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Nonequilibrium Gas-Surface Interactions at High
Temperature, VKI Plasmatron facility and MUTATION++ Library

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14. ABSTRACT In this report, we highlighted the major theoretical, numerical, and experimental research activities, conducted at the von Karman Institute for Fluid Dynamics with the aim of improving our understanding of gas-surface interaction phenomena. The activities were divided in two tasks. During the year 2018-2019, we focused our attention on accomplishing task 1: review of the experimental methods and facility setup as well as of the data concerning the gas surface interaction of different experimental campaigns; furthermore equations describing the the gas-surface interaction were abstracted and included in the VKI library Mutation++. Task 2, continued within the following 2 years, focused on the investigation of complex gas-surface interaction phenomena. Within this framework, equations describing thermal non-equilibrium at the surface were derived and included in the Mutation++ library. It was shown that assuming strong non-equilibrium at the surface better capture the experimentally observed temperature, both in the boundary layer and on the surface, while still well describing the surface recession. As second step, the finite rate chemistry model derived by Prof. Schwartzentruber team in relation to the AFOSR Grant FA9550-17-1-0057 Nonequilibrium Gas-Surface Interactions at High Temperature, was included in the Mutation++ library and validated. Numerical investigations revealed that the model, even if predicting a lower recession rate of the material, is able to capture reaction pressure dependence and nitrogen surface recombination. The VKI team also provided help to the University of Minnesota for the coupling of the Mutation++ library with the US3D solver, making available both the gas surface interaction model and gas phase state-of-the-art modeling. Along with the recent advances in numerical modelling, VKI conducted an experimental campaign on the ablation phenomena of graphite nitrogen plasmas. The nitrogen ablation tests provide experimental data for the further development of phenomenological models of the surface nitridation process and the surface reactivity to nitrogen recombination. The nitrogen tests cases have been conducted at various pressures and plasma power levels. Contrary to numerical predictions, the experimental data suggests increased surface recession and material mass loss at lower test chamber pressures. Additional numerical simulations of each particular test condition at various pressures are required for a better understanding of the obtained test results. Those can in turn be used to update and tune the FRC model coupled to the stagnation line 1D code description.							
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PLASMUT - Nonequilibrium Gas-Surface Interactions at High Temperature, VKI Plasmatron and Mutation++ library

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1. Introduction

Flying through the Earth's atmosphere at hypersonic speeds creates strong shock waves. The resulting chemically reactive boundary layer that envelops the vehicle Thermal Protection System (TPS) leads to Gas-Surface Interaction (GSI) phenomena. The interdisciplinary nature of GSI ranges from physical and numerical modeling to experimental characterization of the material response in high-enthalpy flows.

The von Karman Institute for Fluid Dynamics (VKI) has proposed theoretical, numerical, and experimental research activities, allowing us to better understand such complex GSI phenomena. The two main **objectives** are:

Task 1: to review the current experimental data on GSI collected in the VKI Plasmatron facility that can be made available, as well as the associated physico-chemical models implemented in the VKI MUTATION⁺⁺ library, allowing us to interpret these data.

Task 2: to understand thermo-chemical nonequilibrium in the boundary layer on graphite material by performing a new experimental campaign in the Plasmatron facility, developing and validating advanced computational models for GSI phenomena; a particular task is to couple the MUTATION⁺⁺ library to the US3D CFD solver.

Both tasks were carried out in synergy with a US-team led by Prof. Schwartzentruber at the University of Minnesota (UMN), in relation to the AFOSR Grant FA9550-17-1-0057 *Nonequilibrium Gas-Surface Interactions at High Temperature*.

During the **year 2018-2019**, the Plasmatron data were reviewed for different conditions and materials. Results for carbon matrix composite, carbon bonded carbon fiber and graphite experimental campaigns were made available. A GSI module for treating catalytic and ablative boundary conditions in CFD solvers was also implemented in the MUTATION⁺⁺ library. A Plasmatron experiment on carbon bonded carbon fiber was simulated for validation. Both phenomenological and detailed chemistry models were used, showing good agreement and accomplishing task 1.

During the **year 2019-2020**, an existing nitridation experimental campaign on graphite conducted at VKI was carefully investigated. Optical emission spectroscopy measurements in the boundary layer suggested a departure from thermal equilibrium. The GSI module of the MUTATION⁺⁺ library was further developed by including a surface vibronic energy balance accounting for thermal nonequilibrium. Simulations performed using this new boundary condition showed that thermal nonequilibrium may arise from GSI phenomena. As part of task 2, the coupling between the MUTATION⁺⁺ library and



the US3D solver was also started.

During the **year 2020-2021**, the coupling between MUTATION⁺⁺ and US3D was achieved. The previous nitridation experimental campaign was thoroughly simulated using both the US3D solver and a 1D stagnation line solver developed in-house. The GSI phenomena were modeled by implementing into MUTATION⁺⁺ a finite-rate chemical mechanism for nitridation developed at UMN. The nitridation reaction rate coefficients showed a significant pressure dependence leading to an estimation of the mass blowing rate lower than the one observed experimentally. For this reason, an extensive numerical work was carried out over a wide range of inlet pressure and surface temperature, aiming to design a new experimental campaign. Finally, a new experimental campaign on graphite samples was performed in nitrogen plasmas to investigate the pressure dependence of surface reactions.

2. Review of experimental data and Physico-Chemical modeling

In this section, the results to fulfill task 1 are summarized. The experimental methods are presented and the past experimental campaigns are reviewed. Furthermore, the physico-chemical models developed are also introduced.

2.1. Experimental Methods and Campaigns

This chapter is dedicated to some selected experimental campaigns carried out in the VKI Inductively Coupled Plasma (ICP) Plasmatron facility. Several test series have been run in the past on materials of interest:

- Carbon-Bonded Carbon Fiber (CBCF) material made of carbon fibers connected with a carbonized matrix tested in air flow to understand carbon fiber oxidation of porous materials,
- Pure graphite tested in a nitrogen flow to determine nitridation rate coefficients,
- Ceramic Matrix Composite (CMC) material tested in air flow to determine their limits of operation, i.e., when active oxidation starts to destroy the material.

The objectives of the experimental tasks of the current research activity are:

- a) Providing data for carbon/carbon and carbon/silicon carbide materials with passive/active oxidation and ablation conditions,



- b) Providing spectroscopic data in the near-surface region of carbon/carbon and carbon/silicon carbide materials that indicate breakup of the material and release of volatile species,
- c) Providing data experiments for backup materials such as graphite including detailed characterization of the microstructure and gas-phase investigation.

As part of task 1, we will review those data in the sections below after giving an overview of the experimental setup. This is followed by the new experimental campaign performed under task 2 of this research activity.

2.2. Experimental Set-Up

The experimental setup installed at the Plasmatron facility offers intrusive and non-intrusive (optical) measurement techniques. The instrumentation equipment for this work consisted of a video camera, a 2-color pyrometer, a broad-band radiometer, a digital camera, and a spectrometer with intensified Charge-Coupled Device (CCD) (reviewed below). The main data of interest during this investigation were surface ablation rates of graphite in a pure nitrogen plasma, including measurements of the locally resolved CN boundary layer emission.

The Plasmatron is equipped with a 160 mm diameter ICP torch powered by a high frequency, high power, high voltage (400 kHz, 1.2 MW, 2 kV) generator. The gas is heated by induction through a coil, providing a high purity plasma flow.

The graphite test sample shape was a 25 mm radius hemisphere with a 25 mm afterbody, machined in-house (a photograph can be found in Fig. 2). The raw graphite material is a superfine grain, high density extruded graphite rod obtained from Graphtek LLC. We note that iso-molded graphite might be another possibility for plasma tests due to its uniform properties, of great importance in the field of TPS design. Density of the graphite rod is reported with $\rho_s = 1760 \text{ kg/m}^3$, with a thermal conductivity of $130 \text{ W/(m}\cdot\text{K)}$ at room temperature. The total stagnation point recession can be measured using a digital camera (Nikon D5000) attached to a 400 mm lens, giving a resolution of about 0.03 mm per pixel. The test sample is then pre-heated (cleaned and dried) by the Argon plasma used to start the Plasmatron facility. After starting the plasma on Argon gas, with the test sample in place, the test gas is switched to pure nitrogen.

The strong radiative signature of the CN molecule allows for its easy probing by emission spectroscopy via the strong violet system emission ($\text{B}^2\Sigma^+ - \text{X}^2\Sigma^+$ transition) [1, 2]. One can further benefit from the low surface recession rate of the graphite sample, contrary to air ablation, allowing to average several recorded spectra per ablation test. Our emission spectroscopy setup consists of an Acton Series SP-2750 spectrograph of 75 cm focal length combined with an ICCD PI-MAX camera with a frame of 1024×1024 pixels ($12.8 \mu\text{m} \times 12.8 \mu\text{m}$ pixel size), as illustrated in Fig. 1. For conversion of the data into

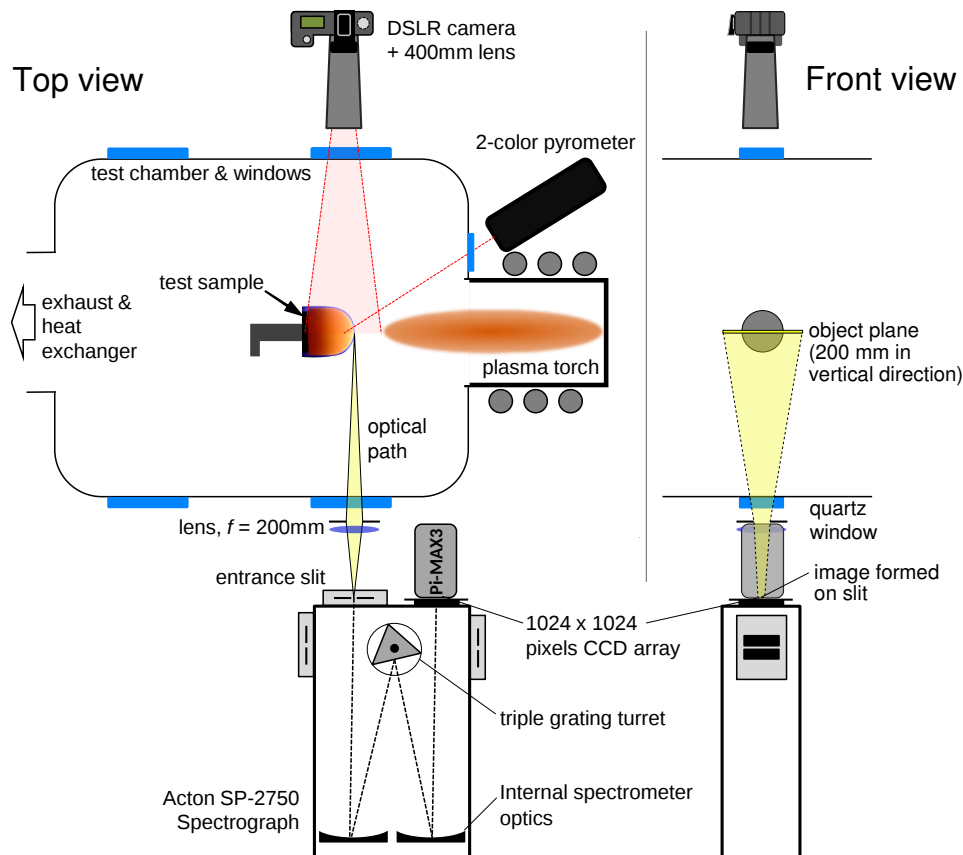


Figure 1: Schematic of experimental setup (seen from top (left) and front (right), not to scale) with spectrometer optical path perpendicular to the plasma flow in front of the ablating sample, recording full radial profile.

spectral intensities $[W/(m^2 \cdot sr \cdot nm)]$ a calibration of the whole system can be performed by placing a tungsten ribbon lamp (OSRAM WI 17G) in the focus of the collection optics inside the test chamber.

For each acquisition, the camera records a data matrix with wavelength distributed along the horizontal axis and the lateral positions of the observed plasma radius distributed along the vertical axis (Fig. 2).

Objective of the spectral measurements is the determination of the locally resolved CN emission.

2.3. Computation of the plasma freestream conditions

A coupled numerical-experimental procedure allows for computation of the finite-rate boundary layer chemistry, plasma freestream enthalpy, and temperature. First, cold-wall heat flux and pitot pressure are being intrusively determined during the Plasmatron ex-

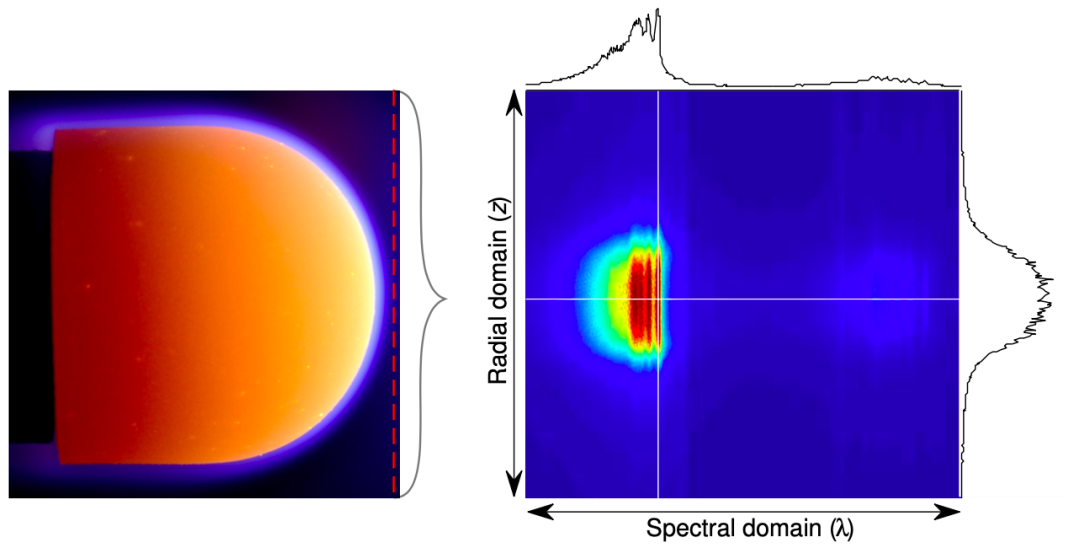


Figure 2: Ablating graphite sample in nitrogen with indication of spectrometer slit position as red dashed line (notice the bright violet boundary layer caused by the strong CN violet (B-X) emission); and example of a single data frame illustrating the spectral emission (horizontal line) and radial emission distribution of CN violet maximum (vertical line).

periment at a certain generator power P_{el} . The subsonic Plasmatron flow field is then numerically simulated using a resistive magnetohydrodynamics solver, characterizing the boundary layer geometry around the heat flux probe under Local Thermodynamic Equilibrium (LTE) and axisymmetric flow assumption (VKI ICP code [3, 4, 5]). The set of magnetohydrodynamics equations combine fluid dynamics (Navier-Stokes) and electromagnetism (Maxwell) in order to compute the flow in the ICP torch and test chamber simultaneously. Input to this procedure are the gas mass flow rate, electrical power, and static pressure p_s in the test chamber. The VKI ICP code makes use of the physico-chemical MUTATION⁺⁺ library¹ [6, 7] to determine thermodynamic and transport properties of a five species nitrogen mixture including N_2 , N_2^+ , N , N^+ , e^- . After simulation of the plasma flow field with the VKI ICP code, hydrodynamic parameters characteristic of the flow are extracted and, along with the experimentally determined heat flux and pitot pressure, serve as input conditions for the VKI boundary layer code [8]. The code solves the axisymmetric, chemically-reacting stagnation-line boundary layer over a catalytic surface under chemical nonequilibrium conditions. A Newton method is used to iterate on the boundary layer outer edge temperature T_e , until experimental and numerical heat fluxes are matched.

The boundary layer code models the catalytic surface reactions as experienced by the

¹for download available at <https://github.com/mutationpp/Mutationpp>



copper calorimeter during the heat flux measurement ($N + N \rightarrow N_2$). The code assumes complete accommodation of exothermic recombination energy. The thermodynamic and transport properties are modeled for a five-species mixture for nitrogen (N , N_2 , N^+ , N_2^+ , e^-). Rate coefficients for the gas phase reactions are taken from the Dunn and Kang chemistry model [9]. The complete procedure including Plasmatron measurements, VKI ICP code simulations, and the boundary layer rebuilding is sketched in Fig. 3.

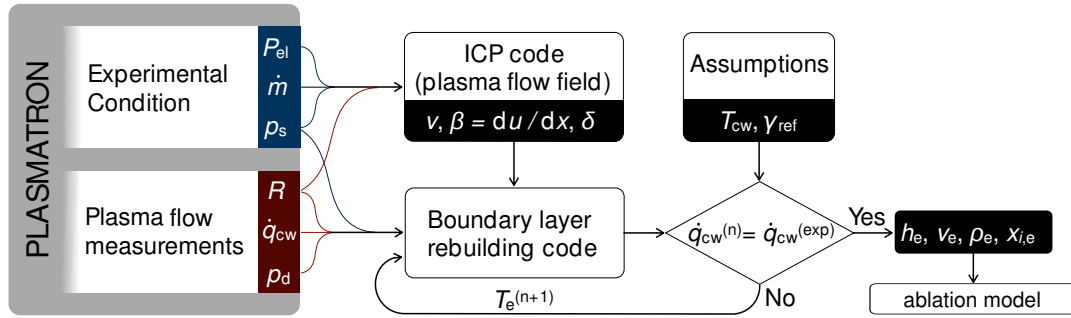


Figure 3: Schematic of experimental-numerical rebuilding procedure combining plasma flow measurements, plasma flow solver (ICP code), and nonequilibrium boundary layer solver for simulation of boundary layer edge (e) parameters. Those may serve as input to ablation simulations.

Output of the whole procedure is the plasma condition at the boundary layer edge, independent of ablation at the surface. This condition can then serve as input to simulations including ablation. In two recent publications, we have presented the impact of the experimental uncertainties on the plasma flow rebuilding [10] and the propagated uncertainty on the ablation model [11].

2.4. Review of the past experimental campaign

2.4.1. Carbon Fiber in air and nitrogen flow

Our experiments of the CBCF compound included in-situ recession and mass loss rates for surface temperatures ranging from 1700 K up to 2850 K, therefore, covering a wide range of ablation regimes (reaction limited, diffusion limited, and sublimation).

Until now, most numerical codes for prediction of the heat shield recession use equilibrium chemistry or sets for finite-rate surface reactions. Both approaches treat the surface in a control volume fixed to the wall, where the ablation products are mixed with the boundary layer gases. A more elaborate approach would describe ablation of the carbon fibers and charred resin at microscale, with ablation treated as a volume phenomenon rather than being restricted to the surface. Such high-fidelity approaches eventually require the intrinsic carbon fiber reactivity for an accurate description of the ablation process at microscale.



From simulations of the preform experiments with tightly coupled material-flow solvers, the diffusion-reaction competition (Th) could be estimated, as well as the fiber intrinsic reactivity k_f .

Table 1: Plasmatron CBCF test conditions: test case reference (cylindrical (CY) and hemispherical (HS)), test gas, static pressure p_s , dynamic pressure p_d , generator power P_{el} , mean cold wall heat flux $\dot{q}_{cw}$, test sample exposure time τ , mean surface temperature T_w , recession rate $\dot{s}$, mass loss rate $\dot{m}$, and emissivity ε .

Test-ID	gas	p_s hPa	p_d Pa	P_{el} kW	$\dot{q}_{cw}^{\S}$ kW/m ²	τ s	T_w K	$\dot{s}$ μm/s	$\dot{m}$ mg/s	$\varepsilon^{\S}$
$CY-A1$	air	15	215	232	1021	90.0	2225	$78 \pm 0.6^{\dagger}$	76.4	-
$CY-A2$	air	100	17	221	1026	90.0	1875	$56 \pm 0.6^{\dagger}$	61.0	-
$CY-A3$	air	200	-	249	1005	90.0	2160	$61 \pm 0.6^{\dagger}$	56.8	-
$HS-A0$	air	15	60	109	312	90.5	1710	31 ± 2.2	30.0	-
$HS-A1a$	air	15	141	166	1019	91.0	2125	48 ± 1.2	48.2	0.85
$HS-A1b$	air	15	342	365	3074	30.7	2735	46 ± 3.5	69.8	-
$HS-A2a$	air	200	-	188	1050	91.2	1975	45 ± 1.4	53.2	0.86
$HS-A2b$	air	200	48	321	2962	30.8	2675	65 ± 6.2	74.6	-
$HS-A3^{\ddagger}$	air	80	-	500	9500	30.8	3135	237 ± 22	68.9	-
$HS-N1a$	N ₂	15	124	154	1057	90.7	1985	0	3.47	0.94
$HS-N1b$	N ₂	15	285	350	3149	31.2	2550	6.9	8.42	-
$HS-N2^{\ddagger}$	N ₂	80	-	500	9500	31.1	3010	82 ± 8.7	15.6	-

[†] Measured with a caliper ruler, precision: ± 0.05 mm, but compression/destruction of char layer can lead to higher measurement uncertainty.

[‡] Supersonic test configuration (sample located 5 cm from nozzle exit, no Pitot pressure measurement, p_s corresponds to the reservoir pressure).

[§] Only reported for hemispherical samples at low heat flux (1MW/m²), uncertainty: ± 0.05 .

[§] $\dot{q}_{cw}$ was measured for CY tests using a standard-shape heat flux probe, and for HS tests using a hemispherical probe.

2.4.2. Graphite in Nitrogen Flow

Many experiments in the past were dedicated to the effects of oxygen as a main driver for carbon heat shield recession [12, 13, 14, 15, 16, 17]. The nitridation reaction on a solid carbon surface, which has been found to increase rapidly when the surface temperature exceeds 1400 K [18, 19], is still weakly understood. Nitridation reaction efficiencies proposed by Park [2] and Suzuki et al. [20] differ by several orders of magnitude. We have also shown in a previous publication the impact of nitridation on a CBCF preform material, which exhibited strong erosion of the carbon fibers at microscale after nitrogen ablation [21]. Even if nitridation does not cause much material ablation, it may significantly alter the N-atom recombination probability at the surface, hence the surface



Table 2: Numerical boundary layer edge characterization for air and nitrogen plasma of cylindrical (CY) and hemispherical (HS) samples: test gas, static pressure p_s , enthalpy h_e , density ρ_e , temperature T_e , velocity v_e , boundary layer thickness δ_e , velocity gradient β_e , and velocity gradient derivative in axial direction $\partial\beta_e/\partial y$.

