an energy input at the end of the test tube. Finally, the temperature far from the end is assumed to be equal to the initial temperature. The reduced, dimensional form of the system to be studied can then be written as

$$\frac{\partial I}{\partial \hat{t}} = -k_d(T)I, \quad I(0) = I_0, \tag{2.7}$$

$$\frac{\partial M}{\partial \hat{t}} = -k_{eff}(T)M\sqrt{I}, \quad M(0) = M_0, \tag{2.8}$$

$$\frac{\partial T}{\partial \hat{t}} = \kappa \frac{\partial^2 T}{\partial \hat{x}^2} + qk_{eff}(T)M\sqrt{I}, \quad T(0, \hat{x}) = T_0, \quad \hat{x} \geq 0, \tag{2.9}$$

$$\frac{\partial T(\hat{t}, 0)}{\partial \hat{x}} = -\hat{h}(\hat{t}), \quad \text{and} \quad T \to T_0 \quad \text{as} \quad \hat{x} \to \infty. \tag{2.10}$$

3. Scaling and nondimensionalization. Because the activation energies are relatively large, the Arrhenius reaction terms are insignificant, provided that the temperature is relatively small. Thus, we will consider a critical value of the temperature T_c at which the reaction terms become appreciable. The value of T_c will be made more precise later. Further, the largeness of the activation energies facilitates a perturbation scheme in solving for the temperature. Hence, we introduce the small parameter

$$\epsilon = \frac{R_g T_c}{E_{eff}}$$

and define the quantities

$$r = \frac{E_d}{E_{eff}}, \qquad \tilde{k}_d^0 = k_d^0 e^{-r/\epsilon}, \qquad \tilde{k}_{eff}^0 = k_{eff}^0 e^{-1/\epsilon},$$

$$t_* = (\tilde{k}_{eff}^0 \sqrt{I_0}\,)^{-1}, \qquad x_* = \sqrt{\kappa t_*}.$$

We also introduce the nondimensional variables

$$\phi = \frac{I}{I_0}, \quad \psi = \frac{M}{M_0}, \quad \theta = \frac{T}{T_c}, \quad \theta_0 = \frac{T_0}{T_c},$$
$$h(t) = \frac{x^*}{T_c}\hat{h}(\hat{t}), \quad t = \frac{\hat{t}}{t_*}, \quad \text{and} \quad x = \frac{\hat{x}}{x_*}.$$

From (2.7)–(2.9), we obtain the corresponding nondimensional system:

$$\frac{\partial \phi}{\partial t} = -A\phi \exp\left\{\frac{r}{\epsilon}\left(1 - \frac{1}{\theta}\right)\right\}, \quad \phi(0) = 1, \tag{3.1}$$

$$\frac{\partial \psi}{\partial t} = -\psi\sqrt{\phi} \exp\left\{\frac{1}{\epsilon}\left(1 - \frac{1}{\theta}\right)\right\}, \quad \psi(0) = 1, \tag{3.2}$$

$$\frac{\partial \theta}{\partial t} = \frac{\partial^2 \theta}{\partial x^2} + B\psi\sqrt{\phi} \exp\left\{\frac{1}{\epsilon}\left(1 - \frac{1}{\theta}\right)\right\}, \quad \theta(0,x) = \theta_0, \tag{3.3}$$

$$\frac{\partial \theta(t,0)}{\partial x} = -h(t), \quad \text{and} \quad \theta \to \theta_0 \quad \text{as} \quad x \to \infty. \tag{3.4}$$

The additional nondimensional parameters A and B appearing in (3.1) and (3.3) are defined by

$$A = \frac{\tilde{k}_d^0}{\tilde{k}_{eff}^0 \sqrt{I_0}} \quad \text{and} \quad B = \frac{M_0 q}{T_c}.$$

The role of initiator consumption in the possible inhibition of initiation is inherent in the scaling of these two parameters. If A is large, for example, we can expect that the amount of initiator will rapidly decay. This rapid decay or an insufficient quantity of initiator at the onset of the experiment will cause the reaction to stop before a thermal front can develop. Similarly, if B is small, the effect of the reaction term in (3.3) is decreased. This can result in insufficient heat to initiate and maintain propagation of the polymer chain. In the present analysis, the following scaling will be assumed:

$$A = A_0\epsilon^{-1} \quad \text{and} \quad B = B_0\epsilon^{-\frac{1}{2}},$$

with $A_0 = O(1)$ and $B_0 = O(1)$ with respect to ϵ. The numerical values of A, B, and ϵ depend on the choice of reactants, their kinetic properties, and the conditions of the

experiment (e.g., pressure and ambient temperature). Extensive tabulated values of activation energies, preexponential factors, and other kinetic parameters for various initiators and monomers can be found in [10]. For typical values of the physical parameters appearing in (2.7)–(2.10), the value of ϵ is expected to be in the range of 10^{-4} to 10^{-3}. Moreover, at room temperature the values of A_0 and B_0 can range between 0.01 and 10. Given the typical range of values for ϵ, this is consistent with the assumption that A_0 and B_0 are $O(1)$ with respect to ϵ.

For fixed A_0, the quantity T_c is defined by the relation

$$A = \frac{k_d(T_c)}{k_{eff}(T_c)\sqrt{I_0}}. \tag{3.5}$$

Equations (3.1) and (3.2) are separable and can be solved explicitly. We have

$$\phi(t) = \exp\left(-A\int_0^t e^{\frac{r}{\epsilon}\left(1-\frac{1}{\theta}\right)}\,ds\right),$$
$$\psi(t) = \exp\left(-\int_0^t e^{\frac{1}{\epsilon}\left(1-\frac{1}{\theta}\right)} \times e^{-\frac{A}{2}\int_0^s e^{\frac{r}{\epsilon}\left(1-\frac{1}{\theta}\right)}\,dq}\,ds\right).$$

Upon substitution of the above into the boundary value problem (3.3)–(3.4), the system reduces to one involving only a single dependent variable. In the next section, an asymptotic solution to (3.3)–(3.4) will be derived.

