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Software Documentation for

Master Equation based Lumping (MEL)

Bridging *ab intio* calculations and large kinetic mechanisms

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Contents

Introduction

1.1 General Purpose

1.2 Copyright and warranty

1.3 Organization

Installation

2.1 Requirements

2.2 Windows Installation

Code Structure

Input setup

The code input is organized in one subfolder `inp` and one input file in the main folder `input_lumping.txt`. The folder name must be unchanged, whereas the input file can be renamed, as the code is run by the command `MEL` *`inputfilename`*.

4.1 inp folder

The input folder must contain the following files:

- kinetic file: depending on the type of input, the kinetic file is called in different ways
  - for MESS input type: both the input to ME calculations and MESS output must be present. Filenames must be `me_ktp.inp` and `rate.out`
  - for CHEMKIN input type: the mechanism file in chemkin format is `kin.CKI`. **Warning** : the reactions in `kin.CKI` must be all expressed in the forward direction only. No thermodynamics is required. In future implementations, also reversible reactions will be processed and the backward rate constants will be automatically derived with `OpenSMOKE++` preprocessor [1].
- `input_OS_template.dic`: input template for OpenSMOKE++ simulations. This file should not be changed, unless default function tolerances or simulation times are inadequate for the case processed. For further information see `https://www.opensmokepp.polimi.it/`.
- `input_preproc.dic`: input to OpenSMOKE++ mechanism preprocessor. This file should not be changed.
- `pseudospecies.txt`: this file is required for jobs `composition_selection`, `lumping`, and `validation`. It contains the names of the pseudospecies considered in the lumped mechanism and the corresponding species of the detailed mechanism. Pseudospecies constituted of single species have the same name both in the lumped and in the detailed mechanism. Pseudospecies constituted of multiple species are indicated with `I_L` and the composition is indicated with `I+J+K+L+M`, where `I` is the first species of the lumped group. For instance, in the case of C_5H_5OH PES (Section 6.2), the pseudospecies file is:

```
R      R
W4_L   W4+W5+W1
W3     W3
P1     P1
P2_L   P2+P5
P3     P3
P4     P4
```

it is noted that:

- the name of the species of the detailed mechanism must correspond to the species names of the kinetic files;
- not all species of the detailed mechanism are necessarily included in pseudospecies;
- `pseudospecies.txt` requires insights into the species to be neglected and those to be grouped together in the lumped mechanism. Automatic species selection is not available yet and it will be implemented in a future release of MEL. To simplify this operation, the jobs `prescreening_equilibium` and `prescreening_allreactive` can be run to check product distribution and characteristic times (Section 4.2.2, 4.2.2). Then, `composition_selection` selects an appropriate composition of the selected groups read from `pseudospecies.txt`.

4.2 input_lumping.txt

The input file is divided into three sections, delimited by an initial keyword and `end`:

- input: specifications about input type and operating conditions;
- jobs: list of jobs to be performed. The code proceeds in series;
- jobs subdictionaries: subdictionaries corresponding to each of the jobs in the job list. The subdictionaries are not read if the job key is inactive (i.e. if it is commented with #).

Comments in the input are preceeded by # and are not read. To activate a job in the list, remove the # sign that preceeds it. An example of a possible input is shown in Figure 4.1, and detailed explanation of each section is provided below.

4.2.1 input

Input specifications include:

- `opensmoke_folder`: absolute path to OpenSMOKE++ bin. Alternatively, the environment variable can be specified between %.
- `mech_type`: type of input mechanism:

```
#########################################################################
                      input for lumping code
#########################################################################

input
    opensmoke_folder = %OPENSMOKEPP_EXE_FOLDER%
    mech_type = MESS/CKI
    P_vect = [1]
    T_range = [400 2400]
    T_skip = [500 700 900 1100 1300 1500 1700 1900 2100 2300]
    units_bimol = molec/mol
    Stoichiometry = [C2 H4 O2]
    cutoff = 0.01-0.99
end

jobs
    #single_simulation
    prescreening_equilibrium
    prescreening_allreactive
    composition_selection
    lumping
    validation
end

############ jobs subdictionaries ########################

dictionary prescreening_equilibrium
    pseudospecies = [all]
end

dictionary prescreening_allreactive
    pseudospecies = [all]

end

dictionary composition_selection
    BF_tolerance = 0.03
    maxiter = 10
end

dictionary single_simulation
    simul_type = composition_selection
    Reac = []
    Prod = []
    pseudospecies = []
    maxiter = 10
    BF_tolerance = 0.03
end
```

FIGURE 4.1: Example of `input_lumping.txt`

  - `MESS`: both `inp/me_ktp.inp` and `inp/rate.out` required;
  - `CKI`: `inp/kin.CKI` contains the kinetic mechanism with reactions written only in the forward direction.

