Entropy Filtered Density Function
for Large Eddy Simulation of
Turbulent Reacting Flows

by

Mehdi Safari

Submitted to the Graduate Faculty of
the Department of Mechanical Engineering in partial fulfillment
of the requirements for the degree of

Doctor of Philosophy

Northeastern University

2014
ENTROPY FILTERED DENSITY FUNCTION FOR LARGE EDDY SIMULATION OF TURBULENT REACTING FLOWS

NORTHEASTERN UNIVERSITY
DEPARTMENT OF MECHANICAL AND INDUSTRIAL ENGINEERING

This dissertation was presented
by
Mehdi Safari

It was defended on
April 4, 2014
and approved by

Professor Reza H. Sheikhi
Department of Mechanical and Industrial Engineering, Northeastern University

Professor Hameed Metghalchi
Department of Mechanical and Industrial Engineering, Northeastern University

Professor Yiannis Levendis
Department of Mechanical and Industrial Engineering, Northeastern University

Professor Youssef M. Marzouk
Department of Aeronautics and Astronautics, Massachusetts Institute of Technology
Entropy Filtered Density Function for Large Eddy Simulation of Turbulent Reacting Flows

Mehdi Safari
Northeastern University, 2014

Analysis of local entropy generation is an effective means to optimize the performance of energy and combustion systems by minimizing the irreversibilities in transport processes. Large eddy simulation (LES) is employed to describe entropy transport and generation in turbulent reacting flows. The entropy transport equation in LES contains several unclosed terms. These are the subgrid scale (SGS) entropy flux and entropy generation caused by irreversible processes: heat conduction, mass diffusion, chemical reaction and viscous dissipation. The SGS effects are taken into account using a novel methodology based on the filtered density function (FDF). This methodology, entitled entropy FDF (En-FDF), is developed and utilized in the form of joint entropy-velocity-scalar-turbulent frequency FDF and the marginal scalar-entropy FDF, both of which contain the chemical reaction effects in a closed form. The former constitutes the most comprehensive form of the En-FDF and provides closure for all the unclosed filtered moments. This methodology is applied for LES of a turbulent shear layer involving transport of passive scalars. Predictions show favorable agreements with the data generated by direct numerical simulation (DNS) of the same layer. The marginal En-FDF accounts for entropy generation effects as well as scalar and entropy statistics. This methodology is applied to a turbulent nonpremixed jet flame (Sandia Flame D) and predictions are validated against experimental data. In both flows, sources of irreversibility are predicted and analyzed.
Acknowledgments

I would like to express my sincere gratitude to my Ph.D. advisor, Professor Reza Sheikhi for his support, patience, and encouragement. I thank him for introducing me to the wonders and frustrations of scientific research. He has exercised the perfect balance between guiding me and allowing me to explore by myself. In addition to his intellectual guidance, his friendship and personal warmth made working with him such a great experience for me. I could not have imagined having a better advisor and mentor through the course of my research. I am grateful to the members of my doctoral committee, Professors Hameed Metghalchi, Yiannis Levendis and Youssef M. Marzouk (MIT) for their support and valuable suggestions.

I would like to thank Professor Behrooz Satvat and Professor John Cipolla, two gifted teachers and great scholars at Northeastern for the wonderful classes I took and insightful discussions we had. I thank my colleagues and friends at the Computational Energy and Combustion Laboratory, Fatemeh Hadi, Ronak Ghandriz, Jim Kopriva and David Hensel. I am also thankful to Dr. Mohammad Janbozorgi (USC) for his friendship and assistance during my earlier years in graduate school. I would like to thank my esteemed colleagues at Northeastern, Reza Khatami and Ali Moghaddas. My deepest gratitude goes to my family for providing me with the best possible education during my younger years. Their support and encouragement had a significant influence in my life. I have been blessed to have the companionship of my wife, Mona. Her love, support and patience through the course of my Ph.D. have been essential in seeing its completion.

I am grateful to the donors of the Petroleum Research Funds administrated by the American Chemical Society for their partial support of this research under Grant ACS-PRF 50912-DNI9. I also acknowledge the College of Engineering Computer Center at Northeastern University and the Texas Advanced Computing Center at the University of Texas at Austin through the National Science Foundation Extreme Science and Engineering Discovery Environment (XSEDE) for providing computational support for this work.
I dedicate this thesis to
my parents and my wife, Mona
for their constant support and unconditional love.
# Contents

## 1 INTRODUCTION  
1.1 Scope ................................................. 3  

## 2 ENTROPY FILTERED DENSITY FUNCTION  
2.1 Introduction ............................................ 4  
2.2 Formulation ............................................ 4  
2.3 Transport of entropy ................................... 6  
2.4 Large eddy simulation .................................. 11  
2.5 Entropy filtered density function ...................... 11  
   2.5.1 Definition .......................................... 12  
   2.5.2 En-FDF transport equations ....................... 13  
   2.5.3 En-FDF modeled transport equations ............. 14  
   2.5.4 Closure of unclosed terms in the En-FDF ........ 16  
2.6 Numerical solution procedure .......................... 18  
2.7 Temporal mixing layer simulation ...................... 20  
   2.7.1 Validation via DNS data ............................ 21  
   2.7.2 Analysis of entropy generation ................... 22  

## 3 MARGINAL ENTROPY FILTERED DENSITY FUNCTION  
3.1 Introduction ............................................ 33  
3.2 Formulation ............................................ 34  
3.3 Definition of Marginal En-FDF ......................... 36
3.4 Marginal En-FDF transport equations ........................................... 37
   3.4.1 Marginal En-FDF modeled transport equations ......................... 38
   3.4.2 Closure of unclosed terms in the marginal En-FDF .................... 40
3.5 Numerical solution procedure ..................................................... 42
3.6 Nonpremixed flame simulation ..................................................... 43
   3.6.1 Validation via laboratory data ............................................ 44
   3.6.2 Analysis of entropy generation ......................................... 45

4 CONCLUSION AND SOME SUGGESTIONS FOR FUTURE WORK 62

Nomenclature 64

Bibliography 68
List of Figures

2.1 Ensemble averaging on three different domains. Black squares denote finite difference grid points and the blue circles are MC particles. Also shown are three different ensemble domains: (1) $\Delta_E = \Delta/2$, (2) $\Delta_E = \Delta$ and (3) $\Delta_E = 2 \times \Delta$. ................................................................. 23

2.2 A schematic of the 3D temporally developing mixing layer. ...................... 24

2.3 Isosurface of instantaneous filtered entropy in temporal mixing layer simulations at $t = 80$, predicted by (a) En-FDF and (b) DNS. .................. 25

2.4 Cross-stream variation of Reynolds-averaged filtered entropy obtained from temporal mixing layer simulations at $t = 80$. The solid line and (+) symbol denote the En-FDF predictions obtained from FD and MC solvers, respectively. The circles denote the filtered DNS data. .................. 26

2.5 Cross-stream variation of Reynolds-averaged streamwise entropy flux components: (a) SGS, (b) resolved and (c) total obtained from temporal mixing layer simulations at $t = 80$. The solid lines denote the En-FDF results and the circles denote the filtered DNS data. .............................. 27

2.6 Cross-stream variation of Reynolds-averaged entropy generation by (a) heat conduction, (b) mass diffusion and (c) viscous dissipation obtained from temporal mixing layer simulations at $t = 80$. The solid lines denote the En-FDF results and the circles denote the filtered DNS data. .............................. 28

2.7 Instantaneous contours of temperature obtained from the En-FDF prediction of temporal mixing layer at $t = 80$ on planes: (a) $z = L$ and (b) $x = L$. .. 29

2.8 Instantaneous contours of SGS mixing frequency obtained from the En-FDF prediction of temporal mixing layer at $t = 80$ on planes: (a) $z = L$ and (b) $x = L$. .................................................. 30

2.9 Instantaneous contours of entropy generation by (a) heat conduction, (b) mass diffusion and (c) viscous dissipation obtained from the En-FDF prediction of temporal mixing layer at $z = L$ and $t = 80$. .............................. 31
2.10 Instantaneous contours of entropy generation by (a) heat conduction, (b) mass diffusion and (c) viscous dissipation obtained from the En-FDF prediction of temporal mixing layer at \( x = L \) and \( t = 80 \).

3.1 Ensemble averaging on three different domains. Black squares denote finite difference grid points and the blue circles are MC particles. Also shown are three different ensemble domains: (1) \( \Delta_E = \Delta/2 \), (2) \( \Delta_E = \Delta \) and (3) \( \Delta_E = 2 \times \Delta \).

