Initially Approximated Quasi Equilibrium Manifold

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Summary: Most commonly, kinetics model reduction techniques are based on exploiting time scale separation into fast and slow reaction processes. Then, a researcher approximates the system dynamically with dimension reduction for slow ones eliminating the fast modes. The main idea behind the construction of the lower dimension manifold is based on finding its initial approximation using Quasi Equilibrium Manifold (QEM). Here, we provide an efficient numerical method, which allow us to calculate low dimensional manifolds of chemical reaction systems. This computation technique is not restricted to our specific complex problem, but it can also be applied to other reacting flows or dynamic systems provided with the condition that a large number of extra (decaying) components can be eliminated from the system. Through computational approach, we approximate low dimensional manifold for a mechanism of six chemical species to simplify complex chemical kinetics. A reduced descriptive form of slow invariant manifold is obtained from dissipative system. This method is applicable for higher dimensions and is applied over an oxidation of CO/Pt.

Keyword: chemical kinetics, model reduction, entropy, invariant manifolds, variation problem, Lagrange multipliers method.

Introduction

The field of chemical kinetics is full of challenges and interesting activities involving complexity which is not only involved in chemistry but also in other areas of science, *i.e*., mathematics and physics.

In order to construct a lower dimensional manifold, many modern model reduction techniques make use of the Multiple Time Scales Method. By considering the behavior of the system for a long time, fast transient dynamical models are assumed to be relaxed within the slowly reduced model approximations [1]. In this way the original system of differential equations is reduced to lower dimensions without losing the general applicability of the system [2, 3].

It is necessary to find a reduction system that does not affect system's accuracy and explain the whole mechanism of the system.

The computational singular perturbation method, developed by Lam (1986) and Gossips (1989), determines the result similar to the analytical singular perturbation method and it is popular for stiff systems.

The most common modern model reduction techniques include lumping, sensitivity and time scale analysis.

In a time scale analysis, the computational singular perturbation (CSP) and intrinsic low-dimensional manifolds (ILDM) [4-6] are very common while the quasi equilibrium (QE) and quasi-steady-state assumption (QSSA) [7] also demands the knowledge of the involved materials.

The classical Quasi Steady State Approximation proposed by Bodenstein (1913- [8]), basically depends on the relative pettiness of concentrations of some of the active reagents like (radicals, substrate-enzyme complexes) [9-11].

Lumping analysis combine the reagents into quasi-components for dimension reduction [12-15].

It is possible to construct QEM analytically with the help of Lagrange multipliers, but the idea fails or becomes more complicated for a larger dimensional QEM.

Here, we consider a general method of constructing the reduced descriptive form of dissipative systems of reaction kinetics. This idea belongs to late 80s and early 90s [16-18]. The new idea of Quasi Equilibrium Grid (QEG) construction will be considered as a discrete analog of QEM in order to avoid all the difficulties faced in large dimension stiff problem. The constructive algorithm is applicable for any dimension and it is implemented on an example of a complex chemical reaction. Accuracy of this method can be easily observed/confirmed and it is possible to get some other SIM approximations as well depending on same algorithms.

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Paper Organized

This paper is organized as follows: we start our work by a formal description of some background and chemical representation uses throughout the paper within a section 2. The role of thermodynamics is explained in section 2.2 as equilibrium is defined by thermodynamics. The main idea of the slow invariant manifold and invariance equation is described in section 2.3 which basically gives invariant grids *i.e*. positively invariant manifolds for dissipative systems. Iterative method for the construction of invariant grid is discussed in section 3.3.

In this section, the main idea of constructing one dimension quasi-equilibrium grid algorithm is presented. This is then implemented on an example of oxidation of carbon monoxide over platinum and a one dimensional manifold is obtained in section 4. The idea is extended for higher dimensions by using a straightforward extension and a two dimensional manifold will be obtained in section 4.1. Finally, in section 5, the paper is concluded.

Background

Chemical Kinetics Representation

For a basic notation of the chemical kinetics and its formalism consider a list of finite set of components along with symbols: $A_1,\ldots,A_n$.

