Non-Equilibrium Reaction Kinetics of an Atmospheric Pressure Microwave-Driven Plasma Torch: a Kinetic Global Model
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Abstract
In the context of microwave-coupled plasmas, within atmospheric pressure nozzle geometries, we have developed a kinetic global model (KGM) framework designed for quick exploration of parameter space. Our final goal is understanding key reaction pathways within non-equilibrium plasma assisted combustion (PAC). In combination with a Boltzmann equation solver, kinetic plasma and gas-phase chemistry are solved with iterative feedback to match observed bulk conditions from experiments; using a parameterized non-equilibrium electron energy distribution function (EEDF) to define electron-impact processes. The KGM is first applied to argon and ‘air’ systems as a means of assessing the soundness of made assumptions. The test with ‘air’ greatly increases the complexity by incorporating a plethora of excited states (e.g. translational and vibrational excitations) and providing new reaction pathways. The KGM is then applied to plasma driven combustion mechanisms (e.g. H2 or CH4 with an oxidizer source) which drastically increases the range of reaction time-scales. As the reaction mechanisms become more complex, availability of data will begin to hinder model physicality, requiring analytical and/or empirical treatment of gaps in data to maintain completeness of the reaction mechanisms.

KGM Methodology
Open-source volume-averaged modeling tools designed for quick parameter space exploration of plasma chemistry systems

- Written in Python ([Num, Sci, Sym]Py)
- Automated data acquisition from public sources
- Visualization of dataset completeness and database comparison
- Symbolic representation and differentiation
- Numerical results with compiled and interactive ODE models

Governing Assumptions and Equations
- Quasi-neutrality, spatial uniformity
  - Spatial effects can be mapped to time (-1D)
  - Electron energy equation is solved for an effective electron temperature ($T_e$)
  - EEDF fixed shape ($x$); included in parameter space until Boltzmann equation solver

Normalized EEDF parameterized by shape, $x$:

$$f_x = \frac{\varepsilon}{(\frac{T_e}{T})^2 \left(\frac{T}{T_e}\right)^x} \exp \left[ -\left(\frac{\varepsilon}{\frac{T}{T_e}}\right)^x \right]$$

- $P_{eff}, D_{eff}, K_{ij}$ depend on $T_e, T_g, n_a$, and/or $\nu_m$

General species continuity equation

$$\frac{dn_i}{dt} = \sum_{j=1}^{R} K_{ij} \int n_j - \frac{D_{eff}}{X} \tag{1}$$

Gas phase temperature equation

$$\frac{dT_g}{dt} = -\frac{\sum_{i=1}^{N} m_i h_i(T_g)n_i + \dot{Q}/V}{\sum_{i=1}^{N} m_i c_{v,i}(T_g)n_i}$$

Electron energy equation

$$\frac{d}{dt} \left( \frac{3}{2} n_e k_B T_e \right) = P_{eff} - \sum_{i=1}^{N} n_i K_{ij} \Delta E_{ij} n_e$$

Dataset Visualization
Data for a model is a collection from database sources and optional input files
- Open DB downloaded files: LXcat, NIST ASD & MSD, Phys4Entry, VAMDC
- Custom models can be partially/entirely input
- Database files: 'CHEMKIN-like'
- Reaction/cross-section data as CSV tables and/or string algebraic expressions

Using ODE Models
Numerical ODE models can be created depending on usage requirements
- LambdaLib: Fast to compile, slowest evaluation time
- Theano: Graph function for hardware acceleration
- Compiled C: Fastest evaluation and recoverable

Rough fitting of timing trends

Spline lookups are used (integrated $K_{ij}$, piecewise thermo data, etc) to preserve a smooth Jacobian. Integrated data is saved for recovery

References

Future Work
- Implementation of custom ODE solvers
  - High-order, stiffly stable, multi-derivative schemes
  - Fast implicit parallel solvers
- Boltzmann equation solver for self-consistent evaluation of the EEDF
  - Multi-term approximation and discretization methods
- An application programming interface for using compiled c code within a fluid code
- Expanding the capabilities of the reaction parsing engine (OCR, automatic updates)

Argon Model Testing
Since the Argon reaction model is well studied => Testing ground of standard assumptions
- Using the explicit time dependence of the MW electric field vs time averaged constant
- Effect of changes to the EEDF shape, $x$, on the species evolution

Both tests assume: pressure of 760 [Torr], gas temperature of 500 [K]. Each Argon 4s and 4p state is tracked individually.

Argon major species evolution. $X = 1$ is solid, $X = 2$, $X = 3$, $X = 4$ is dot-dot

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