3.2 Sandia Flame D configuration [125].

3.3 Instantaneous contours of filtered entropy in Sandia Flame D obtained from (a) MC and (b) FD solvers.

3.4 Radial variation of mean entropy in Sandia Flame D simulations at (a) \( x = 7.5 \) and (b) \( x = 15 \). The lines denote the En-FDF predictions. The circles denote the experimental data.

3.5 Radial variation of the RMS of entropy in Sandia Flame D simulations at (a) \( x = 7.5 \) and (b) \( x = 15 \). The solid and dashed lines denote the resolved and the total contributions, respectively. The circles denote the experimental data.

3.6 Instantaneous iso-surfaces of temperature (1700K, red; 1400K, yellow; 1100K, green) superimposed by contours of entropy generation (color bar) at different axial locations.

3.7 Instantaneous iso-surfaces of mixture fraction (0.3, red; 0.6, yellow; 0.9, blue) superimposed by contours of entropy generation (color bar) at different axial locations.

3.8 Instantaneous contours of: (a) temperature (K), (b) mixture fraction as well as contributions to entropy generation (non-dimensional) due to: (c) heat conduction, (d) mass diffusion and (e) chemical reaction, obtained from En-FDF simulations at \( z = 0 \) plane.

3.9 Instantaneous contours of entropy generation terms predicted by the En-FDF in Sandia Flame D simulations: (a) heat conduction (color) with temperature \([K]\) (black) contours, (b) mass diffusion (color) with mixture fraction (black) contours and (c) chemical reaction (color) with temperature \([K]\) (black) contours.

3.10 Radial variation of mean entropy generation rate due to: (a) heat conduction, (b) mass diffusion and (c) chemical reaction in the En-FDF prediction of Sandia Flame D at \( x = 1 \) (▽), \( x = 5 \) (□), \( x = 10 \) (◇) and \( x = 15 \) (–).
3.11 Radial variation of mean entropy generation rate (dashed lines) and its individual terms: heat conduction ($\nabla$), mass diffusion (□) and chemical reaction (−) at (a) $x = 5$ and (b) $x = 15$ in the En-FDF prediction of Sandia Flame D. 59

3.12 Radial variation of total RMS of mixture fraction (left) and resolved RMS of velocity m/s (right) at $x/D = 10$. Symbols correspond to inflow stream velocity RMS, $U'/u'_{exp}$ = 1.0 (○), 1.014 ($\nabla$), 1.039 (□) and 1.087 (×). . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 60

3.13 Radial variation of entropy generation modes at $x/D = 10$. Symbols correspond to inflow stream velocity RMS, $U'/u'_{exp}$ = 1.0 (○), 1.014 ($\nabla$), 1.039 (□) and 1.087 (×). . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 61
List of Tables

2.1 Temporal mixing layer: summary of simulation parameters .......................... 21

3.1 Sandia Flame D: summary of the LES simulation parameters. ...................... 47

3.2 Effect of turbulent intensity on exergy loss (J/m³.s). The second law efficiency is

\[ \eta_{II} = \left( 1 - \frac{T_0 S_{\infty}}{e_{xin}} \right) \times 100, \]

where \( e_{xin} \) is the rate of exergy influx at the inlet and \( T_0 = 291 K \) is the dead state temperature. ..................................................... 58
Chapter 1

INTRODUCTION

The objective of this work is to predict entropy and entropy generation in turbulent reacting flows using large eddy simulation (LES). Entropy generation is not only an essential part of entropy dynamics, but also a significant quantity in its own right with many applications in diverse fields [1–9]. In fluid systems, production of entropy is a manifest of irreversible dissipation inherent in the underlying transport processes such as fluid flow, heat transfer and mass diffusion. Entropy generation plays a key role in thermodynamic optimization, aiming to minimize the departure from thermodynamic ideality and to approach the theoretical limits of performance [10–13]. Efficient use of energy is one of the major objectives in designing modern energy conversion systems such as turbomachinery, heat exchangers and internal combustion engines. The irreversibility of processes involved in these systems can be effectively investigated by analyzing the entropy production. Entropy generation in a system is proportional to exergy destruction [12,14–16] or loss of available energy due to irreversible processes. The net rate of such loss can be determined by performing a system-level exergy (availability) balance [16–27]. However, to identify the specific irreversible processes, it is necessary to conduct a spatiotemporal (local) analysis of entropy production [28–49]. In this respect, analysis of entropy generation enables identification and subsequently minimization of irreversible losses contributing to availability (exergy) destruction, causing the degradation of available energy into internal energy [16,20,26,36,50]. Prediction and analysis of entropy generation in laminar flows has been the subject of many contributions [23,29,31–33,35,40,51]. Briones et al. [33] studied the entropy generation mechanisms in a partially-premixed flame. Chen et al. [51] investigated the effect of hydrogen enrichment on entropy generation. Teng et al. [29] and Nishida et al. [32] provided a formulation for entropy generation in multicomponent reacting flows. Datta and Som [23] considered energy and exergy balance in a gas turbine combustor and Shuja et al. [35] studied the influence of inlet velocity profiles on efficiency of heat transfer in a laminar jet. Despite the prevalence of turbulence, there have been rather limited investigations devoted to entropy generation in turbulent flows. Contributions in this regime include several direct numerical simulation (DNS) studies [52–57], which demonstrate the influence of turbulence on entropy generation. For example,
Okong’o and Bellan [52, 53] considered a three-dimensional (3D) supercritical mixing layer and analyzed entropy generation effects. Recently, Farran and Chakraborty [57] conducted DNS of entropy generation in a turbulent premixed flame, based on the formulation of Safari et al. [58]. Furthermore, entropy generation is shown to be useful to describe the behavior of small-scale turbulent motions owing to its capacity to incorporate the full range dissipative effects [54].

Despite usefulness of DNS in studying physics of turbulence, the large spatial resolution required makes it prohibitively expensive to solve engineering problems in the foreseeable future. As a remedy, solution of Reynolds averaged Navier-Stokes (RANS) equations has been widely used in engineering applications to predict flows of practical interest. This approach, however, suffers from one principal shortcoming; the fact that the model must represent a very wide range of scales reduces its reliability as a predictive tool. In this regard, LES is a very attractive alternative as it provides a compromise between accuracy and computational cost. This approach is widely acknowledged to be the optimal means of capturing the detailed, unsteady physics of turbulence [59–65]. Application of RANS and LES to predict entropy and its production rate requires modeling of the unclosed entropy generation terms. Previous modeling efforts in this areas have mainly been in the context of RANS [42, 66–68]. Stanciu et al. [38, 39] performed the second law analysis of diffusion flames. Yapıcı et al. [42] considered local entropy generation in methane-air burners and Herwig and Kock [41] used entropy production in turbulent shear flows as a tool to evaluate the local heat transfer performance. The extent of such investigations via LES has been insignificant. Considering the advantages of LES, this approach provides an effective means of predicting and analyzing the local, instantaneous entropy generation mechanisms. The main challenge in LES is accurate modeling of the subgrid scale (SGS) effects, particularly those pertaining to entropy production as shown by Safari et al. [58]. The filtered density function (FDF) methodology is particularly suited for this purpose [47,69]. The methodology was originally introduced by Givi [70] and Pope [71] and has been successfully applied to a variety of turbulent reacting flows [72–85]. In previous contributions, various forms of FDF were developed. These include the scalar FDF [86,87], the velocity FDF (VFDF) [88], the joint velocity-scalar FDF [72, 78] and the frequency-velocity-scalar FDF [80]. Reviews of FDF modeling and its applications are provided in Refs. [89–91].

In the present study, a novel FDF methodology, termed the entropy FDF (En-FDF) [47,69], is developed which contains the SGS variation of entropy. The En-FDF is considered in its comprehensive and marginal forms. The comprehensive En-FDF contains the complete statistical information about the velocity, scalar, frequency and entropy fields and thus, provides SGS closure for all the unclosed filtered moments. The marginal En-FDF is the FDF of entropy and scalar fields and describes the unclosed entropy generation and chemical reaction effects as well as the entropy and scalar statistics. This methodology constitutes a more practical means of predicting entropy generation in complex turbulent reacting flows. However, it requires closure of all the second order SGS moments via the conventional (non-FDF) LES models. The comprehensive En-FDF formulation is employed to perform LES.
of a 3D turbulent temporally developing mixing layer involving transport of passive scalars. The marginal En-FDF is applied to a turbulent nonpremixed jet flame. Entropy generation analysis is performed in both cases and predictions are assessed by comparing with DNS and experimental data.

