



MIXING AND NON-PREMIXED COMBUSTION AT SUPERCRITICAL PRESSURES

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To my dad

ABSTRACT

This thesis is devoted to the numerical investigation of mixing and non-premixed combustion of cryogenic propellants at supercritical pressures. These severe conditions are commonly encountered in high pressure combustion chambers, such as those of liquid-fueled rocket engines (LRE), and lead to significant deviations from the ideal gas thermodynamic behavior of the reacting mixtures.

The non-premixed laminar flame structure of liquid oxygen (LOx) and methane or liquid natural gas (LNG) mixtures, a recently proposed LRE propellants combination, is investigated by means of a general fluid unsteady flamelet solver. Real gas effects are analyzed on prototypical unsteady flame phenomena such as autoignition and re-ignition/quenching caused by strain perturbations. Such effects influence different flame regions depending on pressure, as well as the critical strain values that a laminar flame can sustain before quenching occurs. Moreover the flame structure is also influenced by the composition of the LNG, in particular the early stage soot precursors production and oxidation.

In order to shed light on real gas mixing, a low-Mach approximation for real gas reacting mixtures is presented. A single species non-reacting real gas model is implemented in a highly scalable spectral element computational fluid dynamic (CFD) code with state of the art thermodynamic and transport properties. Transcritical and supercritical planar temporal jets, are chosen as representative test cases for investigating high-pressure mixing by means of direct numerical simulations. The pseudo-boiling phenomenon, occurring in transcritical flows, significantly influences the jet development, mitigating the development of shear layer instabilities and leading to a liquid-like jet break-up. Moreover pseudo-boiling is confined in a narrow spatial region suggesting particular care in the turbulent combustion modeling of non-premixed flames when transcritical thermodynamic conditions are encountered.

The results of the present thesis, its physical insights as well as the modeling considerations involved, can be of support in the development of future CFD tools capable of simulating real engine operative conditions and configurations.

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The purpose of computing is
insight, not numbers

R. Hamming, 1962
*Numerical Methods for Scientists
and Engineers*

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INTRODUCTION

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1.1 HIGH PRESSURE COMBUSTION

Combustion in practical systems, such as aeronautical engines, rockets, gas turbines etc., is usually characterized by high pressures and elevated turbulence levels in order to achieve optimal efficiency and reduced geometrical size. It is known that pressure increases combustion intensity, in terms of energy released per unit volume, resulting in higher energy output as well as higher system efficiency. In fact high pressures combustion devices, such as gas turbines and chemical rocket engines, have been successfully utilized for decades. While these are relatively mature technologies, the complex phenomenology occurring in such devices is only partially understood. New challenges including increased performance of the devices, with constraints such as restricted budgets and short development time as well as reduced pollutants emissions are motivating substantial research interests.

In this framework, the role of computational fluid dynamics (CFD) for simulating turbulent combustion is nowadays becoming crucial. The reason why CFD is becoming more and more attractive, with the ever increasing computing resources, is essentially twofold: on one hand CFD simulations of real engines geometries and operating conditions can lower the development costs acting as a

relatively cheap surrogate of experimental tests, on the other hand it can provide fundamental physical insights on the combustion phenomena using simplified configurations. Generally speaking turbulent combustion involves complex and highly non-linear interactions of turbulent and molecular transport with chemistry over a wide range of time and length scales. Moreover combustion chamber operating conditions characterized by elevated pressures, can cause the propellants to burn under thermodynamic conditions far removed from the ideal gas assumptions, increasing the physical modeling effort needed in order to achieve high fidelity simulations.

Despite the progress in computer science and hardware, direct numerical simulations (DNS) of these multi-scale problems are presently feasible only for a range of prototypical flame configurations. This approach is a useful tool for fundamental research since it can be considered a *numerical experiments*^[20] from which it is possible to extract information difficult or impossible to obtain experimentally. Thus DNS simulations are useful in the development of turbulent combustion models for practical applications, such as sub-grid scale (SGS) models for large eddy simulation (LES) and simplified models for methods that solve Reynolds averaged Navier Stokes equations (RANS) useful at system design level. This can be done by analyzing the results produced by a particular model using the DNS results as an input, in *a priori* fashion, or alternatively using *a posteriori* tests, in which the model results are compared to the DNS data. This is even more important due to the non-trivial nature of high-pressure mixing and combustion experiments. They rarely provide all the data necessary for the development and validation of turbulent combustion and mixing models, especially including pollutants formation in turbulent high pressure flames.

1.2 COMBUSTION IN LIQUID ROCKET ENGINES

Space propulsion is probably one of the most extreme application of energy conversion by means of combustion. This takes places at elevated or even supercritical pressures into chemical liquid rocket engines (LRE) combustion chambers. For this kind of devices the most significant technological trend over the years was increasing the thrust levels. This trend promoted a significant increase of the operating pressures inside the combustion chambers in order to improve performances (which can be estimated by the vacuum specific impulse¹) and allows engine to remain reasonably sized. However, this rise

¹ The specific impulse is defined as the time that 1Kg of propellant can give a thrust of 9.8N in vacuum

in the operating pressure levels causes at least two main drawbacks. Firstly wall heat transfer in combustion chamber of a LRE scales almost linearly with pressure, thus causing additional loads for both the structures and the cooling system. Secondly, typical operating pressures are above the critical pressure of a large part of the propellant combinations which are typically used by LRE. This, combined with the cryogenic conditions usually encountered in the feeding line systems, implies that the propellants will most likely behave like complex fluids rather than an ideal gas or liquid. Even if this does not directly impact engine performance or stability of operations, it poses serious challenges to the physical understanding and the numerical modeling.

1.2.1 Supercritical mixing and combustion

As previously mentioned, the operating conditions can cause the LRE propellants to be injected at pressures and temperatures that approach or exceed their thermodynamic critical point. One or both of the reactants can be injected in a liquid-like state, at a temperature which is below the critical value², in an environment where the pressure exceeds the critical pressure. These conditions are usually referred to as trans-critical, inducing real gas effects on both the mixing and combustion processes. Real gas effects consist in abrupt changes of thermodynamic and transport properties such as mixture density, enthalpy, constant pressure specific heat, viscosity and a vanishing surface tension which eliminates the liquid-gas interface [21].

Trans-critical injection is commonly encountered in high performance liquid rocket engines, which widely utilize liquid oxygen (LOx) [22] in conjunction with fuels such as liquid hydrogen (LH₂), kerosene (RP1) and more recently methane [23]. The fuel is generally injected under supercritical conditions ($T > T_{cr}$, $p > p_{cr}$ where subscript *cr* stands for critical) while the oxidizer, the liquid oxygen (LOx), is invariably in a trans-critical state ($T < T_{cr} = 154.6$ K, $p > p_{cr} = 50.43$ bar) during injection. Indeed, the injection temperature of LOx, typically between 80 K and 120 K, can be significantly lower than its critical temperature thereby enhancing real gas effects and strongly influencing the injection and non-premixed combustion processes.

The injection plate controls the introduction of the propellants to the combustion chamber trying to achieve the best distribution and mixing of fuel and oxidizer. Many injector designs have been used and tested over the years, such as doublet and triplet impinging jets, swirl injectors, shower head and coaxial

² More precisely below the pseudo boiling temperature, which is usually slightly above the critical temperature, more details will be given in section 6

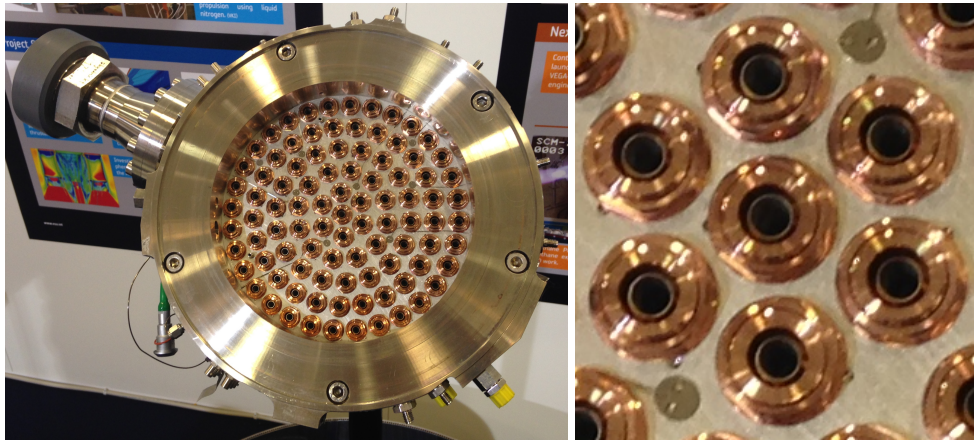


Figure 1.: Injector plate of a reduced-scale liquid rocket engine (left), detail of the coaxial injectors (right). Courtesy of the ESA stand at the Space Propulsion conference in Rome, May 2016.

hollow post injectors. The latter remain one of the most used configuration, due to its geometrical simplicity and mixing efficiency caused by the large shear between the fuel and oxidizer streams as shown in fig. 1.

1.2.2 Methane as a space propulsion fuel

A substantial part of the technological and research efforts of the space industry and agencies is nowadays devoted toward the development of high performance and relatively low-cost engines. This includes the adoption of new technologies such as composite materials and additive manufacturing technique as well as the research of new propellants combinations. Methane or Liquefied Natural Gas (LNG) have been recently considered a promising fuel, together with cryogenic oxygen, for liquid rocket engines applications, having shown some advantages over the commonly used propellants such as liquid hydrogen or kerosene. In particular it has shown reduced costs of supply, tanking, handling with respect to LOx/LH₂ fueled systems and higher performance and flexibility potential with respect to LOx/kerosene propellants combination, resulting in a good trade-off solution between them. This remain true for a large number of propulsion systems applications ranging from first stage and boosters to upper-stage and deep-space devices [24].

Methane, the lightest hydrocarbon (HC), is characterized by a critical temperature of 190.56 K and a critical pressure of 51.72 bar. Therefore it is a low density ($\rho = 0.639 \text{ kg/m}^3$) supercritical gas at standard conditions (room temperature and atmospheric pressure), and it become a liquid ($\rho = 423 \text{ kg/m}^3$) below a boiling temperature of $T = 111.5\text{K}$. These thermodynamic characteristics make

methane a *soft cryogenic* propellant with a relatively low toxicity and corrosively power, thanks to the absence of sulphur compounds in its composition. Therefore it is relatively easy to handle and store, requiring less insulation with respect to comparable hydrogen fuel systems. Being approximately six time denser, methane has significant advantage over hydrogen in terms of volumetric specific impulse. From the performance point of view, a simple measure of propellants performance is the vacuum specific impulse [22], which is ≈ 350 s for RP1-kerosene and ≈ 370 s for methane, the highest out of common hydrocarbons. Moreover, coking and sooting tendencies of methane are relatively low compared to kerosene and other complex hydrocarbon fuels, thus allowing for better characteristics in terms of reusability, multiple-restarts and longer burn times [23].

The mentioned possible technological advantages of the use of methane as a fuel in LRE's have recently promoted the interest of the Italian Space Agency (ASI) and the Italian aerospace Industry promoting research projects. The principal aim is the acquisition of technological and scientific expertise and the development of a methane fueled expander-cycle upper-stage LRE for upgrading the already successful Vega launcher [25] to Vega-E.

1.3 STATE OF THE ART

Despite the great experimental and theoretical/numerical effort in the past decades, supercritical mixing and combustion processes are still to be completely understood, motivating a substantial research effort. Three of the main areas of turbulent combustion modeling of non-premixed combustion (flame structure, turbulent mixing and turbulence chemistry interaction) are explored in the following brief literature review.

1.3.1 Laminar flame structure at supercritical pressures

The inner structure of a diffusive flame can be described by temperature and species distribution as function of the local stoichiometry, or of physical spatial coordinate in a simple laminar configuration [26]. In order to analyze the flame structure characteristics at supercritical pressures, recently the counterflow diffusion flame configuration has been numerically investigated as a prototype for supercritical non-premixed combustion. Fundamental characteristics have been analyzed, such as the dependency of burning rate on the mass transfer from the trans-critical regions [27], the effect of pressure, the effects of flow strain rate

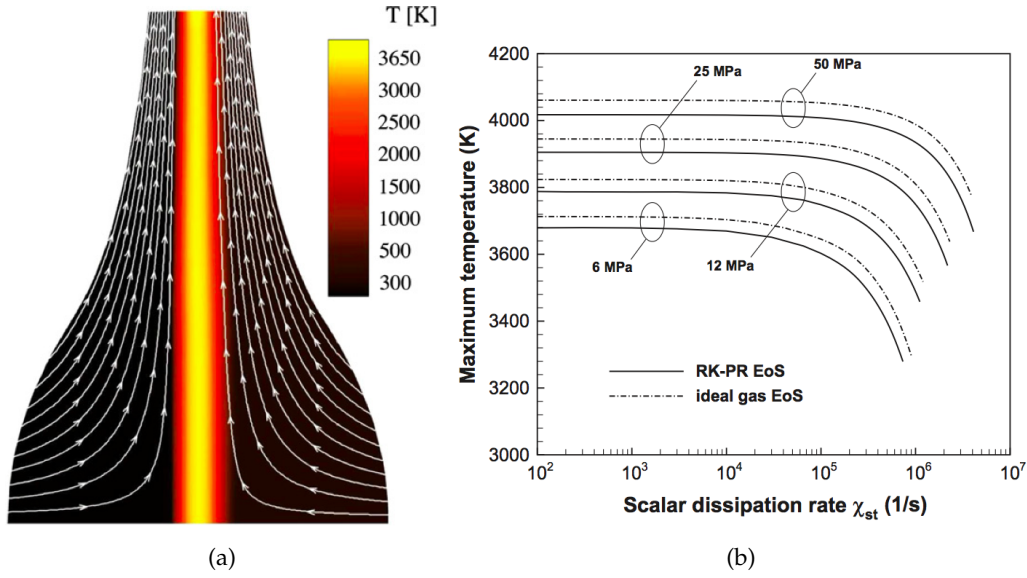


Figure 2.: Laminar flame structures at supercritical pressures: (a) Temperature field and the flow topology of a LOx/Hydrogen supercritical counterflow flame [1], (b) stable branch of the flamelet S-shape diagram for LOx/Kerosene non-premixed supercritical combustion [2].

and inlet temperature on flame structures [28], heat release rate profiles and extinction limits [29, 30]. It has also been observed that, in such configurations, the mixture never reaches a thermodynamic saturated state, wherein two-phase flow may occur, thus demonstrating that the dense-fluid single-phase approach, coupled to an appropriate equation of state and realistic transport and thermodynamic modeling can be indeed used within a flamelet framework [1]. Most of the existing studies of high-pressure counterflow diffusion flames have focused on the oxygen/hydrogen system, while the pure oxygen/methane mixture is less investigated [31].

An alternative approach in the context of supercritical and trans-critical non-premixed combustion is the direct solution of the flamelet equations in mixture fraction space. Such an approach, albeit for ideal mixtures, has been effectively used to analyze transient effects, such as quenching characteristics [32], or autoignition phenomena [33] or to compute libraries in the context of unsteady flamelet progress variable approaches (UFPV) [34, 35]. The direct approach has also been used to analyze supercritical hydrogen/oxygen [36] and kerosene/oxygen [2] flame structures, albeit in the context of steady state flamelet solutions, while unsteady effects remain unexplored.

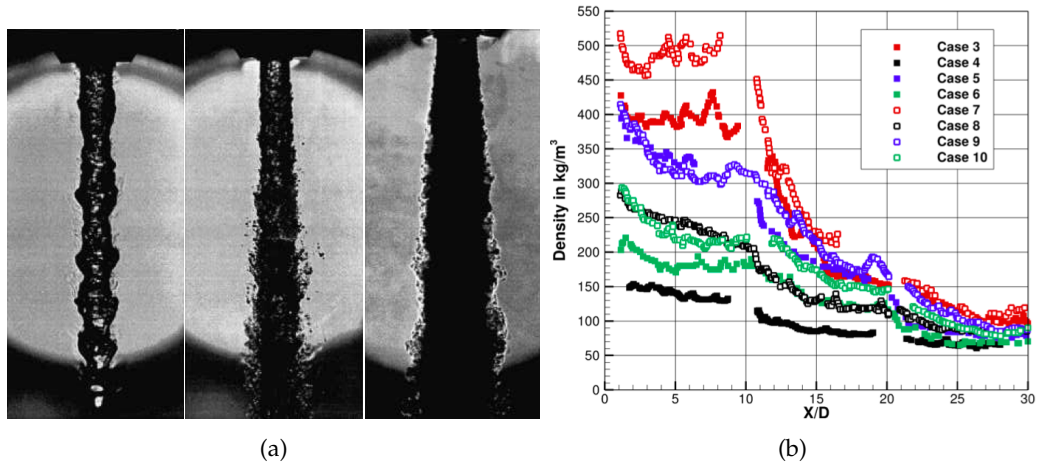


Figure 3.: Injection of nitrogen into pressurized chambers: (a) Experiments from subcritical to supercritical pressures [3](from left to right 20,30 and 40 bar respectively, (b) centerline density profiles of nitrogen jet experiments, figure taken from the thermodynamic interpretation of such data [4].

1.3.2 Mixing at supercritical pressures

Mixing phenomena occurring in devices which uses purely diffusive (non-premixed) flames, such as LRE, are of fundamental importance as they directly impact combustion efficiency [37]. Contrary to premixed flames where a characteristic flame propagation speed is well defined given its combustion wave nature [38], a diffusive flame does not impose directly its own dynamics on the flow field, making it intrinsically more influenced by turbulent motions. Therefore it is important to understand the physical processes involved in turbulent mixing, which is complicated by the supercritical pressure, in particular when transcritical conditions are encountered. These conditions, where large thermodynamic transitions at the pseudo-critical temperature are encountered, are usually referred as *pseudo vaporization* or *pseudo boiling* [39].

Many experiments have been carried out, focused on injection and mixing processes at elevated pressures, mainly at the German Aerospace Center (DLR) and the Air Force Research Laboratory (AFRL). The experiments consisted in injection of cryogenic liquids at subcritical or supercritical pressure and important results of these experimental campaigns have been published by many authors, [40, 41, 42, 43, 16, 44, 45, 46]. Different aspects and data are discussed in each paper, such as: the pressure effect on the thermodynamic characteristic of injection, the jet atomization and break-up mechanism and the strong anisotropy of turbulence due to the large density stratification between

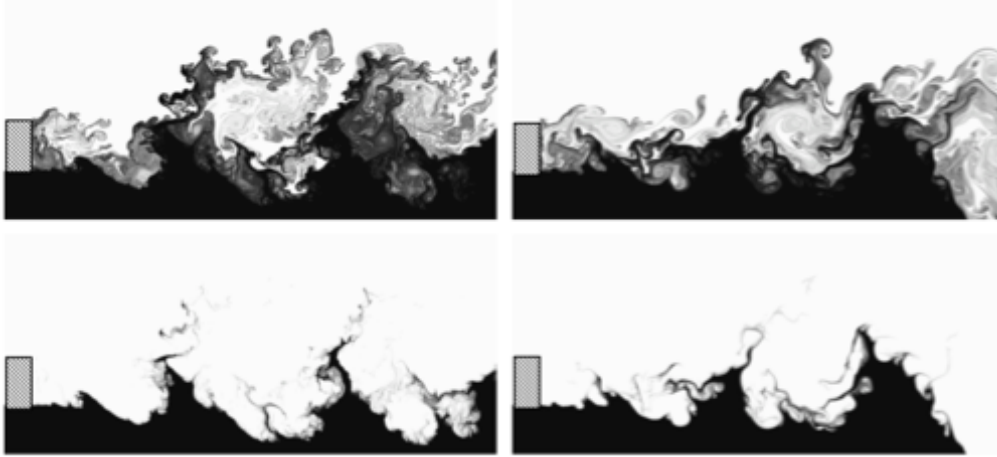


Figure 4.: Two-dimensional numerical benchmark of transcritical mixing of LOx and hydrogen behind a splitter plate [5]. Comparison between two state-of-art CFD tools AVPB-RG [6] (left column) and RAPTOR [7] (right column), in terms of LOx mass fraction (first row) and density (second row).

the injected and ambient fluid. Despite ambiguities in the definition of the experimental injection conditions and some difficulties in the interpretation of the results, which have been highlighted in a recent paper from Banuti and Hanneman [4], the campaign remains one of the most thoroughly documented of pure fluid cryogenic injection at high pressures. Therefore all the experiments mentioned above are of high practical value as they remain very useful for CFD code validation, research groups have simulated it in both RANS [47, 48] and LES context [49, 50, 51, 52] mainly as a starting point to develop reactive CFD solvers. Similar nitrogen thermodynamic conditions have been used for coaxial jets configurations to further investigate the effects of the pseudo vaporization on the jets dynamics. The pseudo vaporization influence on the behavior of the inner core of coaxial jets was investigated by Hosangadi et al. [53] using a hybrid Large-eddy simulation (LES)/Reynolds-averaged Navier-Stokes (RANS) simulation method. In LES context Zong et al. [54, 55] investigated the impact of the large density stratification and of the pseudo vaporization on the round jet shear layer instabilities. However, the investigation on the influence of the pseudo vaporization upon the small-scale turbulence and flow features can be consistently evaluated only by means of DNS.

Pioneering and recent works of Bellan and collaborators [56, 57, 58, 59, 60, 61, 62, 63, 64, 65] highlighted important insights investigating temporal binary-species mixing layers under supercritical conditions in order to examine, by means of DNS, the turbulence characteristics of supercritical fluids from micro- to macro-scale as well as LES sub-grid contributions in both a priori and a

posteriori fashion. Moreover they suggested that the growth and turbulent transition of mixing layers are influenced by the thermodynamic difference between the binary fluids. However, because they focused on mixing layers composed of gas-like fluids above the pseudo-critical temperature, the influence of the pseudo vaporization behavior was never taken into account. Similarly the DNS of Battista et al. [66], focused only on supercritical conditions for nitrogen non-isothermal mixing using a spatially evolving co-flowing jet with simplified real gas EoS. Nitrogen temporal mixing layer under transcritical thermodynamic condition was simulated by Tani et al. [67] to explore the effects of the pseudo vaporization on turbulent structures and transport mechanism. Transcritical conditions effects were also addresses from the numerical method point of view [68, 69, 70] and to establish a CFD benchmark for supercritical flow at high-Reynolds number and high-density ratio using two-dimensional DNS of a binary LOx/hydrogen mixture [5].

1.3.3 Turbulent non-premixed flames at supercritical pressures

The experimental effort on supercritical combustion in the past two decades has focused on coaxial flows at high pressures, representative of actual rocket engines conditions. Most of the existing studies have focused on liquid oxygen and gaseous hydrogen mixtures, investigating supercritical combustion at pressures up to 100 bar. Experimental evidences showed vanishing surface tension of the propellants and that the cryogenic jet flame is always attached to the LOX post because of the creation of a strong recirculation zone. Temperature was shown to be stratified upstream in the radial direction and more homogeneous further downstream where intense turbulent mixing is present supporting the assumption that turbulent mixing is the rate-controlling process [71, 43]. Comparison between the rate of mixing with the rate of the chemistry showed that the flow and chemical time scales were strongly related, highlighting the importance of turbulence chemistry interaction [72].

More recent experiments were performed at ONERA Mascotte test bench on cryogenic combustion with shear-coaxial injector and optical access. Results indicate that the rate of combustion is vaporization-limited when the pressure is below the critical pressure and is mixing-limited when the pressure is above the critical pressure, showing the importance of mixing for rocket combustion chambers designed to operate above the critical pressure of the liquid reactant [73, 74]. The high pressure combustion of LOX and methane were recently investigated [8, 75] showing that the flow and structures formed in the doubly

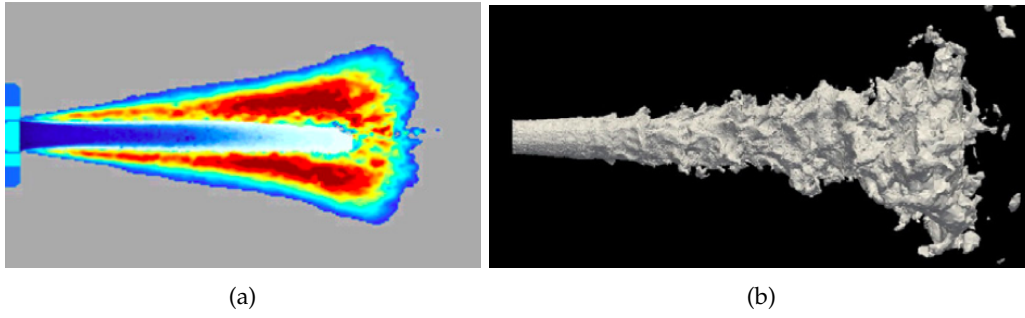


Figure 5.: Transcritical oxygen and gaseous methane injection and combustion: (a) experimental combined Abel transformed emission and backlighting of OH* emission and average jet position [8], (b) temperature q-criterion iso-surface of a large eddy simulation snapshot [9].

trans-critical injection configuration can strongly differ from that where only LOx is injected in a trans-critical state.

Drawing from these experimental findings, recent numerical studies on supercritical combustion are conceptually based on a single-phase mixture model for general fluids that accounts for thermodynamic non-ideality and anomalous transport properties. The general fluid is modeled as a *dense* gas with liquid like density and gas like diffusivities. A unified treatment of fundamental multi-species thermodynamics is commonly employed since the pioneering works of V. Yang [76, 77, 78]. Supercritical combustion simulations, using both LES and DNS in order to characterize the multicomponent diffusion processes in the flame zone of a shear-coaxial injector, were performed in two dimensional configurations [7]. Results show significant real-gas effects in the colder mixing regions and relatively small cross-diffusion ones (Dufour and Soret effects) [79]. The same configuration was used to study the near field flame dynamics of an LOX/methane shear-coaxial injector using LES without any turbulent combustion model and a global chemical mechanism [80]. Flamelet approaches for turbulent combustion models were first adopted in RANS with both hydrogen and methane as fuels [48, 81, 82]. On the other hand fully three dimensional LES of a cryogenic flame was performed using a simplified infinitely fast chemistry flamelet based method [9]. Additional effort has been devoted to the consistent coupling between compressible solvers and supercritical combustion [83].

High pressure turbulent combustion modeling issues were addressed recently, performing compressible DNS of temporal evolving mixing layers of hydrogen and oxygen [84, 85]. However, similarly to the previously mentioned works, these studies are limited to gas-like fluids above the pseudo-critical temperature where real gas effects are present but inherently limited. In this context the

absence of a reliable reactive real gas DNS database, for the development of consistent turbulent combustion models, motivates the development of highly efficient and scalable codes capable of simulating such complex multi-scale phenomena.

1.4 OBJECTIVE AND OUTLINE OF THE THESIS

On the basis of the presented literature review, the need of substantial research effort to improve the current understanding of supercritical mixing and combustion processes is evident. This remains valid for the three main areas of turbulent combustion modeling of non-premixed flames mentioned in the presented literature review. In this framework the aim of this work is essentially threefold.

Firstly develop and validate an efficient real gas mixtures library, capable of add real gas corrections to the well established ideal gas thermodynamic properties, that could be used in the context of reactive solvers. In addition coupling the real gas mixtures library with an unsteady flamelet solver, in order to investigate prototypical unsteady flame configurations such as auto-ignition, re-ignition/quenching as well as analyzing fuel composition effect on the LOx/methane-LNG flame structures at pressures representative of LRE combustion chambers operating conditions.

Secondly derive a low-Mach number approximation for real gas reacting mixtures with arbitrary EoS and transport models since mixing and combustion, in high-pressure combustion chambers, usually occurs at relatively low Mach numbers conditions³. Using this approach is possible to avoid the serious time step restrictions encountered by compressible formulations caused by the extreme speed of sound typical of LRE cryogenic propellants⁴. The EoS independent formulation with its high versatility potential, will allow to include state of the art real gas models for both the EoS, thermodynamic and transport properties.

Finally implement a preliminary non-reacting version of the proposed formulation in the highly scalable open-source spectral element flow solver nek5000. This code has been chosen in order to have a massively parallel infrastructure and to take advantage of high order methods to efficiently resolve the peculiar multi-scale characteristics of supercritical and transcritical reacting flows. Both

³ Some exception can be the ignition sequence and a fast chamber filling

⁴ Cryogenic propellants have usually a liquid-like speed of sound, the LOx speed of sound at 100 K and 60 bar is 1070 m/s, which is at least three time the corresponding standard conditions value (320 m/s)

reason mentioned are of fundamental importance to perform DNS of transcritical and supercritical mixing of a cryogenic nitrogen jets. The mentioned objective are even more motivated since they will allow to set the stepping stones to develop a tool able to perform DNS of high pressure turbulent combustion with detailed chemical kinetics in the low-Mach number limit, in order to shed light on completely unexplored problems such as turbulence-chemistry interaction of complex cryogenic propellants and pollutant formation at supercritical pressures.

The outline of the present dissertation is as follows:

- Chapter 1** A brief overview on the main topics has been presented. In particular it focus on combustion at high pressure and its space propulsion applications as well as state of the art of supercritical mixing and both laminar and turbulent combustion simulations.
- Chapter 2** Real gas thermochemistry concepts and numerical approaches for both pure species and mixtures are recalled. The developed fortran library RGM, for the real gas properties evaluation, using the departure functions formalism, is validated using currently available data.
- Chapter 3** An unsteady real fluid flamelet formulation is presented and used to study the LOx/Methane flame structure at supercritical pressures. Prototypical unsteady laminar flame configurations are used, in order to investigate on autoignition and re-ignition/quenching phenomena.
- Chapter 4** The influence of LNG composition, with respect to the pure methane, on non-premixed combustion at typical LRE operating conditions is analyzed. Qualitatively results on early stage soot precursors and PAH at supercritical pressures are presented.
- Chapter 5** The Low Mach number approximation for real gas reacting mixtures is derived for arbitrary real gas EoS and transport models. An efficient implementation of simplified sub-cases in the highly scalable spectral element code nek5000 is presented and validated.
- Chapter 6** A set of direct numerical simulation of planar temporal evolving nitrogen jets at high pressure are performed using state of the art EoS and transport models. Results are analyzed in order to shed lights on supercritical and transcritical mixing and their structural thermodynamic differences. Sub-grid modeling considerations for LES and RANS approach are addressed and *a priori* evaluated using DNS data.

Appendix A As part of the validation processes of the in-house modifications to the nek5000 code, a deficient reactant combustion model has been implemented. It has been also used to investigate hydrodynamic instabilities in turbulent premixed flames.

2

REAL GAS THERMODYNAMICS

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Combustion under severe thermodynamical conditions, such as those encountered in high pressure combustion devices leads to significant deviation from ideal gas behavior as introduced in chap. 1. In this chapter the effect of molecular interactions is introduced from a statistical mechanics point of view, reviewing the derivation of an equations of state from first principles. Then the critical properties of the pure substances of interest are described as well as classical pressure-volume-temperature ($p - V - T$) considerations. A recently developed and computationally efficient cubic equation of state, written in a general three-parameter fashion, is introduced for pure species and extended to mixtures. In this framework deviations from ideality of the thermodynamic properties are implemented in the RGM library and validated against the National Institute of Standards and Technology (NIST) data for both pure species and mixtures of interest.

2.1 EQUATIONS OF STATE

An equation of state (EoS) is a thermodynamic relation between state variables, which describes the state of matter under a given set of physical conditions [21]. It provides a mathematical relationship between two or more state functions

associated with the matter, such as its temperature, pressure, volume, or internal energy. A fluid is a system that can be identified by two independent thermodynamic variables, usually two among pressure, volume and temperature. Introducing an EoS reduces the three variables $p - V - T$ into two independent variables, commonly expressed as: $p = f_{EoS}(V, T)$.

2.1.1 Statistical mechanics approach

The average behavior of a mechanical system, in which the state is uncertain, can be studied by means of probability theory in a *statistical* sense, hence by statistical mechanics. In this framework the thermodynamic behavior of large system and its macroscopic thermodynamic quantities, such as those usually related by an EoS, can be derived from a statistical characterization of the possible states of the system at a microscopic level. In this sense a gas, can be considered an ensemble of N particles governed by classical Hamiltonian mechanics [86, 87]. An Hamiltonian function $\mathcal{H}$, describing the total energy of the system can be defined as:

$$\mathcal{H}(\mathbf{q}_1, \dots, \mathbf{q}_N, \mathbf{p}_1, \dots, \mathbf{p}_N) = \sum_{k=1}^N \frac{\mathbf{p}_k \cdot \mathbf{p}_k}{2m_k} + \Phi(\mathbf{q}_1, \dots, \mathbf{q}_n) \quad (1)$$

where $\mathbf{q}_k$, $\mathbf{p}_k$ and m_k are respectively position, momentum and mass of the k -th particle. The term $\sum_{k=1}^N \frac{\mathbf{p}_k \cdot \mathbf{p}_k}{2m_k}$ represent the total kinematic energy while Φ is the interaction potential between particles expressed as a function of the particles position only. The latter is responsible for the deviation from the ideal gas behavior under certain thermodynamic conditions. The definition of an Hamiltonian function create a system for the governing equation of the particles position and momentum:

$$\dot{\mathbf{p}}_k = -\frac{\partial \mathcal{H}}{\partial \mathbf{p}_k} \quad \dot{\mathbf{q}}_k = -\frac{\partial \mathcal{H}}{\partial \mathbf{q}_k} \quad (2)$$

together with proper initial conditions:

$$\mathbf{p}_k(0) = \mathbf{p}_k^0 \quad \mathbf{q}_k(0) = \mathbf{q}_k^0 \quad (3)$$

where the superscript 0 indicates initial values.

Macroscopically the instantaneous state of the system can be described by a probability density function of position, momentum and time $\mathcal{F}(\mathbf{p}, \mathbf{q}, t)$ of the possible states. Given an initial condition for the probability density function:

$$\mathcal{F}(\mathbf{p}, \mathbf{q}, t = 0) = \mathcal{F}^0(\mathbf{p}, \mathbf{q}) \quad (4)$$

is possible to obtain a governing equation for $\mathcal{F}$ taking the $\mathcal{F}$ derivative with respect to time, considering that the momentum and the position of the particles are also function of time. Therefore we obtain:

$$\frac{d\mathcal{F}}{dt} = \frac{\partial \mathcal{F}}{\partial t} + \dot{\mathbf{q}}_k \frac{\partial \mathcal{F}}{\partial \mathbf{q}_k} + \dot{\mathbf{p}}_k \frac{\partial \mathcal{F}}{\partial \mathbf{p}_k} \quad (5)$$

then substituting the time derivatives of position and momentum using eq. 2 a Liouville-type governing equation for the statistical description of the mechanical system is obtained [88]:

$$\frac{\partial \mathcal{F}}{\partial t} + \left(\frac{\partial \mathcal{H}}{\partial \mathbf{p}_k} \right) \frac{\partial \mathcal{F}}{\partial \mathbf{q}_k} + \left(- \frac{\partial \mathcal{H}}{\partial \mathbf{q}_k} \right) \frac{\partial \mathcal{F}}{\partial \mathbf{p}_k} = 0. \quad (6)$$

Considering a system macroscopically in thermodynamic equilibrium, a stationary probability distribution $\mathcal{F}_{eq}(\mathbf{p}, \mathbf{q})$ describes the possible states of the system, that can be expressed equivalently as a function of Hamiltonian function of the system $\mathcal{F}_{eq}[\mathcal{H}(\mathbf{p}, \mathbf{q})]$. From this functional dependence thermodynamic state function can be generated expressing $\mathcal{F}_{eq}$ as [89]:

$$\mathcal{F}_{eq} = \frac{e^{-\mathcal{H}/k_B T}}{\mathcal{Z}} \quad (7)$$

where k_B and T are respectively the Boltzmann constant and the temperature representing, by means of an exponential function, a *canonical* energy level and $\mathcal{Z}$ is a partition function [90]. The many body partition function can be expressed as a function of the number of particles, temperature and volume $\mathcal{Z} = \mathcal{Z}(N, T, V)$ [88]:

$$\mathcal{Z} = \frac{1}{N! h^{3N}} \int e^{-\mathcal{H}/k_B T} d^{3N} \mathbf{p} d^{3N} \mathbf{q} \quad (8)$$

where h is the Planck constant and the factor $N! h^{3N}$ takes into account the fact that particles are indistinguishable. Given the presence in $\mathcal{H}$ of the interaction potential (that is a function of the particles position only), $\mathcal{Z}$ cannot be factorized into the product of the single particle partitions functions. Since the hamiltonian function is the sum of the kinetic energy (momentum-dependent) and a potential energy (position dependent), it is possible only to factor out the non interacting part (related to the kinetic energy) of the partition function:

$$\mathcal{Z}_{ideal} = \frac{V^N}{N! h^{3N}} \int e^{\sum_{k=1}^N (\frac{\mathbf{p}_k \cdot \mathbf{p}_k}{2m_k}) / k_B T} d^{3N} \mathbf{p} \quad (9)$$

where V come from integrating over the entire $\mathbf{q}_k$ while the subscript ideal come from the fact that an ideal gas is collection of N particles that do not interact, therefore they have a null interaction potential simplifying the hamiltonian

function expressed in eq.(1). The complete many-body/interacting partition function can be expressed as:

$$\mathcal{Z} = \mathcal{Z}_{ideal} \frac{1}{V^N} \int e^{\sum_{k=1}^N \Phi(\mathbf{q}_1, \dots, \mathbf{q}_n)/k_B T} d^{3N} \mathbf{p} \quad (10)$$

where a *correction* term, which is also known as configuration integral, can be defined as:

$$Q = \frac{1}{V^N} \int e^{\sum_{k=1}^N \Phi(\mathbf{q}_1, \dots, \mathbf{q}_n)/k_B T} d^{3N} \mathbf{p}. \quad (11)$$

The partition function can be written in a compact form:

$$\mathcal{Z} = \mathcal{Z}_{ideal} Q \quad (12)$$

and the configurational integral Q is usually evaluated/approximated by means of a Cluster expansion [91].

This expansion, considering only the leading order terms, leads to the following Q form :

$$Q = 1 + \frac{N^2}{2V} \int [e^{-\Phi(r)/k_B T} - 1] d^3 r \quad (13)$$

where r is the relative distance between two particles. This expression can be further simplified assuming spherical symmetry for the interaction potential, and integrating over the ensuing angular coordinates $\int d^3 r \approx 4\pi \int r^2 dr$ leading to:

$$Q = 1 + 4\pi \frac{N^2}{2V} \int [r^2 e^{-\Phi(r)/k_B T} - 1] dr. \quad (14)$$

A rigorous and detailed treatment of the cluster expansion including third body contributions and higher order terms can be found in [91].

The same functional dependence of complete partition function $\mathcal{Z}$ can be found in the Helmholtz free energy potential $F = F(N, T, V)$ as they are related through the Boltzmann law [89]:

$$F = -k_B T \ln(\mathcal{Z}). \quad (15)$$

Including in eq.(15) the expression previously derived for $\mathcal{Z} = \mathcal{Z}_{ideal} Q$ the free energy can be recast in a non-interacting and a correction term:

$$F = -k_B T \ln(\mathcal{Z}_{ideal} Q) = F_{ideal} + F_{correction}. \quad (16)$$

2.1.2 Deriving a generic EoS

One of the possible way to obtain a generic equation of state in terms of pressure p is taking the Helmholtz free energy derivative with respect to V at constant temperature and particle number:

$$\left(\frac{\partial F}{\partial V}\right)_{N,T} = -p(N, T, V) \quad (17)$$

recalling the Boltzmann law (eq. 15) an equation of state (EoS), hence a function $p(N, T, V)$ can be expressed:

$$p(N, T, V) = -\left(\frac{\partial F}{\partial V}\right)_{N,T} = k_B T \left(\frac{\partial \ln(\mathcal{Z})}{\partial V}\right)_{N,T} \quad (18)$$

drawing back from eq.(12) we can clearly see that the interaction potential, which is included in Q can be regarded as a modifying term, which is added to the ideal part:

$$p(N, T, V) = k_B T \left(\frac{\partial \ln(\mathcal{Z}_{ideal})}{\partial V}\right)_{N,T} + k_B T \left(\frac{\partial \ln(Q)}{\partial V}\right)_{N,T}. \quad (19)$$

2.1.3 Derivation example: ideal gas equation of state

As previously mentioned, in the ideal gas limit the interaction potential Φ tend to zero, so the modifying term of eq. 19 including Q can be neglected and $\mathcal{Z} = \mathcal{Z}_{ideal}$. Evaluating the integral in the partition function ideal part expressed in eq. 9 we obtain:

$$\mathcal{Z} = \mathcal{Z}(N, T, V) = \frac{V^N}{N! h^{3N}} (\sqrt{2m\pi k_B T})^{3N}. \quad (20)$$

Taking the Boltzmann law, the explicit form of the Helmholtz free energy is:

$$F = -k_B T \ln \left(\frac{V^N}{N! h^{3N}} (\sqrt{2m\pi k_B T})^{3N} \right) \quad (21)$$

which can be further simplified using Stirling approximation for the factorial term $\ln(N!) = N \ln N - N$ since N is large enough, typically of the order of the Avogadro's number N_A :

$$F = -Nk_B T \left[\ln V + \frac{3}{2} \ln T + \ln \left(\frac{(2\pi m k_B)^{3/2}}{h^3} \right) - \ln N + 1 \right]. \quad (22)$$

Following eq. 17 the ideal gas equation of state can be found by taking the Helmholtz free energy derivative with respect to V :

$$p(N, T, V) = -\left(\frac{\partial F}{\partial V}\right)_{N,T} = \frac{Nk_B T}{V} \quad (23)$$

that can be rewritten in the common molar form:

$$p(n, T, V) = \frac{n\mathcal{R}T}{V} \quad (24)$$

where $\mathcal{R} = N_A k_B = 8.314 \text{ J/molK}$ is the universal gas constant.

2.1.4 Real gas equations of state

As mentioned before real gas effects or deviation from the ideal gas behavior arises from the interaction potential between molecules $\Phi(\mathbf{q})$. Retaining the configuration integral Q (that includes $\Phi(\mathbf{q})$ effects) in the pressure expression of eq. (19), and using the result obtained in the ideal gas limit, some simple manipulations leads to:

$$p(N, T, V) = -\left(\frac{\partial F}{\partial V}\right)_{N,T} = k_B T \frac{N}{V} - k_B T \frac{N^2}{V^2} 2\pi \int r^2 [e^{-\Phi(r)/k_b T} - 1] dr \quad (25)$$

The net effect of this additional term on the ideal gas one can be either attractive or repulsive, decreasing or increasing respectively the pressure depending on molecules spacing and the interaction potential characteristics.