- `P_vect`: set of pressures. For MESS inputs, this must correspond to a subset of the pressures in `kin/me_ktp.inp`. `[1]` indicates no pressure dependence.
- `T_range`: temperature range of the simulations. For MESS inputs, a subset of the range indicated in `kin/me_ktp.inp`.
- `T_skip`: range of temperatures to be skipped. It is recommended to leave this blank `[ ]` for jobs `composition_selection` and `lumping`.
- `units_bimol`: units for bimolecular reactions. Fixed: cm^3, s. Optional: *molec* or *mol*. Default units for MESS input types are *molec*.
- `Stoichiometry`: number of x carbon, y hydrogen, and z oxygen atoms in the format `[Cx Hy Oz]`. This information is currently not used inside the code.
- `cutoff`: % of cutting of the species profiles to avoid numerical instabilities or accumulation of irrelevant intermediates at low conversions. For instance `0.1-0.99` indicates that output profiles start after 10% conversion of the reactant and end at 99% of reactant consumption.

4.2.2 jobs

Warning: job keys are meant to be activated one after the other. Hence, if the corresponding output subfolders are found, the job is not run. If you want to run a job that was already run, delete all the subfolders in the corresponding output folder. Sometimes you may want to keep the subfolder `BF_INPUT` (see below).

Besides `prescreening _equilibrium` and `prescreening_allreactive`, meant to give information about species selection, once the file `inp/pseudospecies.txt` is set, the three steps `composition _selection`, `lumping` and `validation` may be activated all together. In this way, pseudospecies composition is derived and used for both the derivation of the lumped mechanism and the model validation.

prescreening_equilibrium

This job selects the equilibrium (steady state) composition of the selected isomer pool by simulating a submechanism including only the isomerization reactions within the group. The initial composition of the set of wells is selected randomly from a normal distribution. Subdictionary options:

- `pseudospecies = [all]`: the whole set of wells is considered. This operation is risky if the rate constants of the wells are not defined in the full `T, P` range, as may be the case of MESS inputs.

- `pseudospecies = [A+B+C D+E+F]`: steady state composition of subsets `A+B+C, D+E+F` is derived. Species `A+B+C, D+E+F` must be wells.

prescreening_allreactive

This job analyzes the reactivity of species of the detailed mechanism considering all reactions of the detailed mechanism. The species indicated are the only reactants of the simulations performed (i.e. present at time = 0). Subdictionary options:

- `pseudospecies = [all]`: simulations are performed for each species of the detailed mechanism. In each set, only one species is present at t=0.
- `pseudospecies = [A+B+C D+E+F G H]`: the reactivity of subsets `A+B+C, D+E+F, G, H` is analyzed. The inlet composition of subsets of multiple species (for instance `A+B+C`) is selected randomly from a normal distribution. Species `A+B+C, D+E+F` may be either wells or bimolecular fragments, however one subset must contain only one type of species.

composition_selection

This job is run for pseudospecies constituted of multiple species. It requires the file `inp/pseudospecies.txt` in the format specified in Section 4.1. For all `I_L` pseudospecies, iterative simulations are run with `I_L` as reactants, including all reactions of the detailed mechanism. Iterations stop when the average composition within the chosen subset does not change throughout the simulations according to a given tolerance. The initial composition of `I_L` subset for the first iteration is chosen randomly from a normal distribution if `composition_selection/BF_INPUT/I_L` is not found. This folder may be generated automatically in prior prescreening simulations. Subdictionary options:

- `BF_tolerance`: tolerance for the convergence of the isomer pool composition. It must be a number between 0 (identical braching fractions throughout the simulation) and 1 (any change in the branching fractions is accepted). It is computed as the total time-weighted average variation in the BFs of the pseudospecies components throughout the simulation. A value of `0.03` indicates a maximum tolerance of `3%`.
- `maxiter`: maximum number of iterations. It is recommended to keep it in the order of 10s to avoid too long computational time.

lumping

This job has no subdictionary specifications. However, it requires:

- `inp/pseudospecies.txt`

- `lumping/BF_INPUT`: not strictly necessary; however, random initial composition selection for the simulations results most likely in wrong lumped rate constants. This does not apply to pseudospecies constituted of single species. `lumping/BF_INPUT` is copied automatically from the output of `composition_selection`.

validation

This job has no subdictionary specifications. However, it requires:

