Singular perturbation analysis for the reduction of complex chemistry in gaseous mixtures using the entropic structure

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Abstract   In this Note, we investigate the reduction of complex chemistry in gaseous mixtures. We consider an arbitrarily complex network of reversible reactions, the equilibrium constant of which are compatible with thermodynamics, thus providing an entropic structure. We assume that a subset of the reactions is consituted of fast reactions and define a constant and linear projection onto the partial equilibrium manifold compatible with the entropy production. This reduction step is used for the study of a homogeneous reactor at constant density and internal energy where the temperature can encounter strong variations. We prove the global existence of a smooth solution and of an asymptotically stable equilibrium state for both the reduced system and the complete one. A global in time singular perturbation analysis proves that the reduced system on the partial equilibrium manifold approximates the full chemistry system. ***To cite this article: M. Massot, C. R. Acad. Sci. Paris, Ser. I 335 (2002) 93–98.*** © 2002 Académie des sciences/Éditions scientifiques et médicales Elsevier SAS

Analyse de perturbation singulière pour la réduction de la chimie complexe des mélanges gazeux avec structure entropique

Résumé   Dans cette Note, nous étudions la réduction des mécanismes chimiques complexes pour les mélanges gazeux. Nous considérons un réseau de complexité arbitraire de réactions réversibles dont les constantes d'équilibre sont compatibles avec la thermodynamique ce qui fournit une structure entropique. En suposant qu'il existe un sous ensemble de réactions rapides, nous définissons une projection linéaire constante compatible avec la production d'entropie afin de définir le système réduit sur la variété d'équilibre partiel. Nous considérons un réacteur homogène contenant un mélange gazeux à densité et énergie interne constante, la température pouvant subir de fortes variations. Nous montrons l'existence globale d'une solution régulière et l'existence d'un unique état d'équilibre asymptotiquement stable pour le système complet et pour le système réduit. Une analyse de perturbation singulière globale en temps permet de montrer que le système réduit approxime le système avec chimie complète. ***Pour citer cet article : M. Massot, C. R. Acad. Sci. Paris, Ser. I 335 (2002) 93–98.*** © 2002 Académie des sciences/Éditions scientifiques et médicales Elsevier SAS

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La simulation numérique des écoulements de mélanges gazeux réactifs met en œuvre des mécanismes chimiques détaillés afin de décrire l'influence de la chimie complexe sur les écoulements. Ces mécanismes font intervenir un grand nombre de variables et d'échelles de temps. L'utilisation de mécanismes réduits permet de résoudre le problème de la raideur des systèmes obtenus dans le cas où les plus petites échelles de temps sont dues à des réactions très rapides et où la solution se trouve proche d'une « variété lente ». Il y a eu ces dix dernières années un effort considérable pour définir et résoudre numériquement les systèmes d'équations réduits sur la « variété lente » pour des applications telles que la combustion et la pollution atmosphérique (citons parmi d'autres [6,7,9] et [10]). Dans la plupart des cas, la question de la compatibilité de l'étape de réduction avec la production d'entropie due aux réactions chimiques n'est pas abordée, si ce n'est dans [10] pour un réacteur homogène isotherme, où l'on propose une projection qui ne préserve pas la structure entropique du système dynamique original. Par ailleurs on trouve une analyse de la structure du système d'EDPs régissant les écoulements de mélanges gazeux réactifs à l'équilibre chimique [3] ou sur la variété d'équilibre partiel dans le cas de la chimie réduite [5] ; dans ces deux travaux, l'étape de réduction est linéaire, constante et préserve la structure entropique ; cependant elle reste formelle, l'analyse de perturbation singulière n'y étant pas menée. Finalement, une analyse de perturbation singulière est menée dans [2] dans un cadre mathématique sans lien avec la thermochimie et donc sans la structure entropique du système dynamique d'origine.

Dans cette Note, nous considérons un réacteur homogène contenant un mélange gazeux à densité et énergie interne constante, la température pouvant subir de fortes variations. L'évolution de la composition et de la température est donnée par un système dynamique en les concentrations des espèces et en l'énergie interne totale (1). La chimie est décrite par un réseau arbitrairement complexe de réactions élémentaires réversibles (3) dont les constantes d'équilibre sont compatibles avec la thermodynamique ce qui permet l'obtention d'une structure entropique [4]. Nous étendons les travaux [3] et [4], établis à température constante, en montrant l'existence globale d'une solution régulière, l'existence d'un unique état d'équilibre asymptotiquement stable ainsi que d'un compact invariant pour le système dynamique (Proposition 1 et Théorème 2).