A systematic way to generalize a real gas equation state is the virial expansion [91]. It consist in expressing the EoS by means of a power series of the particles number density N/V :

$$\frac{p}{kT} = \frac{N}{V} + B_2(T) \left(\frac{N}{V}\right)^2 + B_3(T) \left(\frac{N}{V}\right)^3 + \dots \quad (26)$$

where the factor B_i is the i -th *virial coefficient*. Observing this series expansion, it is easy to notice that the simplified form of the EoS (previously found in eq. 25) it is equivalent to a series truncated at the second order. The second coefficient of the virial expansion can be expressed as:

$$B_2(T) = -2\pi \int_0^\infty r^2 [e^{-\Phi(r)/k_b T} - 1] dr. \quad (27)$$

This term can be calculated once the functional form of the interaction potential is known. Many formulations have been proposed for the functional dependence of the interaction potential (some of them are schematically represented in fig. 6) depending on the particular molecules characteristics, giving the rise to a large part of the EoS present in the current literature [21].

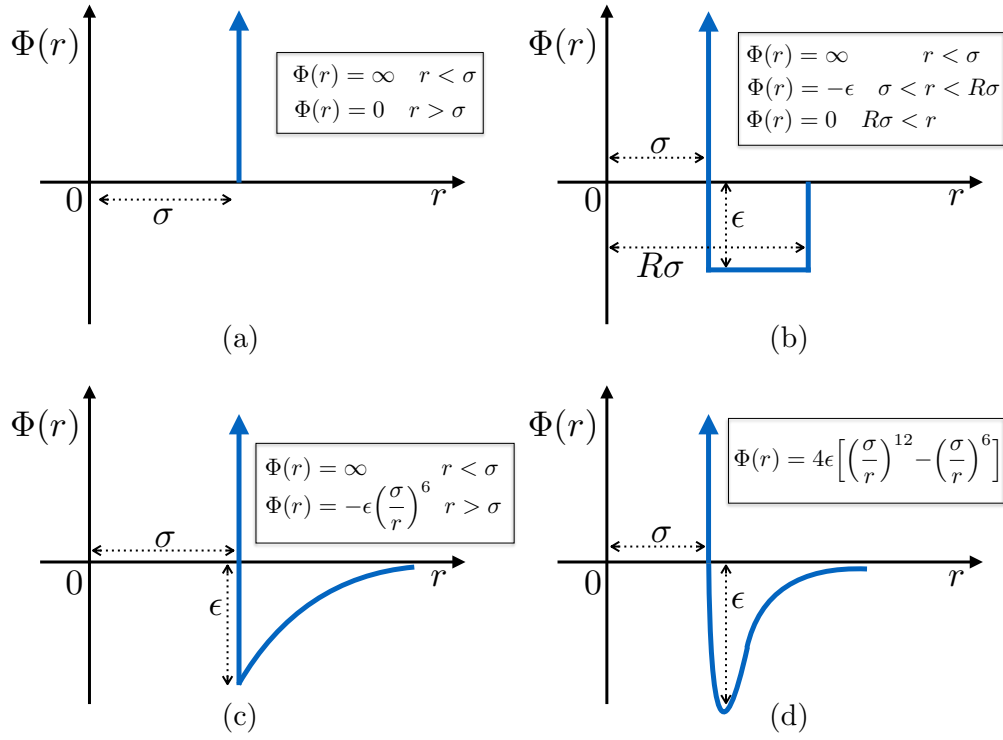


Figure 6.: Examples of simple functional dependence of the interaction potential $\Phi(r)$ based on particle dependent parameters: minimum distance between two particles σ , depth ϵ and elongation $R\sigma$ of the potential well. Panel (a): Hard core potential, panel (b): Square-well potential, panel (c): Sutherland potential and panel (d): Lennard-Jones potential.

Perform an exact calculation in powers of a small parameter, such as the particles number density (or simply the density), is not always an easy task for practical applications. Usually in the engineering field, alternative approaches are used, by means of various approximations of the partition function. These approaches are very often used since, contrary to the virial framework, they are not limited to low densities. The main idea behind this approaches, which start from the pioneering work of van der Waals [92], is to approximate $\mathcal{Z}$ starting from the single particle partition function. In this way, based on the single component molecular characteristics, it is possible to obtain an equation of state that approximates the behavior of a real gas [21]:

$$p = \frac{nRT}{(V - nb)} - \frac{n^2a}{V^2} \quad (28)$$

giving the rise to the class of *van der Waals-type* equations of state which are largely used in engineering [21, 93]. They can also be referred as interpolated [94] or cubic EoS, since pressure is expressed as cubic function of the volume or

density. The two substance dependent parameters a and b , usual dependence on the critical properties as will be mentioned in following section. These can be set to zero to recover the classical ideal gas law. From a physical point of view the parameter a measure of the average attraction between particles, while b the volume excluded by the particles and, in addition, they can be linked to some functional form of $\Phi(r)$. Since in the original van der Waals approach the attractive part and the repulsive part were treated separately, they can be easily related to the Lennard-Jones inter-particle interaction potential (see fig. 6) in terms of σ and ϵ , respectively the closest distance between two particles and the depth of the potential well. Two key points arises from this approach. Firstly the repulsion is strong and particles are correlated each other only when they are very close together. Secondly attraction is weak so there is a very little correlation between particles positions. These considerations with together with some manipulations leads to:

$$a = \frac{16}{9} \pi \sigma^3 \epsilon \quad b = \frac{2}{3} \pi \sigma^3 \quad (29)$$

which completely defines the Van der Waals EoS.

The aforementioned class of EoS have been largely used in CFD simulations, although several sophisticated EoS exist such as the BWR (Benedict-Webb-Rubin) model [95], that have been scarcely applied in CFD due to complex nonlinear forms and the elevated computational costs. Therefore most of the real gas CFD simulations have so far relied on the well establish two-parameter cubic EoS, such as Peng–Robinson (PR) [96] or Soave–Redlich–Kwong (SRK) [97]. Additional correction, case-dependent fix and fitting parameters have also added to these simple formulations, in order to obtain a better agreement with experimental data for CFD applications [98].

2.2 CRITICAL PROPERTIES AND P–V–T BEHAVIOR

Considering a pure substance, its global thermodynamic behavior can be described by the classical pressure-temperature diagram, such as the one represented in fig. 7. It clearly show the solid, liquid and vapor states highlighting the boundaries where two-phase are present. Equilibrium and isobaric/isothermal or combined processes are simply represented by horizontal/vertical lines.

It worth noting the importance, both from a physical and a technological point of view of the critical point. For supercritical conditions we indicate thermodynamic conditions where the liquid and gaseous phases become indistinguishable.

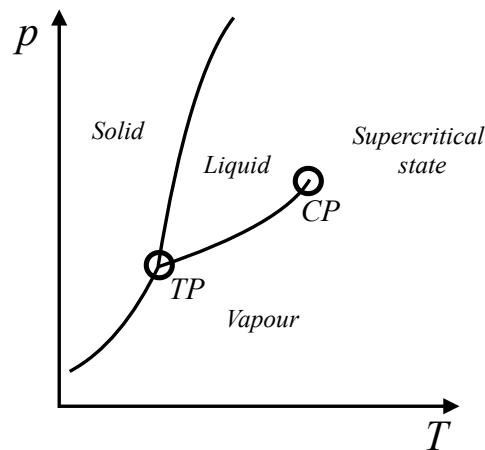


Figure 7.: Schematic of a pressure-temperature diagram for a pure substance.

For temperature below the critical temperature (subcritical) during an isothermal process, as the pressure increases, the intermolecular forces between molecules increases as well, eventually overcoming the kinetic energy which is constant since the temperature is constant. At this point new intermolecular forces are created which give rise to molecule cohesion and surface tension and the vapor transform into liquid (condensed matter). On the other hand for temperature over the critical temperature (supercritical), the kinetic energy is so high that an intermolecular bond cannot be created and no change of state occurs, for any given pressure. Hence, the weaker the intermolecular bond, the lower is the critical temperature. Molecular interactions strongly depend on molecule nature, atoms and its geometry as discuss in the next subsection.

2.2.1 Single species critical data

From a technological standpoint, knowing the critical point coordinates and therefore the conditions in which a substance is liquid, vapor or supercritical is of fundamental importance. For LRE and high pressure combustion devices, in which combustion efficiency and performance are strongly related to the propellants thermodynamic condition at injection [99]. The injection and combustion processes is as an isobaric transformation (combustion chamber pressure) as schematically shown in fig. 8.

Critical temperature T_{cr} , critical pressure p_{cr} and critical volume V_{cr} represent three widely used pure component constants. They are very important properties because a large part of the thermo-chemical properties can be predicted from boiling point and critical constants by means of the corresponding state

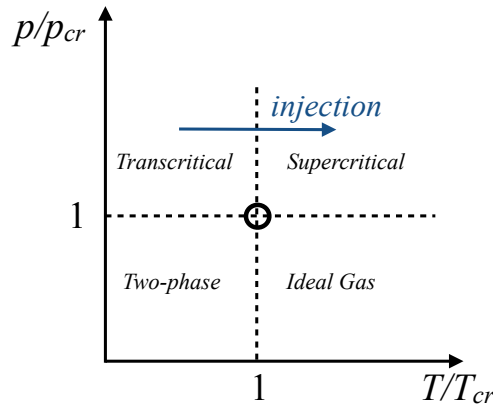


Figure 8.: Thermodynamic path of the injection processes in a LRE using cryogenic propellants

theory. The corresponding state theory assumes that fluids behave in a similar manner when described in terms of their reduced pressure and temperature. Reduced (subscript r) pressure and temperature are simply normalized by the critical one:

$$T_r = \frac{T}{T_{cr}} \quad p_r = \frac{p}{p_{cr}}. \quad (30)$$

Therefore precise prediction of critical constants are needed, and of fundamental importance for deriving consistent thermodynamical properties [21].

Table 1.: Critical properties of pure substance of interest [11].

Substance	Formula	p_{cr} [bar]	T_{cr} [K]
Oxygen	O ₂	50.4	154.6
Water	H ₂ O	220.6	647.01
Nitrogen	N ₂	34.0	126.2
Helium	He	50.4	5.21
Hydrogen	H ₂	12.8	32.94
Methane	CH ₄	46.0	154.6
Ethane	C ₂ H ₆	48.72	154.6
Propane	C ₃ H ₈	42.51	307.32

The critical pressures and temperatures for different substances of interest for this work are listed in tab. 1. The data highlight a quite broad range of values even for similar molecules that can cause some modeling problems dealing with complex mixtures.

2.3 THREE-PARAMETER REAL GAS EQUATION OF STATE

In this work, dealing with complex mixtures arising from the non-premixed combustion of methane and other hydrocarbons, a computationally efficient real gas equation of state (EoS) is used. This choice has been made in order to avoid complex nonlinear formulations, even if several more accurate EoS exist as previously mentioned. The widely used cubic form of the real gas EoS, usually written in a two-parameter form, can be recast in a convenient general three-parameter fashion indicated as RK-PR (Redlich Kwong - Peng Robinson) [100] which, for a pure species, reads:

$$p = \frac{\rho R_u T}{W - b\rho} - \frac{a\alpha(T)\rho^2}{(W + \delta_1 b\rho)(W + \delta_2 b\rho)}, \quad (31)$$

where p , ρ , T are fluid pressure, density and temperature, W is the species molecular weight, R_u the universal gas constant and $\alpha(T)$ is a temperature correction factor usually referred as volume translation [98]. The three parameters characterizing the EoS are a , b and δ_1 ($\delta_2 = (1 - \delta_1)/(1 + \delta_1)$), whereas α is a temperature dependent correction factor which is coupled with a . The choice of parameters in Eq. (31) determines which particular cubic EoS has been chosen. The classical Peng-Robinson form is recovered for $\delta_1 = 1 + \sqrt{2}$ while the Soave-Redlich-Kwong form for $\delta_1 = 1$. A complete three parameter EoS, such as the RK-PR, is obtained for $\delta_1 = \delta_1(Z_c)$, where $Z_c = p_c/(\rho_c T_c R_u/W)$ is the critical compressibility factor [21]. Complete functional definitions for a , b , α and δ_1 can be found in work of Cismondi and Mollerup [100]. Most of the numerical studies on supercritical combustion so far relied on two-parameter cubic EoS, dealing in most of the cases with the simple hydrogen-oxygen chemistry and composition range. This general form of cubic EoS has been used for the first time for modeling kerosene combustion in [2]. It is particularly well suited for methane and other more complex hydrocarbons because of it has shown a simpler handling of mixtures with rather different critical compressibility factor [2].

2.3.1 Mixing rules

In order to extend the validity of the real gas EoS to an arbitrary number of components, a mixture model is needed. A mixture can be considered as a single phase of a unique pure hypothetical fluid. The parameters required by the EoS are calculated from critical characteristics of each species considered [101] together with the use of conventional molar fraction based mixing rules [21].

The critical parameters needed are critical temperature and pressure, as well as the acentric factor of the molecule, used in the following mixing expressions:

$$a\alpha(T) = \sum_{i=1}^{ns} \sum_{j=1}^{ns} X_i X_j a_{ij} \alpha_{ij}(T) \quad (32)$$

$$b = \sum_{i=1}^{ns} X_i b_i \quad (33)$$

$$\delta_1 = \sum_{i=1}^{ns} X_i \delta_{1,i} \quad (34)$$

where subscript i refers to the i -th species and X is the molar fraction. The off-diagonal terms $a_{ij}\alpha_{ij}(T)$, representing binary interactions, are obtained by means of combination rules based on pseudo-critical parameters [102], which are simple estimation of binary mixtures critical properties. The interaction between the pseudo critical parameters and the other mixing component can be expressed by means of interaction parameters, however are commonly neglected [78]. On the other hand the single species parameters b_i and $\delta_{1,i}$ are obtained directly from the i -th species critical properties [2].

2.3.2 Thermodynamic properties of mixtures

In order to ensure the self-consistency of the model, all thermodynamic properties are calculated from the same equation of state [77]. Once the mixture is characterized by the EoS parameters ($a\alpha$, b , δ_1), any thermodynamic relation can be expressed in terms of a reference ideal mixture low-pressure property, denoted by subscript 0, and a real gas departure function [102] derived from the real gas EoS. Generally, such properties are not independent of each other so that an evaluation order has to be chosen. One common choice is to start from internal energy [78]:

$$e(T, \rho) = e_0(T) + \int_{\rho_0}^{\rho} \left[\frac{p}{\rho^2} - \frac{T}{\rho^2} \left(\frac{\partial p}{\partial T} \right)_{\rho_i} \right] d\rho. \quad (35)$$

The above expression of the mass based internal energy allows for the derivation of the single species internal energy e_i by differentiating with respect to the partial density [103]:

$$e_i = \left(\frac{\partial \rho e}{\partial \rho_i} \right)_{T, \rho_j \neq i}. \quad (36)$$

Then the enthalpy of species i is obtained from basic thermodynamical relations for a mixture of general gases.

$$h_i = e_i - \left(\sum_{j=1}^{ns} Y_j e_j - e(T, \rho) - \frac{p}{\rho} \right) \frac{\left(\frac{\partial p}{\partial \rho_i} \right)_{T, \rho_{j \neq i}}}{\left(\frac{\partial p}{\partial \rho} \right)_{T, Y_i}}. \quad (37)$$

where Y_j is the j -th mass fraction and where the specific enthalpy of the mixture can be obtained simply by means of Euler's theorem of first order homogeneous functions:

$$h = \sum_{i=1}^{ns} Y_i h_i. \quad (38)$$

The specific heat capacity at constant volume is evaluated differentiating the internal energy definition with respect to the temperature.

$$C_v = \left(\frac{\partial e}{\partial T} \right)_{Y_i, \rho} \quad (39)$$

Once C_v is determined, constant pressure specific heat can be evaluated using fundamental thermodynamical relationship [103]:

$$C_p = C_v + \frac{T}{\rho^2} \frac{\left(\frac{\partial p}{\partial T} \right)_{\rho_i}^2}{\left(\frac{\partial p}{\partial \rho} \right)_{Y_i, T}}. \quad (40)$$

The above expressions are cast in a form which is EoS-independent, wherein only the explicit form of the thermodynamic derivatives retain a dependence from the particular EoS used. In the present case of RK-PR EoS, such derivatives assume the form derived by Kim et al. [2].

In order to obtain a complete thermodynamic characterization of a real gas mixture, transport properties are needed such as the mixture viscosity and thermal conductivity as well as species diffusion coefficients [77]. In the present version of the RGM library transport properties are not available but are envisaged for future applications. Currently only the thermodynamic properties needed by the laminar flamelet equations (see chap. 3) are implemented and validated in the following section.

2.4 THERMODYNAMIC PROPERTIES VALIDATION

Thermodynamic properties for methane and the oxygen, along with their mixture, are compared against the National Institute of Standards and Technology (NIST) data obtained by means of the Refprop software [11]. In the proximity of the critical point, thermodynamic and transport properties exhibit anomalies in their behavior, usually referred as near-critical enhancement or pseudo-boiling/vaporization. It can be considered like a phase transition between a supercritical liquid-like and a gas-like thermodynamic state when the Widom- or pseudoboiling-line is crossed, which is identified by the peak of specific heat capacity and by a significant reduction in density. The *pseudo* prefix stand in the sense that is a continuous, nonlinear and transcritical process that resemble a classical subcritical vaporization [39].

Thermodynamic variables and properties, needed for laminar flamelet equations (see chap. 3, such as density, mixture enthalpy and specific heat at constant pressure, are compared against NIST data for pure oxygen and pure methane in Fig. 9 and a mixture of both in Fig. 10. The validation is shown for various pressures within temperature range of interest. The comparison shows reasonably good agreement from near critical up to supercritical pressures for both pure species and their mixture. Although for pressures below the critical value, the interface between dense liquid and light gas is represented by abrupt gradients, which are approximated by smooth curves by the cubic EoS, the present study will focus on high pressures, above the critical value of the propellants considered and for which transitions are smooth and reasonably well captured.

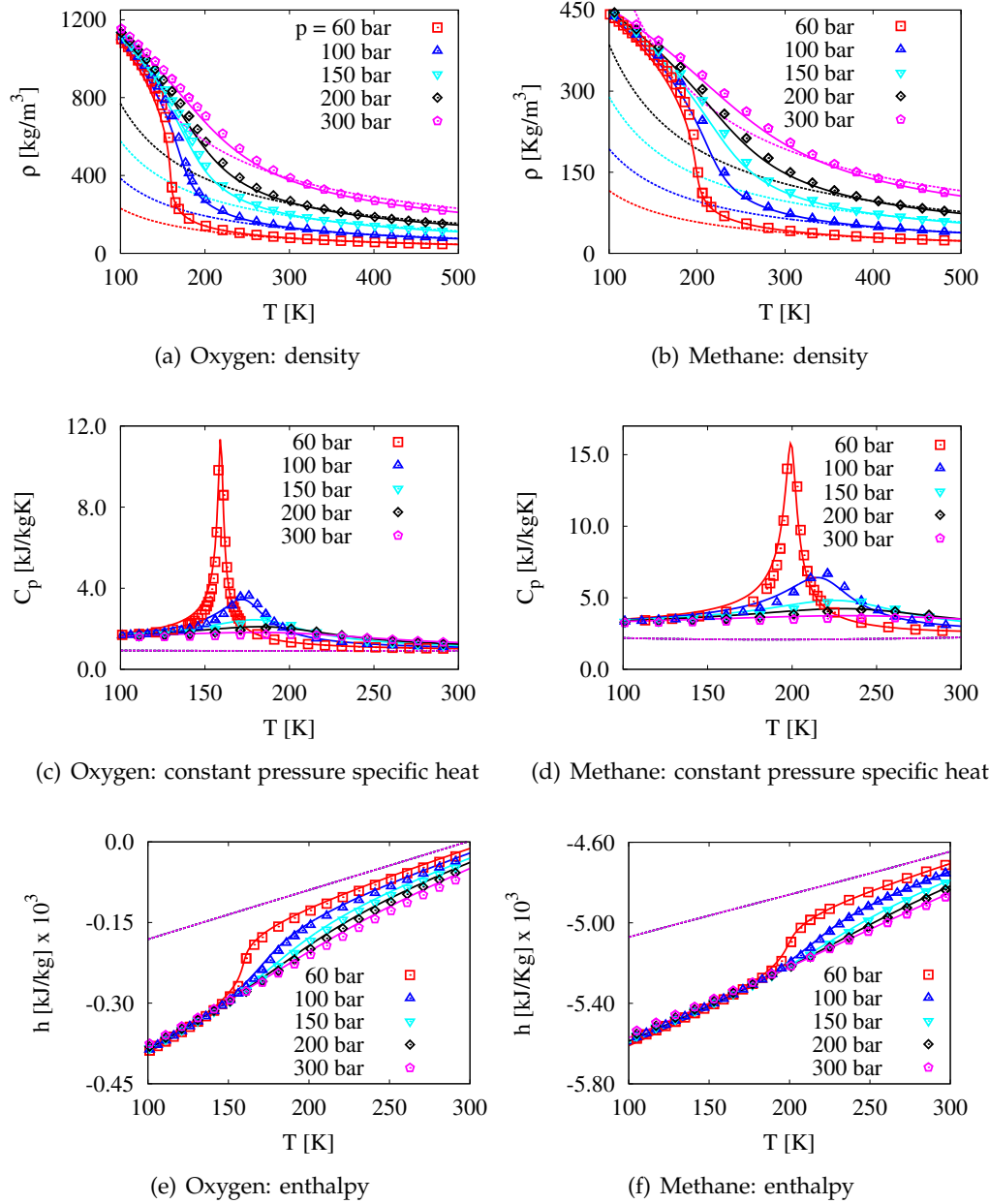


Figure 9.: Real fluid thermodynamic properties of pure oxygen (left) and pure methane (right) as functions of temperature at five different pressures, from 60 bar to 300 bar. Solid lines (—): PR-RK EoS results; dashed lines (---): Chemkin ideal gas EoS results [10]; Symbols: Refprop software results from the NIST database [11].

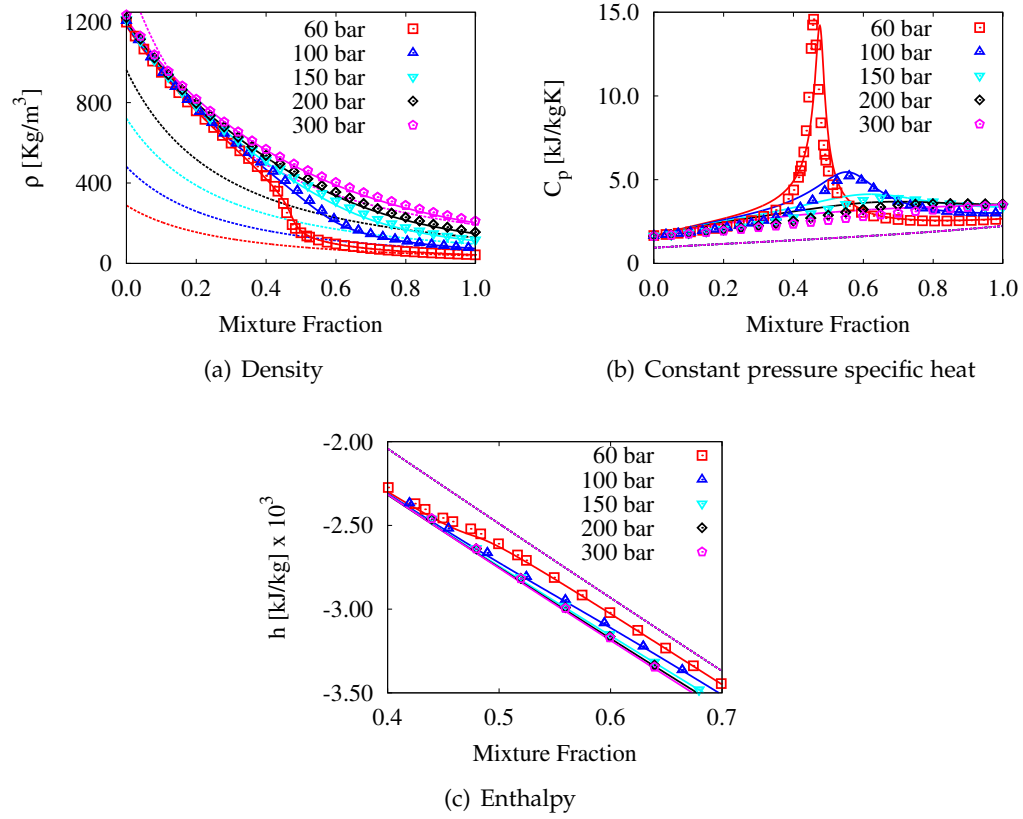


Figure 10.: Real fluid thermodynamic properties of an oxygen-methane mixture as functions of the mixture fraction at five different pressures, from 60 bar to 300 bar. The mixture fraction is defined according to Bilger [12] on a elemental basis and temperature is assumed to vary linearly with the mixture fraction from $T_{LOX} = 120$ K where the mixture fraction is 0 to $T_{CH_4} = 300$ K where the mixture fraction is 1. Solid lines (—): PR-RK EoS results; dashed lines (---): Chemkin ideal gas EoS results [10]; Symbols: Refprop software results from the NIST database [11].

3

SUPERCRITICAL UNSTEADY FLAME STRUCTURE

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Real gas effects on the temporal evolution of supercritical cryogenic LO_x-methane non-premixed flame structures are investigated in this chapter in the framework of the unsteady laminar flamelet equations. Real fluid effects, are taken into account using the developed RGM library described in the previous chapter. Unsteady flame structure calculations are performed at pressures which can be considered representative of a liquid rocket engine chamber operating conditions. Pressure and scalar dissipation rate effects are investigated in the context of prototypical unsteady flame configurations, such as autoignition and re-ignition/quenching. Auto-ignition is achieved by imposing a high fuel temperature boundary condition, while oxygen is maintained at cryogenic temperatures, in order to investigate real-gas effects, such as near-critical enhancement of thermodynamical properties, which can influence the temporal evolution of the ensuing non-premixed flame structure. On the other hand, re-ignition and quenching phenomena are analyzed using a time dependent

forcing function for the scalar dissipation rate, in order to investigate the response to typical turbulent perturbations. An extensive parametric analysis is performed in order to shed light on the effects of the main operating parameters on ignition times, most reactive mixture fraction and re-ignition/quenching characteristics. Real gas effects are evaluated and quantified over the large range of thermodynamic states explored by the evolving flame structures, for pressures ranging from near-critical up to largely supercritical. Such effects are observed to be relevant even at relatively high temperatures.

3.1 FLAMELET EQUATIONS AT SUPERCRITICAL PRESSURES

The local flame structures of a turbulent non-premixed flame, even at supercritical pressures, can be effectively described by the laminar flamelet equations provided the diffusion flame is thin compared to turbulent length scales, or, equivalently, if chemical time scales are shorter than turbulence time scales [26]. This translates into the requirement that the Damköhler number Da relevant in the context of turbulent combustion, defined as the ratio between the turbulence integral time scale τ_T and a chemical time scale τ_c , be sufficiently high. However, such a definition differs from the Damköhler number relevant for the local non-premixed laminar flame structure, which can be defined as $Da^{fl} = \tau_f / \tau_c$, where τ_f is a relevant flow time scale (assumed proportional to the inverse of the scalar dissipation rate). These two Damköhler numbers are roughly connected by the relation $Da \sim \sqrt{Re_t} Da^{fl}$ [37], where Re_t is the turbulent Reynolds number. During unsteady flamelet solutions, Da^{fl} is variable as a result of varying chemical time scales and/or scalar dissipation rate perturbations. In order for the laminar flamelet assumption to hold at all times, Da should still be always high enough. The implicit assumption made is that the turbulence integral time scale τ_T or Re_t should be at all times sufficiently high.

Therefore the flamelet equations can be seen as an unsteady competition between chemical kinetic and molecular diffusion processes enhanced by turbulent mixing [26]. The independent variables of the flamelet equations are a lagrangian flamelet time t and the mixture fraction z which is a measure of the local stoichiometry. The key parameter is the scalar dissipation rate of the mixture fraction, defined as $\chi = \frac{1}{2} D_z (\nabla z)^2$, where D_z is the diffusion coefficient of z . The scalar dissipation rate of the mixture fraction is the only flow-field parameter which influences the flame structure, acting similarly to strain rate for the counterflow diffusion flame configuration [37]. Moreover, the steady-state solution for $\chi = 0 \text{ s}^{-1}$ effectively represents chemical equilibrium for a given

composition range. With the unit Lewis-number assumption, commonly used in methane combustion, for a system of N_s species, the classical form of the flamelet equations reads [26]:

$$\frac{\partial Y_i}{\partial t} = \frac{1}{2}\chi \frac{\partial^2 Y_i}{\partial z^2} + \frac{\dot{\omega}_i}{\rho} \quad ; \quad i = 1, N_s \quad (41)$$

$$\frac{\partial T}{\partial t} = \frac{1}{2}\chi \left[\frac{\partial^2 T}{\partial z^2} + \frac{1}{C_p} \frac{\partial C_p}{\partial z} \frac{\partial T}{\partial z} + \frac{\partial T}{\partial z} \sum_{k=1}^{N_s} \left(1 - \frac{C_{p_k}}{C_p} \right) \frac{\partial Y_k}{\partial z} \right] + \frac{\dot{\omega}_T}{C_p \rho}, \quad (42)$$

where $\dot{\omega}_i$ is the species mass production rate and $\dot{\omega}_T = -\sum_{i=1}^{N_s} h_i \dot{\omega}_i$ is the energy equation source term. The mixture C_p experiences abrupt changes when the mixture undergoes a trans-critical transition, causing discretization issues of its numerical derivative with respect to z . Thus an equivalent energy equation can be used instead of Eq. (42), by recasting it in terms of mixture enthalpy [36]:

$$\frac{\partial T}{\partial t} = \frac{1}{2}\chi \frac{1}{C_p} \left[\frac{\partial^2 h}{\partial z^2} + \sum_{k=1}^{N_s} h_k \frac{\partial^2 Y_k}{\partial z^2} \right] + \frac{\dot{\omega}_T}{C_p \rho}. \quad (43)$$

The functional dependence of the scalar dissipation rate profile on z is assumed to be known a-priori as an amplitude mapping closure model [104]:

$$\chi(z) = \chi_{max}^0 \exp(-2\text{erfc}^{-1}(2z))^2, \quad (44)$$

parametrized according to the peak scalar dissipation rate value χ_{max}^0 . Equations (41) and (43) define the flamelet system, whose solution is the transient flame structure $\{Y_i(z, t), T(z, t)\}$. Such transient solutions can have multiple interpretations in the context of a reacting flow field. In the case of a steady flamelet solution being perturbed by transient variations in scalar dissipation rate, the ensuing transient flamelet solutions can be considered as representative of a local *flame element* subject to a turbulent perturbation. On the other hand, transient flamelet solutions ensuing from auto-igniting boundary conditions, can be considered as describing in the (z, t) plane the steady structure of a laminar edge flame in the physical (x, y) plane, where one spatial dimension will be aligned to the direction of the convective flow and the other to the inflow composition gradient. Both the perturbed and the auto-igniting solutions will be analyzed in this chapter for pressures ranging from near critical (60 bar) up to largely supercritical (200 bar).

The flamelet equations are solved in a fully coupled fashion, thus no operator splitting technique is adopted to tackle the scale separation between reaction and diffusion processes. Stiff solver for ordinary differential equations DVODE [105] is used in conjunction with Chemkin-II package [10] for chemical terms and

for the reference ideal gas properties [106]. The previously validated real gas library RGM, implementing the departure functions for a general cubic equation of state, is coupled to the above scheme to furnish real gas thermodynamical properties.

3.1.1 Real gas initial conditions

A number of numerical studies [81, 36, 2] have so far relied on boundary value problem solvers to determine the steady state solution of the supercritical flamelet equations. In order to investigate the transient supercritical flame structure in the context of an autoignition problem, the unsteady flamelet formulation, Eq. (41),(43), is to be integrated starting from physically sound initial conditions. These are provided by the steady state solutions of the frozen mixing problem emerging from the flamelet system, which yield a pure adiabatic mixing solution. Such solutions in terms of mass fraction and enthalpy are, trivially, linear functions of the mixture fraction, as for $\dot{\omega}_i = \dot{\omega}_T = 0$ they satisfy $\partial_z^2 Y_i = \partial_z^2 h = 0$, irrespective of χ . On the other hand, especially for real fluid mixtures, for which variations of C_p with mixture fraction are substantial in the proximity of the near-critical enhancement, the temperature mixing solution will not be linear as it satisfies the steady, frozen form of Eq. (42), namely $\partial_z^2 T + (1/C_p)\partial_z C_p \partial_z T = 0$.

The nonlinearity in the mixing solution for temperature is equally present under the ideal gas assumption, but it is a far less pronounced effect than in the real gas case which exhibits a large, near critical enhancement in C_p . Figure 11 displays mixing profiles for temperature and C_p corresponding to linear enthalpy profiles ($\partial_z^2 h = 0$). Also shown are enthalpy and C_p profiles corresponding to an unphysical linear temperature profile ($\partial_z^2 T = 0$), highlighting the substantial differences between the two cases and thus the potentially different transient solutions of the flamelet system when using such profiles as initial conditions.

3.1.2 Real gas reaction rates

Detailed reaction mechanisms usually provide Arrhenius rate constants k_f for forward steps only, the reverse rate constant k_r being obtained through the equilibrium constant K_c so that $K_{r_j} = k_{f_j}/k_{c_j}$ for the j -th reaction. While this expression holds for both ideal and real gases, in the former case K_c is a function of the temperature only while in the general case it carries an additional dependence on pressure. Accordingly, a real gas correction is needed such as:

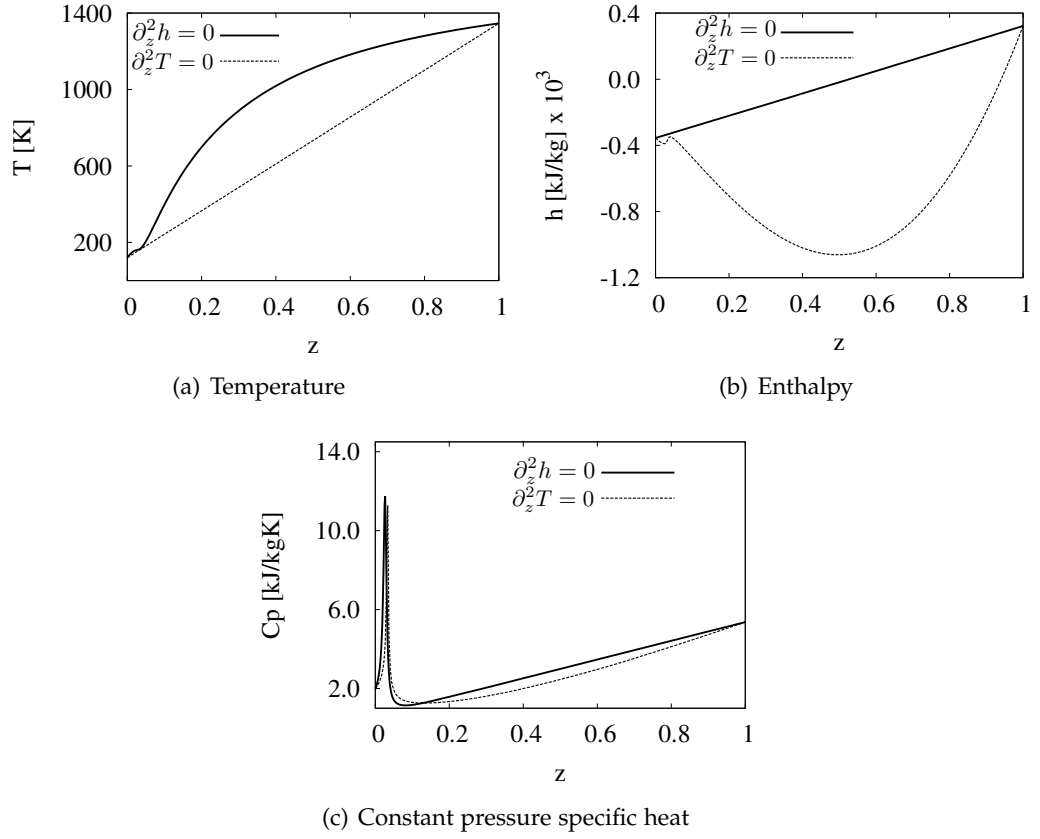


Figure 11.: Difference between temperature and enthalpy mixing lines as initial conditions for supercritical unsteady flamelet calculations, for a near critical pressure of 60 bar. Boundary conditions are the same of section 3.2.

$$K_{c_j}^{real} = K_{c_j}^{ideal} K_{c_j}^{corr} \quad (45)$$

where $K_{c_j}^{corr}$ is a correction factor taking into account fugacity and compressibility effects [101]. These effects are usually neglected in calculations [28], as in the present thesis, although a detailed analysis is still missing in the current literature.

3.1.3 High pressure chemical mechanism

The oxygen/methane chemical mechanism chosen for the present work, referred to as Ramec [13], comprising 38-species and 190-reactions. It was employed here at the high pressures and low temperatures conditions of interest in order to correctly capture ignition delay characteristics (fig .12).

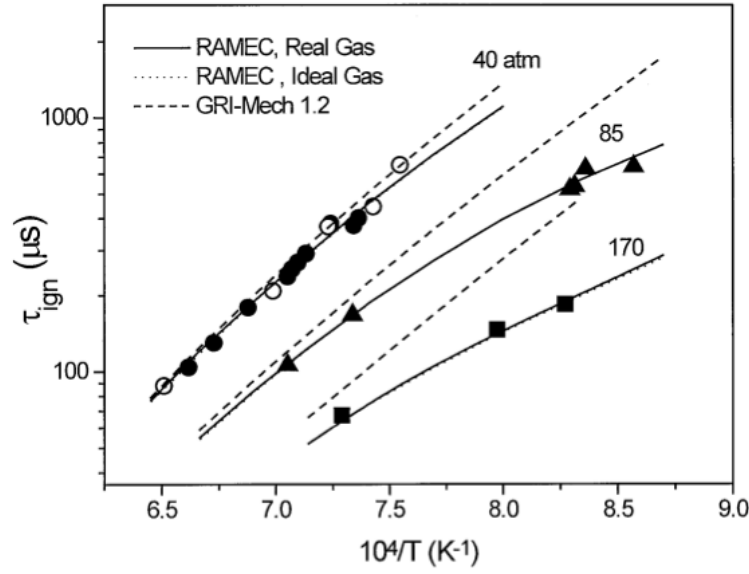


Figure 12.: Ignition delay time calculations and experimental data for fuel(methane)-rich mixtures for a pressure-range between 40-170 atm. Figure taken from [13].

The Ramec mechanism was derived from the GRI-Mech 1.2 [107] adding 12 reactions and 6 species. Among such additional reactions identified to play an important role in the ignition of oxygen/methane mixtures at high-pressures and low temperatures, are those involving the CH_3O_2 radical, which ultimately promote the buildup of H and OH radical pool leading to ignition [13]. In particular, they accurately reproduce experimental data [108] with respect to high pressure ignition delay times, which are consistently smaller than delay times at lower pressure. The employed mechanism was validated in terms of experimental ignition delay times in shock tube experiments at pressures up to 260 atm, for initial mixture temperatures as low as 1040 K and for both lean and rich mixtures. Indeed, the latter validation implies that the mechanism may be employed with confidence over the entire mixture fraction domain.

3.2 AUTOIGNITION RESULTS AND DISCUSSION

An autoignition test case at near-critical pressure is analyzed in order to investigate real gas effects on the time evolution of the flame structure using the adiabatic pure mixing solutions.

3.2.1 Autoignition test case

A background pressure of 60 bar, representative of LOx-methane LRE chamber conditions, is chosen for the unsteady flamelet calculations. This value is challenging from a numerical point of view in that for the chosen pure mixing initial conditions the near critical enhancement is rather pronounced and occurs close to the critical region for pure oxygen (for which $T_{cr} = 154.6$ K, $p_{cr} = 50.4$ bar) in the neighborhood of the pure oxygen boundary. In order to accurately capture such enhancement of thermodynamic properties, a higher resolution and thus lower grid spacing is required towards the lean side in mixture fraction space. This is achieved by using a non-uniform 160-point grid, suitably compressed towards the oxidizer side. A relatively low value of the scalar dissipation rate as been chosen ($\chi_{max}^0 = 100 \text{ s}^{-1}$) in order to analyze the tribrachial structure emanating from the autoignition point and its interaction with near critical enhancement near the LOx side. The boundary condition on the cold oxidizer side, chosen as pure oxygen at $T_{ox} = 120$ K, is representative of the operating temperature of cryogenic LOx injection in LRE combustion chambers, while on the hot fuel side, chosen as dissociated methane at $T_f = 1346$ K at chemical equilibrium, is a suitable condition for autoignition to occur on the rich zone. Note that LRE's using an expander cycle configuration, a pure fluid fuel is generally injected at lower temperatures while in staged combustion cycles fuel-rich mixtures are used at similar equilibrium temperatures.

