

Low-Dimensional Manifold Based on Entropy Production Rate of Reaction Kinetics

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1 Introduction

Model reduction or simplification of detailed chemical kinetic mechanisms is important in order to reduce the CPU time needed for simulating turbulent reactive media and to understand the essential features of the mechanisms. A variety of reduction methods, exemplified by the computational singular perturbation and the intrinsic low-dimensional manifold, have been developed and applied, especially in research into combustion [1]. Both methods are based on spectral decomposition in the time domain, which enables the identification of slow and fast modes of the ordinary differential equations of the chemical kinetics: The identified slow modes represent the low-dimensional manifold of the reduced mechanism. In addition to this type of method, Gorban et al. [2] and Lebiedz [3] have developed methods utilizing the second law of thermodynamics, a corollary of which says that minimum entropy production holds for the system in the linear regime of the non-equilibrium stationary state [4]. In contrast Ziegler [5] has proposed the concept of maximal entropy production, which is still an issue under debate [6]. In the present work, we discuss the relation between the chemical kinetic path and entropy production in regard to model reduction for chemical kinetic mechanisms.

2 Methodology

The purely reactive contribution to the entropy production rate of thermally perfect gases is given by [4]

$$\frac{dS}{dt} = \hat{R}V\sigma \quad (1)$$

where t is time, S is the entropy of the system, $\hat{R}$ is the universal gas constant, V is the volume of the system, and σ is the total reactive contribution to the entropy production rate:

$$\sigma = \sum_{l=1}^{N_R} \sigma_l \quad (2), \quad \sigma_l = (R_{fl} - R_{bl}) \ln \frac{R_{fl}}{R_{bl}} \quad (3).$$

Equation 3 is the contribution of the l th reaction with forward reaction rate R_{fl} and backward reaction rate R_{bl} . The chemical kinetics proceed according to the following ordinary differential equations:

$$\frac{d\vec{y}}{dt} = \sum_{l=1}^{N_R} (\vec{\beta}_l - \vec{\alpha}_l) R_l \quad (4)$$

where

$$R_l = R_{fl} - R_{bl} \quad (5), \quad R_{fl} = k_{fl} \prod_{k=1}^N y_k^{\alpha_{kl}} \quad (6-1), \quad R_{bl} = k_{bl} \prod_{k=1}^N y_k^{\beta_{kl}} \quad (6-2),$$

$$\vec{y} = \begin{bmatrix} y_1 & y_2 & \cdots & y_N \end{bmatrix}^T \quad (7),$$

$$\vec{\alpha}_l = \begin{bmatrix} \alpha_{1l} & \alpha_{2l} & \cdots & \alpha_{Nl} \end{bmatrix}^T \quad (8-1), \text{ and } \vec{\beta}_l = \begin{bmatrix} \beta_{1l} & \beta_{2l} & \cdots & \beta_{Nl} \end{bmatrix}^T \quad (8-2).$$

Here k_{fl} and k_{bl} are the reaction rate constants of the l th forward and backward reactions, respectively, y_k is the concentration of the k th species, and α_{kl} and β_{kl} are the stoichiometric coefficients of the k th species in the l th forward and backward reactions, respectively. In the following we discuss three types of paths on the basis of the entropy production rate in Eq. 2; these paths may be used to approximate the true chemical kinetic path.

2.1 Steepest gradient path

Ziegler [5] has proposed an orthogonality principle for irreversible processes, which is equivalent to a certain extremal principle, that is, the maximal rate of entropy production. However, publications on this topic are fragmented over wide a variety of areas of research, and the thermodynamic and statistical bases of the principle are not clear, although the second law of thermodynamics can be obtained as a corollary of the principle [6]. In the present study, we simply apply the principle by assuming that reactions proceed in the direction opposite to the steepest gradient of the entropy production rate σ given in Eq. 1:

$$\frac{d\vec{y}_{ind}}{ds} = -\nabla \sigma \quad (9)$$

where s is the pseudo time (i.e., an artificial time-marching parameter) and $\vec{y}_{ind}$ is the vector that consists of the species concentrations chosen as the set of independent variables consistent with element conservation (see Section 2.3). The path according to Eq. 9 will be called the steepest gradient path hereafter.

