

Kinetic CH4 Photoionization model

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May 2020

The purpose of this document is to function as a *quick and dirty* brain-dump for my ideas for a kinetic photoionization model to be used in the Afivo-PIC code. This document is not written with the intention of being representable, it may contain:

- an incomplete reference list,
- spelling and grammar errors,
- bad humor,
- crimes against formatting,

and should be shot on sight.
Enjoy!

1 Kinetic Model for Air

Two papers that have photoionization of air in a particle model are [1] and [2], both are based upon the classical model for photoionization of air by [3]. The approach is the same, but I will stick to the notation of [1] for their explanation is more complete. The idea is this (and I quote directly from [1]):

“The emissivity of photons that lead to ionisation of oxygen is assumed to be proportional to the nitrogen ionisation rate. The relative emissivity ψ^* is the number of oxygen photoionisations per impact ionisation:

$$\psi^* = p^* \gamma^* \eta^* \tag{1}$$

where p^* accounts for quenching effects on excited nitrogen, γ^* is the fraction of nitrogen ionisation events that leads to radiation with energy sufficient to ionise oxygen, and η^* the efficiency of those photons to ionise oxygen. [...] To reproduce this proportionality in our particle code, ionising photons are created if a random number $U_p < \psi^*$ for each computer particle that suffers an ionisation event. The number of created photons (N_{ph}) equals the number of electrons the computer particle represents (limited to 10,000). The wave frequency γ

of the photons determines their mean free path. It is chosen randomly in the frequency interval $[\gamma_1, \gamma_2]$ able to ionise oxygen using a random number U_c such that $\gamma = \gamma_1 + U_c(\gamma_2 - \gamma_1)$. ($\gamma_1 = 2.925$ PHz and $\gamma_2 = 3.059$ PHz). The mean free path of the photons before they create an ionisation event of oxygen

$$K_f = K_1 \left(\frac{K_2}{K_1} \right)^{\frac{\gamma - \gamma_1}{\gamma_2 - \gamma_1}} \quad (2)$$

where $K_1 = 3.5P_{O_2}m^{-1}$ and $K_2 = 200P_{O_2}m^{-1}$.”

(Opinion time: The formulation of Eq. 2 in [2] is more intuitive and more concise.) Note that the photon travel distance is drawn from an exponential distribution with the mean-free path as mean value.

2 What about CH4 absorption?

First some properties. The ionization potential of CH4 is around 12.6 eV. For O2 we have: 12.1 eV and for N2 we have 15.6 eV. So in theory, the photons that we consider to be available (i.e. the energy range of the photons that is not strongly suppressed by non-ionizing absorption by N2 and above the ionization potential of O2, [12.1, 12.65] eV or [98, 102.5] nm or [2.925, 3.059] PHz... Whichever units you find the least annoying.) can ionize the CH4 molecule. **However, it turns out that the rate of photoionization of methane in this region is very low and also much lower than the (non-ionizing) dissociative absorption [4], see figure 1.** This leads to the simplification that photoionization of CH4 can be neglected, and we only need to account for photon-absorption by CH4 (Note that this only holds for air-methane mixtures where the ionization of O2 dominates the ionization of CH4. In N2-CH4 mixture, e.g. titans atmosphere, one *should* consider the ionization of CH4 as this is the only molecule available for photoionization [5]. Opinion time: the model from [5] is quite crude. They claim that 9% of the photons have enough energy to ionize CH4 and therefore simply take the Zheleznyak model with 9% of the photons, nothing about the cross-sections of CH4. “This should be punishable by death, or in the very least a community service of 30 days...” Note also, the dissociative photonabsorption leads to neutral fuel fragments, CH3 CH2 or CH, which might be relevant for combustion modelling, but are omitted here)

So... What does this mean for modelling electric discharges? Well, if we listen to the very nice work of [6] we can extend the (continuum) Zheleznyak model by incorporating the absorption rate of methane:

$$k_{CH4} = \sigma_{CH4}n_{CH4}, \quad (3)$$

where k is the absorption rate, σ the cross-section and n the number density. This gives a spatially-dependent coefficient $Z_{CH4}(r) = \exp(-k_{CH4}r)$ that corrects a “photoionization coefficient” Ψ and we can all take the afternoon off.