Using enthalpy mixing lines (adiabatic mixing) as initial conditions, the time evolution of the high pressure flame structure exhibits a similar behavior to the well known low-pressure case but with very different time scales. As shown in Fig. 13, temperature at first exhibits a small increase in the rich region, in the neighborhood of the most reactive mixture fraction value which we analyze later, while some pre-ignition species increase gradually such as CH_2O as shown in Fig. 14, before autoignition occurs. This transient, usually referred to as induction time [33], is clearly considerably shorter, with respect to atmospheric pressure cases, due to decreased chemical timescales [109]. Following the induction time, the concentration of species related to highly exothermic processes, such as the final products of combustion, as well as temperature, increase abruptly, eventually approaching the final steady flamelet profile, while pre-ignition species are rapidly consumed. At this stage autoignition occurs and an autoignition time can thus be defined (see sect. 3.2.3), using, for example, pre-ignition species consumption (such as formaldehyde CH_2O) as a marker. Autoignition time and other time scales involved are expected to be strongly dependent on the boundary conditions used for the flamelet calculation. Since

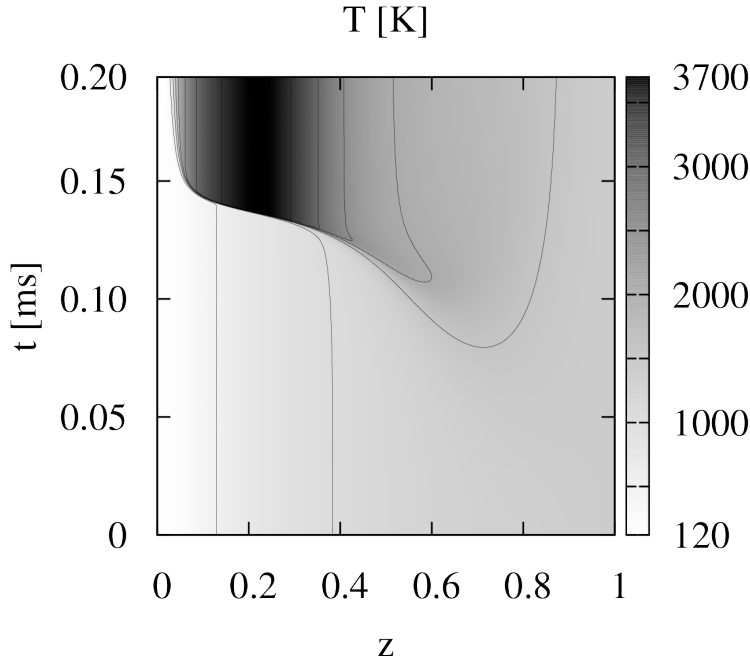


Figure 13.: Transient, real gas, flamelet solution for autoignition test case at near-critical pressure of $p = 60$ bar: temperature field mixture fraction-time space $T(z, t)$.

we are interested exclusively in the qualitative behavior of the transient, real gas, flame structure, no attempt for a quantitative estimation of the influence of boundary conditions (in particular the hot fuel side $z = 1$) on the ignition times has been carried out.

Autoignition time, in the high-pressures regime, is known to be significantly shorter than at lower pressures due to pressure effects on chemical source terms and reaction paths [109]. The Ramec mechanism used herein, models the chemical paths involving CH_3O_2 , not included in the original GRI- Mech 1.2 [13], which has been shown to play a pivotal role in the radical production during the induction time. After autoignition occurs, a typical transient evolution usually exhibits a lean and a rich premixed reaction front propagating in opposite directions in mixture fraction space (see e.g. fig. 14), respectively towards the lean and rich region. A similar scenario unfolds in the tribrachial structure of an edge flame in physical space. In this particular case the rich reaction front is not clearly observable because autoignition occurs for very rich mixtures, close to the fuel boundary ($z = 1$). Fig. 13 show that the lean premixed front soon approaches the stoichiometric zone ($z_{st} = 0.2$) and is then extinguished in the low temperature lean region while the trailing steady state flamelet solution is achieved soon after. The lean premixed reaction front, in its propagation towards the lean side, can also be seen to initially leave in its wake a small temperature and

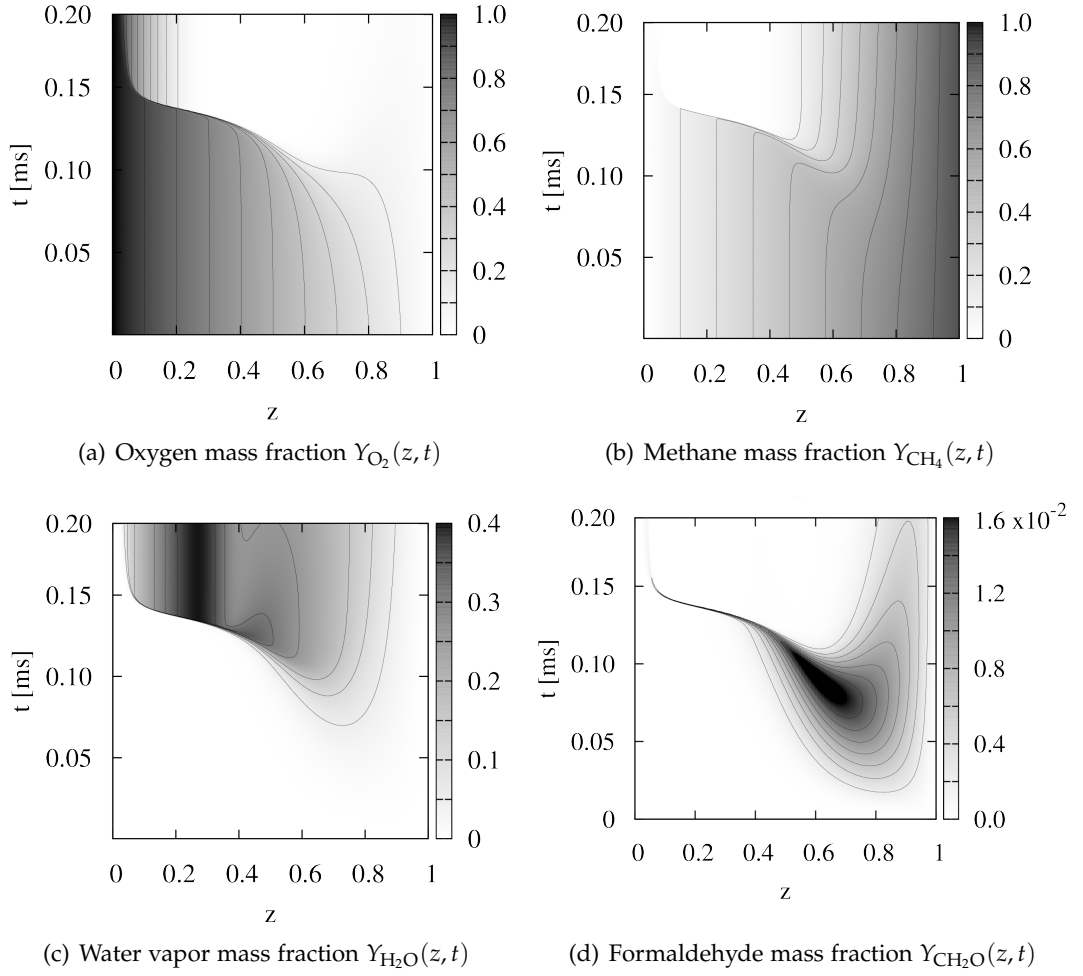


Figure 14.: Transient flamelet solution for autoignition test case at near critical pressure of $p = 60$ bar: oxygen, methane, water vapor and formaldehyde mass fraction field in the mixture fraction-time (z, t) space.

water vapor concentration overshoot (Fig. 13-14), due to kinetic superadiabatic effects [110], before settling onto the steady flamelet solution. Then the overshoot relaxes onto the steady flamelet solution with a time scale related to water vapor recombination reactions.

The propagation speed of the premixed fronts strongly depends on the scalar dissipation rate as well as on its functional profile in z -space and which we assume constant in time. Such autoignition phenomena are analyzed in depth in sect. 3.2.3, at pressures ranging from 60 bar to 300 bar and scalar dissipation rate ranging from $\chi = 0 \text{ s}^{-1}$ to the critical value $\chi = \chi_{cr}$ at which autoignition is inhibited.

3.2.2 Real gas effects and thermodynamic regime

The temporal evolution of an auto-igniting flamelet solution can also be considerably affected by real gas effects. In particular, as mentioned in sect. 3.2.1, an abrupt enhancement of thermophysical properties such as C_p and ρ occurs at near-critical pressures close to the LOx side, as seen in Fig. 11. The higher C_p and density effectively act as heat sinks for the high temperature premixed front, whose propagation towards the lean side in z -space is substantially inhibited.

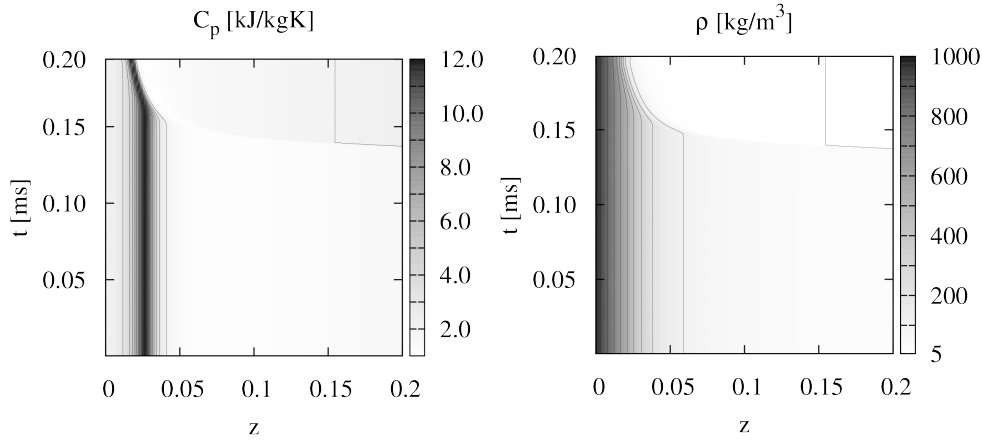


Figure 15.: Ignition in the lean region influenced by constant pressure specific heat enhancement, detail ($0 < z < z_{st}$) of the interaction with a high temperature propagating flame front in terms of constant pressure specific heat and density.

This effect is visible in Fig. 15, displaying a detail of the lean side between $z = 0$ and $z_{st} = 0.2$ for $C_p(z, t)$ and $\rho(z, t)$. Indeed, as the front approaches the property enhancement region, it is observed to slow down. Clearly, given the presence of a vanishing scalar dissipation model, at the LOx boundary, the premixed front is physically inhibited from ever reaching such boundary. Moreover the prior deceleration of the premixed front due to the property enhancement has the effect of reducing the extent of the transcritical region in the mixture fraction space as shown in fig. 16 shifting the pseudo-boiling toward the lean side. It is important to remark that even if the transcritical region and the pseudo boiling are confined to a relatively limited extension in the mixture fraction space, they can have a significant impact in the physical space as pointed out in [81].

As previously mentioned in this work the real gas mixture has been considered as a single phase of a unique pure hypothetical fluid. Since real gas mixtures can undergo a phase separation even at a pressure above the critical pressures of pure the components, provided it is lower than the mixture critical

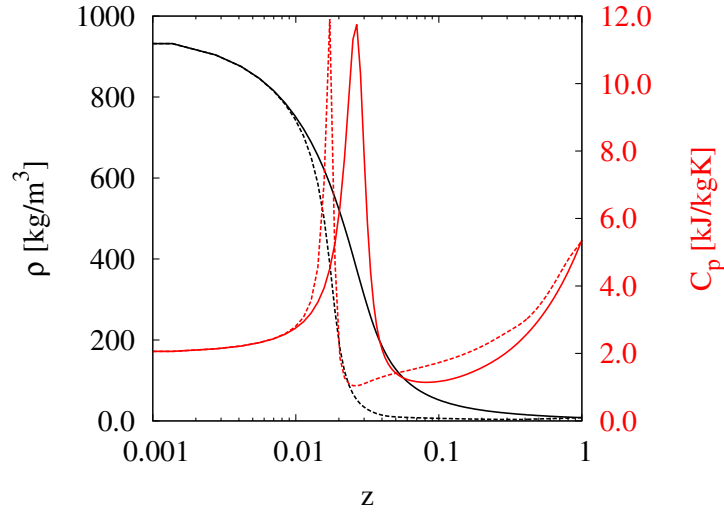


Figure 16.: Traveling, in mixture fraction space, of the pseudo boiling region due to propagating flame front after the autoignition. Bold lines are the initial conditions while the dashed lines are the steady state flamelet solution.

pressure [99], it is important to verify that no phase separation is occurring during the evolution of the flame structure. Experiments and equilibrium calculations have shown that the mixing of different components can cause significant variations in the mixture critical properties [111]. The thermodynamic regime can be determined comparing the local temperature and pressure with the critical temperature and critical pressure values. While for pure substance this comparison is quite straightforward, dealing with real gas mixtures some other assumptions are necessary and in order to determine the thermodynamic regime of real gas mixtures, an estimation of the mixture critical properties is required. Following [1] the critical temperature T_{mix}^c and the critical pressure p_{mix}^c of the mixture are approximated as:

$$T_{mix}^c = \sum_{j=1}^{ns} \frac{X_j V_j^c}{\sum_{i=1}^{ns} X_i V_i^c} T_j^c \quad (46)$$

$$p_{mix}^c = \frac{\sum_{j=1}^{ns} (X_j \frac{p_j^c V_j^c}{T_j^c}) T_{mix}^c}{\sum_{j=1}^{ns} X_j V_j^c} \quad (47)$$

where V_i^c , T_i^c and p_i^c are the critical volume, temperature and pressure of the i -th species respectively. Given the critical properties of the mixture, a reduced temperature $T_r = T/T_{mix}^c$ and a reduced pressure $p_r = p/p_{mix}^c$ can be defined for the entire transient flamelet solution of Fig.13 which can be mapped onto a thermodynamic regime plane (T_r, p_r) as shown in Fig.17.

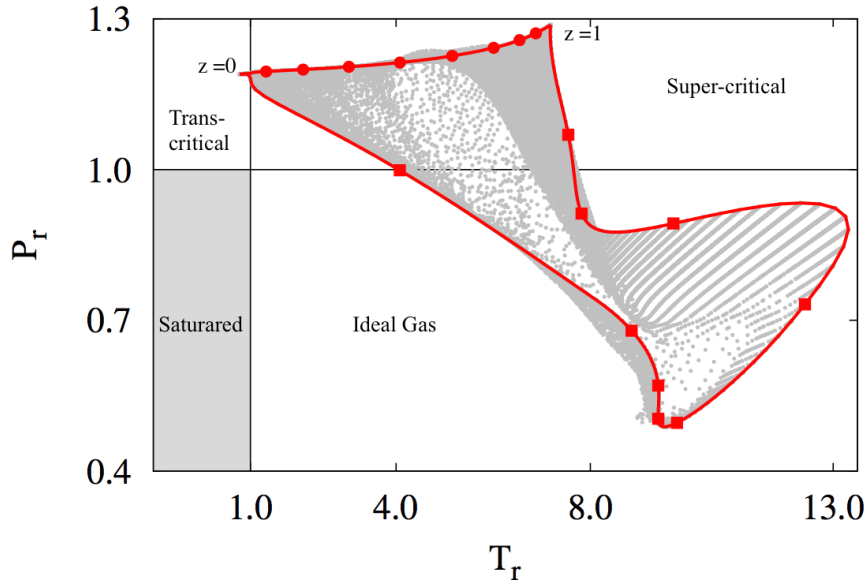


Figure 17.: Flamelet transient solution of Fig.13 represented in the thermodynamic regime plane (T_r, p_r) which is divided in four regions: trans-critical ($T_r < 1, p_r > 1$), super-critical ($T_r > 1, p_r > 1$), ideal ($T_r > 1, p_r < 1$) and saturated ($T_r < 1, p_r < 1$). Bold lines with filled symbols are the initial condition and the steady state solution (circles and squares respectively).

The initial condition (adiabatic pure mixing) lies almost entirely in the super-critical region ($T_r > 1, p_r > 1$) except for the lean boundary region ($z = 0$) where the cryogenic temperature of the oxygen causes an excursion into the trans-critical region. For the entire induction time, the flamelet solution is confined in the supercritical region and then after autoignition occurs the solution moves toward the ideal gas region due to temperature increase, and finally reaches the steady solution. The latter is characterized, similarly to the LOx-Hydrogen flame structure studied in [1], by 4 regions: transcritical lean, supercritical lean, ideal-high temperature and supercritical rich. It is evident that the entire transient never reaches the saturated region, confirming that two-phase flow effects cannot be encountered at these operating pressures (60 bar or higher) and temperature boundary conditions, thus confirming the validity of the single phase approach used here as a real gas mixture model.

Unsteady supercritical flamelet solutions obtained with the unique pure hypothetical fluid assumptions at different pressures, can be therefore used to evaluate real gas effects on the transient evolution of the flame structure. These effects can be conveniently evaluated by means of the compressibility factor Z measuring the mixture deviation from ideality, defined as: $Z = p / [\rho(R_u / \bar{W})T]$ where $\bar{W}$ is the mean mixture molecular weight. A transient flame structure

solution yields a compressibility factor field $Z(z, t)$ which can be analyzed to highlight real gas effects, identified as deviations from $Z = 1$, and to identify their influence on the evolution of such laminar flame structure during autoignition. Auto-igniting solutions at pressures $p = 60 - 300$ bar are analyzed, for the same scalar dissipation values to highlight pressure effects.

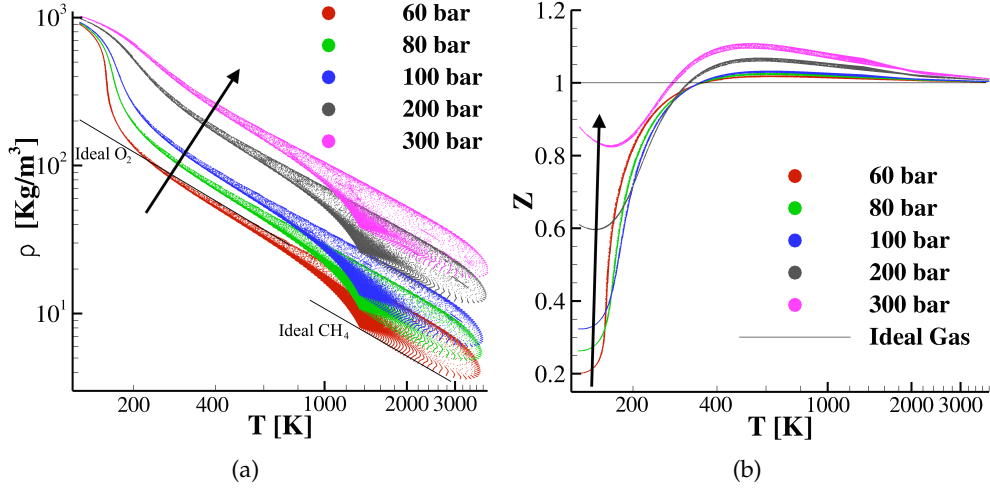


Figure 18.: Real Gas effects on transient flame structure at different pressures, increasing in the arrow direction, from $p = 60$ bar to $p = 300$ bar: Supercritical transient flame structures mapped in the temperature-density plane (a), compressibility factor-temperature plane (b).

A convenient way to analyze real gas effects is to map the complete transient solution on the density-temperature and compressibility factor-temperature planes as shown in Fig. 18. Results for the near-critical pressure of 60 bar show that real gas effects ($Z \neq 1$) are relevant only in the low temperature region, constituted predominantly by LOx. High temperature, low density states, on the other hand, correspond to a near-ideal gas mixture for which $Z < 1.03$ yielding a maximum density error of 3% in the reactive region. Similar conclusions were drawn in turbulent jet flame simulations [81] where real gas effects were observed to be confined exclusively to the cold oxidizer core. Note that the density scatter observed at high temperatures is due to the evolving composition of flame structure solutions at different times. Deviation from ideality can also be seen in terms of density by observing the reference ideal line for pure oxygen in Fig. 18.

At elevated pressures ($p > 100$ bar), deviation from ideality extends to the high temperature region as well while it reduces on the LOx side. Indeed at 300 bar real gas effects become of the same order both in the cold LOx zone ($Z \geq 0.78$) and in the high temperature region ($Z \leq 1.11$), with the exception of the burned near-stoichiometric region at $T > 2000$ K for which $Z \rightarrow 1$. This has

important consequences on a class of simplified methods which confine real gas effects to a single species, such as oxygen, treating the remaining species as an ideal gas mixture [112]. While this can lead to significant time savings by bypassing complex mixing rules such as Eq. (32)-(34), it can be considered acceptable at best for near-critical pressures and simple fuels such as hydrogen, but can lead to considerable errors at higher pressures or more complex fuels.

3.2.3 Influence of pressure and scalar dissipation on ignition

Auto-igniting flamelet solutions can be used to evaluate qualitative temporal behavior in terms of ignition delay time τ_{ign} and a time shift τ_{SH} [33]. An ignition delay time, for each value of z , has been estimated here using the peak concentration of a pre-ignition species such as formaldehyde CH_2O as a marker [113]. The overall ignition delay is then defined as $\tau_{ign} = \min(\tau_{ign}(z))$ as shown in fig. 19. The time shift τ_{SH} is then defined as the difference between $\tau_{ign}(z_{st})$ and τ_{ign} , where z_{st} is the stoichiometric mixture fraction ($z_{st} = 0.2$ in the present case), and represents a measure of the flame spreading time across mixture fraction space [33]. In this particular sub-case the scalar dissipation rate was intentionally deprived of a dependence from the mixture fraction and was therefore kept constant so that the unsteady evolution of the flame structure would not suffer from the adoption of a particular model. This clearly has an effect at the boundaries as considering $\chi \neq 0$ throughout the mixture fraction space implies a residual mass and temperature diffusion as opposed to the case of vanishing scalar dissipation models. While this may alter the premixed front propagation and thus the ignition delay times calculations in the proximity of the boundaries, constant scalar dissipation can be safely assumed in the inner mixture fraction domain (mixture fraction regions important for τ_{ign} and τ_{SH} definition) without loss of generality as shown in fig. 19.

Figure 20 displays a comprehensive parametric analysis of the characteristic times in terms of pressure and scalar dissipation for the auto-igniting solutions considered, both τ_{ign} and τ_{SH} are observed to decrease as pressure is increased due to kinetic effects (see also Fig. 21). For each pressure value, a critical value of the scalar dissipation rate χ_{cr} can be defined for which $\tau_{ign} \rightarrow \infty$ and autoignition becomes inhibited due to excessive heat loss. The critical scalar dissipation χ_{cr} is observed to increase with pressure, as shown in Fig. 21, thereby widening the range of auto-igniting solutions which exist for $\chi \in [0, \chi_{cr}]$. A steady-state parametric analysis was carried out by Kim et al. [36] who observed a similar increase of the quenching value of the scalar dissipation rate χ_q with pressure. This essentially suggests that, for increasing pressures, the typical S-

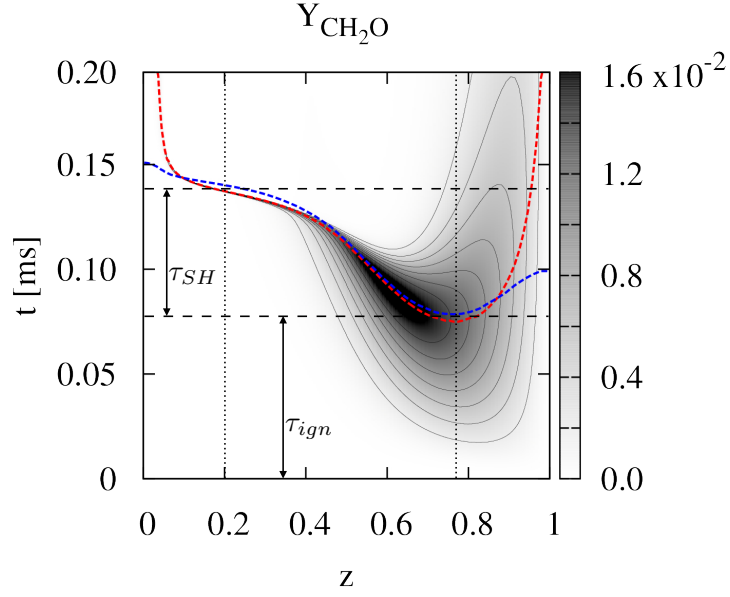


Figure 19.: Definitions of ignition time τ_{ign} and time shift τ_{SH} on the basis of formaldehyde concentration $Y_{CH_2O}(z, t)$. The red dashed line is $\tau_{ign}(z)$ using $\chi(z)$, the blue dashed line is $\tau_{ign}(z)$ using $\chi = const$.

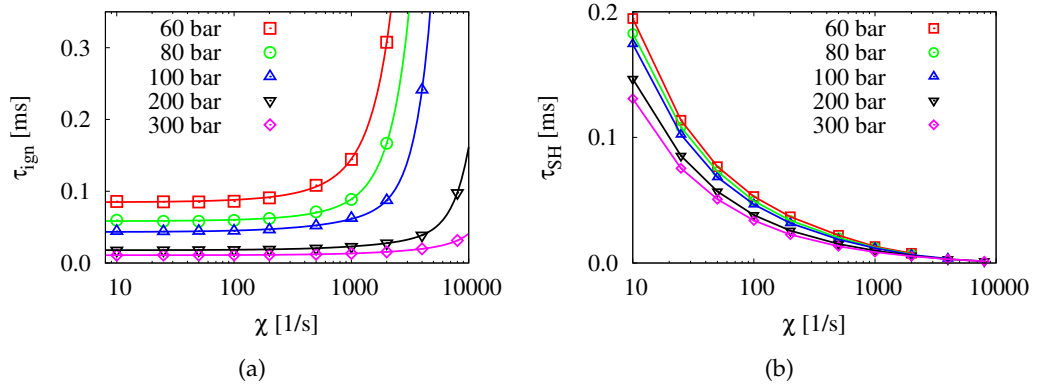


Figure 20.: Parametric analysis from for τ_{ign} (a) and τ_{SH} (b) at various pressures, from $p = 60$ bar to $p = 300$ bar, as functions of the scalar dissipation rate χ .

shaped diagram, for given boundary conditions, is expected to translate towards higher values of scalar dissipation.

Observing Fig. 20, two scalar dissipation regimes can be singled out: a low- χ regime where τ_{ign} remains essentially constant, and a high- χ regime, where τ_{ign} rapidly increases. Such regimes can be better investigated in Fig. 22 by observing $\tau_{ign}(z)$ for each value of z as scalar dissipation is increased in the $[0 \text{ s}^{-1}, \chi_{cr}]$ range.

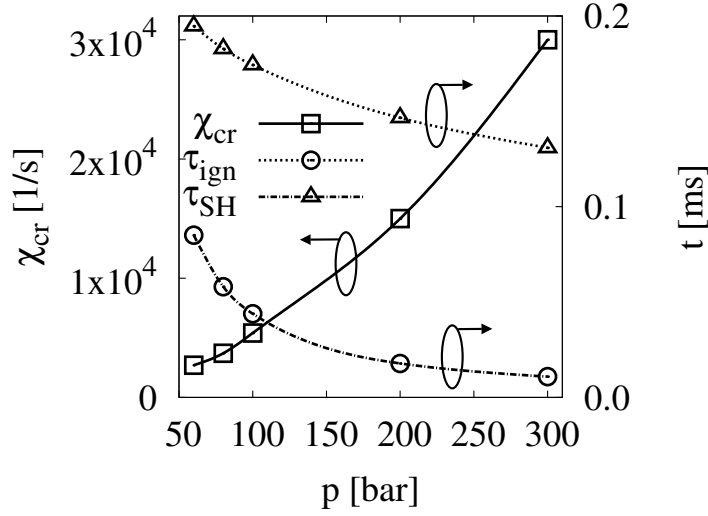


Figure 21.: Pressure influence on critical scalar dissipation rate $\chi = \chi_{cr}$. Also shown, minimum τ_{ign} and maximum τ_{SH} obtained at low scalar dissipation rate $\chi = 10s^{-1}$.

In the low- χ regime (panels (a,b,c) in Fig. 22) it is clear that as χ is increased, while τ_{ign} remains essentially constant, $\tau_{ign}(z_{st})$ decreases significantly. This implies a marked decrease of τ_{SH} with χ , as shown in Fig. 20(b), and in turn a significant decrease in flame spreading time or equivalently an increase in the propagation speed of the flame front towards the lean side in z -space. This is due to the effect of scalar dissipation, which governs the diffusive process in z -space and thus is expected to be proportional to the propagation speed of the premixed front. Therefore, for higher values of scalar dissipation, the complete achievement of the steady state flamelet structure occurs in shorter times as the flame spreading is promoted by the higher diffusivity.

On the other hand, in the high- χ regime (panels (d,e,f) in Fig. 22), the flame spreading time essentially shrinks to zero so that $\tau_{ign}(z)$ becomes essentially uniform in z . A further increase in scalar dissipation, however, results, for each value of z , in an ever enhanced heat loss and radical species diffusion which cause a delay in ignition and ultimately, for $\chi = \chi_{cr}$ the inhibition of autoignition and $\tau_{ign}(z) \rightarrow \infty$ for all z as shown in Fig. 22.

3.2.4 Most reactive mixture fraction

In the autoignition of turbulent non-premixed flows, a key information is given by the location of the ignition kernel which depends on local composition, temperature and scalar dissipation. In particular, such ignition kernels will occur

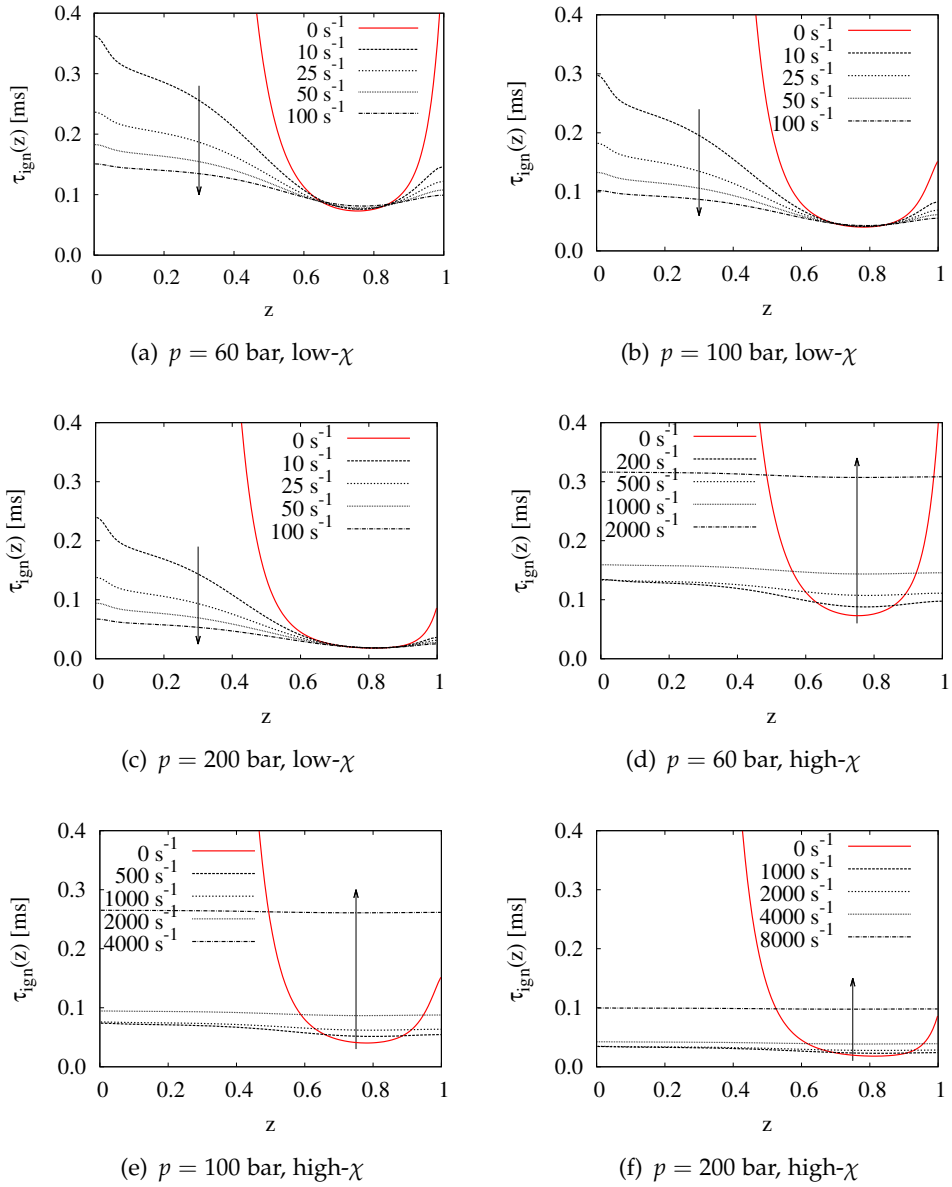


Figure 22.: Ignition delay time $\tau_{ign}(z)$ for low- χ and high- χ regimes at three pressure values of 60 bar, 100 bar and 200 bar.

where mixture fraction approaches a "most reactive" value, provided conditions of low scalar dissipations are met [114, 115]. In the context of auto-igniting flamelet solutions in z -space, the most reactive mixture fraction z_{MR} can be considered a property of the initial and boundary condition and can be defined as the first value of z to exhibit ignition. The definition can thus be taken as the value of z at which the temperature source term $\dot{\omega}_T$ is maximized at the initial state $t = 0^+$ [116].

The effect of pressure on z_{MR} has generally not been analyzed explicitly in the literature, as mentioned in [33], although a dependence is to be expected. In particular, given the expression for $\dot{\omega}_T = -\sum_i h_i \dot{\omega}_i$, such dependence intervenes through the species source terms and, in the case of the present real gas modeling, through the species enthalpies as well. Indeed, analyzing Fig. 22, the value of z at which $\tau_{ign}(z)$ reaches a minimum, which can be taken as an alternate definition for z_{MR} , is clearly seen to shift towards the rich side as pressure is increased, independently of scalar dissipation rate. By explicitly monitoring z_{MR} , using the maximum $\dot{\omega}_T$ definition, we observe the clear dependence shown in Fig. 23 where increasing the pressure from 60 to 300 bar causes an increase in z_{MR} from 0.865 to 0.905. It is important to note that, while the latter change in z_{MR} may seem relatively small in z -space, the same change may correspond to large changes in the physical space location of the ignition kernels depending on the level and pattern of mixture fraction stratification of the turbulent flow.

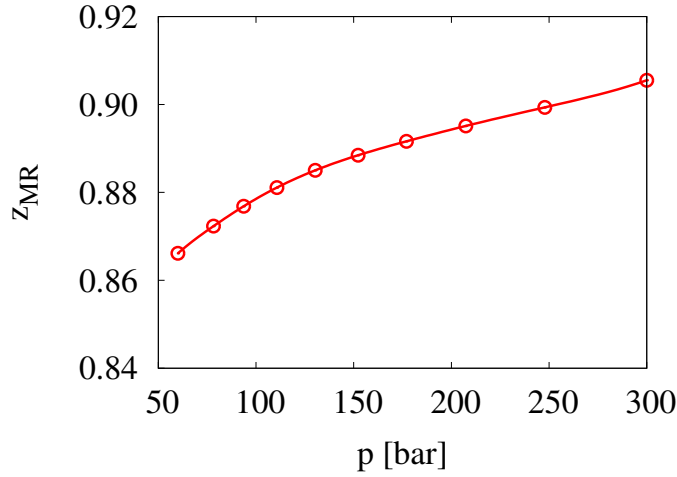


Figure 23.: Most reactive mixture fraction z_{MR} as a function of pressure.

3.2.5 Heat release rate

The total heat release rate per flame unit volume $\dot{q}_s$ can be defined as follows:

$$\dot{q}_s(t) = - \int_0^1 \left(\sum_{k=1}^N h_k \dot{\omega}_k \right) dz. \quad (48)$$

This quantity has been extensively investigated at supercritical pressures both in steady state flamelet solutions [36, 2] and in counterflow configurations [28, 27]. Such studies showed that for a given pressure, $\dot{q}_s$ increases almost linearly

with χ until reaching the maximum heat release rate for χ_q at quenching. Moreover χ_q , which marks the extinction limit of the steady ignited solution branch, was shown to increase with pressure. It was also found that the heat release rates for all supercritical pressure conditions can be linearly correlated with the product of pressure and scalar dissipation rate $\dot{q}_s \sim \chi \cdot p$ [36, 2]. This highlights both the diffusion-controlled nature of steady solutions and a pressure effect on chemical rates.

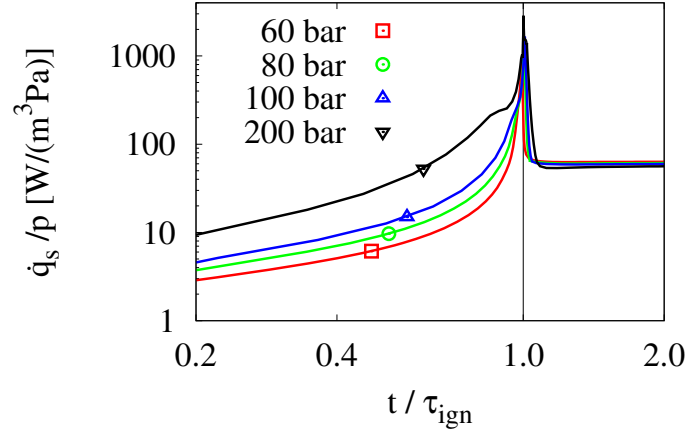


Figure 24.: Heat release rate normalized by pressure $\dot{q}_s/p$ during the flamelet evolution for various pressures (from $p = 60$ bar to $p = 200$ bar) and a single scalar dissipation rate value ($\chi = 1000 \text{ s}^{-1}$)

In the present study $\dot{q}_s$ is analyzed during the whole ignition transient. In Fig. 24 the heat release rate normalized by the pressure is shown for a single scalar dissipation rate ($\chi = 1000 \text{ s}^{-1}$) during the transient. The correlation $\dot{q}_s \sim \chi \cdot p$ is shown to be recovered only at steady state where $\dot{q}_s/p$ collapses onto a single value. This confirms that during the induction time, the heat release rate is controlled by the chemical time scales and not by the diffusion time scales as at steady state.

3.3 UNSTEADY EFFECTS ON BURNING FLAME STRUCTURE

In order to investigate unsteady phenomena such as re-ignition and quenching at supercritical pressures, the response of a flamelet solution to turbulent perturbations is studied. Indeed, state-of-art supercritical combustion simulations currently rely on simplified steady state flamelet models [9, 81, 82] which assume the flame structure to respond infinitely fast to perturbations of the

turbulent flow field. In a high pressure environment, however, the elevated Reynolds number [80] can lead to rapid and intense scalar dissipation variation over time, given its intermittent nature [117, 118], that can in turn give rise to unsteadiness in the flame structure.

3.3.1 Turbulent perturbation modeling

Turbulent effects can be modeled as abrupt variations or sharp time signals of the scalar dissipation rate [119, 32]. Following the work of Xuan and Blanquart [119] the scalar dissipation rate profile $\chi(z, t)$ fluctuates with a characteristic timescale according to a multiplicative factor $\phi(t)$ that can attain values from 0.5 to 2. The functional dependence of the scalar dissipation rate profile on z is assumed to be known a-priori as an amplitude mapping closure model [104]:

$$\chi(z) = \chi_{max}^0 f(z) \quad ; \quad f(z) = \exp(-2\text{erfc}^{-1}(2z))^2, \quad (49)$$

parametrized with the peak scalar dissipation rate value χ_{max}^0 . The unsteady scalar dissipation signal is then obtained from:

$$\chi(z, t) = \phi(t)\chi(z) = A_\chi \tilde{\phi}(t)\chi(z), \quad (50)$$

where the chosen shape of the multiplicative perturbation $\tilde{\phi}(t)$ is a triangular wave of unit amplitude, as in [32] and where $\phi(t) = A_\chi \tilde{\phi}(t)$ is fully characterized by a peak amplitude A_χ and a duration τ_χ as shown in Fig. 25. The ensuing scalar dissipation rate $\chi(z, t)$ will thus constitute a forcing function for the unsteady flamelet system, whose solutions are here considered as representative of a local "flame element" subject to a turbulent perturbation.

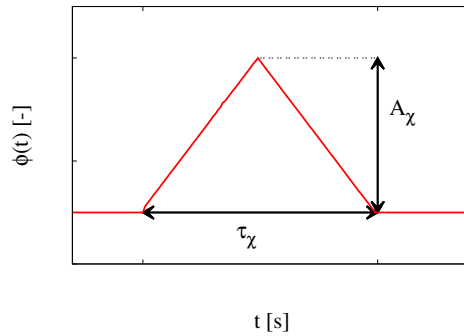


Figure 25.: Multiplicative scalar dissipation perturbation $\phi(t)$ as a triangular wave defined by an amplitude A_χ and duration τ_χ .

3.3.2 Quenching and re-ignition phenomena

Realistic LOx-Methane LRE combustion chamber conditions are here employed for supercritical flamelet calculations to investigate quenching and re-ignition of the flame structure. Coherently with the autoignition calculations in sec. 3.2 a background pressure of 60 bar is chosen, while the boundary conditions are slightly different with pure oxygen at the oxidizer side ($T_{ox} = 120$ K) along with pure methane at the fuel side ($T_{fuel} = 300$ K). The time-varying scalar dissipation rate model is given by Eq. (50) whereas the initial condition is a steady state burning flamelet solution obtained for peak scalar dissipation rate of $\chi_{max}^0 = 5.0 \cdot 10^5 s^{-1}$.

Two representative perturbations in the scalar dissipation rate have been imposed with a characteristic time of $\tau_\chi = 1 \mu s$ and respectively $A_\chi = 1.35$ and $A_\chi = 1.30$ following the definitions of Fig.25. Note that such amplitudes lead to peaks in scalar dissipation exceeding the quenching value for steady solutions which was estimated as $\chi_q \approx 5.93 \cdot 10^5 s^{-1}$. The characteristic time τ_χ , which can be considered of the order of a Kolmogorov timescale τ_K , has been chosen following the experimental and numerical work of Ivancic and Mayer [72], where $\tau_K \approx 1 \mu s$ was estimated for hydrogen and LOx combustion at supercritical pressures.

