

Thermal explosion in a hot gas mixture with organic gel fuel droplets

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Abstract Recent experimental evidence has uncovered the peculiar behavior of certain gel droplets which, under appropriate ambient thermal conditions, evaporate and burn in an oscillatory fashion. In this work a preliminary foray is made into the theoretical analysis of the nature of the evolution of a hot gas mixture containing organic gel fuel droplets with oscillatory evaporation within the context of thermal-explosion theory. The problem is modeled as a system of highly nonlinear singularly perturbed ordinary differential equations. Non-dimensionalization of the equations enables identification of the parameters that play a major role in determining the dynamical regimes of the system of equations. The method of integral manifolds is exploited for the analysis and it is found, that for certain parametric regions, the system exhibits new dynamical behavior that is quite different from that found for conventional liquid droplets.

Keywords Gel fuel droplets · Singularly perturbed system of equations · Theory of integral manifolds · Thermal explosion

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1 Introduction

In a wide variety of applications (from boost motors for micro-spacecraft and large launchers for all kinds of tactical missiles) the need for highly energetic propellants must be balanced against their safety features. The utilization of gel propellants provides a promising response to these essential requirements. However, there is a still lot of ground to be covered before a sound understanding of the unique properties and combustion features of such propellants will be available. The uniqueness of gels, as opposed to conventional liquid or solid propellants, is compactly captured by Brinker and Scherer [1, Chap. 2] in their definition of a gel as a “substance that contains a continuous solid skeleton enclosing a continuous liquid phase. The continuity of the solid structure gives elasticity to the gel”. Essentially, this means that gels are liquids whose rheological properties have been altered by the addition of gelling agents so that their resulting behavior is that of non-Newtonian time-dependent fluids. This change of the rheological behavior can prevent agglomeration, aggregation and separation of a metal solid phase from the fuel during storage. In short, these propellants are advantageous because of their capability to provide full energy management and because of their safety benefits over conventional liquids and solid propellants. Their performance characteristics and operational capabilities, which are similar to liquid propellants, as well as their high density, increased combustion energy and long term storage capability, make them attractive for many applications, especially for volume-limited propulsion-system applications. A thorough review of the background material on gels till the year 2000 is given by Natan and Rahimi [2].

In the present piece of work we focus on an interesting experimental discovery of Solomon and Natan [3]. They found that *organic* gel fuel droplets exhibit a pulsating-type of evaporation behavior, in contrast to the usual d^2 law evaporating behavior of inorganically based gel fuels. Observations indicate that, as heating occurs, the gel structure ceases to exist and a binary mixture of liquids (fuel and gellant) with different properties is produced. The low-boiling-point liquid (the fuel) evaporates and an elastic layer of gellant forms around the droplet, which prevents further fuel vaporization from the droplet surface. Thus, a fuel vapor bubble is formed in the interior and the droplet swells. Eventually the outer layer is perforated, releasing evaporated fuel to the surroundings. After the occurrence of this burst of fuel vapor the droplet shrinks, an elastic outer layer is reformed and the cycle repeats itself a number of times until the liquid fuel in the droplet is completely depleted. The sequence of the aforementioned stages is sketched in a schematic fashion in Fig. 1. The actual complex sequence of mutually interacting physical mechanisms that lead to this pulsating-type of evaporation behavior is far from understood and remains to be thoroughly elucidated. Here, we choose to extract from the experimental observations the phenomenological fact that the organic gellant-based fuel droplets evaporate in an oscillating fashion upon reaching a critical temperature. This behavior is strikingly different, not only from that of inorganic gellant-based fuel droplets, but also from that of purely liquid droplets, that are widely used in a range of combustion engineering applications.

There is some compelling experimental evidence to indicate that the combustion of a spray of liquid fuel droplets in a combustible mixture can be strikingly different from that of an equivalent purely gaseous mixture. The complexity of these two-phase (liquid–gas) systems makes their mathematical analysis rather difficult and the presence of a gel instead of normal liquid fuel just aggravates the situation. In a realistic system one is concerned with simultaneous heat, mass and momentum transfer of a multi-component, multi-phase mixture. Mathematically, one has to contend with a set of strongly nonlinear coupled partial differential equations. In order to disentangle the many physico-chemical processes at play, and to attempt to identify their realms of relevance and importance, it is reasonable to adopt an approach that focuses on singling out the key driving mechanisms. These are analyzed separately as a preliminary stage before building up an integrated picture of their interaction.

In this paper we follow this line of thought in order to carry out a qualitative investigation of thermal-explosion dynamics in a gelled fuel droplet + gas cloud. By “thermal explosion” we exclusively refer to the initial stages of the behavior of a combustible medium as its temperature begins to rise (by about 100–200 K) and various competing physical and chemical processes are called into play. This is what takes

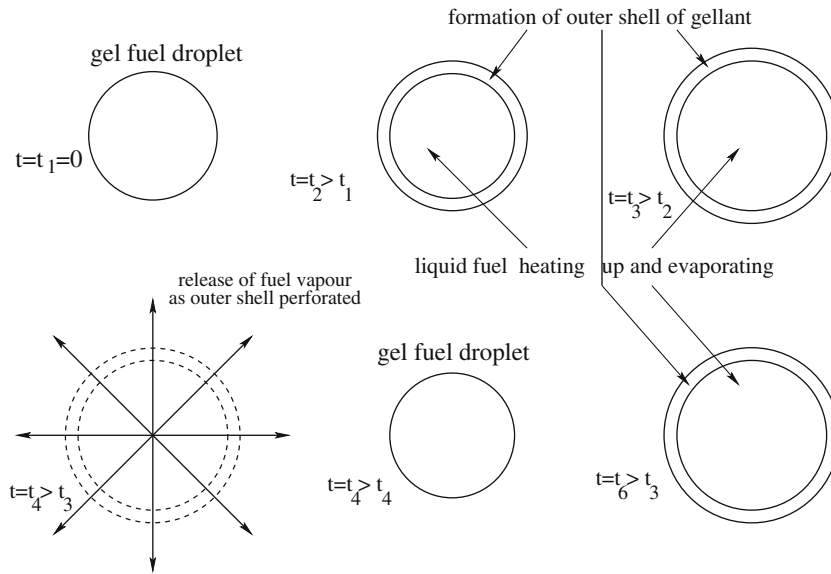


Fig. 1 Sketch of the behavior of an evaporating/combusting organic gel fuel droplet (based on Solomon and Natan [3, 10])

place at this initial evolutionary period that sets the stage for the ultimate behavior of the system. Thus, we only focus on this particular episode in the spray's lifetime, rather than on its entire life history.