4. Solving for the temperature. As stated, we consider the initial temperature to be small so that the reaction terms are negligible at the onset of the experiment—during the inert heating stage. In the formulation above, this means that we take $\theta_0 < 1$ and $1-\theta_0 = O(1)$ with respect to ϵ. This allows us to initially ignore the Arrhenius term, which is mathematically equivalent to taking the limit $\epsilon \to 0$ in (3.1)–(3.3). Let θ_I be given by

$$\theta_I(t,x) = \theta_0 + \int_0^t h(\tau)\frac{e^{\frac{-x^2}{4(t-\tau)}}}{\sqrt{\pi(t-\tau)}}\,d\tau.$$

Then θ_I solves the problem (3.3)–(3.4) in the limit $\epsilon \to 0$; we will call this the inert solution. From $0 < 1-\theta_0$ and $1-\theta_0 = O(1)$, it follows that initially

$$\theta = \theta_I + \text{e.s.t.},$$

where e.s.t. represents terms that are exponentially small with respect to ϵ. However, this remains valid only until such time as $\theta_I \approx 1$. In order to continue the analysis, let us define the critical time t_c to be the smallest value such that

$$1 = \theta_I(t_c,0) = \theta_0 + \int_0^{t_c} \frac{h(\tau)}{\sqrt{\pi(t_c-\tau)}}\,d\tau.$$

For arbitrary $h(t)$, such a critical time need not exist. This suggests a restriction on the class of boundary conditions that can lead to initiation. We will assume that the imposed flux $h(t)$ given is such that this critical time does exist. Also note that the above is evaluated at $x = 0$ because θ_I attains its maximum at the end $x = 0$. The inert stage of the reaction ends in the neighborhood of $(t_c, 0)$, and the system enters a transition stage where the reaction terms first become appreciable. To further

our investigation, we perturb about this point and introduce the new independent variables

$$\xi = \frac{x}{\epsilon}, \qquad \tau = \frac{t - t_c}{\epsilon}.$$

In these inner variables, (3.1)–(3.3) become

$$\phi_\tau = -A_0 \phi \exp\left\{\frac{r}{\epsilon}\left(1 - \frac{1}{\theta}\right)\right\}, \quad \phi \to 1 \quad \text{as} \quad \tau \to -\infty, \tag{4.1}$$

$$\psi_\tau = -\epsilon \psi \sqrt{\phi} \exp\left\{\frac{1}{\epsilon}\left(1 - \frac{1}{\theta}\right)\right\}, \quad \psi \to 1 \quad \text{as} \quad \tau \to -\infty, \tag{4.2}$$

$$\epsilon\theta_\tau = \theta_{\xi\xi} + \epsilon^{3/2} B_0 \psi \sqrt{\phi} \exp\left\{\frac{1}{\epsilon}\left(1 - \frac{1}{\theta}\right)\right\}, \quad \theta \to \theta_0 \quad \text{as} \quad \tau \to -\infty, \tag{4.3}$$

$$\theta_\xi = O(\epsilon) \quad \text{for} \quad \xi = 0 \quad \text{and} \quad \tau > -\infty. \tag{4.4}$$

We note here that the conditions at $t = 0$ in the outer variables correspond asymptotically to conditions in the inner variables as $\tau \to -\infty$. The first two equations can again be solved to obtain

$$\phi(\tau) = \exp\left(-A_0 \int_{-\infty}^{\tau} e^{\frac{r}{\epsilon}\left(1 - \frac{1}{\theta}\right)}\, ds\right), \tag{4.5}$$

$$\psi(\tau) = \exp\left(-\epsilon \int_{-\infty}^{\tau} e^{\frac{1}{\epsilon}\left(1 - \frac{1}{\theta}\right)} \times e^{-\frac{A_0}{2}\int_{-\infty}^{s} e^{\frac{r}{\epsilon}\left(1 - \frac{1}{\theta}\right)}\, dq}\, ds\right). \tag{4.6}$$

Substitution of these integrals into (4.3)–(4.4) yields a single problem in the variable θ.

4.1. An asymptotic expansion. We seek an asymptotic expansion for θ of the form

$$\theta = \theta_I + \epsilon\theta^0 + \epsilon^{3/2}\theta^1 + \cdots.$$

Then we can expand θ_I about $(t_c, 0)$ and write

$$\theta_I = 1 + \epsilon a\tau - \epsilon b\xi + o(\epsilon), \tag{4.7}$$

where

$$a = \lim_{t \to t_c} \frac{\partial \theta_I}{\partial t}, \qquad b = -\lim_{x \to 0} \frac{\partial \theta_I}{\partial x}.$$

For the continued analysis, we must assume that these limits exist and that $a > 0$ and $b > 0$. The latter condition follows from requiring that h be a nonnegative function for all times corresponding to an influx of energy at the end of the test tube. The condition $a > 0$ implies that the temperature is increasing at the onset of the transition phase. Both of these are consistent with the potential for initiation.

Substitution of (4.7) into the expansion of θ yields

$$\theta = 1 + \epsilon(a\tau - b\xi + \theta^0) + \epsilon^{3/2}\theta^1 + o(\epsilon^{3/2}),$$

so that

$$\frac{1}{\epsilon}\left(1 - \frac{1}{\theta}\right) = (a\tau - b\xi + \theta^0) + o(1).$$

Combining this result with (4.5) and (4.6) and substituting into the boundary value problem (4.3)–(4.4), we arrive at the equations governing θ^0 and θ^1:

$$O(\epsilon): \quad \begin{aligned} &\theta^0_{\xi\xi} = 0, \\ &\theta^0(-\infty,\xi) = 0, \quad \theta^0_\xi(\tau,0) = 0, \end{aligned} \tag{4.8}$$

$$O(\epsilon^{3/2}): \quad \begin{aligned} &\theta^1_{\xi\xi} = -B_0 e^{a\tau - b\xi + \theta^0} \exp\left(\tfrac{-A_0}{2}\int_{-\infty}^{\tau} e^{r(as-b\xi+\theta_0)}\,ds\right), \\ &\theta^1(-\infty,\xi) = 0, \quad \theta^1_\xi(\tau,0) = 0. \end{aligned} \tag{4.9}$$

Equation (4.8) has solution

$$\theta^0(\tau,\xi) = f_0(\tau), \quad \text{where} \quad f_0(\tau) \to 0 \text{ as } \tau \to -\infty.$$

This is substituted into (4.9) to obtain

$$\theta^1(\tau,\xi) = -B_0 e^{a\tau + f_0(\tau)} \int_0^\xi \int_0^z e^{-b\hat{z}} \exp\left(\frac{-A_0}{2} e^{-rb\hat{z}} \int_{-\infty}^{\tau} e^{r(as+f_0(s))}\,ds\right) d\hat{z}\,dz + f_1(\tau),$$

with $f_1(\tau) \to 0$ as $\tau \to -\infty$.