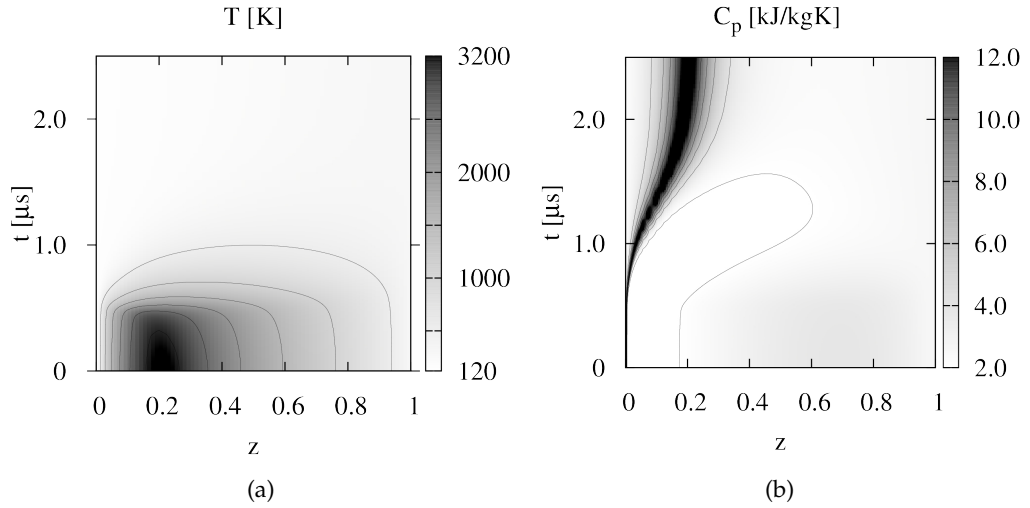


Figure 26.: Real gas flame structure results for a scalar dissipation rate signal characterized by $A_\chi = 1.35$ and $\tau_\chi = 1 \mu s$ leading to quenching: Temperature $T(z, t)$ (a), constant pressure specific heat of the mixture $C_p(z, t)$ (b).

In Fig. 26 the perturbation $A_\chi = 1.35$ is shown to drive the flame structure towards complete quenching. In point of fact, an initial increase in scalar dissipation rate generally causes a temporary rise in heat release $\dot{q}_s$ owing to

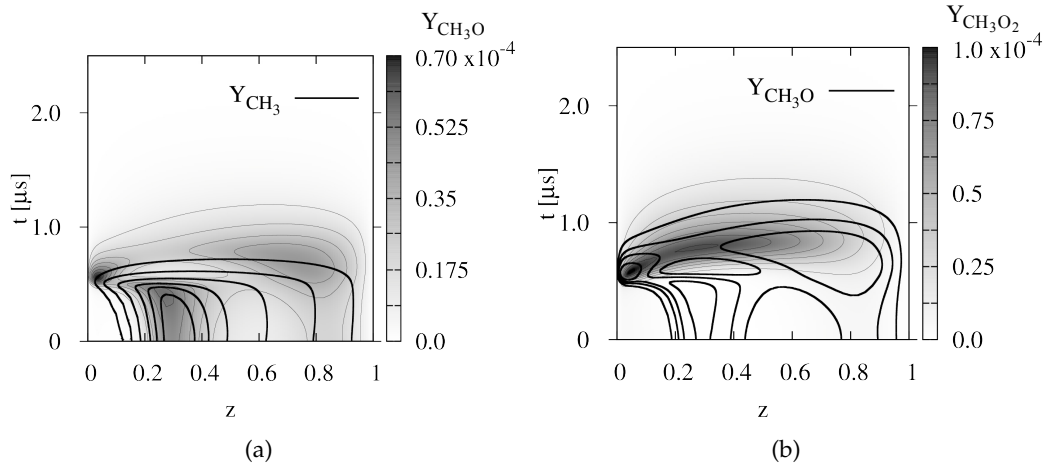


Figure 27.: Radical pool species diffusion in mixture fraction space. Diffusion of $Y_{CH_3O}(z, t)$ with isolines (even increments) of $Y_{CH_3}(z, t)$ superimposed in bold (a). Diffusion of $Y_{CH_3O_2}(z, t)$ with isolines (even increments) of $Y_{CH_3O}(z, t)$ superimposed in bold (b).

an increased supply of reactants in a regime where chemical timescales are still shorter than diffusive timescales. As scalar dissipation is increased further, diffusion timescale become competitive to chemical processes, thus initiating the lateral diffusion of temperature and radical pool species, which are key processes leading to quenching. Also shown in Fig. 26, is the location of the near-critical enhancement of C_p , moving away from the z value relative to the steady burning solution, and approaching the mixture fraction value relative to the pure adiabatic mixing between LOx and methane.

Figure 27 displays the quenching phenomenon in terms of the transient effects on radical species concentration. Before the radical pool diffusion becomes unsustainable for combustion, complex chemical transients may be observed in which some intermediates are formed immediately prior to quenching. In Fig. 27(a), intermediate CH_3 can be seen diffusing towards the LOx side where the pool of atomic oxygen is present. In doing so, it activates reactions such as $CH_3 + O \rightarrow CH_3O$. Indeed a transient pool of CH_3O can be observed (Fig. 27) to appear near the lean side. Such intermediate species soon recombines according to $2CH_3O \rightarrow CH_3O_2 + CH_3$ to yield a final pool of CH_3O_2 (as shown in Fig. 27(b)) which diffuses soon after, prior to quenching. An additional CH_3O pool is observed on the rich side, possibly generated by formaldehyde being diffused into higher methane concentration according to $CH_2O + CH_4 \rightarrow CH_3O + CH_3$.

The second perturbation considered, $A_\chi = 1.30$, leads to the re-ignition of the flame structure as shown in Fig. 28. This means that the excursion of the scalar dissipation rate above χ_q was not sufficient for quenching to occur. In particular,

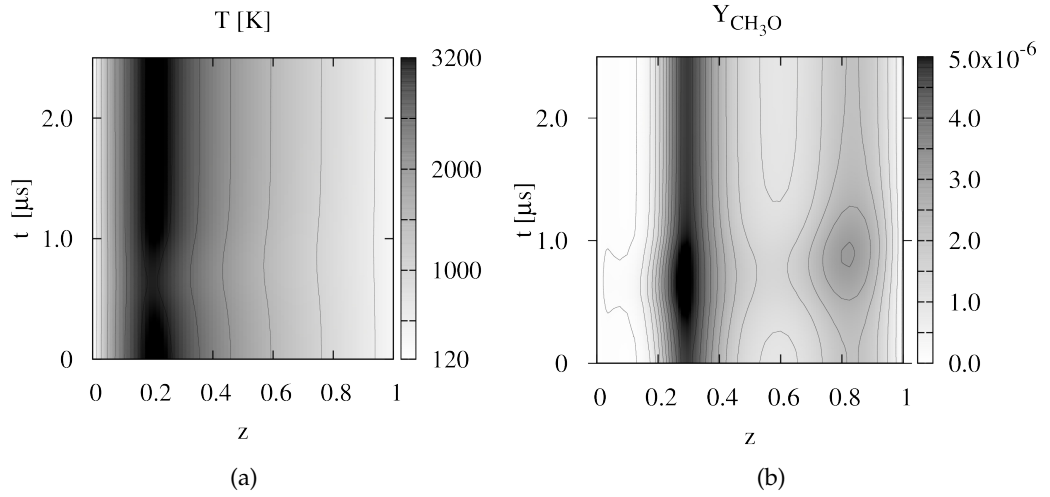


Figure 28.: Real gas flame structure results for a scalar dissipation rate signal characterized by $A_\chi = 1.30$ and $\tau_\chi = 1 \mu\text{s}$ leading to re-ignition: Temperature $T(z, t)$ (a) and an intermediate $Y_{\text{CH}_3\text{O}_2}(z, t)$ (b). Note that the peak value of CH_3O_2 is an order of magnitude smaller than the corresponding value during quenching.

temperature is only slightly reduced before regaining the initial steady state profile. The transient patterns involving intermediates during quenching, are now far less pronounced. Figure 28 (b), for instance, reveals only a partial production of CH_3O on the lean and rich sides, indicating that the diffusive processes involved in such production are insufficient to trigger the related chemical pathways described above. In conclusion, as observed at atmospheric pressures in [32], the discriminating property between a quenching and a re-igniting scalar dissipation rate signal is its excess time integral with respect to the constant background scalar dissipation rate, a quantity referred as critical dissipation impulse [120]. For the constant duration signal in Fig. 25 this is clearly proportional to the amplitude A_χ .

Given the constant perturbation time $\tau_\chi = 1 \mu\text{s}$, a critical perturbation amplitude $A_{\chi_{cr}}$ exists which defines the bifurcation between quenching and re-ignition of an initial steady state flame structure. For the pressure and boundary conditions considered herein, the critical perturbation amplitude is found to be $A_{\chi_{cr}} = 1.329$. Figure 29 shows such bifurcation in terms of ensuing peak temperature T_{max} and heat release rate $\dot{q}_s$ for the two signals $A_\chi = 1.325 < A_{\chi_{cr}}$ and $A_\chi = 1.335 > A_{\chi_{cr}}$, leading to re-ignition and quenching respectively. Note that in Fig 29, χ_{max} is defined as $\chi_{max} = \chi(z = 0.5, t)$. It is worth mentioning that both solutions exhibit increasing heat release rate during the growing part of the scalar dissipation rate signal. The same bifurcation event can be observed in

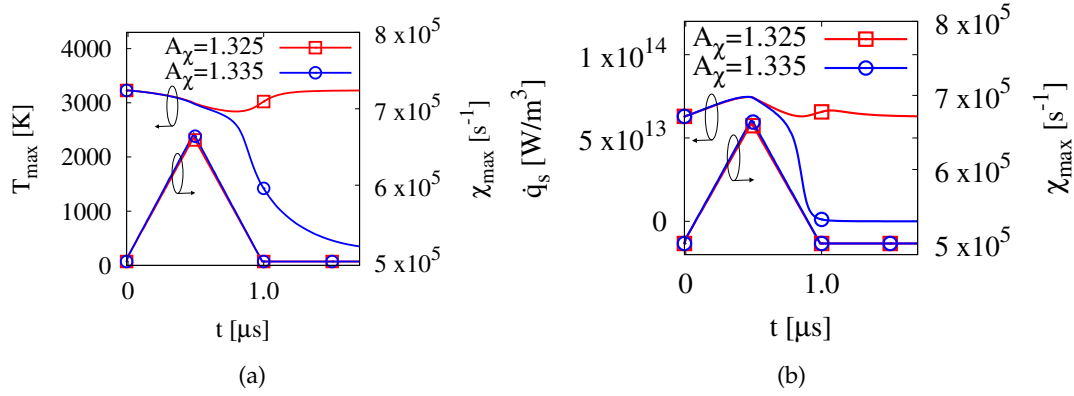


Figure 29.: Time evolution of peak temperature (a) and heat release rate per unit flame (b) during scalar dissipation rate signals around the critical amplitude of $A_{\chi_{cr}} = 1.329$.

the flamelet state space (T_{max}, χ_{max}) in Fig 30, where the two trajectories can be seen to emanate from the stable burning branch.

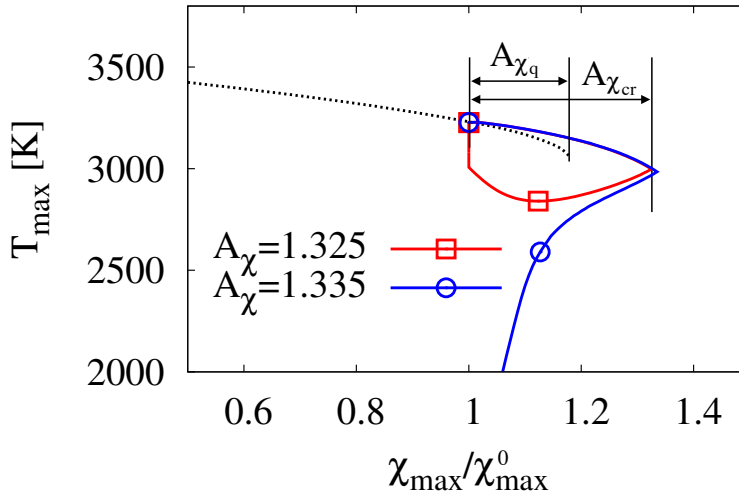


Figure 30.: Trajectory of perturbed flame structure in $(T_{max}, \chi_{max}/\chi_{max}^0)$ -space during scalar dissipation rate signals around the critical amplitude of $A_{\chi_{cr}} = 1.329$. Dashed line: steady burning branch solutions. Also shown, amplitude of reference signal A_{χ_q} and critical amplitude $A_{\chi_{cr}}$.

3.3.3 Pressure effects on critical perturbation amplitude

Steady non-premixed flames at supercritical pressures have been shown to be more resilient to strain rate effects, and consequently the quenching value of the scalar dissipation rate χ_q is observed to increase with pressure [36, 2]. Indeed

higher values of the scalar dissipation rate, and therefore shorter diffusive time scales, are required to compete with the decreased chemical time scales at higher pressures, in order to achieve a steady state solution. In other terms, given the increased heat release rate, the steady non-premixed structure can survive to a wider range of scalar dissipation rates. The steady state peak temperature is also observed to increase with pressure due to the reduction of chemical dissociation [36, 2]. The foregoing properties pertain strictly to steady state flame structures and were, indeed, observed exclusively for such steady solutions.

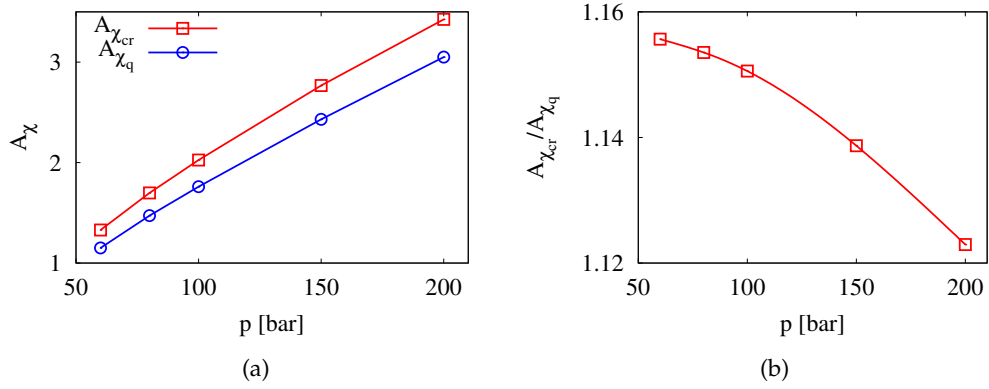


Figure 31.: Critical, $A_{\chi_{cr}}$, and reference, A_{χ_q} , amplitudes of the scalar dissipation rate signal (a) and their ratio (b) as functions of background pressures.

In the present work, which focuses on the unsteady behavior of flame structure at supercritical pressures, the question arises as to the extent to which the amplitude of a transient scalar dissipation rate signal can exceed the steady quenching value χ_q , and in particular, the related role played by pressure. This can be answered by defining a reference scalar dissipation rate signal, whose amplitude A_{χ_q} is such that its peak is attained at the quenching value χ_q as shown in Fig. 30. Although the initial scalar dissipation rate value χ_{max}^0 and the signal duration τ_χ are kept constant, the signal will vary with pressure due to variations in χ_q . Such reference signal can be compared to the critical bifurcating signal having the same duration, whose amplitude is $A_{\chi_{cr}}$. Figure 31 shows the influence of pressure on both such amplitudes. While the monotonic increase of A_{χ_q} and $A_{\chi_{cr}}$ with pressure may be directly attributed to the corresponding increase of χ_q , the ratio $A_{\chi_q} / A_{\chi_{cr}}$ is however observed to decrease. These two effects have a clearly different genesis. An increase of χ_q with pressure signifies that a steady diffusion flame is more resilient at high pressure, surviving to a wider range of steady χ fields. On the other hand, the decrease of $A_{\chi_{cr}} / A_{\chi_q}$ is a purely transient phenomenon pointing to the fact that, at higher pressures, a

diffusive flame can survive to perturbations in excess of χ_q that are relatively smaller than at lower pressures. The reason for this is that the wider range of scalar dissipation rate perturbing a high pressure flame, also implies faster transients due to the higher rates of heat loss. Thus, given a constant duration signal τ_χ , amplitudes leading to quenching, in excess of A_{χ_q} , are relatively smaller at higher pressures. An un-physical limit case would imply transients infinitely faster than the duration τ_χ , in which case the only non-quenching signal amplitude would tend to A_{χ_q} , implying $A_{\chi_q}/A_{\chi_{cr}} \rightarrow 1$.

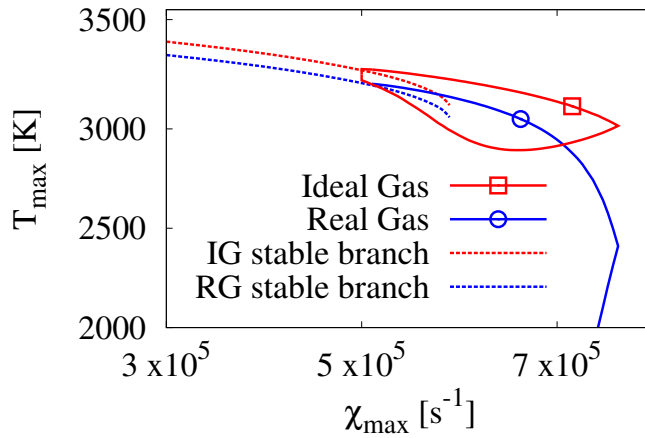


Figure 32.: Time evolution of peak temperature of the ideal and real gas flame structure with respect to χ_{max} during the same scalar dissipation rate perturbation at $p = 60$ bar.

Some authors, based on the similarity of steady state flame structures obtained using ideal and real gas EoS, have suggested that the ideal-gas flame solutions can be used for fluids at supercritical conditions [30]. Others pointed out that the similarity of these flame structures does not translate directly into an equivalent similarity in the multi-dimensional spatial domain [36]. Indeed, every numerical approach must utilize a real gas model to capture fluid effects in and around the cryogenic liquid oxygen region (and at very high pressures also in broader regions of the flow as in Fig. 18). Ideal gas Steady Laminar Flamelet (SLF) approaches to turbulent combustion modeling may yield acceptable results when coupled with real fluid compressible CFD solvers. However, consistent low-mach and compressible [83] formulations must mandatorily utilize real gas flame structures as these act as an effective equation of state.

Additional issues may arise when extending unsteady flamelet methods to supercritical turbulent combustion. Figure 32 shows that for the same perturbation, ($\tau_\chi = 1 \mu s$ and $A_\chi = 1.35$), the ideal gas flame structure experiences a

re-ignition process while the real gas flame structure is quenched. Thus the same turbulent perturbation leads to opposite behaviors owing to the slightly different peak temperatures of the initial condition. While this effect can be dramatic for unsteady flame structure solutions, it is unclear the role it will play in an unsteady turbulent combustion model.

3.3.4 Representation of transient phenomena

It is customary to represent unsteady flamelet phenomena as trajectories in the (T_{max}, χ_{max}) -plane (e.g. as in Fig. 32 or equivalently in the (T_{st}, χ_{st}) -plane) juxtaposed to the standard S-shape locus of steady solutions on the same plane [34, 35]. Time evolving iso- χ solutions, therefore, are represented as vertical lines in the flamelet state space (T_{max}, χ_{max}) . A more complete picture can however be achieved on an alternative (λ, Da) -plane, where λ is the flamelet parameter [35] (the peak value of a progress variable normalized with its equilibrium value) and Da is an appropriately defined Damkhöler number. While λ plays an equivalent role to T_{max} , the Da number sheds light on the role of chemical, as well as diffusive timescales during any transient flamelet evolution. A possible definition of the Damkhöler number is the following:

$$Da = \frac{1}{\chi_{max}(t) \tau_c(t)} = \frac{\rho(z_{st}, t) T(z_{st}, t) C_p(z_{st}, t)}{\chi_{max}(t) \dot{q}_s(t)}. \quad (51)$$

Figure 33 displays both the locus of steady state solutions (stable burning branch) as well as a set of representative transient solutions (trajectories or paths) for a background near critical-pressure of 60 bar and a super-critical pressure of 200 bar. The latter higher pressure exhibits a lower value of the Damkhöler number at quenching conditions Da_q . This is coherent with the increased χ_q value of the scalar dissipation rate as discussed earlier in terms of faster transients due to the higher rates of heat loss.

Transient solutions, regardless of their origin, exhibit two distinct behaviors: (i) an igniting or re-igniting behavior, characterized by $d\lambda/dt > 0$ and terminating on the stable burning branch, and (ii) a quenching or relaxing behavior, with $d\lambda/dt < 0$ and terminating at $Da \rightarrow 0$ or on the stable burning branch respectively. The plane (λ, Da) of Fig. 33, was populated with trajectories originating from the steady burning branch and generated by imposing representative turbulent perturbations, modeled as abrupt changes in the scalar dissipation rate as Heaviside step functions or square waves. A quenching trajectory, for instance, is obtained by imposing a χ -step function of amplitude exceeding χ_q .

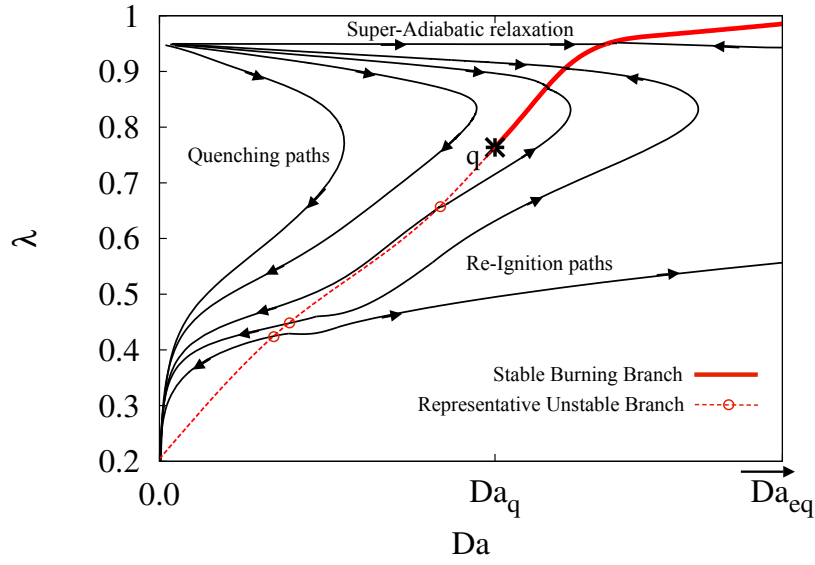
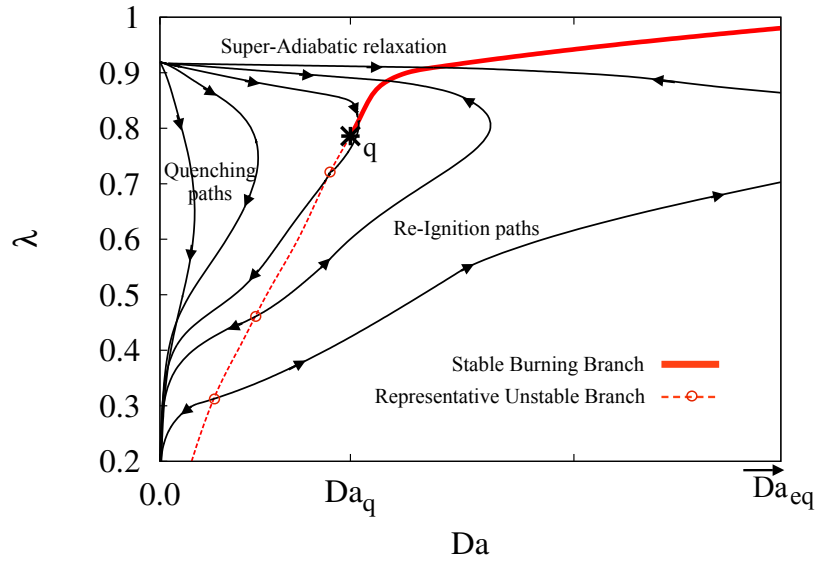
(a) $p = 60$ bar(b) $p = 200$ bar

Figure 33.: Flamelet state space (λ, Da) showing steady and representative unsteady solutions at near-critical and supercritical pressures. Note that $Da_q(60 \text{ bar}) > Da_q(200 \text{ bar})$

Any smaller amplitude signal will result in a super adiabatic relaxation path reverting back to the stable burning branch.

Re-igniting solutions, on the other hand, are obtained by imposing square wave signals characterized by an impulse below the critical value, as discussed earlier in sec. 3.3.2, a greater impulse yielding a quenching solution. The boundary between re-igniting and quenching solutions, displayed as a dashed

line in Fig. 33, is indicative of the unstable branch in the classical S-shape diagram, and subdivides the (λ, Da) state space into an igniting region in which $d\lambda/dt > 0$ and a quenching region or relaxing region where $d\lambda/dt < 0$. In the context of turbulent combustion modeling, the described set of representative quenching and re-igniting trajectories could be employed as tabulated flamelet libraries parametrized in (χ, λ, z) -space, as done in Unsteady Flamelet/Progress variable (UFPV) methods at atmospheric pressure [34, 35].

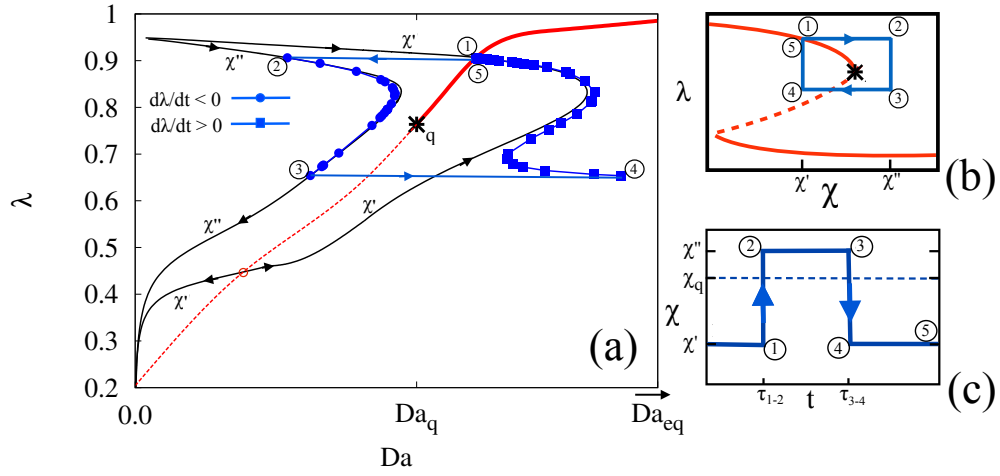


Figure 34.: Representation in the $\lambda - Da$ space (a) and in the $\lambda - \chi$ space (b) of a re-ignition trajectory caused by a prescribed abrupt change in the scalar dissipation $\chi(t)$, as reported in (c).

A particular re-ignition event has been analyzed in Fig. 34. Point 1 represents the initial steady state solution on the stable branch for $\chi = \chi'$. At time τ_{1-2} , the scalar dissipation rate abruptly reaches $\chi'' > \chi_q$, corresponding to point 2 in the figure, after which the flamelet solution follows the iso- χ'' quenching trajectory until point 3 at τ_{3-4} when χ is reduced back to χ' . Such trajectory exhibits a fast relaxation transient before collapsing onto the iso- χ' representative solution which effectively acts as an attractor or *pseudo manifold* and thus represents the solution's asymptotic behavior. We conclude that these fast transient effects will remain undetected by any UFPV method utilizing only the representative trajectories of Fig. 33 as flamelet libraries. However the present dynamical reconstruction on the (λ, Da) plane, reveals that such trajectories furnish the most complete representation of all possible transient phenomena.

3.4 SUMMARY AND CONCLUSIONS

A general fluid, unsteady flamelet solver has been developed in order to investigate unsteady effects, such as autoignition, re-ignition and quenching in the context of flamelet solutions for LOx/Methane non-premixed flame structures at supercritical pressures. Real fluid effects were captured using a general three-parameter equation of state and appropriate mixing rules implemented in the RGM library.

- Auto-igniting flamelet solutions were analyzed at pressures $p = 60 - 300$ bar and constant and uniform scalar dissipation. Real gas effects in terms of compressibility factor were observed, during the ignition transient and at steady state, to be confined to the LOx region for $p < 100$ bar but extend farther into the rich region at greater pressures. Near stoichiometric regions at $T > 2000$ K can be considered ideal at any pressure.
- Auto-igniting flamelets show that while ignition and flame spreading times decrease with pressure, the critical scalar dissipation rate value above which autoignition is inhibited increases. This implies that the S-shape turning points, in terms of χ_{cr} and $\chi_{q,}$ are shifted toward higher scalar rate values. Moreover, as scalar dissipation rate is increased, ignition times decrease uniformly while flame spreading time tends to zero. Further increase at or above the critical value, a uniform increase in ignition time was observed until complete inhibition of the autoignition process.
- Real gas effects in auto-igniting flamelets are manifested by a deceleration of the lean premixed front near the LOx side. This is due to the near-critical enhancement of C_p effectively acting as a localized heat sink.
- The most reactive mixture fraction in auto-igniting solutions was observed, for the particular boundary conditions adopted, to shift towards richer values as the pressure is increased from 60 to 300 bar. The variability of the most reactive mixture fraction may have non negligible effects on the location in the physical space of ignition kernels in high pressure turbulent diffusive flames.
- During the entire autoignition transient at near critical pressure, the mixture is found to never reach the saturated region, confirming that a locally two-phase flow cannot be encountered at the pressures and boundary temperatures considered.

- Quenching and re-ignition phenomena were analyzed by means of transient scalar dissipation signals, mimicking turbulent effects. These events can exhibit complex transient patterns of intermediate species concentration. The location in mixture fraction space of the C_p near-critical enhancement is also susceptible to synthetic turbulent perturbations, during the quenching of the flame structure.
- For an initial steady state flame structure, a critical turbulent perturbation amplitude which defines the bifurcation between quenching and re-ignition has been found. The critical signal amplitude was observed to increase with pressure similarly to the behavior of the quenching value of the scalar dissipation rate. However the relative extent to which the scalar dissipation rate amplitude can exceed the quenching value, for a given signal duration, is observed to decrease with pressure. Thus, while high pressure flames possess higher quenching values of scalar dissipation rate, they can be considered more susceptible to quenching during transient phenomena.
- Transient flamelet solutions were projected onto a comprehensive flamelet-parameter/Damköhler-number state space highlighting chemical and diffusive timescales. A representative subset of such supercritical solutions can be expected to be usefully employed within unsteady flamelet approaches for turbulent combustion modeling.

4

LNG FLAME STRUCTURE

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Methane and Liquefied Natural Gas (LNG) have been recently considered as propellants, together with cryogenic oxygen (LOx), for Liquid Rocket Engines (LRE) applications as pointed out in the introduction . In this framework is of fundamental importance to understand how the composition of LNG, compared to pure methane, can influence non-premixed combustion at typical LRE supercritical operating conditions. In the present chapter, the flame structures of LNG/LOx mixtures at supercritical pressures are investigated by means of the previously developed general fluid formulation for the unsteady laminar flamelet equations (chap. 3). Flame structures are analyzed at elevated pressures ranging from near-critical up to largely supercritical, for pure methane and various representative mixtures models of LNG. The LNG/LOx steady state flame structure characteristics are found to show close similarities to those of pure methane. On the other hand pollutants such as early stage soot precursors (i.e. acetylene) are found to be strongly dependent on the LNG composition. Preliminary analysis on sooting tendencies of LNG are carried out in order to shed light on Polycyclic Aromatic Hydrocarbons (PAH) presence at supercritical pressures. A single representative mixture for LNG composition is analyzed showing significantly larger production of soot precursors, such as benzene and naphthalene.

4.1 THEORETICAL AND NUMERICAL FORMULATION

The previously developed general fluid formulation for the unsteady laminar flamelet equations (see chap. 3) is used here in order to analyze the flame structure of the LNG/LOx mixtures. The idea is to gain insights on the non-premixed combustion at typical LRE supercritical operating conditions and understand how the composition of LNG, compared to pure methane, can influence the flame characteristics. Contrary to the previous chapter the flame structures are analyzed in a stationary sense, paying attention only to the ensuing steady state solution of the supercritical flamelet equations. In order to assess the steadiness of the flamelet solutions, the dependency of mixture enthalpy on mixture fraction $h(z)$ is monitored. At steady state $h(z)$ is a linear function between the two boundary values at the fuel and oxidizer for every scalar dissipation value, with unit Lewis numbers and adiabatic assumptions. This can be easily derived substituting the flamelet species equation (eq. 41) into the energy equation (eq. 43) which implies:

$$\frac{\partial h}{\partial z} = 0. \quad (52)$$

The chemical mechanism used is the GRI 3.0 [107] comprising 53 species with 325 elementary chemical reactions (hydro-carbon + nitrogen chemistry). It includes all the species of the representative LNG mixtures of Tab. 3, and has been shown to give good results for combustion of natural gas. Even if originally developed for atmospheric pressure, it can be used at elevated pressure if only the steady state solution is needed, showing a maximum 3% error (with respect to the high pressure mechanism RAMEC) over the entire flamelet profile of temperature and major species. Moreover, it has been recently used at supercritical pressures for LOx/methane combustion using steady flamelet assumptions [82].

4.2 LIQUID NATURAL GAS CHARACTERISTICS

4.2.1 LNG composition range

LNG is commonly obtained cooling the gaseous natural gas. The composition of the raw natural gas can be largely influenced by processing history and extraction location. Methane is the most abundant species present among others in the raw composition with a molar fraction always exceeding 85%. Carbon dioxide,

nitrogen, and water can also be present together with heavier hydrocarbons such as ethane (C_2H_6) and propane (C_3H_8), [121]. Components that will freeze during the cooling processes, such as carbon dioxide, are removed before starting the processes. In order to ensure non-toxicity and non-corrosiveness of LNG less abundant species, hydrogen sulphide (H_2S) and mercury (Hg), among others, are also removed [122].

Table 2.: LNG composition range [18, 19]

Species	Molar Fraction, %
CH_4	80 – 99
C_2H_6	1 – 17
C_3H_8	0.1 – 5
C_4H_{10}	0.1 – 2
C_5H_{12} and heavier	0 – 1
N_2	0 – 5

Table 3.: LNG representative mixtures in Molar Fraction, % [18, 19]

Mixture	CH_4	C_2H_6	C_3H_8	N_2
MIX0	100	0.0	0.0	0.0
MIX1	92	4.0	2.2	1.8
MIX2	86	9.5	4.0	0.5
MIX3	93	5.0	1.5	0.5
MIX4	88	5.0	2.0	5.0

Commercial LNG composition will be influenced by quality specifications and can vary in the range reported in Tab. 2. Following the work of Urbano and Nasuti [123], in the present study the heaviest hydrocarbon considered is propane. Five representative LNG compositions [123], which are summarized in Tab. 3, have been used for flame structure calculations.

4.2.2 LNG mixtures properties

Before analyzing the LOx/LNG flame structures, the relevant thermodynamic properties of only liquid natural gas are shown. In Fig. 35 real fluid properties of the representative LNG mixtures are compared against pure methane at various pressures in a temperature range of interest. Results for density $\rho(T; p)$ and constant pressure specific heat $C_p(T; p)$ show quite similar behavior for mix1, mix3 and mix4. On the other hand mix2 exhibits the larger discrepancies

from pure methane (mix0), this being mainly due to the high concentration of ethane and propane (respectively 9.5% and 4.0% in moles).

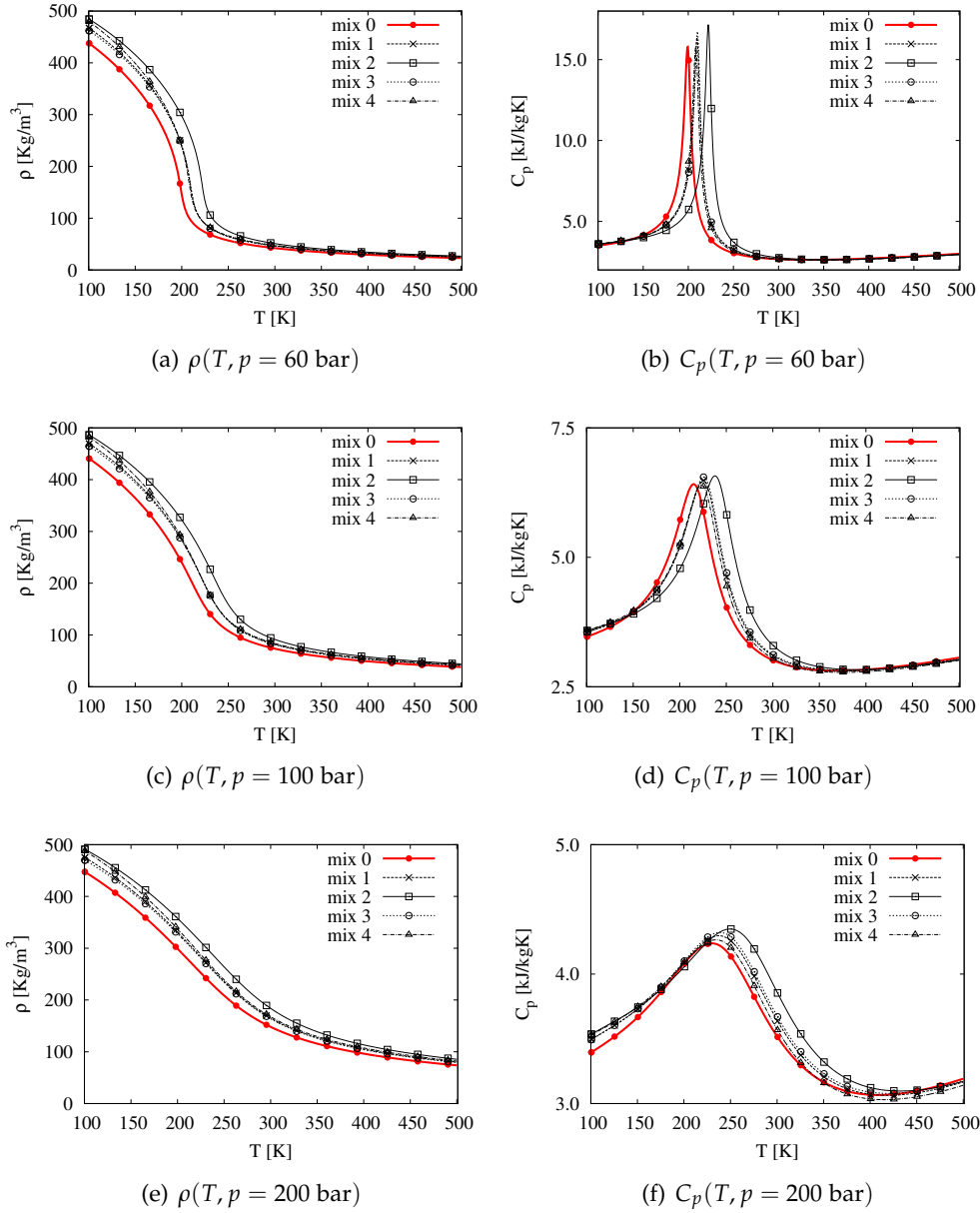


Figure 35.: Real fluid thermodynamic properties of representative LNG mixtures (Tab. 3) as functions of temperature at three different pressures: 60 bar, 100 bar and 200 bar.

4.3 FLAME STRUCTURE CHARACTERISTICS OF LOX/LNG MIXTURES

4.3.1 Steady flame structure overview

Similarly to the previous analysis a background pressures of 60 bar, representative of realistic LOx-methane LRE chamber conditions, is chosen for a set of steady state flame structure. The chosen value $p = 60$ bar is challenging from a numerical point of view because of the pseudo-boiling occurring in the proximity of the pure oxygen boundary occurring in the neighborhood of the critical region for pure oxygen ($T_{cr} = 154.6$ K). In order to accurately capture the enhancement of thermodynamic properties, a higher resolution and thus lower grid spacing is required towards the lean side in mixture fraction space. This is achieved by using a non-uniform grid gradually refined towards the oxidizer side. The same grid of the unsteady analysis of chap. 3 is used.

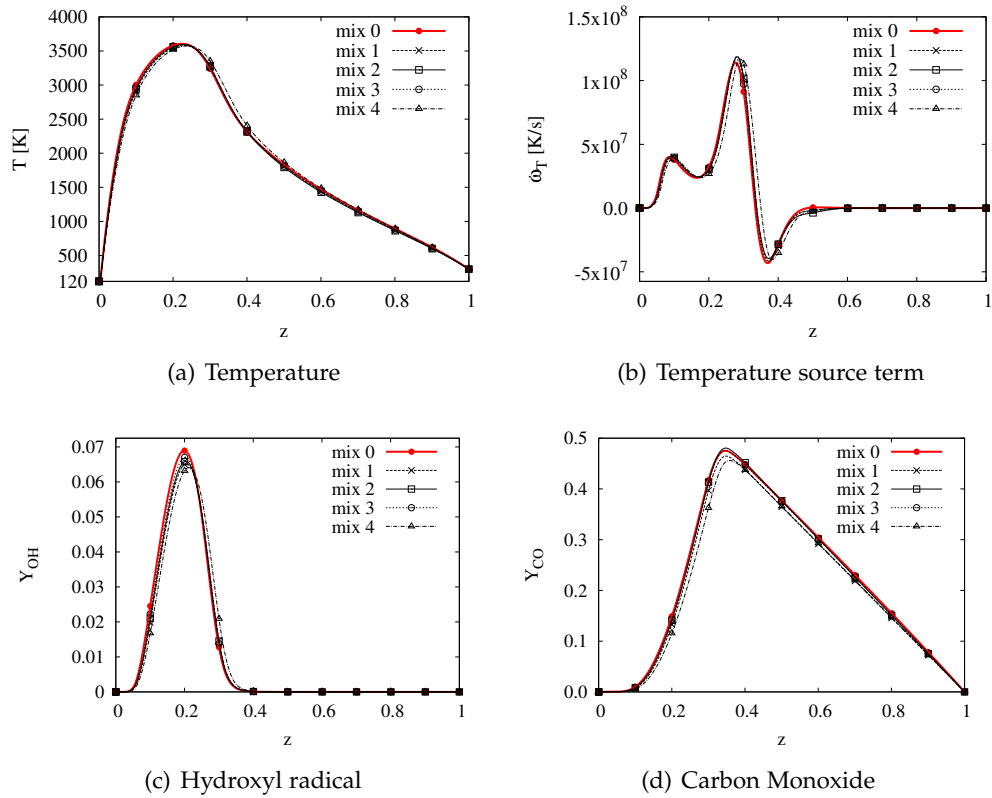


Figure 36.: Steady state real fluid flame structures for a low scalar dissipation value ($\chi_{max} = 1000 \text{ s}^{-1}$) at near critical pressure 60 bar. Results shown in terms of temperature T , temperature source term ω_T , hydroxyl radical OH and carbon monoxide CO for LNG representative mixtures of Tab. 3.