In the present work we pose the question: what is the nature of the evolution of a hot gas mixture containing organic-gel fuel droplets with oscillatory evaporation within the context of thermal explosion theory? Essentially, the behavior of the considered system is driven by two heat-transfer processes: heat loss due to the evaporation of the flammable liquid medium (droplets) and heat release associated with an exothermic oxidation reaction in the gas phase. In turn, the latter is fueled by the production of vapor from the evaporating gel droplets. Competition between these processes determines the main dynamical peculiarities of the system.

After defining the basic model, comparison of typical characteristic time scales is made and reveals that the system of governing equations is multi-scale. This permits us to apply a geometrical asymptotic method (integral manifold method, MIM, [4]) for qualitative analysis of the model. The qualitative analysis enables a complete classification of dynamical behavior to be given, without the need for detailed numerical solution of the governing equations, as well as permitting critical conditions for the main dynamical regimes transitions to be deduced analytically.

The structure of the paper is as follows. Following a description of the governing equations we expose the possible multiple scales necessary for the analysis. The integral-manifold method is then briefly sketched and applied to a reduced set of governing equations. The different possible dynamical regimes are revealed, the influence of the oscillation's amplitude is discussed and delay-time estimates are developed. Finally, we present calculated results in which a comparison is made between the predictions of the theory and direct numerical simulation.

2 Model assumptions and governing equations

We investigate the effect of gel fuel droplets on the ignition of a flammable spray in a pre-heated combustible gas mixture using a simplified physical model. The following main physical assumptions apply. We consider an infinite medium filled with a combustible gas mixture (oxidant and gaseous fuel) and gel

fuel droplets. The combustible gel droplets are distributed uniformly throughout space as a mono-disperse spray undergoing evaporation.

An adiabatic approach is adopted for the analysis. As is appropriate [5, 6] for thermal explosion processes of the type we are studying, the pressure change in the reaction volume is negligible as is its influence on the combustion process. All droplets are at the same constant temperature (on the saturation line) which is equal to the initial gas temperature. Heat flux from the burning gas to the droplets is supposed to be proportional to the temperature difference between the liquid and gas phases. The chemistry is modeled as a one-step highly exothermic chemical reaction of the first order.

In the current model we focus on experimental observations [2] which indicate that the behavior of the internal structure of gellant droplets is quite different from that of liquid-fuel droplets. Heat flux from the surrounding hot gas to a gellant droplet causes internal changes to occur in the droplet. The gellant forms an elastic outer layer on the droplet inside which the liquid fuel heats up and mixes. The evaporation properties of a gel droplet covered by an elastic layer of gellant are quite distinct, whilst the vapor is being produced inside the droplet there is no release of vapor to the surroundings. However, eventually the outer layer ruptures and fuel vapor is released to the surroundings in a burst. After this event the droplet shrinks, an elastic layer is regenerated and the cycle repeats itself a number of times until the liquid fuel in the droplet is completely used up (see Fig. 1).

In view of the lack of detailed experimental information and the complexity of the solid/liquid/gaseous processes occurring within heated organic gel droplets we focus on their main phenomenological bulk feature, namely, their oscillating evaporation behavior. As a result of this behavior the surface area of a typical gel droplet will also change. Here we concentrate on the effect of these periodical changes of the droplets surface area on the dynamics of the ignition.

The governing energy equation is given by

$$C_{pg}\rho_g\varphi_g\frac{dT_g}{dt} = c_f Q_f \mu_f \varphi_g A \exp\left(-\frac{E}{R_u T_g}\right) - 4\pi R_d^2 n_d q_c, \quad (1)$$

where A a constant pre-exponential factor (1/s), E the activation energy (J/kmol), C the specific heat capacity (J/kg/K), R_u the universal gas constant, R_d the radius of the droplets (m), Q_f the specific (per unit mass) combustion energy (J/kg), T is the temperature (K), c_f the molar concentration of the combustible component in the gaseous mixture (kmol/m³), q_c the heat flux from the hot gas to the gel droplets (W/m²), n_d the number of droplets per unit volume (1/m³); t the time (s); ρ the density (kg/m³), μ the molar mass (kg/kmol); φ the volumetric phase content (dimensionless). Subscripts: b refers to boiling conditions; d refers to liquid/gel droplets; g refers to gas mixture; f refers to combustible gas component of the mixture (fuel); p refers to constant pressure; c refers to convection.

Following the aforementioned assumptions, the surface area of an average gel droplet oscillates with some characteristic frequency. As a result the heat flux to/from a gel droplet q_c differs from that of a pure liquid fuel droplet q_c^{normal} by some oscillating factor GF_{gel} :

$$q_c = q_c^{\text{normal}} \cdot GF_{\text{gel}}.$$

Following our previous works [7–9] the heat flux q_c is taken as

$$q_c^{\text{normal}} = \left(\frac{\lambda_{g0}}{R_d}\right) (T_g - T_d),$$

where λ_{g0} is the gas thermal conductivity at $T_g = T_{g0}$, $T_d = T_b$.

For mathematical convenience we model the oscillating factor GF_{gel} as

$$GF_{\text{gel}} = \left(\frac{R_d}{R_{d0}}\right) (1 + \alpha \zeta(t)),$$

where the term R_d/R_{d0} ensures that the factor GF_{gel} disappears when the gel droplet radius R_d tends to zero, α describes the amplitude of the oscillations (the value of α is limited from above by unity to

ensure the radius is a decreasing variable, e.g. $\alpha \leq 1$), and $\zeta(t)$ is the function providing the oscillations. For simplicity $\zeta(t)$ is taken to be the simple sinusoidal function $\zeta(t) = -\sin(t\omega_\zeta)$, where ω_ζ is the frequency. Thus, the heat flux from the hot gas to the gel droplets reads:

$$q_c = \left(\frac{\lambda_{g0}}{R_d}\right) \left(\frac{R_d}{R_{d0}}\right) (1 + \alpha\zeta(t)) (T_g - T_d). \tag{2}$$

To treat the governing system as autonomous, the function $\zeta(t)$ can be described using the equation:

$$\frac{d^2\zeta}{dt^2} + (\omega_\zeta)^2 \zeta = 0,$$

or, equivalently, by a set of two first order ODEs:

$$\frac{d\zeta}{dt} = \omega_\zeta \xi, \quad \frac{d\xi}{dt} = -\omega_\zeta \zeta. \tag{3}$$

The rate of fuel evaporation is given by

$$\frac{dm_d}{dt} = -\frac{4\pi R_d^2}{L} q_c, \tag{4}$$

where m_d is the droplet mass (kg), L is the latent heat of evaporation (J/kg).