Nous supposons que les échelles de temps associées au taux d'avancement des réactions peuvent être partitionnées en échelles rapides et échelles lentes (7). Cette partition repose en pratique sur une étude de sensibilité qui sort du contexte de la présente Note. La structure entropique associé au réseau de réactions réversibles (3) permet alors de définir un modèle réduit sur la variété d'équilibre partiel en utilisant une projection linéaire constante, compatible avec la production d'entropie due aux réactions chimiques. Le système dynamique réduit conserve la structure entropique et reste bien posé (Proposition 4). Finalement nous estimons la distance entre la solution du système complet et la solution réduite en menant une analyse de perturbation singulière globale en temps (Théorème 5). Le détail de cette étude se trouve dans [8] et ces résultats sont un outil important pour mener l'analyse numérique de la séparation d'opérateurs en présence d'échelles rapides [1].

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1. Introduction

Numerical simulations of multicomponent reactive flows raise several difficulties created by the large number of unknowns and the wide range of temporal scales due to large and complex detailed chemical kinetic mechanisms. One way to adress the problem of the stiffness and to reduce the range of time scales to be solved, is to use reduced mechanisms for the complex chemistry. It is valid when the quickest time scales are due to very fast reactions and when, most of the time, the solution is on the so-called 'slow manifold'. There has been a tremendous effort in creating efficient and predictive numerical methods in order to define

and solve reduced system of equations for combustion and air pollution modeling applications (among other studies [6,7,9] and [10]). Most of the time, the question of the the compatibility of the reduction step on the 'slow' manifold with the entropy production due to chemical reaction is not investigated, except in [10] for an isothermal homogeneous reactor, where a nonlinear and nonconstant projection onto the partial equilibrium manifold is proposed, but it does not preserve the original entropic structure. Besides, the structure of the system of partial differential equations governing multicomponent reactive flows at chemical equilibrium is provided in [3] and the one at partial equilibrium for a reduced chemistry in [4]; in these two studies, the reduction step is linear, constant and compatible with the entropy production, however it is formal since the singular perturbation analysis is not conducted. Finally, a singular perturbation analysis is performed in [2] in a mathematical framework without thermochemical assumptions and thus without entropic structure for the original dynamical system.

In this Note, we investigate a homogeneous reactor containing a gaseous mixture at constant density and internal energy, where the temperature can encounter strong variations. We consider an arbitrarily complex network of reversible reactions, the equilibrium constant of which are compatible with thermodynamics thus providing an entropic structure [4]. We extend [3] and [4] and prove the existence of a global in time solution and of an asymptotically stable equilibrium state.

We assume that the time scales associated with the reaction rates can be partitioned into fast scales and slow scales (7). The choice of this partition relies in practice on sensitivity analysis and is beyond the scope of the present Note. The entropic structure associated with the network of reversible reactions (3) then allows to define a linear and constant projection, compatible with the entropy production due to chemical reactions, in order to obtain the reduced system on the partial equilibrium manifold for the fast reactions. The well-posedness and the entropic structure of the reduced system is proved and the distance between the full system and the reduced one is evaluated through a singular perturbation analysis, globally in time. Details of this study can be found in [8] and its application to the numerical analysis of operator splitting techniques in the presence of fast scales can be found in [1].

2. System of equations, thermochemistry and mathematical assumptions

The equations modeling a homogeneous reactor at constant density and energy express the conservation of species mass densities and internal energy of the mixture and can be written:

$$d_t u = \Omega(U), \qquad U(t=0) = U_0, \tag{1}$$

$$U = \left(\varrho^t, \mathfrak{E}\right)^t, \qquad U_0 = \left(\varrho_0^t, \mathfrak{E}_0\right)^t, \qquad \Omega = (M\omega, 0)^t, \tag{2}$$