The boundary condition on the cold oxidizer side, chosen as pure oxygen at $T_{ox}(z = 0) = 120$ K, is representative of the operating temperature of cryogenic LOx injection in LRE combustion chambers. The temperature fuel boundary condition is $T_{fu}(z = 1) = 300$ K, that can be considered representative of a LRE's using an expander-cycle-like configuration. The maximum scalar dissipation rate value chosen for steady state flamelet calculation is $\chi_{max} = 1000 \text{ s}^{-1}$ according to Eq. (49), which can be considered a low value with respect to extinction limits [2] in the range of pressure considered.

Figure 36 displays a similar behavior of the flame structures, between representative LNG mixtures and pure methane. Results are shown in terms of the main flame structure features such as temperature $T(z; p)$ (fig. 36(a)) and temperature source term $\dot{\omega}_T(z; p)$ (fig. 36(b)) as well as relevant species (fig. 36(c)-36(d)). The hydroxyl radical OH and carbon monoxide CO mass fractions were respectively chosen as an important flame marker and an abundant by-products respectively. The two mass fraction profiles ($Y_{OH}(z; p)$ and $Y_{CO}(z; p)$) essentially reveals the same behavior between the representative mixtures and the pure methane flame structure. Only mix 4, due to the elevated nitrogen percentage in the composition (5%) show negligible discrepancies with the profiles peaks shifting slightly toward the rich side.

All these similarities in the profiles analyzed in fig. 36 hints at a substantial equivalence, from the combustion performance point of view, between LNG mixtures and methane as LRE fuels. This result is confirmed by integral quantities such as the total heat release rate per flame unit volume $\dot{q}_s$, defined as:

$$\dot{q}_s(t) = - \int_0^1 \left(\sum_{i=1}^N h_i \dot{\omega}_i \right) dz \quad (53)$$

and shown in Fig. 37 for a wide range of scalar dissipation rates, from near chemical equilibrium up to quenching values. The total heat release rate per flame unit volume, for the representative mixtures mix1-4, is found to bear very close to the pure methane. Slightly different behavior between mixtures are present only in the near extinction region where mix 2 (ethane and propane rich) seem to be more robust to strain.

Moreover, consistently with previous results of the counterflow diffusion flames for hydrogen/oxygen [28] and methane/oxygen [27], as well as the flamelet calculation for hydrogen/oxygen [36] a linear dependence of the heat release rate on the scalar dissipation rate or the strain rate at supercritical pressures is found for all mixtures.

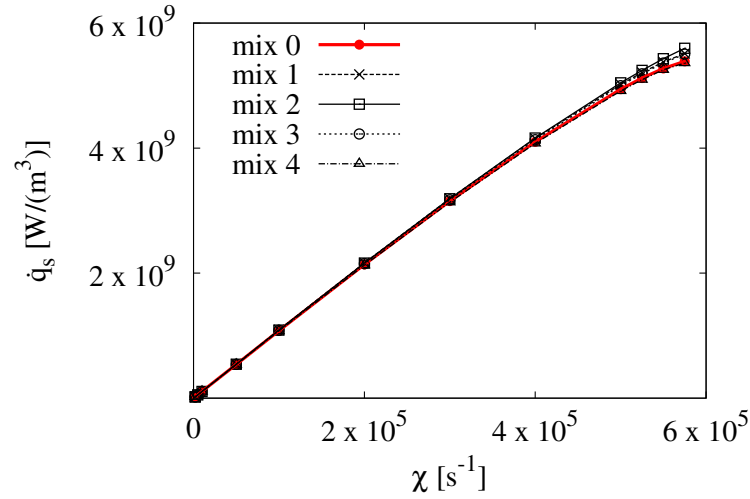


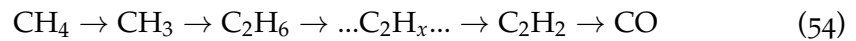
Figure 37.: Substantial equivalence between LNG mixtures and methane: heat release rate per flame unit volume as a function of scalar dissipation rate at near critical pressure $p = 60$ bar.

4.3.2 LNG composition effects

The influence of LNG composition on the steady state flame structure is investigated for two representative hydro-carbon (HC) species: acetylene C_2H_2 and ethylene C_2H_4 . In particular, acetylene is an important PAH precursors that can be correctly represented by steady state flamelet solutions because of its relatively fast chemistry [119, 124]. In addition, simplified and semi-empirical soot models at elevated pressure use acetylene-based chemistry for soot inception and growth [125].

Results show that these early soot precursors (Fig. 38) are directly influenced by the amount of ethane and propane in the LNG composition. A useful parameter to describe the results is the ratio between the carbon and hydrogen content in the chemical compound, which will be indicated as (C/H) [123]. Indeed for acetylene mass fraction $Y_{C_2H_2}$, the lowest values are observed for pure methane (C/H= 0.25) and the highest for MIX2 (C/H= 0.2614).

Computational singular perturbation (CSP) analysis on methane oxidation using GRI3.0 mechanism, even if performed at atmospheric pressure can give important physical insight. It highlighted essentially three pathways for methane oxidation [126], the one involving acetylene is here reported:



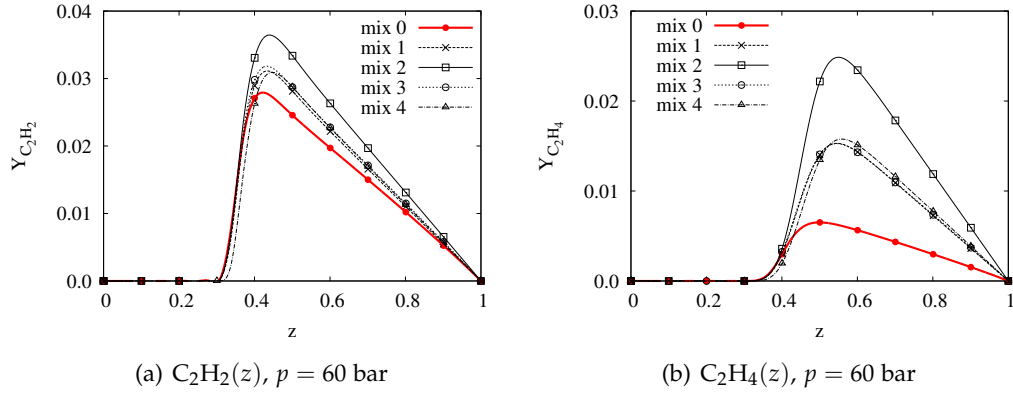


Figure 38.: Steady state real fluid flame structures for a low scalar dissipation value ($\chi_{max} = 1000 \text{ s}^{-1}$) at near critical pressure 60 bar. Results shown in terms of acetylene (C_2H_2) and ethylene (C_2H_4) for LNG representative mixtures of Tab. 3.

which clearly show the pivotal role of ethane toward acetylene formation. For this reason, acetylene mass fraction in the flame structure of LNG mixtures is roughly proportional to ethane mass fraction in the fuel composition and therefore to C/H ratio.

Analyzing the flame structure profiles, for lean mixture fraction values, $z < z_{st}$, it is clearly observable that C_2H_2 and C_2H_4 concentrations approach zero. Such species are therefore oxidized before reaching the flame region in the moderately rich zone $z > z_{st}$ ($z \approx 0.3$ for C_2H_2) for all representative LNG mixtures considered, contributing to CO production. For richer values of the mixture fraction ($z > 0.5$) diffusion becomes the dominant process, showing an almost linear dependence on mixture fraction of the mass fractions for the species considered. This means that the analyzed species have vanishing source terms in that region, since at steady state $\dot{\omega}_i = -1/2\rho\chi\partial^2 Y_i/\partial z^2$.

4.3.3 Pressure Effects

The pressure effect on the LNG/LOx flame structure is here analyzed, taking advantage of the fact that the shape of the flamelet profiles are preserved, not only for different scalar dissipation values, but also through LNG compositions and pressure values. This allows the representation of a flamelet solution by means of a single mixture fraction value at $z^* = z \mid \max(Y_{C_2H_2})$, namely the peak location of acetylene profile. The values at z^* are therefore analyzed in

a range of pressure useful for LRE applications that ranges from near critical (60 bar) up to largely supercritical (200 bar).

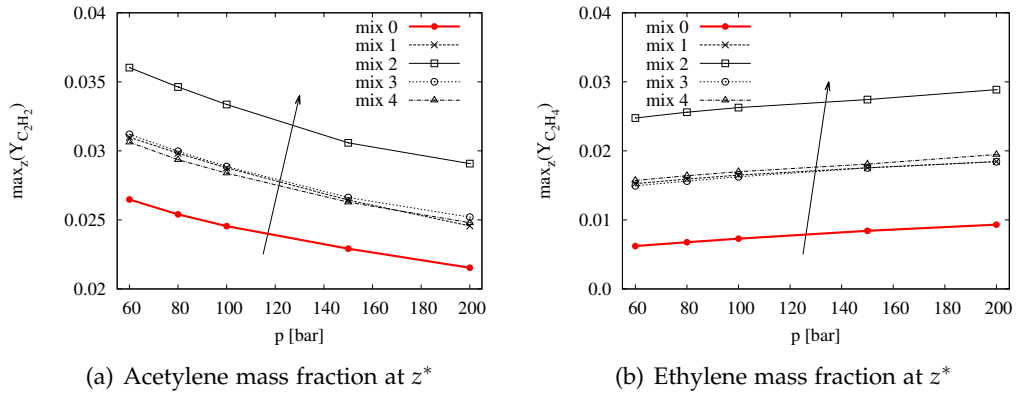


Figure 39.: Acetylene (C_2H_2) and ethylene (C_2H_4) mass fractions at $z = z^*$ for LNG representative mixtures as functions of pressure. The arrow indicates an increasing C/H ratio between mixtures. All the steady state real fluid flame structures are calculated for a fixed low scalar dissipation value ($\chi_{max} = 1000 \text{ s}^{-1}$).

Figure 39, show that acetylene mass fraction is decreasing, while ethylene is slightly increasing as pressure increases for all representative LNG mixtures considered. This behavior of a representative early stage soot precursor, such as C_2H_2 , is consistent with experimental studies on soot formation for methane-oxygen non-premixed combustion at high pressures [127]. The differences between the various mixtures remain in the same range discussed for the 60 bar case, depending on the C/H ratio.

However, in order to correctly evaluate the LNG composition effects on soot precursors, a more detailed chemical mechanism is needed, including a full set of PAH and important reactions such as the well-known mechanisms hydrogen-abstraction-carbon-addition (HACA) mechanism for the creation of the first benzene ring.

4.3.4 Preliminary analysis on soot precursors

Drawing from the supercritical flamelet results, obtained with the GRI3.0 mechanism, a preliminary analysis of the LNG sooting tendencies is presented. The influence of LNG composition on the PAH formation at supercritical pressure is investigated using the C1-C4 mechanism with PAH formation of Marinov et al. [128] consisting in 155 species and 689 reactions. The chosen representative soot precursors are benzene C_6H_6 and naphthalene $C_{10}H_8$. Indeed Attili

et al. [129] found a strong correlation between soot number density and the concentration of naphthalene in a prototypical turbulent jet flame.

Only the LNG representative composition with the higher acetylene and ethylene mass fraction (MIX2) is examined, and compared to pure methane because the main production pathways of benzene and naphthalene involve both C_2H_2 and C_2H_4 .

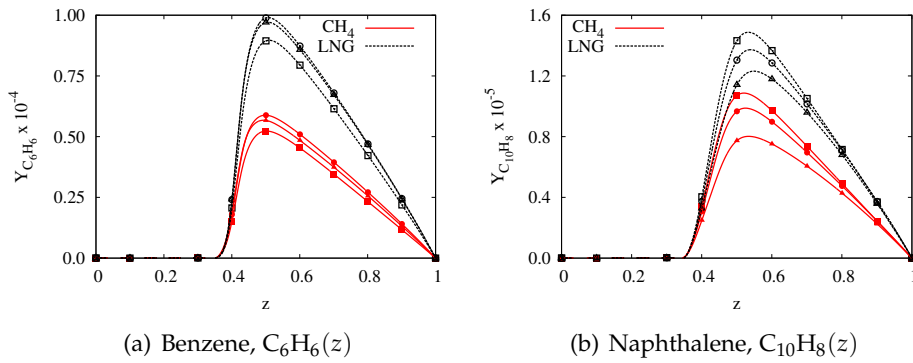


Figure 40.: Soot precursors benzene (C_6H_6) and naphthalene ($C_{10}H_8$) mass fraction profiles for pure methane (bold line and filled symbols) and a representative LNG mixture, MIX2 of Tab.(3) (dashed line and empty symbols) at three different pressures: 60 bar (squares), 100 bar(circles) and 200 bar (triangles).

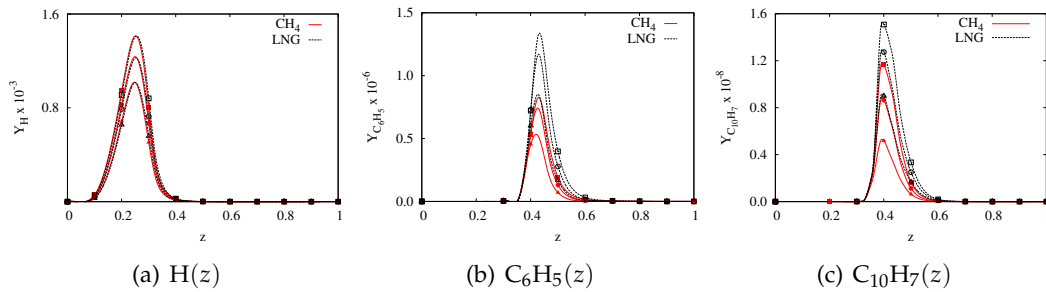


Figure 41.: Atomic hydrogen and representative PAH radicals (C_6H_5 and $C_{10}H_7$) mass fraction profiles for pure methane (continuous line and filled symbols) and a representative LNG mixture, MIX2 of Tab.(3) (dashed line and empty symbols) at three different pressures: 60 bar (squares), 100 bar(circles) and 200 bar (triangles).

The profiles of benzene and naphthalene mass fractions shown in Fig. 40 exhibit the same lighter HC (ethylene and acetylene that were previously analyzed) shape. It is noteworthy important to remark that also pure methane combustion at LRE thrust chamber conditions generates some soot precursors, and therefore its combustion products will not be completely soot-free. However, LNG as

expected, creates roughly two times the amount of PAH mass fraction with respect to pure methane.

In Fig. 41 the mass fraction profiles of a small radical (atomic hydrogen) and two important PAH radicals C_6H_5 and $C_{10}H_7$, for benzene and naphthalene production are presented. Pressure is shown to reduce the peak value of all the radical considered, leading to minor naphthalene production as pressure increases as shown in Fig. 40. The peaks of PAH radicals mark the mixture fraction region where soot precursors are oxidized before reaching the stoichiometric region.

It is important to remark that for a complete description of soot formation in order to help LRE thrust chamber design a soot model, coupled with detailed chemical mechanism for PAH formation is needed.

4.4 SUMMARY AND CONCLUSIONS

The effect of fuel composition on the LNG/LOx flame structure has been analyzed at supercritical pressures representative of LRE operating conditions. Real fluid effects encountered in LRE combustion chambers have been taken into account by means of a comprehensive three-parameter PR-RK cubic equation of state.

The LNG/LOx steady state flame structures have been calculated by means of an in-house code resorting to the GRI3.0 mechanism for methane oxidation. Results have show close similarities to those of the pure methane and LOx mixture from near-critical up to supercritical pressures. Temperature, OH radical profiles and also the total heat release rate per unit flame appear to be not significantly influenced by LNG composition hinting at a substantial equivalence from a combustion efficiency point of view. On the contrary early stage soot precursors as the acetylene, strongly depends on the LNG composition decreasing, as expected, as pressure increases. For the composition range adopted in the present work, the acetylene mass fraction in the flame structure of LNG mixtures is found to be roughly proportional to ethane presence in the fuel composition.

Pure methane and the LNG representative mixture with the higher presence of ethane (MIX-2) has been further analyzed with the more detailed mechanism of Marinov, gaining insights on soot precursors. It is found that LNG creates almost two times the amount of benzene and naphthalene mass fractions with respect to pure methane in the pressure range of interest. From a combustion modeling point of view additional effort is needed in order to take into account

differential diffusion, soot formation and radiative heat losses, which can be crucial for CFD simulations of LRE combustion chamber.

5

THE REAL GAS LOW-MACH NUMBER FORMULATION

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Mixing and combustion under supercritical conditions have been classically studied from the numerical point of view using compressible CFD codes. However these reactive and non-reactive flows are characterized, in many cases, by a very limited range of Mach numbers (usually well below 0.3). This implies that serious time step restriction are encountered due to elevated speed of sound in the liquid-like zones. In order to overcome these limitations, the highly scalable incompressible and low Mach number code nek5000 is here employed and modified. Firstly a low Mach number formulation for arbitrary EoS and chemistry models is developed under supercritical conditions. Secondly the formulation is validated on simply and well-known problems, such as the Rayleigh-Taylor instabilities for the non-reactive case and the propagation of a laminar premixed flame with simplified chemistry for the reactive case.

5.1 EOS INDEPENDENT LOW-MACH NUMBER FORMULATION

In the low-Mach number limit the governing equations of a flow can be recast filtering the acoustic waves propagation. This allows an efficient numerical

integration of the equations while density variations caused by temperature gradients, heat release and composition changes are fully taken into account.

5.1.1 Low-Mach number expansion

Recently the classical ‘Low-Mach expansion’ of Majda and Sethian [130] has been recalled by Battista et al. [66] to allow extension to real gas conditions. Moreover for real fluids the low-Mach number assumptions on the governing equations have been extensively used in the framework of turbulent flows with heat transfer [131]. The compressible, multi-component and reactive Navier-Stokes equations in a dimensional form reads [132]:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0 \quad (55)$$

$$\frac{\partial \rho \mathbf{u}}{\partial t} + \nabla \cdot (\rho \mathbf{u} \mathbf{u}) = \nabla \cdot \mathcal{T} + \rho \mathbf{f} \quad (56)$$

$$\frac{\partial \rho e}{\partial t} + \nabla \cdot (\rho \mathbf{u} h) = \mathcal{T} : \nabla \mathbf{u} - \nabla \cdot \mathbf{q}_e \quad (57)$$

$$\frac{\partial \rho Y_k}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = \nabla \cdot (\rho \mathbf{J}_k) + \dot{\omega}_k \quad (58)$$

where ρ is the mixture density, $\mathbf{u}$ the fluid velocity, e the mass weighted internal energy, h the mass weighted enthalpy and Y_k the mass fraction of the k -th species. To this point no assumptions have been made on the constitutive relations needed for: the stress tensor $\mathcal{T}$, the energy flux vector $\mathbf{q}_e$, the diffusive flux vector $\mathbf{J}_k$ and the reaction rate $\dot{\omega}_k$. We now assume that no body forces are present $\rho \mathbf{f} = 0$ and that the fluid is newtonian: $\mathcal{T} = -pI + 2\mu S + \lambda \text{tr}(S)I$, where μ is the dynamic viscosity, λ the thermal conductivity and $S = \frac{1}{2}(\nabla \mathbf{u} + \nabla \mathbf{u}^T)$ is the strain tensor. The energy flux vector can be expressed as: $\mathbf{q}_e = \mathbf{q}_q + h_k \mathbf{J}_k$ where the first term represents the heat flux vector and the second term the enthalpy flux vector of the species diffusion. From thermodynamic principles the heat flux vector and mass flux vector need to be a linear combination of the thermodynamic forces (temperature, pressure and concentration gradients) [89]:

$$\mathbf{q}_q = -b_{qT} \nabla T + b_{qp} \nabla p + b_{qj} \nabla Y_j \quad (59)$$

$$\mathbf{J}_k = b_{kT} \nabla T + b_{kp} \nabla p - b_{kj} \nabla Y_j \quad (60)$$

where b_{ij} is the matrix of coefficients assuming Fickian like processes.

Governing equations can be conveniently rewritten in a non-dimensional form using:

$$t^0 = \frac{l^0}{u^0}, \quad t^* = \frac{t}{t^0}, \quad u^* = \frac{u}{u^0}, \quad l^* = \frac{l}{l^0}, \quad \psi^* = \frac{\psi}{\psi^0} \quad (61)$$

where the star indicates non-dimensional variables, and the superscript 0 a reference value while ψ stands for all the other variables used. After some manipulations, eq.(55-58) read:

$$\frac{\partial \rho^*}{\partial t^*} + \nabla_* \cdot (\rho^* \mathbf{u}^*) = 0 \quad (62)$$

$$\rho^* \frac{D\mathbf{u}^*}{Dt^*} = -\frac{1}{\gamma_0 \hat{M}a^2} \nabla_* p + \frac{1}{Re} \nabla_* \cdot \Sigma^* \quad (63)$$

$$\rho^* \frac{Dh^*}{Dt^*} = \frac{Dp^*}{Dt^*} + \frac{\gamma_0 \hat{M}a^2}{Re} \mathcal{T}^* : \nabla_* \mathbf{u}^* + \frac{1}{Re Sc} \nabla_* \cdot \mathbf{q}_e^* \quad (64)$$

$$\rho^* \frac{DY_k^*}{Dt^*} = \frac{1}{Re Sc} \nabla \cdot (\rho^* \mathbf{J}_k^*) + \dot{\omega}_k^* \quad (65)$$

where the following non dimensional number have been introduced: $Re = \rho_0 u_0 l_0 / \mu_0$, $Sc = \mu_0 / D_0 \rho_0$ and $\hat{M}a = u_0 / a_0$ which are respectively Reynolds, Schmidt and a pseudo Mach number. It is important to remark that $\hat{M}a$ takes the role of the Mach number, even if the quantity in the denominator a_0 does not directly coincide with the sound speed at reference thermodynamic conditions using a generic EoS [66].

It is now possible to introduce the standard asymptotic expansion [130] for a generic variable f , in terms of a representative Mach number:

$$f(\mathbf{x}, t) = f_0(\mathbf{x}, t) + f_2(\mathbf{x}, t) \hat{M}a^2 + \mathcal{O}(\hat{M}a^4) \quad (66)$$

where the subscript 0 now represents the leading order term in the expansion and the superscript * is now dropped for brevity. All the dependent variables, namely $\rho, \mathbf{u}, e$ and Y_k , that do not explicitly exhibit $\hat{M}a$ in their equation (eq.62-65), will be represented only by their zero-th order contributions. All the terms of $\hat{M}a^2$ order can be dropped out since they can be considered small if the low-Mach assumptions are well posed for the particular case. Therefore the continuity equation reads:

$$\frac{\partial \rho_0}{\partial t} + \nabla \cdot (\rho_0 \mathbf{u}_0) = 0 \quad (67)$$

and applying eq. (66) to the momentum equation, the only term involving $\hat{Ma}$ is $1/\gamma_0 \hat{Ma}^2 \nabla p$ where γ is a reference ideal gas value. Comparing all the remaining terms of the same order in $\hat{Ma}$ we found that $\nabla p_0 = 0$, so the zero-th order pressure alternatively called thermodynamic or background pressure is spatially homogeneous and can vary only with time. The second order pressure term p_2 , which is commonly called hydrodynamic pressure, now appear in the zero-th order momentum equation:

$$\rho_0 \frac{D\mathbf{u}_0}{Dt} = -\nabla p_2 + \frac{1}{Re} \nabla \cdot \mathbf{S}_0. \quad (68)$$

Applying the asymptotic expansion to the energy equation the dissipation term $\gamma_0 \hat{Ma}^2 / Re \mathcal{T} : \nabla \mathbf{u}$ is not zero-th order so is not retained and Dp/Dt becomes simply $\partial p / \partial t$ since $\mathbf{u}_0 \cdot \nabla p_0 = 0$, neglecting spatial gradient of the thermodynamic pressure. Therefore the energy equation reads:

$$\rho_0 \frac{Dh_0}{Dt} = \frac{\partial p_0}{\partial t} + \frac{1}{ReSc} \nabla \cdot \mathbf{q}_{e0} \quad (69)$$

and the species equation simply reads:

$$\rho_0 \frac{DY_k}{Dt} = \frac{1}{ReSc} \nabla \cdot (\rho_0 \mathbf{J}_k) + \dot{\omega}_k \quad (70)$$

since only zero-th order terms are involved. Thermodynamic relations as well as explicit constitutive relations are now needed to completely close the system. These relations, which are commonly expressed in dimensional form, suggest a recasting in a dimensional form of the system without losing in generality. The subscript 0 is retained only for the thermodynamic pressure, while for the other variables is dropped for simplicity.

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0 \quad (71)$$

$$\rho \frac{D\mathbf{u}}{Dt} = -\nabla p_2 + \nabla \cdot \mu \mathbf{S} \quad (72)$$

$$\rho \frac{Dh}{Dt} = \frac{\partial p_0}{\partial t} + \nabla \cdot \mathbf{q}_e \quad (73)$$

$$\rho \frac{DY_k}{Dt} = \nabla \cdot (\rho \mathbf{J}_k) + \dot{\omega}_k. \quad (74)$$

5.1.2 Thermodynamic relations and divergence constraint

In real gases framework, every thermodynamic property depends is in general on temperature, pressure and composition: $\psi = \psi(T, p, Y_k)$. In the low-Mach number limit, this functional dependence is simplified since, considering open domains, the thermodynamic pressure p_0 is constant. This implies that p_0 effectively acts as a constraint for the thermodynamic properties, lowering the dimensionality of problem.

A generic equation of state: $p_0 = f_{EoS}(T, Y_k)$ constrain the evolution of the derived low-Mach system (eq.(71)-(74)). A common choice is to express the constraint in terms of fluid velocity $\mathbf{u}$ divergence, that can be obtained using the mass conservation equation and differentiating the EoS:

$$\nabla \cdot \mathbf{u} = -\frac{1}{\rho} \frac{D\rho}{Dt} = \mathcal{Q}_T \quad (75)$$

where $\mathcal{Q}_T$ is the thermal dilatation and the density is completely determined by the thermodynamic state by means of the equation of state. The imposition of the divergence constraint can be done indirectly, with eq. 75 replaced by an inhomogeneous Poisson problem for the hydrodynamic pressure p_2 , which is obtained by taking the divergence of the momentum equation:

$$\nabla \cdot \left(\frac{\nabla p_2}{\rho} \right) = -\nabla \cdot \frac{D\mathbf{u}}{Dt} + \nabla \cdot \mathbf{u} \left(\frac{4}{3} \mathcal{Q}_T - \nabla \times \nabla \times \mathbf{u} \right) \quad (76)$$

and imposing proper boundary conditions [133, 14]. The hydrodynamic pressure, thus effectively act as a Lagrange multiplier on the system evolution so that the divergence constraint is satisfied. Some numerical problems can arise using this approach because the divergence constraint is imposed only in an indirect way. For instance during the numerical integration, the approximated solution can drift away from the constraint manifold. In particular any numerical method will need to have small residuals on the constraint and to project the numerical solution back onto the manifold.

Without any assumptions on the particular form of the EoS, the energy equation (eq. 69) can be recast in terms of temperature using the general thermodynamic relations derived by Meng and Yang [78]:

$$dh = \left(\frac{\partial h}{\partial T} \right)_{p, Y_i} dT + \left(\frac{\partial h}{\partial p} \right)_{T, Y_i} dp + \sum_i^{ns} \left(\frac{\partial h}{\partial Y_i} \right)_{p, T, Y_{j \neq i}} dY_i = B_T dT + B_p dp + \sum_i^{ns} B_{Y_i} dY_i \quad (77)$$

and applying it to the material derivative of the enthalpy eq.(69) we obtain:

$$\rho \left(B_T \frac{DT}{Dt} + B_p \frac{Dp}{Dt} + \sum_i^{ns} B_{Y_i} \frac{DY_i}{Dt} \right) = \nabla \cdot \mathbf{q}_e \quad (78)$$

where B_T , B_{Y_i} and B_p are respectively C_p and h_i of a real gas mixture and compression factor. In the low-Mach number limit and considering open domains $Dp/Dt = 0$, so eq. 78 reads:

$$\rho C_p \frac{DT}{Dt} = \nabla \cdot \mathbf{q}_e + \rho \sum_i^{ns} h_i \frac{DY_i}{Dt}. \quad (79)$$

It is now possible to rewrite the thermal dilatation parameter $\mathcal{Q}_T$, using an alternative general thermodynamic relation for the enthalpy [78]:

$$dh = \left(\frac{\partial h}{\partial p} \right)_{\rho, Y_i} dp + \left(\frac{\partial h}{\partial \rho} \right)_{p, Y_i} d\rho + \sum_i^{ns} \left(\frac{\partial h}{\partial Y_i} \right)_{p, \rho, Y_j} dY_i = A_p dp + A_\rho d\rho + \sum_i^{ns} A_{Y_i} dY_i \quad (80)$$

and using it to obtain an expression for the material derivative of the density, recalling the open domain assumption:

$$\frac{D\rho}{Dt} = \frac{1}{A_\rho} \left(\frac{Dh}{Dt} - \sum_i^{ns} A_{Y_i} \frac{DY_i}{Dt} \right) \quad (81)$$

where the explicit form of the thermodynamic coefficients A_ρ and A_{Y_i} include thermodynamic derivatives that directly depend on the particular EoS chosen [78]. Taking eq. 81 and 75 the thermal expansion term $\mathcal{Q}_T$ can be expressed as:

$$\mathcal{Q}_T = \nabla \cdot \mathbf{u} = -\frac{1}{\rho} \frac{1}{A_\rho} \frac{D\rho}{Dt} = -\frac{1}{\rho} \frac{1}{A_\rho} \left(\nabla \cdot \mathbf{q}_e - \sum_i^{ns} A_{Y_i} \frac{DY_i}{Dt} \right) \quad (82)$$

and the complete EoS independent low-Mach number system can be rewritten:

$$\rho \frac{D\mathbf{u}}{Dt} = -\nabla p_2 + \nabla \cdot (\mu \mathbf{S}) \quad (83)$$

$$\rho C_p \frac{DT}{Dt} = \frac{1}{ReSc} \nabla \cdot \mathbf{q}_e + \sum_i^{ns} h_i (\dot{\omega}_i + \nabla \cdot \rho \mathbf{J}_i) \quad (84)$$

$$\rho \frac{DY_k}{Dt} = \nabla \cdot \rho \mathbf{J}_k + \dot{\omega}_k \quad (85)$$

together with the constraint on $\nabla \cdot \mathbf{u}$ of eq. 82. The constitutive relations read:

$$\mathbf{q}_q = -b_{qT} \nabla T + b_{qj} \nabla Y_j \quad (86)$$

$$\mathbf{J}_k = b_{kT} \nabla T - b_{kj} \nabla Y_j \quad (87)$$

since the thermodynamic pressure is constant ($\nabla p_0 = 0$) presso-diffusion and presso-heating are neglected, and the real gas coefficients: $b_{qT} = \lambda$, b_{qj} , b_{kT} and $b_{kj} = D_{kj}$ are respectively the diffusion coefficients of Fourier, Dufour, Soret and Fick effects. On the other hand the thermodynamic properties needed by the system are: ρ , e_i , h_i , C_V , C_p , A_ρ and A_{Y_i} . They can be expressed following [78] in terms of fundamental thermodynamic derivatives:

$$\rho = f_{EoS}(Y_i, T; p_0) \quad (88)$$

$$A_\rho = -C_v \left(\frac{\partial T}{\partial p} \right)_{\rho_i} \left(\frac{\partial p}{\partial \rho} \right)_{T, Y_i} + \frac{1}{\rho} \sum_{i=1}^{ns} Y_i e_i - \frac{e}{\rho} - \frac{p}{\rho^2} \quad (89)$$

$$A_{Y_i} = -\rho C_v \left(\frac{\partial T}{\partial p} \right)_{\rho_i} \left(\frac{\partial p}{\partial \rho_i} \right)_{T, \rho_i} - e_i \quad (90)$$

the explicit expression of each thermodynamic derivative depend on the particular EoS chosen. The expression of the thermodynamic properties not present here can be found in Chap. 3.

5.2 LOW MACH NUMBER FLOW SOLVER

In order to numerically solve the low-Mach number system defined in the previous section, the open source spectral element flow solver Nek5000 [15] is used. It is a CFD solver based on the spectral element method [134] developed at Mathematics and Computer Science Division of Argonne National Laboratory. The code is written in Fortran 77 and C and use the standard MPI paradigm for parallel computing. It has demonstrated high parallel efficiency on state of the art high performance computing infrastructures, additional information can be found in the official homepage [15].

5.2.1 Pseudo-Spectral spatial discretization

While most of the CFD codes relies on finite differences/volumes methods, the spectral element method, a particular application of the weighted residuals [135], is used in the present work. This method for the discretization of partial differential equations (PDE), arises from a particular choice of the test

functions used in a general method of weighted residuals, where trial functions ϕ_i are employed as basis functions for a truncated series expansion for the approximated solution of a PDE u :

$$u = \sum_{i=0}^{\infty} C_i \phi_i \quad (91)$$

where C_i are the i -th expansion coefficient of the series. A key characteristic of this kind of methods is that dispersion errors are exponentially convergent. Moreover minimal numerical diffusion is introduced compared to higher order finite difference and finite volume methods. In order to achieve exponential convergence to the exact solution of the PDE, test and trial functions need to be carefully chosen. In case of spectral-Galerkin methods trial and test functions are intentionally chosen to be the same, as the N th-order tensor product polynomials based on Gauss quadrature points [136].

In this work the spectral element method (SEM) proposed by Patera [134], and implemented in nek5000 is used for the discretization of the governing equations. The SEM discretization is based on splitting of the computational domain into E hexahedral elements and then each element is subdivided based on the polynomials order chosen N in the spatial directions. In this approach the efficiency of the tensor product based global spectral methods is merged with the finite element methods geometric and numerical flexibility. For these reasons SEM method combines the advantages of spectral-Galerkin methods (exponentially convergent dispersion errors) with those of finite element methods (arbitrary domains and geometries) due to the application of the spectral method per each element [136].

From the numerical point of view, the computational grids used by nek5000 are locally structured, with the solution, data, and geometry efficiently expressed as sums of N th-order tensor product polynomials, based on the Gauss-Lobatto-Legendre quadrature points. Globally, the mesh is an unstructured array of E spectral elements which can be distorted, allowing the implementation of efficient parallel algorithms for domain decomposition and parallel computing.

Compared to the commonly used finite elements methods (FEM), SEM has been designed for higher approximation orders, that are typically higher than fourth. This is a useful characteristics in multi-scale problems, such as real fluids mixing and combustion, using DNS since it requires the propagation of small-scale features with minimal dissipation over many characteristic length and time scales.

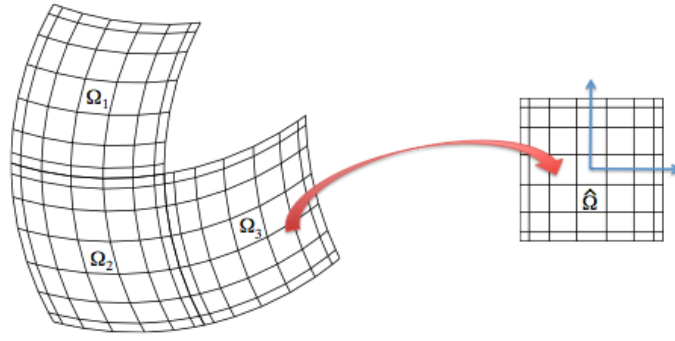


Figure 42.: Spectral element mapping from canonical 7th-order quadrilateral domain to physical subdomain, figure from [14].

5.2.2 Thermochemistry and hydrodynamic subsystems

The solution algorithm for the SEM discretized governing equation is based on the high-order splitting scheme for low-Mach number reactive flows described in Tomboulides et al. [137]. In the low Mach number formulation the thermochemistry subsystem (energy and species equations) is decoupled from the hydrodynamic subsystem (momentum equations and divergence constrain). Dealing with reactive flows, that are usually characterized by a large range of time scales, this has two main advantages for the solution of the thermochemistry subsystem. Firstly an appropriate stiff ordinary differential equation solver can be used, and secondly the integration can be done in a fully-coupled way, avoiding additional splitting errors [138, 139]. The solution of the hydrodynamic subsystem is based on the scheme formulated by Orszag et al. [133], which is a projection type velocity correction scheme. The density ρ and the divergence constrain imposed by Q_T are the connecting links between the two subsystems. In particular Q_T accounts for the density variations on the velocity field, in this term much of the real gas effects are included.

The complete solution algorithm for low-Mach number reactive flows implemented in nek5000 and developed in [14, 140] can be briefly summarized in the following steps [141]:

- **Step 1**

The spatially discretized thermochemistry subsystem yield a system of ordinary differential equations (ODE), that can be integrated in time by means of the variable-step integrator CVODE [142]. The equations are solved implicitly with the exception of the velocities which are calculated with an high-order explicit extrapolation scheme. Alternatively if the

system does not have any particularly stiff time scale, usually related with chemical kinetics, the thermochemistry subsystem can be simply integrated with the standard Helmholtz solver [15].

- **Step 2**

The thermal divergence is calculated and imposed in the right hand side (RHS) of the inhomogeneous Poisson problem expressed by eq.(76).

- **Step 3**

By means of the mentioned splitting scheme a pressure Poisson equation is solved using a 3rd-order extrapolation scheme for velocities in the viscous term. Once the hydrodynamic pressure p_2 is known the velocity is corrected in a second implicit viscous correction step.

The briefly reported low Mach number formulation have shown minimal splitting errors and an high accuracy for all hydrodynamic variables [137, 133].

5.2.3 Code extension

In the open source version of nek5000, the ideal gas EoS is hard coded in the provided non reacting low mach formulation. The extension proposed in the present work is the implementation of the EoS independent low Mach number formulation for real gas mixtures. Therefore the main idea is to take advantage of the comprehensive thermal divergence expression of eq.(82). A set of thermodynamic and transport variables are needed by the equations for momentum energy and species. In particular the key quantities for accounting real gas effects A_ρ and A_{Y_i} can be calculated, by means of case dependent routines and EoS, at the same time of other properties such as density and viscosity, a schematic representation is given in fig. 43 for the solution of the governing equations.

It is worth nothing the elevated versatility of the present approach, for instance a simple flamelet model can be implemented simply using a single species for the mixture fraction transport. All other thermodynamic properties will be tabulated, such as A_ρ , including completely any EoS information.

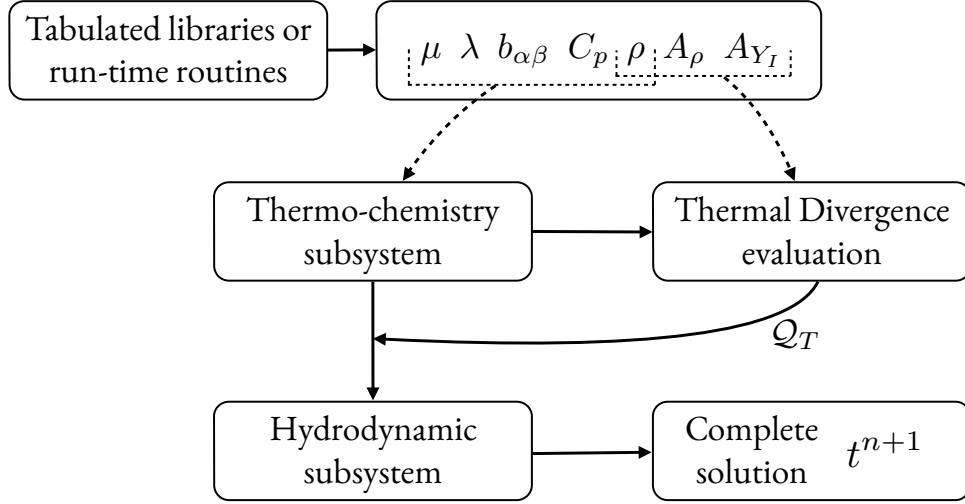


Figure 43.: Schematic representation of the solution strategy of the high-order splitting scheme for low-Mach number reactive flows implemented in nek5000 [15], the properties box is the key part of the EoS independent formulation presented.

5.3 VALIDATION TEST CASES

In order to validate and check the EoS independent formulation and implementation in nek5000, two simple flow test cases, respectively non-reactive and reactive, have been carried out.

5.3.1 Non reactive flow: Rayleigh–Taylor instabilities

Supercritical flows are usually characterized by highly stratified flows resulting in large density and properties gradient. The ability to accurately simulate variable density flow is verified considering a standard two-dimensional Rayleigh–Taylor instability problem. The same test case was used in the validation processes of the NGA code developed at Stanford University [143, 129].

In this case momentum equation is solved together with a conserved scalar ξ (i.e. a non dimensional temperature) that represents mixing:

$$\rho \frac{D\xi}{Dt} = \nabla \cdot (\rho D_\xi \nabla \xi) \quad (92)$$

where D_ξ is the passive scalar diffusivity. This equation is solved using the standard Helmholtz scalar solver since no stiff time scales are present. Then density is computed from ξ using a simple EoS:

$$\rho(\xi) = \frac{1}{a\xi + b} \quad (93)$$

imposing a density ratio of 10 ($a = 9, b = 1$). The computational domain is a two-dimensional box $L_x = [-0.5, 0.5] \times L_y = [-0.5, 0.5]$ and the two miscible fluids are separated horizontally by a perturbed interface with the mean interface located at $y = 0$. Following [144] the exact location of the interface is given by the following expression:

$$y_{int} = -\alpha \sum_{k=0}^7 \cos(\omega_k \pi x) \quad (94)$$

where $\alpha = 0.001$ is the amplitude of the perturbation and the wave number are $\omega_k = 4, 14, 23, 28, 33, 42, 51, 59$. The initial condition for density is given by eq. (93) imposing a mixture fraction field:

$$\xi(x, y; t = 0) = \frac{1}{2} \left[1 + \tanh\left(\frac{y_{int}(x) - y}{2\delta}\right) \right] \quad (95)$$

where $\delta = 0.002$ is the thickness of the interface. The fluids have the same kinematic viscosity and diffusivity ($\nu = 0.001, D_\xi = 0.0005$) and the gravitational acceleration is $\mathbf{g} = 9$, the Reynolds number is $Re = \sqrt{gL_y}L_x/\nu = 3000$. The computational domain is subdivided into $E = 32 \times 32$ spectral elements and various polynomial orders N have been used from 6 up to 12.

