# Non-Equilibrium Reaction Kinetics of an Atmospheric Pressure Microwave-Driven Plasma Torch: a Kinetic Global Model

Guy Parsey, Yaman Güçlü, John Verboncoeur and Andrew Christlieb
[parseygu,yguclu,johnv,christli]@msu.edu

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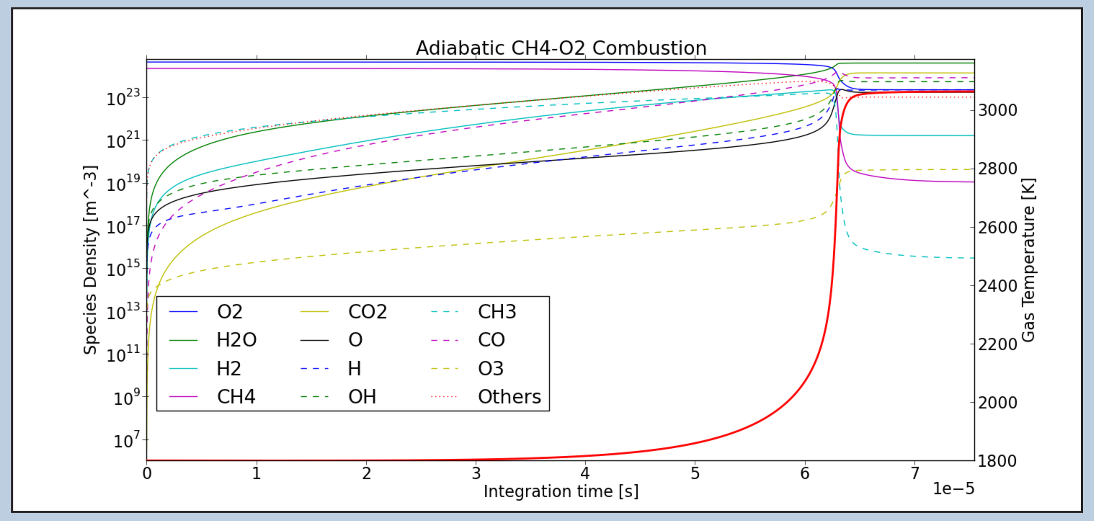
## Abstract

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. $H_2$ or $CH_4$ 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.

## (Plasma Assisted) Combustion

Classical combustion is highly dependent on chain-branching chemistry

- Increase in chain-carriers drives termination
- Autoignition related to rate of carrier dissociation
- Restricted by flammability limits
- Non-linear effects typically ignored for simplicity




Adiabatic - 760 Torr $CH_4 - H_2$ combustion. $T_g$ in red

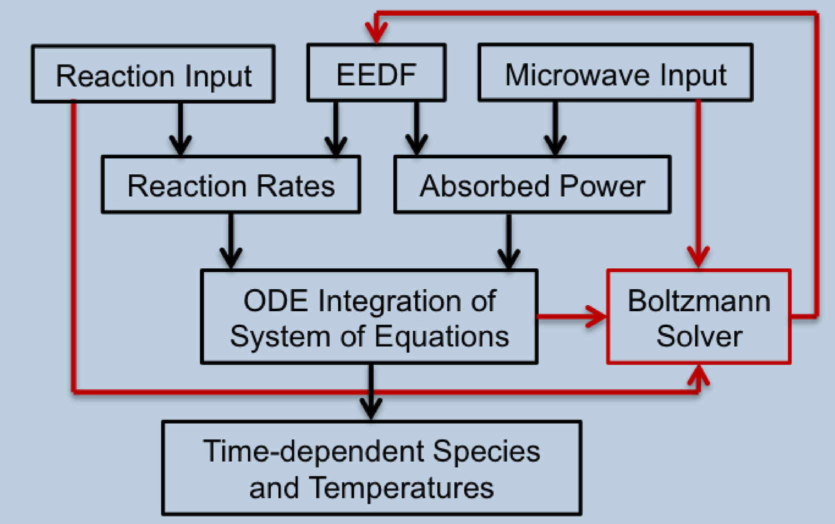
Using plasma discharges to augment combustion characteristics such as operating regimes or efficiency

