Network community detection based combustion reaction mechanism coarse graining method

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1 Introduction

Combustion mechanism reduction is the bridge between micro chemical processes and macro characters such as ignition delay times, laminar flame speeds that have vital implications for the engine design. Currently, there are generally two kinds of mechanism reduction methods: skeleton reduction and time-scale splitting-based mechanism reduction. Many of these methods need the model user to select a proper screening threshold to pick out the important reaction components and pathways in the specific conditions, which may resulting in artificial influence and experience differences. Additionally, the obtained scheme is still described by elementary reactions, and for complex system like those of surrogated fuels, the size of the reduced mechanism exceeds the engineering requirements. The time-scale splitting-based methods mainly analyze reaction system mathematically, paying less attention to the chemical essence of the reaction. Getting macro combustion characteristics from the microscopic mechanism expressed in elementary reactions needs essentially cross-scale mechanism expression. Similar as the hierarchical structure of molecule, cell, tissue and organ in life systems, a natural cross-scale expression strategy is to take the group of closely interactive subunits as the "agent" of interactions of higher level. Combustion reaction is no doubt a complex system whose interactions could be conveniently represented by a complex network. One of the cross-scale expression methods under network framework is community detection[1,2], which aims to identify the functional modules and possibly the potential hierarchical organization. The obtained community structure (module) with tight connections between nodes with similar features within groups, and loose connections between nodes across groups, would help to obtain a clear coarse-grained picture of the original systems.

Chemical reactions networks with their native pathways have always been views as bipartite species-reaction network. Reactants and reactions are highly coupled in this kind of network. For a simple reaction like $A + B \Leftrightarrow C + D$, it is not easy to tell what the relation between A and C is, since the transformation from A to C also needs B. It is also difficult to describe the relation between A and B. This sort of bipartite structure is a barrier to elucidating the relations of species in the network. In this work, the reactant and reactions are decoupled by quantitatively defining the relative reaction flux as edge weight between species,

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and thus successfully mapped the bipartite reaction network onto an unipartite network with only species nodes. A coarse-grained system is obtained by finding functional modules through a nonmetric community detection method, and the effectiveness of the method is further tested in the hydrogen explosion system. Our method provides effective way to express the combustion network in a higher level and makes necessary preparation for the cross-scale express of the combustion reaction mechanism by a bottom-up approach.

2 Method

As for combustion reaction system, there are generally hundreds or thousands of species reacting together in just as many reactions. To capture the global properties of such a complex interactive system, the critical step is to model it as a network whose nodes represent the dynamical units (such as the neurons in the brain) and the links stand for the interactions between the units. The combustion mechanism is first represented as a network, whose nodes are defined as the reactants. If two compounds participate in one reaction, a link is established between the corresponding nodes. In order to facilitate data analysis, a reaction network with N species can be completely represented by the adjacency (or connectivity) matrix $\mathcal{A}$, i.e. a N ×N square matrix whose entry a_{ij}(i, j =1, …, N) is 1 if the link l_{ij} exists, and zero otherwise. Let's take the following reaction network as example:

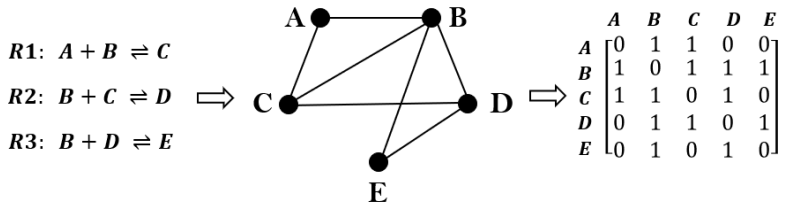

Fig 1: Transformation from reaction mechanism to network

Such networks depict the binary relation, that is, the edges between nodes are either present or not, qualitatively describing the transformation connections between the reactant pairs but losing a lot of quantitative dynamical information. Nevertheless, many real networks display a diversity in the interactions, .e.g. strong and weak ties between individuals in social networks[3], uneven fluxes in metabolic reaction pathways[5]. These systems can be better described by weighted networks. How to properly define the edge weight according to elementary reactions, that is, to decouple the relationship between reactants, is the key issue. Here we define the edge weight as:

$$w_{ij} = \frac{\sum_{r=1,R}|v_{i,r}\eta_r\delta_r|}{\sum_{r=1,R}|v_{i,r}\eta_r|} \quad (1)$$

where η_r represents the contribution of reaction r to the connection between i and j, $v_{i,r}$ indicates stoichiometric coefficients of i in reaction r. The function δ_r is equal to 1 when i and j participate in the reaction r, and zero otherwise.