The function $f_0(\tau)$ governs the first order correction to the inert solution in the transition stage.

4.2. The transition stage solution. In order to determine the nature of f_0 we need a matching condition for large ξ. To this end, we consider the stretched space variable

$$X = \sqrt{\epsilon}\xi.$$

Let $\hat{\Theta}$ represent the solution in the boundary layer. From (4.3) we have

$$\hat{\Theta}_\tau = \hat{\Theta}_{XX} + O(\epsilon^{1/2}).$$

Assuming that θ has the following form in the boundary layer,

$$\theta = \theta_I + \epsilon\hat{\Theta}^0 + \epsilon^{3/2}\hat{\Theta}^1 + \cdots,$$

the $O(\epsilon)$ problem is

$$\hat{\Theta}^0_\tau = \hat{\Theta}^0_{XX}, \quad \hat{\Theta}^0 \to 0 \text{ as } \tau \to -\infty.$$

Additional conditions at $X = 0$ are needed and are determined by matching to the outer solution. Observe that as $X \to 0$ and $\xi \to \infty$,

$$\epsilon\hat{\Theta}^0 + \epsilon^{3/2}\hat{\Theta}^1 + \cdots = \epsilon\theta^0 + \epsilon^{3/2}\theta^1 + \cdots, \tag{4.10}$$

$$\begin{aligned} \epsilon\hat{\Theta}^0_X + \epsilon^{3/2}\hat{\Theta}^1_X + \cdots &= 0 + \epsilon^{3/2}\theta^1_X + \cdots \\ &= 0 + \epsilon^{3/2}(\epsilon^{-1/2}\theta^1_\xi) + \cdots. \end{aligned} \tag{4.11}$$

Equating by powers in ϵ, the above implies that

$$\lim_{X\to 0} \hat{\Theta}^0(\tau,X) = \lim_{\xi\to\infty} \theta^0(\tau,\xi), \qquad \lim_{X\to 0} \hat{\Theta}_X(\tau,X) = \lim_{\xi\to\infty} \theta^1_\xi(\tau,\xi).$$

The equation that $\hat{\Theta}^0$ satisfies is

$$\begin{aligned} \hat{\Theta}^0_\tau &= \hat{\Theta}^0_{XX}, \\ \hat{\Theta}^0_X(\tau,0) &= -B_0 e^{a\tau+f_0(\tau)} \int_0^\infty e^{-bz} e^{\frac{-A_0}{2} e^{-rbz} \int_{-\infty}^{\tau} e^{r(as+f_0(s))}\,ds}\,dz \\ &\equiv J(\tau), \\ \hat{\Theta}^0 &\to 0 \text{ as } \tau \to -\infty. \end{aligned} \tag{4.12}$$

The additional condition

$$\hat{\Theta}^0(\tau,0) = f_0(\tau)$$

determines the unknown function f_0. The solution of (4.12) can be expressed in terms of the Green's function

$$\hat{\Theta}^0(X,\tau) = -\int_{-\infty}^{\tau} J(\sigma) G(X,\tau;0,\sigma)\,d\sigma,$$

where

$$G(X,\tau;0,\sigma) = \frac{1}{\sqrt{\pi(\tau-\sigma)}} e^{\frac{-X^2}{4(\tau-\sigma)}}.$$

Finally, applying the condition on $\hat{\Theta}^0$ at $X=0$, we arrive at the nonlinear integral equation governing the temperature in the transition stage:

$$f_0(\tau) = -\int_{-\infty}^{\tau} \frac{J(\sigma)}{\sqrt{\pi(\tau-\sigma)}}\,d\sigma = \frac{B_0}{b}\int_{-\infty}^{\tau} \frac{e^{f_0(\sigma)+a\sigma}}{\sqrt{\pi(\tau-\sigma)}} Q(\sigma)\,d\sigma, \tag{4.13}$$

where

$$Q(\sigma) = \int_0^\infty b e^{-bz} \exp\left(-e^{-rbz}\frac{A_0}{2}\int_{-\infty}^{\sigma} e^{r(f_0(s)+as)}\,ds\right)\,dz.$$

In the next section, we will examine the integral equation (4.13). We will perform a coordinate change resulting in the appearance of an additional parameter governing the qualitative behavior of the solution. Existence considerations will be addressed, and both analytical and numerical results presented.

5. Analysis of the integral equation. The parameter r was defined as the ratio of the decomposition activation energy to the effective activation energy obtained by applying the QSSA. Typical experimental values of the activation energy for decomposition, propagation, and termination are such that $E_d \gg E_p \gg E_t$. It follows that the ratio r is roughly 2. We will consider only values of r such that $1 < r \le 2$, with special attention given to the case $r = 2$.

