1. INTRODUCTION

Heterogeneous combustion takes place at the interface separating two different physical phases. The burning of solid propellants for rocket propulsion represents typically this type of combustion. So-called composite solid propellants are mixtures of finely ground salts, such as NH$_4$ClO$_4$ (ammonium perchlorate = AP), and a polymer binder (for instance polybutadiene) in a ratio of order 4:1. At operational pressures combustion of AP-based solid propellants takes place in a thin zone close to the interface solid/gas. On the solid surface itself the polymer pyrolyzes forming gaseous products, and the AP decomposes into NH$_3$ and HC1O$_4$ that react exothermically between themselves and with the polymer vapor in a diffusion flame. Details of the physics and chemistry of this type of combustion may be found elsewhere$^1$-$^2$. The purpose of this study is to present a mathematical model of the solid phase-gas system reacting at the interface, and to show that depending on the external variables (pressure, heat flux by radiation) and on the physico-chemical characteristics of the propellant (energy content, activation energies of the condensed phase decomposition reaction, etc.) burning occurs in different regimes. In mathematical terms, the response of the system (e.g., the interface temperature) bifurcates when some particular parameters are varied. Experimental evidence of this behavior has already been obtained and is presented elsewhere$^3$.

2. MATHEMATICAL MODEL

The one-dimensional deterministic energy conservation equation for the condensed phase, written in a coordinate system x fixed to
the burning interface regressing with velocity $r_b$, is a reaction/diffusion (Fourier) equation. Together with its boundary and initial conditions, its dimensionless form is\(^4\):

$$
\frac{\partial \Theta}{\partial \tau} + R \frac{\partial \Theta}{\partial X} = \frac{\partial}{\partial X} \left( K \frac{\partial \Theta}{\partial X} \right) + \int_{\lambda_1}^{\lambda_2} f_1(X, \lambda) d\lambda + \varepsilon c H_c - \dot{q}_{\text{out}} \frac{S \, d \, ref}{A} = 0
$$

(2.1)

\(X \leq 0, \tau \geq 0\)

\(\Theta(X, \tau = 0) = \text{assigned}\)

\(\Theta(X \to -\infty, \tau) = \Theta_{-\infty}\)

$$
(K \frac{\partial \Theta}{\partial X})_{c,s} = \left( \frac{k}{k_{\text{ref}}} \right) \frac{\partial \Theta}{\partial X}_{g,s} + R H_s - \dot{q}_{\text{out}} (\Theta)
$$

(2.2)

The radiative flux term in (2.1) may be \(\geq 0\) and assumes a condensed phase absorbing between the wavelengths $\lambda_1, \lambda_2$. The dimensionless burning, or regression, rate $R$ is given by

$$
R = \exp(-E_s \left( \frac{1}{T_s} - 1 \right)) \, p^{ns} \quad T_s > T_k
$$

$$
R = \left( \frac{T_s - T_m}{1 - T_m} \right) \, p^{ns} \quad T_k < T_s < T_m
$$

and $H_s$ by

$$
H_s = \frac{Q_{s, \text{ref}} + T_{s, \text{ref}} (c_g - c_s(T_{s, \text{ref}})) - T_s (c_g - c_s(T_s))}{Q_{\text{ref}}}
$$

Coupling with the gas phase occurs via (2.2) at the interface. The gas phase equations (continuity, momentum and energy equations) simplify if, as is the case with AP-based propellants, the characteristic times of the gas are much smaller than those for the solid and interface. The longest time of the gas, the convective transport time $\alpha_g/u_g^2$, is about $O(10^2)$ times smaller than the condensed phase thermal conduction time $\alpha_c/\bar{T}_D^2$. Physically this means that the gas chemical reactions are restricted to a very thin region close to the interface. Mathematically the coupling between the two phases becomes simpler, since inertial terms in the gas equations can be dropped, and the gas can be treated as quasi-steady with respect to the condensed phase. With a different terminology, the gas is a "slave" of the solid\(^5\): it is determined by it, but at the same time feeds energy back to it through (2.2). With this assumption the gas phase equations reduce to:

$$
m(t) = \rho_g (x,t) u_g (x,t) = \rho_c r_b(t) \quad \text{dim. continuity}
$$

(2.3)