Test-ID	gas	p_s hPa	h_e MJ/kg	ρ_e g/m ³	T_e K	v_e m/s	δ_e mm	β_e 1/s	$\partial\beta_e/\partial y$ 1/(m·s)
<i>CY-A1</i>	air	15	22.7	0.60	5525	351	9.7	9944	743900
<i>CY-A2</i>	air	100	22.5	3.76	6002	46.5	9.5	1193	89941
<i>CY-A3</i>	air	200	20.4	7.78	6059	25.6	8.5	702	54341
<i>HS-A0</i>	air	15	8.1	1.2	3680	121	5.9	7740	817050
<i>HS-A1a</i>	air	15	21.4	0.62	5460	232	5.7	12735	1.34E6
<i>HS-A1b</i>	air	15	54.1	0.26	9229	687	5.7	29790	3.47E6
<i>HS-A2a</i>	air	200	21.4	7.57	6122	14.0	5.1	1620	182245
<i>HS-A2b</i>	air	200	42.0	4.32	8079	54.5	4.6	4480	534435
<i>HS-N1a</i>	N ₂	15	22.6	0.63	5600	232	5.7	12935	1.42E6
<i>HS-N1b</i>	N ₂	15	63.0	0.24	9448	624	5.2	38150	4.87E6

heating rate. This becomes especially important for carbon silicon carbide composites, which ideally inhibit a low catalytic, highly emissive, and highly oxidation resistant surface. Studies beyond active oxidation of C/SiC materials in air plasmas suggested that nitrogen reactants actively participate to the chemistry of the surface.

Intensive ablation research has been carried out in the VKI Plasmatron on basic carbon materials such as graphite and a CBCF preform [21]. For example, our basic experiments on graphite in nitrogen flows allowed us with an experimental-numerical approach to determine the nitridation reaction efficiency of a carbon surface at increasing temperature [22]. The proposed ablation model accounts for the carbon injection into the boundary layer in a coupled fashion, considering the species distribution throughout the whole computational domain. Up to now, such evaluation of the nitrogen concentration at the wall and ablation-flowfield coupling was not taken into account by approaches of other researchers for determination of the nitridation reaction efficiency. Based on our findings, we propose an updated Arrhenius form, fitting our data with that of equivalent studies for evaluation of nitridation reaction efficiencies as a function of wall temperature. We envisage application of this model to simulations aiming at the coupling of high temperature flows and surface ablation.

The nitridation reaction efficiencies for different surface temperatures were evaluated by fitting the data collected over different experiments. The procedure developed for the extraction of the nitridation reaction efficiencies is based on the described ablation model. If the only active surface reaction is the nitridation, the surface mass blowing flux can be expressed as:

$$\dot{m}_s = \dot{\omega}_{N_w}^{CN} \frac{\mathcal{M}_C}{\mathcal{M}_{CN}} = \dot{s}\rho_s \quad (1)$$

and it is directly linked to the measured recession rate ($\dot{s}$) through the known material



density. The superscript CN indicates the source terms for atomic nitrogen due to the nitridation reaction ($C_s + N \longrightarrow CN$). Assuming this reaction to be first order in reactant concentrations, the surface reaction velocity is evaluated by multiplying the number flux of the reactant species (N) arriving at the surface, given by the kinetic theory, by the probability of the reaction to take place [23]. Then, recalling the definition of surface source term per unit area and reaction velocity:

$$\dot{\omega}_{N_w}^{CN} = k_{N_w}^{CN} \rho_{N_w} \quad (2)$$

with

$$k_{N_w}^{CN} = \frac{\gamma_N^{CN}(T_w)}{4} \sqrt{\frac{8 \mathcal{R} T_w}{\pi \mathcal{M}_N}} \quad (3)$$

we can express the unknown nitridation reaction efficiency as:

$$\gamma_N^{CN}(T_w) = \frac{\dot{m}_s}{\rho_{N_w}} \frac{\mathcal{M}_{CN}}{\mathcal{M}_C} \left(\frac{\mathcal{R} T_w}{2\pi \mathcal{M}_N} \right)^{-1/2}. \quad (4)$$

By imposing the experimental mass blowing rate and surface temperature in Eq. (4) one can evaluate the nitridation reaction efficiency through the gas-surface interaction model. The unknown nitrogen density is computed by accounting in a fully-coupled way the effect of the ablation product injection. We point out that this approach does not take any changes in the surface microstructure during ablation into account and is solely based on steady-state ablation. In addition, it is almost impossible to observe changes of the surface state during ablation in the plasma windtunnel in-situ and only pre- and post-test micrographs have been carried out as presented in the next section.

All test conditions, including cold-wall heat flux, steady-state surface temperature, recession rate, and total mass loss are listed in Table 3 (plasma mass flow rate $\dot{m}_{N_2} = 16 \text{ g/s}$). The test time was taken as the period of constant surface temperature until shutdown. Surface temperature and recession increased with increasing heat flux, the highest measured recession was 0.75 mm for a steady state of 300 s.

Within the current work, the numerical approach for determining the nitridation efficiency did not take this change of surface microstate into account as only a solid carbon surface was modeled. More detailed material models would be required for such analysis but their implementation is difficult [24] and until now they have only been applied to carbon oxidation studies [25].

The boundary layer edge values of flow velocity v_e , density ρ_e , temperature T_e , and dissociation degree $1 - x_{N_2}$, computed using the procedure described in Sec. 2.3, are given in Table 4. We recall from Table 3 that no recession or mass loss could be observed for test conditions *G1* and *G2* and was almost negligible for *G3*. The degree of dissociation reported in Table 4 therefore indicates that the onset of nitrogen dissociation acts also as the onset of increased nitridation reactions.



Table 3: Plasmatron test conditions (15 hPa, nitrogen): dynamic pressure p_d , generator power P_{el} , mean cold wall heat flux $\dot{q}_{cw}$, test sample exposure time τ taken from steady state (ss), mean surface temperature T_w , recession rate $\dot{s}$, and total mass loss Δm .

ID	p_d Pa	P_{el} kW	$\dot{q}_{cw}$ kW/m ²	τ_{ss} s	T_w K	$\dot{s}$ μm/s	Δm g
<i>G1</i>	56.7	120	486	125	1540	-	-
<i>G2</i>	153	205	1022	165	1940	-	-
<i>G3</i>	182	235	1520	205	2140	(0.17)	1.67
<i>G4</i>	231	280	2130	266	2225	1.41	2.00
<i>G5</i>	268	330	2730	250	2410	1.64	2.05
<i>G6</i>	312	370	≈3500	300	2535	2.60	2.4
<i>G7</i>	330	390	3580	277	2575	2.51	2.1

Table 4: Overview of numerical and experimental results: Computed plasma freestream condition at the boundary layer edge including velocity v_e , density ρ_e , temperature T_e , and dissociation degree $1 - x_{N_2}$; mean surface temperature T_w ; T_{tr} and T_{ve} from fitting of experimental CN spectra with SPECAIR; nitridation reaction efficiency γ_N^{CN} provided by the stagnation-line code with ablation.

ID	Simulation				Exp.	CN Spectral fitting		Nitridation efficiency
	v_e m/s	ρ_e g/m ³	T_e K	$1 - x_{N_2}$	T_w K	T_{tr} K	T_{ve}	γ_N^{CN}
<i>G1</i>	131	0.748	5371	0.45	1540	n/a	n/a	-
<i>G2</i>	283	0.491	6192	0.89	1940	n/a	n/a	-
<i>G3</i>	365	0.325	8306	0.99	2140	n/a	n/a	0.0030 [†]
<i>G4</i>	554	0.236	10005	1.0	2225	6920±450	10650±650	0.0032–0.0074
<i>G5</i>	562	0.225	10280	1.0	2410	7360±450	10040±650	0.0040–0.0086
<i>G6</i>	846	0.184	11040	1.0	2535	7215±450	8500±650	0.0079–0.0120
<i>G7</i>	859	0.189	10970	1.0	2575	7615±450	9940±650	0.0081–0.0125

[†] only upper bound value reported

The assumption that carbon sublimation is negligible for our test conditions was verified with a preliminary analysis: We considered two heterogeneous surface reactions, nitridation $C_s + N \longrightarrow CN$ (using the reaction efficiency of Suzuki [20]) and sublimation $3C_s \rightleftharpoons C_3$. We recall that C_3 is reported to be the main sublimation product [26]. Its equilibrium concentration was evaluated through the saturated carbon vapor pressure ($p_{C,eq.} = 5.19 \times 10^{15} \exp(-90845/T_w)$ [27]). This preliminary analysis showed that the ablated mass blowing flux due to sublimation is always two orders of magnitude lower than that of nitridation for the present conditions.

The approach described by Eq. 4 uses as alternative input to the reaction efficiency data the steady-state stagnation-point mass blowing flux obtained from the post-processing of the camera images. Output of this procedure were the values of nitridation reaction



efficiency $\gamma_N^{\text{CN}}(T_w)$ given in Table 4, and CN mole fractions along the boundary layer stagnation line. The uncertainty range given on the determined nitridation reaction efficiencies is mainly due to the uncertainty on the measured mass blowing flux (Eq. 4) caused by the spatial resolution of the Digital Single-Lens Reflex camera (DSLR) images for recession analysis (± 0.03 mm). In addition, T_{tr} and T_{ve} , output of the fitting procedure with SPECAIR, are also listed in this table.

The translational-rotational temperatures (T_{tr}) listed in Table 4 are all below the computed boundary layer edge temperature T_e . This is an expected effect of the boundary layer cooling towards the wall. Vibronic temperatures were still not fully equilibrated, i.e., $T_{\text{tr}} \neq T_{\text{ve}}$, possibly due to the longer characteristic relaxation time required for CN vibrational states [28, 29], especially at the low pressure used in this study (15 hPa). However, we assume that for this conditions a Boltzmann distribution is valid, allowing for computation of the integrated electronic CN violet intensity ϵ_{CN} . This assumption should be further assessed in future analysis, e.g., by a closer investigation of the plasma thermodynamic state with extensive investigation of the atomic nitrogen emission in the freestream. Other researchers have also investigated CN violet emission originating from an ablating surface [30, 31, 32, 33, 34], some of them also including temperature estimations from the spectral data. With temperatures in the range of 6000 K to 10000 K those data are close to our values. However, no spatially resolved data is up to now available that would allow determination of CN species densities.

CN species densities from the ablation model are plotted versus the stagnation-line distance from the surface including uncertainty bounds caused by the measurement uncertainties in Fig. 4. The same figure shows the experimental CN densities. Only one single experimental value was obtained for each condition, according to the placement of the spectrometer. A dislocation of the spectrometer during the experiment was not performed due to a too low sensitivity of the movable diagnostic bench.

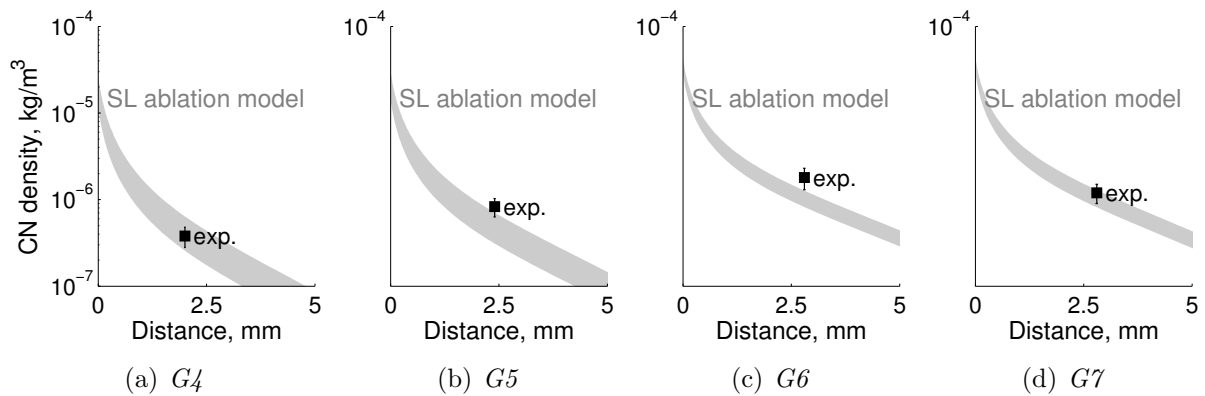


Figure 4: Experimentally determined CN densities are in very good agreement with the stagnation-line (SL) ablation model; gray areas comprise experimental uncertainty used to compute γ_N^{CN} .



All retrieved CN species densities agree very well with the values predicted by the ablation model, with two measurements (*G4*, *G7*) lying within the bounds of the model. In the worst case (*G6*), measurement uncertainties and bounds of the model are still overlapping. Main drawback of the application of emission spectroscopy is the probing of atoms and molecules restricted to their electronically excited states only. Estimation of ground-state populations of the investigated volume has to be based on multiple assumptions. In the current analysis, we assume that electronic excitation can be estimated from the vibrational temperature ($T_{\text{vib}} = T_{\text{el}}$), and that the electronic populations follow a Boltzmann distribution. More elaborate techniques such as Laser Induced Fluorescence (LIF) spectroscopy have successfully been applied to the investigation of ground state species populations in the plasma freestream [35, 36]. But boundary layer investigations using LIF are relatively rare, and missing for ablative surfaces, in particular, concerning the CN molecule. The consistent agreement of the experimental data with the numerical model provides confidence in the chosen experimental procedure. The obtained nitridation efficiencies $\gamma_{\text{N}}^{\text{CN}}$ (Table 4) are compared in Fig. 5 to values from literature. Our data (blue dots) span one order of magnitude from 0.0030 (2140 K) to 0.0125 (2575 K). We recall the limited temperature range of our experiments based on the onset of sublimation of the carbon surface as described before. At higher temperatures, a separate experimental study is advised in order to first quantify the carbon mass blowing rate caused by sublimation. Zhang et al. [18] and Goldstein et al. [37] performed nitridation measurements in a quartz tube furnace coupled to a microwave discharge at lower pressures (1.33 hPa to 6.66 hPa) and temperatures than in our study (15 hPa). Like us, they found increasing reaction efficiencies with increasing temperature. In contrast to those long-duration experiments are the shock-tube experiments of Park and Bogdanoff [2], which resulted in nitridation efficiencies of three orders of magnitude higher than in our study. The reason for this difference remains up to now unknown.

2.4.3. Nonequilibrium phenomena

Spectroscopic measurements on both graphite and CBCF in the VKI Plasmatron facility suggest that the internal temperatures $T_{\text{trans-rot}}$ and $T_{\text{vib-elect}}$ depart from equilibrium close to the ablating surface (Fig. 6) [21]. The gathered data indicate that non-dissociated nitrogen in the boundary layer might play a significant role in the vibrational excitation of the CN molecule.

Until now, we have not investigated a possible deviation from thermal equilibrium of the N_2 molecule, which might be one reason for causing the vibrational CN excitation. Therefore, an additional analysis of the nitrogen freestream could help to identify non-equilibrium effects of the N_2 molecule, which may have a strong influence on the surface energy balance, formation of CN, and energy transfer with CN [39]. Additional measurements should be targeted towards the CN A-X transition. By this, a possible deviation

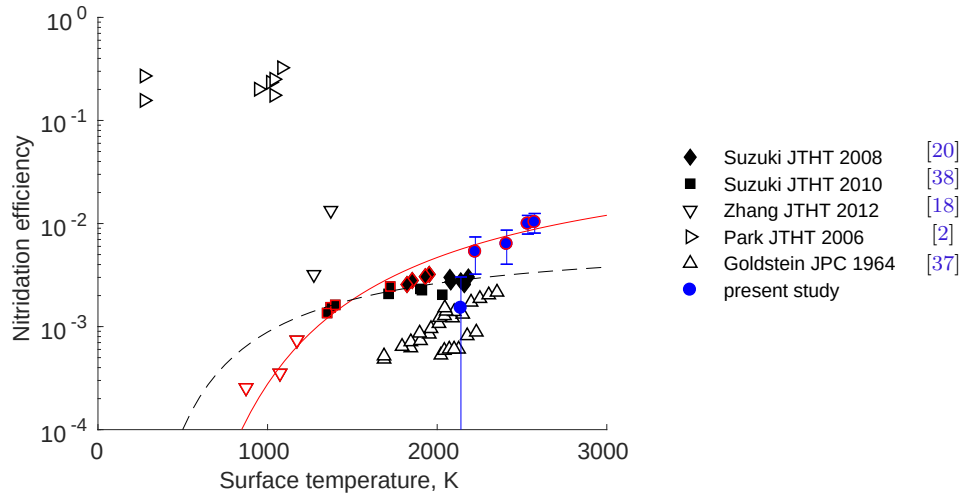


Figure 5: Active nitridation reaction efficiencies comparison with data from literature including fitted Arrhenius laws; our data compare well to Suzuki [38] and extend to higher temperatures.

- model proposed by Suzuki et al. [38]: $\gamma_N^{CN} = 8.441 \times 10^{-3} \exp\left(-\frac{2322}{T_w}\right)$;
- model including our data and selected values of Zhang et al. [18] and Suzuki et al. [38] (markers with red edge): $\gamma_N^{CN} = 7.91 \times 10^{-2} \exp\left(-\frac{5653}{T_w}\right)$.

of electronically excited states from a Boltzmann distribution could be studied, which was not possible with the existing setup due to the limited spectrometer wavelength range.

2.4.4. Operational limits of Ceramic Matrix Composites in air flow

Beside determination of the catalytic properties of carbon silicon carbides, the main interest lies in the identification of the Passive to Active Transition (PAT) for oxidation in different atmospheres for different materials. Beyond active oxidation, which is a destructive process for C/SiC materials, several authors have observed a sharp surface temperature jump of several hundred Kelvin during exposure of silicon carbide specimens to high heat flux, low pressure oxidation environments [40, 41, 42, 43]. Some initial studies were carried out in the von Karman Institute for Fluid Dynamics (VKI) Plasmatron in order to identify the limits of Ultra-High Temperature Ceramics (UHTC) and CMC materials [44, 45].

A more detailed analysis was carried out by Panerai et al. and Balat-Pichelin et al. [46, 47, 48]. The test materials in this study between VKI and PROMES were those selected for Intermediate eXperimental Vehicle (IXV), with a lifting trajectory similar to that of the Space Shuttle, mounting carbon/silicon carbide TPS on the nose-cap, the

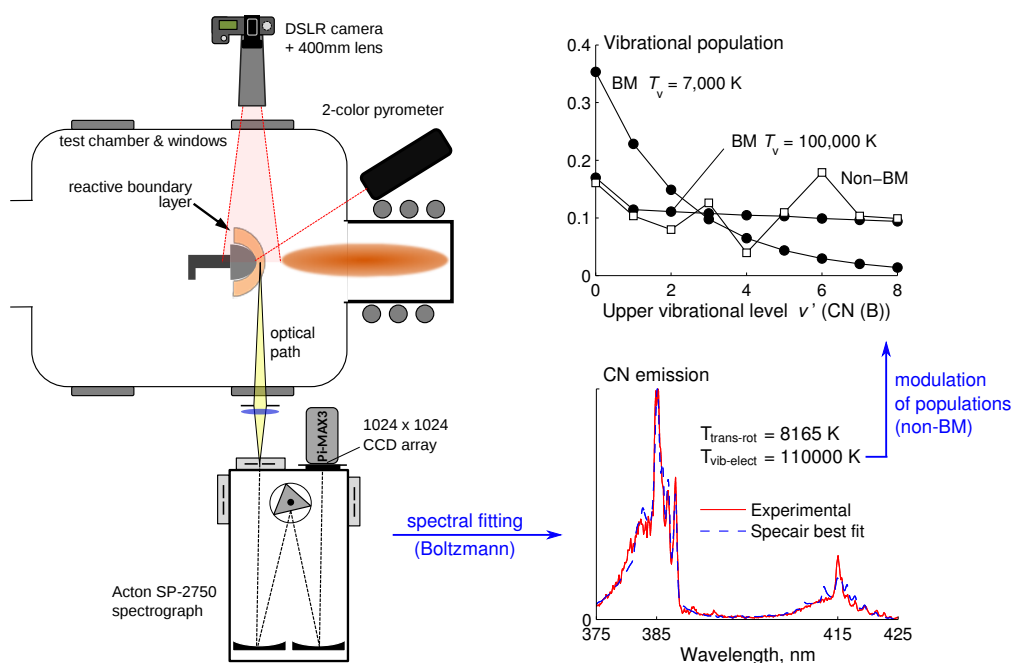


Figure 6: Experimental setup and post processing: Recorded CN spectrum (graphite ablation) serves as input for spectral fitting procedure for estimation of $T_{\text{trans-rot}}$ and $T_{\text{vib-elect}}$; the strong thermal nonequilibrium condition based on Boltzmann populations can also be fit by manually modulating the vibrational CN populations.



windward side, and the controllable flaps. The CMC materials were provided by Herakles (Safran Group, Le Haillan, France) and MT Aerospace (Augsburg, Germany). Herakles material (SEPCARBINOX L6) manufacturing starts from a carbon fiber preform, based on a multi-layer woven architecture [49]. The preform is constructed from a lay-up of prepreg that is cured in a mold, and densified with consecutive depositions of silicon carbide by Chemical Vapor Infiltration (CVI) [50]. The last CVI cycle allows at the same time to achieve the requested density, and to ensure a full coating of the composite surface by a β -SiC layer of approximately 80 μm thickness as stated by the manufacturer².