The integral Q appearing in (4.13) can be expressed in terms of gamma functions. Note that

$$\int_0^\infty b e^{-bz} \exp\left(-e^{-rbz}\frac{A_0}{2}\int_{-\infty}^{\sigma} e^{r(f_0(s)+as)}\,ds\right)\,dz = \frac{\Gamma\left(\frac{1}{r}\right)}{r}\,\gamma\left(\frac{1}{r}, q(\sigma)\right),$$

where

$$q(\sigma) = \frac{A_0}{2}\int_{-\infty}^{\sigma} e^{r(f_0(s)+as)}\,ds,$$

Γ is the gamma function, and γ is the incomplete gamma function defined by

$$\gamma(\alpha, z) = \frac{z^{-\alpha}}{\Gamma(\alpha)} \int_0^z e^{-t} t^{\alpha-1}\, dt.$$

To facilitate the analysis of the integral equation, let us introduce the change of variables

$$\eta = a\tau + \log\left(\frac{B_0}{b\sqrt{a}}\right) \quad \text{and} \quad u(\eta) = f_0(\tau).$$

In these new coordinates, (4.13) takes the form

$$u(\eta) = \int_{-\infty}^{\eta} \frac{e^{u(\sigma)+\sigma}}{\sqrt{\pi(\eta-\sigma)}} F_r\left(\lambda_r \int_{-\infty}^{\sigma} e^{r(u(s)+s)}\, ds\right) d\sigma. \tag{5.1}$$

The function F_r appearing above is defined by

$$F_r(x) = \frac{\Gamma\left(\frac{1}{r}\right)}{r}\, \gamma\left(\frac{1}{r}, x\right) \quad \text{for} \quad x > 0, \quad \text{with} \quad F_r(0) = 1,$$

and the parameter λ_r is the ratio

$$\lambda_r = a^{r/2-1} \frac{A_0 b^r}{2B_0^r} \geq 0.$$

Note that in the limiting case $r = 2$,

$$F_2(x) = \frac{\sqrt{\pi}}{2} \frac{\operatorname{erf}(\sqrt{x})}{\sqrt{x}}$$

and

$$\lambda_2 = \frac{A_0 b^2}{2B_0^2}.$$

A number of observations should be made about the parameter λ_r and the function F_r defined above. First, in the limiting case, $\lambda = 0$ ($F_r \equiv 1$), equation (5.1) reduces to the integral equation derived by Liñàn and Williams [1], Kapila [2], and Olmstead [3]. It is known that this equation has a solution u that is positive and monotonically increasing, with the asymptotic behavior

$$u \sim e^{\eta} + \frac{1}{\sqrt{2}} e^{2\eta} + \cdots \quad \text{as} \quad \eta \to -\infty,$$
$$u \sim -\frac{1}{2} \log(\eta^* - \eta) + \cdots \quad \text{as} \quad \eta \to \eta^*,$$

with $\eta^* \approx -0.431$ determined numerically. Also, for every value of r, F_r is positive monotonically decreasing, with $F_r \to 0$ as its argument tends to infinity. If $r = 1$, then (5.1) is exactly that obtained by Lasseigne and Olmstead [4] governing ignition of a solid half-space with first order Arrhenius reaction and accounting for reactant consumption. They found that there is a critical value of the parameter λ_1 such that, for values less than this critical value, the solution u becomes unbounded in finite time—it is this unbounded behavior that is taken to signal the onset of ignition.

For values of λ_1 larger than this critical value, the solution remains bounded for all finite time. It is the decaying nature of F_r that serves to inhibit initiation of a polymerization front. This is the case for all r on $1 < r \leq 2$. However, for fixed x note that $(d/dr)\, F_r(x) > 0$. Hence, as r increases, F_r decays less rapidly. As will be shown in section 5.3, $r = 2$ appears to be an upper limit for the possible existence of solutions exhibiting the type of logarithmic singularity analogous to those discussed in [3] and [4].

5.1. Existence of solutions to the integral equation. We continue the analysis by establishing the existence of solutions to (5.1). This is useful because it will establish a lower bound on the time of initiation. To that end, let us consider the class of bounded functions

$$S = \{u : (-\infty, \tilde{\eta}] \to [0, N]\},$$

where $\tilde{\eta} > -\infty$ and $0 < N < \infty$. Additionally, let the integral operator T be given by

$$Tu \longmapsto \int_{-\infty}^{\eta} \frac{e^{u(\sigma)+\sigma}}{\sqrt{\pi(\eta-\sigma)}} F_r\left(\lambda_r \int_{-\infty}^{\sigma} e^{r(u(s)+s)}\, ds\right) d\sigma \quad \text{for} \quad \eta \leq \tilde{\eta},\ u \in S.$$

Conditions on $\tilde{\eta}$ and N are sought to ensure that T is a contraction on S. First, observe that, for $u \in S$,

$$Tu \leq e^N I_0(\eta; r, \lambda_r),$$

where

$$I_0(\eta; r, \lambda_r) = \int_{-\infty}^{\eta} \frac{e^{\sigma}}{\sqrt{\pi(\eta-\sigma)}} F_r\left(\frac{\lambda_r}{r} e^{r\sigma}\right) d\sigma.$$

Second, let u_1 and u_2 be elements of S. Then

$$|Tu_1 - Tu_2| \leq \sup_{u_1, u_2 \in S} |u_1 - u_2| \left\{ e^N I_0(\eta; r, \lambda_r) + e^{(r+1)N} I_1(\eta; r, \lambda_r) \right\},$$

where

$$I_1(\eta; r, \lambda_r) = \lambda_r \int_{-\infty}^{\eta} \frac{e^{(r+1)\sigma}}{\sqrt{\pi(\eta-\sigma)}} \left| F_r'\left(\frac{\lambda_r}{r} e^{r\sigma}\right) \right| d\sigma.$$

Since I_0 and I_1 are monotonic increasing in η, we can conclude that T is a contraction on S, provided

$$I_0(\tilde{\eta}; r, \lambda_r) \leq N e^{-N} \tag{5.2}$$

and

$$e^N I_0(\tilde{\eta}; r, \lambda_r) + e^{(r+1)N} I_1(\tilde{\eta}; r, \lambda_r) < 1. \tag{5.3}$$

For given λ_r, there exists a unique pair $\hat{N} < 1,\ \hat{\eta} > -\infty$ such that (5.2) and (5.3) are satisfied as equalities. That is,

$$e^{\hat{N}} I_0(\hat{\eta}; r, \lambda_r) = \hat{N},$$
$$e^{\hat{N}} I_0(\hat{\eta}; r, \lambda_r) + e^{(r+1)\hat{N}} I_1(\hat{\eta}; r, \lambda_r) = 1.$$

