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Knowledge-based probabilistic representations of branching ratios in chemical networks

Sylvain Plessis[a,b], Nathalie Carrasco[c], Pascal Pernot[a,b1]

a Laboratoire de Chimie Physique, UMR 8000, CNRS, Orsay F-91405
b Université Paris-Sud 11, Orsay F-91405
c Laboratoire Atmosphères, Milieux, Observations Spatiales,
Université de Versailles Saint-Quentin, UMR 8190 Verrières le Buisson F-91371

Abstract

We present the use of Nested Dirichlet distributions to represent uncertain branching ratios in chemical networks. The interest is twofold: (1) to preserve the structure of experimental data by imposing sum-to-one representations; and (2) to be able to introduce totally unknown subsets of branching ratios (missing data). These points are central to sound uncertainty propagation and sensitivity analysis in complex chemical networks.

Keywords: *Nested Dirichlet distributions*; *uncertainty propagation*; *probabilistic uncertainty representation*; *sum-to-one variables*

1. Dirichlet-type representations of tree-structured sum-to-one variables

Branching ratios are sum-to-one variables giving the probability to form the different products of a chemical reaction. Carrasco and Pernot (2007) proposed to elicit uncertain sets of branching ratios with the Dirichlet distribution (Evans et al., 2000;), *e.g.* $\{b_1,b_2,b_3\}\sim\mathrm{Diri}(\beta_1,\beta_2,\beta_3\ ;\gamma)$, where β_1,β_2,β_3 are the measured values and γ is a precision factor, estimated from the measurement uncertainties. Recent developments of this topic (Plessis et al., 2010) led us to use the more flexible generalized Dirichlet distribution (Lingwall et al., 2008), Dirg. The Dirg distribution enables to handle more precisely individual uncertainties for each channel, *e.g.* $\{b_1,b_2,b_3\}\sim\mathrm{Dirg}(\beta_1,\beta_2,\beta_3\ ;\Delta\beta_1,\Delta\beta_2,\Delta\beta_3)$.

In many instances, the set of branching ratios is incomplete, with total indetermination within subsets of products. Such cases cannot be handled by the abovementioned distributions and require a specific treatment. Let us consider a typical example where one experiment measured the relative efficiencies of the productions of M_1+M_2 (B_1) and M_3 (B_3), and another experiment, independent of the first one, was able to measure the branching ratios between M_1 (B_{11}) and M_2 (B_{12}). Each experiment comes with it's own set of uncertainty ΔB_i, which should be preserved as well as possible when generating branching ratios for the whole set of products.

The final branching ratios for the three products can be computed from both data sets: M_1 ($b_1=B_1*B_{11}$), M_2 ($b_2=B_1*B_{12}$) and M_3 ($b_3=B_3$). The preservation and proper treatment of the initial information involves the use of a

[1] Corresponding author. Tel.: +33 1 69 15 54 28
E-mail address: pascal.pernot@u-psud.fr.

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Nested Dirichlet distribution, in this case $\{b_1,b_2,b_3\}\sim\mathrm{Dirg}\big(B_1\otimes\mathrm{Dirg}(B_{11},B_{12};\Delta B_{11},\Delta B_{12}),B_3;\Delta B_1,\Delta B_3\big)$. Practically, two sets of random numbers, for $\mathrm{Dirg}(B_1,B_3;\Delta B_1,\Delta B_3)$ and $\mathrm{Dirg}(B_{11},B_{12};\Delta B_{11},\Delta B_{12})$, are sampled independently, and the adequate products are performed. This construction is particularly useful when the set of branching ratios contains subsets with total uncertainty. For our example, only the set $\{B_1,B_3\}$ would be characterized by experimental data, and the subset $\{B_{11},B_{12}\}$ would be inferred without information on the values of the branching ratios. This can be represented by the distribution $\{b_1,b_2,b_3\}\sim\mathrm{Dirg}\big(B_1\otimes\mathrm{Diri}(1/2,1/2;2),B_3;\Delta B_1,\Delta B_3\big)$, where $\mathrm{Diri}(1/2,1/2;2)$ is the uniform distribution for $\{B_{11},B_{12}\}$. As seen in Fig.1, due to the large and dominant uncertainty on b_1 and b_2, one-level sampling using standard uncertainty propagation for $\{b_1=B_1*B_{11},\ b_2=B_1*B_{12},\ b_3\}$ violates the sum-to-one constraint on $B_{11}+B_{12}$, and is unable to preserve the accurate information about b_3. Sampling with a nested Dirichlet scheme preserves this information.

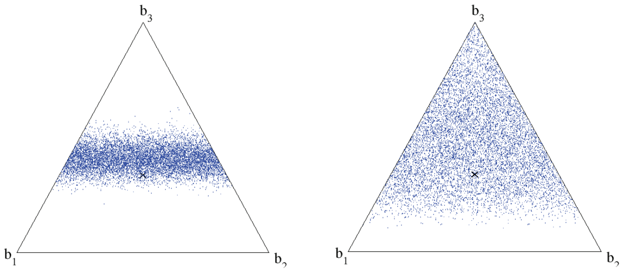

Figure 1. Difference between the nested sampling $\{b_1,b_2,b_3\}\sim\mathrm{Dirg}(0.6\otimes\mathrm{Diun}(2),0.4\ ;\ 0.1,0.05)$ (left) and the standard "one-level" sampling $\{b_1,b_2,b_3\}\sim\mathrm{Dirg}(0.3,0.3,0.4\ ;\ 0.3,0.3,0.05)$ (right) for the measured values $B_1=0.6\pm0.1$, $B_3=0.4\pm0.05$ and $B_{11}=0.5\pm0.5$, $B_{12}=0.5\pm0.5$. Such differences have a strong impact on model predictions.

The nested Dirichlet approach is very versatile and offers a powerful technique: (i) to preserve the independence of complementary experimental information about branching ratios; and (ii) to implement partial knowledge into kinetic modeling.

2. References

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