A reaction mechanism, defined by a finite set of elementary reactions, provides a set of stoichiometric equations.

$$\sum_i^n \alpha_{\rho i} A_i \rightarrow \sum_i^n \beta_{\rho i} A_i, \qquad (1)$$

$\alpha_{\rho i}, \beta_{\rho i}$, are *stoichiometric coefficients* (nonnegative integers) and $\rho = 1, \ldots, m$ gives the reaction number. n-dimensional *stoichiometric vector* γ_ρ of the reaction (1) is

$$\gamma_{\rho i} = \beta_{\rho i} - \alpha_{\rho i}, \qquad (2)$$

Roughly speaking it is, 'gain minus loss' in the $\rho\ th$ reaction.

The reaction rate, $r_\rho, (or\ W_\rho)$, which corresponds to each reaction, (1) is a non-negative extensive quantity given by mass action law

$$r_\rho(c,T) = k_\rho(T)\prod_i c_i^{\alpha_{\rho i}}, \qquad (3)$$

As a function of concentration $\mathbf{c}$ and temperature. Whereas $k_\rho(T)$ is a reaction rate constant.

As an intensive variable $c_i = N_i / V$ ($V > 0$ Volume), the vector $\mathbf{c} = \mathbf{N} / V$ is a vector of concentration while $N_i \in A_i$ is an extensive variable. The kinetic equations for a system (without external flux) will become:

$$\frac{d\mathbf{N}}{dt} = V\sum_\rho r_\rho \gamma_\rho, \quad or$$
$$\dot{\mathbf{N}} = VJ(c), \quad J(c) = \sum_\rho \gamma_\rho W_\rho(c). \qquad (4)$$

When a system (4) moves towards equilibrium, the relation between the quantities is defined by the principle of detail balance *i.e*,

$$W_\rho^+(c^{eq}) = W_\rho^-(c^{eq}), \quad \rho = 1...m. \qquad (5)$$

$c^{eq}(T)$ is the equilibrium. For isolated or isothermal conditions, we get an extra equation in the form of U, V or $T = Cnt$ (*i.e*, constant). Finally, the above system (4) will take a form

$$\dot{c} = \sum_\rho \gamma_\rho W_\rho(c) = J(c). \qquad (6)$$

Similarly, other constraints (linear) *i.e*. conservation of atoms are taken into account as well.

$$Dc = Cnt. \qquad (7)$$

Once, if we become able to define thermodynamic structure of the system, then we will be able to transform our system into a dissipative system.

Thermodynamics Potential and Thermodynamics Projector

Due to the dissipative property of our system, it has a thermodynamic potential, *i.e*. Lyapunov function G which has an important role for the stability and convergence of the system and it follows the second

law of thermodynamics. This means the Lyapunov function decreases monotonically until it reaches global minimum c^{eq} of the phase space. It is also possible to get a number of positively closed invariant sets in a dissipative system.

An ideal case under the constant volume and at a constant temperature of perfect free gas energy is given by [2]

$$G = \sum_{i=1}^{n} c_i [ln(c_i / c_i^{eq}) - 1]. \quad (8)$$

knowing the G function, we are able to find its gradient ∇G and also its second derivatives matrix H such as:

$$\nabla G = |\, ln(c_i / c_i^{eq}) \,|, H = |\, \partial^2 G / \partial c_i \partial c_j \,|. \quad (9)$$

Use thermodynamic scalar product $\langle , \rangle$ as follows

$$\langle x, y \rangle = (x, H y), \quad (10)$$

where (,) implies Euclidean scalar product.

An operator (thermodynamic projector) projects the vector field at each point of the manifold into the tangent space to give the induced vector field $PJ(\mathbf{c})$, defines the "slow and fast motions" duality [19]. In this way, a projector depends on two things, tangent space of the manifold Ω and concentration point c. Now the differential of a linear functional G, and induced vector field are:

$$DG(x) = (\nabla G(c), x).$$

$$DG(PJ) \le 0, \quad \forall \; c \in \Omega. \quad (11)$$

where the projector P considers the above condition if and only if:

$$ker(P) \subset ker(DG), \quad \forall \; \mathbf{c} \in \Omega \quad (12)$$

ker is the null space of an operator.