Inequalities (5.2) and (5.3) are satisfied for $N = \hat{N}$ and any choice of $\tilde{\eta} < \hat{\eta}$. We note that the value of $\hat{\eta}(\lambda_r)$ provides a lower bound on the time of initiation for given λ_r. Moreover, $\hat{N}$ and $\hat{\eta}$ have the following asymptotic expansions for $\lambda_r \ll 1$ and $\lambda_r \to \infty$:

$$\hat{N} \sim 1 - \frac{\lambda_r}{(r+1)^{3/2}} + \cdots,$$
$$\hat{\eta} \sim -1 + \frac{\lambda_r}{re^r(r+1)^{3/2}} + \cdots \quad \text{as} \quad \lambda \to 0$$

and

$$\hat{N} \sim \hat{N}_\infty + \cdots,$$
$$\hat{\eta} \sim \lambda_r^{2/r}\left(\frac{\pi}{4\Gamma^2(\frac{1}{r})} r^{2-2/r}\right)\hat{N}_\infty^2 e^{-2\hat{N}_\infty} + \cdots \quad \text{as} \quad \lambda \to \infty.$$

The value $\hat{N}_\infty$ is the solution to the transcendental equation $\hat{N}_\infty = (1 - \hat{N}_\infty)e^{-r\hat{N}_\infty}$. For $1 < r \leq 2$, the value of $\hat{N}_\infty$ is such that $0.33 \leq \hat{N}_\infty < 0.41$. Also, $r \leq 2$ and $\hat{\eta} = O(\lambda_r^{2/r})$ as $\lambda_r \to \infty$ suggests that the onset of initiation can be delayed as long as desired by taking λ_r sufficiently large.

We anticipate two qualitatively different types of solutions to (5.1), depending on the value of λ_r. Self-consistent analyses for solutions that remain bounded in finite time and those that exhibit an unbounded singularity at a finite time are sought. Such solutions are interpreted as indicating noninitiation and initiation of a front, respectively. Moreover, for a given r, there is a critical value λ_r^c separating the initiation and noninitiation regimes.

5.2. Noninitiation solutions. First, we consider the existence of solutions bounded for all finite η. To this end, assume that the solution u has the following form:

$$u \sim C\eta^d \quad \text{as} \quad \eta \to \infty, \tag{5.4}$$

where C and d are constants to be determined. If $\lambda_r > 0$ and $d < 1$, then (5.4) implies

$$e^{u+\eta}F_r\left(\lambda_r \int_{-\infty}^{\eta} e^{r(u+s)}\,ds\right) \sim \frac{\Gamma(\frac{1}{r})}{r}\left(\frac{r}{\lambda_r}\right)^{1/r} \quad \text{as} \quad \eta \to \infty.$$

For each $\eta \gg 1$, we can write

$$u(\eta) = C_0 + J(\eta),$$

where J is defined as

$$J(\eta) = \frac{1}{\sqrt{\pi}}\int_0^{\eta} \frac{e^{u+\eta}}{\sqrt{\eta - \sigma}} F_r\left(\lambda_r \int_{-\infty}^{\sigma} e^{r(u+s)}\,ds\right)\,d\sigma.$$

Employing the asymptotic techniques given in [7], we find that, as $\eta \to \infty$,

$$J(\eta) \sim \frac{2\Gamma(\frac{1}{r})}{r\sqrt{\pi}}\left(\frac{r}{\lambda_r}\right)^{1/r}\eta^{1/2} + \cdots.$$

Hence, u has the form given in (5.4), with the constants determined as

$$C = \frac{2\Gamma(\frac{1}{r})}{r\sqrt{\pi}}\left(\frac{r}{\lambda_r}\right)^{1/r} \quad \text{and} \quad d = \frac{1}{2}.$$

Note that $d < 1$, which is consistent with our initial requirement. If λ_r is large enough so as to advance the damping effect of F_r appearing in the integrand of (5.1), the leading order behavior of the solution is expected to be square root growth. In section 5.4, numerical confirmation of this is presented.

5.3. Initiation solutions. Next, we look for solutions of (5.1) that become unbounded at some finite time value η^*. In the case $\lambda_r = 0$, we know that the solution of (5.1) has a logarithmic singularity as previously discussed. This motivates looking for behavior of the form

$$u \sim -\beta \log(\eta^* - \eta) + \cdots \quad \text{as} \quad \eta \to \eta^*, \tag{5.5}$$

where $\beta = \beta(\lambda_r)$ and $\eta^* = \eta^*(\lambda_r) < \infty$. The analysis is facilitated by translating the singularity to the point at infinity. The techniques given in [7] and [8] can then be used. In the coordinates

$$\rho = (\eta^* - \eta)^{-1}, \qquad v(\rho) = u(\eta),$$

equation (5.1) becomes

$$v(\rho) = \sqrt{\rho}\, e^{\eta^*} \int_0^\rho \frac{e^{v - s^{-1}}}{\sqrt{\pi(\rho - s)}} s^{-3/2} F_r \left(\lambda_r e^{r\eta^*} \int_0^s t^{-2} e^{rv - rt^{-1}}\, dt \right) ds, \tag{5.6}$$

and the asymptotic behavior of v is sought as ρ tends to infinity. The cases $1 < r < 2$ and $r = 2$ must be considered separately as they give rise to different matching requirements.

Suppose $1 < r < 2$ and

$$v \sim \log(\rho^{1/2}) + \log(P) + \log(1 + o(\rho^{1/2})) \quad \text{as} \quad \rho \to \infty, \tag{5.7}$$

where P is constant. Then, as $\rho \to \infty$,

$$\frac{e^{v - 1/\rho}}{\rho^{3/2}} F_r \left(\lambda_r e^{r\eta^*} \int_0^\rho t^{-2} e^{rv - rt^{-1}}\, dt \right) \sim P \rho^{-1} F_r(\lambda_r e^{r\eta^*} I_r(\infty)) + o(\rho^{-1}),$$

where

$$I_r(\infty) = \int_0^\infty \frac{e^{rv - r/t}}{t^2}\, dt < \infty.$$

By the results in [7] and [8], it follows that

$$\int_0^\rho \frac{e^{v - 1/s}}{s^{3/2}} F_r(\lambda_r e^{r\eta^*} I_r(s)) \frac{ds}{\sqrt{\pi(\rho - s)}} \sim \frac{P}{\sqrt{\pi}} F_r(\lambda_r e^{r\eta^*} I_r(\infty)) \rho^{-1/2} \log(\rho) \tag{5.8}$$

as $\rho \to \infty$. Comparison of (5.7) and (5.8) yields

$$P = \frac{\sqrt{\pi} e^{-\eta^*}}{2 F_r(\lambda_r e^{r\eta^*} I_r(\infty))}.$$

Hence,

$$v \sim \frac{1}{2} \log(\rho) + O(1) \quad \text{as} \quad \rho \to \infty,$$

and, returning to the previous coordinates, we have

$$u \sim \frac{-1}{2}\log(\eta^* - \eta) + O(1) \quad \text{as} \quad \eta \to \eta^*.$$