1.1 Scope

This dissertation is organized as follows. In Chapter 2, the comprehensive En-FDF is presented. The equations governing fluid flow and species transport are introduced. The entropy transport equation is derived, followed by filtered form of equations in LES. The En-FDF methodology is introduced to describe the unclosed subgrid effects in LES. Closure of unclosed terms in transport equations are presented, including that for each individual entropy generation terms. The simulation results are presented after an overview of the numerical solution procedure. To assess the methodology, simulations are conducted of a non-reacting temporal mixing layer. This flow has been studied in previous works [72, 80], in which extensive validation of hydrodynamics and scalar fields are demonstrated. The focus in this dissertation is to provide the same appraisal for entropy and entropy generation statistics against DNS results. In Chapter 3, a marginal form of the En-FDF is presented, which is useful for more practical turbulent combustion simulations. Following an overview of the formulations and numerical simulation procedure, simulation results are presented. Simulations are conducted of a non-premixed jet flame and results are validated via laboratory data. This flow has been the subject of previous FDF study [73]. The concentration of this work is on assessment of entropy and entropy generation statistics using data derived from laboratory measurements. For convenience of the reader, Chapters 2 and 3 are self-contained. In Chapter 4, some final remarks are made, with some suggestions for future research. The work described in this dissertation has been presented at several conferences [92–96]; published as conference papers [97–101] and journal articles [47, 58, 69]. It is also under review for publication in Journal of Fluid Mechanics [102]. Part of this dissertation published in Ref. [97] has received the ASME Systems Analysis Best Paper Award.
Chapter 2

ENTROPY FILTERED DENSITY FUNCTION

2.1 Introduction

In this chapter, the En-FDF methodology is developed to account for the joint SGS statistics of velocity, frequency, scalar and entropy fields. An overview of governing equations are provided followed by derivation of a transport equation for entropy in a form consistent with LES formulation. Subsequently, the En-FDF is introduced to describe the unclosed terms in the transport equations of mass, momentum, scalar and entropy. Following its mathematical definition, the “exact” En-FDF transport equation is derived. The unclosed terms in this equation are modeled using an equivalent system of stochastic differential equations. A hybrid Eulerian/Lagrangian numerical solution procedure is developed. In the Eulerian part, the filtered transport equations are solved by finite-difference method. In the Lagrangian part, the solution of the modeled En-FDF transport equation is obtained by Monte Carlo method. The unclosed statistics in the Eulerian part are obtained from the Monte Carlo solver. Simulations are conducted of a temporally developing mixing layer. The consistency and accuracy of the methodology in predicting entropy and entropy generation are shown. The predictive capabilities of the En-FDF is shown by comparing the simulation results with data generated via DNS of the same layer.

2.2 Formulation

In turbulent reacting flows involving $N_s$ number of chemical species, the transport variables are fluid density $\rho(x,t)$, velocity vector $u_i(x,t)$ ($i = 1, 2, 3$), pressure $p(x,t)$, specific enthalpy $h(x,t)$ and species mass fractions $Y_\alpha(x,t)$ ($\alpha = 1, 2, \ldots, N_s$). Equations that govern the
transport of these variables in space \( x_i \) \((i = 1, 2, 3)\) and time \( t \) are the conservation laws of mass, momentum, enthalpy (energy) and species mass fraction, together with an equation of state,

\[
\begin{align*}
\frac{\partial \rho}{\partial t} + \sum_{i=1}^{3} \frac{\partial \rho u_i}{\partial x_i} &= 0 \quad (2.1) \\
\frac{\partial \rho u_i}{\partial t} + \sum_{j=1}^{3} \frac{\partial \rho u_i u_j}{\partial x_j} &= -\frac{\partial p}{\partial x_i} + \sum_{ij} \frac{\partial \tau_{ij}}{\partial x_j} \quad (2.2) \\
\frac{\partial \rho \phi_\alpha}{\partial t} + \sum_{i=1}^{3} \frac{\partial \rho u_i \phi_\alpha}{\partial x_i} &= -\sum_{i} \frac{\partial J_\alpha^i}{\partial x_i} + \rho S_\alpha \quad (2.3) \\
p &= \rho R_u T \sum_{\alpha=1}^{N_s} \phi_\alpha M_\alpha = \rho RT \quad (2.4)
\end{align*}
\]

where \( R_u \) and \( R \) are the universal and the mixture gas constants; \( M_\alpha \) denotes the molecular weight of species \( \alpha \) and \( T \) is the temperature. Equation (2.3) governs the transport of scalars \( \phi = [\phi_1, \phi_2, \ldots, \phi_{N_s+1}] \), wherein \( \phi_\alpha \equiv Y_\alpha \) \((\alpha = 1, 2, \ldots, N_s)\) and \( \phi_{N_s+1} \equiv h \). In Eq. (2.3), \( S_\alpha \) is the chemical reaction source term for the chemical species \( \alpha \), defined as,

\[
S_\alpha = \frac{1}{\rho} M_\alpha \dot{\omega}_\alpha \quad (2.5)
\]

where \( \dot{\omega}_\alpha \) for \( \alpha = 1, 2, \ldots, N_s \) is the molar rate of production/destruction of species \( \alpha \) due to chemical reaction. The molar rate of production/destruction of species, is described by the gas-phase reaction mechanisms. In a chemical mechanism containing \( r \) reactions, the molar rate of production/destruction of species \( \alpha \) is,

\[
\dot{\omega}_\alpha = \sum_{j=1}^{r} \nu_{\alpha j} W_j \quad (2.6)
\]

In this equation, \( W_j \) is the rate of reaction \( j \) in chemical mechanism

\[
W_j = k_{fj} \prod_{\alpha=1}^{N_s} \left( \frac{\rho Y_\alpha}{M_\alpha} \right)^{\nu'_{\alpha j}} - k_{bj} \prod_{\alpha=1}^{N_s} \left( \frac{\rho Y_\alpha}{M_\alpha} \right)^{\nu''_{\alpha j}} \quad (2.7)
\]

where \( k_{fj} \) and \( k_{bj} \) are the rate coefficients of the forward and backward reactions, respectively. In general, they are functions of temperature and may also depend on pressure. The exponents \( \nu'_{\alpha j} \) and \( \nu''_{\alpha j} \) are the stoichiometric coefficients of reaction \( j \) in forward and backward directions, respectively. The chemical reaction source term in Eq. (2.3) is the production rate of species \( \alpha \) per unit mass and unit time and is defined as the sum over all reactions in the mechanism,

\[
\rho S_\alpha = M_\alpha \sum_{j=1}^{r} \nu_{\alpha j} W_j \quad (2.8)
\]
where $\nu_{\alpha j} = \nu''_{\alpha j} - \nu'_{\alpha j}$. Since mass is conserved, the sum over all source terms vanishes,

$$
\sum_{\alpha=1}^{N_s} \rho S_{\alpha} = 0 \quad (2.9)
$$

In low Mach number flows, $S_{\alpha} \equiv S_{\alpha}(\phi)$ is function of the composition variables $\phi = [Y_1, Y_2, \ldots, Y_{N_s}, h]$ and is independent of pressure [103]. The source term for enthalpy ($S_{N_s+1}$) contains the effect of viscous dissipation, pressure variation and radiation. For low Mach number flows the former two effects are small. For the non-sooting flames, the heat loss by radiation is typically negligible compared to the overall rate of heat transfer. Therefore, the source term in enthalpy transport equation is set to zero ($S_{N_s+1} \approx 0$).

We consider a Newtonian fluid and employ the Fick’s law of mass diffusion and Fourier’s law of heat conduction. The viscous stress tensor $\tau_{ij}$ and the scalar flux $J_{\alpha i}$ are thus represented by,

$$
\tau_{ij} = \mu \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} - \frac{2}{3} \frac{\partial u_k}{\partial x_k} \delta_{ij} \right) \quad (2.10a)
$$

$$
J_{\alpha i} = -\gamma \frac{\partial \phi_{\alpha}}{\partial x_i} \quad (2.10b)
$$

where $\mu$ is the fluid dynamic viscosity and $\gamma$ denotes the thermal and mass molecular diffusivity coefficients for all the scalars. We assume $\mu = \gamma$ (thus, we have unity Schmidt $Sc$, Prandtl $Pr$ and Lewis $Le$ numbers). Equations (2.1 - 2.4) accompanied by Eq. (2.5) and Eqs. (2.10) form a closed set of equations.