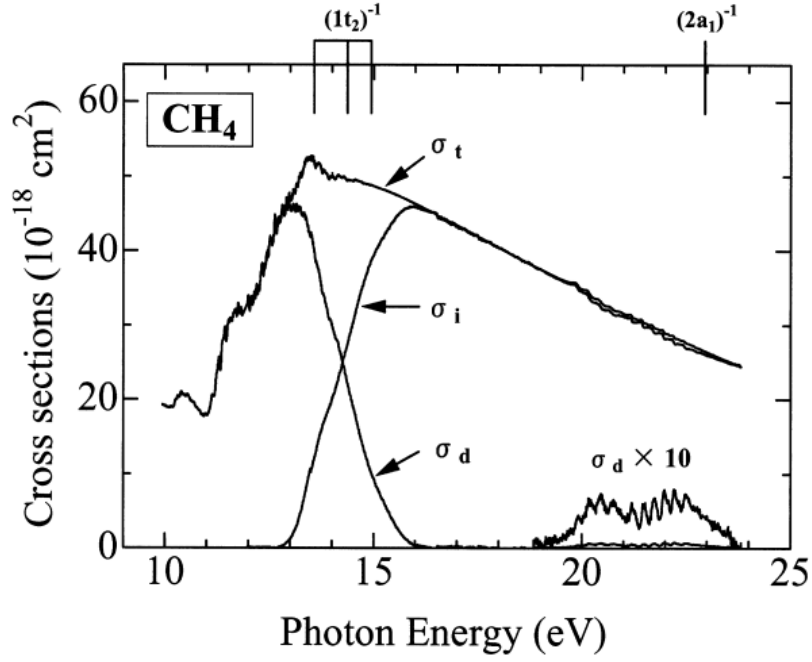


Fig. 2. The photoabsorption (σ_t), photoionization (σ_i), and neutral-dissociation (σ_d) cross sections of CH_4 as a function of the incident photon energy measured in this experiment with a bandpass of 0.1 nm, which corresponds to the energy width of 32 meV at the incident photon energy of 20 eV. The vertical ionization potentials of the ionic states involved are also indicated by the vertical bars [53].

Figure 1: figure and caption from

The value $\sigma_{CH_4} = 3 \cdot 10^{-17} \text{ cm}^2$ is taken (in other publication by the same author one can find a value of $4 \cdot 10^{-17} \text{ cm}^2$ [7], so the sweetspot should be somewhere in between those two values).

3 Correcting for CH4 absorbtion

A kinetic variant of the above paragraph would be nice to include in our particle model. In order to obtain this, we first need to take a small step back because the correction in the above paragraph corrects two processes at the same time, namely: (1) reduced mean free path of the photons (eq. 2) and (2) reduced number of photons interacting with O2 due to absorption of CH4 (eq. 1). In a particle code, the influence of these quantities is handled separately and requires some extra thinking beforehand.

First, let us consider the mean free path of a photon with energy $12.1 < \gamma < 12.65 \text{ eV}$.

$$l_{mfp}(\gamma) \approx (\sigma_{CH_4} n_{CH_4} + \sigma_{O_2}(\gamma) n_{O_2})^{-1}, \quad (4)$$

where we have neglected the influence of N2 due to low cross-sections and taken a constant value for σ_{CH_4} . Furthermore, the absorbtion of O2 can be approximated with a simple power law (e.g. in [8] eq 14 and fig 7) Therefore, to get the travel-distance l of the photon. Draw random photon energy γ , compute l_{mfp} and draw l from an exponential distribution with mean l_{mfp} . Which is a sufficient correction wrt photon travel distance in CH4-O2-N2 mixtures. In Figure we can see the mean free paths for photon energies at the extremity of our energy interval (12.10 eV and 12.65 eV) at a pressure of 1.0 bar for varying CH4 fractions (CH4 is mixed with air, i.e. gas with a ratio N2:O2 8:2)

Second, if one remembers from eq 1 that ψ^* resembles the number of oxygen photoionisations per impact ionisation. Now we have to include in this coefficient the probability of absorption by CH4. The relative probability of a photon with energy γ colliding with O2 is given by:

$$P = \frac{\sigma_{O_2}(\gamma) n_{O_2}}{\sigma_{O_2}(\gamma) n_{O_2} + \sigma_{CH_4} n_{CH_4}},$$

where we again neglected the presence of N2 due to small cross-sections. Thus, to get the number of photons that lead to photon ionization of O2, draw random γ , compute P , and continue the routine presented by [1] using the coefficient $P\psi^*$ (instead of ψ^*) (Brainfart: it would be fun to check if the values of P are close to 0.09 and couple this to the crude model used in [5]...). This is a sufficient correction wrt number of ionizing photons produced in CH4-O2-N2 mixtures. The plot of P is omitted here. Later its effect will be shown combined with the quenching correction.