- Equilibrium plasmas result in local heating
- Non-equilibrium plasmas used to impart energy on specific DoF within the gas
  - Non-linear interactions between species
  - Reaction dependency on EEDF

## 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, $x$.

$$f_e = \frac{x\varepsilon^{\frac{1}{2}}}{(\frac{3}{2}T_e)^{\frac{3}{2}}}\frac{(\Gamma(\frac{5}{2x}))^{\frac{3}{2}}}{(\Gamma(\frac{3}{2x}))^{\frac{5}{2}}}\exp\left[-\left(\frac{\Gamma(\frac{5}{2x})}{\Gamma(\frac{3}{2x})}\frac{\varepsilon}{\frac{3}{2}T_e}\right)^x\right]$$

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

General species continuity equation

$$\frac{dn_\alpha}{dt} = \sum_i^R K_{i,j}\prod_j n_j - \frac{D_{\rm eff}}{\Lambda^2}$$

Gas phase temperature equation

$$\frac{dT_g}{dt} = \frac{-\sum_{k=1}^N m_k h_k(T_g)\dot{n}_k + \dot{Q}/V}{\sum_{l=1}^N m_l c_{vl}(T_g) n_l} \qquad (1)$$

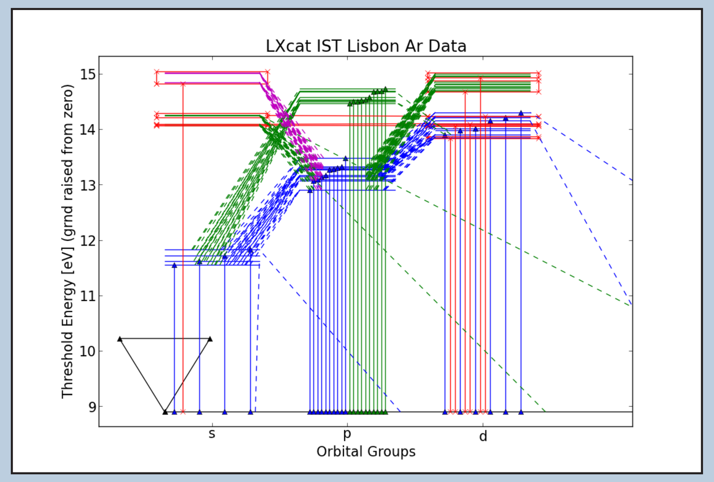
Electron energy equation

$$\frac{d}{dt}\left[\frac{3}{2}n_e k_B T_e\right] = \frac{P_{\rm eff}}{V} - \sum_i^{R_{\rm EI}} n_i K_{ij}\Delta E_{ij} n_e$$

## 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



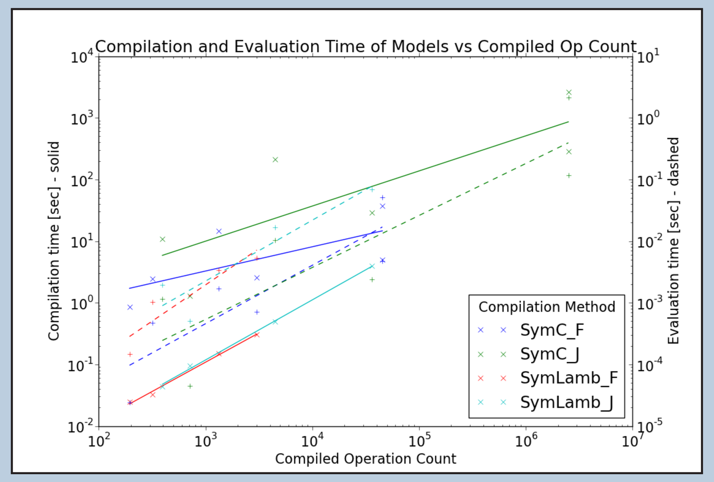

Line style, color and direction describe a given reaction and involved species

## Using ODE Models

Numerical ODE models can be created depending on usage requirements

- Lambdify: Fast to compile, slowest evaluation time
- Theano: Graph function for hardware acceleration
- Compiled C: Fastest evaluation and recoverable

Rough fitting of timing trends
Operation count is math ops, neglects spline lookups