### 2.3 Transport of entropy

The thermodynamic efficiency of a device or a process, which is related to the degree of irreversibilities generated, has widely been evaluated using the second law analysis. Practical energy conversion processes are always accompanied by an irreversible increase in entropy, which leads to a decrease in exergy (available energy). Thus, even though energy is conserved, exergy decreases because energy is converted into a different form, from which less work can be extracted. Reduced entropy generation results in more efficient use of available energy in combustion systems. To improve the performance of these systems, exergy analysis is essential to explain the sources of exergy loss. The exergy balance equation reads as,

$$
\frac{dE_x}{dt} = E_{xt} - E_{xD} \quad (2.11)
$$

where $E_x$ is the exergy and the term on the left hand side specifies the rate of change of exergy within the system. $E_{xt}$ is the rate of exergy transfer due to heat, work and flow
interactions and $E_{xD}$ denotes the rate of exergy destruction due to irreversibility and can be expressed as,

$$E_{xD} = T_0 S_g$$

where $T_0$ is the ambient (dead state) temperature and $S_g$ is the rate of entropy generation due to irreversibilities which appears in the transport of entropy, as described below.

Using Gibbs fundamental relation [104],

$$T \, ds = de + pdv - \sum_{\alpha=1}^{N_s} \mu_\alpha \, d\phi_\alpha$$

a transport of entropy can be derived,

$$T \rho \frac{Ds}{Dt} = \rho \frac{De}{Dt} + p \rho \frac{Dv}{Dt} - \sum_{\alpha=1}^{N_s} \mu_\alpha \rho \frac{D\phi_\alpha}{Dt}$$

where $T$, $e$ and $v$ denote the temperature, internal energy and the specific volume, respectively. $D/Dt = \partial/\partial t + u_i \partial/\partial x_i$ denotes the material derivative. $\mu_\alpha$ denotes the chemical potential (per unit mass of species $\alpha$),

$$\mu_\alpha = h_\alpha - T s_\alpha^o$$

in which,

$$s_\alpha^o = \frac{1}{M_\alpha} \left( \frac{\partial S}{\partial n_\alpha} \right)_{T,p,n_\beta} \quad (\beta \neq \alpha)$$

is the partial entropy. $n_\alpha$ is the number of moles of species $\alpha$. $S$ denotes the extensive entropy,

$$S = m s = m \sum_{\alpha=1}^{N_s} \phi_\alpha s_\alpha^o$$

where $m$ is the total mass. For an ideal gas, the partial entropy can be expressed in terms of entropy of pure substance as,

$$s_\alpha^o = s_\alpha - R_\alpha \ln X_\alpha$$

In this equation, $s_\alpha$ denotes the entropy of pure species $\alpha$, $X_\alpha$ denotes the mole fraction and $R_\alpha$ is the gas constant for species $\alpha$ ($R_\alpha = R_u/M_\alpha$). In Eq. (2.15), $h_\alpha$ is the enthalpy of species $\alpha$,

$$h_\alpha = h_\alpha^0 + \int_{T_0}^T c_{p\alpha}(T')dT'$$

in which $h_\alpha^0$ denotes the enthalpy of species $\alpha$ at reference temperature $T_0$ and $c_{p\alpha}$ represents specific heat at constant pressure for species $\alpha$. By substituting for $De/Dt$ and $D\phi_\alpha/Dt$
from conservation equations of energy and chemical species mass fraction [61], we obtain a transport equation for entropy,

$$\frac{\partial \rho s}{\partial t} + \frac{\partial \rho u_i s}{\partial x_i} = \frac{1}{T} \left[ \tau_{ij} \frac{\partial u_i}{\partial x_j} - \frac{1}{T} \left( q_i - \sum_{\alpha=1}^{N_s} h_{\alpha} J_{\alpha}^i \right) \frac{\partial T}{\partial x_i} - \sum_{\alpha=1}^{N_s} \mu_{\alpha} \frac{\partial J_{\alpha}^i}{\partial x_i} - \sum_{\alpha=1}^{N_s} \rho \mu_{\alpha} S_{\alpha} \right]$$ \hspace{1cm} (2.20)

In Eq. (2.20), $q_i$ is the energy flux term, expressed as

$$q_i = -\lambda \frac{\partial T}{\partial x_i} + \sum_{\alpha=1}^{N_s} h_{\alpha} J_{\alpha}^i$$

$$= -\lambda \frac{\partial T}{\partial x_i} - \sum_{\alpha=1}^{N_s} \gamma_{\alpha} h_{\alpha} \frac{\partial \phi_{\alpha}}{\partial x_i}$$

where the rate of heat transfer by radiation is neglected. In this equation $\lambda$ denotes the thermal conductivity. The entropy transport equation, Eq. (2.20), can be written in a form consistent with that in Ref. [104],

$$\frac{\partial \rho s}{\partial t} + \frac{\partial \rho u_i s}{\partial x_i} = \frac{1}{T} \left[ \tau_{ij} \frac{\partial u_i}{\partial x_j} - \frac{1}{T} \left( q_i - \sum_{\alpha=1}^{N_s} h_{\alpha} J_{\alpha}^i \right) \frac{\partial T}{\partial x_i} - \sum_{\alpha=1}^{N_s} \rho \mu_{\alpha} S_{\alpha} \right]$$

$$- \frac{\partial}{\partial x_i} \left[ \frac{1}{T} \left( q_i - \sum_{\alpha=1}^{N_s} h_{\alpha} J_{\alpha}^i \right) + \sum_{\alpha=1}^{N_s} s_{\alpha} J_{\alpha}^i \right]$$

$$\hspace{1cm} (2.22)$$

Utilizing Eq. (2.19), the term $IV$ on the right hand side (RHS) of this equation can be expressed as,

$$- \sum_{\alpha=1}^{N_s} J_{\alpha}^i \left( \frac{\partial \mu_{\alpha}}{\partial x_i} + s_{\alpha}^o \frac{\partial T}{\partial x_i} \right) = - \sum_{\alpha=1}^{N_s} J_{\alpha}^i \left( c_{p\alpha} \frac{\partial T}{\partial x_i} - T \frac{\partial s_{\alpha}^o}{\partial x_i} \right)$$ \hspace{1cm} (2.23)

For an ideal gas, taking derivative of Eq. (2.18) results in,

$$\frac{\partial s_{\alpha}^o}{\partial x_i} = \frac{c_{p\alpha}}{T} \frac{\partial T}{\partial x_i} - \frac{R_{\alpha}}{X_{\alpha}} \frac{\partial X_{\alpha}}{\partial x_i} - \frac{\rho \beta_{\alpha}}{p} \frac{\partial p}{\partial x_i} \approx 0$$ \hspace{1cm} (2.24)

where the last term can be neglected in low Mach number combustion processes [39,64,105]. By employing Eq. (2.24), the term $IV$ in Eq. (2.22) can thus be written as

$$- \sum_{\alpha=1}^{N_s} J_{\alpha}^i \left( \frac{\partial \mu_{\alpha}}{\partial x_i} + s_{\alpha}^o \frac{\partial T}{\partial x_i} \right) = - \sum_{\alpha=1}^{N_s} R_{\alpha} J_{\alpha}^i \left( \frac{R_{\alpha}}{X_{\alpha}} \frac{\partial X_{\alpha}}{\partial x_i} \right)$$ \hspace{1cm} (2.25)
In Eq. (2.22), the term $V$ can be further simplified by using Eqs. (2.10b), (2.21) as,

$$-rac{\partial}{\partial x_i} \left[ \frac{1}{T} (q_i - \sum_{\alpha=1}^{N_s} h_\alpha J^\alpha_i) + \sum_{\alpha=1}^{N_s} s^\alpha_i J^\alpha_i \right] = \frac{\partial}{\partial x_i} \left[ \frac{\lambda}{T} \frac{\partial T}{\partial x_i} + \sum_{\alpha=1}^{N_s} \gamma^\alpha s^\alpha_i \frac{\partial \phi_\alpha}{\partial x_i} \right]$$

(2.26)

This equation can further be simplified by employing Eq. (2.24) and assuming equal mass diffusivity for all species ($\gamma_\alpha = \gamma$, $\alpha = 1, \ldots, N_s$) and unity Lewis number ($Le = \lambda/(\gamma c_p) = 1$, where $c_p = \sum_{\alpha=1}^{N_s} c_{p,\phi} \phi_\alpha$ is the specific heat capacity at constant pressure for the mixture). Therefore, the term $V$ in Eq. (2.22) reduces to diffusion of entropy,

$$-rac{\partial}{\partial x_i} \left[ \frac{1}{T} (q_i - \sum_{\alpha=1}^{N_s} h_\alpha J^\alpha_i) + \sum_{\alpha=1}^{N_s} s^\alpha_i J^\alpha_i \right] = \frac{\partial}{\partial x_i} \left( \gamma \frac{\partial s}{\partial x_i} \right)$$