The combustible gas-component content is controlled by oxidation (flammable substance consumption) and gel droplets evaporation (fuel vapor source):

$$\varphi_g \frac{dc_f}{dt} = -c_f \varphi_g A \exp\left(-\frac{E}{R_u T_g}\right) + \frac{4\pi R_d^2 n_d}{L \mu_f} q_c. \tag{5}$$

The governing system of Eqs. 1–5 is to be solved subject to the following initial conditions:

$$t = 0 : T_g = T_b = T_{g0}, \quad R_d = R_{d0}, \quad c_f = c_{f0}, \quad \zeta = 0, \quad \zeta' = -\frac{1}{t_\zeta}. \tag{6}$$

Equations 1–5 can be rewritten in dimensionless form:

$$\gamma \frac{d\theta}{d\tau} = \eta \exp\left(\frac{\theta}{1 + \beta\theta}\right) - \varepsilon_1 (1 + \alpha\zeta) r^2 \theta, \tag{7}$$

$$\frac{d\eta}{d\tau} = -\eta \exp\left(\frac{\theta}{1 + \beta\theta}\right) + \psi_f \varepsilon_1 (1 + \alpha\zeta) r^2 \theta, \tag{8}$$

$$\frac{dr^3}{d\tau} = -\varepsilon_1 \varepsilon_2 (1 + \alpha\zeta) r^2 \theta, \tag{9}$$

$$\frac{d\zeta}{d\tau} = \varepsilon_3 \xi, \quad \frac{d\xi}{d\tau} = -\varepsilon_3 \zeta. \tag{10}$$

The dimensionless initial conditions are:

$$\tau = 0 : \theta = 0; \quad \eta = \eta_0, \quad r = 1, \quad \zeta(0) = 0, \quad \xi(0) = -1. \tag{11}$$

The following dimensionless parameters have been introduced:

$$\begin{aligned} \beta &= \frac{R_u T_{g0}}{E}; \quad \gamma = \frac{C_{pg} T_{g0} \rho_{g0}}{c'_f Q_f \mu_f} \beta; \quad c'_f = \frac{\varphi_d \rho_{d0}}{\mu_f}; \quad \varepsilon_1 = \frac{4\pi R_{d0} \lambda_{g0} n_d T_{g0} \beta \exp(1/\beta)}{A c'_f Q_f \mu_f \varphi_g}; \\ \varepsilon_2 &= \frac{c'_f Q_f \mu_f \varphi_g}{(4/3) \pi R_{d0}^3 n_d \rho_{d0} L}; \quad \varepsilon_3 = t_{\text{react}} \omega_\zeta; \quad \psi_f = \frac{Q_f}{L}; \\ \theta &= \frac{T_g - T_{g0}}{\beta T_{g0}}; \quad \eta = \frac{c_f}{c'_f}; \quad r = \frac{R_d}{R_{d0}}; \quad \tau = \frac{t}{t_{\text{react}}}; \quad t_{\text{react}} = A^{-1} \exp(1/\beta). \end{aligned} \tag{12}$$

Here, t_{react} is the time required for the reactant concentration to fall by a factor e from its initial value under isothermal conditions and c'_f is the fuel vapor concentration after all droplets have evaporated but not burnt.

The parameters β and γ are the conventional parameters of the Semenov theory of thermal explosion: β is the reduced initial temperature, γ represents the final dimensionless adiabatic temperature of the thermally insulated system after the explosion has been completed. Characteristic values of the parameters β and γ are small compared with unity for most gaseous mixtures due to the high exothermicity of the chemical reaction and the large activation energy. The parameter ε_1 describes the competition between the combustion and evaporation processes whereas ε_2 relates to the heat released during combustion and energy needed to evaporate all fuel droplets. The parameter ε_3 is the ratio of t_{react} and the characteristic time of the oscillations, which is proportional to the reciprocal of the frequency, ω_ζ . Finally, ψ_f is the ratio of specific combustion energy and latent heat of vaporization. Typically, the values of ψ_f are large.

3 Preliminary analysis

3.1 Governing equations—simplifications

The governing system is adiabatic, and, therefore, it has an energy integral which can be obtained by combining Eqs. 7–9:

$$\frac{d(\gamma\theta + \eta)}{dr^3} = -\frac{(\psi_f - 1)}{\varepsilon_2}.$$

Integrating the last equation subject to the initial conditions (11) yields:

$$\eta = \eta_0 - \gamma\theta + \frac{(\psi_f - 1)}{\varepsilon_2} (1 - r^3). \quad (13)$$

The system under consideration describes a thermal-explosion phenomenon for any parameter values. This study concentrates on the initial stages of such an event when the combustible gas temperature is comparatively low, $\theta \sim O(1)$. It is reasonable to apply the Frank–Kamenetskii approximation (which is known to work well for $\beta\theta < 1$) [6, Chapter 4]: $\exp\left(\frac{\theta}{1+\beta\theta}\right) \approx \exp(\theta)$.

The reduced system is then given by

$$\gamma \frac{d\theta}{d\tau} = \eta(\theta, r) \exp(\theta) - \varepsilon_1 (1 + \alpha\zeta) r^2 \theta, \quad (14)$$

$$\frac{1}{\varepsilon_2} \frac{dr^3}{d\tau} = -\varepsilon_1 r^2 (1 + \alpha\zeta) \theta, \quad (15)$$

$$\frac{1}{\varepsilon_3} \frac{d\zeta}{d\tau} = \xi, \quad \frac{1}{\varepsilon_3} \frac{d\xi}{d\tau} = -\zeta, \quad (16)$$

subject to

$$\tau = 0: \theta = 0, \quad r = 1, \quad \zeta = 0, \quad \xi = -1, \quad (17)$$

where $\eta(\theta, r)$ is given by Eq. 13.