where d_t is the time derivative operator, U the conservative variable, $\varrho^t = (\rho_1, \ldots, \rho_{n_S})$ the vector of species mass densities; n_S is the number of species, $S = [1, n_S]$ the set of species indices, $\rho = \sum_{k \in S} \rho_k = \langle \varrho, \mathcal{U} \rangle$, the total density, $\langle \, , \, \rangle$ the Euclidean scalar product, $\mathcal{U}^t = (1, \ldots, 1)$, the unit vector, m_k the molar mass of the kth species, $M = \mathrm{diag}(m_1, \ldots, m_{n_S})$ the mass weights matrix, $\omega = (\omega_1, \ldots, \omega_{n_S})^t$, the vector of molar chemical production rates. The internal energy $\mathfrak{E}$ can also be expressed as a function of the natural variable $Y^t = (\varrho^t, T)$: $\mathfrak{E} = \langle \varrho, e \rangle$, with $e = (e_1, \ldots, e_{n_S})^t$, where $e_k(T), T \geqslant 0$, is the specific internal energy of the kth species. The system (1) can also be written in terms of the natural variable $d_t Y = (M\omega, -\langle M\omega, e \rangle / \langle \varrho, c_v \rangle)^t$, so that the temperature may vary; $c_v = (c_{v1}, \ldots, c_{vn_S})^t$, is the vector of specific heats at constant volume of the species.

The (physical) entropy $\mathfrak{S}$ can be written $\mathfrak{S} = \sum_{k \in S} \rho_k s_k$, and the reduced chemical potential of the kth species, $\mu_k(\rho_k, T)/T = e_k/T + r_k - s_k, T \geqslant T_{\mathrm{ref}} > 0$, where s_k is the specific entropy of the kth species, $r_k = R/m_k$, the specific gas constant of the kth species, R the universal gas constant and T_{ref} a positive reference temperature chosen such that $\min_{k \in S}\{e_k(T_{\mathrm{ref}})\} > \max_{k \in S}\{e_k(T=0)\}$ [4].

We consider a system of N_R reversible reactions for n_S species

$$\sum_{k \in S} v'_{ki} \mathcal{S}_k \rightleftharpoons \sum_{k \in S} v''_{ki} \mathcal{S}_k, \quad i \in \mathcal{R}, \tag{3}$$
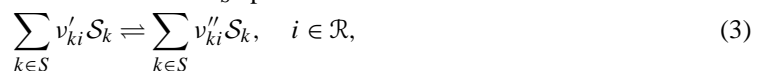
where $\mathcal{S}_k$ is the chemical symbol of the kth species, ν'_{ki} and ν''_{ki} the stoichiometric coefficients of the kth species in the ith reaction and $\mathcal{R} = [1, N_R]$ the set of reaction indices. The chemical species are assumed to be constituted by elements and we denote by $\mathcal{E}_{kl}$ the number of lth element in the kth species. We also denote by $\mathcal{E} = [1, N_E]$ the set of element indices and by N_E the number of elements. The vector of molar production rate is given by $\omega_k = \sum_{i \in \mathcal{R}} \nu_{ki} \tau_i$, where the global stoichiometric coefficients are $\nu_{ki} = \nu''_{ki} - \nu'_{ki}$, $k \in S$, $i \in \mathcal{R}$, and where τ_i are the rates of progress, of the ith reaction. We make the following assumptions on the thermochemistry:

(C$_1$) The specific heats c_{vk}, $k \in S$, are C$^\infty$ functions of $T \in [0, \infty)$. Moreover there exists a positive constant a with $0 < a \leqslant c_{vk}(\xi)$, for $\xi \geqslant 0$ and $k \in S$.

(C$_2$) The element vectors $\mathcal{E}_l$, $l \in \mathcal{E}$, defined by $\mathcal{E}_l = (\mathcal{E}_{1l}, \ldots, \mathcal{E}_{n_S l})^t$, and the reaction vectors ν_i, $i \in \mathcal{R}$, defined by $\nu_i = (\nu_{1i}, \ldots, \nu_{n_S i})^t$, satisfy the element conservation relations: $\langle \nu_i, \mathcal{E}_l \rangle = 0$, $i \in \mathcal{R}$, $l \in \mathcal{E}$, which can be rewritten $\mathcal{R} \subset \mathcal{E}^\perp$, where $\mathcal{R} = \text{span}\{\nu_i, \ i \in \mathcal{R}\}$ is of dimension n_R, and where $\mathcal{E} = \text{span}\{\mathcal{E}_l, \ l \in \mathcal{A}\}$, with $\mathcal{A} = \mathcal{E}$, is assumed of dimension $n_E = N_E$.