2.2 Newton-direction path

The method described in the previous section can be interpreted as a version of a well-known optimization method, the method of steepest ascent or descent: the standard algorithm uses line search along a definite length in the search direction, whereas Eq. 9 uses the pseudo time and differential. Another well-known optimization method is Newton iteration, in which the function to be optimized is approximated by the second-order Taylor series expansion in the direction of line search, the so-called Newton direction [7]. The Newton-direction path can be calculated according to

$$H \frac{d\vec{y}_{ind}}{ds} = -\nabla \sigma \quad (10)$$

where

$$H \equiv \nabla^2 \sigma \quad (11)$$

is the Hessian of σ . The Newton direction is also utilized by the method of conjugate gradient, and the direction of the steepest conjugate gradient is the Newton direction.

2.3 Path of linear non-equilibrium

The third method described here is a completely new method. This path is calculated according to

$$2Q \frac{d\vec{y}_{ind}}{dt} = -\nabla \sigma \quad (12)$$

where

$$Q \equiv \begin{bmatrix} \sum_{k=K+1}^N (B_3)_{k-K,1} \frac{1}{y_k} (B_3)_{k-K,1} & \sum_{k=K+1}^N (B_3)_{k-K,1} \frac{1}{y_k} (B_3)_{k-K,2} & \cdots & \sum_{k=K+1}^N (B_3)_{k-K,1} \frac{1}{y_k} (B_3)_{k-K,K} \\ \sum_{k=K+1}^N (B_3)_{k-K,2} \frac{1}{y_k} (B_3)_{k-K,1} & \sum_{k=K+1}^N (B_3)_{k-K,2} \frac{1}{y_k} (B_3)_{k-K,2} & \cdots & \sum_{k=K+1}^N (B_3)_{k-K,2} \frac{1}{y_k} (B_3)_{k-K,K} \\ \vdots & \vdots & \ddots & \vdots \\ \sum_{k=K+1}^N (B_3)_{k-K,K} \frac{1}{y_k} (B_3)_{k-K,1} & \sum_{k=K+1}^N (B_3)_{k-K,K} \frac{1}{y_k} (B_3)_{k-K,2} & \cdots & \sum_{k=K+1}^N (B_3)_{k-K,K} \frac{1}{y_k} (B_3)_{k-K,K} \end{bmatrix} + \begin{bmatrix} \frac{1}{y_1} & 0 & \cdots & 0 \\ 0 & \frac{1}{y_2} & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & \frac{1}{y_K} \end{bmatrix} \quad (13)$$

Here it should be noted that t is not the pseudo time. The matrix B_3 is defined by

$$B_3 \equiv B_2^{-1} B_1 \quad (14)$$

where B_2 and B_1 are the coefficient matrices of the equations of element conservation:

$$B_1 \vec{y}_{ind} + B_2 \vec{y}_{dep} = \vec{c} \quad (15)$$

where

$$\vec{y}_{ind} = \begin{bmatrix} y_1 & y_2 & \cdots & y_K \end{bmatrix}^T \quad (16-1), \quad \vec{y}_{dep} = \begin{bmatrix} y_{K+1} & y_{K+2} & \cdots & y_N \end{bmatrix}^T \quad (16-2)$$

$$\vec{c} = \begin{bmatrix} c_1 & c_2 & \cdots & c_M \end{bmatrix}^T \quad (17),$$

K is the number of independent species concentrations (the components of the vector $\vec{y}_{ind}$), M is the number of elements and also the number of dependent species concentrations (the components of the vector $\vec{y}_{dep}$), $N = K + M$, and c_i for $i = 1, \dots, M$ is the total number density of the i th element in the system. It can be proved that Eq. 12 coincides with the true chemical kinetic equation Eq. 4 to first order in the variable ε_l defined by

$$R_{fl} = (1 + \varepsilon_l) R_{bl} \quad (18).$$

However, the proof is not shown here due to the limit on the length of papers.