(2.27)

By substituting Eqs. (2.25), (2.27) into Eq. (2.22), another useful form of entropy transport equation can be obtained,

$$\frac{\partial \rho s}{\partial t} + \frac{\partial \rho u_i}{\partial x_i} = \frac{\partial}{\partial x_i} \left( \gamma \frac{\partial s}{\partial x_i} \right) + \frac{1}{T} \tau_{ij} \frac{\partial u_i}{\partial x_j} + \frac{\gamma c_p}{T^2} \frac{\partial T}{\partial x_i} \frac{\partial T}{\partial x_i} + \sum_{\alpha=1}^{N_s} \gamma R_\alpha \frac{\partial \phi_\alpha}{\partial x_i} \frac{\partial X_\alpha}{\partial x_i} - \frac{\rho}{T} \sum_{\alpha=1}^{N_s} \mu_\alpha S_\alpha$$

(2.28)

In this equation, the last four terms on the RHS constitute the volumetric rate of generation of entropy $S_g$,

$$S_g = S_{g_v} + S_{g_h} + S_{g_m} + S_{g_c}$$

(2.29)

which constitute the irreversible part of entropy transport, and is comprised of individual contributions,

$$S_{g_v} \equiv \frac{1}{T} \tau_{ij} \frac{\partial u_i}{\partial x_j} \geq 0$$

(2.30a)

$$S_{g_h} \equiv \frac{\gamma c_p}{T^2} \frac{\partial T}{\partial x_i} \frac{\partial T}{\partial x_i} \geq 0$$

(2.30b)

$$S_{g_m} \equiv \sum_{\alpha=1}^{N_s} \gamma R_\alpha \frac{\partial X_\alpha}{\partial x_i} \frac{\partial \phi_\alpha}{\partial x_i} \geq 0$$

(2.30c)

$$S_{g_c} \equiv -\frac{\rho}{T} \sum_{\alpha=1}^{N_s} \mu_\alpha S_\alpha \geq 0$$

(2.30d)

where $S_{g_v}, S_{g_h}, S_{g_m}$ and $S_{g_c}$ denote entropy generation by viscous dissipation, heat conduction, mass diffusion and chemical reaction, respectively. These terms are positive semidefinite according to the second law of thermodynamics. The first three terms are associated with dissipation inherent in viscous flows, heat conduction and mass diffusion. They are dependent on the molecular diffusion and the gradients in the corresponding fields. The last term,
arising due to the irreversibility associated with chemical reaction, depends on the rate of chemical reaction along with the chemical composition of the mixture. The significance of entropy generation effects is further elucidated by considering the normalized form of the entropy transport equation (Eq. (2.28)) [54]. We nondimensionalize the specific entropy by $U_o^2/T_o$ where $U_o$ and $T_o$ are the reference velocity and temperature, respectively. The reference values for length and density are $L_o$ and $\rho_o$, respectively. The chemical reaction source term scales with $1/t_c$, where $t_c$ denotes the time scale associated with chemical reaction. For an ideal gas, the reference gas constant is $R_o = U_o^2/T_o k_o Ma_o$, where $k_o = c_{po}/c_{vo}$ is the reference heat capacity ratio; $c_{po}$ and $c_{vo}$ are the reference specific heat capacity at constant pressure and volume, respectively; $Ma_o$ denotes the reference Mach number. Normalizing Eq. (2.28) results in the following non-dimensional entropy generation terms,

\[ S_{gv}^* = \frac{1}{Re_o \, T_o^*} \frac{\partial u_i^*}{\partial x_j^*} \quad \text{(2.31a)} \]
\[ S_{gh}^* = \frac{1}{Re_o \, Pr_o (k_o - 1) \, Ma_o^2 T_o^*} \frac{\gamma^* c_p^*}{\partial x_i^*} \frac{\partial T^*}{\partial x_j^*} \quad \text{(2.31b)} \]
\[ S_{gm}^* = \frac{1}{Re_o \, Sc_o \, k_o \, Ma_o^2} \sum_{\alpha=1}^{N_s} \frac{\gamma^* R_o^*}{X_\alpha} \, \frac{\partial X_\alpha}{\partial x_i^*} \, \frac{\partial \phi_\alpha}{\partial x_i^*} \quad \text{(2.31c)} \]
\[ S_{gc}^* = -Da_o \frac{\rho^*}{T_o^*} \sum_{\alpha=1}^{N_s} \mu_\alpha^* S_\alpha^* \quad \text{(2.31d)} \]

where the $(\cdot)^*$ denotes the non-dimensional variables. In these equations, $Re_o$, $Pr_o$ and $Sc_o$ are the reference Reynolds, Prandtl and Schmidt numbers, respectively; $Da_o = L_o/t_c U_o$ denotes the reference Damköhler number. It is evident that the chemical reaction contribution is only influenced by Damköhler number and therefore, as anticipated, its associated irreversibility increases as the reaction becomes faster. These equations also indicate that the entropy generation by viscous dissipation, heat conduction and mass diffusion are inversely proportional to Reynolds number owing to their dissipative nature. The relative importance of these effects are shown by considering the ratios,

\[ \frac{S_{gv}^*}{S_{gh}^*} \sim Pr_o (k_o - 1) \, Ma_o^2 \quad \text{(2.32a)} \]
\[ \frac{S_{gv}^*}{S_{gm}^*} \sim Sc_o \, k_o \, Ma_o^2 \quad \text{(2.32b)} \]
\[ \frac{S_{gh}^*}{S_{gm}^*} \sim Le_o \, \frac{k_o}{k_o - 1} \quad \text{(2.32c)} \]

It is noticed that while the effect of viscous dissipation is more significant in high Mach number flows; the entropy generation by heat conduction and mass diffusion are in fact important at low speeds. Moreover, for fluids with $Le_o \approx 1$, the contribution of heat conduction is larger than that of mass diffusion by a factor of $k_o/(k_o - 1)$. 

10
2.4 Large eddy simulation

In LES, we filter the transport equations using the spatial filtering operation \[106\],

\[
\langle Q(x, t) \rangle = \int_{-\infty}^{+\infty} Q(x', t) G(x', x) \, dx'
\] (2.33)
in which \(G(x', x)\) represents the filter function and \(\langle Q(x, t) \rangle\) is the filtered value of a variable \(Q(x, t)\). We consider spatially invariant and localized filter functions, \(G(x', x) \equiv G(x' - x)\), with filter size \(\Delta\) and with the properties: \(G(r) = G(-r)\), \(\int_{-\infty}^{+\infty} G(r) \, dr = 1\), \(G(r) \geq 0\), and for which all the moments \(\int_{-\infty}^{+\infty} r^m G(r) \, dr (m \geq 0)\) exist. In variable density flows, it is convenient to consider the Favre filtered quantity, \(\langle Q(x, t) \rangle_L = \langle \rho Q \rangle / \langle \rho \rangle\). Application of LES filtering to the transport equations, (Eqs. (2.1 - 2.3) and Eq. (2.28)), yields

\[
\frac{\partial \langle \rho \rangle}{\partial t} + \frac{\partial \langle \rho \rangle \langle u_i \rangle_L}{\partial x_i} = 0
\] (2.34)

\[
\frac{\partial \langle u_i \rangle_L}{\partial t} + \frac{\partial \langle u_i \rangle_L \langle u_j \rangle_L}{\partial x_j} = -\frac{\partial \langle p \rangle}{\partial x_i} + \frac{\partial \langle \tau_{ij} \rangle_L}{\partial x_j} - \frac{\partial \langle \rho \rangle \tau(u_i, u_j)}{\partial x_i}
\] (2.35)

\[
\frac{\partial \langle \phi_\alpha \rangle_L}{\partial t} + \frac{\partial \langle u_i \rangle_L \langle \phi_\alpha \rangle_L}{\partial x_i} = \frac{\partial}{\partial x_i} \left( \gamma \frac{\partial \langle \phi_\alpha \rangle_L}{\partial x_i} \right) - \frac{\partial \langle \rho \rangle \tau(u_i, \phi_\alpha)}{\partial x_i} + \langle \rho \mu_\alpha \rangle
\] (2.36)

\[
\frac{\partial \langle s \rangle_L}{\partial t} + \frac{\partial \langle u_i \rangle_L \langle s \rangle_L}{\partial x_i} = \frac{\partial}{\partial x_i} \left( \gamma \frac{\partial \langle s \rangle_L}{\partial x_i} \right) - \frac{\partial \langle \rho \rangle \tau(u_i, s)}{\partial x_i} + \left\langle \frac{1}{T} \tau_{ij} \frac{\partial u_i}{\partial x_j} \right\rangle + \left\langle \gamma \frac{c_p}{T^2} \frac{\partial T}{\partial x_i} \frac{\partial T}{\partial x_i} \right\rangle + \sum_{\alpha=1}^{N_s} \left\langle \gamma \frac{R_\alpha}{X_\alpha} \frac{\partial \phi_\alpha}{\partial x_i} \frac{\partial X_\alpha}{\partial x_i} \right\rangle - \left\langle \frac{\rho}{T} \sum_{\alpha=1}^{N_s} \mu_\alpha S_\alpha \right\rangle
\] (2.37)

In these equations, \(\tau(a, b) = \langle ab \rangle_L - \langle a \rangle_L \langle b \rangle_L\) denotes the second order SGS moments which appear as unclosed. In addition, the filtered chemical reaction source term and the filtered entropy generation terms require SGS modeling. It is clear that filtered entropy and entropy generation fields cannot be determined from other filtered variables because of their nonlinear dependence. Moreover, the knowledge of entropy is not sufficient to identify the individual processes contributing to its generation.