Different initial assumptions are needed when $r = 2$. In this case, we look for the solution of (5.6) to have the asymptotic form

$$v \sim \log(\rho^\beta) + \log(1 + o(\rho^\beta)) \quad \text{as} \quad \rho \to \infty. \tag{5.9}$$

Under the assumption (5.9), observe that the integral in the argument of F_2 appearing in (5.6) is finite only if $\beta > 1/2$. That is, matching can occur only if we restrict $\beta > 1/2$; this becomes a consistency condition on the analysis. Supposing that this is the case and that (5.9) holds, we find that

$$\frac{e^{v-\rho^{-1}}}{\rho^{3/2}} F_2\left(\lambda_2 e^{2\eta^*}\int_0^\rho \frac{e^{2v-2t^{-1}}}{t^2}\,dt\right) \sim \frac{\sqrt{\pi}}{2} e^{-\eta^*}\lambda^{-1/2}\rho^{-1}\sqrt{2\beta-1} + o(\rho^{-1})$$

as $\rho \to \infty$. Then, employing the results in [7] and [8],

$$\rho^{-1/2}e^{-\eta^*}v(\rho) \sim \frac{\lambda_2^{-1/2}}{2} e^{-\eta^*}\sqrt{2\beta-1}\rho^{-1/2}\log(\rho) \quad \text{as} \quad \rho \to \infty. \tag{5.10}$$

Comparing the left- and right-hand sides of this relation and using (5.9), we arrive at the equation for β:

$$\beta(\lambda_2) = \frac{1}{4\lambda_2}\left(1 - \sqrt{1 - 4\lambda_2}\right). \tag{5.11}$$

The following observations should be made about this result. First, note that $\beta > 1/2$, as was required for the derivation. Also, we see that this result makes sense—insofar as β is real—only for values of λ_2 between 0 and 0.25. This seems to suggest an upper bound of 0.25 on the critical value of λ_2. In fact, the numerical analysis confirms this where we find that $\lambda_2^c = 0.11998$. Finally, we note that $\beta \to 1/2$ as $\lambda_2 \to 0$, which is consistent with the results for $r < 2$ and those in [1] and [3] for the $\lambda = 0$ case. In terms of the variables u and η, the asymptotic results for the initiation case are summarized:

$$u \sim -\frac{1}{2}\log(\eta^* - \eta) + \cdots \quad \text{as} \quad \eta \to \eta^*(\lambda_r)$$

for $1 < r < 2$, and

$$u(\eta) \sim -\beta(\lambda_2)\log(\eta^*(\lambda_2) - \eta) + \cdots \quad \text{as} \quad \eta \to \eta^*(\lambda_2)$$

for $r = 2$ with β given by (5.11). In both cases, the value of η^* is to be determined numerically.

5.4. Numerical analysis. Equation (5.1) was solved numerically for several values of r and λ_r. Because the lower bound of the integral is infinite, the asymptotic form of the solution u as $\eta \to -\infty$ is useful. Using the properties of the incomplete

gamma function and the identity

$$\int_{-\infty}^{\eta} \frac{e^{\alpha\sigma}}{\sqrt{\pi(\eta-\sigma)}}\, d\sigma = \frac{e^{\alpha\eta}}{\sqrt{\alpha}} \quad \text{for all} \quad \alpha > 0,$$

we have

$$u \sim e^{\eta} + \frac{1}{\sqrt{2}} e^{2\eta} + \cdots \quad \text{as} \quad \eta \to -\infty, \tag{5.12}$$

$$\int_{-\infty}^{\sigma} e^{r(u+s)}\, ds \sim \frac{1}{r} e^{r\sigma} + \frac{r}{r+1} e^{(r+1)\sigma} + \cdots \quad \text{as} \quad \sigma \to -\infty. \tag{5.13}$$

We then fix $\eta_0 > -\infty$ and assume that for all $\eta, \sigma < \eta_0$ the relations (5.12) and (5.13) hold. Substituting (5.12) and (5.13) into (5.1), we arrive at the following equation, which is solved numerically:

$$\begin{aligned} u(\eta) = {} & e^{\eta} \operatorname{erfc}\sqrt{\eta-\eta_0} + \frac{1}{\sqrt{2}} e^{2\eta} \operatorname{erfc}\sqrt{2(\eta-\eta_0)} \\ & + \int_{\eta_0}^{\eta} \frac{e^{u+\sigma}}{\sqrt{\pi(\eta-\sigma)}} F_r\left(\lambda_r I_r(\sigma)\right)\, d\sigma, \end{aligned}$$

where

$$I_r(\sigma) = \frac{1}{r} e^{r\eta_0} + \frac{r}{r+1} e^{(r+1)\eta_0} + \int_{\eta_0}^{\sigma} e^{r(u+s)}\, ds.$$

This approach is similar to that applied by Lasseigne and Olmstead [4]. Moreover, if $r = 1$, the above reduces to the integral equation considered in [4] for a first order reaction term. The accuracy of the numerical methods employed in the current work was tested by comparing the results obtained for $r = 1$ with those in [4]. The value $\eta_0 = -10$ was found to be sufficient to produce reliable results, and this was used for all numerical trials given in this paper.

