SELFORGANIZATION IN HIGH TEMPERATURE REACTION KINETIC SYSTEMS

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Abstract

Models of homogeneous explosions and one-dimensional laminar flames of hydrogen and methane were analysed by a series of mathematical tools. The results indicated that the real dynamical dimension of these systems is 1 to 3, while the number of variables is from 10 to 38. This dimension reduction indicates strong couplings in the model, exhibited in the similarity relations among the sensitivity functions. It has consequences in areas of practical importance, like determination of rate parameters from experimental data or search for a minimal equivalent model.

Introduction

Selforganization is usually investigated in solution phase chemical or biological systems. In this paper we should like to demonstrate that some high temperature gasphase chemical kinetic systems are not only highly non-linear, but also may show surprising signs of selforganization.

The systems investigated were the homogeneous explosions and one-dimensional laminar flames of hydrogen and methane. We have investigated both freely propagating and burner stabilized laminar flames. The methane combustion simulations used the Leeds Methane Oxidation Mechanism [1], [2], which contains 37 species and 350 (irreversible) reactions. The hydrogen oxidation calculations were carried out with a subset of the Leeds Mechanism, having 9 species and 46 reaction steps.

The number of variables of the explosion and flame models was equal to the number of reactive species plus one when temperature was also calculated. It has been shown recently, that the real dynamical dimension of high temperature chemical kinetic systems is lower; in the case of the adiabatic explosion of hydrogen it is one instead of ten and in the case of the adiabatic explosion of methane it is three instead of 38. The reason of this huge dimension reduction is the existence of low-dimensional slow manifolds in the variable space of high-temperature chemical kinetic systems.

Lam and Goussis [3] have investigated the presence of different time-scales in a series of single points of the variable space. Roussel and Fraser [4] described the evolution of kinetic systems in connection with slow manifolds. They stated that the existence of very different time scales in chemical kinetic systems causes the trajectory of the solution to move on slow manifolds. The trajectory originally moves on an N dimensional manifold, but as time advances usually the dynamical dimension of the movement decreases and after some time the trajectory moves close to a two-dimensional surface (curved plate), then close to a one-dimensional curve, and finally arrives to the zero-dimensional equilibrium or stationary point if it exists. Maas and

Pope [5] elaborated algorithms and computer codes for the approximate numerical calculation of slow manifolds. They also studied the existence of manifolds in several combustion models and generated reduced models having few variables only.

We have shown [6], [7] that the presence of low-dimensional manifolds in the composition space of dynamical systems may result in the similarity of local sensitivity functions, which is a sign of several unusual features of such systems. Sensitivity analysis investigates the effect of parameter change on the solution of mathematical models. The local sensitivity coefficient $s_{i,k} = \partial Y_i/\partial p_k$ shows the effect of the minor change of parameter p_k on model result Y_i. In the case of a general model, no relation can be expected among the rows and columns of a local sensitivity matrix. However, the sensitivity functions may exhibit three types of similarity.

The Similarity of Sensitivity Functions

The local sensitivity functions ($s_{ik} = \partial Y_i / \partial p_k$) of chemical kinetic models may show the following types of similarity:

(1) *Local similarity*: $\lambda_{ij}(z) = s_{ik}(z)/s_{jk}(z)$ is equal for any parameter k, but depends on the results Y_i and Y_j investigated,

(2) *Scaling relation*: $\lambda_{ij}(z)$ is equal to $\left(d Y_i(z)/d z\right)/\left(d Y_j(z)/d z\right)$,

(3) *Global similarity*: $\mu_{kl} = s_{ik}(z)/s_{il}(z)$ is constant in a range of the independent variable z (time or distance).

Scaling relation and global similarity (the latter under the name of self-similarity) have been described [8], but local similarity existing without scaling relation was detected by us.