2.5 Entropy filtered density function

To model the SGS effects in Eqs. (2.35 - 2.37) we use the En-FDF methodology. This is a novel methodology and is developed based on the previous velocity-frequency-scalar FDF formulation. In the En-FDF, the effects of the unresolved SGS are taken into account by considering the joint probability density function of the velocity, frequency, scalar and
2.5.1 Definition

The En-FDF denoted by $\mathcal{F}_{\text{en}} \left( \hat{\mathbf{u}}, \hat{\phi}, \hat{\omega}, \hat{s}; \mathbf{x}; t \right)$, is formally defined as,

$$
\mathcal{F}_{\text{en}} \left( \hat{\mathbf{u}}, \hat{\phi}, \hat{\omega}, \hat{s}; \mathbf{x}; t \right) = 
\int_{-\infty}^{+\infty} \rho(x', t) \zeta \left[ \hat{\mathbf{u}}, \hat{\phi}, \hat{\omega}, \hat{s}; \mathbf{u}(x', t), \phi(x, t), \omega(x, t), s(x, t) \right] G(x' - x) dx'
$$

(2.38)

in which,

$$
\zeta \left[ \hat{\mathbf{u}}, \hat{\phi}, \hat{\omega}, \hat{s}; \mathbf{u}(x, t), \phi(x, t), \omega(x, t), s(x, t) \right] = \delta (\hat{s} - s(x, t)) \times 
\delta (\hat{\omega} - \omega(x, t)) \prod_{i=1}^{3} \delta (\hat{u}_i - u_i(x, t)) \prod_{\alpha=1}^{N_\alpha+1} \delta (\hat{\phi}_\alpha - \phi_\alpha(x, t))
$$

(2.39)

is the fine-grained density [64] and $\delta$ denotes the Dirac delta function. In this formulation, the sample space variables $\hat{\mathbf{u}}, \hat{\phi}, \hat{\omega}$ and $\hat{s}$ correspond to velocity vector, scalar array, turbulent frequency $\omega(x, t)$ and entropy, respectively.

For further developments, it is useful to define the conditional filtered value of the variable $Q(x, t)$ by, [72, 78, 80, 88]

$$
\left\langle Q(x, t) \right| \hat{\mathbf{u}}, \hat{\phi}, \hat{\omega}, \hat{s} \rightangle = \left\langle Q(x, t) \right| \mathbf{u}(x, t) = \hat{\mathbf{u}}, \phi(x, t) = \hat{\phi}, \omega(x, t) = \hat{\omega}, s(x, t) = \hat{s} \rightangle
$$

$$
= \frac{\int_{-\infty}^{+\infty} \rho(x', t) Q(x', t) \zeta \left[ \hat{\mathbf{u}}, \hat{\phi}, \hat{\omega}, \hat{s}; \mathbf{u}(x', t), \phi(x', t), \omega(x', t), s(x', t) \right] G(x' - x) dx'}{\mathcal{F}_{\text{en}}}
$$

(2.40)

where $\langle \mid \rangle$ denotes the “conditional” filtered values. Equation (2.40) has the following properties [72],

$$
Q(x, t) = c : \quad \left\langle Q \right| \hat{\mathbf{u}}, \hat{\phi}, \hat{\omega}, \hat{s} \rightangle = c
$$

(2.41a)

$$
Q(x, t) = \tilde{Q} (\mathbf{u}(x, t), \phi(x, t), \omega(x, t), s(x, t)) : \quad \left\langle Q \right| \hat{\mathbf{u}}, \hat{\phi}, \hat{\omega}, \hat{s} \rightangle = \tilde{Q} (\hat{\mathbf{u}}, \hat{\phi}, \hat{\omega}, \hat{s})
$$

(2.41b)

$$
\langle \rho(x, t) \rangle \langle Q(x, t) \rangle_L = \int_{-\infty}^{+\infty} \left\langle Q \right| \hat{\mathbf{u}}, \hat{\phi}, \hat{\omega}, \hat{s} \right\rangle \mathcal{F}_{\text{en}}(\hat{\mathbf{u}}, \hat{\phi}, \hat{\omega}, \hat{s}; \mathbf{x}; t) d\hat{\mathbf{u}} d\hat{\phi} d\hat{\omega} d\hat{s}
$$

(2.41c)
Following Eqs. (2.41), the filtered value of any function \( \tilde{Q}(\hat{u}, \hat{\phi}, \hat{\omega}, \hat{s}) \), is obtained from the En-FDF as,

\[
\langle \rho(x,t) \rangle \langle Q(x,t) \rangle_L = \int_{-\infty}^{+\infty} \tilde{Q}(\hat{u}, \hat{\phi}, \hat{\omega}, \hat{s}) F_{en}(\hat{u}, \hat{\phi}, \hat{\omega}, \hat{s}, x; t) \, d\hat{u} \, d\hat{\phi} \, d\hat{\omega} \, d\hat{s} \quad (2.42)
\]

### 2.5.2 En-FDF transport equations

The En-FDF is governed by an exact transport equation \([72, 78, 80, 88]\). Differentiating Eq. (2.39) with respect to time we have,

\[
\frac{\partial \zeta}{\partial t} = \frac{\partial \zeta}{\partial s} \frac{\partial s}{\partial t} + \frac{\partial \zeta}{\partial \omega} \frac{\partial \omega}{\partial t} + \frac{\partial \zeta}{\partial u_i} \frac{\partial u_i}{\partial t} + \sum_{\alpha=1}^{N_s+1} \frac{\partial \zeta}{\partial \phi_\alpha} \frac{\partial \phi_\alpha}{\partial t} \quad (2.43)
\]

Substituting for \( \partial s/\partial t \), \( \partial u_i/\partial t \) and \( \partial \phi_\alpha/\partial t \) from transport Eqs. (2.28), (2.2), (2.3) into Eq. (2.43) yields,

\[
\frac{\partial \rho \zeta}{\partial t} + \frac{\partial \rho u_i}{\partial x_i} = -\frac{\partial}{\partial x_i} \left( \frac{\gamma}{\rho} \frac{\partial s}{\partial x_i} \right) \frac{\partial \rho}{\partial x_i} - \frac{\rho}{\rho} \frac{\partial \omega}{\partial t} - \frac{\partial}{\partial x_i} \left( \frac{\gamma}{\rho} \frac{\partial s}{\partial x_i} \right) \frac{\partial \rho}{\partial x_i} + \frac{\partial}{\partial x_i} \left( 1 \right) \frac{\partial \tau_{ij}}{\partial \phi_\alpha} \frac{\partial \zeta}{\partial \phi_\alpha} \quad (2.44)
\]

Integrating Eq. (2.44) according to Eq. (2.38) while employing properties in Eqs. (2.41) yields,

\[
\frac{\partial F_{en}}{\partial t} + \frac{\partial (\hat{u}_i F_{en})}{\partial x_i} = \frac{\partial}{\partial u_i} \left[ \left( \frac{1}{\rho} \frac{\partial \rho}{\partial x_i} \right) \hat{u}_i \hat{\phi} \hat{\omega} \hat{s} F_{en} \right] - \frac{\partial}{\partial \phi_\alpha} \left[ \left( \frac{1}{\rho T} \frac{\partial T}{\partial x_i} \right) \hat{u}_i \hat{\phi} \hat{\omega} \hat{s} F_{en} \right] - \sum_{\alpha=1}^{N_s+1} \frac{\partial}{\partial \phi_\alpha} \left[ \left( \frac{1}{\rho} \frac{\partial \rho}{\partial x_i} \right) \frac{\partial \tau_{ij}}{\partial \phi_\alpha} \hat{u}_i \hat{\phi} \hat{\omega} \hat{s} F_{en} \right] \quad (2.45)
\]

which is exact En-FDF transport equation. It is noticed that the SGS convection (the second term on the LHS) and the effects of chemical reaction (the last two terms on the RHS) are
in closed forms. However, all terms involving conditional filtered values are unclosed and require closure [72, 88].