Since the following relations also hold *to first order in ε_l* when Eq. 18 is satisfied, the path according to Eq. 12 can be called the path of linear non-equilibrium:

$$\sigma = \sum_{l=1}^{N_R} \varepsilon_l^2 R_{bl} = \sum_{l=1}^{N_R} X_l J_l \quad (19), \quad J_l \equiv \varepsilon_l R_{bl} = R_{bl} X_l \quad (20-1), \quad X_l \equiv \varepsilon_l \quad (20-2)$$

where J_l and X_l are, respectively, interpreted as the thermodynamic flux and thermodynamic force due to the l th reaction.

3 Results

In addition to the chemical kinetic path (Eq. 4), the paths given by Eqs. 9, 10, and 12 have been calculated for the following examples of simple reaction systems. All the (dimensionless) calculations here are under constant volume with fixed reaction-rate constants, which enables the graphical representation of σ with respect to only the species concentration.

3.1 $A \rightleftharpoons 2B \rightleftharpoons C$: 1-D manifold

Figure 1 shows the four paths (chemical kinetic path, the steepest gradient path, the Newton-direction path, and the path of linear non-equilibrium) for the reactions $A \rightleftharpoons 2B \rightleftharpoons C$ projected onto the concentration (y_A, y_B) phase plane with a contour plot of σ ; y_C is determined by element conservation:

$$y_A + 0.5y_B + y_C = c \quad (21).$$

These calculations were made with the rate constants given in Table 1.

The following observations can be made from Fig. 1 and other figures that are not shown here:

1. The path of linear non-equilibrium has the same 1-D manifold as that of the chemical kinetics (Fig. 1a) expected from the path coinciding with the chemical kinetic path *to first order in the variable* ε_l .
2. The Newton-direction path has no 1-D manifold except when the initial non-equilibrium composition is far from the final equilibrium (Fig. 1b).
3. The steepest gradient path (Fig. 1b) has a slightly different 1-D manifold from that of chemical kinetics because the Jacobian of Eq. 9 is the Hessian H (Eq. 11), which is different from the Jacobian of Eq. 4. However, one of the eigenvectors of H at equilibrium (corresponding to a 1-D manifold) is very similar to that of the Jacobian of Eq. 4, especially for stiffer ordinary differential equation systems, and accordingly the 1-D manifold of the steepest gradient path is almost the same as that of the chemical kinetics.

3.2 $A \rightleftharpoons B \rightleftharpoons C \rightleftharpoons D$: 2-D and 1-D manifolds

Figure 2 shows the four paths (chemical kinetic path, the steepest gradient path, the Newton-direction path, and the path of linear non-equilibrium) for the reactions $A \rightleftharpoons B \rightleftharpoons C \rightleftharpoons D$ projected into the concentration (y_A, y_B, y_C) phase space; y_D is determined by element conservation:

$$y_A + y_B + y_C + y_D = c \quad (22)$$

These calculations were made with the rate constants given in Table 2.

The following observations can be made from Fig. 2 and other figures that are not shown here:

1. The path of linear non-equilibrium has the same 2-D manifold as that of the chemical kinetics (Fig. 2a), though the former is appreciably different from the latter in the same 2-D manifold.
2. The steepest gradient path (Fig. 2b) has a 2-D manifold that differs from both that of the chemical kinetics and that of the path of linear non-equilibrium, but the extent of the difference varies depending on the ratio of rate constants among different reactions.
3. The Newton-direction path has no 2-D and 1-D manifolds except when the initial non-equilibrium composition is far from the final equilibrium (Fig. 2b).