- `inp/pseudospecies.txt`
- `validation/BF_INPUT`: this should the same as `lumping/BF_INPUT` and is copied automatically from the output of `composition_selection`.
- `lumpedmech`: folder containing the files of the lumped mechanism `kin.txt, therm.txt` in CHEMKIN format, automatically generated in the lumping step.
- `lumpedmech_opt`: additional folder in case another lumped mechanism is present (for instance an optimized version of the lumped mechanism previously generate). Files must be named `kin.txt, therm.txt` and are in CHEMKIN format.

single_simulation

Single simulations of any type of those listed above may be performed. In this case, the selected pseudospecies for simulations must be specified. Before running, make sure that the corresponding output folder does not exist; results are not automatically overwritten to avoid loss of information. The subdictionary includes:

- `simul_type`: one of the job types.
- `pseudospecies`: to be specified for jobs `composition_selection`, `prescreening_equilibrium`, `prescreening_allreactive`. Only one pseudospecies must be indicated.
- `maxiter, BF_tolerance`: to be specified for `composition_selection` jobs.
- `Reac, Prod`: to be specified for jobs `lumping, validation`. Only one set of species must be selected as reactant, such as `[A+B+C]` or `[A]`. Products are written as `[D+E+F G H L+M]`. For `validation` jobs, the list of products does not affect the results. For `lumping` jobs, the selected products are set as infinite sinks (i.e. unreactive), therefore the products selection does affect the simulation profiles.

Output

The output of each job is stored in a folder named after the job type. If the folder is not found, it is automatically generated. All output folders share the same structure, as described in Section 5.1. Specific information of each job output are instead found in Section 5.2.

5.1 Output folders structure

Folders `jobtype/` share the same set of subfolders:

- `pseudospeciesname`: contain simulation profiles. Each folder is named after the pseudospecies, i.e. `I` for single species and `I_L` for multiple species. Subfolders contain simulation inputs and outputs performed at isobaric and isothermal conditions:
  - `I(_L)/Pressure/Temperature/input_OS.dic`: input of the simulation. For `I_L`, only the lumped pseudospecies (rather then the subset of species) is specified. When no pressure dependence is considered, Pressure folder is `1.0atm` by default.
  - `I(_L)/Pressure/Temperature/Temperature.txt`: simulation output profiles. Each profile is described by three columns `time, mole fraction, relative error`. This format allows further optimization with OptiSMOKE++ [2, 3] if needed.
  - `I(_L)/Path_to_Exp_Datasets.txt, I(_L)/Path_to_OS_inputs.txt`: List of relative pathways to all the inputs and outputs stored in `I(_L)`.
- `BF_INPUT`: input branching fractions for pseudospecies `I_L`. Files are named `I_L/Pressure.txt` and contain the composition of pseudospecies `I_L` with varying temperature. If the sum is not exactly 1, the BFs are renormalized before each simulations. These files are generated automatically. In particular, `prescreening_*` jobs generate `BF_INPUT` subfolders in `composition_selection`, which in turn generates `BF_INPUT` subfolders for `lumping` and `validation`.
- `BF_OUTPUT`: output branching fractions for all pseudospecies constituted of multiple species. Files are named `I(_L)/J_L/Pressure.txt`, where `I(_L)` is the

reactant and J_L is a pseudospecies produced in the simulation of I(_L) reactivity. These outputs may be copied as BF_INPUT of folders of successive steps.

- PLOTS: Prof_EXP_I(_L)_Pressure.png contain simulation output profiles at a given pressure in the selected range of temperature. For pseudospecies with multiple components I_L, figures Prof_EXP_I_L_composition_Pressure.png show the time variation in pseudospecies composition.

5.2 Jobs Output

In the following sections, specific information about the subfolders of each job is provided.

5.2.1 prescreening_equilibrium

- pseudospeciesname: only multiple species subfolders I_L are present. Species are all wells. If pseudospecies = [all] is specified in the input, only one subfolder I_L is generated, where I_L is a mixture of all wells of the PES.
- BF_INPUT: not present. Prescreening simulations aim at selecting input BFs for simulations of the following steps of the lumping procedure.
- BF_OUTPUT: steady state BFs of the selected isomer pools (or the full set of wells for pseudospecies = [all]). Only reactant BFs are reported in I_L/I_L/Pressure.txt, because no products are formed (only isomerization reactions are considered in the simulations). These outputs are automatically copied to composition_selection/BF_INPUT if the subfolder does not exist.
- PLOTS: plots Prof_EXP_I_L and Prof_EXP_I_L_composition_Pressure.png of the simulation profiles of the isomer mixture I_L. The time-weighted average of the composition shown in Prof_EXP_I_L_composition_Pressure.png corresponds to that reported in BF_OUTPUT/I_L/I_L/Pressure.txt.