2.5.3 En-FDF modeled transport equations

The transport equations for the En-FDF (Eq. (2.45)) is modeled by a system of stochastic differential equations which provide one-point, one-time description of the En-FDF. We consider the general diffusion process [107], obtained by the system of SDEs,

\[
\begin{align*}
    dX_i^+ & = U_i^+ dt + \sqrt{\frac{2\mu}{\langle \rho \rangle}} dW_i \\
    d\phi_i^+ & = -C_\phi \Omega \left( \phi_i^+ - \langle \phi_i \rangle_L \right) dt + S_\phi(\phi_i^+) dt \\
    d\omega^+ & = -C_\omega \Omega \left( \omega^+ - C_f k_{s}^{1/2} \Delta \right) dt
\end{align*}
\]

(2.46a)
(2.46b)
(2.46c)

where \(X_i^+\), \(U_i^+\), \(\omega^+\) and \(\phi_i^+\) are the stochastic representations of position, velocity, frequency and scalars, respectively. This model consists of SDEs for position, velocity, scalars and frequency. These variables, as appeared in Eqs. (2.46) are developed in Ref. [80]. The set of SDEs include the linear mean square estimation (LMSE) [64] and the generalized Langevin (GLM) models [108], with

\[
G_{ij} = -\Omega \left( \frac{1}{2} + \frac{3}{4} C_0 \right) \delta_{ij}
\]

(2.47)

which corresponds to Rotta’s model in RANS [109]. The \(W_i\), \(W'_i\) terms denote the Wiener-Lévy processes [110–112]. The model parameters \(C_0 = 2.1\), \(C_\phi = 1\), \(C_f = 2\), \(C_\omega = 1\) and \(C_\Omega = 0.9\) are set according to previous work [72, 78, 80]. In these equations, \(k_s = \tau(u_i, u_i)/2\) denotes the SGS kinetic energy and \(\Omega\) is the SGS mixing frequency, modeled as \(\Omega \equiv C_\Omega \langle \omega^+ \mid \omega^+ \geq \langle \omega \rangle_L \rangle_L [80].\)

The stochastic process corresponding to entropy \(s^+(t)\) is governed by the Gibbs relation (Eq. (2.13)), in which the transport of internal energy is governed by the first law of thermodynamics [113],

\[
de^+ = \epsilon_i dt - C_\phi \Omega (h^+ - \langle h \rangle_L) dt - p^+ dv^+
\]

(2.48)
where \( e^+, h^+, p^+ \) and \( v^+ \) are the stochastic processes for the specific internal energy, specific enthalpy, pressure and specific volume, respectively; and \( \epsilon_t \) denotes the total rate of turbulent dissipation, including the SGS and the resolved contributions,

\[
\epsilon_t = k_s \Omega + \frac{1}{\langle \rho \rangle} \langle \tau_{ij} \rangle \frac{\partial \langle u_i \rangle}{\partial x_j}
\]

(2.49)

Substituting Eqs. (2.46c), (2.48) into Eq. (2.13), we obtain a SDE for the specific entropy,

\[
ds^+ = \frac{\epsilon_t}{T^+} dt + \frac{1}{T^+} \sum_{\alpha=1}^{N_s} \mu^+ \varphi \Omega \left[ (\varphi^+ - \langle \varphi^+ \rangle) \right] dt - \frac{1}{T^+} C\varphi \Omega \left[ (h^+ - \langle h^+ \rangle) \right] dt
\]

(2.50)

where \( T^+ \) and \( \mu^+ \) are the stochastic representation of temperature and chemical potential per unit mass of species \( \alpha \), respectively.

The set of SDEs in Eqs. (2.46), (2.50) constitute the modeled En-FDF transport. The Fokker-Planck equation [114] conjugate to the set of SDEs is the modeled En-FDF transport equation,

\[
\frac{\partial F_{en}}{\partial t} + \frac{\partial \langle u_i F_{en} \rangle}{\partial x_i} = \frac{\partial}{\partial x_j} \left( \mu \frac{\partial \langle F_{en}/\langle \rho \rangle \rangle}{\partial x_j} \right) + \frac{1}{\langle \rho \rangle} \frac{\partial \langle \rho \rangle}{\partial x_i} \frac{\partial F_{en}}{\partial \hat{u}_i}
\]

(2.51)

Comparing Eq. (2.51) with Eq. (2.45), it is evident that exact and modeled En-FDF
transport equations are statistically equivalent. The En-FDF implied closure is,

\[
\frac{\partial}{\partial \hat{u}_i} \left[ \langle \frac{1}{\rho} \partial \rho \partial x_i \rangle \hat{u}_i, \phi, \hat{\omega}, \hat{s} \right] F_{en} - \frac{\partial}{\partial \hat{u}_i} \left[ \langle \frac{1}{\rho} \partial \tau_{ij} \partial x_i \rangle \hat{u}_i, \phi, \hat{\omega}, \hat{s} \right] F_{en}
\]

\[
- \frac{\partial}{\partial \hat{\omega}} \left[ \frac{1}{\rho} \partial \omega \frac{\partial x_i}{\partial x_i} \right] \hat{u}_i, \phi, \hat{\omega}, \hat{s} \right] F_{en} - \sum_{\alpha=1}^{N_s+1} \frac{\partial}{\partial \phi_\alpha} \left[ \langle \frac{1}{\rho} \partial \phi_\alpha \partial x_i \rangle \hat{u}_i, \phi, \hat{\omega}, \hat{s} \right] F_{en}
\]

\[
- \frac{\partial}{\partial \hat{s}} \left[ \frac{1}{\rho} \partial \hat{s} \left( \gamma \frac{\partial \hat{s}}{\partial x_i} \right) \hat{u}_i, \phi, \hat{\omega}, \hat{s} \right] F_{en} - \frac{\partial}{\partial \hat{s}} \left[ \langle \gamma \frac{\partial T}{\partial T} \partial x_i \partial x_i \rangle \hat{u}_i, \phi, \hat{\omega}, \hat{s} \right] F_{en}
\]

\[
- \frac{\partial}{\partial \hat{s}} \left[ \frac{1}{\rho} \partial \hat{s} \left( \gamma \sum_{\alpha=1}^{N_s} \frac{R_\alpha}{X_\alpha} \partial x_i \partial x_i \right) \hat{u}_i, \phi, \hat{\omega}, \hat{s} \right] F_{en} - \frac{\partial}{\partial \hat{s}} \left[ \langle \gamma \sum_{\alpha=1}^{N_s} \frac{R_\alpha}{X_\alpha} \partial x_i \partial x_i \rangle \hat{u}_i, \phi, \hat{\omega}, \hat{s} \right] F_{en}
\]

\[
= \frac{1}{\langle \rho \rangle} \frac{\partial}{\partial x_i} \frac{\partial F_{en}}{\partial \hat{u}_i} - \frac{1}{\langle \rho \rangle} \frac{\partial}{\partial x_j} \left( \mu \frac{\partial \langle u_i \rangle}{\partial x_j} \frac{\partial F_{en}}{\partial \hat{u}_i} \right) - \frac{1}{\langle \rho \rangle} \frac{\partial}{\partial x_j} \left( \langle \rho \rangle \frac{\partial F_{en}}{\partial \hat{u}_i} \right)
\]

\[
- G_{ij} \frac{\partial}{\partial \hat{u}_i} \left[ \langle \hat{u}_j - \langle u_j \rangle_L \rangle \right] F_{en} \right] + \frac{\mu}{\langle \rho \rangle} \frac{\partial}{\partial x_k} \frac{\partial F_{en}}{\partial \hat{u}_i} + \frac{1}{2} C_0 k_s \Omega \frac{\partial^2 F_{en}}{\partial \hat{u}_i \partial \hat{u}_i}
\]

\[
+ C_\phi \Omega \frac{\partial}{\partial \phi_\alpha} \left[ \langle \phi_\alpha - \langle \phi_\alpha \rangle_L \rangle \right] F_{en} + C_\omega \Omega \frac{\partial}{\partial \omega} \left[ \langle \omega - C_f \frac{k_s}{\Delta} \rangle \right] F_{en} \right] - \frac{\epsilon_s}{T} \frac{\partial F_{en}}{\partial \hat{s}}
\]

Note that the implied closure is obtained by comparing exact En-FDF transport equation (Eq. (2.45)) with modeled En-FDF transport equation (Eq. (2.51)).