These results are qualitatively very similar to those described in the previous section.

3.3 0-D manifold (equilibrium state)

Figures 1 and 2 indicate that all four paths lead to the final equilibrium point (0-D manifold). Accordingly, they can be utilized to determine the equilibrium states and all of the three thermodynamic paths (the steepest gradient path, the Newton-direction path, and the path of linear non-equilibrium) can be used for equilibrium calculation without detailed information about the

reaction-rate constants. Any values of the rate constants consistent with the equilibrium constant produce good results, and only the equilibrium constants for each reaction must be known precisely.

4. Summary

In addition to the chemical kinetic path, three types of paths considered (the steepest gradient path, the Newton-direction path, and the path of linear non-equilibrium) have been calculated for simple reactive-system examples. The latter three paths are all based on the entropy production rate of reaction kinetics. We have found that the path of linear non-equilibrium (a completely new method) provides good approximations to the low-dimensional manifolds of the chemical kinetics, and all three paths based on the entropy production rate can be used for equilibrium calculation without any information other than the equilibrium constant of each reaction that occurs in the system. In principle our path of linear non-equilibrium is applicable to any non-isothermal cases with variable rate constants, and application for more complex reactive systems such as autocatalytic reactions is in progress.

Table 1: The dimensionless values of the rate constants employed for the calculations shown in Fig. 1

Reaction	A $\rightarrow$ 2B		2B $\rightarrow$ C	
Figure	Forward	Backward	Forward	Backward
1	1	1	0.5	0.5