(C$_3$) The rates of progress τ_i are given by the law of mass action [4] with a compatibility condition of the equilibrium constants: $\log K_{ei}(T) = \sum_{k \in S} \nu_{ki} \mathcal{F}_k(T)$, where $\mathcal{F}_k = \mu_k(m_k, T)/r_k T$. The direct rate constants are C$^\infty$ positive bounded functions of $T \in [0, \infty)$.

(C$_4$) The initial internal energy verifies $\mathfrak{E}_0 > \alpha_{\text{ref}}$, with $\alpha_{\text{ref}} = \max_{k \in S}\{e_k(T_{\text{ref}})\}$ so that the reaction simplex, where ϱ lives, is the affine subspace $(\varrho_0 + M\mathcal{R}) \cap (0, \infty)^{n_S}$. There is no boundary point of the closure of the reaction simplex where the source term vanishes [3].

We define $M\mathcal{R}^{\text{Orth}} = (M\mathcal{R})^\perp \cap (M^{-1}\mathcal{E})^\perp$ so that:

$$\mathbb{R}^{n_S} = M^{-1}\mathcal{E} \overset{\perp}{\oplus} M\mathcal{R}^{\text{Orth}} \overset{\perp}{\oplus} M\mathcal{R}, \tag{4}$$

$M\omega \in M\mathcal{R}$ and the mass conservation relations $\sum_{k \in S} m_k \omega_k = 0$ can also be written $\mathcal{U} \in M^{-1}\mathcal{E}$.

PROPOSITION 1. – *Let us assume $\varrho_0 \in (0, \infty)^{n_S}$ and properties* (C$_1$)–(C$_4$). *Then there exists a C$^\infty$ global in time solution of the dynamical system* (1) *such that the species densities are positive and bounded; there exists two positive temperatures, T_1 and T_2, such that $T_{\text{ref}} < T_1 \leqslant T(t) \leqslant T_2$.*

Proof. – The expression of ω_k allows to prove that ϱ can not approach the frontier of the reaction simplex in finite time and that a global solution exists. The reaction simplex is bounded from $\mathcal{U} \in (M\mathcal{R})^\perp$; (C$_4$) and the fixed internal energy provide the bounds on the temperature. $\quad\square$

3. Global asymptotic stability of equilibrium states

For system (1), we define the mathematical entropy function σ as the opposite of the physical mixture entropy density per unit volume $\sigma = -\mathfrak{S}$ and consider the entropic variables [4]:

$$V = \mathfrak{d}_U \sigma^t = \left(\mathcal{Y}^t, -1/T\right)^t, \qquad \mathcal{Y} = (\mu_1/T, \ldots, \mu_{n_S}/T)^t, \tag{5}$$

where $\mathcal{Y}$ is the vector of reduced chemical potential. The maps $U \to V$ and $U \to Y$ are C$^\infty$ diffeomorphisms from $\mathcal{O}_U$ onto $\mathcal{O}_V$ and $\mathcal{O}_Y$ [4], where $\mathcal{O}_U = \{u \in (0, \infty)^{n_S} \times (0, \infty); \ u_{n_S+1} > \alpha_{\text{ref}} \sum_{k \in S} u_k\}$, with $\mathcal{O}_V \subset (0, \infty)^{n_S} \times (-\infty, -1/T_{\text{ref}})$ and $\mathcal{O}_Y \subset (0, \infty)^{n_S} \times (T_{\text{ref}}, \infty)$.

Using decomposition (4), we define P^{Orth} and P^{a}, two matrices of dimension $n_S \times (n_S - n_E - n_R)$ and $n_S \times n_E$ which are the coordinates of two bases of $M\mathcal{R}^{\text{Orth}}$ and $M^{-1}\mathcal{E}$ in the canonical base. We define $\varrho^{\text{a}} = (P^{\text{a}})^t \varrho$, $\varrho^{\text{Orth}} = (P^{\text{Orth}})^t \varrho$, which are invariant through (1). Making use of the entropic structure, extending [3,4], we prove the following theorem.