After finding a reduced description form, our SIM will become a q (let us suppose) dimensional SIM. It plays an important role for the construction of method of invariant grids (MIG). Let us consider g as a discrete subset of q dimension parametric space. If we are able to find such an approximation in order to restore a smooth map F from the discrete map $F \| g$ then the derivatives $f_i = \partial F / \partial y_i$ at each grid point is available, and the tangent space will become:

$$T_y = Lin(f_i), \quad i = 1 \ldots n \quad (13)$$

Further, if $y \in g$ acquires equilibrium, while for other points $(DG)F(y)(x) \neq 0$ for some $x \in T_y$. Now the thermodynamic projector can be defined [2] for any subspace $T_{oy} = T_y \cap ker(DG)$, where $T_{oy} = T_y \cap ker(DG)$, by introducing a new vector with certain conditions.

$$e_y \in T_y,$$

$$\langle e_y, x \rangle = 0, \quad \forall \; x \in T_{oy}, \quad (14)$$

$$DG(e_y) = 1.$$

If P_o is orthogonal projector on T_{o} w.r.t entropic scalar product (10), then vector projection (thermodynamic) of x is defined as:

$$T_{oy} \neq T_y \Rightarrow P_x + P_{ox} + e_y \, DG(x)$$

$$T_{oy} = T_y \Rightarrow P_x + P_{ox} \quad (15)$$

Invariant Manifold and Invariance Condition

In order to avoid the complexity of systems, we normally move towards the reduce description.

Although, there is no specific definition for invariant manifold (positive), the behaviour of the immersed manifold along the trajectories in a phase space will be measured. In this way, we shall obtain a new equation for the dynamics of the manifold in phase space. Invariant manifolds are the fixed points for this extended dynamics and slow invariant manifold are the Lyapunov stable fixed points.

The invariance condition for reduce decrypted manifold Ω is

$$[1 - P]J(c) = 0, \quad \forall \; t \ge c \quad (16)$$

P is the projector over any tangent bundle of the manifold Ω. If this condition of invariance is not satisfied by the manifold, then it is not invariant manifold.

Slow Invariant Manifold

Several methods are available to measure the slow invariant manifold. Here, we consider a '*Newton method with incomplete linearization*', an efficient method for the invariance equation. For detail of this method, we refer to (Chapter Six [19]). It is a basis of an iterative construction of the manifolds of slow motions [20].

The best initial approximation for this method is quasi-equilibrium manifold. Since it naturally obeys the conditional maxima of the entropy and it is also widely used in non-equilibrium thermodynamics *i.e.* dealing with (or without) the corrections to quasi equilibrium approximation.

Quasi Equilibrium Manifold

Quasi equilibrium approximation basically deals with two entities: entropy S and the slow variables M. Entropy is a Lyapunov function (concave) depending on equilibrium data and it does not depend directly on kinetic coefficients and increase in time. Due to this property, it is called universal. [21].

$$\frac{dS}{dt} \geq 0 , \qquad (17)$$

Slow variables are the differentiable functions of variables x: $M = m(x)$.

Selecting slow variables means believing on hypothesis about separation of motion into slow and fast motion depending on two assumptions, *i.e.* the assumption of small fast-slow projection and slave assumption [21].

According to QE approximation, we obtain functions x_M^* as solutions of the *MaxEnt* optimization problem.

$$S(x) \rightarrow \max \quad \text{w.r.t} \quad m(x) = M . \qquad (18)$$

The rationale behind this approach is simple: during the fast motion entropy S increases while M almost remains unchanged.

Therefore, it's natural to assume that x_M^* is close to the solution of the MaxEnt optimization problem (18). Also, x_M^* represents a solution to the MaxEnt problem.

Being more precise and considering the concentration vectors l, which satisfy the atomic balance constraints defined by the equation (7). Within the space l, we are interested only in those points which minimize the Lyapunov function. The manifold we obtained is called as Quasi Equilibrium Manifold, In an $n-$ dimensional chemical species if l is atomic balance constraint then we are left with $n-l$ degrees of freedom. If $q < (n-l)$ is the dimension of the QEM, then we are left with the reduced descripted variables of $\xi_1 \ldots \xi_q$, mentioned as:

$$(m_1, c) = \xi_1, \ldots, (m_q, c) = \xi_q , \qquad (19)$$

whereas, m_i are n-dimensional vectors. Now, the solution of the variation problem $G \rightarrow min$, under consideration of constraints (6) which represent the QEM and it must respect the following conditions:

$$G = \sum_{i=1}^{n} c_i [ln(c_i / c_i^{eq}) - 1] \rightarrow min$$

$$(m, \mathbf{c}) = \xi$$

$$Dc = (cnt_1, cnt_2)^T . \qquad (20)$$

Spectral Quasi Equilibrium Manifold

By choosing different vector sets m_i we obtained different QEM. If the choice of selecting the vectors m_i is done from the q left eigenvectors x_i^{st} of the Jacobian matrix $L(c^{eq})$ corresponding to small absolute eigen values. Then we are dealing with a Spectral Quasi Equilibrium manifold (SQEM) [2, 22].