The east and west boundary conditions are periodic while the north and south boundary are no-slip walls. The governing equations are integrated keeping constant the convective Courant number to $CFL = u/\Delta x = 0.35$. The comparison of the density fields with the NGA code results for both the high resolution and the low resolution are shown in fig. (44) highlighting the same overall instability features.

Moreover the integral kinetic energy of the system is in good agreement with the NGA results [143], and is essentially independent from the polynomial order used, as shown in fig. 45.

In order to further investigate the differences between the solutions obtained with different N , a slice of the density profiles at $y = 0$ are compared in fig. (46). From $N = 7$ up to $N = 12$ the density profiles collapse onto the same curves showing a reliable prediction of the exact solution. While the low resolution curve with $N = 6$ is clearly unable to correctly predict the dips in density along x justifying the little shift observable in kinetic energy in fig. (45).

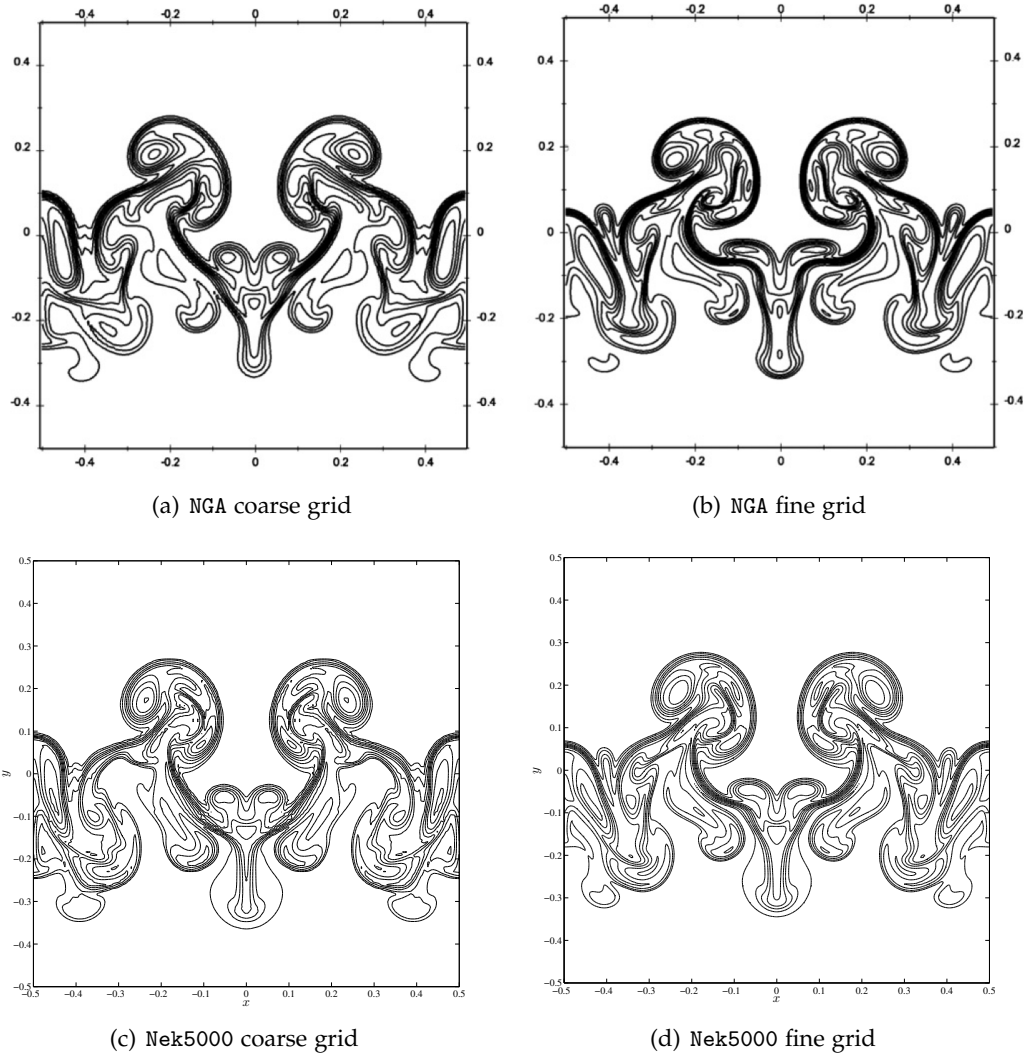


Figure 44.: Density contours of the two-dimensional Rayleigh–Taylor instability at $t = 0.75$: comparison between the EoS independent version of Nek5000 and the Stanford NGA code. Coarse mesh results (NGA: 128×128 , Nek5000: $E = 32, N = 6$) are shown on the left column and fine mesh results (NGA: 512×512 , Nek5000: $E = 32, N = 12$) are shown on the right.

5.3.2 Reactive flow: laminar premixed flame

In order to validate the reactive part of the CFD code, a laminar premixed flame is here simulated. The thermochemistry subsystem is here solved by means of CVODE, as described in the previous section. A simple chemistry model, for which asymptotic solutions of the laminar profile are available in the literature, has been chosen. This model assumes that the reacting mixture is sufficiently off-stoichiometric, and the combustion processes can be considered

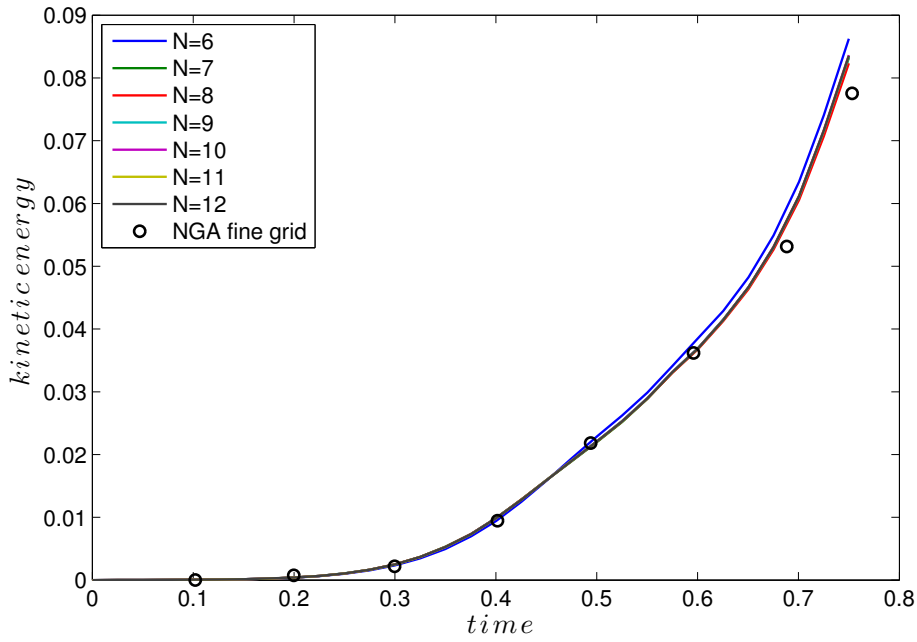


Figure 45.: Temporal evolution of the integral kinetic energy of the system, for the various polynomial order used and NGA fine grid results as a reference.

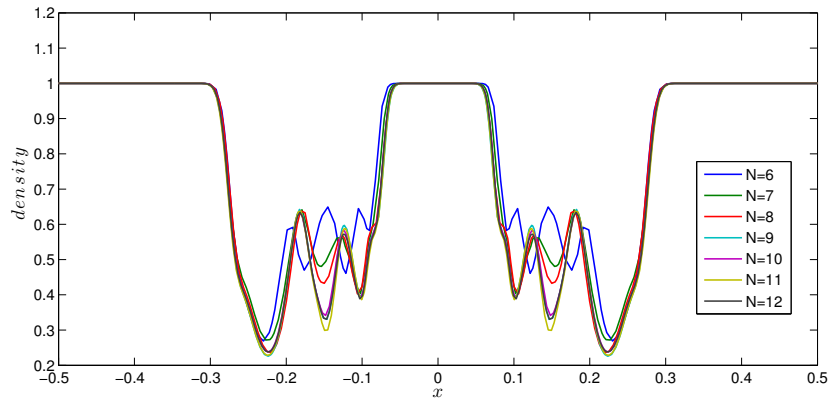


Figure 46.: Slice of the density profiles at $y = 0$, for the various polynomial order used.

to be governed by the concentration of a deficient reactant Y which is completely consumed crossing the premixed flame [145].

Detailed information on the model are available in the appendix A where the model is described and applied to simulate hydrodynamic instabilities of turbulent premixed flames. The asymptotic profile for the temperature and the deficient reactant are the following for $x < x^*$, where x^* is the location of the flame front:

$$T(x) = \exp((1/\delta)(x - x^*)) \quad (96)$$

$$Y(x) = 1 - \exp((1/\delta)(x - x^*)Le) \quad (97)$$

while behind the flame front for $x > x^*$: $T(x) = 1$ and $Y(x) = 0$. In this formulation δ is the non-dimensional flame thickness and Le is the Lewis number, chosen respectively equal to 0.004 and 1.2.

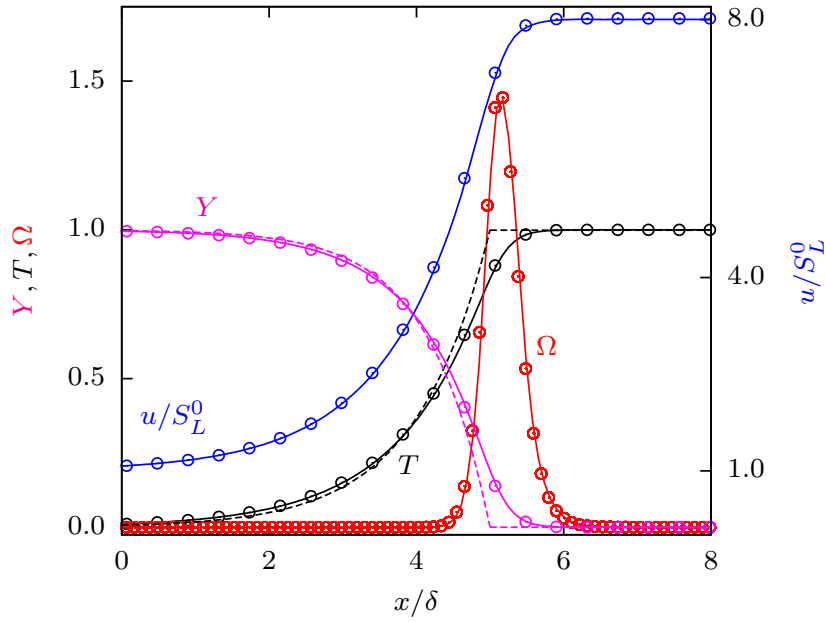


Figure 47.: Planar premixed flame profiles comparison between coarse mesh results (solid lines), sampled fine mesh results (circles) and asymptotic solutions for the temperature T and the deficient reactant Y (dashed lines).

A coarse ($N = 4$) and a fine ($N = 10$) mesh have been used for the planar premixed flame calculation. Figure 47 show good agreement between the two flame profiles and the asymptotic solutions of eq. (96)-(97). The increase across the flame front of the velocity u/S_L^0 is found to be 7 as expected from jump relation:

$$[u] = u_b - u_u = (\sigma - 1)S_L^0 \quad (98)$$

where σ is the density ratio between the unburnt and burnt gases, which is here imposed as $\sigma = \frac{\rho_b}{\rho_u} = 8$ and S_L^0 is the laminar unstretched flame speed.

The consistency between the two resolution used for the numerical solution confirms that flame front can be correctly captured by the discrete system with a reasonable number of point in the flame structure. In particular for the coarse

mesh ≈ 8 grid points are present in the non-dimensional flame thickness δ demonstrating the advantage of using high-order methods.

5.4 SUMMARY AND CONCLUSIONS

A low Mach number formulation for arbitrary EoS, chemistry models and constitutive relations has been developed. The aim of this formulation is to consistently describe mixing and combustion under supercritical conditions. The formulation allows for the use variable fidelity real gas EoS and thermochemistry models. The classical time step restrictions, encountered under supercritical conditions by compressible formulations, are circumvented by means of the low-Mach approximation. This formulation is envisioned as the starting point for future development of a CFD tool able to perform DNS of high pressure turbulent combustion with detailed chemical kinetics and transport. It will allow the investigation of complex turbulence-chemistry interactions in the presence of real gases and, in particular, cryogenic propellants.

The open source spectral element flow solver `nek5000` has been selected as the proper numerical and computational framework, in particular for its portability and parallel scalability. As first steps toward a complete implementation of the described formulation in `nek5000`, two representative sub-cases have been considered and implemented: a highly stratified non reacting flow and a reacting flow with simplified thermochemistry. The two sub-cases have been used as validation test cases for the implemented EoS independent formulation. Two well-known standard problems have been chosen for the validation, such as the Rayleigh-Taylor instabilities and the propagation of a laminar premixed flame propagation. Indeed both the problems were successfully simulated and compared with available validation benchmarks showing good agreement.

6

MIXING AT SUPERCRITICAL PRESSURE

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In order to shed light on real gas mixing at supercritical pressure, direct numerical simulations of non-isothermal nitrogen mixing are carried out. The complete formulation, derived in the previous chapter for reacting real gas mixtures, is used here for a nitrogen non-reacting flow. The mixing of nitrogen at supercritical pressures has been largely investigated both experimentally and numerically, and it is of particular importance in turbulent combustion modeling (TCM) of high pressure non-premixed flames. The main reason for this is that experimental work (for LRE injection) on supercritical combustion have shown that the rate of combustion is mainly controlled by turbulent mixing [8]. Real gas effects on scalar mixing are investigated by means of DNS, in particular exploring the transcritical regime. DNS simulations, even if limited to relatively low Reynolds numbers, can be used to evaluate and analyze sub-grid scale (SGS) contributions and assumptions for LES and RANS models.

6.1 NUMERICAL FORMULATION

Mixing problems at supercritical pressures have been classically tackled using compressible CFD solvers even if these flows are usually characterized by a very limited range of Mach numbers (usually well below the typical threshold

of 0.3). This implies that serious time step restrictions are encountered due to the elevated speed of sound in the liquid-like/cryogenic phase (the maximum experimental Mach number for reference case of cryogenic injection of nitrogen at supercritical pressures [16] is ≈ 0.03). Some works relied on preconditioning and dual time stepping techniques [78, 79] in order to increase the computational time step.

In the low-Mach number limit, the acoustic wave propagation is filtered out from the governing equations allowing an efficient integration of the equations, while taking into account the density variations caused by the non-isothermal conditions enhanced by real gas effects. Therefore, the idea is to take advantage of the low-Mach approximation of the governing equations in order to simulate a relevant configuration with state of the art thermo-physical and transport properties. The governing equations can be rearranged and simplified for a non reacting single species flow, and are cast in the following dimensional form:

$$\rho \frac{D\mathbf{u}}{Dt} = -\nabla p_1 + \nabla \cdot (\mu S) \quad (99)$$

$$\rho c_p \frac{DT}{Dt} = \nabla \cdot (\lambda \nabla T) \quad (100)$$

The energy equation can be recast in terms of $\xi = \xi(T) = T - T_{jet}/T_{env} - T_{jet}$ for simplicity, which is a non-dimensional temperature or equivalently a *mixture fraction* using non-premixed flames nomenclature:

$$\rho c_p \frac{D\xi}{Dt} = \nabla \cdot (\lambda \nabla \xi). \quad (101)$$

Equation (101) is equivalent to eq.(100) since the relationship between T and ξ is known, while the divergence constrain reads:

$$\nabla \cdot \mathbf{u} = -\frac{1}{\rho} \frac{D\rho}{Dt} = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial \xi} \right)_{p_0} \frac{D\xi}{Dt}. \quad (102)$$

where the real gas term A_ρ of the complete formulations eq.(75) is reduced into $A_\rho = \left(\frac{\partial \rho}{\partial \xi} \right)_{p_0}^{-1}$. The thermodynamic and transport properties needed are a reduced number compared to the complete set of the general formulation described in sec.5.1, and they depend only the non dimensional temperature ξ and on background pressure p_0 as a parameter:

- $\rho = \rho(\xi; p_0)$
- $C_p = C_p(\xi; p_0)$
- $\mu = \mu(\xi; p_0)$

- $\lambda = \lambda(\xi; p_0)$
- $\frac{\partial \rho}{\partial \xi} = \frac{\partial \rho}{\partial \xi}(\xi; p_0)$.

The above relations are evaluated using the latest NIST database using the Refprop software [146], and efficiently tabulated for the simulations using 10000 points in ξ to have a proper resolution of large thermodynamic non-linearities. The value of the tabulated properties are shown in fig. 48 as functions of the dimensional temperature in order to highlight the difference between the thermodynamic conditions explored in the simulations.

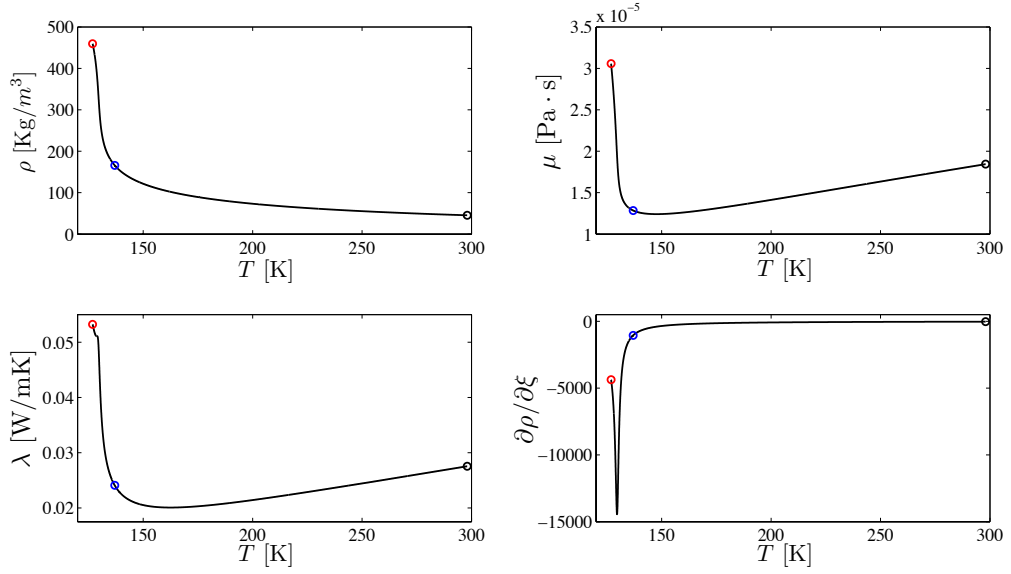


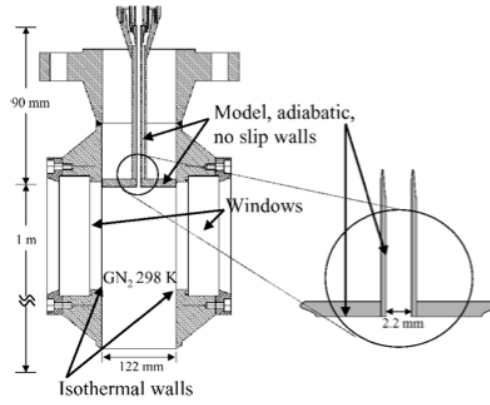
Figure 48.: Thermodynamic properties used for the direct numerical simulation. The circle represent the environment conditions ($\circ$) and the initial jet conditions for case 3 ($\circ$) and case 4 ($\circ$) of the experiments of cryogenic injection of nitrogen characterized by supercritical pressures [16], complete description of these conditions are reported in subsection 6.1.1.

6.1.1 Temporal Jet Configuration and thermodynamic conditions

In the present work, the thermodynamic conditions are chosen to match the experiments of cryogenic injection of nitrogen at supercritical pressures, performed at DLR by Mayer et al. [16, 41]. The experiment consisted in liquid nitrogen at a pressure above its critical value ($p_{cr} = 33.9$ bar) injected through an axisymmetric injector, into a pressurized chamber filled with warm (ambient temperature) gaseous nitrogen. The jet mixing and development was investigated by means of 2-D Raman imaging, comparing density and divergence

Case	Target Pressure (MPa)	Target Velocity (m/s)	Target Temperature (K)	Chamber Pressure (MPa)	Average jet velocity (m/s)	$T_{a_{inj}}(K)$
1	4	2	120	3.96	1.8	130.0
2	4	2	130	3.95	2.7	140.0
3	4	5	120	3.97	4.9	126.9
4	4	5	130	3.98	5.4	137.0
5	5	2	120	4.90	2.0	131.0
6	5	2	130	4.90	1.9	140.0
7	5	5	120	5.01	4.5	126.2
8	5	5	130	5.00	4.9	135.7
9	6	2	120	5.85	2.0	135.0
10	6	2	130	5.88	1.9	140.5
11	6	5	120	5.98	4.9	128.7
12	6	5	130	5.96	4.9	135.4

(a)



(b)

Figure 49.: Experimental setup of Mayer experiment, taken from [16]: (a) original test matrix with target and measured injection conditions of chamber pressure and jet data at injection tube outlet, (b) geometry of the axisymmetric injector and pressurized chamber

angles with simple computational models. The thermodynamic conditions of the injection and chamber were chosen in order to examine the effects of temperatures, pressures and injection velocities on the real gas mixing. The complete test matrix together with geometrical setup of experiment are reported in fig. 49

On the other hand the fluid dynamics conditions are not matched since the Reynolds number amenable to DNS is significantly less than the experimental values of order of $\mathcal{O}(10^5 - 10^6)$. The configuration used in the present DNS study is a geometrically simple planar temporally evolving jet, where the jet stream consist of cold nitrogen mixing into a warm nitrogen environment mimicking the experimental thermodynamic conditions. Two cases from the original experimental test matrix have been considered: a transcritical and a supercritical case corresponding respectively to cases 3 and 4 of the experiments [16].

Table 4.: Thermodynamic conditions of the two cases considered in this work from the experimental test matrix [16], the operating pressure is the same for both cases $p_0 = 39.7$ bar.

	T_{jet} (K)	T_{jet}/T_{pb}	ρ_{jet} (Kg/m ³)	ρ_{jet}/ρ_{env}
Case 3	126.9	0.98	456.8	10.14
Case 4	137.0	1.06	163.4	3.63

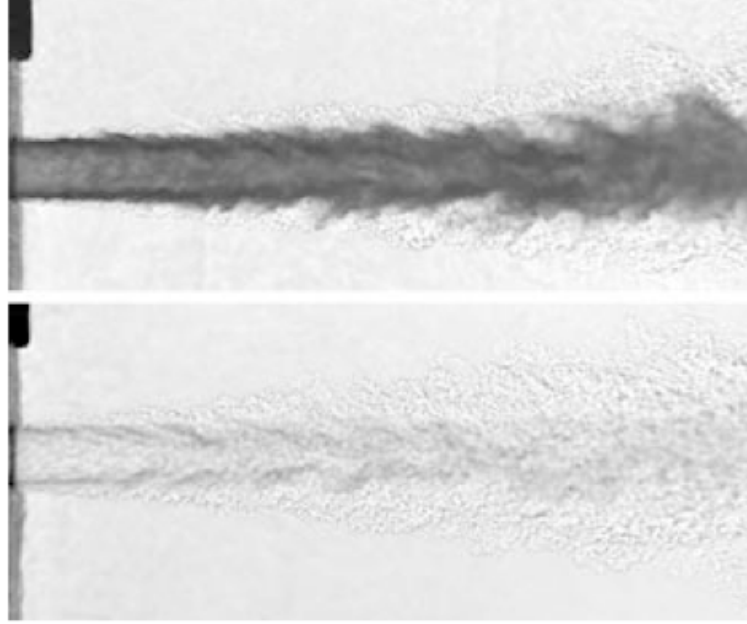


Figure 50.: Shadowgraph images taken from Mayer experiment [16] of case 3 (top panel) and case 4 (bottom panel). The transcritical jet (case 3) is dark for the elevated density that makes it difficult for light to pass through, while the supercritical jet (case 4) is almost transparent since it is much less dense.

The thermodynamic conditions used for the simulations of these two cases are summarized in tab. 4.

Given a background pressure above the critical one, the conditions are considered transcritical (supercritical) if the injection temperature is initially below (over) the pseudo-boiling temperature T_{pb} of nitrogen as shown in the diagram of fig. 51. The pseudo-boiling temperature T_{pb} is the temperature in which, for given pressure, C_p reaches its maximum; it is the prolongation of the gas/liquid phase-change line, which is also known as the Widom-line [39].

The injection/mixing processes can be considered an isobaric transformation at near-critical pressure $p_0/p_{cr} = 1.17$, so the near-critical enhancement of properties is of fundamental influence. Despite the relatively small temperature

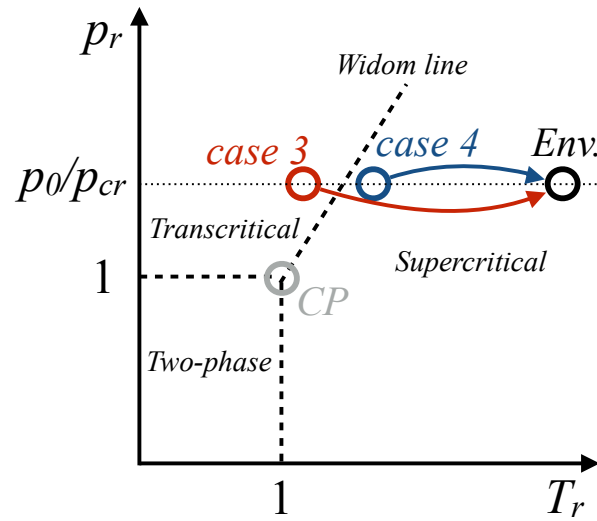


Figure 51.: Thermodynamic regime diagram in terms of reduced temperature and pressure. The circles represent the environment conditions ($\circ$) and the initial jet conditions for case 3 ($\circ$) and case 4 ($\circ$) of the cryogenic injection of nitrogen at supercritical pressures experiments [16]. The arrows indicate the global isobaric thermodynamic transformation during the mixing processes.

difference between the two cases, the fact that the pseudo boiling temperature ($T_{pb} = 129.5$ K at $p = 39.7$ bar) lies between case 3 and case 4 both qualitatively and quantitatively different behaviors. Case 3 during the development and mixing of the jet stream (represented as a red arrow in fig. 51) will experience pseudo-boiling, a continuous non-linear process from the transcritical injection conditions (liquid-like) to the supercritical environment conditions (gas-like). Associated to pseudo boiling, a huge density reduction is present together with elevated specific heat capacity values resembling the standard subcritical vaporization. In fig. 48 it is clearly observable that the great variability of the thermodynamic and transport properties are experienced only in case 3, to the author's knowledge never explored consistently by a direct simulation.

The computational domain of the planar temporally evolving jet considered, is illustrated in fig. 52. It is periodic in the streamwise (x) and spanwise (z) directions, while in crosswise (y) direction an open boundary condition is imposed to have a constant background pressure p_0 and avoid a constant volume domain with a variable pressure.

The domain dimensions in the periodic directions are $L_x = 6H$ and $L_z = 3H$ while in the crosswise direction extend from $-L_y/2$ to $+L_y/2$ where $L_y = 6H$ and $H = 1$ mm is the initial jet width. One of the main advantages of this configuration is the possibility to investigate mixing without the influence of complex injector geometries and wall boundary conditions. This is particularly

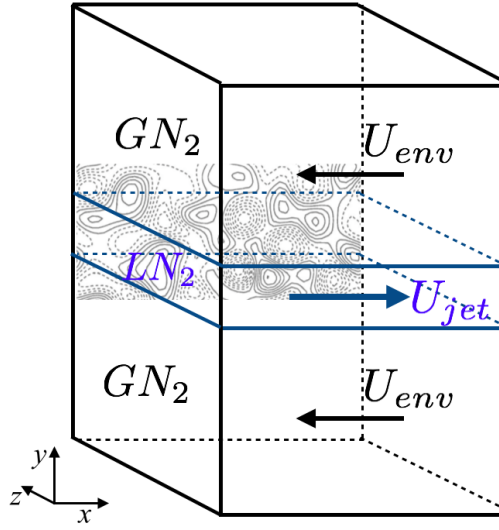


Figure 52.: Temporal jet configuration, the central stream consist in cold nitrogen mixing into a warm nitrogen environment, the jet core velocity is perturbed with three- dimensional isotropic, homogeneous turbulence intended to trip instabilities in the shear layers between the cold and warm streams.

important for the real gas conditions investigated in this work, taken directly from two relevant cases of the experimental campaign [16]. This central role of the injector conditions has been recently pointed out in a critical review and re-interpretation of Mayer's experiments by Banuti and Hanneman [4], explaining that some heat transfer seems to have taken place in the injector giving rise to ambiguities in the boundary conditions definition for CFD simulations. In this framework, having a computational domain characterized by simple boundary condition allows to gain general insights about the mixing processes and to address consistently some LES and RANS thermodynamic modeling considerations.

6.1.2 Initial conditions

The identification of proper initial conditions for temporal evolving jets, even for simple configurations such as the one used here, is not trivial since there a reference geometry to reproduce is not present. Therefore the initial temperature and velocity profiles are chosen as simple and replicable as possible in order to obtain significant qualitative results, while quantitative results will remain strictly dependent from the particular choice.

The velocity initial conditions are such that the initial jet Reynolds number $Re_{jet} = \Delta U H / \nu_{ref}$ is 1500 where $\Delta U = U_{jet} - U_{env}$ and ν_{ref} is a reference

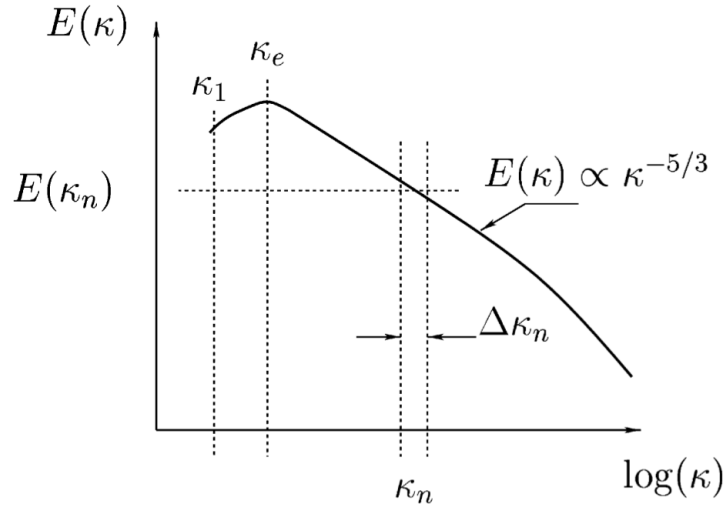


Figure 53.: Modified von Kármán spectrum used for the initial turbulent disturbances of velocity components.

kinematic viscosity value, usually chosen as the minimum in the initial field (see Tab 5) . The three-dimensional velocity field is initialized with a mean field with a superimposed homogeneous and isotropic synthetic turbulence disturbance, generated using random Fourier modes with prescribed probability distributions of the components following [147]. The input parameters, for the synthetic turbulence generation, are a velocity root mean squared (rms) u_{rms} and an integral length l_0 , which are used to characterize a modified von Kármán spectrum as shown in fig. 53.

The prescribed kinetic energy spectrum $E(\kappa)$ is expressed as:

$$E(\kappa) = \alpha \frac{u_{rms}^2}{\kappa_e} \frac{(\kappa/\kappa_e)^4}{[1 + (\kappa/\kappa_e)^2]^{17/6}} e^{[-2(\kappa/\kappa_e)^2]} \quad (103)$$

where κ is the wave number, $\kappa_\eta = \epsilon^{1/4} \nu_{ref}^{-3/4}$ is the highest wave number (ϵ is the dissipation rate per unit mass), $\kappa_e = \alpha 9\pi / (55l_0)$ is the most energetic wave number (α is a constant set to 1.453) and $\kappa_1 = \kappa_e / p$ is smallest wave number (p is a constant set such that $p = H/l_0$).

The perturbations thus generated are superimposed to the mean field $U(y)$ in order to trigger shear instabilities:

$$\mathbf{u}(x, y, z) = U(y) + \mathbf{u}'(x, y, z) \mathcal{F}_N(y) \quad (104)$$

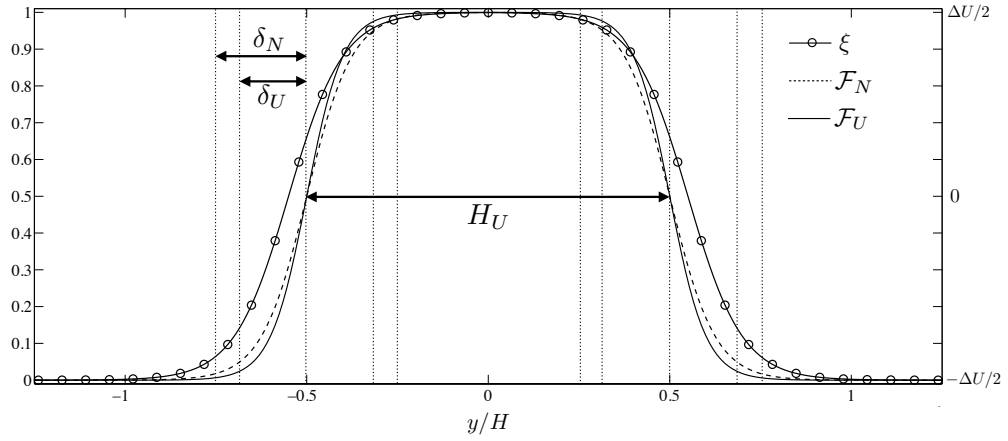


Figure 54.: Initial conditions for the two simulations, note that ξ and $\mathcal{F}_N$ profiles are plotted with respect to left y-axis while U to right y-axis. The point spacing of the ξ curve is chosen to be representative of the spectral element distribution.

where $\mathcal{F}_N(y)$ is a filter isolating disturbances only to the jet core and mixing layers. The root mean square and the integral length scale of the disturbances have been chosen similarly to [148] as $\mathbf{u}_{rms} = 5\%\Delta U$ and $l_0 = H/3$.

The initial profiles of U and ξ as well as the disturbance filter $\mathcal{F}_N$ in the crosswise direction y are chosen as follows:

$$\mathcal{F}_U = \frac{\Delta U}{2} \left[\tanh\left(\frac{H_U - 2|y|}{\delta_U}\right) \right] \quad (105)$$

$$U(y) = \mathcal{F}_U + \frac{\Delta U}{2} \left(\frac{2}{1 + \sqrt{\rho_{jet}/\rho_{env}}} - 1 \right) \quad (106)$$

$$\mathcal{F}_N(y) = \frac{1}{2} - \frac{1}{2} \tanh\left(\frac{H_N - 2|y|}{\delta_N}\right) \quad (107)$$

$$\xi(x, y, z) = \xi(y) = \frac{1}{2} + \frac{1}{2} \tanh\left(\frac{H_\xi - 2|y|}{\delta_\xi}\right) \quad (108)$$

where $H_U = H_N = H$ is the initial jet width and $H_\xi = H_U + \delta_\xi - \delta_U$, the initial thickness of the crosswise profiles are $\delta_U = 0.2H$, $\delta_N = 0.25H$ and $\delta_\xi = 0.3H$ referred respectively to velocity, disturbances and non-dimensional temperature. Note that the last term in eq.(106) is a density correction which modify the velocity initial condition distributing ΔU across the mixing layers according to ρ as in [67]. These profiles are represented in fig. 54 and the values of all the parameters involved in the definition of the initial conditions of the DNS are summarized in Tab 5.

6.1.3 Grid requirement for DNS

In order to perform a direct simulation, the grid spacing is set to be small enough to resolve the smallest length scale of the flow [20]. In a typical isothermal single component flow, the Kolmogorov scale defined as:

$$\eta_K = \left(\frac{\nu^3}{\epsilon} \right)^{(1/4)} \quad (109)$$

where ϵ is the dissipation rate per unit mass, is the smallest length scale present, since below this scale molecular viscosity effectively damps out the flow inhomogeneities. Therefore a DNS-type grid resolution requires $\Delta x \approx \eta_K$ [118]. If thermal or composition inhomogeneities are present in the flow, there is a smallest scalar length that, depending on the relative magnitude between kinematic viscosity and diffusivity of temperature or species, can be smaller or larger than η_K . The ratio between the kinematic viscosity ν and temperature or species diffusivities, respectively $\alpha = \lambda/C_p$ and D leads the definition of the Prandtl and Schmidt numbers:

$$Pr = \frac{\nu}{\alpha} \quad Sc = \frac{\nu}{D}. \quad (110)$$

Considering a flow configuration in which the integral length and a velocity scale are fixed, the size of η_K will depend only on the kinematic viscosity. It is important to remark that the amount of dissipation in the flow is not determined by ν , since it controls only the scales at which dissipation take place. In a similar way the smallest length scale of a scalar (temperature or species) is determined by its diffusivity (α or D). Qualitatively, for the non-isothermal mixing of a single species, the following three scenarios are possible:

- $Pr \sim 1$ ($\nu \sim \alpha$) : the two reference smallest scale of the flow (velocity and scalars) are expected to be of the same order.
- $Pr > 1$ ($\nu > \alpha$) : the velocity fluctuations are dissipated at scales larger than scalar fluctuations, the scalar dissipation has no influence on the inertial range of the kinetic energy spectrum.
- $Pr < 1$ ($\nu < \alpha$) : the velocity fluctuations are dissipated at scales smaller than scalar fluctuations, and the scalar dissipation will influence the inertial range of the kinetic energy spectrum.

The Prandtl number values, which can be expected in the present case by the nitrogen supercritical and transcritical injection are shown in fig.55. The large values of Pr suggest that a length scale smaller than η_K is to be expected, usually

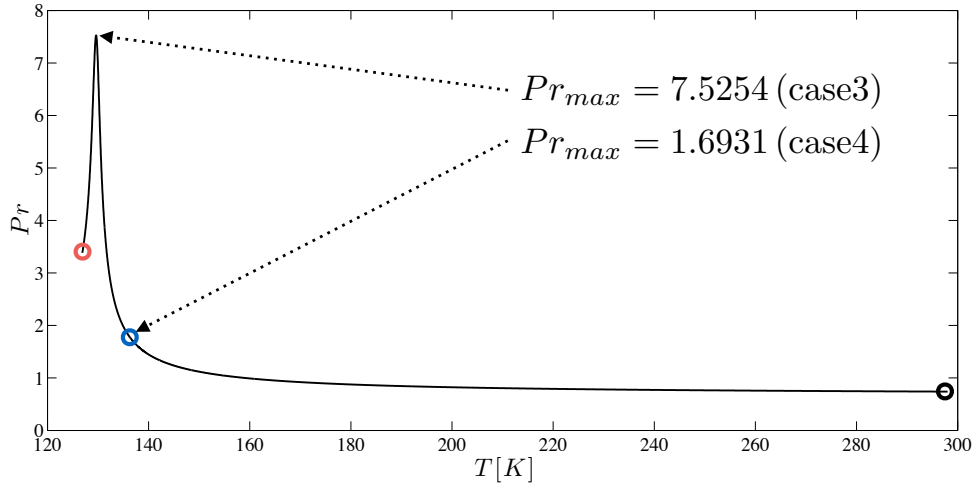


Figure 55.: Prandtl number as a function of temperature, the circles represent the environment conditions ($\circ$) and the initial jet conditions for case 3 ($\circ$) and case 4 ($\circ$). Maximum values for the two simulation conditions are reported to address Batchelor scale considerations.

referred as Batchelor scale η_B [149, 150]. An estimate of such length scale can be found starting from scaling considerations for the diffusion equation:

$$\mathcal{L}^2 \sim \alpha t \quad (111)$$

where t is a reference time and $\mathcal{L}$ is a characteristic length scale. Since in the present work we are interested in the $Pr > 1$ scenario, the region over which the scale analysis is applied is the smallest length scale, thus $\mathcal{L} = \eta_B$. In this length scale region, the temperature scalar field is subject to fluctuation of the complete strain rate since $\eta_B < \eta_K$, therefore the Kolmogorov time scale $\tau_K = (\nu/\epsilon)^{1/2}$ can be used as a reference time scale. This implies using eq.(111) that:

$$\eta_B^2 \sim \alpha (\nu/\epsilon)^{1/2} \quad (112)$$

and using the definition of the Kolmogorov length scale it is possible to obtain the classical scaling result between η_K and η_B [149, 150]:

$$\frac{\eta_B}{\eta_K} \sim \left(\frac{\alpha}{\nu}\right)^{1/2} \quad (113)$$

and consequently, the smallest length scale in $Pr > 1$ flow can be expressed as:

$$\eta_B \sim \eta_K Pr^{-1/2} \quad (114)$$

and the DNS-type grid resolution need to be rearranged to $\Delta x \approx \eta_B$. As shown in fig. 55 the maximum Prandtl number in the transcritical simulation is ≈ 7.5 . Therefore at least 2.75 grid points are needed in the Kolmogorov scale, which is a serious grid limitation since, as an example, a three dimensional simulation with $Pr \approx 7.5$ will have ≈ 20 times the grid points required by a $Pr \approx 1$ simulation.

In some cases, these scalar resolution requirements have been satisfied by means of hierarchical grid approaches, in which different grid resolution are used for the scalars and the momentum equation, in particular for channel flows [151]. Such an approach could be a possible future development for the numerical investigation of $Pr \gg 1$ transcritical flows. It is important to remark that this scalar resolution constrain has been avoided or blended by previous DNS simulations of real gas mixing. Tani et al. [67] increased the background pressure in the DNS investigation of transcritical temporal mixing layers, causing the flattening of the properties profiles and downsizing the effect of the pseudo boiling. Battista et al. [66] used a non accurate EoS (van der Waals) which underestimate the critical point coordinates, obtaining a $Pr < 1$ flow away from the near critical enhancement.

The previously reported scaling considerations are applied to the transcritical jet (case 3) and, in order to resolve the smallest Batchelor scale, the computational grid is composed of 110x110x55 spectral elements, respectively in the x, y, z directions. Every spectral element is internally subdivided by Gauss-Lobatto-Legendre quadrature points of order $N = 6$, corresponding to ≈ 144 million grid points. Additional information on the scales and on DNS resolutions are summarized in Tab 5. For the supercritical jet (case 4) the same grid of the transcritical jet has been used (case 3), in order to have a grid independent comparison, even if not strictly necessary from scaling considerations.