3.2 Method of integral manifolds—brief description

The method of integral manifolds (MIM) enables an analytical study of dynamical models to be carried out that can be developed as singular-perturbed systems of ordinary differential equations. According to

the MIM, the processes involved can be examined sequentially, from the fastest to the slowest. Suppose a particular process is associated with a certain scale. Then, to leading order, all slower processes can be “frozen”, whereas all faster processes have reached their quasi-stationary states. Note that quasi-stationary states can be temporary, with the process becoming fast again in a finite period of time. Assuming, for example, that one process varies the fastest, the rest of the variables can be “frozen”. This situation is maintained till the fastest variable approaches its “steady state” where there is a balance between the rates of change. Mathematically, this balance represents a functional relation determining a hyper-surface (slow integral manifold) that reduces the dimension of the system and therefore simplifies the analysis. If there is a hierarchy on the slow integral manifold, a similar approach can be repeated. The MIM was adopted for combustion problems by Gol’dshstein and Sobolev [4] and has proved to be very successful in a variety of problems including thermal explosions in multi-phase reactive systems [7–9].

4 Analysis, results and discussion

Equations 16, which have the solution $\zeta = -\sin(\varepsilon_3\tau)$, are independent of Eqs. 14 and 15 and it would apparently be desirable to use this fact to reduce the dimension of the system and simplify the analysis. However, it turns out to be more beneficial mathematically to treat the entire system as autonomous (at least initially) in order to obtain a detailed classification of its possible dynamical behavior. It is this approach that we describe here.

The initial hierarchy of the system (14–16) is determined by the right-hand sides of the differential equations calculated at the initial point I given by the conditions (17). There are three possible cases:

- (i) $(\varepsilon_3 \sim \eta_0/\gamma)$, when the rates of the variables changes are comparable;
- (ii) $(\varepsilon_3 < \eta_0/\gamma)$, when the gas temperature is a fast varying variable, while the rest are slowly varying variables;
- (iii) $(\varepsilon_3 > \eta_0/\gamma)$, when the function $\zeta(\tau) = -\sin(\varepsilon_3\tau)$ is oscillating rapidly, while the rest are slowly varying variables.

This work deals with multi-scales so that case (i) will not be considered here.

4.1 Analysis for case (ii) $(\varepsilon_3 < \eta_0/\gamma)$

The initial hierarchy of the system (14–17) is as follows: the gas temperature θ is a fast varying variable, while the three other variables (r, ζ, ξ) vary slowly. The solution of the system (14–17) can be represented as a trajectory in the (θ, r, ζ, ξ) -phase space. The trajectory can be subdivided into ‘fast’ and ‘slow’ parts. The ‘fast’ parts are those characterized by constant values of the slow variables, while the ‘slow’ parts are quasi-stationary states of the fast (θ) -variable which are located on the slow integral manifold. The slow integral manifold can be defined analytically in powers of the relevant small parameter $(\gamma\varepsilon_3/\eta_0)$. We restrict our analysis to the zeroth-order approximations of the slow integral manifolds (abbreviated to slow manifolds or slow surfaces). The slow surface of the system (14–16) is given by

$$G(\theta, r, \zeta) = \left(\eta_0 + \frac{(\psi_f - 1)}{\varepsilon_2} (1 - r^3) \right) e^\theta - \varepsilon_1 (1 + \alpha\zeta) r^2 \theta = 0. \tag{18}$$

The slow surface has a turning line defined as $G(\theta, r, \zeta) = 0, G_\theta(\theta, r, \zeta) = 0$, where the slow surface changes the stability in terms of attracting or repelling trajectories. The turning-line equations read:

$$\theta = 1, \quad \left(\eta_0 + \frac{(\psi_f - 1)}{\varepsilon_2} (1 - r^3) \right) e - \varepsilon_1 (1 + \alpha\zeta) r^2 = 0. \tag{19}$$

In terms of Semenov’s thermal-explosion theory, the value $\theta = 1$ is considered as a pre-explosive critical dimensionless temperature. The slow surface (18) has a ‘near’ stable part characterized by low values of the

dimensionless temperature ($\theta < 1$), and an unstable part where ($\theta > 1$). These two parts are separated by the turning line (19). In general, there exists a ‘far’ stable part of the slow surface, at high θ -values. Recall that this study is aimed at the initial stages of the thermal explosion when the θ -values are reasonably low, and when the Frank–Kamenetskii approximation is satisfactory. Due to this approximation we obtained the unique turning line (19) which separates the ‘near’ stable part of the slow surface from its unstable part.

The initial part of the system trajectory is described by

$$r = 1, \zeta = 0, \xi = -1, \gamma \frac{d\theta}{d\tau} = (\eta_0 - \gamma\theta) e^\theta - \varepsilon_1 \theta, \quad \theta(0) = 0. \tag{20}$$

The asymptotic description of the trajectory changes when the trajectory reaches a stable part of the slow surface, namely a ‘near’ part where ($\theta < 1$) or a ‘far’ part where ($\theta > 1$). Substituting the values $r = 1, \zeta = 0$ in the turning-line equations (19) supplies the critical condition $\varepsilon_1/\eta_0 = e$ (see I_2B in Fig. 2). For $\varepsilon_1/\eta_0 < e$, the system exhibits fast explosive behavior, for which the temperature θ jumps to values higher than unity, whilst the other variables remain equal to their initial values (I_1A in Fig. 2). For $\varepsilon_1/\eta_0 > e$ the system exhibits a delayed explosion, for which there is a significant delay before the final temperature jump (I_3N in Fig. 2). Among these scenarios we focus on the delayed-explosion regime because of its practical importance.