The MT Aerospace samples are produced using a near net shaped layup technique via Polymer Vapor Infiltration. A pre-impregnated carbon fiber structure (7 μm filament diameter) is cured before undergoing pyrolysis, which turns the polymer into an amorphous carbon phase. The pyrolyzed carbon-fiber-reinforced polymer is then coated with β -SiC by a Chemical Vapor Deposition (CVD) process. The SiC coating has an average thickness between 60 μm and 80 μm [52].

From this study, the transition between passive and active oxidation regimes, including the jump condition can be well identified in a classical oxygen partial pressure versus reciprocal temperature plot (Fig. 7).

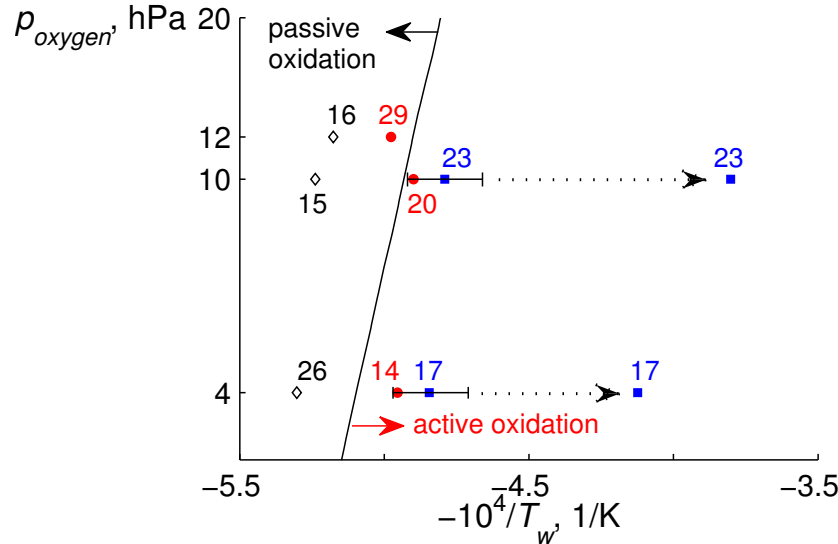


Figure 7: Passive/active oxidation transition and the temperature jump regimes: Triangles represent passive oxidation, red circles represent active oxidation regimes, blue squares are test conditions that experienced a temperature jump. The transition law was taken from Balat [53]. Labels on the data points correspond to the sample number in reference [46].

²SiC exists in many crystalline forms; the most common polymorphs are the 3C (β -SiC) and hexagonal (α -SiC) 2H, 4H, and 6H phases [51].



The reference boundary, represented by a solid black line, was taken from Balat [53], reporting oxidation experiments on a similar material. We consulted sample mass loss and post-test micrographs of tested samples to identify the transition regime:

- **Passive:** relative mass loss ($\frac{\Delta m}{m}$) between 0 % and 1 % and presence of a thin and uniform silica (SiO_2) layer,
- **Active:** mass loss between approximately 1 % and 10 % together with eroded silica layer, and holes/damages on the SiC coating,
- **Jump:** high mass loss (>20 % to 50 %) and strong surface ablation, i.e., complete oxidation of the β -SiC coating and uncovering of bare carbon fibers, which may also be oxidized (needle shape).

Three optical paths connected to three emission spectrometers have been focused along the stagnation-line within 6 mm in front of the test specimen. Calibration of the whole system in relative intensity, consisting of the light collection mechanism and spectrometer efficiencies, was performed using a deuterium lamp in the UV range (<400 nm) in addition to the tungsten lamp. Intensities are therefore comparable throughout the different tests, but presented in arbitrary units.

Main contributors radiating in the UV range between 200 nm to 450 nm are shown in Fig. 8. The spectrum was taken just after occurrence of the temperature jump (80 s). Atomic silicon emission was most dominant in the range 200 nm to 300 nm. Most of those emission lines were the focus of several other experimental studies of C/SiC composites in air plasmas [54, 55, 56, 41, 42]. In addition, CN emission appeared in form of the electronically excited CN violet (B-X) system.

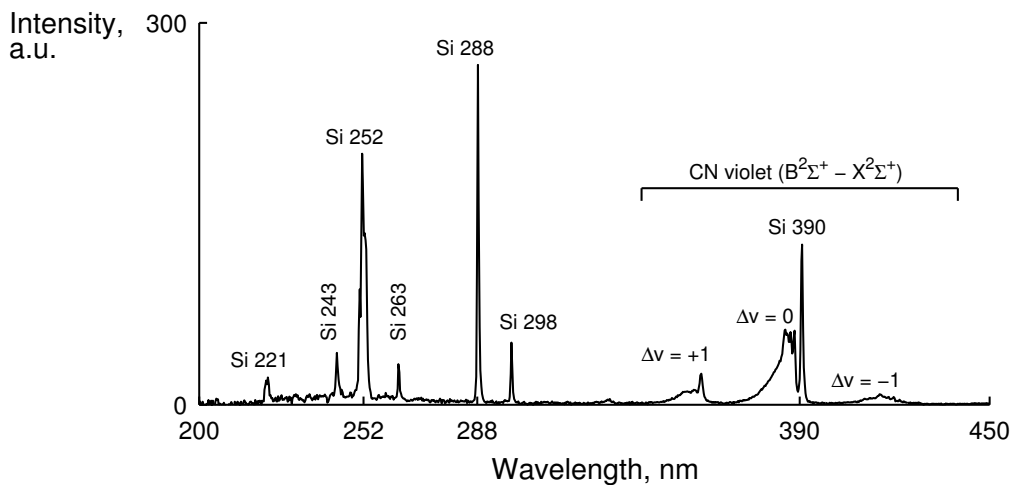


Figure 8: Clear emission of silicion (Si) and CN during test taken 80 seconds after injection approximately 5 mm from the surface (1.2 MW/m^2 , 20 hPa, air).



The sharp rise of silicon emission during the temperature jump, starting around second 65 in Fig. 9(a). Interestingly, the high intensity emission was followed by attenuation and final steady emission until the end of the run. By comparison, only a weak silicon emission signal was observed during the lower heat flux (0.9 MW/m^2) test (Fig. 9(b)). Post-test micrographs confirmed that this test experienced active oxidation, i.e., the protective silica layer was slowly eroded. Those micrographs are not presented here but can be found in the corresponding references [46, 47].

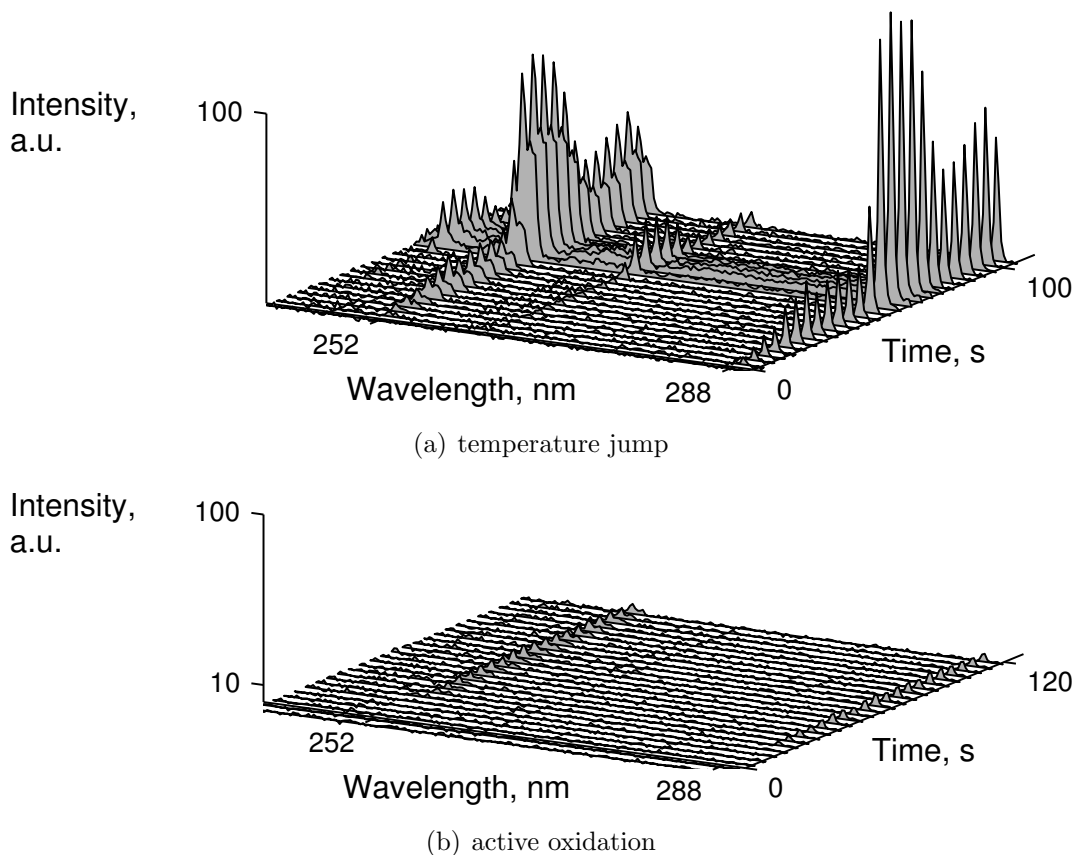


Figure 9: Temporal spectra of erosion products during two experiments at 20 hPa resulting in a temperature jump with a sudden rise of silicon emission (a) and active oxidation with low, constant silicon emission (b). The spectra were taken approximately 2 mm in front of the surface.

To better illustrate the temporal behavior, Fig. 10(a) presents Si and CN violet emission histories for the jump experiment at different locations in the boundary layer over time together with the surface temperature response. We can again appreciate the delayed pyrometer response compared to the spectrometer. Si and CN violet emission started rising before the temperature increase reached the field-of-view of the pyrometer. Si



emission peaked right after completion of the temperature jump, followed by a strong decrease and a steady emission. Further, Si emission collected 5.5 mm in front of the sample was stronger than emission close to the wall during the temperature jump (67 s until 100 s).

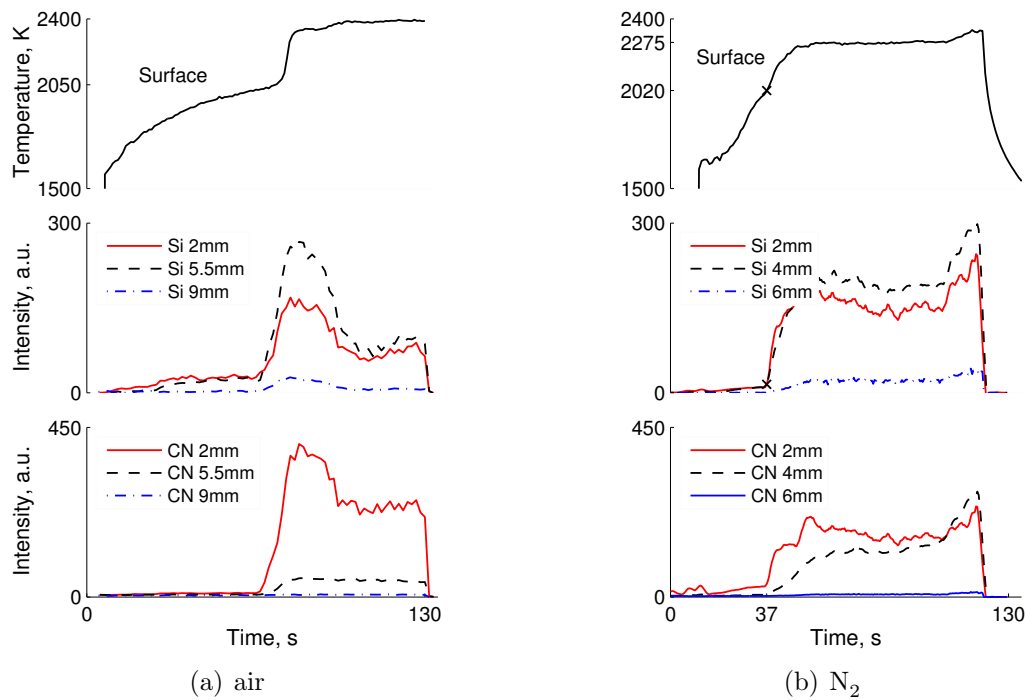


Figure 10: Air (left) and nitrogen (right) surface temperatures (up) along with Si (middle) and CN violet (bottom) emission histories at three locations in the boundary layer prove high species volatilization: Si and CN violet emission signatures strongly rose during the temperature jump in air, indicating sublimation of the β -SiC coating; this is followed by an emission drop once the coating was consumed. (1.2 MW/m^2 , 20 hPa).

It is plausible that SiO molecules break up as they travel away from the wall encountering increasing temperatures. This effect might be enhanced during the temperature jump due to the increasing rate of SiO production and due to an injection of sublimation products into the boundary layer. Feigel [43] found during arc-jet tests on SiC samples with the same geometry that the zone of detectable SiO by LIF extends to 9 mm at 30 Pa ambient pressure. It is hence assumed, that the production of SiO at the surface and its dissociation throughout the boundary layer may lead to a Si emission peak at around 5 mm ahead of the sample. Interestingly, Si emission was almost identical at the two locations (2 mm and 5.5 mm) prior and post to the jump (before 67 s and after 100 s). From this we conclude that the Si overshoot at 5.5 mm resulted from decomposition of



the β -SiC coating.

Another virgin sample was tested in the same freestream condition in terms of pressure and heat flux but in nitrogen plasma (Fig. 10(b)). Although the surface temperature rose more gradually (no sudden jump), Si and CN violet emission rose strongly once the surface temperature exceeded 2020 K, 37 s after injection. Contrary to the test in air, Si emission did not drop anymore after the strong increase, but stayed rather constant until the end of the test³. This observation gives support to the argument that the sudden temperature rise in air was caused by oxidation and depletion of the β -SiC coating of the surface.

Fig. 10(a)) also presents the temporal emission of CN violet, possibly created by nitridation of the surface ($C_{(s)} + N \rightarrow CN$) or through gaseous monoxide ($CO + N \rightarrow CN + CO$). The strong emission increase of CN violet during the temperature jump is consistent with the removal of the SiC coating and the onset of carbon fiber oxidation and nitridation, as the material's protective behavior vanishes. In contrast to silicon emission, CN violet emission considerably decayed with distance from the surface and was not detected by the spectrometer pointed 9 mm in front of the sample.

Numerical interpretation We conclude that in air plasma, a clear temperature jump occurred on the surface (2040 K to 2390 K), contrary to nitrogen plasma where surface temperatures increased gradually. However, silicon emission in the boundary layer experienced a sharp rise in both environments at almost identical surface temperature (approximately 2020 K). This temperature is consistent with occurrence of the temperature jump (2040 K). At this temperature, the β -SiC coating sublimates, leading to increased Si emission in the boundary layer, as well as formation of CN.

Thermochemical equilibrium simulations at 20 hPa using Mutation++ further support the experimental observation of silicon sublimation (Fig. 11). The elemental composition of the simulation represented 50 % SiC and 50 % air by moles ($C:N:O:Si = 0.25:0.4:0.1:0.25$), including solid (Si, SiO_2 , β -SiC) and liquid (SiO_2) phases. The calculation showed that Si mole fractions sharply rise above 2050 K, following the decomposition of β -SiC, with some contribution of Si_2C and SiC_2 . A high production of CO and SiO at temperatures above 1500 K is also apparent.

Concluding remarks

1. **In air plasma**, oxidation of the SiC coating enhances its removal as well as additional oxidation and nitridation of the underlying C/SiC structure, adding exothermicity to the process. A possibly formed silica layer during the first seconds of the test, at low enough surface temperature, is almost fully decomposed at this stage. Upon complete ablation of the β -SiC coating, the C/SiC composite, including the SiC filler matrix and carbon fibers, is actively ablated by oxidation,

³The slight temperature increase at test end (see text), led also to a Si and CN violet emission increase.

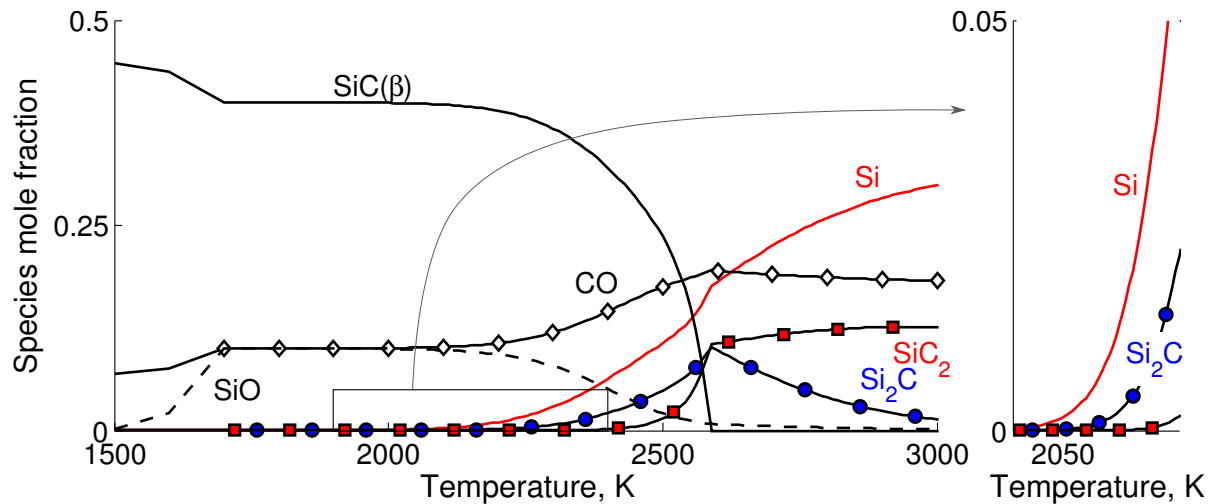


Figure 11: LTE composition at 2000 Pa for a mixture of $\text{C:N:O:Si} = 0.25:0.4:0.1:0.25$, including solid phases such as $\beta\text{-SiC}$ computed with MUTATION^{++} . Decomposition of $\beta\text{-SiC}$ starts at 2050 K along with a strong increase of Si (indicated rectangular detail).

with lower Si emission signature until the end of the test run. Volatilization of Si into the boundary layer might promote additional exothermic reactions with incoming N-atoms ($\text{Si} + \text{N} \rightarrow \text{SiN}$, followed by $\text{SiN} + \text{N} \rightarrow \text{Si} + 2\text{N}$) [57].

2. **In nitrogen plasma**, sublimation of the $\beta\text{-SiC}$ coating causes a rise of the Si emission signal at the same temperature (2020 K) and pressure (20 hPa) as in air. But due to lacking oxidation, the coating is only slowly removed by sublimation as well as via nitridation into gaseous silicon and cyanogen ($\text{SiC} + \text{N} \rightarrow \text{Si} + \text{CN}$) [58]. This results in lower thickness reduction and a significantly smaller mass loss in nitrogen.

With the help of experimental data it is possible to identify the range of ‘reusability’ of a certain material in terms of heat flux and partial oxygen pressure. It is further possible to experimentally investigate the onset of active oxidation, and present clear boundaries to the community when reusability limits are reached. However, numerical prediction of active oxidation still remains a major challenge to the community and further, the thermochemical mechanisms that lead to a sudden surface temperature rise of several hundred Kelvin are up to now not fully understood.

The emission spectroscopy measurements on active oxidation and the temperature jump phenomenon proved as a powerful technique for their temporal analysis: changes of the surface state, for instance, the sublimation onset of silicon, may not be well captured using HD-video analysis or pyrometers, but appeared in the emission spectrum.



2.5. MUTATION++

The MULTicomponent Thermodynamic And Transport properties for IONized gases library written in C++ (MUTATION⁺⁺ [59]) is an open-source library which can be downloaded from <https://github.com/mutationpp/Mutationpp>. It was originally developed at the von Karman Institute for Fluid Dynamics to help centralize physico-chemical models, algorithms, and data into a single software package, which may be shared among several CFD tools. It provides thermodynamic, transport, chemistry, and energy transfer closure needed to treat the gas phase properties to any coupled CFD solver. This presents several advantages: I) the equations implemented in the library can be verified separately, and the CFD code verification process is replaced by a verification of the coupling, as sketched in fig. 12, II) MUTATION⁺⁺ being open-source, different CFD solvers share the same features, helping with code-to-code comparisons, as well regular updates of the library. Further information about MUTATION⁺⁺ gas phase modeling

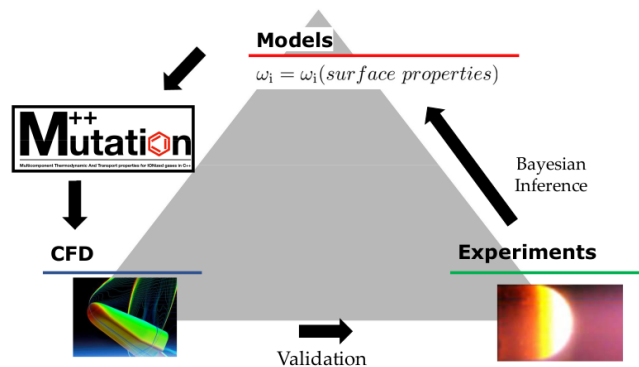


Figure 12: Developing predictive engineering tools for hypersonic flow applications: CFD is a key link between models and experiments.

can be found in the article [59]: *Mutation++: Multicomponent Thermodynamic And Transport properties for IONized gases in C++*. In the next section, attention will be given to the development of the GSI module.

2.6. Gas-Surface Interaction in MUTATION++

A GSI module was implemented in MUTATION⁺⁺ as part of task 1 during the year 2018-2019. It provides the Boundary Condition (BC) closure for the surface characterization of the catalytic and ablative phenomena. The following options are currently available:

- Mass balance: the temperature is imposed, while species concentrations are returned.



- Mass-energy balance: surface emissivity is imposed, while temperature(s) and species concentrations are returned.
- Phenomenological gamma approach and Finite Rate Chemistry (FRC) models for chemical production computations.
- Surface thermal equilibrium, adiabatic vibronic temperature or vibronic energy balance for vibronic temperature closure.