This new procedure is better than the Lagrange multiplier because it can deal with the higher dimensional problem (*i.e.* number of species), where Lagrange method usually fails or becomes more complicated to be handled. An algorithm developed by Quasi Equilibrium Grid (QEG) easily implements a discrete analogue set of QEM in a 1D and can be further extended to higher dimensions.

Construction of Quasi equilibrium Grids (CQEG)

Let us now discuss a one dimensional quasi-equilibrium manifold with an assumption that node c_p lies on the manifold and we are interested to find the next one c_{p+1} which also lies on it. This can be done by adding a shift vector $hc_p : c_{p+1} = c_p + hc_p$ as shown in Fig. 1 a,

The procedure of selecting a new QEM-node c_{p+1} is applicable till each QEM-node c_p is calculated and it satisfies the condition (7).

A convenient way is to describe the process by [23] that takes the conditions (7) automatically into account to express any shift $\mathrm{h}c_p$ as a linear combination of vectors υ_i

$$\mathrm{h}c_p = \sum_i^z \upsilon_i \rho_i \qquad (21)$$

where, ρ_i are the basis in a null space of matrix D having a dimension $z = n - l$. Now the tangent space T at any QEM-node c_{p+1} lies on a surface G is a linear constraint for the system. Although many points c satisfy these constants but we are interested only in those which minimize the G function.

The line l passing from c_{p+1} and c has parametric form $c = \phi t + c_{p+1}$, where t is a vector of T spanning l and ϕ is a parameter.

Now the linear constraints for (20) can be written as

$$\begin{aligned}(m_1,c) &= \phi(m_1,t)+(m_1,c^i_{p+1}) \Rightarrow (m_1,t)=0, \quad \forall t \in T\\ (m_q,c) &= \phi(m_q,t)+(m_q,c^i_{p+1}) \Rightarrow (m_q,t)=0, \quad \forall t \in T\\ (d_i,c) &= \phi(d_i,t)+(d_i,c^i_{p+1}) \Rightarrow (d_i,t)=0, \quad \forall t \in T \qquad (22)\end{aligned}$$

In matrix form it can be represented as:

$$E = \begin{bmatrix} \mathbf{m_1} \\ \mathrm{M} \\ \mathbf{m_q} \\ D \end{bmatrix} \qquad (23)$$

Here, m_1 is the first reduced variable vector $(q=1)$ and for a higher dimension we have $\mathrm{m}_1,..,\mathrm{m}_q$ Then, the dimension of basis t_j in $ker(E)$ will be $(z-q)$.

As we are interested in all the points c_{p+1} of T which minimize the G function (by definition QEM). This can be calculated by taking the orthogonal condition.

$$(\nabla G(c_{p+1}), t_j) = 0, \quad \forall t \in T, \ j = 1,...,z-1 \qquad (24)$$

In spite of above equation, the QEG algorithm based on two more assumptions [23] that is known node c_n is close to the QEM, although it is not necessary that it belongs to QEM.

Secondly, the shift vector $\mathrm{h}c_p$ is also close enough so that the gradient $\nabla G(c_{p+1})$ can be approximated to the first order.

$$\nabla G(c_{p+1}) = \nabla G(c_p) + H(c_p)\mathrm{h}c_p, \qquad (25)$$

where $H(c_p) = [\frac{\partial^2 G}{\partial c_i \partial c_j}]$ denotes the matrix of second derivatives of the function G evaluated at the point c_p. By substituting equations (25) and (21) in (24), we obtain:

$$\sum_{i=1}^{z} (t_j, H(c_p)\rho_i)\upsilon_i = -(t_j, \nabla G(c_p)), \quad \forall j = 1,...,z-1 \qquad (26)$$

By using the entropic scalar product (14), above equations can be written as,

$$\sum_{i=1}^{z} \langle t_j, \rho_i \rangle \upsilon_i = -(t_j, \nabla G(c_p)), \quad \forall j = 1,...,z-1 \qquad (27)$$

Matrix H and ∇G are calculated at each known node c_p. If the node belongs to equilibrium point, then the right hand side of the above equation will become zero. The node collection which has been subsequently evaluated through (27), will be called a Quasi Equilibrium Grid (QEG).

