Chain Branching Model

The chain-branching model is a simplified kinetic model usually adopted to illustrate isothermal explosive behaviors. It consists of the following initiation, propagation and termination steps

$$
\begin{aligned}
R &\rightarrow C \quad (1)\\
C + R &\rightarrow P + \alpha C \quad (2)\\
C &\rightarrow P \quad (3)
\end{aligned}
$$

where R, P and C are the reactant, the product and the chain carrier respectively and α is a positive branching constant. Indicating with k_i, k_p and k_t the rate constants of the three steps, the rate equations for the reactant and chain carrier read

$$
\begin{aligned}
\frac{dc_R}{d\tau} &= -k_i c_R - k_p c_R c_C \quad (4)\\
\frac{dc_C}{d\tau} &= k_i c_R + (\alpha - 1) k_p c_R c_C - k_t c_C \quad (5)
\end{aligned}
$$

where c_R and c_C are the molar concentrations of the reactant and chain carrier respectively.

Introducing the following dimensionless variables $x = c_R/c_R^0$, $y = c_C k_p/k_i$, $t = k_i\tau$ and the parameters $\varepsilon = k_i/(k_p/c_R^0)$ and $\gamma = k_t/(k_p/c_R^0)$, with c_R^0 a reference concentration, the nondimensional rate equations attain the form

$$
\begin{aligned}
\frac{dx}{dt} &= -x - xy \quad (6)\\
\frac{dy}{dt} &= \frac{1}{\varepsilon}\left[x + (\alpha - 1)xy - \gamma y\right] \quad (7)
\end{aligned}
$$

When $\varepsilon << 1$, i.e. the propagation step is faster than the initiation step, the above is a singularly perturbed planar system with x being the slow variable and y the fast variable.

The system possesses a unique equilibrium point at $(x, y) = (0, 0)$. The eigenvectors of the Jacobian matrix *at the equilibrium point* provide the invariant subspaces of the system. While this is true only at the equilibrium point, the corresponding eigenvalues represent intrinsic timescales near the equilibrium. Such eigenvalues, $\lambda_1 = -1$ and $\lambda_2 = -\gamma\varepsilon^{-1}$, exhibit timescale separation if $\gamma\varepsilon^{-1} >> 1$, i.e. $\varepsilon << \gamma$. We therefore consider only the latter case by setting, say, $\gamma = 2$ and letting $\gamma\varepsilon^{-1} > 10$, i.e. $\varepsilon < \gamma/10 = 0.2$. This guarantees more than one ordere of magnitude in time scale separation at the equilibrium point. Note also that the behavior of the system near the equilibrium point is independent of the branching constant α.

The present system should be analyzed as ε and α are varied while γ is kept fixed.