The GSI equations are derived by balancing the fluxes/surface sources on the infinitesimal volume containing both the the surface and the gas.

The **mass balance**, drawn for each i species in the mixture, reads:

$$[\rho_i(\mathbf{u}_g - \mathbf{u}_r) + \mathbf{j}_i - \mathbf{F}_{s,i}] \cdot \mathbf{n} = \dot{\omega}_i, \quad (5)$$

where $\mathbf{u}_g = \sum_{i=1}^{n_s} \dot{\omega}_{\text{abla},i} / \sum_{i=1}^{n_s} \rho_i$ is the gas velocity at the interface and $\mathbf{u}_r = \sum_{i=1}^{n_s} \dot{\omega}_{\text{abla},i} / \rho_s$ is the recession velocity (negligible for reusable TPS). The term $\mathbf{F}_{s,i}$ takes into account the flux incoming from the inside of the material (for example pyrolysis products). The vector $\mathbf{j}_i$ is the diffusion of the species i and $\dot{\omega}_i$ is its chemical production. MUTATION⁺⁺ is equipped with different fidelity routines to compute this term. Phenomenological (gamma) models are widely used in the hypersonic community because of their simplicity; they only require the definition of the probability (γ_i) that a macroscopic reaction takes place:

$$\gamma_i^{\text{rea}} = \frac{\mathcal{N}_i^{\text{rea}}}{\mathcal{N}_i}, \quad (6)$$

where quantity $\mathcal{N}_i^{\text{rea}}$ is the number flux of species i subject to the reaction and $\mathcal{N}_i = n_i \sqrt{k_b T_s / (2\pi m_i)}$, the number flux of species i impinging the surface. Symbol k_b stands for Boltzmann's constant, T_s the surface temperature, and m_i , the mass of species i . A fully catalytic behavior is obtained when the probability γ approaches unity; whereas a non-catalytic behavior is reached when γ is equal to zero. In this case, the chemical production rate reads:

$$\dot{\omega}_i = \gamma_i \mathcal{N}_i m_i. \quad (7)$$

Alternative formulations to phenomenological approaches are Finite-Rate Chemistry (FRC) models, also available in MUTATION⁺⁺, describing each elementary reaction occurring on the surface (adsorption/desorption, nitridation, recombination, ...). They have the advantage of capturing the pressure dependence of chemical reactions and the surface coverage. In this case the chemical production rate reads:

$$\dot{\omega}_i^s = \sum_{r \in R} N_A m_i k_r \prod_{j \in S} [X_j]^{\nu_j}, \quad (8)$$

where R is the set of surface reactions, k_r , the rate coefficient for reaction r , $[X_j] = \rho_j / (N_A m_j)$, the concentration of species j , ν_j , its stoichiometric coefficient, and N_A ,



Avogadro's number.

In case of ablative materials, the GSI module returns to the CFD solver also the mass blowing rate, computed by summing up all the ablative contributes ($\dot{m} = \sum_{i=1}^{n_s} \dot{\omega}_{\text{abla},i}$). The **total energy balance** can be written as:

$$[\rho(\mathbf{u}_g - \mathbf{u}_r)h + \mathbf{q}_g - \mathbf{F}_s] \cdot \mathbf{n} = \dot{S}_{\text{rad}} \quad (9)$$

where $\mathbf{q}_g$ is the gas heat flux (conductive and diffusive) to the surface, $\mathbf{F}_s$ is the energy incoming from the bulk and $\dot{S}_{\text{rad}}$ the energy radiated by the surface treated as a grey body.

The set of equations (5) and (9) are solved by means of a Newton method: the gas state of the first cell close to the surface and its distance, necessary for computing transport gradients, is imposed as well as the set of chemical reactions. The surface state, output of the procedure, is returned to the CFD solver for the computation of interfaces fluxes, for example by using ghost cells.

3. Development and validation of advanced models for GSI phenomena and new experimental campaign

In this sections, the results to fulfill task 2 are reviewed.

Firstly, the modeling of complex GSI phenomena (finite rate chemistry model and thermal non equilibrium) are presented, as well as the associated numerical results. The coupling of MUTATION⁺⁺ with US3D is detailed, as well as the verification test cases. Secondly, the numerical analysis of graphite in nitrogen testing conditions is presented, followed by the experimental results of graphite in nitrogen plasma.

3.1. Oxidation Finite rate chemistry model

The experimental campaign performed on carbon fiber preform detailed in section 2.4.1 was numerically investigated by means of the COSMIC code [60]. The aim is to compare the phenomenological model for carbon oxidation of Park [12] with the higher fidelity PSMM finite-rate chemistry model [61]. The mass balance was coupled with the energy balance to determine the surface temperature of the sample. Simulation free stream conditions were provided by the rebuilding procedure explained in section 2.3. Specifically it was imposed a free stream pressure of 20000 Pa, a velocity of 41.2 m/s, and a temperature of 6088 K. The air composition was imposed to be at equilibrium.

The PSMM rate coefficients for each surface reactions are also shown in table 5, where B is the active site density on the surface [mol m^{-2}], s , the surface density of empty sites [mol m^{-2}], and h , the Planck constant. The set of equations (8) is closed by steady-state assumption ($ds/dt = 0$, meaning that the net production of empty sites in time is zero)



and the system is solved by means of a Newton method.

Table 5: PSMM carbon oxidation mechanism as proposed in [61].

Reaction	Reaction Rate	Rate Coefficient
$O + s \rightarrow O_s$	$k_1[O][s]$	$\frac{1}{B} \sqrt{\frac{8k_b T_s}{2\pi m_o}}$
$O_s \rightarrow O + s$	$k_2[O_s]$	$\frac{2\pi m_o k_b^2 T_s^2}{B h^3} \exp\left(-\frac{44277}{T_s}\right)$
$O + O_s + C_b \rightarrow CO + O_s$	$k_3[O][O_s]$	$\frac{57.37}{B} \sqrt{\frac{k_b T_s}{2\pi m_o}} \exp\left(-\frac{4667}{T_s}\right)$
$O + O_s + C_b \rightarrow CO_2 + s$	$k_4[O][O_s]$	$\frac{8.529 \cdot 10^{-6}}{B} \sqrt{\frac{8k_b T_s}{2\pi m_o}} \exp\left(-\frac{6958}{T_s}\right)$
$O + C_b + s \rightarrow CO + s$	$k_5[O][s]$	$\frac{0.1203}{B} \sqrt{\frac{8k_b T_s}{2\pi m_o}} \exp\left(-\frac{2287}{T_s}\right)$

Figure 13 shows the surface temperature (left) and surface recession rate for three cases. The black lines represent the full phenomenological model, the blue lines the phenomenological model ignoring nitridation and sublimation and the red lines the PSMM model of table 5. The last two models agree excellently with each other. The comparison with the original full model including nitridation shows a non-negligible difference. This indicates that nitridation, even though a secondary effect, can have an impact on the predicted conditions on the surface.

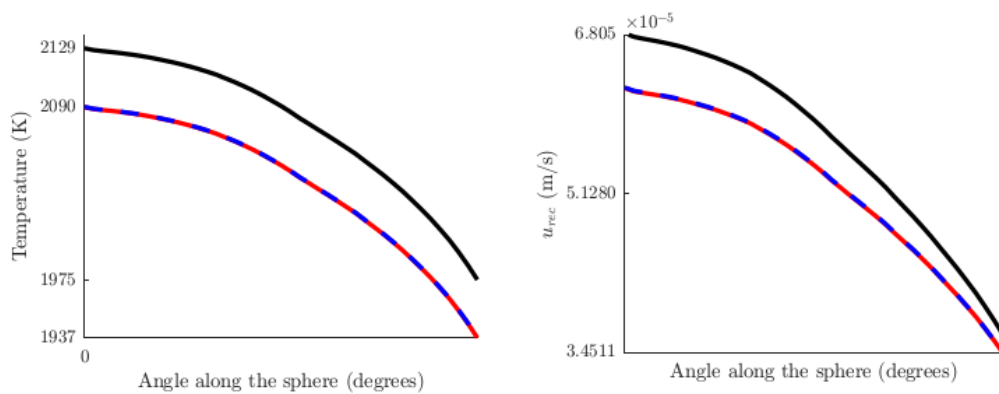


Figure 13: **Left:** Surface temperature (K) along the semi-spherical surface as a function of the angle in degrees. **Right:** Recession rate (m/s) along the semi-spherical surface as a function of the angle in degrees. **Black line:** Park model including nitridation; **Blue line:** Park model only oxidation; **Red line:** PSMM model.



3.2. Nitridation Finite rate chemistry model

Numerical simulations were performed to validate the nitridation Finite-Rate Chemistry (FRC) model developed in UMN [62] by means of a in-house code (appendix A). An experimental campaign was used as validation test case.

The FRC module available in MUTATION⁺⁺ was further extended to accommodate the above-mentioned mechanism, whose considered reactions are reported in table 6.

Table 6: FRC reactions for nitrogen flows[62].

Reaction	Reaction Rate	Rate Coefficient
$N + s \longrightarrow N_s$	$k_1[N][s]$	$\frac{F_N}{B} \exp \frac{-2500}{T_s}$
$N_s \longrightarrow N + s$	$k_2[N_s]$	$\frac{2\pi m_N k_b^2 T_s^2}{N_A B h^3} \exp \frac{-73971}{T_s}$
$N + N_s + C_b \longrightarrow CN + N + s$	$k_3[N][N_s]$	$\frac{F_N}{B} 1.5 \exp \frac{-7000}{T_s}$
$N + N_s \longrightarrow N_2 + s$	$k_4[N][N_s]$	$\frac{F_N}{B} 0.5 \exp \frac{-2000}{T_s}$
$N_s + N_s \longrightarrow N_2 + 2s$	$k_5[N_s][N_s]$	$\sqrt{\frac{N_A}{B}} F_{N,2D} 0.1 \exp \frac{-21000}{T_s}$
$N_s + C_b \longrightarrow CN + s$	$k_6[N_s]$	$10^8 \exp \frac{-20676}{T_s}$

The rate coefficients for each surface reactions are also shown in table 6, where B is the active site density on the surface [mol m^{-2}], s , the surface density of empty sites [mol m^{-2}], $F_N = \sqrt{k_b T_s / 2\pi m_N}$, a quarter of the mean thermal speed of atomic nitrogen, $F_{N,2D} = \sqrt{\pi k_b T_s / 2m_N}$, the mean thermal speed of the mobile adsorbed nitrogen on the surface, and h , the Planck constant. The set of equations (8) is closed by steady-state assumption ($ds/dt = 0$, meaning that the net production of empty sites in time is zero) and the system is solved by means of a Newton method.

In order to compare these results with the ones presented in table 4, an equivalent probability value was computed by dividing the chemical production rate term by the flux of the species impinging the surface:

$$\gamma_N^{CN} = \frac{\dot{\omega}_{CN}}{m_{CN} \mathcal{N}_N}, \quad \gamma_N^{N_2} = \frac{\dot{\omega}_{N_2}}{m_{N_2} \mathcal{N}_N}. \quad (10)$$

Input conditions for the simulations and surface measurements are reported in table 4. Simulations were carried imposing a mixture composed of the following species: N , N_2 , N^+ , e^- , CN , C , C^+ , C_2 , C_3 . Stagnation point results for four cases, namely G4, G5, G6 and G7 are shown in fig. 14 together with the predicted mass blowing rate and the related nitridation efficiency uncertainties reported in table 4.

The value of the nitridation probability γ_{CN} given in fig. 14(a) is within the uncertainty reported for the first two cases, while a lower value is predicted for the second two cases. The predicted recombination efficiency is very important and it increases with the wall

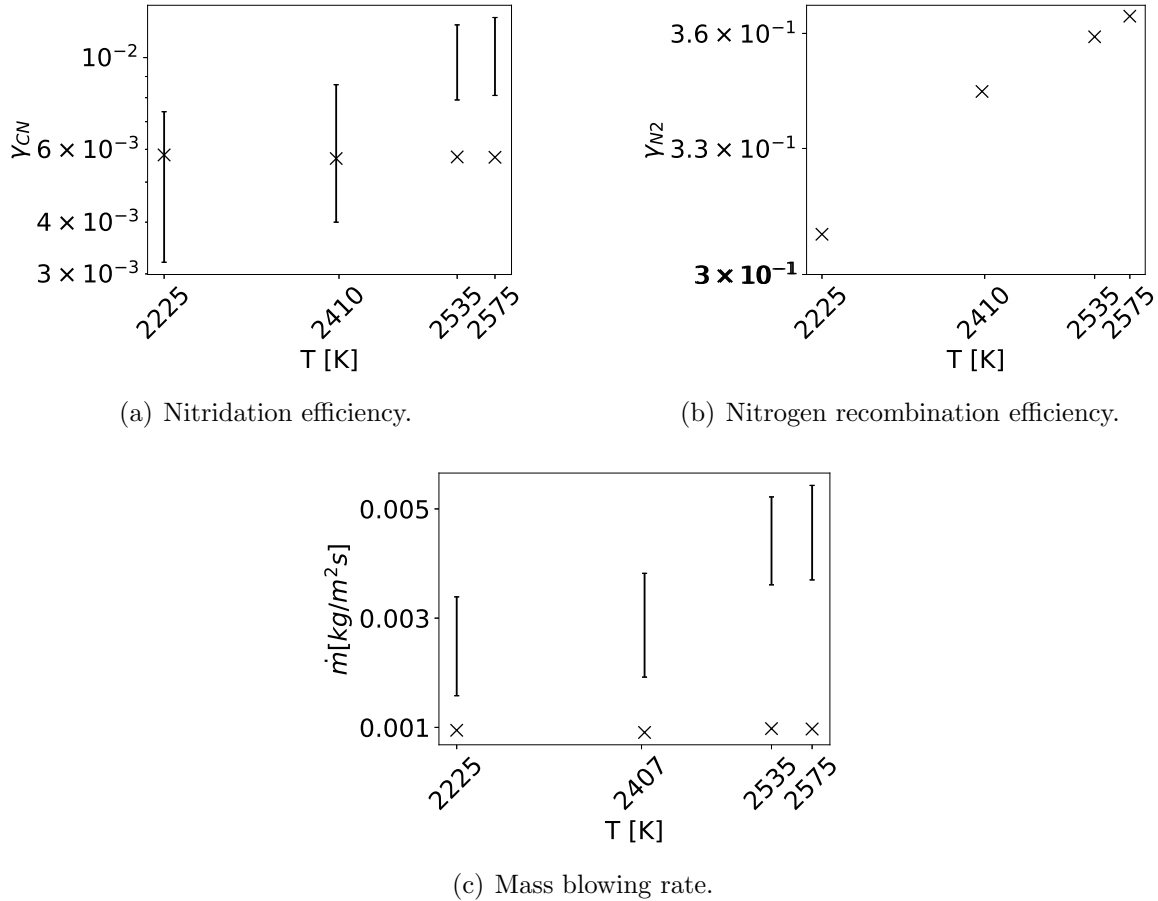


Figure 14: Solution obtained with the in-house code (appendix A) relative to a nitrogen flow over a 25 mm radius hemisphere carbonaceous sample: quantities of interest at the stagnation point for four cases, namely G4, G5, G6 and G7 detailed in table 4 are plotted as function of the surface temperature (cross). Nitridation efficiency and mass blowing rate from the same table are reported with error bars.

temperature, as shown in fig. 14(b). Such a high recombination decreases the atomic nitrogen available near the surface for nitridation reaction (fig. 25(c)) and, thus, the CN production. As a result, the model predicts lower mass blowing rate, as one can see in fig. 14(c).

Though the FRC model does not accurately calculate the mass blowing rate measured in the Plasmatron experiments, the model takes into account the surface recombination reaction. Inclusion of both nitridation and recombination reactions allows for accurate model calibration through direct flow simulations such as those performed in the current work, rather than relying on 0D simulations as in [62].



3.3. Thermal nonequilibrium in gas surface interaction

Boundary layer spectroscopy measurements performed on the nitridation experimental campaign suggested a strong departure from thermal equilibrium. Moreover when it was numerically simulated using a mass-energy balance BC, the surface temperature was over-predicted, assuming it to be in thermal equilibrium (table 7). For these reasons, a numerical study was performed to assess whether this thermal nonequilibrium would arise from a nonequilibrium in the gas surface layer and how this can affect surface properties.

For the closure of the vibronic temperature at the surface, a vibronic energy balance was derived and included in the MUTATION⁺⁺ library, in a 1D frame it reads:

$$\rho u_g h^V + q^V = S_s^{VT} + S_s^{CV}. \quad (11)$$

where the LHS is the sum of the vibronic energy advected out, as well as of the vibronic gas heat flux to the surface (conductive and diffusive); the first term in the RHS takes into account the vibronic relaxation of particles by collisions with the surface (eq. 12, modeled adapting the Landau-Teller gas-gas formulation [63], with collision efficiency α), and the second term takes into account that not all the chemical energy of a reaction is accommodated on the surface but rather transferred to internal modes of the reaction product (eq. 13, two temperature adaptation of the Halpern energy accommodation term, β , [64]).

$$S_s^{VT} = \sum_{i=0}^{n_s} \alpha_i \mathcal{N}_i m_i (h_i^V(T^V) - h_i^V(T^T)). \quad (12)$$

$$S_s^{CV} = \sum_{i \in \mathcal{C}} (1 - \beta_i) \dot{\omega}_i (h_i^V - h_i). \quad (13)$$

For describing the flow, Park's 2-temperature model [65] was assumed and the field solved using a in-house code (appendix A). The surface was modelled using a mass-energy balance with a vibronic mode closure; a nitrogen ion mixture was considered; the nitridation reaction was described using the phenomenological gamma. Inlet condition of the test can be found on table 4. In figure 15(a) the results along the stagnation line for the G5 test-case are given for two extreme solutions of the 11: 1) surface in thermal equilibrium ($T_{\text{wall}}^T = T_{\text{wall}}^V$), 2) surface vibronically adiabatic ($\nabla T_{\text{wall}}^V = 0$). The latter condition better capture the experimentally observed thermal nonequilibrium in the flowfield; moreover it showed that the vibronic excitation is mainly due to the diffusion of electronic excited atomic nitrogen in the BL. In figure 15(b) the behaviour of surface temperature as function of α and β is shown; the translational temperature decreases with α , reducing the numerical/experimental temperature mismatch. Opposite trend is observed for the vibrational temperature, while the blowing mass rate, figure 15(c), being depended on T_{wall} , decreases with it. The chemical term contributes less to the variation of the solution. From these results it can be concluded that thermal nonequilibrium may



arise from GSI phenomenon and potentially may explain some of the observed nonequilibrium features. The results of surface quantity (temperature (T_{wall}) and blowing mass

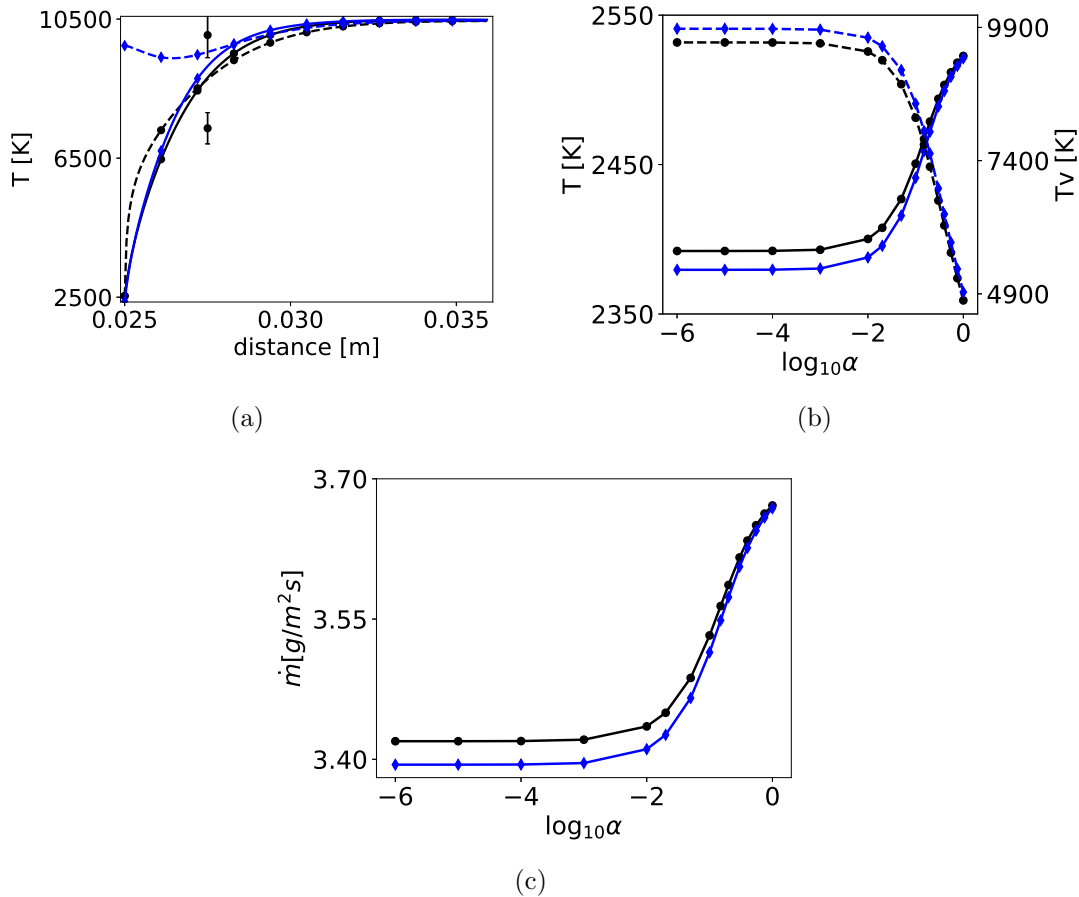


Figure 15: Two temperature GSI BC G5 results:15(a) Results along the stagnation line. Translational temperature in solid lines. Vibronic temperature in dashed lines. Upper error bar relative to experimental measure of vibronic temperature, lower of translational. Surface in thermal equilibrium with circle marker. Surface vibrationally adiabatic with diamond markers.15(b) Surface translational and vibronic temperature as function of α respectively with continuous and dashed line. $\beta = 1$ with circles, $\beta = 0$ with diamond 15(c) Surface blowing rate as function of α respectively with continuous and dashed line. $\beta = 1$ with cycles, $\beta = 1$ with diamond.

rate($\dot{m}$)) are given in table 7, for the two extreme cases. It is also given the error with respect to the experimental temperature. The error on the prediction of surface temperature decreases moving toward the adiabatic condition, while the mass blowing rate is within the experimental uncertainty for both cases.