As we have just mentioned the initial ‘fast’ part of the trajectory is denoted by I_3N (Fig. 2). Here the initial point I_3 is given by the conditions (17), and the point N at which the trajectory hits the attractive part of the slow surface is calculated by substituting $r = 1, \zeta = 0$ in Eq. 18:

$$N: r = 1, \zeta = 0, \theta = \theta_N < 1: e^\theta - \frac{\varepsilon_1}{\eta_0} \theta = 0. \tag{21}$$

Now, having decided on the initial regime of physical interest, we turn to the continuing dynamics which is governed by the reduced system on the slow surface:

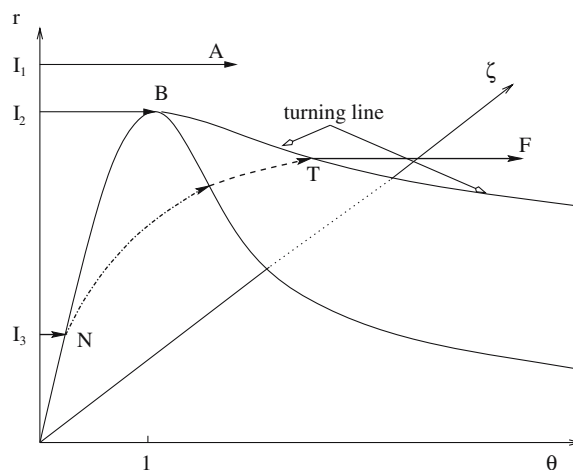
$$\frac{dr}{d\tau} = -\frac{\varepsilon_1 \varepsilon_2}{3} (1 + \alpha \zeta) \theta(r, \zeta), \tag{22.1}$$

$$\frac{d\zeta}{d\tau} = \varepsilon_3 \xi, \quad \frac{d\xi}{d\tau} = -\varepsilon_3 \zeta, \tag{22.2}$$

where $\theta(r, \zeta)$ is given by the slow surface equation (18).

This system (22.1)–(22.2) admits a hierarchy of solutions for the initial conditions (21) which is determined by the following possible cases:

Fig. 2 Schematic of possible dynamical trajectories. I_1A —trajectory does not approach the slow curve, corresponds to immediate explosion; I_3A —trajectory does approach the slow curve (case, considered in the paper) at the point N , stage NT “sits” on the slow surface, at the point T final explosion occurs; I_2A —trajectory separating two previous scenarios (critical trajectory)



- (a) $\varepsilon_3 \sim \frac{\varepsilon_1 \varepsilon_2}{3} \theta_N$, when the rates of the variables changes are comparable;
- (b) $\varepsilon_3 < \frac{\varepsilon_1 \varepsilon_2}{3} \theta_N$, when the radius is decreasing rapidly;
- (c) $\varepsilon_3 > \frac{\varepsilon_1 \varepsilon_2}{3} \theta_N$, when the radius is decreasing slowly.

As already mentioned, this study deals with multi-scales so that case (a) will not be considered here. Thus, to reiterate, we now analyze the cases (b) and (c), *within the context of the parameter domain we have opted for, namely, $\varepsilon_3 < \eta_0/\gamma, \varepsilon_1/\eta_0 > e$.*

4.1.1 Case (b) $\varepsilon_3 < \frac{\varepsilon_1 \varepsilon_2}{3} \theta_N$

On the slow manifold, the system (22.1)–(22.2) reduces to:

$$\zeta = 0, \quad \xi = -1, \quad \frac{dr}{d\tau} = -\frac{\varepsilon_1 \varepsilon_2}{3} \theta(r), \tag{23}$$

where $\theta(r)$ is given by the slow surface equation (18) with $\zeta = 0$, namely:

$$\theta(r) : \left(\eta_0 + \frac{(\psi_f - 1)}{\varepsilon_2} (1 - r^3) \right) e^\theta - \varepsilon_1 r^2 \theta = 0. \tag{24}$$

The radius decreases rapidly to the value r_T given by

$$\theta = 1, \quad 0 < r = r_T < 1 : \left(\eta_0 + \frac{(\psi_f - 1)}{\varepsilon_2} (1 - r^3) \right) e - \varepsilon_1 r^2 = 0. \tag{25}$$

at which point the trajectory reaches the turning line (19). The trajectory then departs from the slow surface; this corresponds to the final ignition event. In this case the delay time can be calculated via the life-time of the droplets on the stable surface, using the third part of Eq. 23, whereby

$$t_{\text{drop}} = \frac{3}{\varepsilon_1 \varepsilon_2} \int_{r_T}^1 \frac{dr}{\theta(r)}, \tag{26}$$

where the function $\theta(r)$ and the lower integral limit r_T are given by Eqs. 24 and 25, respectively.

We recall that the main aim of this work is to disclose effects of the pulsating evaporation of gel droplets on the explosion event, via the relevant function ζ . In this sense, the case considered is seen to be of secondary interest as ζ is a slow variable that does not influence the system’s dynamics.

4.1.2 Case (c) $\varepsilon_3 > \frac{\varepsilon_1 \varepsilon_2}{3} \theta_N$

We note that the parameter condition can be replaced by a simpler (but stronger) condition: $\varepsilon_3 > \frac{\varepsilon_1 \varepsilon_2}{3}$, since θ_N given by (21) is less than unity.

Now, the system (22.1)–(22.2) involves the slow equation (22.1) and the fast equations (22.2). The fast sub-system (22.2) is independent of the variable r , and has the solution $\zeta(\tau) = -\sin(\varepsilon_3 \tau)$. Thus, the reduced system (22.1)–(22.2) on the slow surface (18) becomes:

$$r = 1, \quad \zeta(\tau) = -\sin(\varepsilon_3 \tau), \quad \eta_0 e^\theta - \varepsilon_1 (1 + \alpha \zeta(\tau)) \theta = 0. \tag{27}$$

In terms of the phase-space analysis, this gives the second ‘slow’ part of the trajectory (*NT*) which is on the attractive part of the slow surface (18) (Fig. 2). The transition from the delay to the final explosion event happens when the trajectory reaches the turning line (19). Thus the ‘slow’ part of the trajectory starts at the point *N* (conditions (21)), at which the trajectory hits the stable slow surface (18), and ends at the point *T* on the turning line. The stage *TF* corresponds to the final thermal-explosion event.

The condition when the trajectory reaches the turning line is obtained by substituting $\theta = 1$ in Eq. 27:

$$\theta = 1, \quad r = 1, \quad \zeta = -\sin(\varepsilon_3 \tau), \quad \varsigma = \frac{1}{\alpha} \left(\frac{e \eta_0}{\varepsilon_1} - 1 \right). \tag{28}$$

The function $\zeta(\tau) = -\sin(\varepsilon_3\tau)$ implies the following parameter restriction:

$$\alpha \geq 1 - \frac{e\eta_0}{\varepsilon_1}. \quad (29)$$

Note that the lower bound in (29) is always positive for the delayed explosion. We investigate two alternatives when condition (29) is or is not satisfied (dubbed large amplitude and small amplitude, respectively).