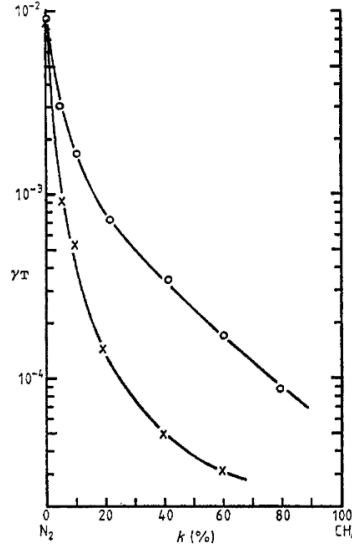


Figure 4. Variation of the total secondary ionisation coefficient γ_T with the fractional CH₄ partial pressure k . $E/p_{20} = (\times) 99.3 \text{ V cm}^{-1} \text{ Torr}^{-1}$, $(\circ) 200 \text{ V cm}^{-1} \text{ Torr}^{-1}$.

Figure 2: figure and caption from [9]

4 What about CH4 quenching?

So far I have been quiet about the quenching of excited nitrogen states. However, one should not be surprised to see a correction in the total quenching rate due to the pressure of CH₄. An example of the influence of quenching due to CH₄ can be seen for example in [9] where the authors ascribe the variations in the measured total secondary electron coefficient (I am assuming due to ion bombardement of the electrode *and* due to photoionization, not entirely clear to me) in N₂-CH₄ mixtures to a stronger quenching rate because of CH₄. For good measure I have copied one graph in Figure 2. This graph shows a very strong slope in the ‘secondary ionisation coefficient’ as a function of CH₄ partial pressure k in the lower gas fraction regime ($0\% < k < 20\%$). Although the direct relevance (i.e. no O₂) of this result is questionable, it shows that strong variations due to elevated quenching rates can occur.

Measurements for the quenching of the $C^3\Pi_u$ states of N₂ due to various gases (e.g. N₂, O₂ and CH₄ but also CO₂) is given in [10] with comparisons to even earlier work. It is mentioned (in [9] they claim this with reference to [12]. The latter is in German, which made it a bit difficult to read. Another possibly important paper which is in German, and contains formulas similar to what is to come, that might be useful is [11]) that this excited state dominates photon emission. Therefore, I will summarize the values here and propose to

use these reaction rates for all excited states. Two values are given for each quenching rate k_q corresponding to the lowest two levels (quote: “since the radiative transitions 2P(0-0) and 2P(1-0) under these levels (proceeding to the level $v'' = 0$ for the state $B^3\Pi_g$) produce bands which lie within the most intense band of the emission spectrum of nitrogen excited by alpha particles at pressures of several hundred of torr” [10]. I must admit that this quote is slightly out of reach of my comprehension.)

pressure (torr)	$v' = 0$	$v' = 1$
$p_q^{N_2}$	91	40
$p_q^{CH_4}$	1.8	1.75
$p_q^{O_2}$	3.7	3.4

Note that $p_q^{N_2}$ is an order of magnitude higher than the other rates and $p_q^{O_2}$ is roughly twice as high as $k_q^{CH_4}$. This shows the strong quenching behaviour of methane. Since the gas fraction of CH4 is comparable to the gas fraction of O2 (default N2:O2:CH4 as 0.715 : 0.19 : 0.095, but this might be subjected to variations) a correction for the quenching rate of methane seems to be appropriate.

QUESTION TIME: Why is the quenching pressure that is normally used for air (40 torr = 30 mbar) the quenching pressure for pure nitrogen?? Shouldnt we have calculated:

$$p_q^{AIR} = \left(\frac{0.8}{40} + \frac{0.2}{3.5} \right)^{-1} \approx 13 \text{ torr} = 17.3 \text{ mbar}$$

[insert interrobang here]

5 Correcting for CH4 quenching

The equation describing the evolution of nitrogen excited states is given by:

$$\partial_t[N_2^*] = Q - \frac{[N_2^*]}{\tau_0} - \sum_{i \in [N_2, O_2, CH_4]} k_q^i \cdot [N_2^*][M^i] \quad (5)$$

where τ_0 is ‘a’ radiative decay time for the excited states of nitrogen and $[M^i]$ is the number density of the i-th gas component. Now, for simplicity, we assume that $[N_2^*]$ is in steady state. With this assumption we are neglecting the build-up of a pool of excited states. More importantly, this assumption allows us to express the rate of radiative decay proportional to the excitation rate, since the production of states must be balanced by either quenching or radiative decay (To see why this is important, take a look at section 1 ;P) This proportionality will follow by following the following steps. First:

$$\begin{aligned} Q &= [N_2^*] \left(\frac{1}{\tau_0} + k_q^{N_2}[N_2] + k_q^{O_2}[O_2] + k_q^{CH_4}[CH_4] \right), \\ &= \frac{[N_2^*]}{\tau_0} \cdot \left(1 + \frac{p}{k_B T} \cdot \tau_0 (k_q^{N_2} \chi^{N_2} + k_q^{O_2} \chi^{O_2} + k_q^{CH_4} \chi^{CH_4}) \right). \end{aligned}$$