Table 7: Surface numerical results relative to the equilibrium and adiabatic BC.

CASE	$T_{\text{wall}}^{\text{equi}}$ [K]	$T_{\text{wall}}^{\text{adi}}$ [K]	$\dot{m}_{\text{equi}}$ [m/g ² s]	$\dot{m}_{\text{adi}}$ [m/g ² s]	ϵ_{equi} [%]	ϵ_{adi} [%]
G4	2440	2300	3.40	3.10	9.7	3.4
G5	2530	2385	3.69	3.40	5.0	-1.0
G6	2750	2575	4.29	4.00	8.5	1.6
G7	2740	2571	4.30	4.05	6.4	-0.1

3.4. Coupling between the MUTATION++ library and the US3D solver

MUTATION++ was coupled to US3D [66] using its user defined functions, allowing for high fidelity ablative simulations. The coupling comprises the following MUTATION++ options:

1. Chemistry library;
2. Transport library: viscosity and thermal conductivity (Gupta-Yos, Wilke, polynomial approximation of Chapman-Enskog(LDT^T decomposition or *CG* method), Eucken correction), and diffusion (Stefan-Maxwell);
3. Roto-translational/vibronic energy transfer;
4. Gas-surface Interaction library: mass and mass-energy balance.

The set of test cases used to verify the coupling is presented below.

3.4.1. Chemistry Box

A 0D adiabatic box was simulated in order to verify the chemistry and multi temperature sources terms coupling. Starting from the chemical non-equilibrium initialization provided in table 8, the system was left free to time-march toward the equilibrium configuration, using both US3D chemical library (referred as US3D) and the US3D solver calling MUTATION++ (referred as MPP). Both the libraries use the chemical rates and the two-temperature source terms provided by Park[65].

Table 8: Initial condition for chemistry box test.

Index	ρ_0 [kg/m ³]	T_0 [K]	T_0^V [K]	u_0 [m/s]	$Y_0(\text{N}_2)$	$Y_0(\text{O}_2)$
I	$1.0 \cdot 10^{-2}$	7000.0	7000.0	0.0	0.767	0.233
II	$1.0 \cdot 10^{-2}$	10000.0	10000.0	0.0	0.767	0.233
III	0.479171	15000.0	300.0	0.0	0.767	0.233



The results obtained for an air 5 mixture assuming thermal equilibrium, index I of table 8, are shown in figure 16(a). They show excellent agreement. No increment of computational time is observed.

A second the test-case was performed, still assuming thermal equilibrium, but with a 11 species air mixture, index II of table 8; also in this case the results, fig. 16(b) and 16(c), show excellent agreement. The only exception is the N_2^+ evolution, which is slightly faster for the US3D library. The same solution is compared to the one obtained with the MUTATION⁺⁺ ODE solver. Being the results in agreement, the differences are due to little differences in the two codes, and not to the coupling itself.

The last simulation, index III of table 8, was run to verify the coupling of 2-temperatures

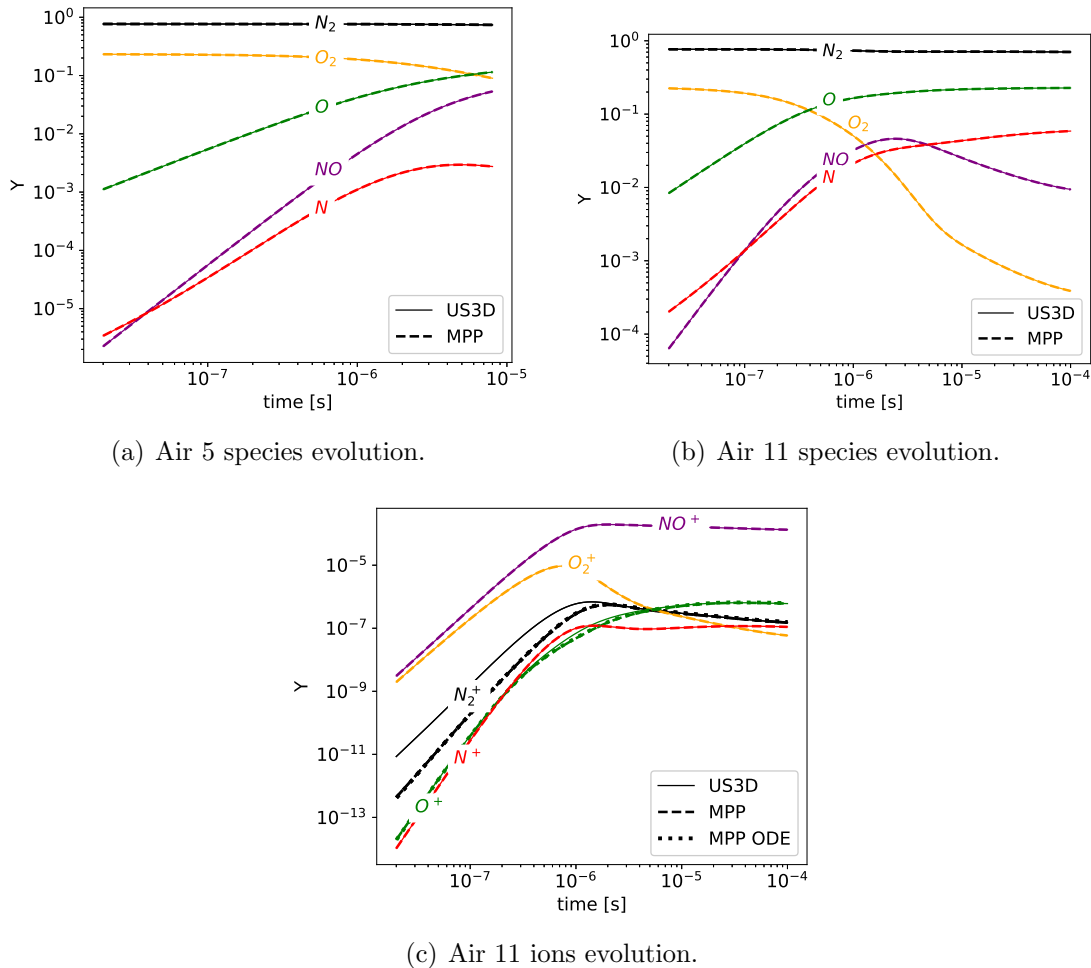


Figure 16: Time evolution of species mass fraction in a 0D reactor.

source terms. Results of the mass fractions and temperatures evolution are respectively plotted in fig. 17(a) and 17(b). Also in this case the agreement is excellent.

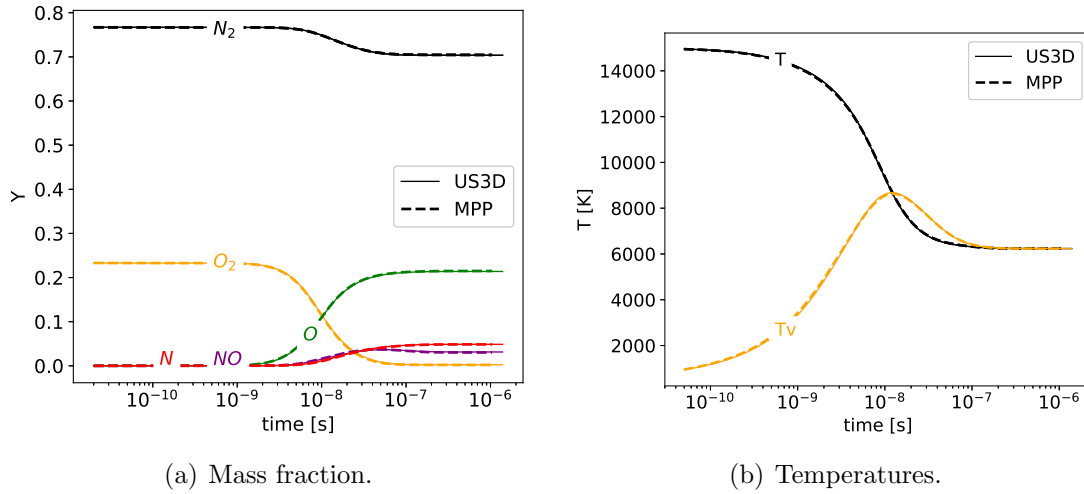


Figure 17: Air 5 time evolution in a 0D reactor.

3.4.2. Supersonic Cylinder: Air 5 species

Another test-case was performed assuming a supersonic inlet flow of 5 species air (chemical rates by Park[65]) over an isothermal cylinder ($T_{\text{wall}} = 300$ K) of radius equal to 0.045m. The relative inlet conditions are given on table 9. The simulation was run using both US3D internal library and using the coupled library MUTATION⁺⁺.

Table 9: Boundary condition for the 5 species supersonic flow over a cylinder.

ρ_∞ kg/m ³	$T_\infty = T_\infty^V$ K	u_∞ m/s	$Y_\infty(N_2)$	$Y_\infty(O_2)$	$Y_\infty(NO)$	$Y_\infty(N)$	$Y_\infty(O)$
$1.547 \cdot 10^{-3}$	901.0	5956.0	0.754	0.007	0.010	-	0.228

Firstly the chemistry of the coupling was re-assessed by performing an Euler simulation, after that the transport coupling was assessed by running a Navier-Stokes simulation.

Euler

The results, shown in fig. 18, show good agreement for the quantities of interest. The increment of computational time linked to the call of MUTATION⁺⁺ library is about the 22.93%.

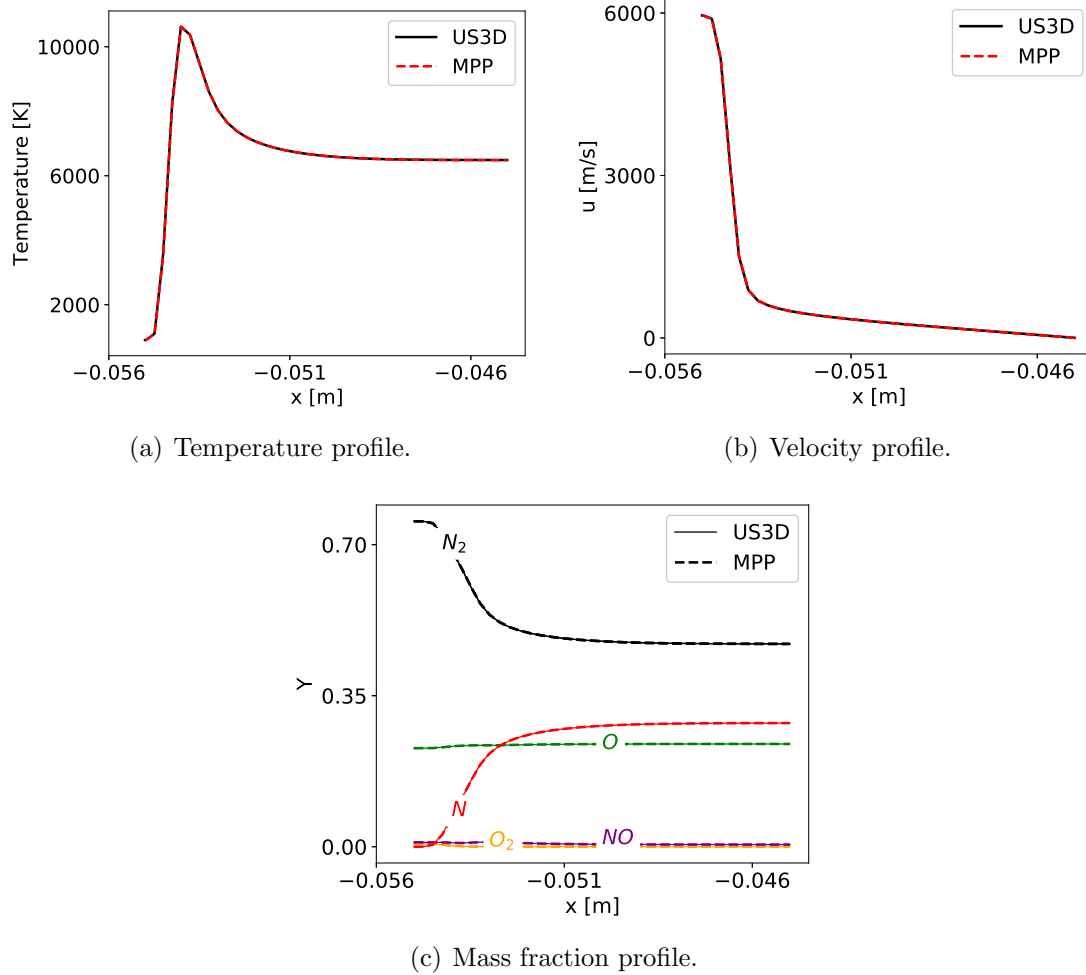


Figure 18: Euler solution extracted along the stagnation line for 5 species air.

Navier-Stokes

For the simulation using US3D internal library, the viscosity and the translational thermal conductivity were computed according to Gupta-Yos mixing rule [67] and the diffusion using the self-consistent effective binary diffusion models[68]. For the simulation calling MUTATION⁺⁺ library, the viscosity and the thermal conductivity were computed according to the polynomial approximations of the Chapman-Enskog expansion, while the diffusion according to the Stefan-Maxwell equation[59]. Eucken correction was used in both the codes for accounting for internal thermal conductivity.

Quantities of interest, shown in figure 19 and 20, show good agreement. The increment of computational time linked to the call of MUTATION⁺⁺ is about the 74.33%.

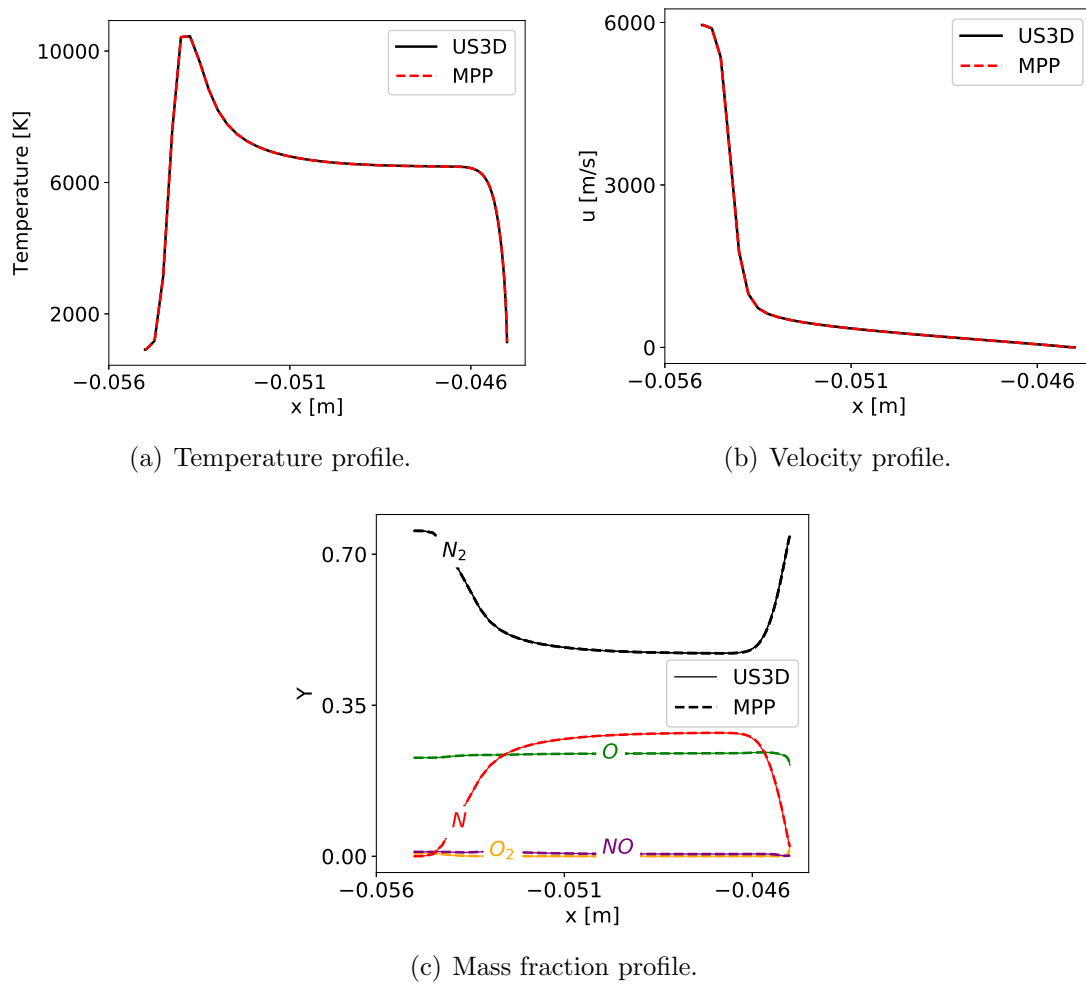


Figure 19: Navier-Stokes solution extracted along the stagnation line for 5 species air.

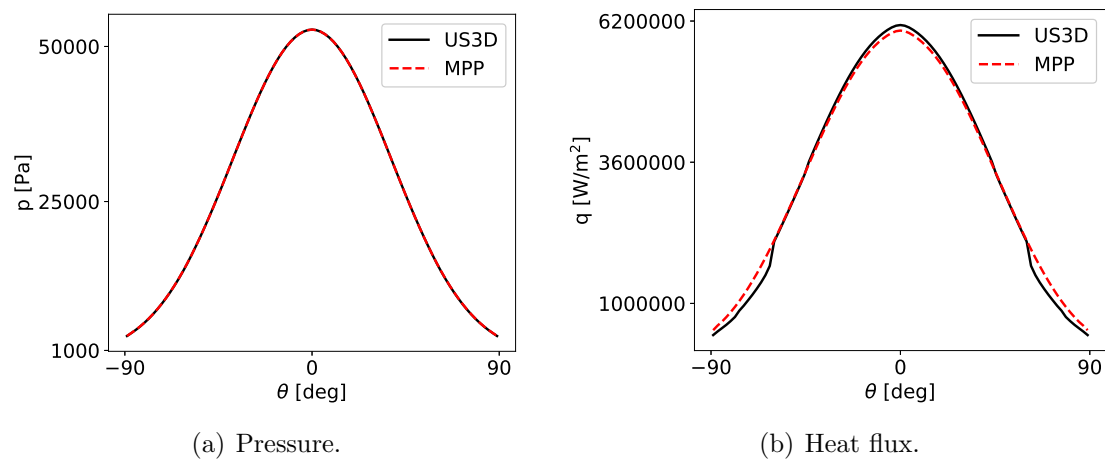


Figure 20: Navier-Stokes solution along the surface for 5 species air.



3.4.3. Hypersonic Cylinder: Air11, Navier-Stokes

Another test-case was performed assuming a supersonic inlet flow of 11 species air (chemical rates by Park[65]) over an isothermal cylinder ($T_{\text{wall}} = 300 \text{ K}$) of radius equal to 0.4m. The relative inlet condition are given on table 10. The transport proprieties are the same used in the air 5 Navier-Stokes test case.

Table 10: Boundary condition for the supersonic 11 species flow over a cylinder.

ρ_{∞} kg/m ³	$T_{\infty} = T_{\infty}^V$ K	u_{∞} m/s	$Y_{\infty}(\text{N}_2)$	$Y_{\infty}(\text{O}_2)$
$2.135 \cdot 10^{-2}$	325.0	6500.0	0.767	0.233

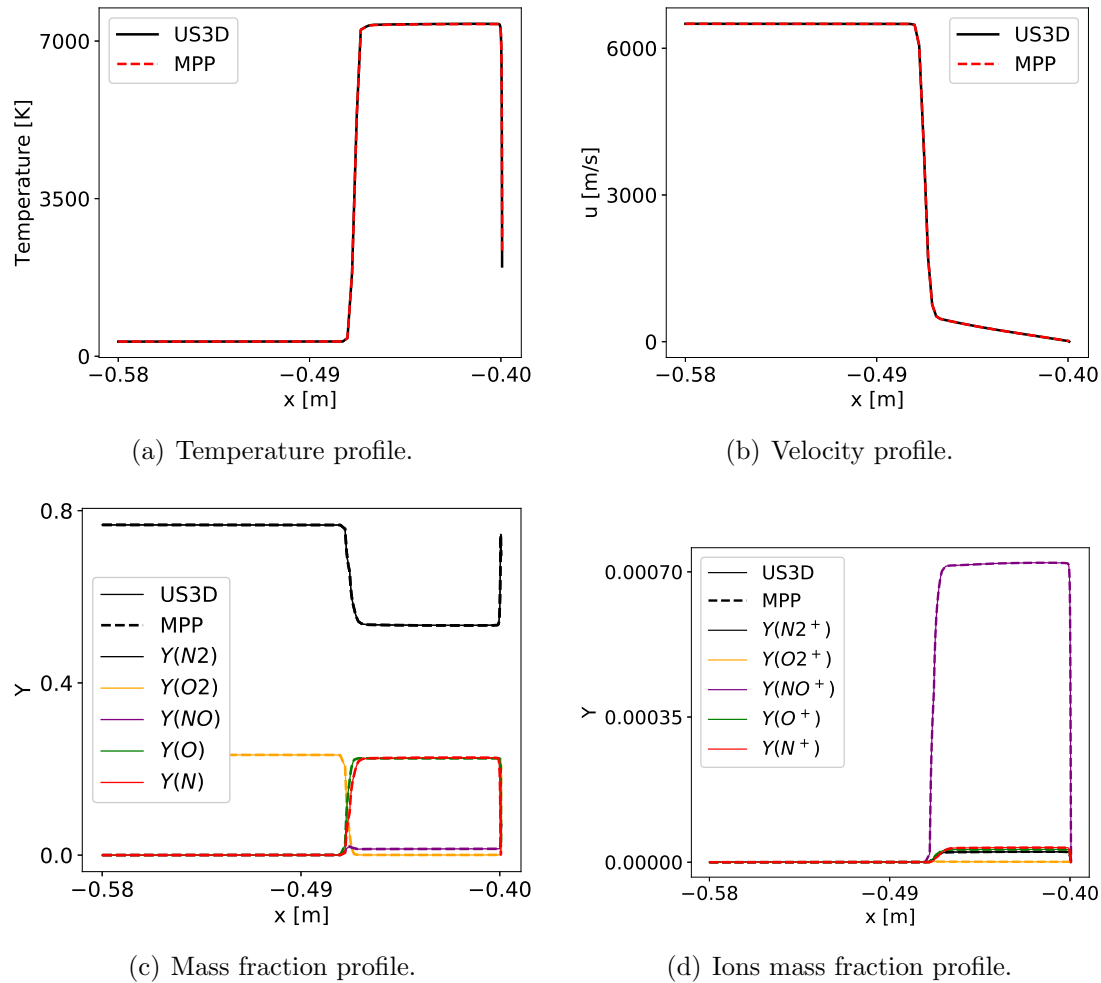


Figure 21: Navier-Stokes solution extracted along the stagnation line for 11 species air.