4.1.3 Large amplitude, α

When condition (29) is satisfied, the delay time τ_{delay} can be calculated directly using equations (28) as:

$$\zeta = -\sin(\varepsilon_3\tau) = \frac{1}{\alpha} \left(\frac{e\eta_0}{\varepsilon_1} - 1 \right).$$

whence, the delay-time formula reads:

$$\tau_{\text{delay}} = -\frac{1}{\varepsilon_3} \arcsin \left\{ \frac{1}{\alpha} \left(\frac{e\eta_0}{\varepsilon_1} - 1 \right) \right\}. \quad (30)$$

The delay time (30) is plotted in Fig. 3 as a function of the amplitude, α . It is readily seen that the delay time decreases as α grows. It is also important to mention that the effective radius of the gel droplets decreases. Our previous studies showed that, for a given number of *liquid* fuel droplets, the smaller the droplets radius, the less is their effect on the dynamics of the thermal-explosion process. In the current case, the effective radius of the gel droplet is reduced as the amplitude α is increased. In turn, the less is the total effect of gel droplets addition to the hot gas on the dynamics of the thermal explosion.

Typical time-histories of the original system of Eqs. 7–11 when condition (29) holds are shown in Fig. 4. The theoretical delay time (30) agrees well with the direct numerical simulations.

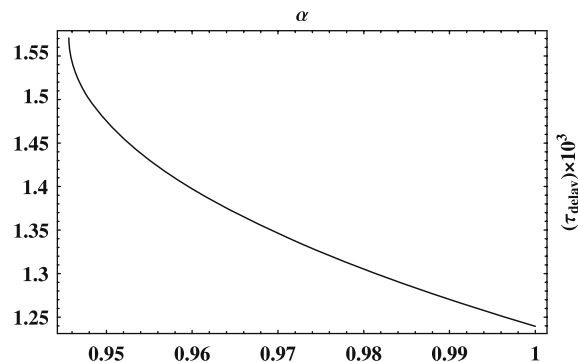
4.1.4 Small amplitude, α

Assume that condition (29) is not valid, namely:

$$0 \leq \alpha < 1 - \frac{e\eta_0}{\varepsilon_1}. \quad (31)$$

This implies that Eq. 27 has no solution in terms of θ . Thus, the system trajectory on the slow surface does not reach the turning curve ($\theta = 1$) and continues to “travel” on the slow surface. In turn, a final explosion (when the trajectory jumps from the slow surface at its turning curve) does not occur. It would seem that this behavior is a result of the zeroth-order approximation that has been used in the analysis

Fig. 3 Dependence of delay time on oscillations amplitude as predicted by Eq. 30; Case 4.1 (c) with large amplitude; data: $\beta = 0$, $\gamma = 10^{-5}$, $\varepsilon_1 = 5$, $\varepsilon_2 = 1$, $\varepsilon_3 = 100$, $\psi_f = 10$, $\eta_0 = 0.1$



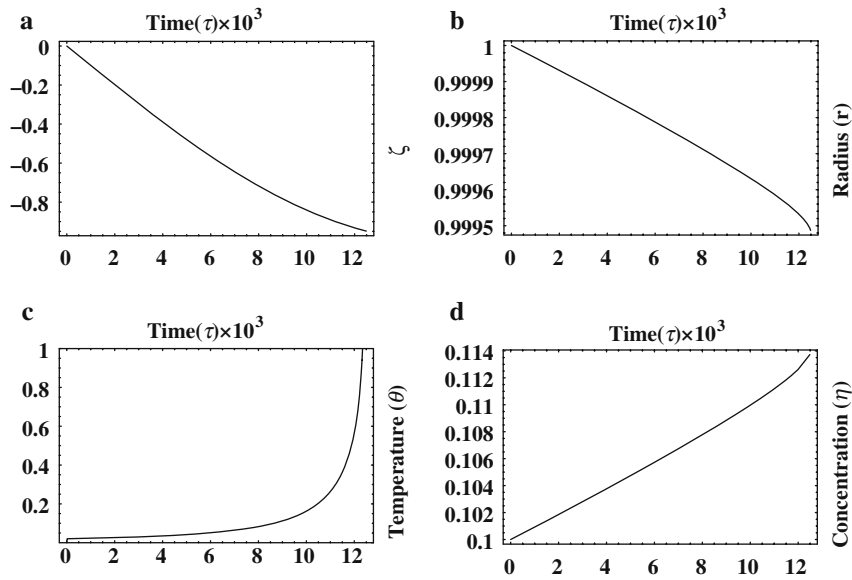


Fig. 4 Behavior of the system for case 4.1 (c) with large amplitude; (a) $\zeta(\tau) = -\sin(\varepsilon_3\tau)$; (b) radius evolution; (c) temperature evolution; (d) concentration evolution; data: $\alpha = 1$ satisfying condition (29), other data as in Fig. 3

and that in order to study the explosion phenomenon and, in particular, the delay time in this situation, higher-order approximations of the MIM should be developed. This is beyond the scope of the present paper. However, some conclusions can be drawn based on direct numerical calculations. Specifically, it turns out that if the parameter value ε_3 is big enough so that the period of oscillations of the function $\zeta(\tau) = -\sin(\varepsilon_3\tau)$ is shorter than the numerically computed delay time, then the formula $\alpha = 1 - \frac{e\eta_0}{\varepsilon_1}$ separates parameter zones with delay periods which are within a single oscillation from parameter zones characterized by long time delays (a number of periods of oscillations). In the latter situation the model exhibits a novel bi-hierarchical dynamical behavior during the delay period. Theoretical prediction of the delay time in this case is the subject of further research. Figure 5 gives typical time-histories of the system, for a large value of the parameter ε_3 and for the parameter α satisfying condition (31). For comparison, Figs. 4 and 5 use the same value of the parameter ε_3 , while α is taken using conditions (29) and (31), respectively. In Fig. 5, the dimensionless temperature θ exhibits oscillations which coincide with those of the function $\zeta(\tau) = -\sin(\varepsilon_3\tau)$. The amplitude of the temperature’s oscillations grows, and when the turning curve of the slow surface, $\theta = 1$, is reached, the final explosion occurs. One can also see that the dimensionless radius of the gel droplets r remains quite close to its initial value (unity) over the considered process. This observation justifies our assumption concerning the bi-hierarchical structure of the system.