Where χ^i is the i-th mole-fraction. Next, by introducing the i-th quenching pressure as $p_q^i = \frac{k_B T}{\tau_0 k_q^i}$ we find the proportionality between the number of photomissions per unit volume per unit time and the excitation rate:

$$\frac{[N_2^*]}{\tau_0} = \left(1 + p \cdot \left(\frac{\chi^{N_2}}{p_q^{N_2}} + \frac{\chi^{O_2}}{p_q^{O_2}} + \frac{\chi^{CH_4}}{p_q^{CH_4}} \right) \right)^{-1} \cdot Q \quad (6)$$

Note that in the special case where only one gas component is considered (or I should say, only one *total* quenching pressure is considered) we can rewrite even further by combining gas-component-specific terms which results in:

$$\frac{[N_2^*]}{\tau_0} = \frac{p_q}{p_q + p} \cdot Q,$$

the right-hand side of which should be familiar to the reader.

However for gas mixtures other than ‘vanilla’ air it is less convenient to talk about *the* quenching pressure. Instead some weighted inverse law allows us to fabricate an effective quenching pressure \tilde{p}_q by solving:

$$\frac{1}{\tilde{p}_q} = \frac{\chi^{N_2}}{p_q^{N_2}} + \frac{\chi^{O_2}}{p_q^{O_2}} + \frac{\chi^{CH_4}}{p_q^{CH_4}} \quad (7)$$

which allows us to recover the well-known form:

$$\frac{[N_2^*]}{\tau_0} = \frac{\tilde{p}_q}{\tilde{p}_q + p} \cdot Q, \quad (8)$$

The combined *relative* influence of effective quenching of excited states and photon absorption by CH4 at 1 bar for variable methane gas fractions is shown in Figure 4. This quantity, i.e.

$$\underbrace{P(\gamma) \frac{\tilde{p}_q}{\tilde{p}_q + p}}_{\text{photon loss in AIR-CH4}} \cdot \underbrace{\frac{p_q^{AIR} + p}{p_q^{AIR}}}_{\text{inverse photon loss in AIR}}$$

represents the fraction of photons that are lost due to the introduction of CH4. (After looking at the figure, think back to [5] where they model Titan’s atmosphere with 9% of the photons in the Zheleznyak model for air... There is no oxygen, so a one-to-one correspondence between their model and mine cannot be made. But still one must question the validity of their results corresponding to 80% CH4.)

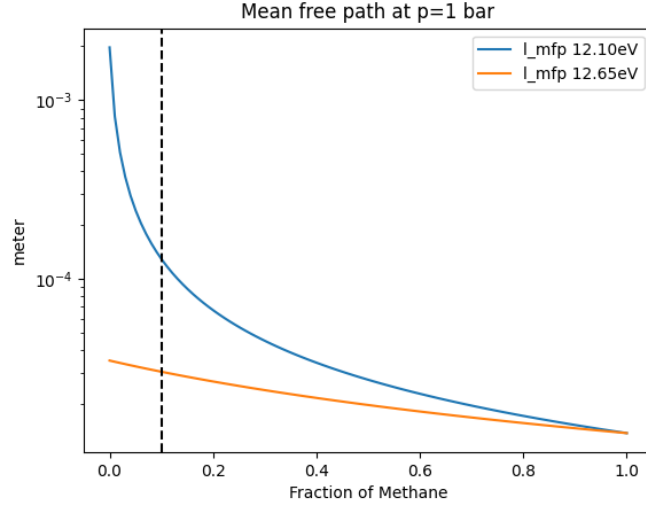


Figure 3: Mean free paths for photon energies in STP air mixed variable methane fraction. The black line denotes your average air-methane mixture used for combustion applications (10%)

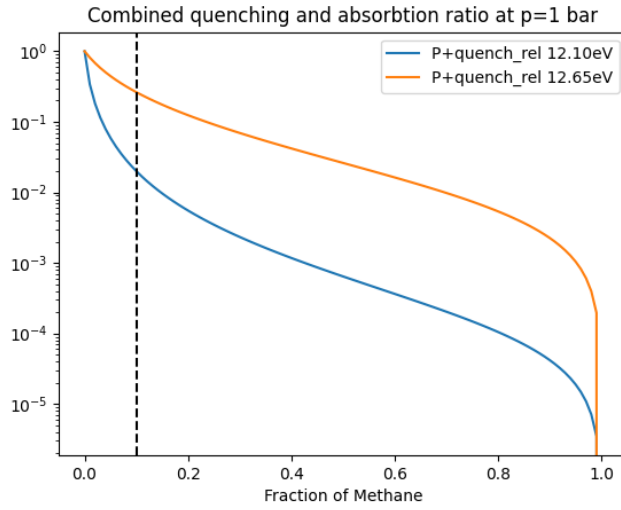


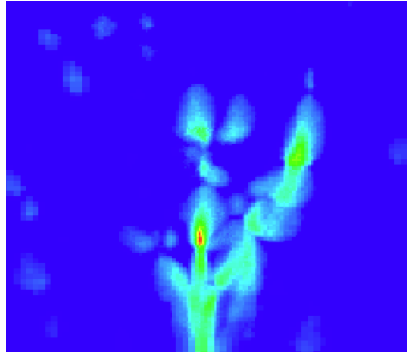
Figure 4: The combined **relative** effect (see text) of methane-promoted quenching of excited states and non-ionizing photon absorption for variable methane gas fractions. The black line denotes your average air-methane mixture used for combustion applications (10%)