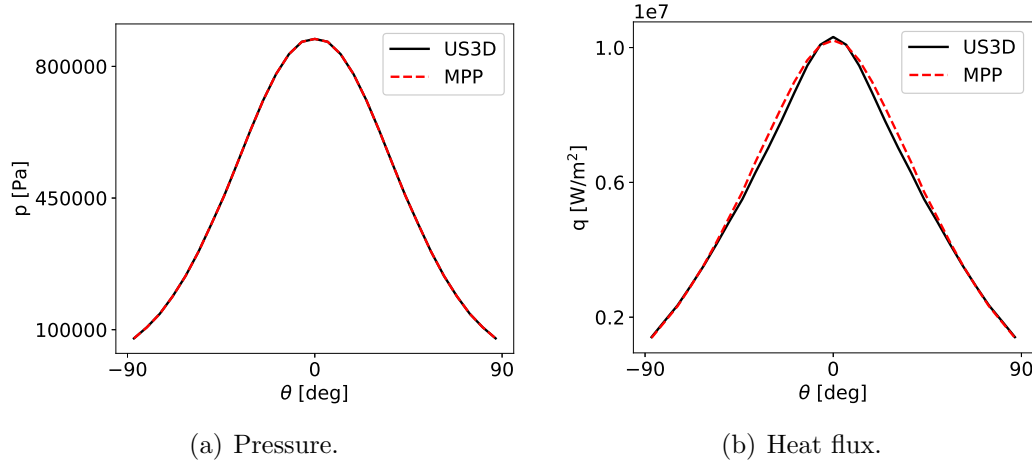


Figure 22: Navier-Stokes solution along the surface for 11 species air.

The results, shown in figure 21 and 22, show good agreement. The increment of computational time linked to the call of MUTATION⁺⁺ library is about the 394%.

3.4.4. Nitridation testcase

The experimental campaign was simulated using the US3D solver imposing the GSI mass balance from MUTATION⁺⁺. Results, extracted on the stagnation line, were compared to the ones obtained from the in-house flow solver to validate the GSI coupling.

The numerical grid is represented in fig. 23, it was rotated around the axis to obtain an axisymmetric domain. An uniform inlet was imposed: its state (density, temperature, and velocity) is reported in table 2.3, assuming local thermodynamic equilibrium. The pressure of the chamber (1500 Pa) was prescribed at the outlet while, on the sample, the surface mass balance eq. (5) was imposed, using the FRC closure. Past the hemispherical part of the sample (at $x = 0.0$ m), an isothermal, non reacting surface boundary condition was imposed. Mach and temperature contours are shown in fig. 24.

As one can see in fig. 25, the agreement between the two codes is excellent for all the quantities of interest (temperature, velocity and mass fraction distribution). The small differences in the results can be attributed to the different sets of equations solved and the numerical methods.

In fig. 26(a), the angular distribution of the mass blowing rate is shown for the four test cases. Also in this case, the differences between the results obtained by the two solvers are minimal, verifying the implementation of the boundary condition. Another important quantity is the heat flux distribution along the sample, plotted in fig. 26(b). The value obtained using the FRC model (continuous line) is shown against the one predicted by assuming an inert surface (dotted line). Specifically, in the hemispherical part, we can see that the strong catalytic nature of the surface in the FRC model,

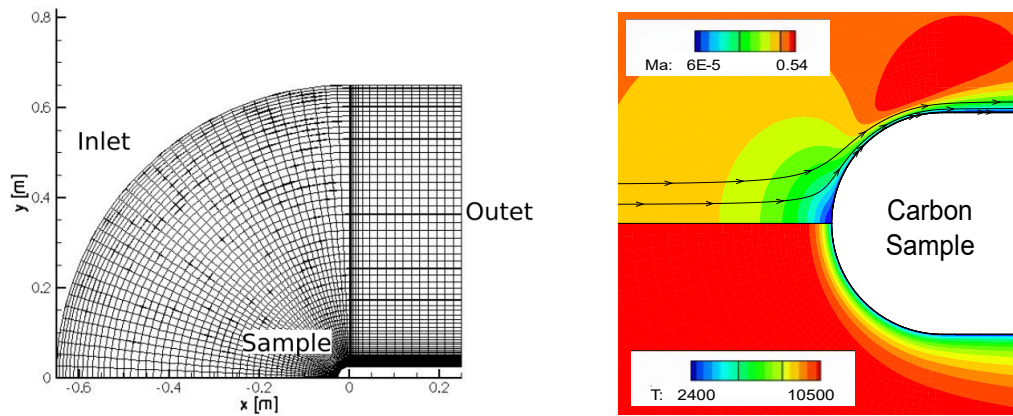


Figure 23: Numerical domain used to solve the axisymmetric flow-field of the nitridation experimental campaign (sec. ??).

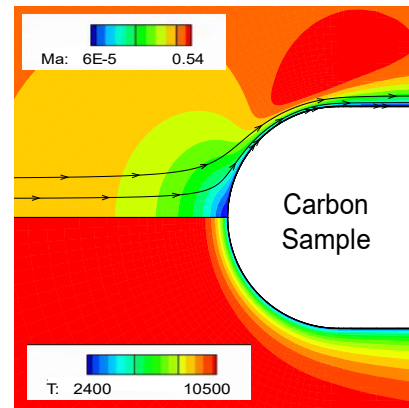


Figure 24: Mach number (top) and temperature (bottom) contour.

increases the surface heat flux by 3 times.

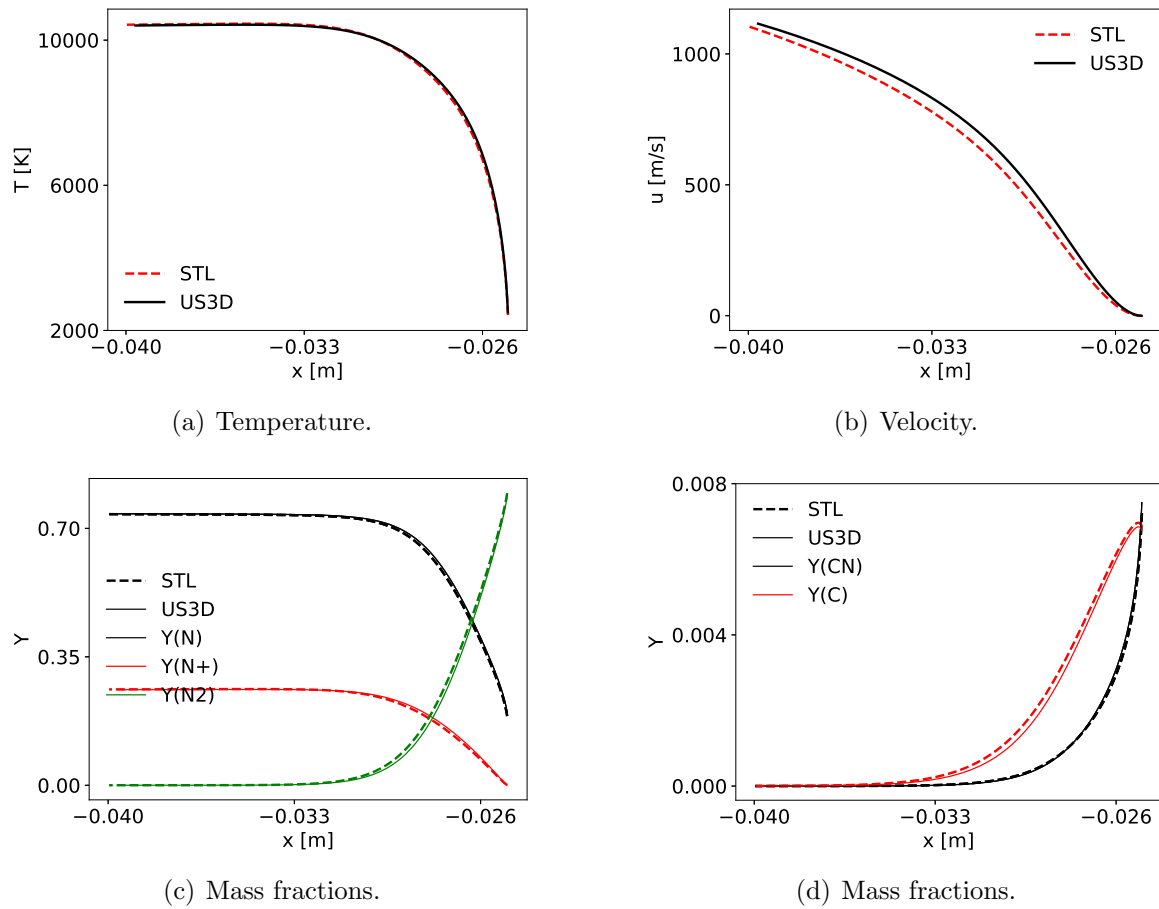
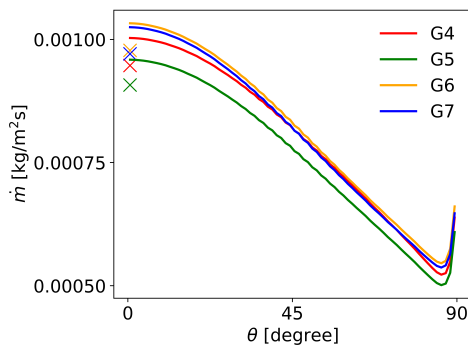
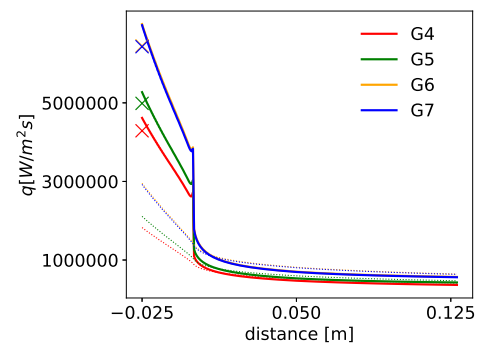


Figure 25: Simulation results for the test-case G5 of table 4. Quantities of interest extracted on the stagnation line in the US3D simulation within the boundary layer are compared to the ones obtained through the stagnation line code (STL in the legend).



(a) Mass blowing rate.



(b) Heat Flux.

Figure 26: Quantities of interest for the four cases detailed in table 4. US3D surface results (lines) are plotted against the stagnation point values from the stagnation line code (cross). Mass blowing rate is plotted as function of angular coordinate, and the heat flux as function of x-coordinate. The heat flux plot contains the results for a reactive surface (solid lines), and also for an inert surface (dotted lines).



3.4.5. Graphite in Nitrogen Flow - numerical pre-analysis regarding pressure dependency

As is detailed above, current models of the gas-surface chemistry relevant to carbon-based ablation are incomplete. While the development of higher fidelity finite rate chemistry (FRC) models seeks to close these gaps, there remains much uncertainty on the performance of these models over the wide range of conditions that may be experienced during re-entry. Moreover, re-entry conditions notwithstanding, the lack of a systematic, experimental approach in understanding the impact of pressure on carbon ablation needs to be addressed, particularly due to the fact that new FRC models often include an implicit pressure dependence, which can significantly impact the overall chemistry. Due to this lack of information, a series of simulations was conducted in order to better inform the definition of an experimental campaign in the Plasmatron facility. The overall goals of these simulations were: (1) consider the impact of variations in the Plasmatron facility static pressure for a range of gas-surface chemistry models, (2) how does the performance of a newer, higher fidelity FRC model [62] compare to the more commonly used empirical (phenomenological) alternatives [69].

All simulations in this section were conducted for a graphite-pure nitrogen flow case for a number of reasons. The first is that the rate of nitridation is two orders of magnitude slower than oxidation. This results in some practical considerations for ablation studies, especially with respect to experimental testing, where both macroscopic measurements (recession rate) and spectral measurements (species) become more reliable. Furthermore, testing in pure nitrogen allows for abstraction in the suite of chemical reactivity, allowing for the reduction in parameters that may impact the overall chemistry. Finally, the VKI Plasmatron facility is well configured for CN spectroscopy, making the study of carbon-nitrogen ablation straightforward.

All simulations were conducted using STAGLINE, the 1D finite volume solver for the axisymmetric Navier-Stokes equations, outlined in [Appendix A](#). STAGLINE computes the flowfield along the stagnation line from the boundary layer edge (nominally) down to the stagnation point of the ablating sample. STAGLINE boundary and inlet conditions were as follows: in all cases a subsonic inlet was used, with a boundary layer edge temperature and pressure computed by the VKI ICP code for the G4, G5, and G7 test conditions, as is detailed in [Table 3](#) ([Sec. 2.4.2](#)). Equilibrium species mole fractions, computed based on the boundary layer edge temperature complete the inlet condition. A general ablation-mass balance, boundary condition was enforced at the stagnation point, detailed in [Sec. 2.6](#), where the sample surface temperature was imposed (given also in [Table 3](#)), and species concentrations were returned based on the gas-surface interaction model employed and its associated kinetics. Note that the GSI model itself is implemented within the MUTATION++ library, which provides the requisite thermodynamic, kinetic, and transport data.

Two different gas-surface interaction models were employed in these simulations, one being the Helber & Turchi phenomenological model and the Minnesota FRC model.



Table 6 details the suite of chemical reactivity specified by the Minnesota FRC to occur at the surface, while Table 11 below details reactivity associated with the much simpler Helber & Turchi phenomenological model. It is important to note that the chemical reactivity at the surface is distinct from the reactivity in the gas phase: for all simulations the carbon-nitrogen Olynick (1999) mechanism was used, which contains nine species (e^- , C^+ , C_2 , C_3 , CN , C , N , N^+ , N_2) and eight reactions.

Table 11: Chemical reactivity included in Helber & Turchi's phenomenological model [69].

Nitridation	$N + C_b \rightarrow CN$	$\gamma_N^{CN} = 7.91 \times 10^{-2} \exp \frac{-5653}{T_w}$
Nitrogen Recombination	$N + N \rightarrow N_2$	$\gamma_N^{N_2} = 1 \times 10^{-3} - 0.5$

For the phenomenological model, the chemical production of molecular nitrogen and CN is prescribed by reaction efficiencies or γ s, given on the right-hand side of Table 11. More details on the development of the reaction efficiencies can be found in Sec. 2.6. While the reaction efficiency associated with production of CN is temperature dependent, the nitrogen recombination efficiency was prescribed in the simulations, detailed in Table 11. Heat flux conditions considered in the studies ranged from 2130-3580 kW/m² (G4-G7 in Table 3 respectively) resulting in sample wall temperatures from 2225-2575 K. Simulated static pressures ranged from 5-500 mbar.

Simulation results suggest significant divergence between predictive capability of both the phenomenological model and the finite rate chemistry model. Figure 27 below details the CN production in terms of the reaction efficiency at the wall. Please refer to Eq. 10 for details on this conversion.

This divergence is immediately apparent when considering Fig. 27, note that the FRC model predicts a non-negligible variation in CN production with respect to increasing pressure. On the other hand, unsurprisingly, with no pressure dependence included in the phenomenological model, we see a slight increase in the predicted CN production with respect to temperature, but none with respect to pressure. Interestingly, the influence of temperature on CN production seems to be much more significant with respect to the phenomenological model than the FRC model, a fact that requires more detailed investigation. It is also worth noting that the phenomenological model can be considered to be the ground truth prediction, as it was constructed on the basis of ablation experiments in the VKI Plasmatron (an ICP facility). In contrast, the Minnesota FRC model was constructed based on results from molecular beam experiments, at conditions that are both different from flight and those accessible in an ICP facility. At a base level, this implies that experimental testing at higher pressures is required. Moreover, it also indicates that the more complex FRC model may need to be tuned further in order to approach empirical predictions.

This same contradiction is evident when the simulation results for recombination of atomic to molecular nitrogen are considered. Again, for the phenomenological model,

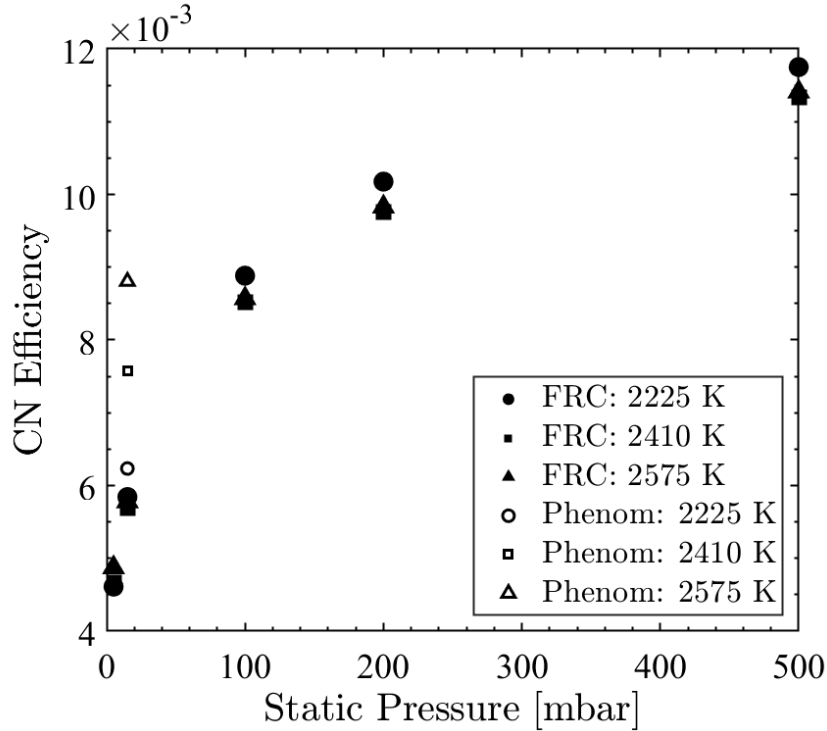


Figure 27: Simulated CN efficiencies across a range of sample wall temperatures (given in the legend) and facility static pressures. All filled markers correspond to the results with the FRC GSI implemented, unfilled markers to the phenomenological model implemented.

these values are prescribed, but for the FRC model, which includes higher fidelity kinetics, the associated values require additional study. The nitrogen recombination efficiencies computed from the simulations are given in Fig. 28 below.

As can be seen, the FRC GSI model predicts significant recombination of atomic nitrogen at the wall. While the fact that the recombination occurs to a significant extent at the wall is not surprising, the computed magnitude is. For reference, the maximum reported experimentally determined value of the nitrogen recombination efficiency is $\gamma_{N^2}^{N_2} = 0.22$ (Gordeev et al., 1985). The FRC model predicts recombination efficiencies in excess of 50% over all the pressure conditions simulated. If the recombination is indeed this significant, this will have significant impacts on the heat flux delivered to the surface of the ablating sample. However, it is more likely that the significant number of parameters associated with FRC model require additional tuning, in order to better approach what is seen empirically. Finally, note that the fall off in recombination efficiency at higher pressures is expected, as the gas phase reactivity consumes atomic nitrogen before it can reach the ablating surface as the pressure is increased.

Clearly, the simulation results imply that study of the impact of pressure is requisite to

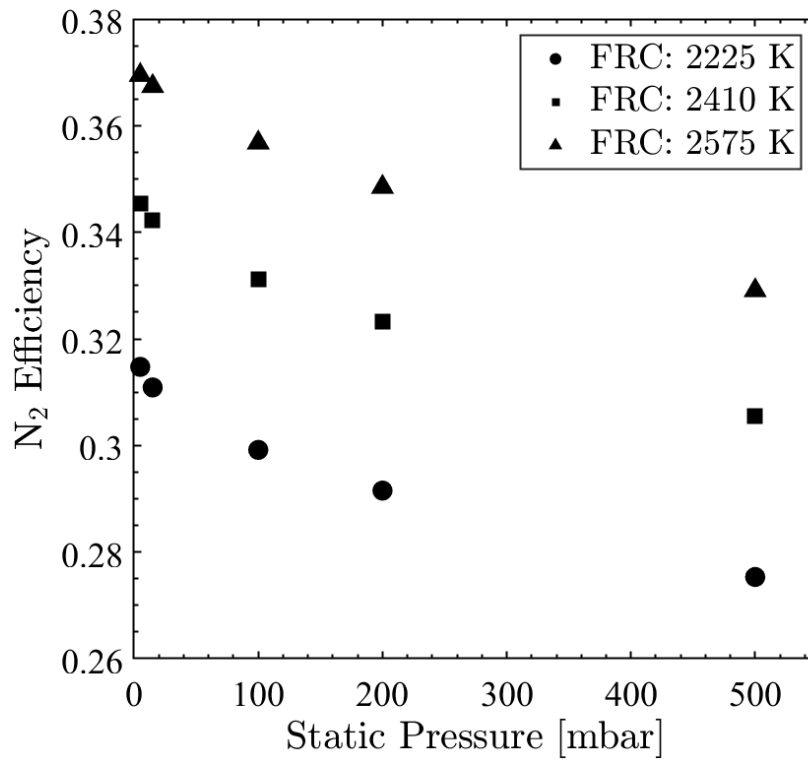


Figure 28: Simulated N_2 recombination efficiencies across a range of sample wall temperatures (given in the legend) and facility static pressures for the FRC model.

the full understanding of the performance of the GSI models, and to the overall physics associated with ablation. Because of this, Plasmatron testing at various facility static pressures is currently on-going.