Edge weights are generally provided by fluxes/traffic related to transportation in networks such as the metabolic, Internet, railway networks. Some existing mechanism reduction methods, e.g. PFA, DRG, CSP, are also based on the reaction flux analysis. In Eq.1 η_r indicates the net reaction flux of reaction r, as described in Eq. 2:

$$\eta_r = k_{fr} \prod_{i=1}^{N} \chi_i^{v'_{i,r}} - k_{br} \prod_{i=1}^{N} \chi_i^{v''_{i,r}} \quad (2)$$

where χ_i is the molar concentration of the i^{th} specie. The k_{fr} and k_{br} are the forward and backward rate constants of the r^{th} reactions.$v'_{i,r}$ indicates the forward stoichiometric coefficients of species i in reaction r, while $v''_{i,r}$ is the reverse stoichiometric coefficients.

On the basis of this weighted network, community detection results could easily help us to extract potential functional modules, in which the reactants have similar dynamical roles..The quality of the obtained community structures resulting from these methods is often measured by modularity Q, which evaluates the density of links inside communities as compared to links between communities[5,6]. Typically, the higher modularity values, the stronger community structures or better network partition quality. Thus, modularity is wildly used as an objective optimization function for finding optimum community detection solutions. For weighted networks, it is given as Eq. 3[7]:

$$\mathrm{Q} = \frac{1}{2m} \sum_{ij} \left(a_{ij} - \frac{k_i k_j}{2m} \right) \delta(c_i, c_j) \quad (3)$$

where a_{ij} is the element of the adjacency matrix that represents the weight of edge between node i and j. The node strength $k_i = \sum_j a_{ij}$ is sum of the edge weights attached to node i, c_i indexes the community to which node i is assigned, and the function $\delta(c_i, c_j)$ is 1 if u=v and 0 otherwise. $m = \frac{1}{2} \sum_{ij} a_{ij}$ is the total of edge weight.

We choose the Louvain algorithm[8] based on modularity optimization, which consists of two phases (Fig 2). First, we assign different community to each node. Then move i from its community to the neighbor community j. If the modularity of newly formed network increases, i.e., $\Delta \mathrm{Q} > 0$, we keep this topological structure. If no positive gain is possible, i is supposed to be in its original community. The second phase is to construct a new network whose nodes are the communities found during the last phase, and repeat iteratively the previous two steps until modularity no longer increases.The gain in modularity $\Delta \mathrm{Q}$ obtained by moving an isolated node i into a community C can easily be computed by Eq. 4:

$$\Delta Q = \left[\frac{\Sigma_{in} + 2k_{i,in}}{2m} - \left(\frac{\Sigma_{tot} + k_i}{2m} \right)^2 \right] - \left[\frac{\Sigma_{in}}{2m} - \left(\frac{\Sigma_{tot}}{2m} \right)^2 - \left(\frac{k_i}{2m} \right)^2 \right] \quad (4)$$

where Σ_{in} is the sum of the weights of the links inside C, Σ_{tot} is the sum of the weights of the links incident to nodes in C, $k_{i,in}$ is the sum of the weights of the links from i to nodes in C.

This algorithm is fit for finding high modularity partitions of large hydrocarbon fuel networks. The validity of this method is checked in the H_2 explosion system. The dynamics simulations are performed with CHEMKIN-II software package in closed homogeneous reactor. Simulations are performed covering various initial conditions with initial temperatures and pressures, with the equivalence ratio fixed at 1.0. Reaction rate files obtained under different initial conditions are turned into network information of nodes and weighted edge, which are further used to find community structure through Louvain Algorithm.