THEOREM 2. – *Assume properties* (C$_1$)–(C$_4$). *There exists a unique equilibrium point $U^{\text{e}} = (\varrho^{\text{e}}, \mathfrak{E}_0) \in \mathcal{O}_U$, where ϱ^{e} is in the reaction simplex, such that*

$$\omega_k(U^{\text{e}}) = 0, \quad k \in S, \qquad \tau_i(U^{\text{e}}) = 0, \quad i \in \mathcal{R}, \qquad \mathcal{Y}^{\text{e}}(U^{\text{e}}) \in (M\mathcal{R})^\perp. \tag{6}$$

$\varrho^{\text{e}} = \varrho^{\text{e}}(\varrho_0^{\text{a}}, \varrho_0^{\text{Orth}}, \mathfrak{E}_0)$ *is a smooth function of its arguments. The linearization of the source term at U^{e} has nonpositive eigenvalues and exactly n_R negative real eigenvalues. The entropy production due to chemical*

reactions at $\mathfrak{E}_0$ admits 0 as a strict maximum at ϱ^e over the reaction simplex. Given $\mathfrak{E}_0$, there exists a closed convex polyhedron K, a compact subset of the reaction simplex containing ϱ^e, invariant by (1), such that for any $\varrho_0 \in K$, the equilibrium point, U^e, is asymptotically stable.

4. Fast and Slow chemistry

Let us now introduce the 'Fast' and 'Slow' scales in the system :

$$\Omega = \Omega^{\text{Slow}} + \frac{\Omega^{\text{Fast}}}{\varepsilon}, \qquad \Omega^\alpha = \left(M\omega^\alpha, 0\right)^t, \qquad \omega^\alpha = \sum_{i \in \mathbb{S}^\alpha} \tau_i^\alpha \nu_i^\alpha, \qquad \alpha = \text{Fast, Slow}, \tag{7}$$

where ω^{Fast} relates to the subset of 'Fast' reactions, the reaction vectors of which are spanning $\mathcal{R}^{\text{Fast}}$ of dimension n_R^{Fast} and are given by ν_i^{Fast}, $i \in \mathcal{R}^{\text{Fast}}$, and ω^{Slow}, to the subset of 'Slow' reactions, the reaction vectors of which are spanning $\mathcal{R}^{\text{Slow}}$ of dimension ν_i^{Slow} and are given by ν_i^{Slow}, $i \in \mathcal{R}^{\text{Slow}}$. We define $M\mathcal{R}^{\text{Orth}} = \left(M\mathcal{R}^{\text{Fast}}\right)^\perp \cap M\mathcal{R}$, denote $n^{\text{Orth}} = n_E + \nu_i^{\text{Slow}}$ and assume that $n^{\text{Orth}} + n_R^{\text{Fast}} = n_S$, for the sake of simplicity. In order to take into account the internal energy variable, which is invariant through the dynamical system, we extend the previous spaces to $\mathbb{R}^{n_S+1}$ by considering $\mathbb{R}^{n_S} \hookrightarrow \mathbb{R}^{n_S+1}$ and adding e_{n_S+1} of the canonical basis to the element conservation subspace. We get the same orthogonal decomposition as (4), with obvious notations: $\mathbb{R}^{n_S+1} = (M^{-1}\mathcal{E})^\star \oplus^\perp (M\mathcal{R}^{\text{Orth}})^\star \oplus^\perp (M\mathcal{R}^{\text{Fast}})^\star$ and define $\mathcal{A}^\star = \mathcal{A} \cup \{n_S + 1\}$.

DEFINITION 3. – A partial equilibrium point $U^{\text{pe}} \in \mathcal{O}_U$ and the associated $V^{\text{pe}} \in \mathcal{O}_V$ are defined by

$$\omega^{\text{Fast}}\left(U^{\text{pe}}\right) = 0, \quad \text{or equivalently,} \quad V^{\text{pe}} \in \left(\left(M\mathcal{R}^{\text{Fast}}\right)^\star\right)^\perp. \tag{8}$$