3.4.6. Graphite in Nitrogen Flow - experimental reaction rate pressure dependency investigation

This section is organized as follows:

- A: Plasmatron test facility overview
- B: Experimental setup overview
- C: Experimental results

3.4.6-A: Plasmatron test facility overview: This section reviews the Plasmatron facility as well as associated measurement techniques planned to be applied during this test campaign.

The Plasmatron facility (Fig. 29) is a high enthalpy wind tunnel in which plasma is generated by electromagnetic induction and blown in the form of a jet inside a test chamber at sub-atmospheric pressure (between 10 mbar and 400 mbar) [70].

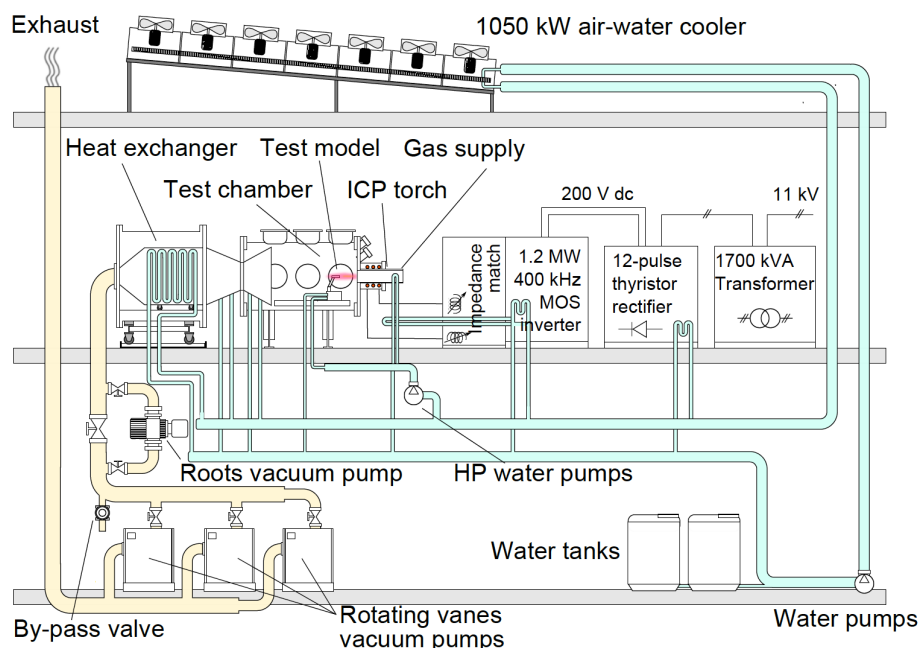


Figure 29: Overview of the VKI Plasmatron facility including cooling and vacuum circuits.

The facility, which is the most powerful induction-coupled plasma (ICP) wind tunnel in the world, uses a high frequency, high power, high voltage (400 kHz, 1.20 MW, 2 kV) solid state (MOS technology) generator, feeding the single-turn inductor of the 160 mm



diameter plasma torch. The torch is mounted on a 1.40 m diameter, 2.50 m long, water-cooled test chamber, fitted with different portholes that allow unrestricted optical access to the test section. Hot gas from the test chamber exits through a 700 kW heat exchanger to a group of three DRYVAC vacuum fore pumps, each backed-up by roots pump. A 1050 kW cooling system using a closed loop deionized water circuit (2090 l/min) and fan-driven air coolers provide cooling to all facility components. The facility is computer controlled using a 719 I/O lines PLC, and two PCs for controlling and monitoring the Plasmatron operation.

The Plasmatron chamber is equipped with an absolute pressure transducer (Membra-novac DM 12, Leybold Vacuum, OC Oerlikon Corporation AG, Switzerland) that measures the static pressure with an accuracy of ± 0.700 hPa. Given that the static pressure measurement is affected by the performance and stability of the vacuum pumps of the facility, an accuracy of $\pm 2\%$ is obtained. The same pressure transducer is installed at the reservoir at the torch exit to obtain the total pressure.

Before and/or after each experimental run, the plasma condition set in the Plasmatron test chamber can be characterized by two intrusive probes injected into the plasma stream. Those are a water-cooled calorimeter for measuring the heat flux level provided by the high temperature gas, as well as a pitot pressure measurement from which the dynamic pressure is obtained. In addition, the test chamber hosts a static pressure port outside the flowfield in order to record the test chamber static pressure during the experiment. A water-cooled (~ 350 K) copper calorimeter is used during the test to measure the stagnation-point cold-wall heat flux. It is placed in the center of the front face of a copper water-cooled probe holder. This probe holder has the same shape and dimensions as the test sample (i.e., hemisphere with 25 mm radius). This is determined by measuring the mass flow (controlled by a calibrated rotameter) and the temperature difference in the cooling water supply and return lines. Two type-E thermocouples are used for this measurements. In order to have correct measurements (i.e., one-dimensional conduction through the copper thickness), the sidewalls of the calorimeter have to be adiabatic. Therefore a Teflon insulator is installed between the calorimeter and the wall of the probe.

Both the probe and the calorimeter have polished copper surfaces which are assumed to be high catalytic to nitrogen and oxygen atom surface recombination. The heat flux is then given by:

$$\dot{q}_{cw} = \frac{\dot{m}c_p(T_{out} - T_{in})}{S} \quad (14)$$

where: $\dot{m}$ is the mass flow rate of the calorimeter in kg/s, c_p is the water heat capacity in J/(kg K), T_{out} is the temperature at the outlet of the calorimeter in K, T_{in} is the temperature at the inlet of the calorimeter in K, and S is the front surface of the calorimeter in m^2 .

A pitot probe with the European Space Agency (ESA)-Standard geometry is used to perform dynamic pressure measurements at stagnation point configuration. The Pitot



line is connected to a Validyne variable reluctance pressure transducer (DP-15, Validyne Engineering Corp., USA) and the output is amplified by a voltage demodulator (CD-15, Validyne Engineering Corp., USA). Both Validyne and amplifier are calibrated with a Betz water manometer, leading to an uncertainty of $\pm 0.2\%$ in dynamic pressure.

3.4.6-B: Experimental setup overview: The experimental setup closely resembled that one presented in Sec. 2.1 and Sec. 2.2. We had three radiometric devices observing the test sample surface temperature (Fig. 30), as reviewed below. The DSLR camera provided absolute recession measurements in addition to the intrusive caliper.

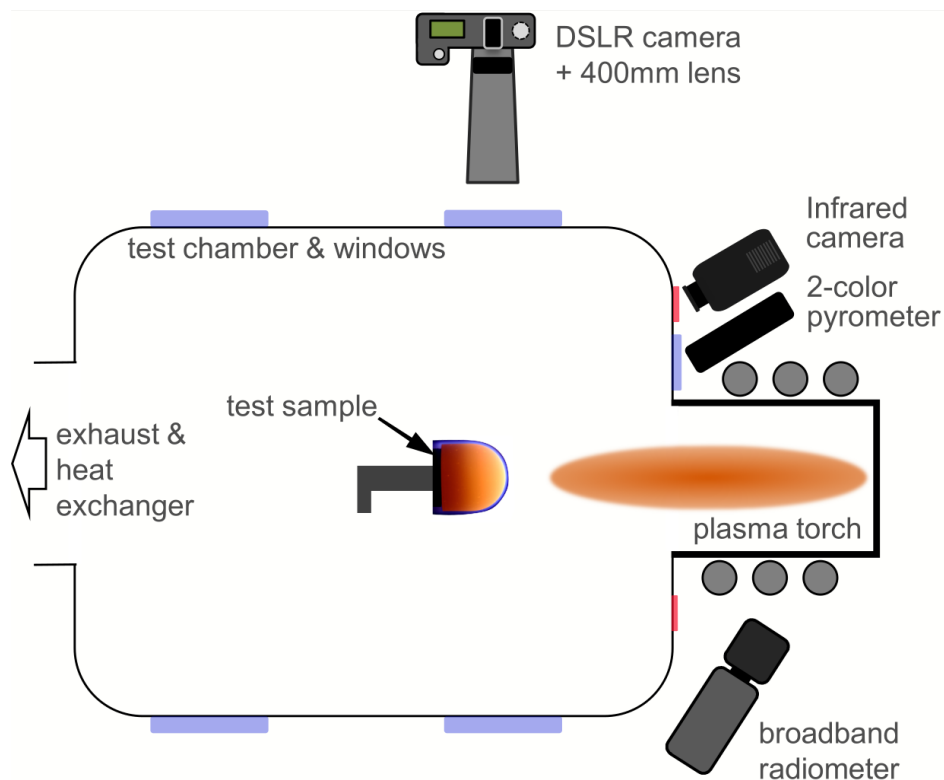


Figure 30: Schematic of experimental setup with observing instruments.

The 2-color infrared pyrometer is used to record the front surface (exposed to plasma) temperature of the sample. The instrument is a RM MR1SC series pyrometer for temperature ranges between 1000°C - 3000°C , which measures over two overlapping narrow wavebands between $0.750\mu\text{m}$ to $1.10\mu\text{m}$, providing an output value independent on emissivity. It is pointed to the stagnation point of the sample.

A certified calibration of the MR1SC series pyrometer, 1000°C to 3000°C , has been carried out at the National Physical Laboratories in London. For this, a high temperature



graphite blackbody (estimated emissivity of 0.995) with an aperture of 25 mm diameter is used. The temperature of the blackbody is determined in terms of the International Temperature Scale of 1990 (ITS-90) using a calibrated linear pyrometer at wavelengths of nominally 650 nm and 900 nm. The measured distance from the back wall of the graphite blackbody to the front of the thermometer was 1000 mm.

During the previous calibration, the effect of the positioning of the optical window in front of the Raytek thermometer was checked at a number of temperatures over the calibration range by moving each window nominally ± 10 mm horizontally and vertically from the nominal center position and recording the thermometer indicated temperature. The effect of changing the angle of the glass window with respect to the thermometer was also checked by positioning the window at $\pm 15^\circ$ from the nominal perpendicular position. The size-of-source effect of the thermometer was also investigated using a NPL standard blackbody source (emissivity > 0.999) held at a nominal temperature of 1010 °C. The thermometer was positioned at a distance of 1000 mm from a water-cooled aperture plate placed immediately in front of the blackbody source, and was aligned and focused onto the center of the aperture. The aperture size was adjusted using a number of different apertures, which were mounted in turn onto the water-cooled aperture plate. For each aperture size the temperature indicated by the thermometer was recorded. The uncertainty analysis resulted in $\delta T_w = \pm 10 - 15$ K in the observed temperature range. The highest uncertainty was attributed to the positioning of the pyrometer with respect to the quartz window, introducing measurement inaccuracies.

The infrared broadband radiometer has been used as an additional front surface temperature measurement device. The instrument is a special version of Heitronics IR-radiation-thermometer KT19.xx specifically designed for the VKI with a broad spectral range of 0.600 μm to 39 μm within a temperature range of 0 °C to 3000 °C. Applications of this type of IR radiometer are the estimation of material emissivities.

In operative Plasmatron conditions, a KRS-5 window, also known as thallium-bromiodide (TlBr-TII) is used along with the IR radiometer to provide optical access to the test chamber. This window enables measurements in the infrared range up to 40 μm . Such material is in fact one of the few existing crystals that offers about 70% transparency in the whole radiometer waveband. The raw IR radiometer output is the uncalibrated temperature evaluated from the measured radiance assuming an emissivity of 1.

A certified calibration of the Heitronics radiometer, 1000 °C to 3000 °C, has been also carried out at the National Physical Laboratories in London, in accordance to the protocol for the pyrometer given above.

The acquisition rate of the instrument is 1 Hz. The process for the surface emissivity estimate combines measurements of the surface temperature, using the two-color pyrometer, and the surface radiance by the IR radiometer [71]. Assuming a gray body behaviour, the material can be characterized by a constant emissivity $\varepsilon < 1$ over the



whole spectral range, emitting less energy than a black body,

$$\varepsilon = \frac{L_{\lambda}}{L_{\lambda}^{\text{bb}}}. \quad (15)$$

Many carbon-based materials such as graphite behave like gray bodies in a certain wavelength range, beneficial for determination of the surface temperatures by radiometers (providing L_{λ} integrated over wavelength range λ) once the surface temperature is known (providing L_{λ}^{bb} integrated over wavelength range λ through Stefan-Boltzmann's law). First, the IR radiometer calibration curve is used to correct the measured temperature value and obtain the surface radiance assuming an emissivity of 1. Then, using the surface temperature measured by the two-color pyrometer, the corresponding blackbody radiance is computed. Finally, the integral value of the emissivity, within the instrument spectral band, is estimated as the ratio between the measured (calibrated) radiance and the blackbody one.

A new infrared thermocamera (FLIR A6750sc MWIR, FLIR SYSTEM, Hong Kong) with thermal filter (ND3) was used to assess the temperature distribution over the probe and sample surfaces. It offers a resolution of 640 x 512 pixels and a maximum spectral sensitivity in the long-wavelength infrared range between 3 μm and 5 μm . The temperature range for the camera is 350°C to 3000°C. The camera is placed at $\sim 1\text{m}$ distance from the probe, with an inclination of 47° with respect to the sample surface normal and optical access to the Plasmatron chamber is assured through a 1 cm thick KRS-5 window. Temperature uncertainties of the camera are $\pm 1.5\%$.

The camera was calibrated together with the high temperature ND3 filter by FLIR up to 3000°C. To account for the proper line-of-sight transmissivity, the optical path encountered during the test conditions is reproduced. The calibration source is held at the same distance of the test probe w.r.t. the instrument and suitable windows are placed in front of the instrument lens.

After proper intensity calibration, IR thermography provides a two-dimensional projection of an object temperature map. To exploit the multidimensional temperature information for quantitative measurements, however, it is required to establish the correspondence between the points of the observed object and the pixel of the thermal image. This procedure requires dedicated tools and non trivial processing if the object has a non-planar geometry, as it often happens in wind tunnel testing.

An optical calibration technique has been newly introduced at VKI, with specific application to the Plasmatron facility. The purpose is to provide the relationship between real world coordinates and image pixels, in order to rebuild the surface radiance map obtained by means of the IR camera on the test object. In practice, to perform such a calibration, one needs:

1. an optical calibration model and a calibration algorithm;
2. a calibration target;



3. the generation of a grid, representative of the observed surface, and a projection function.

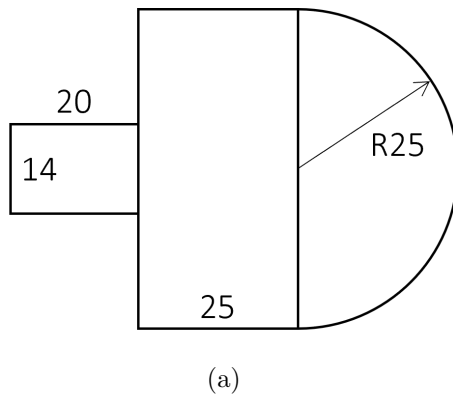
The optical calibration model, extrinsic parameters (translation and rotation matrices) and intrinsic parameters (focal length, pixel position and pixel ratio) are then employed to project a point from the real world coordinates to the image frame. Additionally, radial and tangential distortion components are used to compensate for the deviation of the light rays by the lens system. The model requires as an input the space coordinates and image position (i.e., pixel location) of the calibration points.

This is generally accomplished with the help of a calibration target. A calibration thermogram is then acquired and the image position of the control points is detected by means of suitable image processing techniques. Hence, one can apply the camera calibration algorithm: the extrinsic and intrinsic parameters, along with the distortion constants, can be estimated.

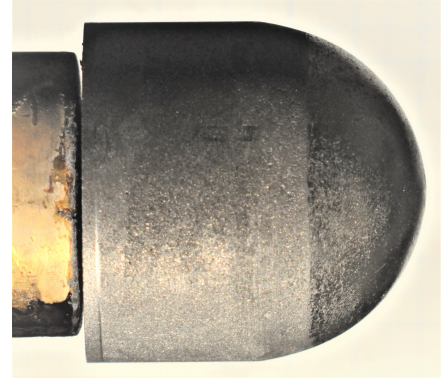
Owing to the difficulties arising in mounting and properly orienting a calibration plate in the Plasmatron facility, an ad-hoc calibration cap has been designed and manufactured, which will have to be adapted for hemispherical test samples. The desired contrast, which allows the calibration spots to be detected in a thermal image, is achieved exploiting different emissivity values. This cap is placed on the probe before the test to acquire a calibration thermogram and removed for the test. Typical reprojection errors associated to the calibration procedure are in the order of ± 0.5 pixel. Once the optical calibration of the camera has been performed, a 3D map of the radiation intensity on the test object can be rebuilt. This is particularly useful because an angular average can be performed, in order for the axisymmetric thermal model to be better representative of the experimental results. The spatially averaged radiation intensity profile is then calibrated and corrected for in-band emissivity to obtain a temperature profile.

Sec. 3.4.6-C: Experimental results: The monolithic test sample was a 50 mm diameter hemisphere with a 25 mm cylindrical part and a 20 mm plug for mounting on the holding arm, all machined in one single piece (Fig. 31). The full sample length was measured before and after each test by a Mitutoyo Digital ABS Height Gauge with ± 0.03 mm maximum permissible error. The mass was measured before and after each test run by a Kern EW150-3M balance with 0.01 g precision.

During the new experimental campaign in nitrogen plasma flow we performed 14 test runs summarized in Table 12. Three test samples of two different bulk graphite grain sizes were machined for this study (six samples total); grain size 0.008 inch (0.2 mm) and 0.001 inch (0.025 mm) denoted as G8 and G1 in the following. The 0.008 grain size graphite was machined from an high density extruded graphite rod with density 1760 kg/m^3 , the 0.001 grain size from an isostatically pressed high strength graphite rod of density 1810 kg/m^3 ; more material data related to the two graphite types is given in Appendix B.



(a)



(b)

Figure 31: Test sample geometry (monolithic) and mounted on sample holder.

Table 12: Summary of the test results for the two graphite grains: G8 stands for grain size 0.008 inch (0.2 mm) and G1 for 0.001 inch (0.025 mm); the table lists test and sample ID (three samples, once reused at higher heat flux), test chamber static pressure p_s , dynamic pressure p_{dyn} , electric power P_{el} , average wall temperature T_w , total recession s , and total mass loss m .

Test-ID	sample ID	p_s hPa	p_{dyn} Pa	P_{el} kW	T_w K	Δs mm	Δm g
<i>G8-1.15_370</i>	008A-1	1500	n/a	370	2413	0.60	2.81
<i>G1-1.15_370_bis</i>	001-1	1500	n/a	370	2481	0.62	2.58
<i>G8-2.100_370</i>	008A-2	10000	58.8	370	2596	0.29	1.17
<i>G1-2.100_370</i>	001-2	10000	56.7	370	2613	0.24	1.51
<i>G8-3.200_370</i>	008A-3	20000	33.4	370	2609	0.20	0.68
<i>G1-3.200_370</i>	001-3	20000	36.2	370	2663	0.16	0.98
<i>G8-1.15_400</i>	008A-1	1500	n/a	400	2492	0.52	2.18
<i>G8-2.100_400</i>	008A-2	10000	70.2	400	2694	0.39	1.07
<i>G8-3.200_400</i>	008A-3	20000	39.3	400	2678	0.26	0.67
<i>G1-1.15_400</i>	001-1	1500	n/a	400	2531	0.52	2.37
<i>G1-2.100_400</i>	001-2	10000	66.9	400	2729	0.22	1.18
<i>G1-3.200_400</i>	001-3	20000	42.5	400	2709	0.28	0.69
<i>G8-1.15_370_bis</i>	008-1	1500	n/a	370	2426	0.46	1.98
<i>G8-2.15_300</i>	008-2	1500	n/a	300	2190	0.21	1.81
<i>G8-3.200_400</i>	008-3	10000	n/a	300	2370	0.15	0.65

The first test runs have been performed for samples of both grain sizes at a Plasmatron electric power of 370 kW at test chamber static pressures of 15 hPa, 100 hPa, and 200 hPa. Then another set of test runs was performed at higher Plasmatron power of 400 kW, reusing the already tested graphite samples (which had suffered from barely any recession due to the nitrogen atmosphere).



The plasma flow was started with pure argon before switching to the nitrogen test gas. The test sample remained injected during the argon startup for a pre-heating, surface cleaning and removal of any possibly trapped water. The test sample was then removed and the test gas switched to nitrogen. Once the plasma flow was stabilized, data acquisition was triggered and the test sample was injected for a total duration of 360 s. It took approximately one minute for the surface temperature to settle at steady state and the sample remained for another five minutes in a steady ablation condition (Fig. 33 and Fig. 34).

Table 12 presents a summary of the test results for the two graphite grains, listing test and sample ID (three samples, once reused at higher heat flux of 400 kW), test chamber static pressure p_s , dynamic pressure p_{dyn} , electric power P_{el} , average wall temperature T_w , total recession s , and total mass loss m . For the low chamber pressure of 15 hPa no dynamic pressure measurements were available (n/a) due to the measurement limit of the used Validyne membrane (max. 300 Pa). This was selected in order to have higher sensitivity at low dynamic pressure (higher static chamber pressure). Another calibration run is foreseen to obtain those values.

A visual summary of the test results is given in Fig. 32 plotting total recession Δs and total mass loss Δm in dependence of surface temperature. Circles indicate test samples made of G008 graphite whereas triangles indicate G001 graphite samples.