3 Results

We use the H_2/O_2 kinetic model that LI et. al proposed[9] and employ different temperature and pressure on both sides of the crossover temperature to discuss the dependence of the clustering results on the initial conditions. As shown in Fig3 and Tab.1, H, O and OH are divided into one group in explosive region A and C, but in nonexplosive region B, H is classified into another group with HO_2, and H_2O_2. It is reported that the following low-pressure chain branching circle reactions (1)-(3) (Tab. 2) are crucial between the first

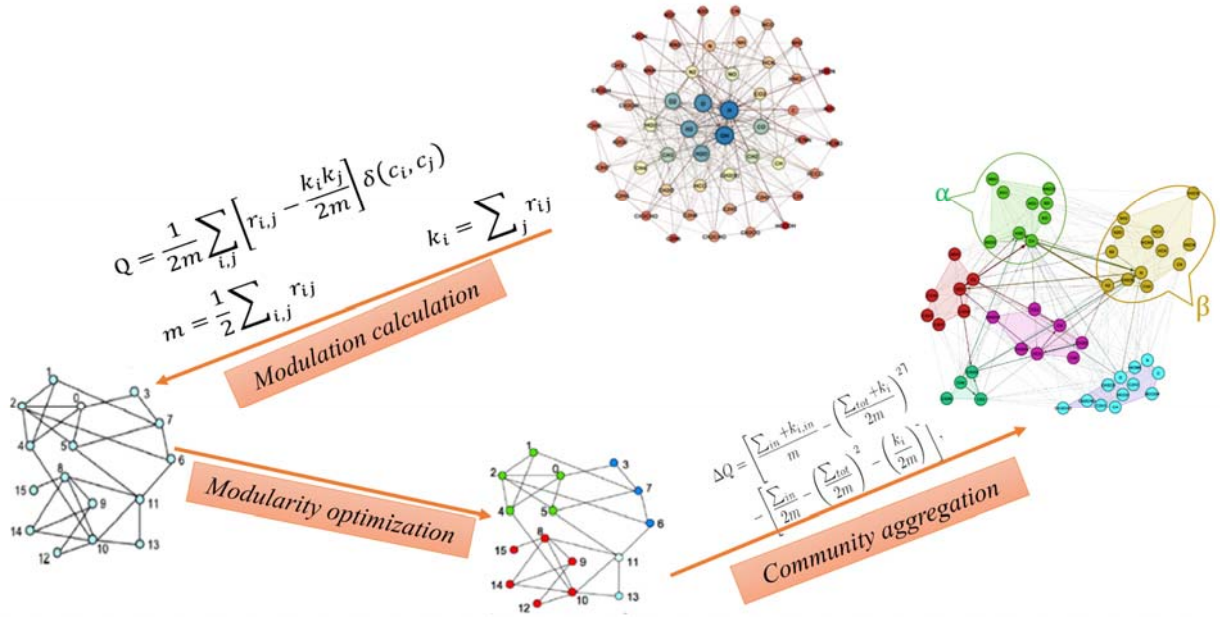

Fig 2: Visualization of the steps of fast-unfolding community detection algorithm

explosion limit and the second explosion limit (region A). This provides detailed information that shows H, O and OH are closely connected in this region.

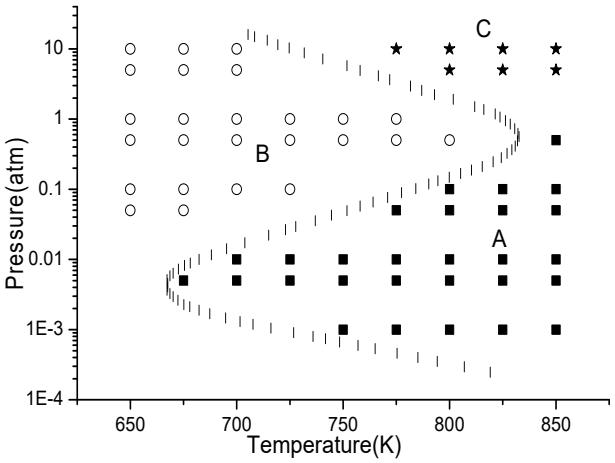

Fig.3. Clustering results in the H_2 explosion system

In region B, the three-body collision reaction (4) speeds up due to the increase of pressure. Because the concentration of M is proportional to pressure, the frequency with which H atoms enters into the three-body collision reaction is proportional to the square of the pressure. However, for binary collision reaction (1), the frequency that H enters into the reaction is linearly dependent on the pressure. So branching path initiated reaction by (1) is precluded by the faster recombination reaction (4). At the same time, as HO_2 concentration increases with pressure, the free radicals HO_2 are destroyed by reactions (5) and (6)[10]. These reactions

generate H_2O_2, forming high-pressure HO_2-H_2O_2 branched-chain mechanisms, which decreases the free radical production rate and neutralizes the ignition. These analyses agree with our result that H, HO_2, and H_2O_2 should be in the same group in this region.