6.2 RESULTS AND DISCUSSION

The DNS results are initially presented in terms of general field overview then first and second order statistics of the velocity and thermodynamic variables are analyzed in the crosswise direction at various time instants. Additional statistical analysis over the entire computational time is carried out for the jet centerline. From this analysis the need of a statistical description for the sub-grid variance of the temperature, for sub-grid scale LES/RANS models is assessed.

Table 5.: Physical and numerical parameters of the simulations. The computational cost is given in core hours on the Galileo supercomputer available at CINECA. The simulations was performed on 1024 cores.

	Case 3	Case 4
Difference in velocity streams ΔU_{jet} (m/s)	0.09	0.116
Initial jet width H (mm)	1	1
Initial jet Reynolds number Re_{jet}	1500	1500
Reference kinematic viscosity ν_{ref} (m/s ²)	$5.92 \cdot 10^{-8}$	$7.74 \cdot 10^{-8}$
Jet time unit $t_{jet} = H/\Delta U$ (ms)	11.3	8.6
Jet Mach number $Ma = \Delta U/a$	$3.4 \cdot 10^{-4}$	$5.7 \cdot 10^{-4}$
Density ratio ρ_{jet}/ρ_{env}	10.14	3.63
Domain size $L_x \times L_y \times L_z$ (mm)	6x6x3	6x6x3
Minimum grid size Δ (mm)	≈ 0.0091	≈ 0.0091
Grid points	≈ 144 Million	≈ 144 Million
Initial velocity perturbations $\mathbf{u}_{rms}$	$5\% \Delta U$	$5\% \Delta U$
Initial velocity perturbations integral scale l_0	$H/3$	$H/3$
Kolmogorov scale (initial) (mm)	0.0297	0.0297
Batchelor scale (initial) (mm)	0.0106	0.0228
Fixed CFL	0.30	0.35
Computational cost (core hours)	≈ 25000	≈ 17000

6.2.1 Flow field overview

The temporal evolving planar jets are analyzed at various non dimensional time instants $t^* = t/t_{jet}$, where the jet time unit is defined as $t_{jet} = t/(H/\Delta U)$ ($t_{jet} = 11.3$ ms for case 3 and $t_{jet} = 8.6$ ms for case 4). The simulations have been run up to $t^* = 20$, until the flow structure can no longer be considered domain independent.

Figure 56 and 57, corresponding respectively to case 3 and case 4, represent five time instants ($t^* = 1, 5, 10, 15, 20$) of ξ , C_p and ρ fields in a span-wise cut ($z = 0.5H$) of the three dimensional jet. The computational domain is shown to be large enough to accomodate at least two large scale Kelvin-Helmoltz instability (KH) vortical structures as prescribed in previous DNS studies of real gas temporal mixing layers (see the work of Bellan [62] for a review). For both the supercritical and transcritical case the initial disturbances begin to trigger shear layer instabilities ($t^* = 1$) and some large scale structure begin their growth ($t^* = 5$). At least two large scale Kelvin-Helmholtz instabilities are generated by the shear layers ($t^* = 10$) that eventually interact giving rise to three dimensional transitional turbulence ($t^* = 15$ and $t^* = 20$). The development and growth of large scale turbulent structures is found to be more evident for the supercritical jet, with respect to the transcritical case where the elevated density stratification

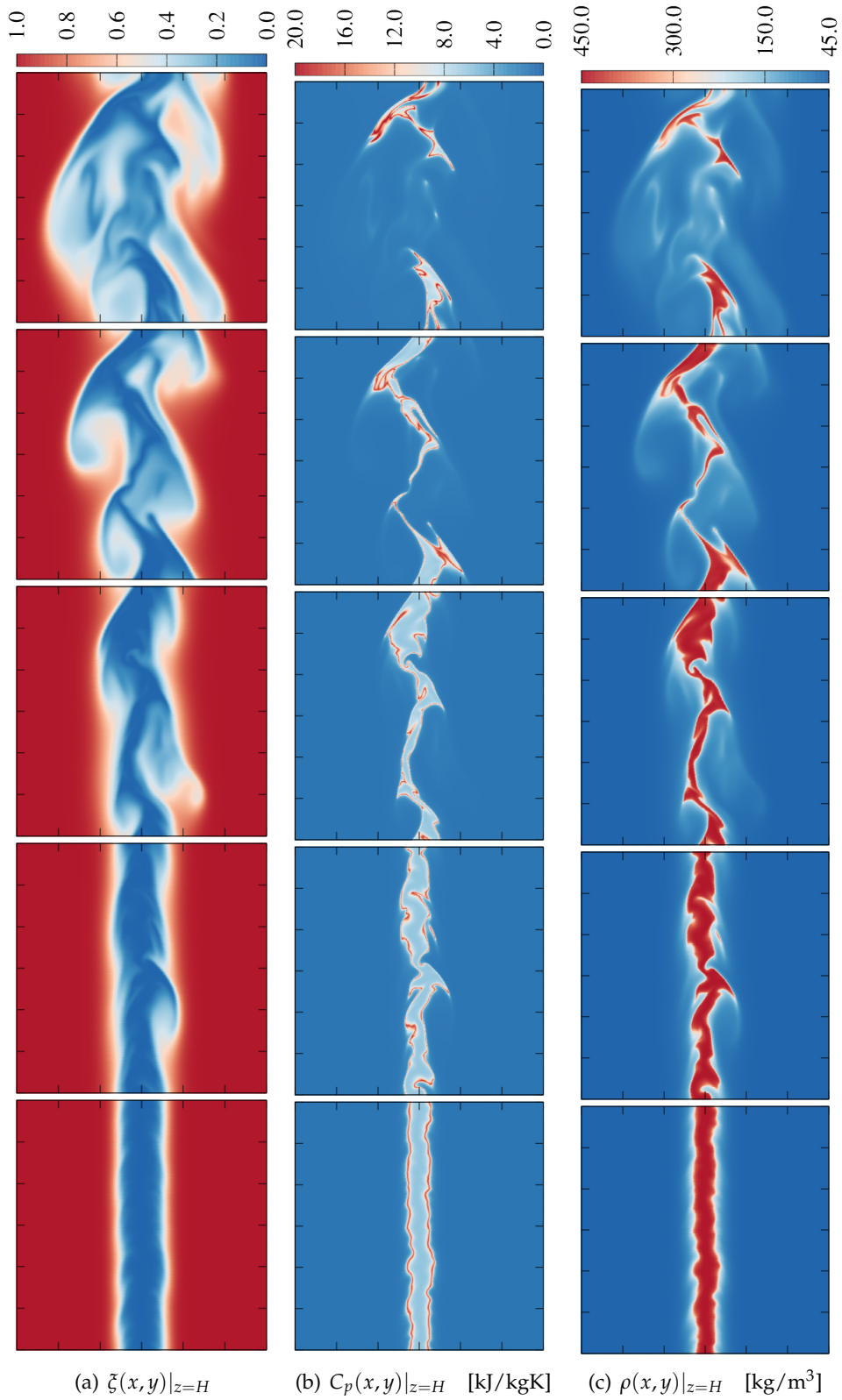


Figure 56.: Evolution of the temporal transcritical jet (case 3), the five time instants represented are $t^* = 1, 5, 10, 15, 20$.

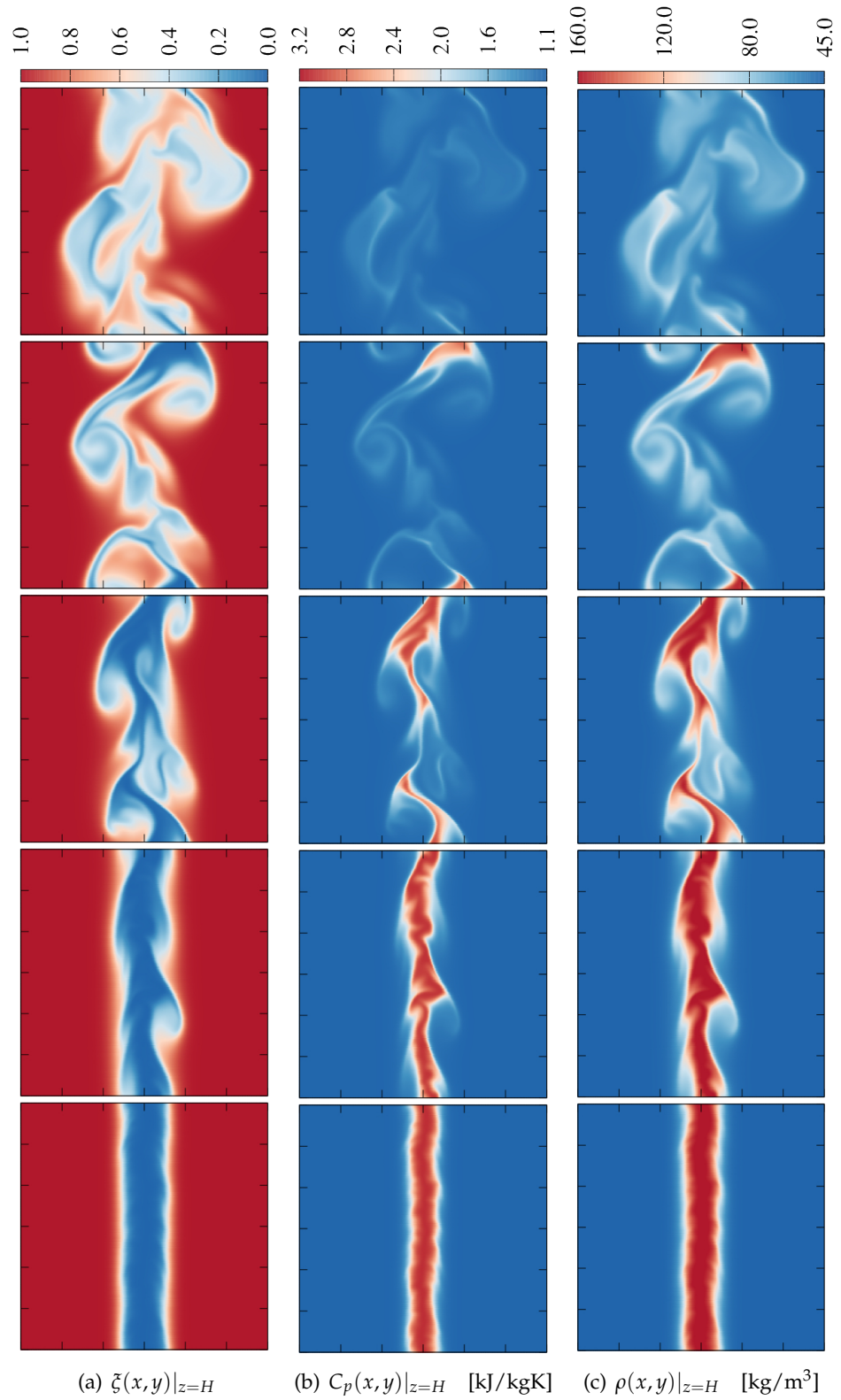


Figure 57.: Evolution of the temporal supercritical jet (case 4), the five time instants represented are $t^* = 1, 5, 10, 15, 20$.

seems to dampen the growth of KH structures. This finding is consistent with the analysis of Zong et al. [54] for spatially evolving two dimensional axisymmetric jets characterized by transcritical thermodynamic conditions with various density stratifications. They evaluated the power spectral densities (PSD) of the axial and radial velocity fluctuations, highlighting the influence of density stratification on the large scale flow motion. They found that as the density stratification increases, it acts like a solid wall in the flow, amplifying the axial turbulent fluctuations and damping the radial one, responsible for the KH formation and growth.

Some common features of free shear highly stratified flows can be observed in the present simulations, such as the so-called ligaments [56], albeit relatively low Reynolds number. The dynamics of such ligament formation, growth, and evolution was deeply analyzed in a spatial co-flowing jet configuration by Battista et al. [66]. However the DNS simulations analyzed in [66] were exclusively supercritical and, using van der Waals EoS, the Prandtl number involved was way out of the realistic range ($Pr < 1$). In the present work, the ligaments formation, growth, and evolution is shown to occur also in the transcritical jet. In the last two temporal panels of the field visualizations of fig. 56 and 57, it can be observed that the KH instability force the extrusion of dense gas structures that are consequently elongated by velocity gradients to form the ligaments. It is important to remark, as pointed out in [66], that the presence of ligament formation is not strictly related to real gas effects but exists as long as a strong density and velocity contrast exists between the two streams. This behavior is far more evident for the transcritical jet of fig. 56 given the higher initial density ratio. While the non dimensional temperature field bears some similarities between the two cases considered, as previously mentioned describing the shear layers instabilities evolution, the thermodynamic properties such as C_p and ρ clearly highlight some structural differences. The transcritical jet, observing fig. 56(c), visually resembles a liquid-like jet break-up during its time evolution, even if no surface tension is present and the fluid is therefore represented as a single supercritical phase. This liquid-like behavior is induced by the pseudo vaporization process between the core of the jet, which is characterized by liquid-like densities, and the warm environment which has, on the contrary, gas-like properties. Contrary to the commonly encountered subcritical vaporization, the pseudo-vaporization is a continuous processes having a diffuse interface without showing a phase change. While this allows a simple single phase approach, it needs to be taken into account in sub-grid scale modeling, since the pseudo-vaporization, at near critical pressure

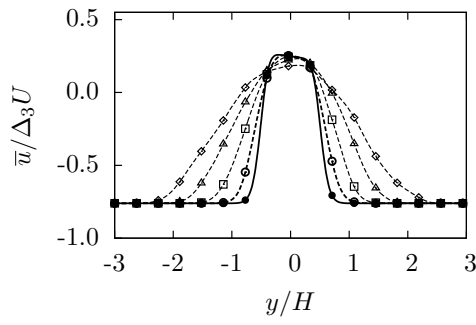
(as in the present case) will have a characteristic length scale well below LES filters and RANS cell grid size. This problem will be discussed in section 6.2.3.

6.2.2 First and second order crosswise jet statistics

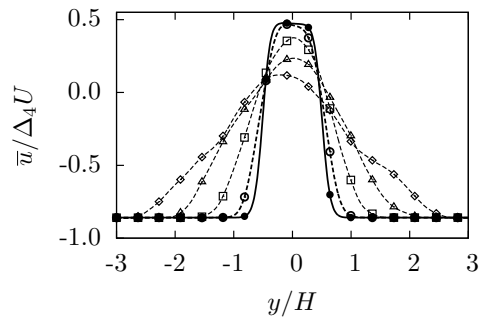
An overview of the supercritical and transcritical jet evolution has been given in the previous section, represented by five time instants in fig. 56 and 57. The same instants are now considered in order to analyze first and second order statistics in the crosswise direction of the jet. Crosswise statistics are obtained averaging in the stream-wise (x) and span-wise (z) directions, and the averaged variables are denoted by an overbar while the fluctuations are defined with respect to the averages. All the statistics are normalized using an average value between the jet and the environment at the initial time $\Delta = (\phi_{jet} + \phi_{env})/2$ where ϕ is a generic scalar field. The normalizing values, respectively for the transcritical and supercritical case, are denoted as Δ_3 and Δ_4 .

Figure 58 shows the mean in the y -direction of two integrated variables, the stream-wise velocity $\bar{u}$ and the non dimensional temperature $\bar{\xi}$ for case 3 and case 4. The initial profiles of $\bar{u}$ and $\bar{\xi}$ are turbulently diffused across the y -direction by the mixing layers, and the simulation ends before these mean values profiles variations reach the open boundaries. The mixing rate of the initial temperature profile is more intense in the supercritical case as shown in fig. 58(b) and 58(d), due to the larger KH instabilities. This leads to a more rapid mixing compared to the transcritical case as shown in fig. 58(a) and 58(c), in which it is evident that the time variation of the mean velocity and temperature in the center of the jet, $y/H = 0$ is less important. A tentative explanation is that the higher density stratification of the transcritical case damps more effectively the crosswise perturbations delaying the complete mixing of the jet stream. This leads to strong anisotropy of the turbulence in the proximity of the density interface, where large eddies flattens and the y -component of the turbulent kinetic energy is transferred to the streamwise component. However, further investigation on this complex phenomenology would be of significant interest, and can be envisaged in future works addressing the influence of Reynolds number and pressure.

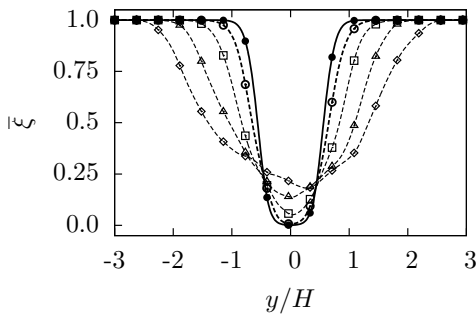
Figure 59 shows the variance in the y -direction for the stream-wise velocity $\overline{u''u''}$ and the non dimensional temperature $\overline{\xi''\xi''}$ for both the transcritical and supercritical case. The variances peak approximately where the maximum mean shear is present, while in the jet centerline the values can be observed to be relatively low. This behavior is due to the relatively low initial jet Reynolds number and, more importantly, to the fact that the present jets do not reach the



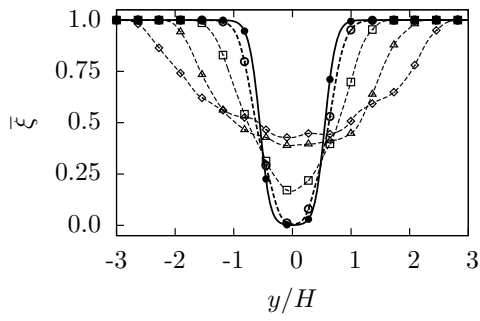
(a) Case 3: mean stream-wise velocity



(b) Case 4: mean stream-wise velocity



(c) Case 3: mean non-dim. temperature



(d) Case 4: mean non-dim. temperature

Figure 58.: Mean of stream-wise velocity and non-dimensional temperature of the transcritical and supercritical jets at several time instants: $t^* = 1$ ($\bullet$), $t^* = 5$ ($\circ$), $t^* = 10$ ($\square$), $t^* = 15$ ($\triangle$) and $t^* = 20$ ($\diamond$). The crosswise coordinate y is scaled with the initial jet thickness H .

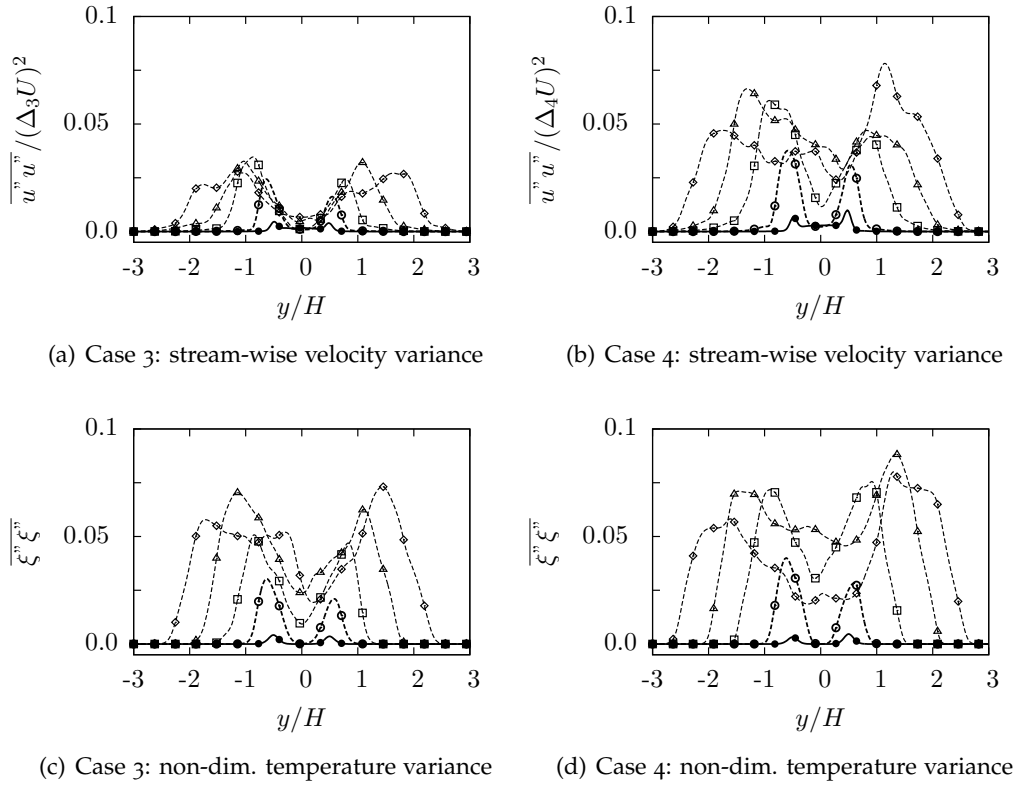


Figure 59.: Variance of streamwise velocity and non dimensional temperature of the transcritical and supercritical jets at several time instants: $t^* = 1$ ($\bullet$), $t^* = 5$ ($\circ$), $t^* = 10$ ($\square$), $t^* = 15$ ($\triangle$) and $t^* = 20$ ($\diamond$). The crosswise coordinate y is scaled with the initial jet thickness H .

self similar state. In fact experiments on planar jets [152] measured velocities variances in the self-similar regions profiles approximately flat over the entire jet width with centerline values close to the peak values. The variance profiles along y observed in the present simulations are strongly influenced by the thermodynamic state of the initial jet stream, even if the two jets considered are characterized by the same Re_{jet} , their second order statistics behave quite differently. While the transcritical jet shows a maximum variance of the stream-wise velocity ≈ 0.035 (fig. 59(a)) the supercritical jet has a peak over ≈ 0.075 (fig. 59(b)) in the last time instant considered, as a result of the very different KH large scale development and growth. Considering the variance ζ shown in fig. 59(c) and 59(d), the difference between the two jets are still present but far less evident. Comparable scalar variances were found in other DNS studies by Pantano [153] in the framework of reactive planar ideal gas jets. The resulting mean and variance of the thermodynamic properties, such as ρ and C_p are shown in fig. 60 and 61 respectively. In particular, fig. 60 shows the mean of C_p

and ρ , highlighting the great variability of the thermodynamic properties. The peaks of the $\bar{C}_p / \Delta_3 C_p$ (fig. 60(a)) at $t^* = 1$ are located in the inner part of the jet mixing layers indicating the mean position of the pseudo-boiling region. Then the turbulent mixing spreads this initial configuration as the pseudo-boiling isoline $\zeta = 0.0159$ is corrugated by turbulent motion as the jet gets mixed and pseudo-vaporized. This phenomenon is clearly not present in the supercritical case, where a pseudo vaporization/boiling processes does not occur, and a typical gas like mixing of the density is observable in fig. 60(b).

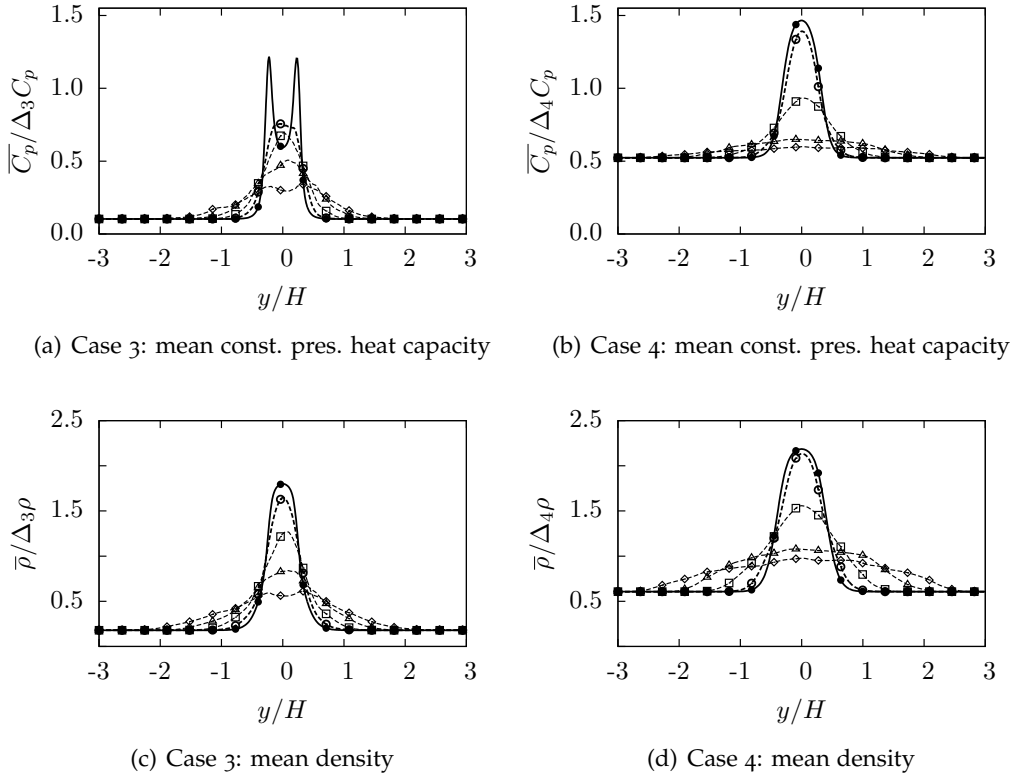


Figure 60.: Mean of representative thermodynamic properties, density and constant pressure heat capacity, of the transcritical and supercritical jets at several time instants: $t^* = 1$ ($\bullet$), $t^* = 5$ ($\circ$), $t^* = 10$ ($\square$), $t^* = 15$ ($\triangle$) and $t^* = 20$ ($\diamond$). The crosswise coordinate y is scaled with the initial jet thickness H .

Figure 61, which display the variance in y -direction of ρ and C_p , highlights a peculiar difference between the transcritical and the supercritical jet. In particular, the peak variance of the thermodynamic properties considered are, in case 3, higher than in case 4, in contrast to the integrated variables (u and ζ) variance which show the opposite behavior (as shown in fig. 59). This is another effect caused by the large non-linearities in thermodynamic properties induced by the pseudo boiling phenomenon.

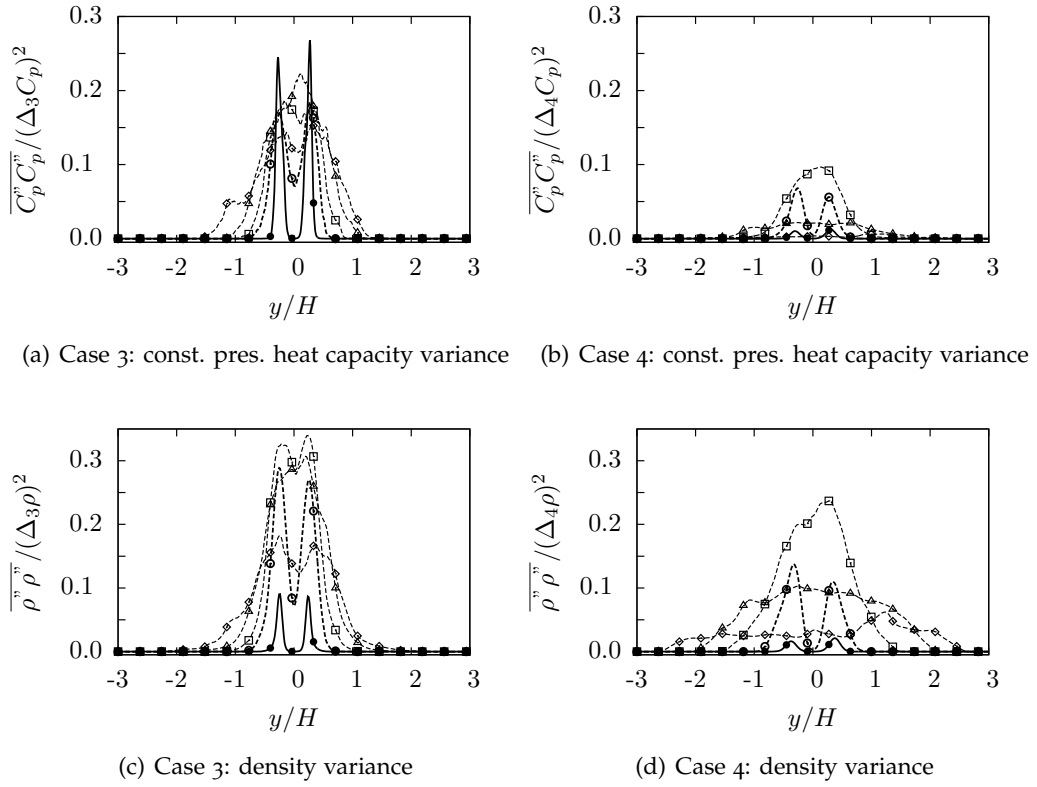


Figure 61.: Variance of representative thermodynamic properties, density and constant pressure heat capacity, of the transcritical and supercritical jets at several time instants: $t^* = 1$ ($\bullet$), $t^* = 5$ ($\circ$), $t^* = 10$ ($\square$), $t^* = 15$ ($\triangle$) and $t^* = 20$ ($\diamond$). The crosswise coordinate y is scaled with the initial jet thickness H .

First and second order crosswise statistics exhibit a range of difference between the supercritical and the transcritical jets. Despite having the same jet Reynolds number the two jets behave quite differently suggesting particular care, in LES and RANS framework, for the modeling of sub-grid scale contributions related to the local thermodynamic state.

6.2.3 Centerline statistics and modeling considerations

In commonly employed LES and RANS approaches each integrated variable, namely ϕ , is filtered into a *resolved* part and a *sub-grid* contribution:

$$\phi = \bar{\phi} + \phi' \quad (115)$$

where the resolved part is $\bar{\phi}$ and the sub-grid contribution is ϕ' . This filtering procedure of the variables leads to a modified or filtered system of the governing

equations, generating a number of unclosed terms that need to be modeled, since they contain information on the sub-grid scales which are not resolved. While important unclosed terms, such as sub-grid turbulent stresses and filtered heat flux vector, have been already investigated in the context of multi-species real gas flows [154, 155, 84], others, such as the filtered thermodynamic and transport properties, have not been analyzed. Generally speaking this modeling problem is particularly important when dealing with transcritical conditions, where large thermodynamic variations occur in a thin portion of the flow field. In the framework of non reacting transcritical and supercritical flows, a relevant part of LES/RANS approaches (see [4, 49, 50, 156, 157] among others) simply evaluate local filtered/averaged values of the thermodynamic and transport properties based on the average value of the integrated variable from which they depend, neglecting its sub-grid contribution:

$$\bar{\Psi}(\phi) \approx \Psi(\bar{\phi}) \quad (116)$$

where Ψ is a generic thermodynamic or transport property that is a function of an integrated variable ϕ . The approximation of eq.(116) can be safely used if an almost linear dependency exist between the thermodynamic or transport properties (Ψ) and the integrated variables (ϕ). In the presence of complex and highly non-linear relations between Ψ and ϕ , the so-called *no-model* approximation of eq.(116) can lead to a large error, which can be estimated as:

$$\varepsilon = [\bar{\Psi}(\phi) - \Psi(\bar{\phi})] \quad (117)$$

and it clearly depends on the characteristic grid or filter dimension Δ_{filt} . In order to reduce this error some statistical considerations can be used, drawing from turbulent combustion modeling (TCM) strategies [37] and in particular from conditional moment closure (CMC) for non-premixed combustion [158]. The expectation of a deterministic function such as Ψ , which depends from a stochastic variable ϕ , at a particular location of the flow field $(\mathbf{x}, t)$ can be expressed, without any assumption, as:

$$\bar{\Psi}(\phi(\mathbf{x}, t), \mathbf{x}, t) = \int \Psi(\phi|\phi^*) p(\phi^*; \mathbf{x}, t) d\phi^* \quad (118)$$

where ϕ^* is the sample space value of the stochastic variable ϕ , $p(\phi^*; \mathbf{x}, t)$ is the pdf of ϕ^* in space and time and $\Psi(\phi|\phi^*)$ is the conditional expectation of the deterministic function. In LES and RANS context, the exact profile of the pdf of ϕ^* is not available (it can only be calculated as a by-product from DNS data)

therefore it can be presumed from the available statistical parameters of the integrated variable ϕ , which are usually its mean and variance:

$$p(\phi^*; \mathbf{x}, t) \approx p(\phi^*; \bar{\phi}(\mathbf{x}, t), \overline{\phi''\phi''}(\mathbf{x}, t)) \quad (119)$$

where $\bar{\phi}$ and $\overline{\phi''\phi''}$ are respectively mean and the variance of ϕ . The commonly employed presumed shape for $p(\phi^*; \bar{\phi}(\mathbf{x}, t), \overline{\phi''\phi''}(\mathbf{x}, t))$, in the context of passive scalar mixing for TCM, is the beta-pdf [37, 159, 160, 161]. It is important to remark that the general expression of eq.(118) includes, as a particular subcase, the no-model approximation expressed in eq.(116), in which the probability density function of the stochastic/integrated variable ϕ is simply a Dirac delta centered in the mean variable value:

$$p(\phi^*; \mathbf{x}, t) = \delta(\phi^* - \bar{\phi}(\mathbf{x}, t)) \quad (120)$$

completely neglecting sub-grid scalar fluctuations. The latter is of particular importance for the thermodynamic conditions of transcritical and supercritical mixing explored in the present work, which are characterized by strong nonlinearities of thermodynamic and transport properties, as shown in fig. 48.

In order to analyze this modeling problem, *a priori* tests have been performed, in which the input data for the model is taken from the previously analyzed DNS simulations. Since p_0 is a constant parameter, in the present case, the only stochastic/integrated variable is the non-dimensional temperature ξ , that determine the thermodynamic or transport properties: ρ , C_p , μ and λ as previously mentioned in sec.6.1. Using eq.(119) the mean or the filtered values of properties can be expressed as:

$$\bar{\rho}(\xi(\mathbf{x}, t), \mathbf{x}, t) = \int_0^1 \rho(\xi|_{\xi^*}) p(\xi^*; \mathbf{x}, t) d\xi^* \quad (121)$$

$$\overline{C_p}(\xi(\mathbf{x}, t), \mathbf{x}, t) = \int_0^1 C_p(\xi|_{\xi^*}) p(\xi^*; \mathbf{x}, t) d\xi^* \quad (122)$$

$$\bar{\mu}(\xi(\mathbf{x}, t), \mathbf{x}, t) = \int_0^1 \mu(\xi|_{\xi^*}) p(\xi^*; \mathbf{x}, t) d\xi^* \quad (123)$$

$$\bar{\lambda}(\xi(\mathbf{x}, t), \mathbf{x}, t) = \int_0^1 \lambda(\xi|_{\xi^*}) p(\xi^*; \mathbf{x}, t) d\xi^* \quad (124)$$

where the conditional expectation of the deterministic function ($\rho(\xi|_{\xi^*})$, $C_p(\xi|_{\xi^*})$, $\mu(\xi|_{\xi^*})$ and $\lambda(\xi|_{\xi^*})$) are simply the profiles of fig. 48. These conditional expectations will be kept fixed for the present *a priori* analysis, i.e. the thermodynamic

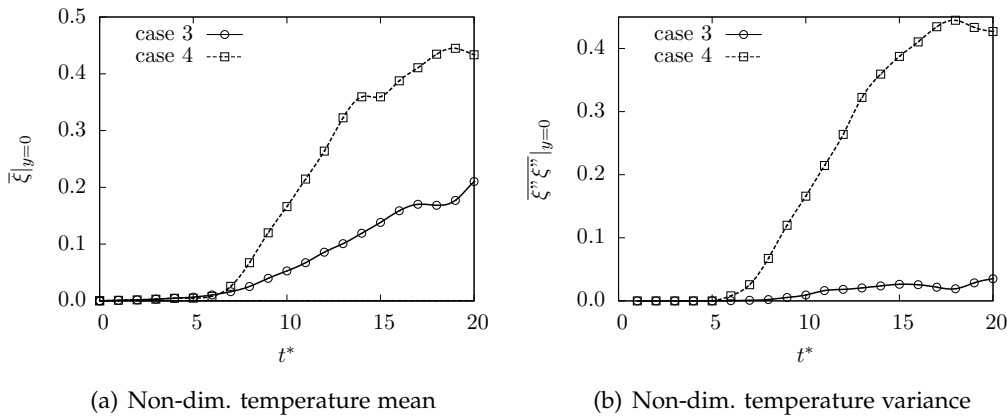


Figure 62.: Time evolution of mean and variance of the non-dimensional temperature ζ in the centerline plane ($y = 0$)

models will not change, while three different level of approximation will be considered for the probability density function of the non-dimensional temperature:

- **Exact or DNS:** The pdf $p(\zeta^*; \mathbf{x}, t)$ is extracted from the previously presented fully resolved DNS data.
- **β -model:** The pdf $p(\zeta^*; \mathbf{x}, t)$ is assumed to be a β -function type distribution based on DNS extracted mean and variance of ζ .
- **No-model:** The pdf $p(\zeta^*; \mathbf{x}, t)$ is assumed to be a Dirac delta centered in the mean $\bar{\zeta}$ value extracted from the DNS data, this assumption is equivalent to expression of eq.(116).

The DNS database for the two jet considered is now restricted to the centerline plane ($y = 0$) to have a reasonable number of realizations of the stochastic variable ζ and a simple physical interpretation of the statistical results.

Figure 62 shows the time evolution of the mean and the variance of the non dimensional temperature in the centerline plane. Both the mean and variance do not show large deviations from the initial values until $t^* = 6$ is reached, where the terminal point of the potential core of a canonical spatially evolving jet is reached. As time increases, which is equivalent to moving downstream in a spatially evolving jet, the supercritical case shows the signature of the more intense KH instabilities as the mean and the variance of ζ suddenly increase reaching peak values just before the end of the simulation. On the other hand the transcritical jet shows a flatter profile without a defined sudden increase of the mean and variance. The latter, remains very limited trough the entire simulation time, due to the higher density stratification of the transcritical case

in which, as pointed out discussing fig. 56, the complete mixing of the jet is delayed.

These considerations are consistent with the results shown in fig. 63, where the exact pdfs of the non-dimensional temperature are compared with the β -function type distribution based on the DNS-extracted first and second order statistical moments and with the no-model approximation. The results show a good agreement between the β -model and the exact distribution over the four representative time instants considered, and for both the transcritical and supercritical cases. On the other hand the no-model exhibits limitations especially when the pdf profiles become wider due to turbulent mixing (see fig. 63(c) and 63(c)). This happens since the no-model has only very limited information (only $\bar{\xi}$) about the sub-grid fluctuations of the stochastic variable available. These limitations directly impact on point-wise evaluation of the thermodynamic and transport properties in a LES/RANS framework, since they depend on the local distribution of ξ inside the computational cell.

Figure 64 displays the time evolution of the mean density and mean constant pressure heat capacity values, averaged over the centerline plane $y = 0$, for the two temporal jets considered, using the previously described three levels of approximation for the ξ distribution. Thus the mean values are obtained using eq.(121) and eq.(122) with the same conditional expectations (tabulated values of $\rho(\xi)$ and $C_p(\xi)$) and different non-dimensional temperature pdfs $p(\xi)$. The exact or DNS mean density profiles exhibit some qualitative differences between the transcritical (see fig. 64(a)) and the supercritical jet (see fig. 64(b)): the former shows an almost regular decrease during its time evolution while the latter exhibits a sudden drop in the profile at the same $t^* \approx 6$ at which variance of ξ start to increase(fig. 62). Similar considerations can be drawn for the exact $\overline{C_p}$ profile, which is quite regular for the transcritical case (see fig. 64(c)), while for the supercritical case (see fig. 64(d)) show similar trend to the density profile, with a slope change right after $t^* \approx 6$. Moreover looking at figure 64, it possible to notice the large discrepancies between the exact means and the predicted *a priori* means using the no-model approach. For both density and constant pressure heat capacity, the errors for case 4, albeit present and relevant, remain limited over the entire time considered. Larger discrepancies are present for case 3 (transcritical) where the large nonlinearities of the thermodynamic properties magnify the error of the no-model approach. Observing in fig. 64(c) the $\overline{C_p}$ profile obtained using the no-model approximation, it is evident that the lack of modeling for the temperature sub-grid fluctuations leads to large errors, as high as $\approx 250\%$, when $\bar{\xi}$ approaches the pseudo-boiling value ξ_{pb} . These large errors in the evaluation of $\overline{C_p}$ are strictly related to the pseudo-boiling phenomenon

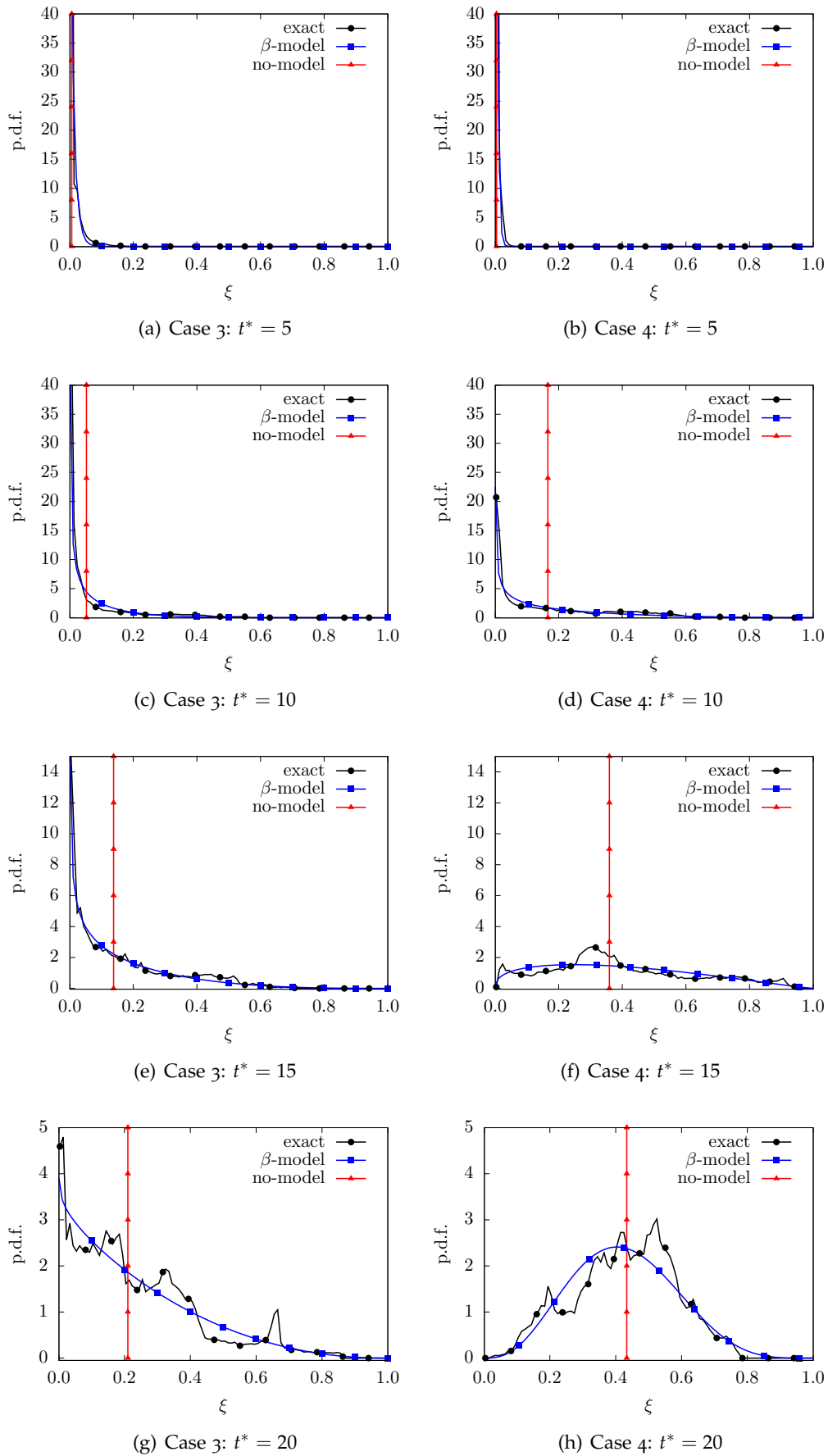


Figure 63.: Non-dimensional temperature pdf for the transcritical and supercritical jet (respectively left and right column), at four representative time instants.