Similarity of local sensitivity functions was investigated in hydrogen–air explosion and flame models. A series of models were created, consisting of homogeneous explosions and burner-stabilized and freely propagating flames. In all the cases the temperature profiles were either calculated using the assumption of adiabatic conditions, or these profiles were fixed to the previously calculated ones. All calculations were carried out at four different equivalence ratios ($\varphi = 0.5, 1.0, 2.0,$ and 4.0). Carefully choosing the initial and boundary conditions, the results of all these models could be meaningfully compared. In the cases of the adiabatic explosions of hydrogen–air mixtures, all the three types of similarity were found. In other cases, either similarity existed only for some parameters or no similarity was found for any of the parameters.
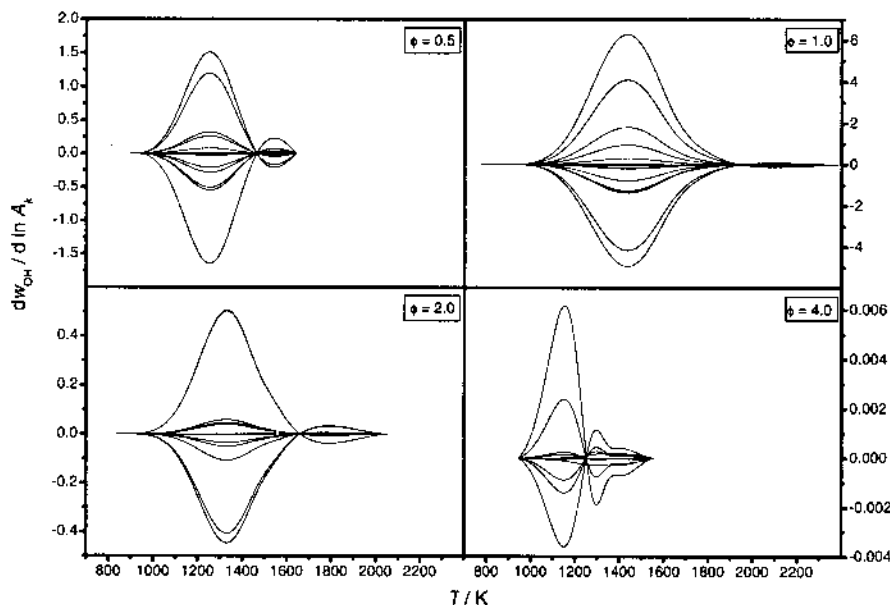
Figure 1. Local sensitivity functions of the mass fraction of OH with respect to the natural logarithm of the 46 pre-exponential coefficients of the reaction steps as a function of temperature, calculated for the adiabatic explosion of hydrogen–air mixtures for equivalence ratios $\varphi = 0.5$, 1.0, 2.0 and 4.0. The sensitivity curves end at the burnt equilibrium temperature.

Adiabatic explosions of methane–air mixtures were also investigated and local similarity was found. The calculations were carried out using three different mechanisms; the similarity relations were similar in all the cases showing that this feature does not depend on the details of the reaction mechanism.

The consequence of the global similarity of the sensitivity functions is that models with different parameter sets can give almost identical simulation results for all variables in a wide range of the independent variable. This statement was illustrated with a series of numerical experiments using modified hydrogen and methane oxidation mechanisms. We have called the attention to the possible problem that using a chemical kinetic model of global similarity, fitted rate coefficients can be determined with large error, while this is not expressed in the deviation of the experimental and fitted model results.

Based on the theory of slow manifolds, an explanation was given to the local similarity and the scaling law. We have shown that scaling relation appears if the trajectory of the simulation is close to a one-dimensional slow manifold. Global similarity appears if the sensitivity functions are locally similar and the sensitivity ODE is pseudohomogeneous.

Couplings among the reaction steps and the minimal size of the mechanisms

In the case of adiabatic models, heat effect of a reaction step may change the temperature of the reaction mixture, thus affecting the rate of others. This is called the *thermal coupling* among the reaction steps. In the case of models of spatially inhomogeneous systems, a reaction step at one location may produce a reactive species that increases the rate of other reaction steps at another location. This is called the *diffusion coupling* among the reaction steps. We have investigated the thermal and diffusion couplings among the reaction steps of hydrogen combustion models [9].

Reduced mechanisms were created using the principal component analysis of the local sensitivity matrix (PCAS method) and that of the rate sensitivity matrix (PCAF method). Global similarity was found to appear in the results of the PCAS method and its origin was explained. Our calculations indicated that the PCAS and PCAF methods have the same efficiency in mechanism reduction and produce the same results; neither the thermal coupling nor the diffusion have impact on the importance of the reactions at the oxidation of hydrogen. A 31-step minimal reduced mechanism was created that described the combustion of hydrogen at all conditions investigated. The same reactions were important in homogeneous explosions and flames, therefore diffusion coupling did not influence the importance of reactions. The same reactions were important in burner-stabilized and freely propagating flames, although the corresponding sensitivity functions were very different. Rich flames could be modelled by much fewer reaction steps than the stoichiometric and lean ones. Instead of the original 46-step mechanism, the combustion of hydrogen could be described by 15-step to 28-step mechanisms at the various conditions investigated and a 31-step mechanism could replace the original mechanism at all conditions studied.

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