Although there is no restriction for the construction of geometric structure of the grid, but the best possible condition can be applied by fixing the Euclidean norm of shift vector $\|\mathrm{h}c_n\|$. For further details of fixing the Grid spacing, we refer the readers to [2]. By fixing the parameters and $(q-1)$ independent vectors m_i, geometric closure can be achieved. In general, it can be written as:

$$\begin{aligned}\sum_{i=1}^{z} \langle t_j, \rho_i \rangle \upsilon_i &= -(t_j, \nabla G(c_p)), \quad \forall j = 1,...,z-1\\ \sum_{i=1}^{z} (m, \rho_i)\upsilon_i &= 0, \qquad (28)\end{aligned}$$

$\| h c_p \| = \grave{o}^2$.

By solving the system (28) at each node point, we generally obtain two real value solutions c_p^{l} and c_p^{l} as shown in Fig. [1] b.

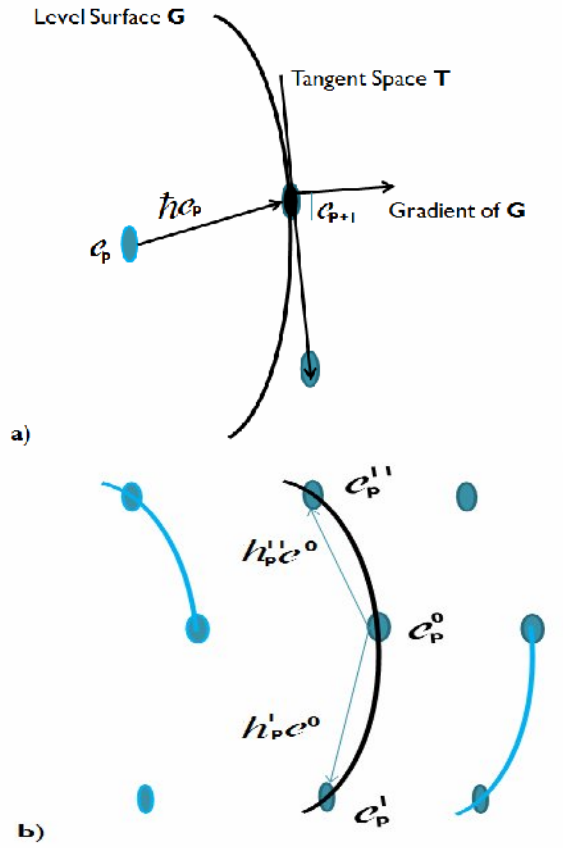


Fig. 1: a) Variation from one grid to next grid point. b) Two solutions from one grid towards the left and right branch.

Now the q dimension grid construction is split into q subsequent steps. Starting from the equilibrium point c^{eq} the system (28) is solved by choosing first slow variable vector m_1 among the q available vectors. In this way, we obtain first SQEM trajectory given by QEG nodes Fig. 2: **a**.

Similarly, by selecting the second m_2 among the remaining $q-1$ available vectors, we obtain some more combinations of nodes Fig. 2 b. The procedure can be extendable to $q\,th$ step to get all the possible combination of vectors. This idea is used to construct the higher dimensional manifold and is illustrated with example in the next section.

Example at Work

Let us describe four step reversible reaction involving six chemical substances, defined as: $O_2 = A_1, CO = A_2, CO_2 = A_3, Pt = A_4, PtO = A_5, PtCO = A_6$, Whereas oxygen, carbon monoxide and carbon dioxide are gases, and platinum and its oxides are surfaces. The conservation law given by (7) is 2 x 6 matrix, $D\ c = c\ n\ t$.