6. Results and discussion. For convenience, we restate the definition of the parameter λ_r here,

$$\lambda_r = a^{r/2-1} \frac{A_0 b^r}{2B_0^r},$$

and recall that A_0 and B_0 are measures of the consumption rate of initiator and heat release due to conversion of monomer, respectively; r $(1 < r \leq 2)$ is the ratio of activation energies associated with decomposition of initiator and polymer chain propagation. We see that λ_r is small, provided that A_0 is relatively small and B_0 relatively large. Hence, we can consider large values of λ_r to indicate an inadequate amount of initiator (i.e., initiator is consumed too rapidly) or that heat release is insufficient to sustain further reaction. Conversely, small values of λ_r represent a sufficiently exothermic reaction, in which the consumption rate of initiator is small relative to the amount of initiator present in the mixture. Small λ_r values are therefore expected to lead to initiation, while large values of λ_r are not. The appearance of a and b in the ratio is the effect of the inert heating, and the values of these parameters are controlled by the choice of heat source applied. As suggested by the results in [4] and the self-consistent analyses in sections 5.2 and 5.3 of this paper, there exists a critical value of λ_r separating the initiation and noninitiation regimes.

TABLE 6.1
The critical parameter value, λ_r^c, as a function of r.

r	1.5	1.8	1.9	2
λ_r^c	0.6645	0.31086	0.21058	0.11998

TABLE 6.2
Initiation time η^* for selected values of λ_2.

λ_2	0	0.01	0.1	0.117	0.11997
η^*	-0.4310	-0.4287	-0.4088	-0.4048	-0.4037

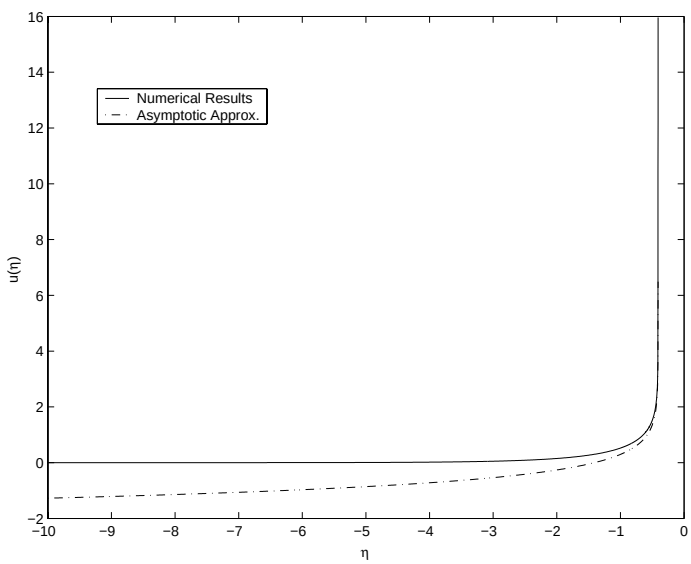

FIG. 6.1. *Initiation solution of the integral equation for $r = 2$ and $\lambda_2 = 0.1$ The solution approaches the asymptotic approximation $U = -\beta(0.1)\log(\eta^* - \eta)$ as $\eta \to \eta^* \approx -0.4088$.*

The critical parameter value, λ_r^c, was determined numerically for different r values. The results are given in Table 6.1. If $\lambda_r < \lambda_r^c$, then the solution exhibits a logarithmic singularity, with the asymptotic behavior described in section 5.3. For values of λ_r larger than λ_r^c, the solution to (5.1) exists and is finite for all η. When λ_r is only slightly larger than the critical value, the solution exhibits behavior on two time scales (see Figure 6.3). The temperature grows slowly while oscillating on a short time scale. This results from the competing effects of the exponential term appearing in (5.1) and the decaying function F_r. If λ_r is increased further, the solution has the leading form described in section 5.2.

The time at which initiation occurs for the case $r = 2$ is given in Table 6.2 for various λ_2, with the critical value found to be 0.11998. Solutions of the types described above for $r = 2$ are shown in Figures 6.1–6.4. In Figure 6.1, λ_2 is less than the critical value. The solution becomes unbounded at $\eta = -0.4088$. The asymptotic results are shown as a dashed curve for comparison. Similarly, Figure 6.2 shows the initiation solution for $\lambda_2 = 0.11997$, just slightly less than the critical value. In both cases, the singular behavior indicates that the temperature progresses beyond the transition stage, and a polymerization front is formed. In contrast, Figures 6.3 and 6.4 show the solution when λ_2 is above the critical value. In Figure 6.3, $\lambda_2 = 0.4$ and the

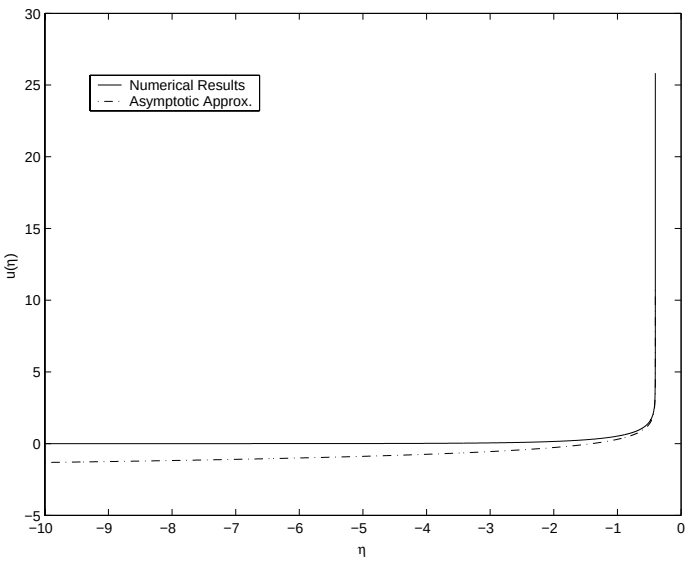

FIG. 6.2. *Initiation solution of the integral equation for* $r = 2$ *and* $\lambda_2 = 0.11997$*, just below the critical value of* 0.11998*. The solution approaches the asymptotic approximation* $U = -\beta(0.11997)\log(\eta^* - \eta)$ *as* $\eta \to \eta^* \approx -0.4037$*.*