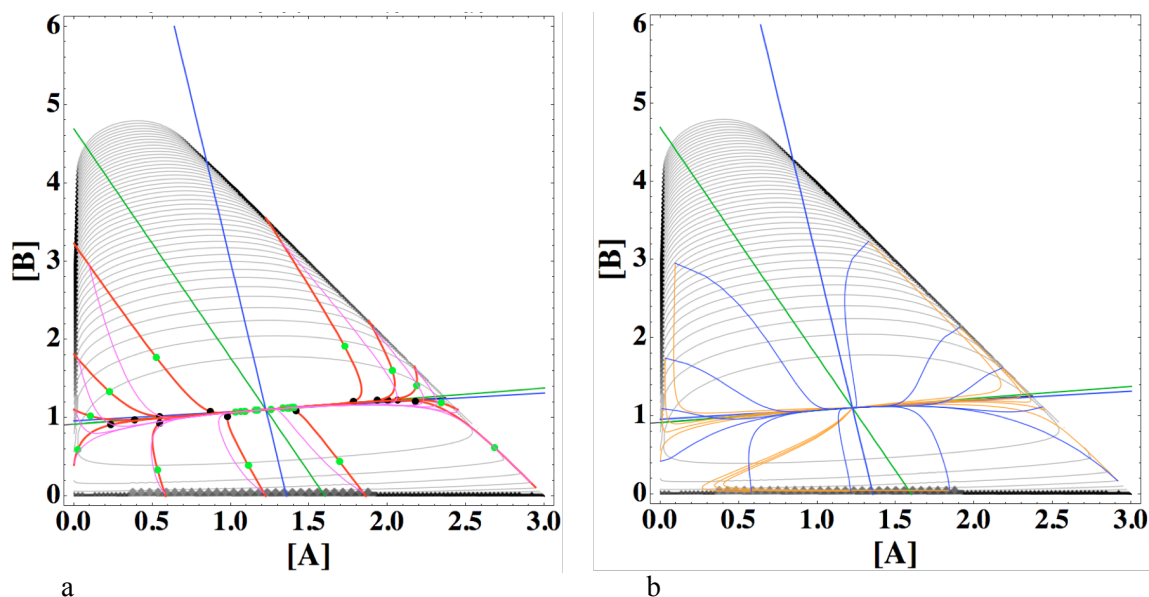


Figure 1. All four paths of the reactions $A \rightleftharpoons 2B \rightleftharpoons C$ projected onto the concentration (y_A, y_B) phase plane with a contour plot of σ . (a) Chemical kinetic paths and the paths of linear non-equilibrium. (b) Steepest gradient paths and Newton-direction paths. Bold red lines are the chemical kinetic paths, magenta lines are the paths of linear non-equilibrium, orange lines are the Newton-direction paths, blue lines are the steepest gradient paths, green straight lines are in the direction of the eigenvectors of the chemical kinetic Jacobian at the equilibrium point, and blue straight lines are in the direction of the eigenvectors of the Hessian of σ . A black straight line that is hidden behind the green and blue straight lines indicates the quasi-steady state approximation with $dy_B/dt = 0$. Points on the chemical kinetic paths indicate the dimensionless time from the initial states: 0.1 (green), 0.5 (black), and 3 (green). The values of reaction rate constants are given in Table 1.

Table 2: The dimensionless values of the rate constants employed for the calculations shown in Fig. 2

Reaction	A $\rightarrow$ B		B $\rightarrow$ C		C $\rightarrow$ D	
Figure	Forward	Backward	Forward	Backward	Forward	Backward
2	1	1	0.3	0.3	0.09	0.09

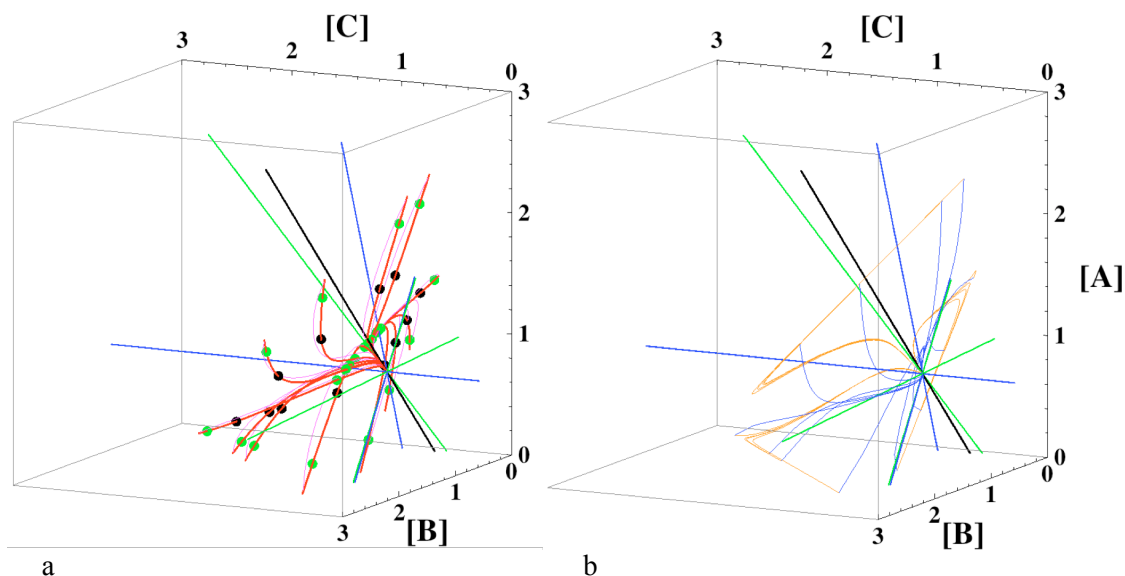


Figure 2. All four paths of the reactions $A \rightleftharpoons B \rightleftharpoons C \rightleftharpoons D$ projected into the concentration (y_A, y_B, y_C) phase space. (a) Chemical kinetic paths and the paths of linear non-equilibrium. (b) Steepest gradient paths and Newton-direction paths. All the lines and points have the same meaning as described in the caption of Fig. 1, except for the black straight line that here indicates the quasi-steady state approximation with $dy_B/dt = 0$ and $dy_C/dt = 0$. The values of reaction rate constants are given in Table 2.

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