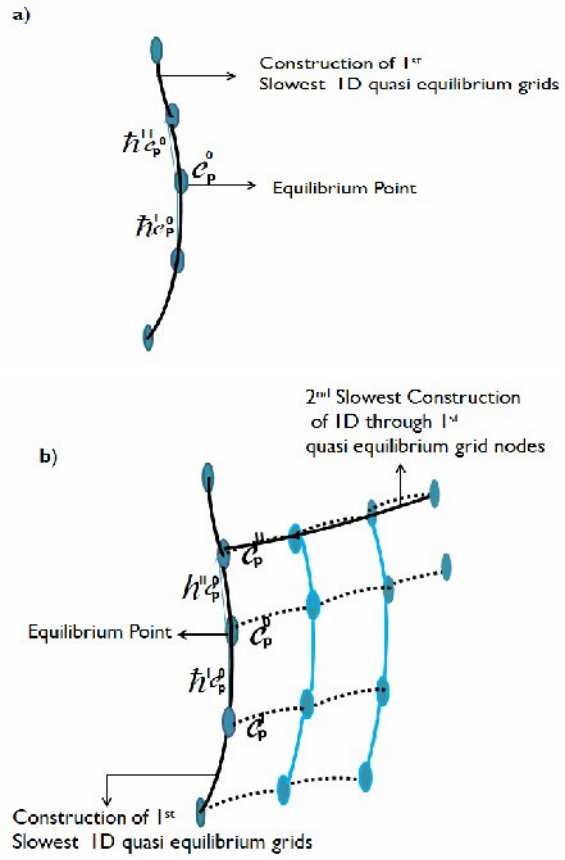
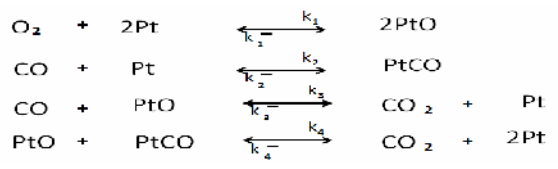


Fig. 2: **a)** First 1D QEG construction starting from the equilibrium point which then extended to both sides. **b**) 2D QEG construction obtained from the 1D invariant grid in the node.



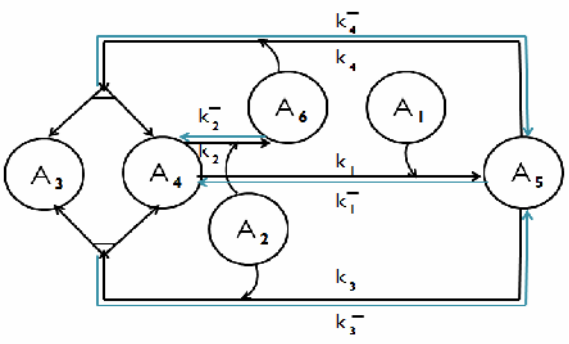


Fig. 3: Mechanism and graph for the *oxidation of carbon monoxide over platinum.*

$$\begin{bmatrix} 2 & 1 & 2 & 0 & 1 & 1 \\ 0 & 0 & 0 & 1 & 1 & 1 \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \\ c_5 \\ c_6 \end{bmatrix} = \begin{bmatrix} cnt_1 \\ cnt_2 \end{bmatrix} \qquad (29)$$

$$J(c) = \begin{bmatrix} k_1^- c_5^{\,2} - k_1 c_1 c_4^{\,2} \\ k_2^- c_6 - k_2 c_2 c_4 + k_3^- c_3 c_4 - k_3 c_2 c_5 \\ k_3 c_2 c_5 - k_3^- c_3 c_4 + k_4 c_5 c_6 - k_4^- c_3 c_4^{\,2} \\ 2k_1^- c_5^{\,2} - 2k_1 c_1 c_4^{\,2} + k_2^- c_6 - k_2 c_2 c_4 + k_3 c_2 c_5 - k_3^- c_3 c_4 + 2k_4 c_5 c_6 - 2k_4^- c_3 c_4^{\,2} \\ -2k_1^- c_5^{\,2} + 2k_1 c_1 c_4^{\,2} - k_3 c_2 c_5 + k_3^- c_3 c_4 - k_4 c_5 c_6 + k_4^- c_3 c_4^{\,2} \\ -k_2^- c_6 + k_2 c_2 c_4 - k_4 c_5 c_6 + k_4^- c_3 c_4^{\,2} \end{bmatrix} \qquad (31)$$

Now, we are using the following set of parameters in this case:

$k_1^+ = 1, k_2^+ = 1, k_3^+ = 1, k_4^+ = 1,$

$$c_1^{eq} = 0.1, c_2^{eq} = .025, c_3^{eq} = 0.35, c_4^{eq} = 0.5, c_5^{eq} = 0.9, c_6^{eq} = 0.2$$

Two left eigenvectors of the Jacobian matrix $\{L = \frac{\partial J_i}{\partial c_j}|_{c^{eq}}\}$ will become,

$$x_1^{sl} = [-0.9075 \ -0.1471 \ 0.1830 \ -0.1141 \ 0.1305 \ -0.3019]$$

$x_2^{sl} = [0.0023 \ -0.9969 \ 0.0302 \ -0.0067 \ -0.0122 \ 0.0718]$.