6 Time for some action!

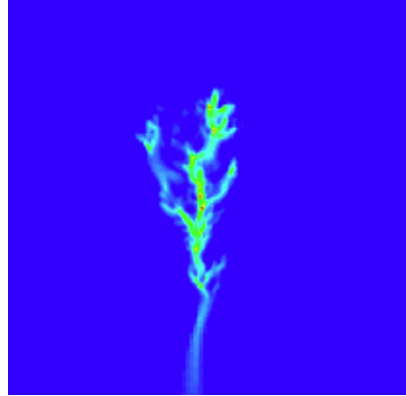
Lets see some discharge simulations in air-methane. First I am obliged to give some boring details before I start. Two mixtures of $\text{N}_2:\text{O}_2:\text{CH}_4$ are considered, 8:2:0 (AIR) and 7.15:1.9:0.95 (FUEL). Furthermore:

- pressure = 1.0 bar (STP)
- $E_0 = 6.0 \cdot 10^6$ (Twice the breakdown voltage in AIR)
- No dielectrics are considered
- No background ionization
- simulated time = 6.2 ns

Only the gas-components (and therefore the photoionization related parameters) and electron impact cross-sections are different.



(a) AIR



(b) FUEL

Figure 5: Positive streamers in both gases. Both images are (roughly) to scale, height of image corresponds to 2.0 mm. Snapshots taken at 6.2 ns.