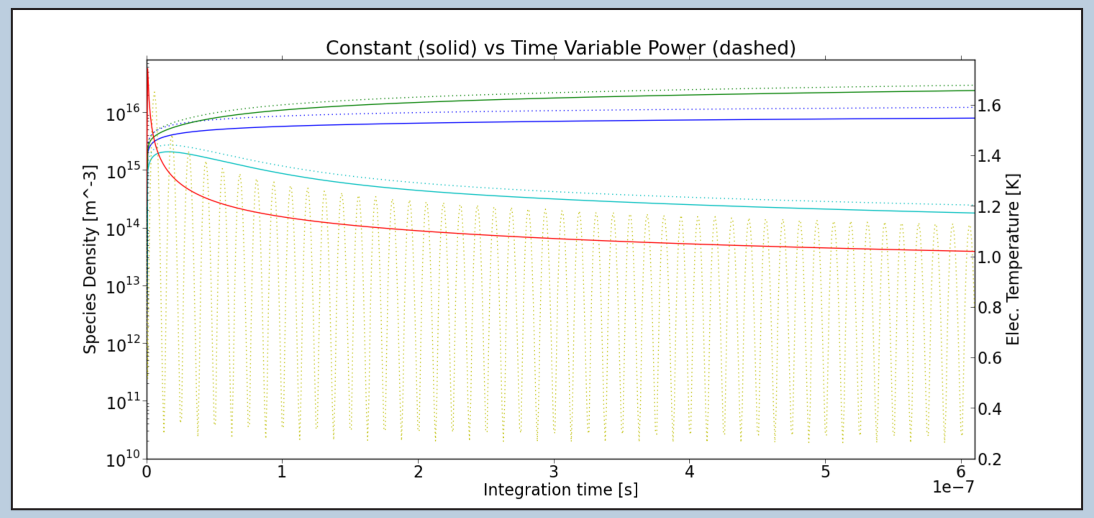

Spline lookups are used (integrated $K_{ij}$, piecewise thermo data, etc) to preserve a smooth Jacobian. Integrated data is saved for recovery

## Argon Model Testing

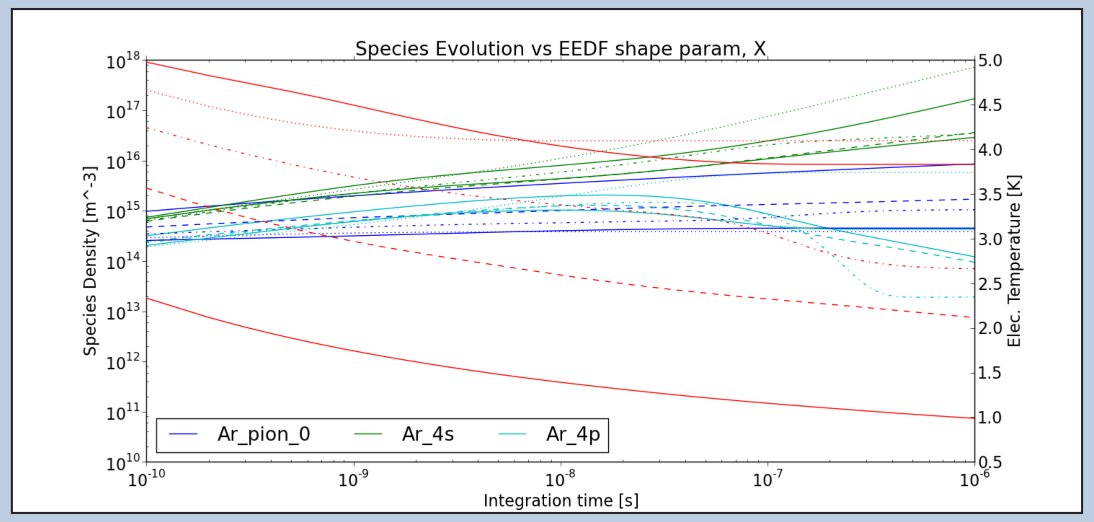
Since the Argon reaction model is well studied
⇒ Testing ground of standard assumptions

- 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.




Explicitly time dependent power vs its time averaged




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

## 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 )

## References

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