It is instructive to make a comparison between the afore-described dynamical behavior and that of pure liquid droplets that do not evaporate in a pulsating manner. In Fig. 6 such a comparison is illustrated using the evolution of the temperature. Operating conditions are identical to those of Figs. 4 and 5. It is interesting to observe that, in both instances shown, the delay time before explosion exhibited by the liquid droplets is much longer than that of the gel droplets. This can be attributed to the fact that, for the conditions considered here, the pulsating evaporation releases less vapor per unit of time than does the constantly evaporating liquid fuel. As a result the lead-up to explosion in the case of the gel droplets is dominated by the exothermic chemical reaction using all *available* vapor, even though the droplets have not yet surrendered all the vapor they could potentially release. In the case of the liquid fuel the evaporation term *competes* with the reaction term until the droplets are completely vaporized and this process prolongs the delay time till explosion occurs.

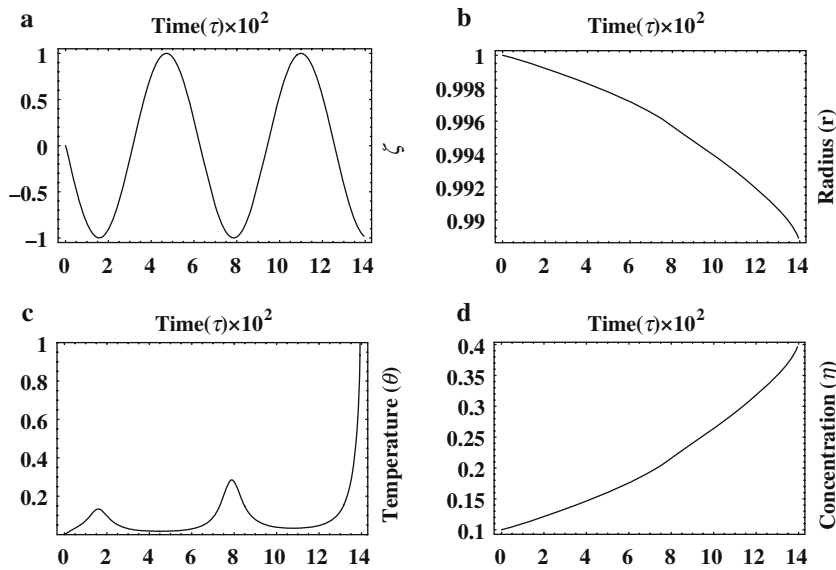


Fig. 5 Behavior of the system for case 4.1 (c) with small amplitude; (a) $\zeta(\tau) = -\sin(\varepsilon_3\tau)$; (b) radius evolution; (c) temperature evolution; (d) concentration evolution; data: $\alpha = 0.8$ satisfying condition (31), other data as in Fig. 3

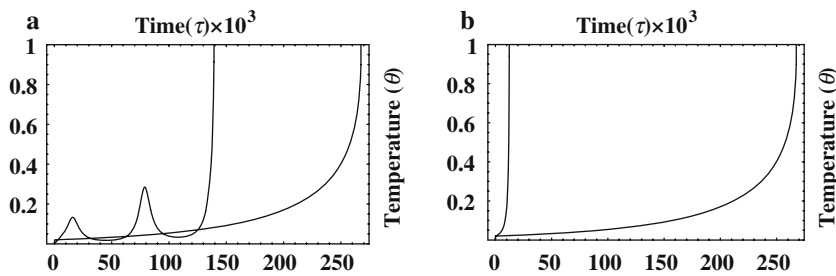


Fig. 6 Comparison between temperature evolution of organic gel droplets and of liquid droplets; Data as in Figs. 4 and 5

4.2 Analysis for case (iii) ($\varepsilon_3 > \eta_0/\gamma$)

Having analyzed the details of the situation of case (ii) for which ($\varepsilon_3 < \eta_0/\gamma$), we briefly turn to case (iii). Now, initially, Eqs. 14–16 represent a multi-scale system with the fast independent sub-system (16) and the slow sub-system (14). The solution of (16) is the function $\zeta(\tau) = -\sin(\varepsilon_3\tau)$ that reduces the governing system to the following equations:

$$\gamma \frac{d\theta}{d\tau} = \eta(\theta, r) e^\theta - \varepsilon_1 (1 - \alpha \sin(\varepsilon_3\tau)) r^2 \theta, \tag{32}$$

$$\frac{3}{\varepsilon_2} \frac{dr}{d\tau} = -\varepsilon_1 (1 - \alpha \sin(\varepsilon_3\tau)) \theta, \tag{33}$$

where $\eta(\theta, r)$ is given by the energy integral equation (13).

The initial conditions are:

$$\tau = 0 : \theta = 0, r = 1, \tag{34}$$

Now suppose that (γ/η_0) is small. This is reasonable as γ is small. Under this assumption, the initial hierarchy of the reduced system (32)–(33) is as follows: the temperature θ increases rapidly, while the radius decreases slowly. The slow manifold of the system in the (θ, r, τ) -space is given by