We define $P^\perp = (P^a, P^{\text{Orth}})$ and P^{Fast}, two matrices which are the coordinates of two bases of $\left(M\mathcal{R}^{\text{Fast}}\right)^\perp$ and $M\mathcal{R}^{\text{Fast}}$, and $\varrho^\perp = (P^\perp)^t \varrho = (\varrho^a, \varrho^{\text{Orth}})^t$, $\varrho^{\text{Fast}} = (P^{\text{Fast}})^t \varrho$, where ϱ^a is the element density vector [3]. In order to use the previous decomposition on U, we define the basis matrices:

$$\Pi^\perp = \begin{pmatrix} P^\perp & 0_{n_S \times 1} \\ 0_{1 \times n^{\text{Orth}}} & 1 \end{pmatrix}, \quad \Pi^{\text{Fast}} = \begin{pmatrix} P^{\text{Fast}} & 0_{n_R^{\text{Fast}} \times 1} \\ 0_{1 \times n_R^{\text{Fast}}} & 1 \end{pmatrix},$$

$$I = \Pi^\perp J^\perp \left(\Pi^\perp\right)^t + \Pi^{\text{Fast}} J^{\text{Fast}} \left(\Pi^{\text{Fast}}\right)^t, \tag{9}$$

where the metric matrices $J^\perp$ and J^{Fast} are defined by $(J^\perp)_{i,j}^{-1} = \langle \Pi_i^\perp, \Pi_j^\perp \rangle$, $i, j \in \mathcal{A}^\star \cup [n_E + 1, n^{\text{Orth}}]$, and $(J^{\text{Fast}})_{i,j}^{-1} = \langle \Pi_i^{\text{Fast}}, \Pi_j^{\text{Fast}} \rangle$, $i, j \in [n^{\text{Orth}} + 1, n_S]$.

5. Reduced chemistry at partial equilibrium and singular perturbation analysis

The algebraic constraints of partial equilibrium are linear in the variable V (8). We then take as a new variable on the partial equilibrium manifold $V_{\text{ext}}^\perp$, the coordinates of $V = \Pi^\perp V_{\text{ext}}^\perp$ in the basis of $\left(\left(M\mathcal{R}^{\text{Fast}}\right)^\star\right)^\perp$. We also define $U_{\text{ext}}^\perp = (\Pi^\perp)^t U = (\varrho^a, \varrho^{\text{Orth}}, \mathfrak{E})^t$. We prove that $V_{\text{ext}}^\perp$ is the entropic variable of $U_{\text{ext}}^\perp$ through σ and derive the reduced system in the next proposition [4,8].

PROPOSITION 4. – *The reduced dynamical system on the partial equilibrium manifold is defined by*

$$d_t U_{\text{ext}}^\perp = \left(\Pi^\perp\right)^t \Omega^{\text{Slow}}\left(U\left(U_{\text{ext}}^\perp\right)\right), \qquad U\left(U_{\text{ext}}^\perp\right) = \Pi^\perp J^\perp U_{\text{ext}}^\perp + \Pi^{\text{Fast}} J^{\text{Fast}} \left(\varrho^{\text{Fastpe}}\left(U_{\text{ext}}^\perp\right), 0\right)^t. \tag{10}$$

The entropy $\sigma^\perp = \sigma(U(U_{\text{ext}}^\perp))$ is a C^∞ convex function of $U_{\text{ext}}^\perp$; the corresponding entropic variable on the partial equilibrium manifold is such that

$$V_{\text{ext}}^\perp = \left(\partial_{U_{\text{ext}}^\perp} \sigma^\perp\right)^t, \qquad V = \Pi^\perp V_{\text{ext}}^\perp, \qquad V \in \left(\left(M\mathcal{R}^{\text{Fast}}\right)^\star\right)^\perp. \tag{11}$$

The map $U_{\text{ext}}^\perp \to V_{\text{ext}}^\perp$ is a C^∞ diffeomorphism from the open convex set $\mathcal{O}_{U_{\text{ext}}^\perp} = \{u \in \mathfrak{p} \times (T_{\text{ref}}, \infty);$

$u_{n^{\text{Orth}}+1} > \alpha_{\text{ref}} \sum_{l \in \mathcal{A}} u_l\}$, where $\mathfrak{p} \subset (0, \infty)^{n^{\text{Orth}}}$ is the convex set of element conservation and slow variable,

onto $\mathcal{O}_{V_{\text{ext}}^{\perp}}$. The entropy production on the partial equilibrium manifold is negative and there exists a unique asymptotically stable point $U_{\text{ext}}^{\perp\,\text{e}}$ which is the full equilibrium, $\Omega(U(U_{\text{ext}}^{\perp\,\text{e}})) = 0$.