(32)

where, x_1^{sl} and x_2^{sl} are the first and second slowest vectors respectively. The gradient of the Lyapunov function G and its second derivatives matrix H will become:

Here, cnt are balances of oxygen and platinum *i.e.*

$$cnt_1 = b_{O=oxygen} = b_1,$$
$$cnt_2 = b_{Z=platinum} = b_2.$$

The Lyapunov function (8) has the form,

$$G = \sum_{i=1}^{6} c_i [ln(c_i / c_i^{eq}) - 1]. \qquad (30)$$

Thus, the dimension of the phase space is six and our aim is to get its reduced description.

The kinetic equations (4) will acquire a form

$$\nabla G = \begin{bmatrix} \ln c_1 - \ln c_1^{eq} \\ \ln c_2 - \ln c_2^{eq} \\ \ln c_3 - \ln c_3^{eq} \\ \ln c_4 - \ln c_4^{eq} \\ \ln c_5 - \ln c_5^{eq} \\ \ln c_6 - \ln c_6^{eq} \end{bmatrix}, \quad H = \begin{bmatrix} 1/c_1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1/c_2 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1/c_3 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1/c_4 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1/c_5 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1/c_6 \end{bmatrix}.$$

(33)

The matrix E (23) will take a form:

$$E = \begin{bmatrix} 2.00000 & 1.00000 & 2.00000 & 0.00000 & 1.00000 & 1.00000 \\ 0.00000 & 0.00000 & 0.00000 & 1.00000 & 1.00000 & 1.00000 \\ -0.9075 & -0.1471 & 0.1830 & -0.1141 & 0.1305 & -0.3019 \\ 0.0023 & -0.9969 & 0.0302 & -0.0067 & -0.0122 & 0.0718 \end{bmatrix}$$

(34)

An orthonormal basis ρ_i in the null space of the matrix D has dimension $z = 4$ and it can be chosen as follows:

$$\rho=\begin{bmatrix} -0.5929 & -0.2512 & 0.7587 & 0.0804 & -0.0402 & -0.0402 \\ -0.0446 & 0.6075 & 0.0636 & 0.6455 & -0.3227 & -0.3227 \\ -0.3411 & 0.4819 & -0.0570 & -0.3143 & 0.6572 & -0.3428 \\ -0.3411 & 0.4819 & -0.0570 & -0.3143 & -0.3428 & 0.6572 \end{bmatrix} \quad (35)$$

Vector t spanning $ker(E)$ is:

$$\begin{bmatrix} 0.1769 & -0.0361 & -0.3918 & -0.4658 & 0.7271 & -0.2613 \\ -0.2197 & 0.0550 & -0.1129 & -0.6100 & -0.1296 & 0.7396. \end{bmatrix} \quad (36)$$

Now the system (28) will become:

$$\sum_{i=1}^{4} <t_j, \rho_i > \upsilon_i = -(t_j, \nabla G(c_p)), \quad \forall j = 1,2.$$

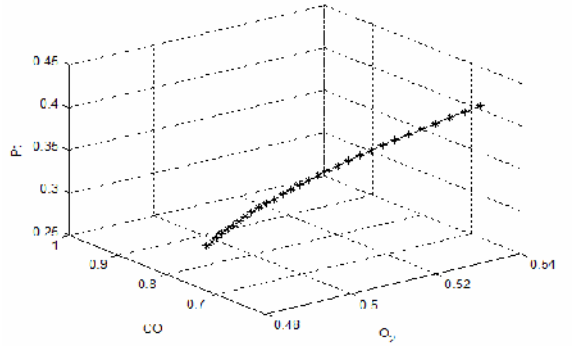
$$\sum_{i=1}^{4} (m, \rho_i)\upsilon_i = 0, \quad (37)$$

$$\| \mathrm{h}c_p \| = 0.5\times10^{-2}.$$

Solving the above system with respect to QEG algorithm *(CQEG)* starting from equilibrium point $c_0 = c^{eq}$, we firstly move towards the right direction $c_{p+1} > c_p$ and then moving towards the left direction $c_{p+1} < c_p$. We stop calculating the next node c_{p+1} when it becomes negative and in this way we obtain first SIM approximation through SQEG. Here, the system was solved by imposing $\delta^2 = 0.5 \times 10^{-2}$ and $m = x_2^{sl}$: In this way, the grid nodes, denoted by cross, were obtained.