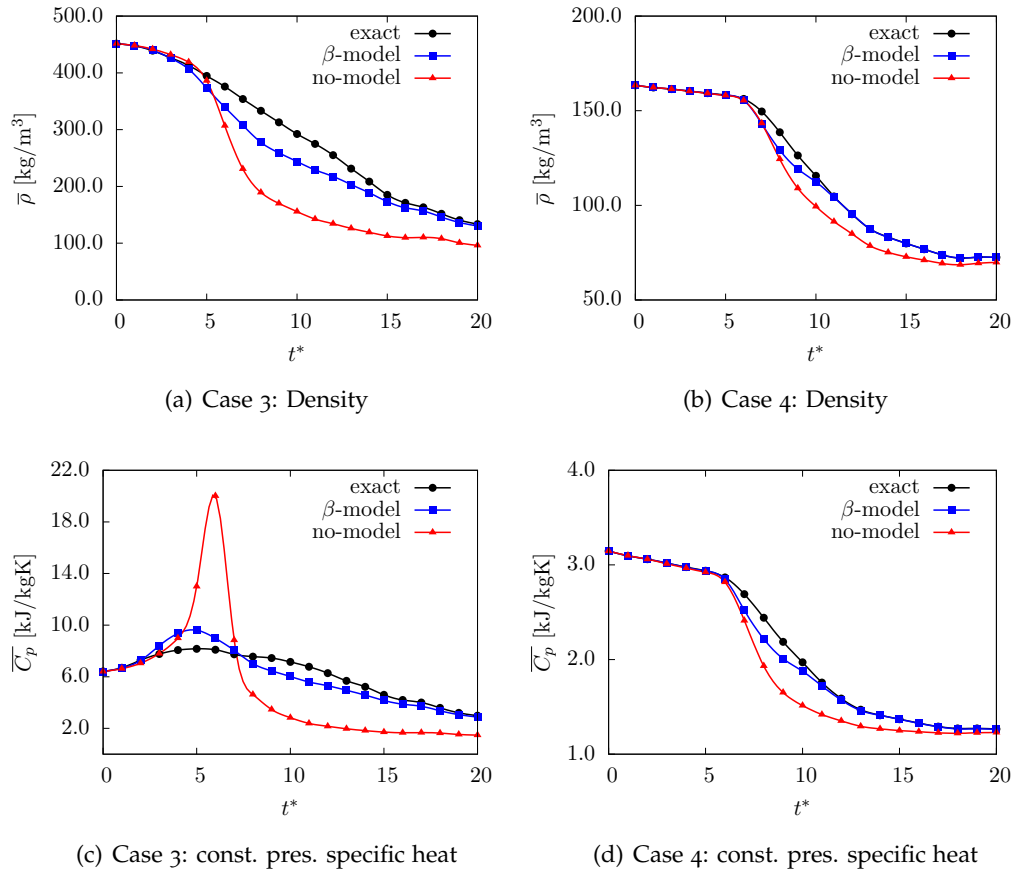


Figure 64.: Time evolution of averaged thermodynamic properties in the centerline plane ($y = 0$), for the transcritical and supercritical jet (respectively left and right column).

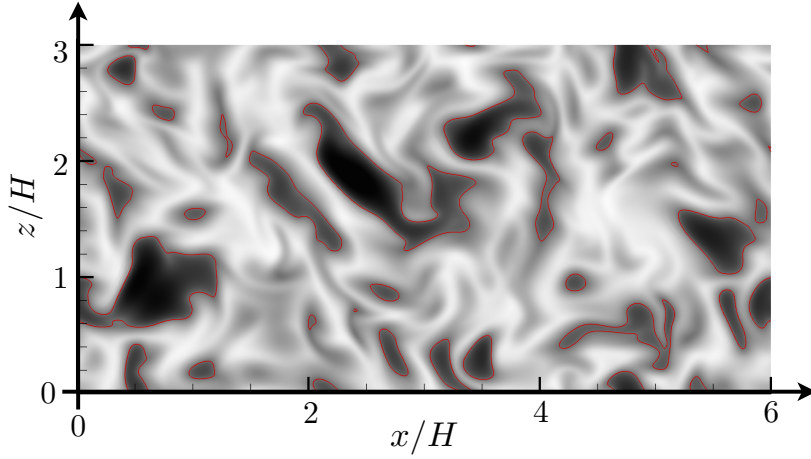


Figure 65.: Centerline cut ($y = 0$) visualization of the non dimensional temperature field $\zeta(x, z)$ at $t^* = 6$, for the transcritical jet (case 3). The color code varies logarithmically from $\zeta = 0$ (white) to the maximum value $\zeta = 0.173$ (black) of the slice considered, while the red line is the pseudo-boiling isoline $\zeta_{pb} = 0.0159$.

since, even if the mean value of ζ corresponds to ζ_{pb} , it does not necessarily imply that the entire region on which the average is performed is in a pseudo boiling state.

Indeed fig. 65, displaying the ζ field of the transcritical jet (case 3), shows the narrow yet resolved region around $\zeta \approx \zeta_{pb}$. This highlights the need for a consistent sub-grid modeling of the pseudo boiling phenomenon. Moreover the no-model density profile of fig. 64(a), also shows large errors which are most evident after $t^* = 6$ where the increase in $\overline{\zeta'''\zeta''}$ begins, and $\bar{\zeta}$ approaches the pseudo-boiling value. These errors are eventually reduced later in the simulation, since the jet is almost completely mixed. In addition, the shape of the no-model density profile (fig. 64(a)) can lead to some misleading interpretation of the jet characteristics itself, showing a fictitious dense core that begins to disintegrate at $t^* = 6$. This can be a major concern in the interpretation of LES and RANS results, representative of the flow conditions of the supercritical injection experiments of Mayer et al. [16]. In addition, dealing with transcritical injection, non-classical jet features can be encountered, such as the absence of a dense potential core (thermal break-up mechanism) recently discussed by Banuti and Hannemann [4], adding even more complexity to the interpretation of LES/RANS results.

Drawing from turbulent combustion modeling of non-premixed flames, a simple way to take into account sub-grid temperature fluctuations, is to approximate the exact pdf $p(\zeta^*; \mathbf{x}, t)$ with a β -function type distribution as introduced

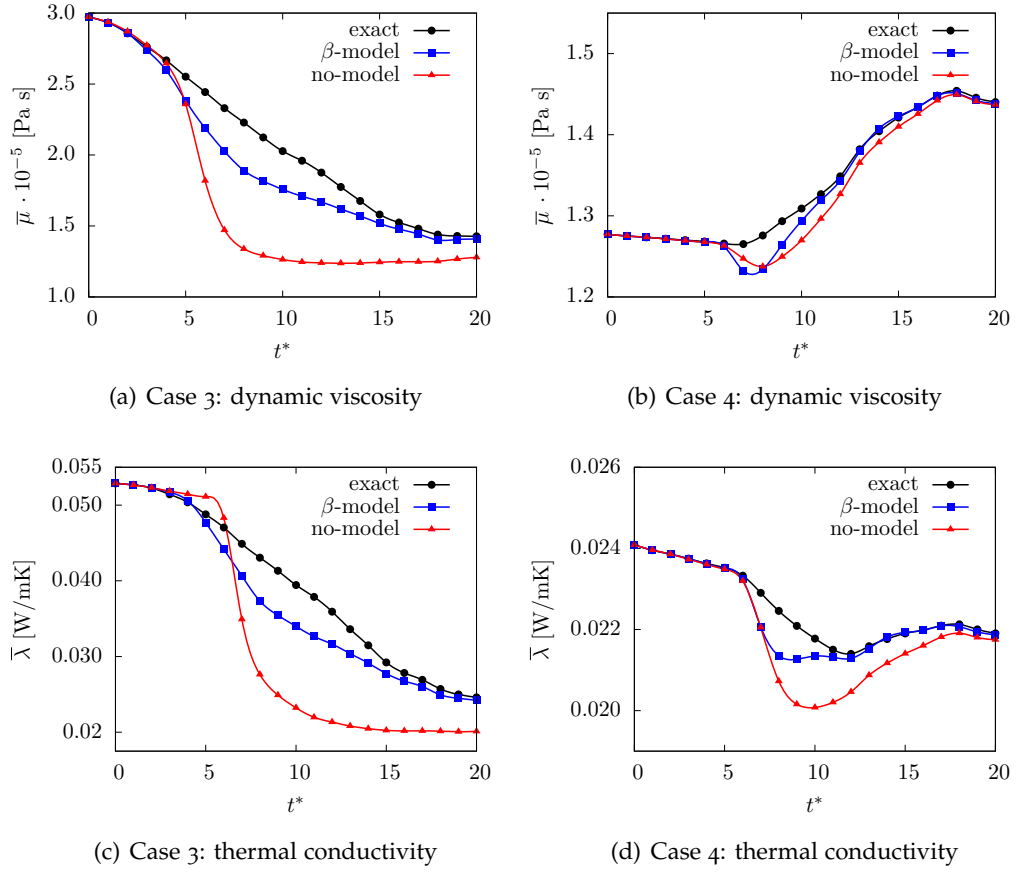


Figure 66.: Time evolution of averaged transport properties in the centerline plane ($y = 0$), for the transcritical and supercritical jet (respectively left and right column).

earlier. Figure 64 shows, along with the exact and no-model results, the mean of the thermodynamic properties $\bar{\rho}$ and $\bar{C}_p$ calculated using a β -function type distribution as in eq. (121) and eq. (122), based on the first and second order moments of the exact distribution. Results show that, for both case 3 and case 4, the use of a presumed pdf for the sub-grid fluctuations of ξ , can lead to a significant improvement of the mean values estimation. In particular, for the transcritical case, the inaccurate results presented by the no-model approach, showing a $\bar{C}_p$ peak (see fig.64(c)) and an abrupt decrease in $\bar{\rho}$ (see fig.64(a)) are both mitigated and therefore improved by the presumed pdf. Although not perfectly accurate at intermediate times ($t^* = 5 - 15$), the β -model shows a good agreement with DNS, with a bounded error which vanishes (for case 4 in particular) towards the end of the simulation time.

In the same way, the time evolution of the transport properties, averaged over the centerline plane $y = 0$, are displayed in fig. 66 comparing the exact mean values with the no-model and β -model approach. Coherently with the previous considerations on thermodynamic properties (ρ and C_p) the β -model averaged values show a much better agreement with the exact averages with respect to the no-model results, showing a confined and vanishing error over the entire *a priori* test. As expected, larger deviations from the exact values are experienced by the transcritical case (see fig.66(a) and fig.66(c)), while the supercritical case shows very good results after $t^* = 14$ as shown in fig. 66(b) and fig. 66(d).

The discrepancies between the DNS results and the two models considered have been presented for mean quantities evaluated over the entire centerline jet plane $y = 0$. The error ε associated to each model, however, will strictly depend on the LES/RANS filter size Δ_{filt} used and will be vanishingly small as Δ_{filt} approaches the DNS grid size Δ_{DNS} . This dependence is analyzed by subdividing a representative square portion of the jet centerline plane in a number of representative LES cells, using variable filter sizes Δ_{filt} up to the DNS resolution Δ_{DNS} . Then the overall averages over the LES cells using the no-model and the β -model, $\bar{\Psi}_{mod}$, are compared to the DNS averages, $\bar{\Psi}_{DNS}$, in order to define an error ε :

$$\varepsilon(\Delta_{filt}, t^*) = \frac{|\bar{\Psi}_{DNS} - \bar{\Psi}_{mod}|}{\bar{\Psi}_{DNS}} \quad (125)$$

which is a function of the filter size used and of the time instant t^* considered. In order to better characterize the models' performance, a total error ε^* is estimated, integrating $\varepsilon(\Delta_{filt}, t^*)$ over the simulation time:

$$\varepsilon^*(\Delta_{filt}) = \int_0^{20} \varepsilon(\Delta_{filt}, t^*) dt^*. \quad (126)$$

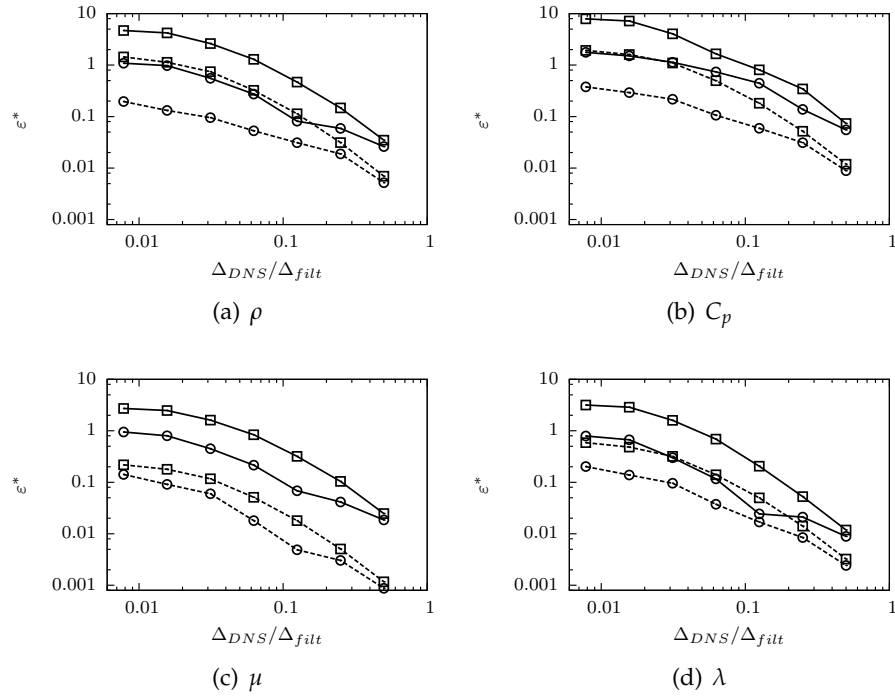


Figure 67.: Total modeling error ε^* of thermodynamic and transport properties as a function of the ratio between the DNS grid Δ_{DNS} and the filter size Δ_{filt} . Continuous lines (—) represent the transcritical jet (case 3) while the dashed lines (---) represent the supercritical jet (case 4), the no-model is denoted by squares symbols ($\square$) and the β -model by circles ($\circ$).

Figure 67 displays the error defined by Eq. (126) for both the transcritical and supercritical case using the β -model and the no-model, as functions of the ratio between the LES/RANS a priori filter size Δ_{filt} and the DNS grid size Δ_{DNS} . As expected, the error tends to zero when the filter size tends to the DNS resolution, progressively reducing the relevance of a sub-grid model for the scalar variance. It is however evident that accounting for the sub-grid scalar variance by means of a presumed β -pdf reduces the total error and substantially improves the results when a relatively coarse grid is used. The error of the β -model is shown to be systematically lower than the no-model, allowing similar accuracies with rather coarser grids. This implies that, given an appropriate resolution and a turbulence closure model, using a sub-grid model for the scalar variance of the non-dimensional temperature allows the use of a coarser LES/RANS grid for $Pr > 1$ flows. Note that the larger errors are shown in the evaluation of C_p (as shown in Fig. 67(b)), which is the thermodynamic property characterized by the most severely non-linear behavior of its conditional values. Nevertheless, the errors in density are also shown to be relevant (see Fig. 67(a)), in particular when

using the no-model approach with coarse grids. Transport properties, such as dynamic viscosity and thermal conductivity, shown in Fig. 67(c) and Fig. 67(d) respectively, are shown to be less sensitive to the filter grid size used. The relative magnitude of the errors suggests that neglecting the sub-grid variance of ζ leads to large but relatively confined errors ($\varepsilon^* < 2$) in the supercritical jet (case 4), while they cannot be neglected in the presence of the pseudo-boiling phenomenon as shown by the transcritical jet results of case 3 where errors up to $\varepsilon^* \sim 10$ are observed for relatively fine LES grids ($\Delta_{DNS}/\Delta_{filt} \approx 0.01$). This finally suggests that pseudo-boiling, occurring in a transcritical flow, is an effective sub-grid phenomenon that needs to be taken into account in LES/RANS modeling for accurate high fidelity simulations.

6.3 SUMMARY AND CONCLUSIONS

Real gas mixing at supercritical pressure, has been investigated by means of DNS in a temporal jet configuration. The NIST reference database has been used for thermodynamic and transport properties. The thermodynamic conditions are chosen to match the experiments of cryogenic injection of nitrogen at supercritical pressures [16, 41]. Two representative cases from the experimental test matrix have been chosen, a supercritical and a transcritical case. The latter, exhibiting pseudo-boiling phenomenon, is to the author's knowledge explored for the first time within a DNS framework.

- Grid requirements for DNS of the transcritical jet simulation with real thermodynamic and transport properties have been assessed. The grid limitations, ensuing from the resulting $Pr \approx 7.5$ in the pseudo boiling region, have been evidenced and discussed in terms of relative magnitude between Kolmogorov and Batchelor scale.
- The transcritical jet was found to visually resemble a liquid-like jet break-up, even if a single phase flow is present without any surface tension. This behavior, is induced by the pseudo boiling process between the core of the jet (liquid-like density) and the warm environment (gas-like density).
- The formation and growth of large scale turbulent structures (KH) is shown to be more evident for the supercritical jet. The elevated density stratification of the transcritical case, where pseudo boiling occurs, damps the growth of KH structures acting like a solid wall. However, additional research effort is needed to consistently analyze this phenomenology and

assess the influence of fundamental parameters on shear layer instability, such as the Reynolds number and background pressure.

- First and second order crosswise statistics of the two DNS simulations have been extracted and compared. Some qualitatively and quantitative differences have been shown between the two jets, despite having the same initial Reynolds number. In particular, the peak variance of thermodynamic properties of the transcritical jet, are found to be greater than the supercritical jet, contrary to the integrated variables (u and ξ) variance which highlighted the exact opposite behavior.
- Sub-grid scale modeling of ξ for the evaluation of thermodynamic and transport properties has been investigated *a priori* by means of DNS data. The no-model approach (which neglects the ξ sub-grid variance), largely used in LES and RANS framework, has been shown to lead to relevant errors and misleading jet properties interpretation.
- Drawing from TCM, a presumed β -pdf based model is used to introduce the ξ sub-grid variance influence on the thermodynamic and transport properties evaluation. The resulting *a priori* estimated error of the β -model is found, for a representative set of LES/RANS filter sizes, by far lower than the error of no-model.
- The evaluation of transport properties has been shown to be less sensitive, with respect to thermodynamic properties, to the filter grid size used, for both the no-model and the β -model.

The present study suggest that, under certain transcritical conditions, pseudo-boiling is an effective sub-grid phenomenon. Therefore it needs to be taken into account in a LES/RANS modeling framework. A possible way to address this problem is the use of a presumed β -pdf, which has been demonstrated to improve significantly the thermodynamic and transport properties evaluation.

7

CONCLUSION AND OUTLOOK

Although supercritical mixing and combustion, prompted by LREs applications, have been extensively studied both experimentally and numerically over the past decades, it remains relatively unexplored compared to its atmospheric pressure counterpart. In this thesis the effect of supercritical thermodynamic conditions on non-premixed laminar flames and on turbulent mixing has been investigated and discussed. Particular attention has been devoted to methane combustion together with LOx, since this propellant combination is a foreseeable future choice for next generation LREs.

In order to numerically account for molecular interactions and real gas effects, usually encountered in LRE combustion chambers, an efficient fortran thermodynamic library has been developed and validated. It is based on the departure function formalism [102] and on recently proposed three parameters EoS [100, 2] to deal with complex real gas mixtures. This tool has been successfully integrated in an unsteady flamelet solver to investigate the non-premixed laminar flame structures of LOx/methane mixtures. Typical unsteady flame configurations such as autoignition and re-ignition/quenching caused by strain perturbations have been studied. Real gas effects were found to be confined to the LOx region at near critical pressure (60 bar) while extending in a broader flame region, even with relatively low impact, for largely supercritical pressures (100 bar and higher). Moreover they influence the critical amplitude of strain perturbation that a laminar flame can sustain before quenching.

Since methane for space propulsion applications comes from the purification of the LNG, the effect of fuel composition on the supercritical flame structure has been investigated. Early stage soot precursors were found to strongly depend from the LNG composition. Moreover their mass fraction was found to decrease with increasing pressure.

As a first step toward the investigation of supercritical flames in a turbulent flow field using DNS, a low-Mach approximation for real gas reacting mixtures has been presented. The formulation allows the use of arbitrary EoS and constitutive relations, avoiding the numerical time step restrictions encountered by the widely used compressible formulations. A relevant sub-case, a single

species non-reacting real gas model, has been implemented in the highly scalable spectral element code nek5000 [15].

Real gas mixing has been investigated using DNS and state of the art thermodynamic and transport properties. Transcritical and supercritical temporal jets, with thermodynamic conditions perfectly matching the cryogenic nitrogen injection experiments at supercritical pressures [16], have been simulated. To the best of the author's knowledge these conditions have been simulated directly for the first time in this thesis. The pseudo-boiling phenomenon, occurring in transcritical flows, has been demonstrated to significantly influence the jet development. A liquid-like jet break-up and a mitigating effect on the development of shear layer instabilities have been observed. Moreover its presence is limited in a narrow spatial region suggest particular care in the sub-grid modeling for LES and RANS approaches. A statistical approach based on a standard presumed sub-grid pdf of temperature has been discussed and a priori tested on DNS data. Results have clearly shown significant improvement over the commonly used approximation in the thermodynamic and transport properties evaluation.

The wide range of results presented in this work provides useful physical insights as well as modeling considerations. The latter are of particular importance in the development of CFD tools capable of consistently simulate real engines configurations and operative conditions. Future effort will be devoted to the complete implementation of the proposed real gas reacting mixture formulation in nek5000, in order to take advantage of the ever increasing computing resources available and perform as relevant as possible DNS. Indeed, the real gas turbulence-chemistry interaction of complex cryogenic propellants and the high pressure pollutant formation remain substantially unexplored research areas, which pose a broad range of serious, as well as interesting, theoretical, numerical and computing challenges.



HYDRODYNAMIC INSTABILITY IN TURBULENT PREMIXED FLAMES

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Hydrodynamic or Darrieus-Landau (DL) instabilities in weakly turbulent Bunsen flames are numerically investigated under low-Mach number assumptions and a simplified deficient reactant thermochemistry. The DL instabilities are responsible for the formation of sharp folds and cusps in the flame front. Varying the ratio between the flame thickness and the Bunsen diameter the cut-off wavelength is modified and the instabilities induced. It is shown that stability criteria developed in the framework of asymptotic theory for planar flames can adequately predict the behavior of turbulent premixed flames in Bunsen configurations. A statistical characterization of flame morphology in the presence/absence of hydrodynamic instability is given in terms of flame curvature. Similar flame conformations were obtained in a recent experimental work. The statistical analysis highlight that the skewness of the flame curvature probability density function is a consistent marker of the instability presence and two different turbulent modes of flame propagation are identified.

A.1 INTRODUCTION

Premixed combustion is commonly encountered in many practical combustion devices from domestic to industrial burners. The premixed combustion processes can be greatly influenced by the onset of Darrieus-Landau (DL) hydrodynamic instabilities [162]. In large scale combustion devices DL instability is expected to be often present given its long wavelength nature. The impact of DL instabilities were experimentally investigated mainly in the wrinkled flamelet regime [163, 164, 165, 166, 167, 168, 169] while a number of numerical studies [170, 171,

[172, 173] focussed on the role of DL instability in deriving scaling laws for the turbulent flame speed S_T . Two very distinct turbulent modes of flame propagation were identified and described for planar premixed flames, denoted by the presence or absence of DL instability.

In a recent experimental work [174] evidence for this dual behavior within the wrinkled and corrugated flamelet regimes was conjectured using a propane-air Bunsen flame. The existence of an equivalence ratio range within which flames exhibit DL instability was predicted analytically for planar flames and then observed experimentally for bunsen flames. Moreover the flame front morphology was characterized in terms of curvature p.d.f. and its skewness assessing the presence of DL structures coexisting with the active turbulent wrinkling.

In the present work a low-Mach number formulation with a deficient reactant approach is implemented in nek5000 [15] a highly-scalable incompressible flow solver, in order to simulate the propagation of turbulent premixed flame and hydrodynamic instabilities in the less investigated Bunsen configuration. In order to induce DL instabilities the ratio between the flame thickness and the Bunsen diameter is modified within a range analytically derived for planar flames and induce DL instability. A parametric statistical analysis is carried out to confirm that the skewness of the flame curvature probability density function can be considered a consistent marker of the instability presence. Finally the influence of instabilities on the mean profiles and on the turbulent flame speed is investigated.

A.2 THEORETICAL AND NUMERICAL FORMULATION

In the low-Mach number limit the governing equations of a flow can be recast filtering out the acoustic waves propagation [130]. This allows an efficient integration of the equations while density variations caused by heat release and composition changes are fully taken into account [137]. Assuming that reacting mixture is sufficiently off-stoichiometric, the combustion processes can be considered to be governed by the concentration of a deficient reactant Y which is completely consumed crossing the premixed flame [145]. Therefore all the transport properties can be considered constant since they are not influenced by the presence/absence of the deficient reactant.

Under these assumption the non-dimensional form of the governing equations reads:

$$\rho \frac{Du}{Dt} = -\nabla p_1 + \frac{1}{Re} \nabla \cdot (\nabla u + (\nabla u)^T - \frac{2}{3}(\nabla \cdot u)I) \quad (127)$$

$$\rho \frac{DT}{Dt} = \nabla \cdot (\delta \nabla T) + \frac{\dot{\omega}}{\delta} \quad (128)$$

$$\rho \frac{DY}{Dt} = \nabla \cdot \left(\frac{\delta}{Le} \nabla Y \right) - \frac{\dot{\omega}}{\delta} \quad (129)$$

while the continuity equation is replaced by a constrain on the velocity divergence:

$$\nabla \cdot u = (\sigma - 1) \left[\nabla \cdot (\delta \nabla T) + \frac{\dot{\omega}}{\delta} \right] \quad (130)$$

where the non-dimensional state variables are the velocity u , the temperature T and the deficient reactant mass fraction Y . The source/sink term and the equation of state are expressed as:

$$\dot{\omega} = \frac{Ze^2}{2Le} Y \exp\left(\frac{Ze(1-T)}{1 - (1 - \frac{1}{\sigma})(1-T)}\right) \quad \rho = \frac{1}{(\sigma - 1)T + 1} \quad (131)$$

The non-dimensional parameters are defined as:

- expansion ratio $\sigma = \frac{\rho_u}{\rho_b}$ where subscript u and b are referring respectively to the unburnt and burnt regions.
- flame thickness $\delta = \frac{l_d}{L}$ where l_d is the dimensional flame thickness and L the characteristic hydrodynamic scale.
- Lewis number $Le = \frac{\lambda}{\rho_u c_p D}$ where λ is the thermal conductivity, c_p the constant pressure specific heat and D the diffusivity of the deficient reactant.
- Reynolds number $Re = \frac{\rho_u S_L^0 \delta}{\mu}$ where S_L^0 is the laminar flame speed and μ the dynamic viscosity.
- Zeldovich number $Ze = \frac{T_a(T_{ad} - T_u)}{T_{ad}^2}$ where T_{ad} is the adiabatic flame temperature.

The spatial discretization of the governing equations is based on the spectral element method [134], with conforming rectangular elements. Sums of tensor products of Legendre polynomials of order N , based the Gauss-Lobatto-Legendre quadrature points, are used to express both the geometry and the solution. The discrete form of the governing equation are solved with the highly scalable code nek5000 [15]. A semi-explicit time integration is used together with high-order splitting scheme for the low-Mach number variable density

flows [137], the stiffness deriving from finite-rate chemistry is tackled solving the energy and species equations implicitly using CVODE [142].

A.3 RESULTS AND DISCUSSION

The configuration considered is a two dimensional Bunsen flame. Homogeneous turbulence ($u_{rms} = 1.5$) is superimposed to the injected unburnt mixture while the surrounding co-flow is burnt mixture with a velocity such that no shear turbulence is induced. The other in order to be representative of hydrocarbons combustion and are summarized in Table 6.

Table 6.: Parameters settings

Parameter	Value
σ	8
δ	[0.004, 0.0325]
Le	1.2
Re	200
Ze	9.0

The non dimensional flame thickness change in a range chosen based on asymptotic theory for the stability of planar flames. Figure 68 show the stability region for a fixed σ value as a function of Le and δ following [17]. This region can be identified imposing a single unstable wavelength $N_c = 1$. Given a single value for the Lewis number a critical value of δ can be found, for the particular conditions chosen $\delta_{cr} = 0.0155$.

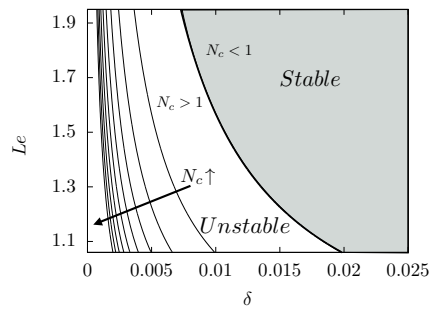


Figure 68.: Stable region (grey) in the Le - δ plane for planar premixed flames [17]. The bold line identify the $N_c = 1$.

Figure 69 shows single realizations for three representative δ values ($\delta_1 = 0.008$, $\delta_2 = 0.015$, $\delta_3 = 0.0275$). Different morphology are clearly observable, the δ_1 realization shows sharp cusps visibly indicating the presence of DL instabilities while the δ_3 realization is characterized by a smooth and round

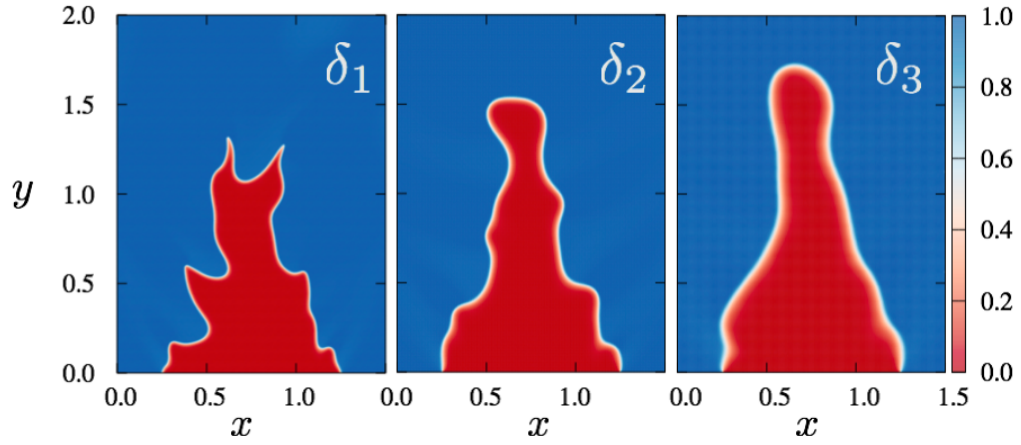


Figure 69.: Instantaneous representation of the non-dimensional temperature fields for three representative δ values ($\delta_1 = 0.008$, $\delta_2 = 0.015$, $\delta_3 = 0.0275$).

conformation hinting at a stable behavior of the flame front. The different morphology are then analyzed statistically, investigating the probability density function (p.d.f.) of the flame front curvature κ . The flame front is conventionally identified as a deficient reactant iso-line $Y = 0.9$. Therefore all the statical informations are conditioned to $Y = 0.9$.

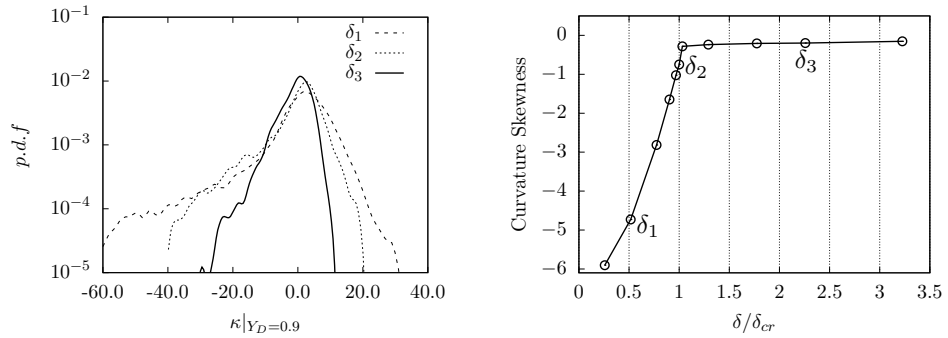


Figure 70.: Flame front curvature probability density function for three representative delta values (left panel). Skewness of curvature probability density function as a function of the ratio between the non-dimensional flame thickness and its critical value (right panel).

The left panel of figure 70 show the curvature p.d.f. for the three cases considered. The asymmetry of the p.d.f. is accentuated by decreasing δ indicating that its skewness can be a consistent marker of the instabilities. The skewness of the κ p.d.f. is therefore analyzed for each value of δ normalized by its critical value δ_{cr} . As shown in the right panel of figure 70 two very distinct trends can be observed: (i) for $\delta/\delta_{cr} > 1$ an almost constant null values of the skewness indicates that a preferential curvature of the flame front is not present, hence

the flame can be considered as stable; (ii) for $\delta/\delta_{cr} < 1$ the skewness decreases monotonically highlighting a general preference for negative curvature of the flame front that can be attributed to DL instabilities.

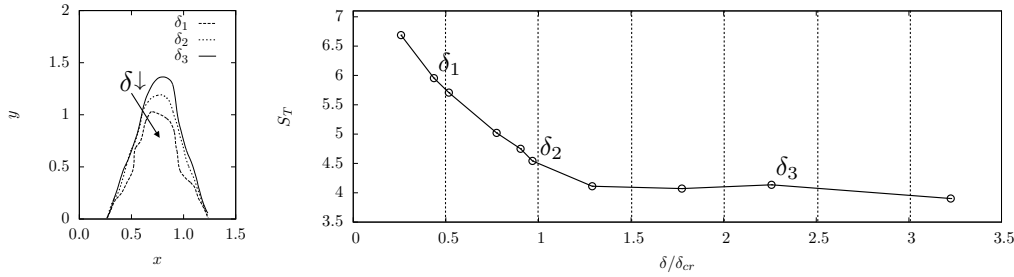


Figure 71.: Averaged flame profile for three representative δ values (left panel). Turbulent flame speed as a function of the ratio between the non-dimensional flame thickness and its critical value (right panel)

In order to evaluate the influence of hydrodynamic instabilities on the premixed flame propagation, the effect of δ on turbulent flame speed S_T is investigated. For a correct evaluation of S_T the mean flame front profiles have been calculated averaging a large number of realizations of the turbulent flow-field. The left panel of fig. 71 shows the averaged flame profile for the three representative δ values considered ($\delta_1 = 0.008$, $\delta_2 = 0.015$, $\delta_3 = 0.0275$). The flame area decreases as the flame becomes thinner and therefore the turbulent flame speed increases. As shown in the right panel of fig. 71 and consistently with the previous analysis and fig. 70 two distinct modes of propagation are evidenced. In the stable region ($\delta/\delta_{cr} > 1$) the turbulent flame speed remains almost constant while a substantial increase is shown in the unstable region ($\delta/\delta_{cr} < 1$). The DL instabilities inducing preferential negative curvature to the flame front modify the flame topology reducing the height of the averaged flame profile and, therefore, its propagation characteristics. In particular as the flame becomes more unstable the turbulent flame speed increases.

A.4 SUMMARY AND CONCLUSION

Hydrodynamic instabilities in weakly turbulent Bunsen flames have been numerically investigated. A low-Mach number formulation with simplified thermochemistry has been successfully implemented in the highly scalable code nek5000. DL instabilities have been induced by varying the ratio between the flame thickness and the Bunsen diameter, modifying the cut-off wavelength. The stability criteria developed in the framework of asymptotic theory for

planar flames have shown to correctly predict the behavior of the Bunsen flames investigated in the present work. The statistical analysis of the flame morphology have confirmed that the skewness of the flame curvature probability density function is a consistent marker of the instability presence. Finally two very distinct turbulent modes of flame propagation were identified analyzing the turbulent flame speed and the DL enhancement of it. Additional numerical effort is envisioned in order to asses the turbulence-flame interaction in the presence of DL instabilities and its effects on flame stretch and induced flow patterns

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LIST OF PUBLICATIONS

Some of the ideas and figures presented in the thesis may have previously appeared in the following publications:

Journal Publications

- F.Creta, R.Lamioni, P.E.Lapenna and G.Troiani "*Interplay of Darrieus-Landau instability and weak turbulence in premixed flame propagation*", Physical Review E 94.5 (2016): 053102
- P.E. Lapenna, P.P. Ciottoli and F.Creta "*An unsteady flamelet-based analysis of LOx-Methane flame structures at supercritical pressures*", (Submitted to Combustion Science and Technology)
- P.E. Lapenna, P.P. Ciottoli and F.Creta "*The effect of fuel composition on the non-premixed supercritical flame structure of LNG/LOx*", (in preparation for publication)
- P.E. Lapenna and F.Creta "*Mixing under transcritical and conditions: an a priori analysis using DNS*", (Submitted to Journal of Supercritical Fluids)

Conference Papers

- P.E. Lapenna, P.P. Ciottoli, F. Creta and M. Valorani "*Numerical investigation of unsteady laminar methane/LOx flamelet at supercritical pressures*", 7th European Combustion Meeting, Budapest, March30-April 2 2015.
- P.E. Lapenna and F. Creta "*Towards an Unsteady/Flamelet Progress Variable method for non-premixed turbulent combustion at supercritical pressures*" XXXVIII Meeting of the Italian Section of the Combustion Institute, Lecce, September 20-23 2015.
- P.E. Lapenna, P.P. Ciottoli and F. Creta "*The effect of fuel composition on the non-premixed flame structure of LNG/LOx mixtures at supercritical pressure*", 54th AIAA Aerospace Science Meeting, San Diego, January 4-8 2016.
- P.E. Lapenna, R. Lamioni and F. Creta "*LNG/LOX mixing and combustion under supercritical conditions*", Space Propulsion Conference, Rome, May 2-6 2016.
- D. Bianchi, P.E. Lapenna, F. Creta and F. Nasuti "*Numerical Simulations of Flowfield and Combustion in Hybrid Rockets*", Space Propulsion Conference, Rome, May 2-6 2016.

- P.E. Lapenna, R. Lamioni, G. Troiani and F. Creta "*Darrieus-Landau induced regime of propagation of turbulent premixed flames in Bunsen configurations*", XXXIX Meeting of the Italian Section of the Combustion Institute, Naples, July 4-6 2016
- R. Malpica Galassi, P.E. Lapenna, P.P. Ciottoli, G. Leccese, D. Bianchi, F. Nasuti, F. Creta and M. Valorani "*Simplified chemical kinetic mechanisms for hybrid rocket propulsion*", XXXIX Meeting of the Italian Section of the Combustion Institute, Naples, July 4-6 2016
- P.E. Lapenna, D. Cecere and F. Creta "*Scalar mixing and transport modeling under transcritical conditions for turbulent combustion modeling*", Submitted for 8th European Combustion Meeting 2017
- R. Lamioni, P.E. Lapenna, G. Troiani and F. Creta "*Interaction of Hydrodynamic instability and turbulence in premixed flame propagation*", Submitted for 8th European Combustion Meeting 2017
- P.P. Ciottoli, R. Malpica Galassi, P.E. Lapenna, G. Leccese, D. Bianchi, F. Nasuti, F. Creta and M. Valorani "*Skeletal chemical kinetic mechanism for HTPB-based hybrid rockets*", Submitted for 8th European Combustion Meeting 2017
- G. Troiani, F. Creta, P.E. Lapenna and R. Lamioni "*Experimental assessment of suppression and role of turbulence in Darrieus-Landau instability*", Submitted for 8th European Combustion Meeting 2017
- H. Muller, M. Pfitzner, P.E. Lapenna, P.P. Ciottoli, F. Creta and M. Valorani "*Analysis of the flame structure in non-premixed methane/oxygen flames at high-pressure conditions*", Submitted for 8th European Combustion Meeting 2017
- P.P. Ciottoli, B.J. Lee, P.E. Lapenna, R. Malpica Galassi, M. Valorani and H. Im "*Large eddy simulation on the effects of pressure on syngas/air turbulent nonpremixed flames*", Submitted for 8th European Combustion Meeting 2017