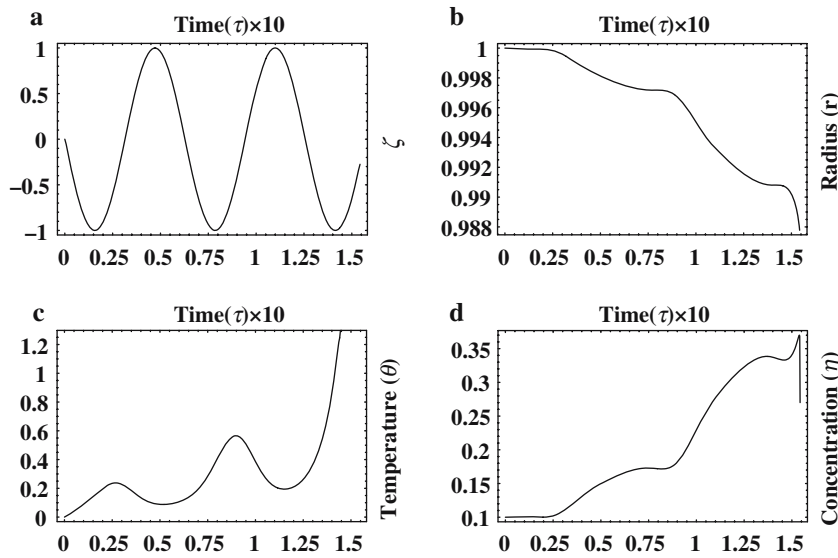


Fig. 7 Behavior of the system for case 4.2 ($\varepsilon_3 > \eta_0/\gamma > 1$); (a) $\zeta(\tau) = -\sin(\varepsilon_3\tau)$; (b) radius evolution; (c) temperature evolution; (d) concentration evolution; data: $\beta = 0$, $\gamma = 10^{-2}$, $\varepsilon_1 = \varepsilon_2 = 1$, $\varepsilon_3 = 100$, $\psi_f = 10$, $\eta_0 = 0.1$, $\alpha = 1$

$$G(\theta, r, \tau) = \left(\eta_0 + \frac{(\psi_f - 1)}{\varepsilon_2} (1 - r^3) \right) e^\theta - \varepsilon_1 (1 - \alpha \sin(\varepsilon_3\tau)) r^2 \theta = 0. \tag{35}$$

The turning curve of the slow surface reads:

$$\theta = 1, \left(\eta_0 + \frac{(\psi_f - 1)}{\varepsilon_2} (1 - r^3) \right) e - \varepsilon_1 (1 - \alpha \sin(\varepsilon_3\tau)) r^2 = 0. \tag{36}$$

It can be shown that in the parameter domain ($\varepsilon_3 > \frac{\eta_0}{\gamma} > 1$) the system exhibits delayed thermal explosion. In terms of the MIM, the delay time is determined theoretically by the part of the trajectory on the stable slow surface, between the initial point (34) and the turning curve (36). Typical time-histories of the original system of Eqs. 7–11 for this case are strikingly illustrated in Fig. 7. The entire system manifests an oscillating-type of behavior until explosion occurs. This behavior is in tandem with the evaporation oscillations and, unlike under the conditions considered in Fig. 5, extends quite clearly to the evolution of the droplets radius, the fuel production and the temperature. In addition, there is some qualitative agreement with experimental results (see [3, 10]) for burning gel droplets, albeit under somewhat different laboratory operating conditions.

5 Conclusions

In this paper a preliminary attempt has been made to study the effects of the oscillatory evaporation of organic gel fuel droplets on a gaseous thermal explosion. A detailed mathematical analysis has been carried out of this new physical model that encompasses pulsating-type of evaporation of organic gellant-based fuel droplets. The effect of the oscillatory evaporation on the thermal explosion of a hot combustible mixture of gases and cool evaporating gellant-based fuel droplets has been studied. The closed mathematical formulation involves a singularly perturbed system of five highly nonlinear ordinary differential equations. The entire dynamical picture of the system is qualitatively uncovered by exploiting the geometrical version of the powerful asymptotic approach known as the method of integral manifolds (MIM).

It was found that the system’s behavior can be classified according to the values of a number of key dimensionless parameters (α , γ , η_0 , ε_1 , ε_2 , ε_3). Possible types of dynamical behavior of the system were

studied and the parametric regions of their existence were delineated, with emphasis being on the underlying physico-chemical processes at play. Both conventional explosive and delayed regimes were found to occur. Due to its practical importance the delayed regimes were analyzed in detail and explicit analytical formulae for the delay times and evaporation times were extracted. In particular parametric regions the model was shown to exhibit interesting novel dynamical behavior. Specifically, when the parameter ε_3 (defined as the ratio of a typical reaction time to the characteristic time of droplet evaporation oscillations) is large, and under certain parameter restrictions, there exist long-time oscillations before the final explosion event. Their predictions were found to agree rather well with the results of direct numerical simulations.

Finally, we note that, although the current use of a suggested model does provide a broader more accurate perspective than that previously obtained with a model based on pure liquid fuel droplets, it is not without its own deficiencies. The data generally used for the liquid fuel, the pre-exponential factor and the activation energy are derived from correlations with experimental measurements or detailed computational results for physical situations that are not necessarily identical to those under consideration here. Nevertheless, it can be argued that the data must somehow express some driving mechanisms that are surely called into play in the ignition process. However, it is indisputable that a more realistic description should ideally include more details of the chemistry and physics of the process of an evaporation of gellant-based droplets and further combustion of the fuel vapor. This direction of further improvement of our model is currently under investigation. Additionally, our ongoing work is directed towards ascertaining mathematically the delay times associated with the new dynamical characteristics that have been disclosed in this paper.

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References

1. Brinker CJ, Scherer GW (1990) Sol-gel science. Academic Press, Boston
2. Natan B, Rahimi S (2001) The status of gel propellants in year 2000. In: Kuo KK, deLuca L (eds) Combustion of energetic materials Begel House, Boca Raton, pp 172–194
3. Solomon Y, Natan B (2003) Combustion characteristics of organic-gellant-based gel fuels, In: De Luca L (ed) Rocket propulsion: present and future. Politecnico di Milano, Naples, pp 31.1–31.11
4. Gol'dshtein V, Sobolev V (1992) Singularity theory and some problems of functional analysis, AMS Transl Series 2 153:73–92
5. Semenov NN (1928) Z Phys 48:571–581
6. Frank-Kamenetskii DA (1969) Diffusion and heat exchange in chemical kinetics, 2nd edn. Plenum Press, New York
7. Goldfarb I, Gol'dshtein V, Kuzmenko G, Greenberg JB (2000) Thermal explosion in a droplet-gas cloud. Combust Theory Modell 4:289–316
8. Goldfarb I, Gol'dshtein V, Zinoviev A (2002) Delayed thermal explosion in porous media: method of integral manifolds. IMA J Appl Math 67:263–280
9. Goldfarb I, Sazhin S, Zinoviev A (2004) Delayed thermal explosion in flammable gas containing fuel droplets: asymptotic analysis. J Eng Math 50:399–414
10. Solomon Y, Natan B (2006) Experimental investigation of the combustion of organic-gellant-based gel fuels. Combust Sci Technol 178:1185–1199