Table 1: Specie clustering information of H_2 explosion system

	Group 1	Group 2
A	H, O, OH, H_2O, H_2	O_2, HO_2, H_2O_2
B	O, OH, H_2O	H, H_2, O_2, HO_2, H_2O_2
C	H, O, OH, O_2	H_2O, HO_2, H_2O_2

These elaborate conditional dependencies of the mechanism can be accurately captured by our method through detecting the community relation between the reactants, reactants, without the particular requirement of user's prior chemical knowledge. Thus mechanism obtained based on the community structures obtained in our method will provide an effective coarse grained, phenomenological understanding of the reactions.

Table 2 Important reactions of H_2/O_2 system

Reaction	No.
$H + O_2 \rightarrow OH + O$	(1)
$H_2 + O \rightarrow OH + H$	(2)
$H_2 + OH \rightarrow H_2O + H$	(3)
$H + O_2 + M \rightarrow HO_2 + M$	(4)
$2HO_2 \rightarrow H_2O_2 + O_2$	(5)
$HO_2 + H_2 \rightarrow H_2O_2 + H$	(6)

Summary

A bran-new network community detection based coarse-graining representation method for combustion reaction mechanism is proposed. The detailed kinetic mechanism was first translated into a complex weighted network, whose nodes are reactants and edge weights integrate dynamic information. Then, community structures were found by the Louvain network unfolding algorithm. The grouping information obtained in H_2 explosion system agrees well with previous detailed mechanism and kinetic investigations under a variety of conditions, which suggests that the proposed method is feasible for coarse-graining the combustion mechanism. Under our framework, it is also possible to extract the non-equilibrium characteristics by describing the reaction with entropy growth rate, thermal dissipation rate and other thermodynamic parameters. The network constructed by the time-dependent unsteady reaction flow may be useful for the investigation of turbulent combustion. Besides, the hierarchy exploration function of the Louvain algorithm allows users to employ suboptimal partitions under the different resolutions, thus making it possible to achieve desirable multi-scale expression.

References

[1] Fortunato, S., Community Detection in Graphs. *Physics Reports* **2010**, *486*, 75-174.

[2] Newman, M. E., Scientific Collaboration Networks. I. Network Construction and Fundamental Results. *Phys Rev E* **2001**, *64*, 016131.

[3] Csermely, P., Strong Links Are Important, but Weak Links Stabilize Them. *Trends Biochem Sci* **2004**, 29, 331-334.

[4] Boccaletti, S.; Latora, V.; Moreno, Y.; Chavez, M.; Hwang, D., Complex Networks: Structure and Dynamics. *Physics Reports* **2006**, *424*, 175-308.

[5] Clauset, A.; Newman, M. E.; Moore, C., Finding Community Structure in Very Large Networks. *Phys Rev E* **2004**, *70*, 066111.

[6] Newman, M. E., Analysis of Weighted Networks. *Phys Rev E* **2004**, *70*, 056131.

[7] Blondel, V. D.; Guillaume, J.-L.; Lambiotte, R.; Lefebvre, E., Fast Unfolding of Communities in Large Networks. *Journal of Statistical Mechanics: Theory and Experiment* **2008**, *2008*, P10008.

[8] Fortunato, S.; Hric, D., Community Detection in Networks: A User Guide. *Phys Rep* **2016**, *659*, 1-44.

[9] Li, J.; Zhao, Z.; Kazakov, A.; Dryer, F. L., An updated comprehensive kinetic model of hydrogen combustion. *International Journal of Chemical Kinetics* **2004,** *36* (10), 566-575

[10] Wang, X.; Law, C. K., An Analysis of the Explosion Limits of Hydrogen-Oxygen Mixtures. *J Chem Phys* **2013**, *138*, 134305.