We can reformulate system (1) using the projections $(U^{\perp}, U^{\text{Fast}})$ of U and $\Omega(U) = \overline{\Omega}(U^{\perp}, U^{\text{Fast}})$ and compare this system with full chemistry to the reduced system (10) in the following theorem.

THEOREM 5. – *Let us define the internal layer by*:
$$d_{\tau} U_{\text{int}}^{\text{Fast}} = \left(\Pi^{\text{Fast}}\right)^{t} \overline{\Omega}^{\text{Fast}}\left(U_0^{\perp}, U_{\text{int}}^{\text{Fast}}\right), \quad U_{\text{int}}^{\text{Fast}}(t=0) = U_0^{\text{Fast}}, \tag{12}$$
with $\tau = t/\varepsilon$, and the external layer by Eq. (10) *with the initial condition $U_{\text{ext}}^{\perp}(t=0) = U_0^{\perp}$.*

Assuming (C$_1$)–(C$_4$), *there exists a convex compact polyhedron K, $K \subset (\varrho_0 + M\mathcal{R}) \cap (0, \infty)^{n_S} \times \{\mathfrak{E}_0\}$, invariant by both systems* (1), (10) *and* (12). *System* (12) *admits a unique asymptotically stable partial equilibrium state $\varrho^{\text{pe}}(U_0^{\perp})$ in $(\varrho_0 + M\mathcal{R}^{\text{Fast}}) \cap (0, \infty)^{n_S}$.*

Besides, there exists U^{e} an asymptotically stable equilibrium point for both the complete system (1) *and for the exterior solution* (10).

Finally, for ε sufficiently small, there exists $\gamma > 0$ such that for $t \in [0, +\infty)$:
$$U^{\text{Fast}}(t, \varepsilon) = U^{\text{Fastpe}}\left(U_{\text{ext}}^{\perp}(t)\right) + \text{O}\left(\exp\left(-\gamma\frac{t}{\varepsilon}\right)\right) + \text{O}(\varepsilon), \qquad U^{\perp}(t, \varepsilon) = U_{\text{ext}}^{\perp}(t) + \text{O}(\varepsilon). \tag{13}$$

Proof. – The internal layer problem is related to a regular perturbation problem, the study of which relies on Theorem 2. For a given $\mu > 0$, it insures that, after a time interval $[0, t_0]$ as small as we want depending on ε, the solution is at a small distance of the partial equilibrium manifold; it can be rewritten in terms of the entropic variable $V = \Pi^{\perp} V^{\perp} + \Pi^{\text{Fast}} V^{\text{Fast}}$ through $|\Pi^{\text{Fast}} V^{\text{Fast}}| < \mu$. The asymptotic stability of the unique full equilibrium point V^{e} provides the existence of a time t_1 such that for all $t \geqslant t_1$, $|\Pi^{\perp}(V^{\perp} - V_{\text{ext}}^{\perp\,\text{e}})| < \mu$, and $|\Pi^{\text{Fast}} V^{\text{Fast}}| < \mu$. We first prove that there exists a neighborhood of $t = t_0$, say $[t_0, t_2)$ where $|\Pi^{\text{Fast}} V^{\text{Fast}}| < \mu$ still holds and thus, for sufficiently small ε, $|\Pi^{\perp}(V^{\perp} - V_{\text{ext}}^{\perp})| < \mu$, also. In order to prove that $t_2 > t_1$, we assume that there exists $t_3 \leqslant t_1$ such that $|\Pi^{\text{Fast}} V^{\text{Fast}}| = \mu$ and use the dynamical system in the entropic variable V. Indeed, it can be proved that there exists a symmetric positive definite matrix $D(V^{\perp})$ such that $d_t \langle V^{\text{Fast}}, D\, V^{\text{Fast}} \rangle = \langle V^{\text{Fast}}, (\Pi^{\text{Fast}})^t \Omega(U(V)) \rangle / \varepsilon + \Psi$, where Ψ is bounded and $\langle V^{\text{Fast}}, (\Pi^{\text{Fast}})^t \Omega(U(V)) \rangle < 0$ is the entropy production due to fast chemical reactions. For sufficiently small ε, one can prove that the distance of V^{Fast} from 0 has to decrease at t_3 such that $|\Pi^{\text{Fast}} V^{\text{Fast}}|$ can not reach μ at this point. Finally the asymptotic expansion is obtained through a proof which is close to the one in [11]. $\quad\square$

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