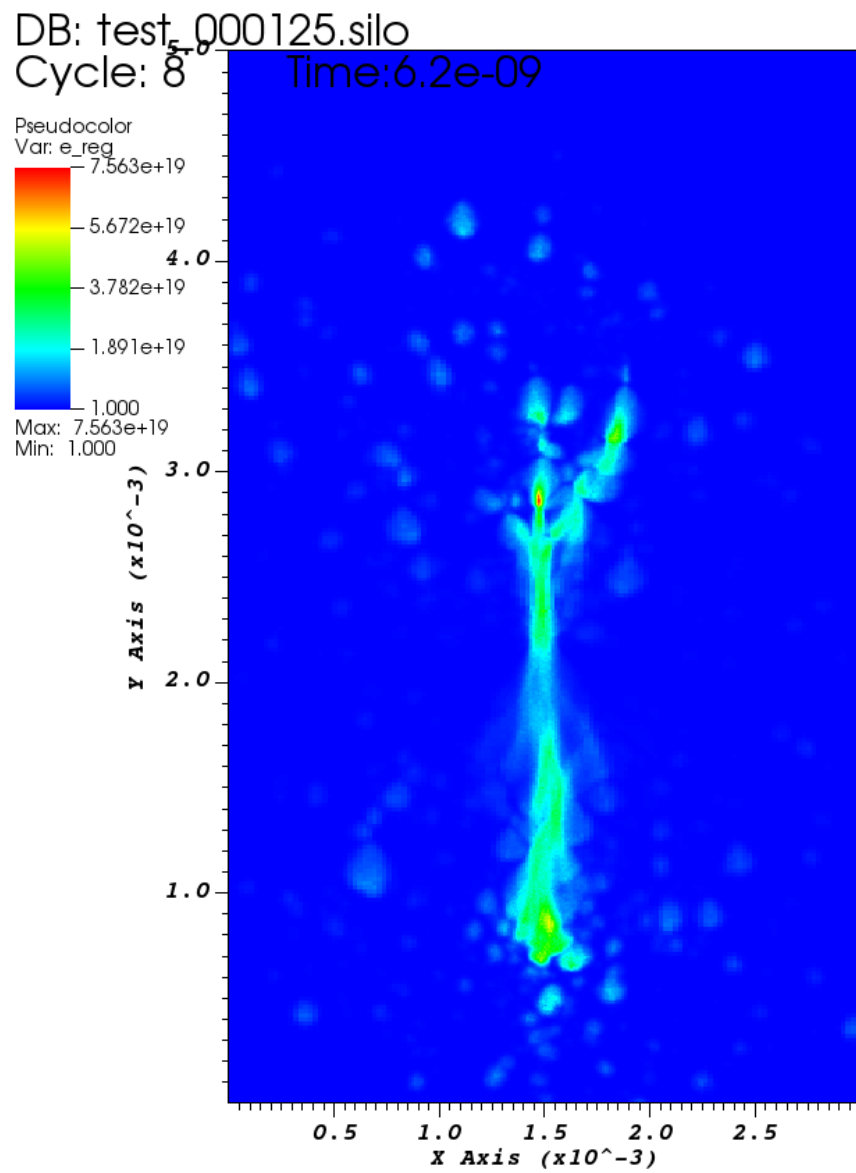


Figure 6: AIR

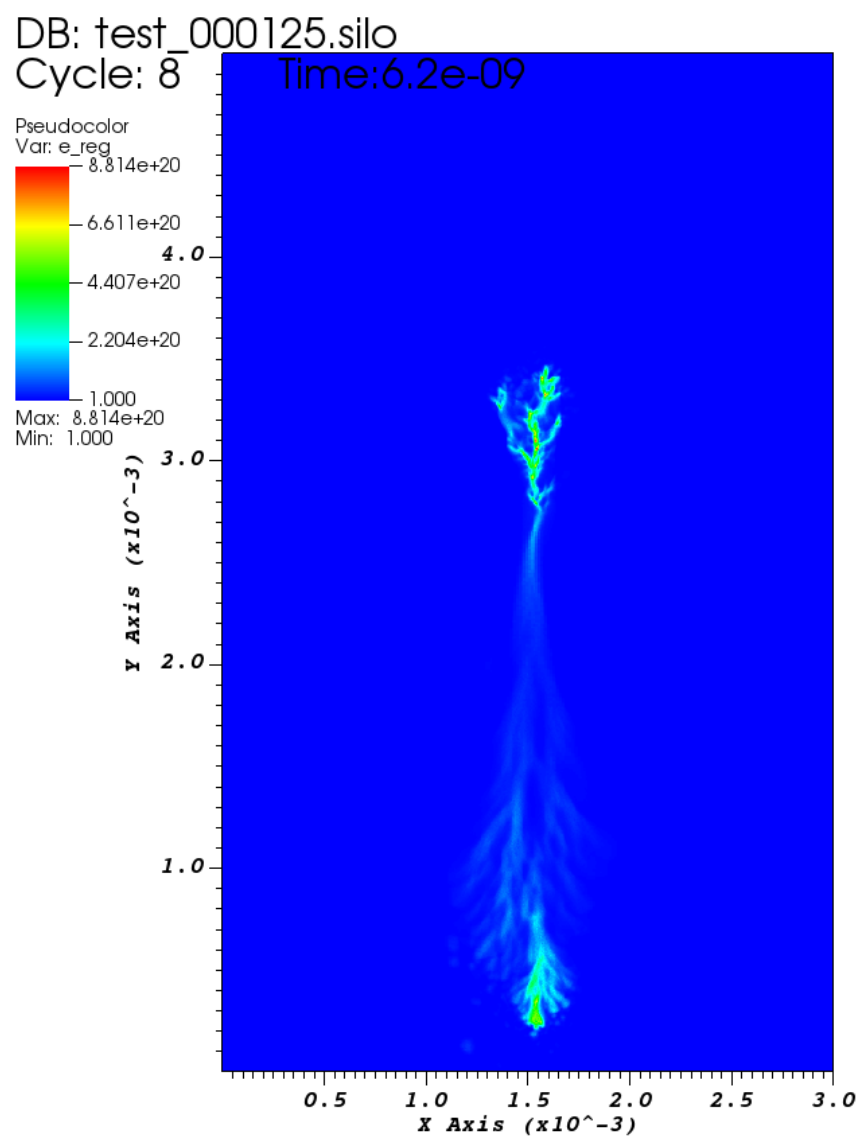


Figure 7: FUEL

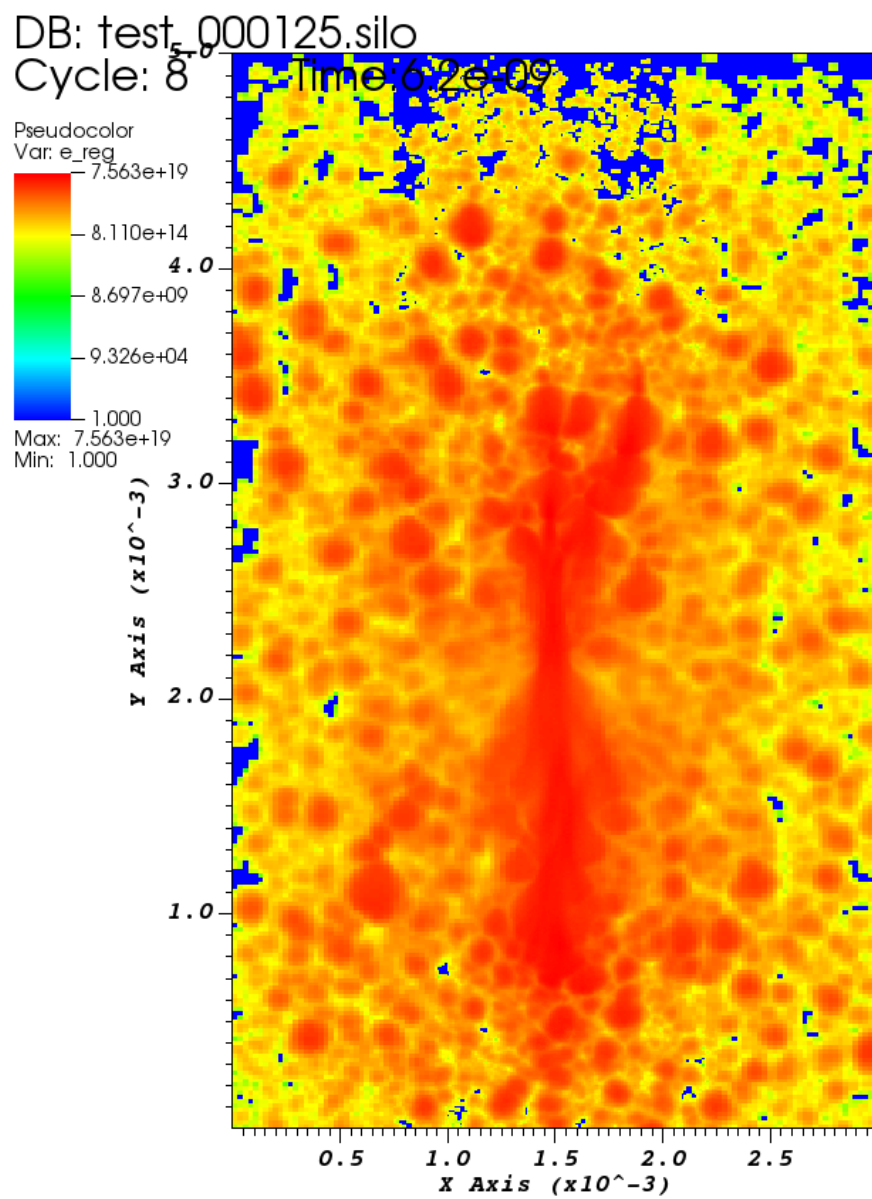


Figure 8: AIR on logplot

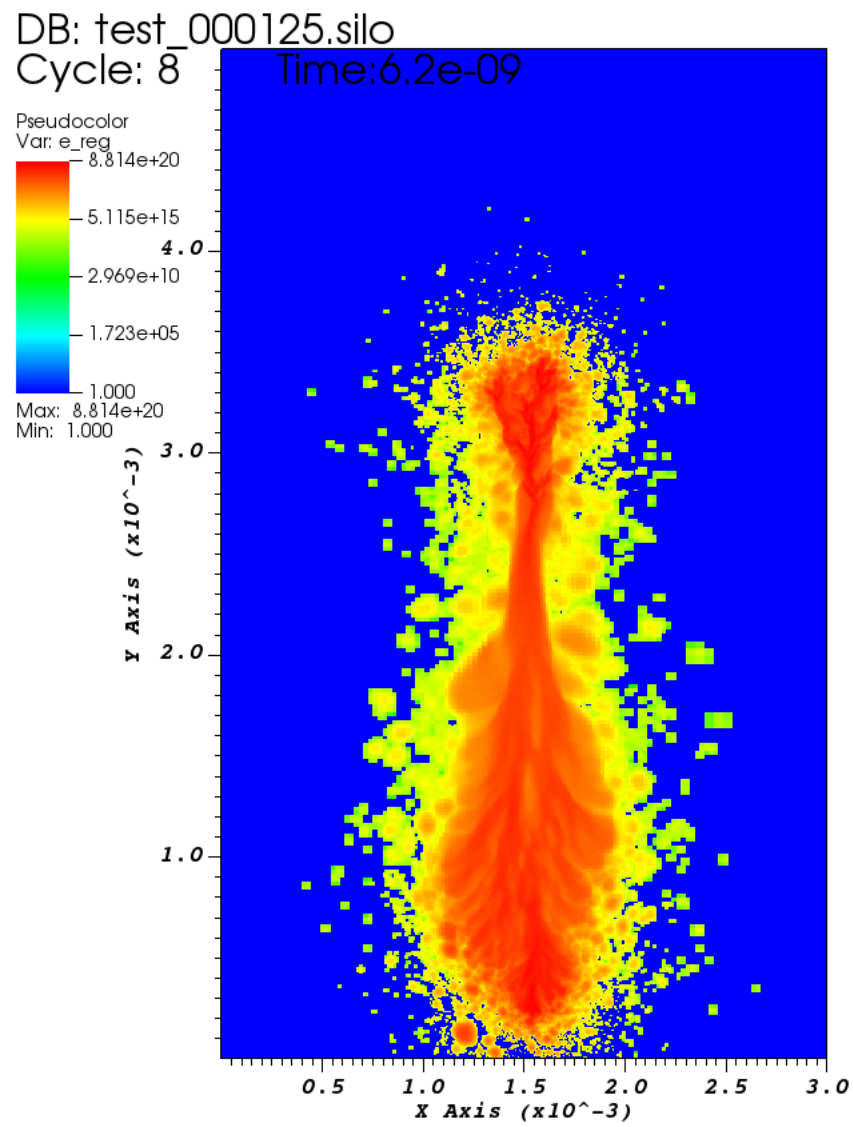


Figure 9: FUEL on logplot

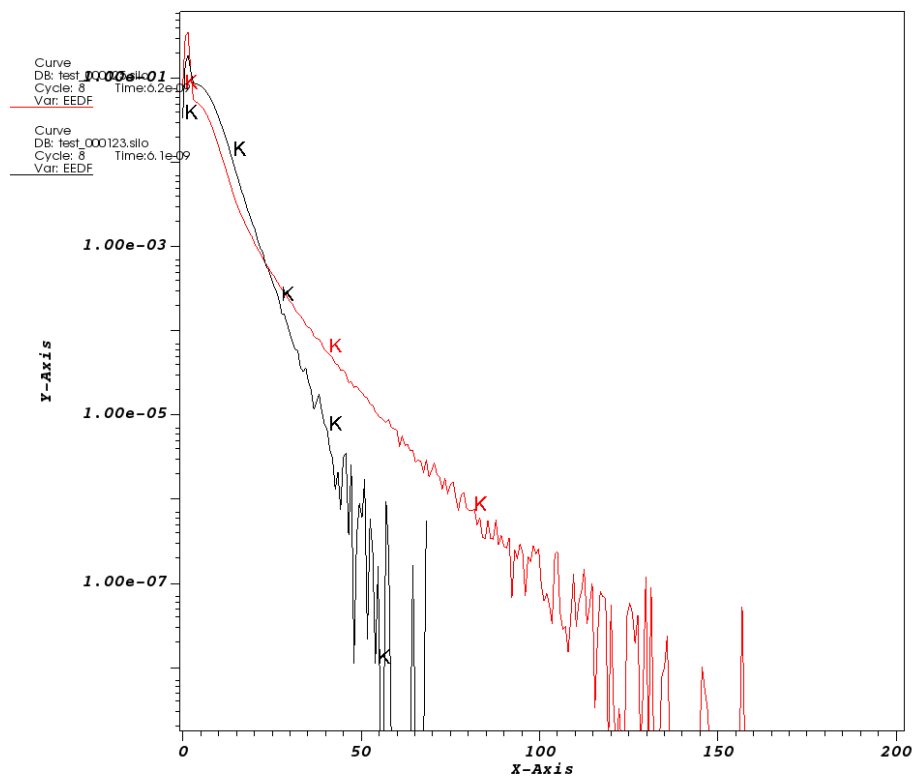


Figure 10: Electron energy distributions of FUEL (red) and AIR (black). x-axis in eV.

6.1 Some thoughts

Simulating a positive streamer in air above breakdown feels a little bit unintuitive (c.f. [13]) since the non-localized effect of photoionization prevents the discharge from evolving into a sharp streamer (i.e. screening of interior and local field enhancement at the tip due to space-charge effects). This is less influential in fuel streamers since the nonlocal effect of photoionization is strongly suppressed. It is a good idea to perform simulations of a streamer discharge below breakdown field, but for now we will put this idea aside and continue with our story:

- Since the photon mean-free path in fuel is highly suppressed. The fuel discharge does not have “freckels” and regions of high electron density are much more localized when compared to air discharges (easy to see on the log plots)
- The fuel streamer has a much finer structure. The width of plasma channels is much thinner and it has significantly more branches than in air.
- Both streamers seem to have covered roughly the same amount of distance, however the positive methane streamer appears to be slightly ahead of its air-counterpart
- The electron density in the fuel streamer is much higher (around an order of magnitude in both streamer tips)
- Electric fields at the tips are roughly twice as high in the fuel streamers (not shown)
- The tail of the fuel-EEDF is significantly enhanced. Hence electrons at the tip of the streamers have much higher energies

7 Next

Quantitative analysis of streamer properties? Track the evolution of the pool of active species relevant for combustion modelling.

References

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