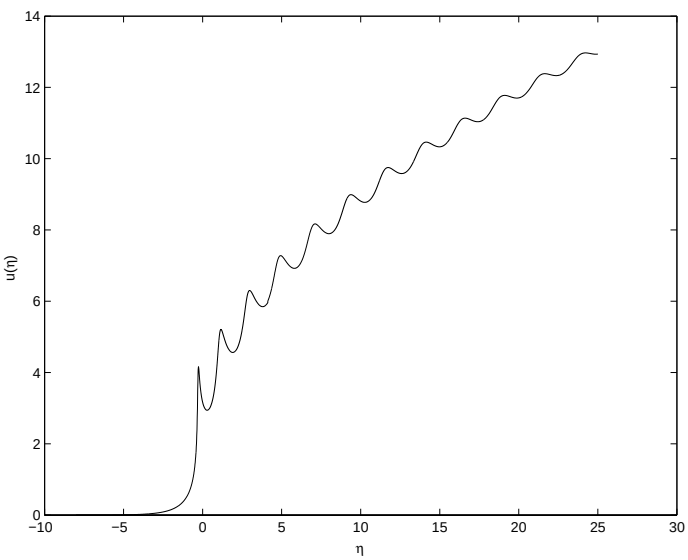

FIG. 6.3. *The noninitiation solution showing oscillation for* $r = 2$ *and* $\lambda_2 = 0.4$*.*

temperature oscillations described can be seen. However, the large scale behavior is slow growth with the oscillations damping as η increases. Figure 6.4 is a plot of the solution when $\lambda_2 = 1$. Here, the solution is monotonic with a change of concavity occurring in a neighborhood of $\eta = 0$. The temperature remains bounded, indicating that a reaction front does not form.

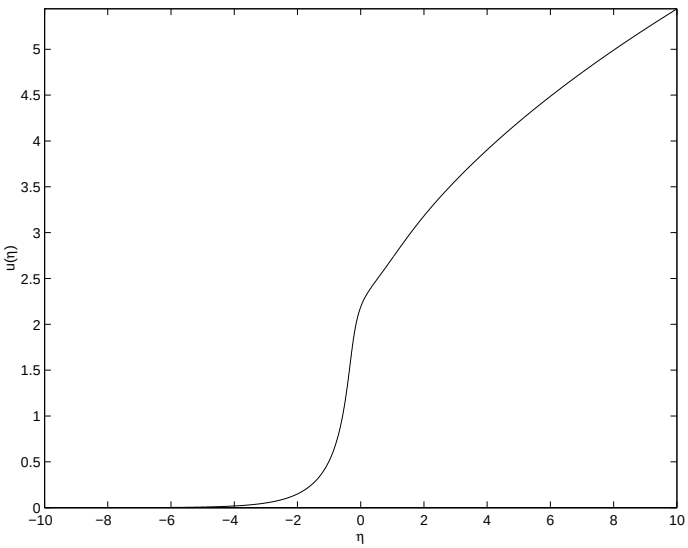

FIG. 6.4. *The noninitiation solution for $r = 2$ and $\lambda_2 = 1$.*

7. Summary and conclusion. A reduced system governing a five species reaction model of free radical frontal polymerization was considered, and the temperature was tracked from the inert heating to the transition stage. Through an asymptotic analysis, the integral equation (4.13) arose as the first correction to the inert solution. This integral equation was then rewritten by a change of variables as (5.1), where there appears the parameter λ_r which governs the qualitative behavior of the solution. For a fixed ratio of the activation energies, there is a critical value of the parameter λ_r^c such that the solution of (5.1) has an infinite singularity in finite time if $\lambda_r < \lambda_r^c$ but remains bounded for all time if $\lambda_r > \lambda_r^c$.

The unbounded and bounded types of solutions are taken to indicate initiation and noninitiation in the underlying system, initiation being the formation and onset of propagation of a polymerization front. In the noninitiation case, but for values of λ_r close to the critical value, an oscillatory type of solution was found numerically. The solution remains bounded in this case, and it appears that the oscillations dampen with the growth of the independent variable.

The experimental parameters can be chosen so as to ensure the onset of a thermal front. The critical temperature T_c used in the scaling can be determined by taking $A_0 = 1$ in the relation (3.5). This results in a transcendental equation for T_c,

$$\frac{E_{eff}}{R_g T_c} = \frac{k_d(T_c)}{k_{eff}(T_c)\sqrt{I_0}}.$$

Then, B_0 can be found in terms of the initial amount of monomer and the heat release parameter q, and the values a and b are given in terms of the known flux condition.

Some additional comments regarding the relationship of the integral equation (5.1) to the original system (3.1)–(3.4) and the limitations of the results are in order. First, we have shown that, under certain conditions, the solution to the integral equation (5.1) exhibits an infinite singularity at a finite time. This singular behavior is interpreted as thermal runaway and hence initiation of a polymerization front. This

does not, however, correspond to blow-up of the solution of the original system (3.1)–(3.4) of interest in this study. For the system (3.1)–(3.4), there exists a unique, global solution as indicated by the classical theory of parabolic equations. However, the Arrhenius reaction term produces a large temperature gradient at the site of initiation so that the temperature profile at the end of the tube exhibits a steep increase to the maximum temperature in a thin reaction zone. It is this sharp increase in temperature that is modeled asymptotically by the thermal runaway phenomenon of the integral equation (5.1).

Second, we note that even in the case when thermal runaway occurs in (5.1)—i.e., when the parameter values are such that $\lambda_r < \lambda_r^c$—the front formed requires a sufficiently large amount of initiator present in the mixture for propagation throughout the tube. While it is possible to induce runaway by imposing a sufficiently high level of external energy input at $x = 0$, this case is not of interest since the reaction will die off and the polymer will not be produced. Hence, for the results obtained in this paper to be of practical use, the values of a and b must be assumed to be $O(1)$ and fixed as prescribed by the externally imposed heat flux. Then, the variation in the magnitude of λ_r can be viewed as due to changes in the values of A_0 and B_0, which correspond to the physical and chemical properties of any particular mixture.

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