This initial approximation can be further modified by applying different methods like MIG, CSP, etc to get an accurate SIM approximation. Here, we just have obtained the first SIM as shown in (Fig. 4 a) and now extending the idea for 2D (Fig. 4b) explained in the next section.

a)



b)

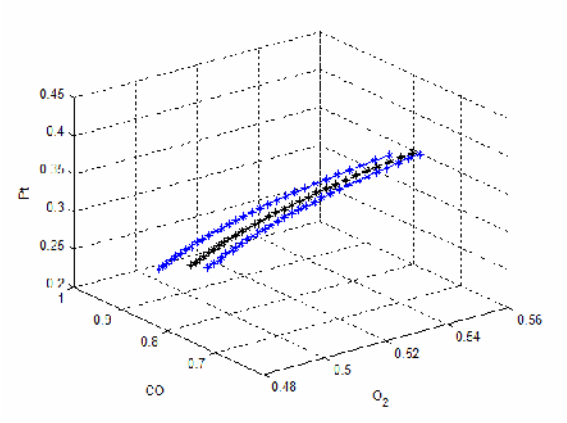


Fig. 4: (a) One dimensional Spectral Quasi Equilibrium Manifold *i.e.* 1D SQEM, starting from equilibrium. b) Two solutions obtained *i.e.* 2D SQEG extended from the 1D invariant grid. The grid spacing, in both the cases are $\varepsilon^2 = 0.5 \times 10^{-2}$.

Multidimensional Case

In order to construct the two dimensional spectral quasi-equilibrium grids, the same method discussed in section *(CQEG)* is applied. Starting from the equilibrium point, first SQEG is constructed, dark cross line and imposing $\delta^2 = 0.5 \times 10^{-2}$ and $\mathbf{m} = x_2^{sl}$. Then in the next time system, (28) is solved again by starting from any grid (cross) imposing $\delta^2 = 0.5 \times 10^{-2}$ and using vector $\mathbf{m} = x_1^{sl}$. This time, it gives horizontal dots. By selecting first twenty five points in each case, we obtain 2D-Spectral Quasi Equilibrium Manifold as shown in Fig. 5.

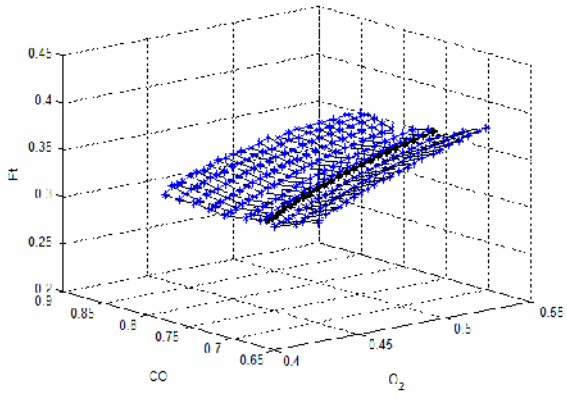


Fig. 5: Further extension in 2D SQEG from the 1D invariant grids (dark cross line) for first twenty points. The grid spacing, in this case is $\varepsilon^2 = 0.5 \times 10^{-2}$.

Conclusion

The non-linear ODEs of the system lead towards the interesting phenomena of mathematical as well as chemical point of view. It is difficult to get direct solution of such a complex problem. Therefore, we stress on reducing the system by getting slow invariant manifold. At here we have discussed a numerical method which allows an efficient calculation of low dimensional manifolds for the simplification of complex chemical kinetics. It is based on a multi dimensional continuation process and allows us to calculate manifolds of arbitrary dimensions. The computation method discussed here not only exploits the fact of chemical kinetics but also provides the information about how Chemistry approaches equilibrium and later it approaches its first and second dimension.

Initial approximation is obtained through QEM and it is further extended to higher dimensions. The stability of the system is provided by the Lyapunov function which plays an important role in thermodynamics. We have presented Quasi Equilibrium Manifold approximation by means of a method of invariant grid for reducing the system of chemical kinetics. Through construction of proper algorithm, this idea has been numerically extended for higher dimensions and illustrated through an example. Avoiding the analytical difficulties of Lagrange multipliers method, we have obtained a very good QEM approximation through QEGA.

The idea presented here also gives the geometrical construction and its reduction in the form of slow invariant manifold approximations. By considering the other possibilities of the same problem, this idea can be further extendable and it is possible to implement it to the grid based approximation.

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