5.2.2 prescreening_allreactive

- pseudospeciesname: subfolders I(_L). Species may be either wells or bimolecular fragments. If pseudospecies = [all] is specified in the input, subfolders I correspond to each species of the detailed mechanism (no I_L subfolders generated).
- BF_INPUT: not present. Prescreening simulations aim at selecting input BFs for simulations of the following steps of the lumping procedure.
- BF_OUTPUT: time-weighted average BFs of the selected pseudospecies (only if constituted of multiple species). Only reactant BFs are reported as I_L/I_L/Pressure.txt. These outputs are automatically copied to composition_selection/BF_INPUT if the subfolder does not exist.

- PLOTS: plots Prof_EXP_I(_L), Prof_EXP_I_L_composition_Pressure.png of the simulation profiles of pseudospecies reactivity. The time weighted-average of the composition shown in Prof_EXP_I_L_composition_Pressure.png corresponds to that reported in BF_OUTPUT/I_L/I_L/Pressure.txt.

5.2.3 composition_selection

- pseudospeciesname: subfolders I_L with simulation outputs of pseudospecies reactivity considering all reactions of the detailed mechanism. Only pseudospecies constituted of multiple species are considered. The set of pseudospecies is read from inp/pseudospecies.txt.

- BF_INPUT: guess inlet composition of I_L for the iterative simulations performed. Derived automatically from prescreening simulations and updated at each iteration from BF_OUTPUT/I_L/I_L until reaching convergence or the maximum number of iterations.

- BF_OUTPUT: time-weighted average BFs of the selected pseudospecies I_L. Resulting BFs for reactants and products are in I_L/J_L/Pressure.txt. The final outputs for reactant composition I_L/I_L/Pressure.txt are automatically copied to lumping/BF_INPUT and validation/BF_INPUT if the subfolders do not exist.

- PLOTS: plots Prof_EXP_I_L and Prof_EXP_I_L_composition_Pressure.png of the simulation profiles of the pseudospecies reactivity. The time-weighted average of the composition shown in Prof_EXP_I_L_composition_Pressure.png corresponds to that reported in BF_OUTPUT/I_L/I_L/Pressure.txt.

5.2.4 lumping

- pseudospeciesname: subfolders I(_L) with simulation outputs of pseudospecies reactivity considering all other pseudospecies as unreactive. The set of pseudospecies is read from inp/pseudospecies.txt. Lumped submechanisms (I_L -> prods) are reported in I(_L)/kin.txt

- BF_INPUT: inlet composition of I_L copied from composition selection.

- BF_OUTPUT: time-weighted average BFs of the selected pseudospecies I_L. Resulting BFs for both reactants and products are reported as I_L/J_L/Pressure.txt.

- PLOTS: plots Prof_EXP_I(_L) and Prof_EXP_I_L_composition_Pressure.png of pseudospecies reactivity. Simulation results of the detailed submechanisms are compared to those of the lumped submechanisms lumping/I(_L)/kin.txt. The time weighted average of I_L composition shown in Prof_EXP_I_L_composition_Pressure.png corresponds to that of BF_OUTPUT/I_L/I_L/Pressure.txt.

- `lumpedmech`: lumped mechanism combined from the `lumping/I(_L)/kin.txt` outputs. Contains both kinetics and fictitious thermodynamic files `kin.txt` and `therm.txt`.

5.2.5 validation

- `pseudospeciesname`: subfolders `I(_L)` with simulation outputs of pseudospecies reactivity considering all reactions of the detailed mechanism. The set of pseudospecies is read from `inp/pseudospecies.txt`.

- `BF_INPUT`: inlet composition of `I_L` derived automatically from composition selection. This should correspond to `lumping/BF_INPUT`.

- `BF_OUTPUT`: time-weighted average BFs of the selected pseudospecies `I_L`. Resulting BFs in terms of both reactants and products are reported as `I_L/J_L /Pressure.txt`.

- `PLOTS`: plots `Prof_EXP_I(_L)` and `Prof_EXP_I_L_composition_Pressure.png` of the simulation profiles of pseudospecies reactivity. Detailed mechanism simulations are compared those using the lumped mechanism `lumpedmech/kin.txt` and its optimized version if present `lumpedmech_opt/kin.txt`. The time-weighted average of `I_L` composition shown in `Prof_EXP_I_L_composition_Pressure.png` corresponds to that of `BF_OUTPUT/I_L/I_L/Pressure.txt`.

Examples

6.1 CH_3COOH

6.2 C_5H_5OH

6.3 $C_{10}H_{10}$

6.4 C_9H_9

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