As introduced above, the G8 samples have a slightly lower density (1760 vs 1810 kg/m³) and a higher thermal conductivity (130 vs 85 W/(m².K/m)) than the G1 samples, which may explain the slightly higher surface temperature for G1 samples for each single test condition. The water-cooled holding stem acts as a heat sink and removes heat from the sample during steady condition.

From both plots of Fig. 32 a very slight increase of recession and mass loss with surface temperature is apparent for each pressure. But more importantly, low pressure tests (15 hPa, black) lead to highest recession and mass loss whereas lowest recession and mass loss appear for high pressure tests (200 hPa, red). We note that mass loss measurements count the total mass loss of the test sample, including possible side- and backwall ablation, whereas recession measurements with the caliper were solely taken at the stagnation point region (total length for the test sample, assuming the holding plug inside the cooled holder did not ablate).

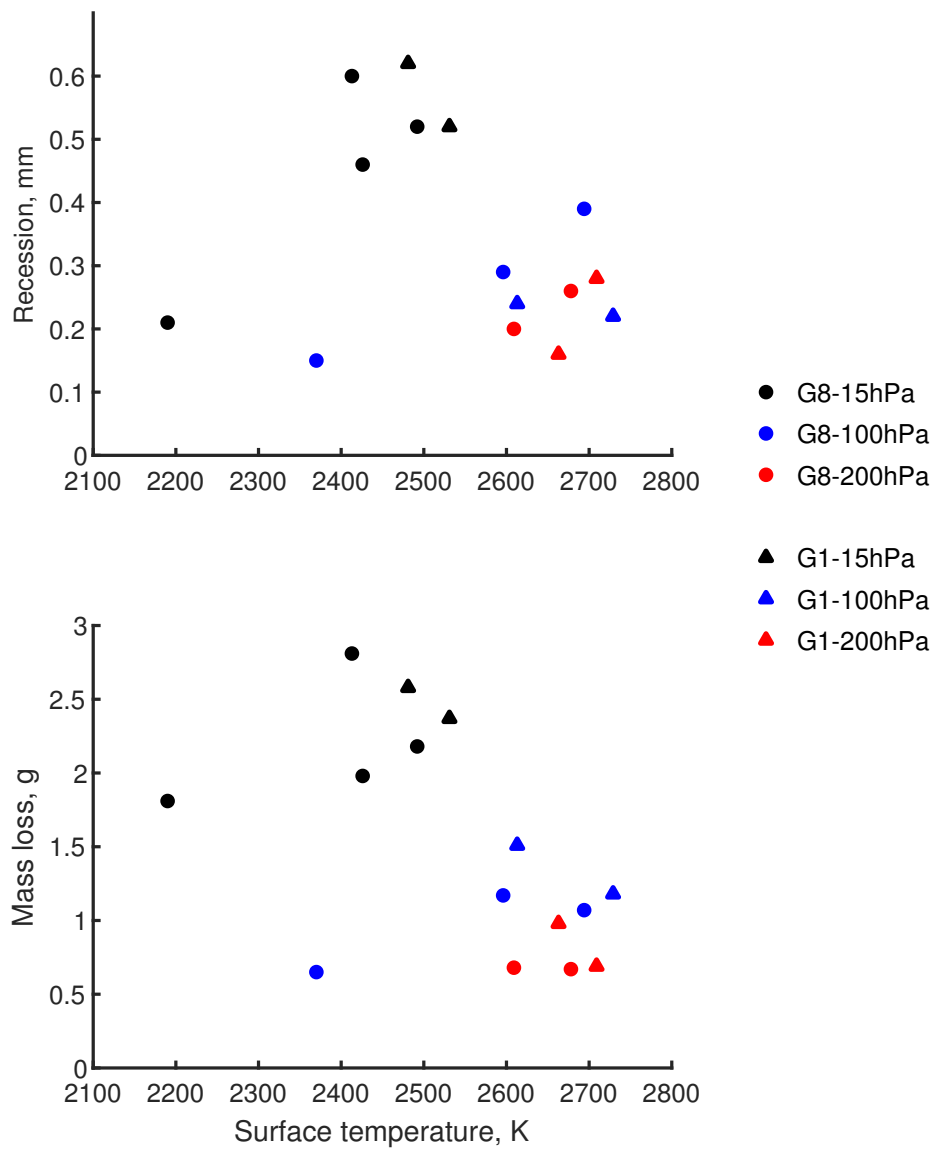
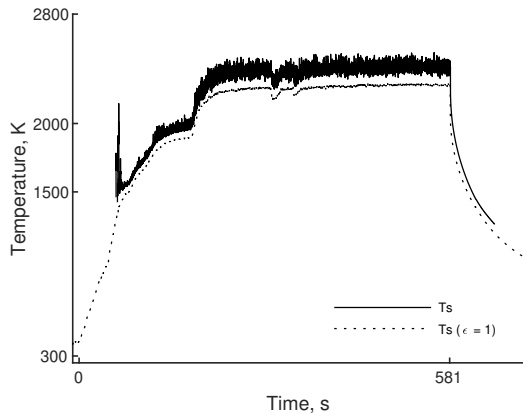
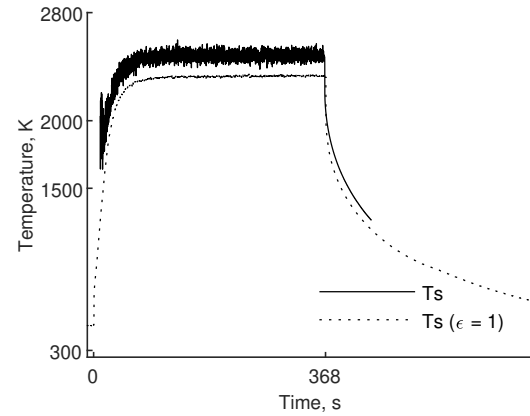


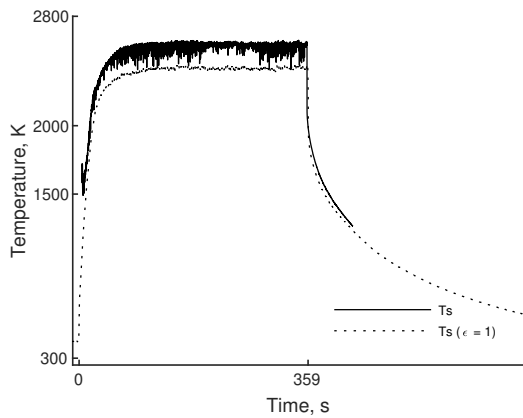
Figure 32: Summary of mass loss and recession for the three static chamber pressures (black: 15 hPa, blue: 100 hPa, red: 200 hPa) for the two different grains (G008: circle, G001: triangle); the data suggests higher mass loss and recession at low pressure and a higher mass loss for the smaller grain size (which responded with higher surface temperature for all test conditions); accuracies: $\delta s = \pm 0.03$ mm, $\delta m = \pm 0.01$ g.



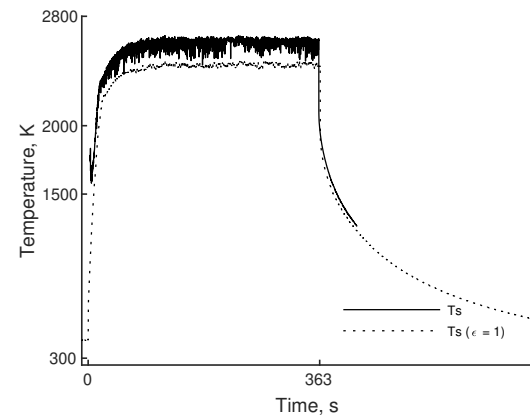
(a) G008, 15 hPa



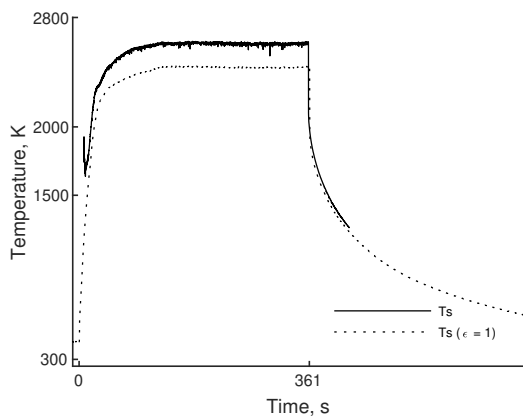
(b) G001, 15 hPa



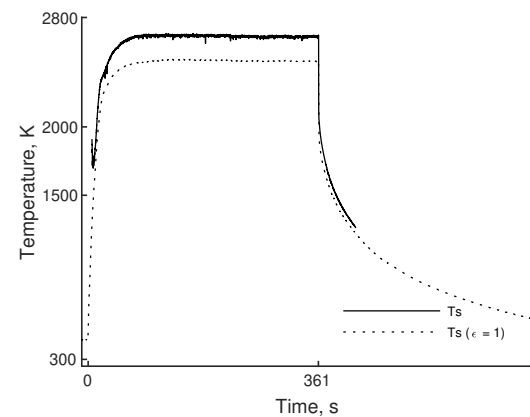
(c) G008, 100 hPa



(d) G001, 100 hPa

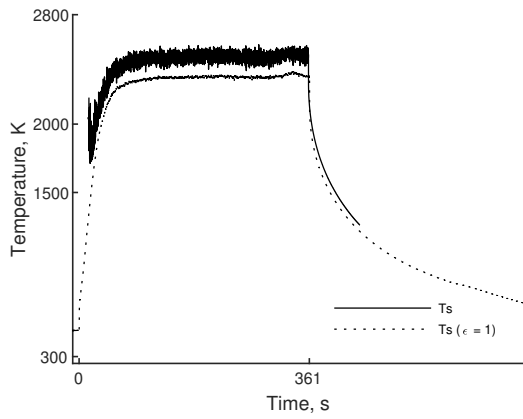


(e) G008, 200 hPa

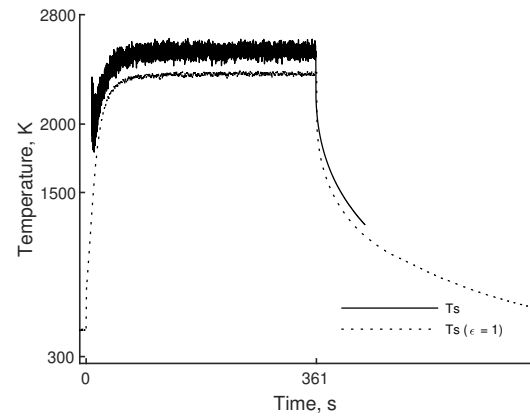


(f) G001, 200 hPa

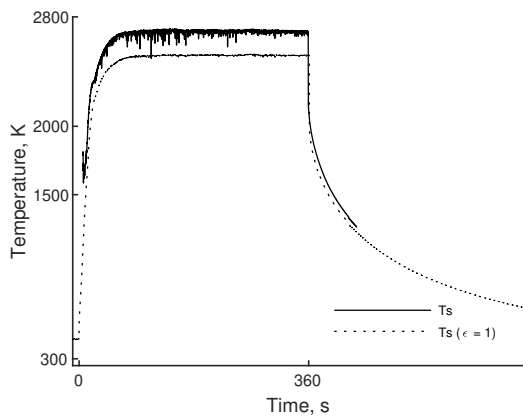
Figure 33: Surface temperatures for G008 and G001 at 370 kW and pressures of 15, 100, and 200 hPa static chamber pressure.



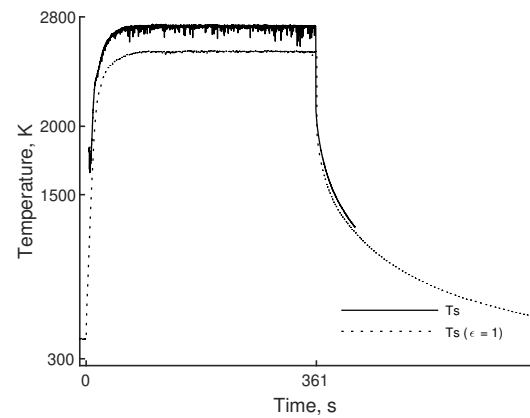
(a) G008, 15 hPa



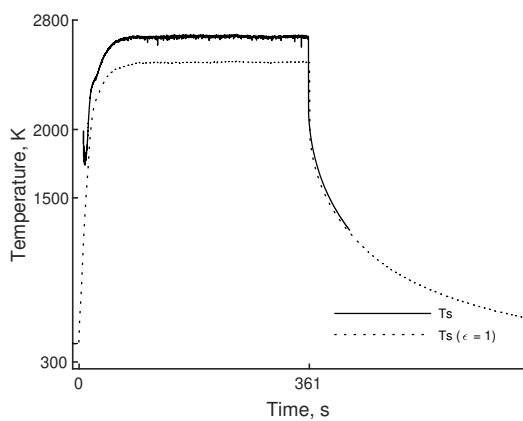
(b) G001, 15 hPa



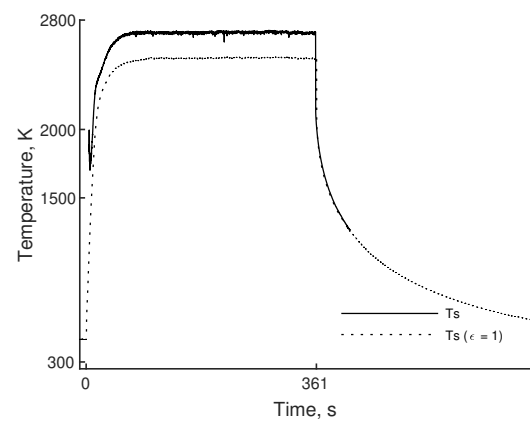
(c) G008, 100 hPa



(d) G001, 100 hPa



(e) G008, 200 hPa



(f) G001, 200 hPa

Figure 34: 400 kW.



4. Conclusion

In this report, we highlighted the major theoretical, numerical, and experimental research activities, conducted at the von Karman Institute for Fluid Dynamics with the aim of improving our understanding of gas-surface interaction phenomena.

The activities were divided in two tasks. During the year 2018-2019, we focused our attention on accomplishing task 1: review of the experimental methods and facility setup as well as of the data concerning the gas surface interaction of different experimental campaigns; furthermore equations describing the the gas-surface interaction were abstracted and included in the VKI library MUTATION⁺⁺.

Task 2, continued within the following 2 years, focused on the investigation of complex gas-surface interaction phenomena. Within this framework, equations describing thermal non-equilibrium at the surface were derived and included in the MUTATION⁺⁺ library. It was shown that assuming strong non-equilibrium at the surface better capture the experimentally observed temperature, both in the boundary layer and on the surface, while still well describing the surface recession. As second step, the finite rate chemistry model derived by Prof. Schwartzentruber team in relation to the AFOSR Grant FA9550-17-1-0057 *Nonequilibrium Gas-Surface Interactions at High Temperature*, was included in the MUTATION⁺⁺ library and validated. Numerical investigations revealed that the model, even if predicting a lower recession rate of the material, is able to capture reaction pressure dependence and nitrogen surface recombination. The VKI team also provided help to the University of Minnesota for the coupling of the MUTATION⁺⁺ library with the US3D solver, making available both the gas surface interaction model and gas phase state-of-the-art modeling.

Along with the recent advances in numerical modelling, VKI conducted an experimental campaign on the ablation phenomena of graphite nitrogen plasmas. The nitrogen ablation tests provide experimental data for the further development of phenomenological models of the surface nitridation process and the surface reactivity to nitrogen recombination. The nitrogen tests cases have been conducted at various pressures and plasma power levels. Contrary to numerical predictions, the experimental data suggests increased surface recession and material mass loss at lower test chamber pressures. Additional numerical simulations of each particular test condition at various pressures are required for a better understanding of the obtained test results. Those can in turn be used to update and tune the FRC model coupled to the stagnation line 1D code description.

In total, two post-doctoral and one post-graduate student received funding from this activity for pursuing the above mentioned tasks:

- J. Scoggins, one year of Postdoc, work summarized in the article attached at pag.;



- G. Bellas-Chatzigeorgis, one year of Postdoc, article in preparation;
- M. Capriati, two year of PhD, work summarized in the proceedings at pag. and pag. .

Furthermore, it allowed to support the *master after master* degrees of visiting Belgian and American students K. Devesse and G. Kale, who were followed by the VKI team.

Hypersonic in-flight experiments, being no longer of prohibitive cost, can offer a complementary approach to study the complexity of hypersonic flows and related phenomena, which are generally duplicated and decoupled in ground-test facilities. As future prospective, thus, we propose a synergy between on-ground and a potential in-flight experiment, defined through numerical simulations and Plasmatron ground testing. Both will be coherently linked through state-of-the-art uncertainty quantification techniques for definition of the test conditions.

Appendices

A. STAGLINE

When dealing with axisymmetric problems, a Dimensionally Reduced Navier-Stokes Equations (DRNSE) formulation [72] can be used to simulate the flowfield on the stagnation line. The set of equations is written in spherical coordinates (r, θ, ϕ):

$$f(r, \theta) = f^*(\theta)\bar{f}(r). \quad (16)$$

Exploiting the axial symmetry of the problem, $f^*(\theta)$ is equal to $\cos \theta$ for u, p, T , and ρ_i and to $\sin \theta$ for u_θ .

Applying the Newtonian theory for hypersonic flow the wall pressure reads:

$$p_{wall} - p_\infty = \frac{1}{2}\rho_\infty u_\infty^2 \cos^2 \theta, \quad (17)$$



leading the variables to be expressed as:

$$\begin{aligned}\rho_i(r) &= \bar{\rho}_i(r), \\ u_r(r, \theta) &= \bar{u}_r(r) \cos \theta, \\ u_\theta(r, \theta) &= \bar{u}_\theta(r) \sin \theta, \\ p(r, \theta) - p_\infty &= \bar{p}(r) \cos^2 \theta, \\ T(r) &= \bar{T}(r), \\ T^\nu(r) &= \bar{T}^\nu(r).\end{aligned}$$

Letting $\theta \rightarrow 0$, the Navier-Stokes equations can be reduced to a quasi one-dimensional formulation. It reads:

$$\frac{\partial \mathbf{U}}{\partial t} + \frac{\partial \mathbf{F}^{\text{inv}}}{\partial r} + \frac{\partial \mathbf{F}^{\text{diff}}}{\partial r} = \mathbf{S}, \quad (18)$$

where, omitting the overline for sake of simplicity, the conservative variables vector is:

$$\mathbf{U} = (\rho_i, \rho u_r, \rho u_\theta, \rho E, \rho e^\nu)^T, \quad (19)$$

the inviscid flux is:

$$\mathbf{F}^{\text{inv}} = (\rho_i u_r, p + \rho u_r^2, \rho u_\theta u_r, \rho E, \rho u_r e^\nu)^T, \quad (20)$$

and the diffusive flux is:

$$\mathbf{F}^{\text{diff}} = (\rho_i V_i^D, \tau_{rr}, \tau_{r\theta}, \tau_{rr} u_r - q, q^\nu)^T. \quad (21)$$

The right-hand side of equation 18 is a vector containing the sources due to chemistry and energy transfer, and geometrical sources as a result of the coordinate system change ($\mathbf{S}^G$) reading:

$$\begin{aligned}\mathbf{S}^{\text{NV}} &= (\dot{\omega}_i, 0, 0, 0, \sum_m^{\mathcal{I}} \Omega^m)^T, \quad (22) \\ \mathbf{S}^G &= -\frac{1}{r} \begin{bmatrix} 2\rho_i(u_r + u_\theta + V_i^D) \\ 2(\rho u_r(u_r + u_\theta) - \bar{\tau}_{rr} - \bar{\tau}_{r\theta} + \bar{\tau}_{\theta\theta}) \\ 3\rho u_r(u_r + u_\theta) - 2(p - p_\infty) - 3\bar{\tau}_{r\theta} + \bar{\tau}_{\theta\theta} \\ 2\rho(u_r + u_\theta)H - 2(\bar{\tau}_{rr}u_r + \bar{\tau}_{r\theta}u_r + \bar{\tau}_{\theta\theta}u_\theta - q) \\ 2\rho(u_r + u_\theta)e^\nu - 2q^\nu \end{bmatrix}. \quad (23)\end{aligned}$$

Munafò [73] developed a CFD solver for the DRNSE equations based on a finite volume discretization method, together with an implicit local time-stepping technique to reach the steady state. The code interfaced to MUTATION++ helps us to verify the coupling of US3D to MUTATION++, using the Roe scheme [74] for the numerical fluxes.



B. Graphite data sheets

Grade: GR008G

Manufacturer: Graphtek LLC
Method of Manufacturing: Extruded
Description: Superfine grain, high density extruded graphite rod
Comparable Grades: 580

Property	US Value		Metric Value	
Particle Size	0.008	in	0.02032	cm
Density	0.064	lb/in ³	1.76	gr/cm ³
Flexural Strength	4200	psi	29.0	MPa
Compressive Strength	8200	psi	55.8	MPa
Resistivity	5.5	ohmXinX10 ⁻⁴		
Thermal Conductivity	75	BTU/(h.ft ² °F/ft)	130	W/(m ² .K/m)
CTE	1.1	in/in °F x 10 ⁻⁶	2.0	Microns/m °C
Temperature (Air)	750	°F	399	°C
Temperature (Inert)	5000	°F	2760	°C
Ash	0.06	%		%

Grade: GR001CC

Manufacturer: Graphtek LLC
Method of Manufacturing: Isostatically Pressed
Description: High Strength, wear resistant graphite

Property	US Value		Metric Value	
Density	0.065	lb/in ³	1.81	gr/cm ³
Shore Hardness	60			
Flexural Strength	7250	psi	50	MPa
Oxidizing Atmosphere	801	°F	427	°C
Neutral Atmosphere	5000	°F	2760	°C
Porosity	12	% VOL		% VOL
Electrical Resistivity	0.00055	Ω·in		Ω·m
Thermal Conductivity	750	BTU/(h.ft ² °F/ft)	85	W/(m ² .K/m)
Ash Content	100	ppm		
CTE	2.6	in/in °Fx10 ⁻⁶	4.6	Microns/m °C



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