### 2.5.4 Closure of unclosed terms in the En-FDF

The transport equations for the filtered variables are obtained by integration of Eq. (2.51) according to Eq. (2.41c),

\[
\frac{\partial \langle \rho \rangle}{\partial t} + \frac{\partial \langle \rho \rangle \langle u_i \rangle_L}{\partial x_i} = 0 \tag{2.53}
\]

\[
\frac{\partial \langle \rho \rangle \langle u_i \rangle_L}{\partial t} + \frac{\partial \langle \rho \rangle \langle u_i \rangle_L \langle u_j \rangle_L}{\partial x_j} = - \frac{\partial \langle \rho \rangle}{\partial x_i} + \frac{\partial}{\partial x_j} \left( \mu \frac{\partial \langle u_i \rangle_L}{\partial x_j} \frac{\partial \langle u_j \rangle_L}{\partial x_i} \right) \tag{2.54}
\]

\[
\frac{\partial \langle \rho \rangle \langle \phi_\alpha \rangle_L}{\partial t} + \frac{\partial \langle \rho \rangle \langle \phi_\alpha \rangle_L}{\partial x_i} \frac{\partial \langle \phi_\alpha \rangle_L}{\partial x_i} = \frac{\partial}{\partial x_i} \left( \gamma \frac{\partial \langle \phi_\alpha \rangle_L}{\partial x_i} \right) \tag{2.55}
\]

16
\[
\frac{\partial \langle \rho \rangle \langle s \rangle_L}{\partial t} + \frac{\partial \langle \rho \rangle \langle u_i \rangle_L \langle s \rangle_L}{\partial x_i} = \frac{\partial}{\partial x_i} \left( \frac{\gamma}{T} \frac{\partial \langle \rho \rangle \langle s \rangle_L}{\partial x_i} \right) - \frac{\partial \langle \rho \rangle \tau (u_i, s)}{\partial x_i} + \langle \rho \rangle \epsilon_t \left\langle \frac{1}{T} \right\rangle_L \\
+ \langle \rho \rangle C_\phi \Omega \sum_{a=1}^{N_a} \tau (\phi_\alpha, \frac{g_\alpha}{T}) - \langle \rho \rangle C_\phi \Omega \tau \left( h, \frac{1}{T} \right) \\
+ \langle \rho \rangle C_\phi \Omega \sum_{a=1}^{N_a} R_\alpha \tau (\phi_\alpha, \ln X_\alpha) - \left( \frac{\rho}{T} \sum_{a=1}^{N_a} \mu_\alpha S_\alpha \right)
\]

(2.56)

where \( g_\alpha \) is the Gibbs free energy of species \( \alpha \). It is clear that the transport equations implied by the model (Eqs. (2.53 - 2.56)) are consistent with the original LES equations (Eqs. (2.34 - 2.37)). As mentioned before, the entropy generation by chemical reaction appears closed in En-FDF formulation (last term in Eq. (2.56)) and does not need modeling. Comparing Eq. (2.56) with exact filtered entropy transport equation (Eq. (2.37)), we find the closure for entropy transport equation,

\[
\langle S_{gv} \rangle = \left\langle \frac{1}{T} \frac{\partial u_i}{\partial x_j} \right\rangle \approx \langle \rho \rangle \left\langle \frac{1}{T} \right\rangle \epsilon_t \tag{2.57a}
\]

\[
\langle S_{gh} \rangle = \left\langle \frac{c_p}{T} \frac{\partial T}{\partial x_i} \right\rangle \approx \langle \rho \rangle C_\phi \Omega \left[ \sum_{a=1}^{N_a} \tau (\phi_\alpha, \frac{g_\alpha}{T}) - \tau \left( h, \frac{1}{T} \right) \right] \tag{2.57b}
\]

\[
\langle S_{gm} \rangle = \left\langle \sum_{a=1}^{N_a} \gamma R_\alpha \frac{1}{X_\alpha} \frac{\partial \phi_\alpha}{\partial x_i} \partial X_\alpha \right\rangle \approx \langle \rho \rangle C_\phi \Omega \sum_{a=1}^{N_a} R_\alpha \tau (\phi_\alpha, \ln X_\alpha) \tag{2.57c}
\]

To verify Eqs. (2.57) we use the LMSE model, which reads as [103],

\[
\langle \rho \rangle C_\phi \Omega \tau (\phi_\alpha, \phi_\beta) \approx \left\langle \gamma \frac{\partial \phi_\alpha}{\partial x_i} \frac{\partial \phi_\beta}{\partial x_i} \right\rangle \tag{2.58}
\]

Considering forth and fifth terms on RHS of Eq. (2.56) and applying Eq. (2.58) we have,

\[
\langle \rho \rangle C_\phi \Omega \sum_{a=1}^{N_a} \tau (\phi_\alpha, \frac{g_\alpha}{T}) - \langle \rho \rangle C_\phi \Omega \tau \left( h, \frac{1}{T} \right) \approx \sum_{a=1}^{N_a} \left\langle \gamma \frac{\partial \phi_\alpha}{\partial x_i} \frac{\partial (g_\alpha / T)}{\partial x_i} \right\rangle \\
- \left\langle \gamma \frac{\partial h}{\partial x_i} \frac{\partial (1/T)}{\partial x_i} \right\rangle \tag{2.59}
\]

By taking derivative of \( g_\alpha = h_\alpha - Ts_\alpha \) and \( h \) we have,

\[
\frac{\partial (g_\alpha / T)}{\partial x_i} = \frac{h_\alpha}{T^2} \frac{\partial T}{\partial x_i} \tag{2.60a}
\]

\[
\frac{\partial h}{\partial x_i} = \frac{c_p}{T^2} \frac{\partial T}{\partial x_i} + h_\alpha \frac{\partial \phi_\alpha}{\partial x_i} \tag{2.60b}
\]

and substituting Eqs. (2.60) into Eq. (2.59), the closure in Eq. (2.57b) is verified,

\[
\langle \rho \rangle C_\phi \Omega \left[ \sum_{a=1}^{N_a} \tau (\phi_\alpha, \frac{g_\alpha}{T}) - \tau \left( h, \frac{1}{T} \right) \right] \approx \left\langle \gamma \frac{c_p}{T^2} \frac{\partial T}{\partial x_i} \frac{\partial T}{\partial x_i} \right\rangle \tag{2.61}
\]

17
Similarly, using Eq. (2.58) we can verify Eq. (2.57c),
\[
\langle \rho \rangle C_{\phi} \Omega \sum_{\alpha=1}^{N_s} R_\alpha \tau (\phi, \ln X_\alpha) \approx \left( \sum_{\alpha=1}^{N_s} \gamma R_\alpha \frac{1}{X_\alpha} \frac{\partial \phi_\alpha}{\partial x_i} \frac{\partial X_\alpha}{\partial x_i} \right) \tag{2.62}
\]
Also, for entropy generation by dissipation [47],
\[
\left\langle \frac{1}{T} \tau_{ij} \frac{\partial u_i}{\partial x_j} \right\rangle \approx \left\langle \frac{1}{T} \right\rangle L \langle \rho \rangle \epsilon_t \tag{2.63}
\]
By substitution for total dissipation \(\epsilon_t\) from Eq. (2.49), Eq. (2.57a) is being developed,
\[
\left\langle \frac{1}{T} \tau_{ij} \frac{\partial u_i}{\partial x_j} \right\rangle \approx \left\langle \frac{1}{T} \right\rangle L \left( \langle \rho \rangle k_s \Omega + \langle \tau_{ij} \rangle \frac{\partial \langle u_i \rangle}{\partial x_j} \right) \tag{2.64}
\]

### 2.6 Numerical solution procedure

Numerical solution of the En-FDF is obtained by a hybrid Eulerian-Lagrangian finite difference (FD)/Monte Carlo (MC) method, similar to that used in previous FDF simulations [72, 78, 80, 86–88]. For numerical solution of the hydrodynamic field in LES, a high order accurate FD procedure is being used. This discretization procedure is based on the compact parameter scheme [115,116] which yields fourth order accurate results and the solution is obtained on equally spaced Cartesian grid points. A second order accurate symmetric predictor-corrector sequence is employed for time integration of Eqs. (2.34 - 2.37). The filtered pressure \(\langle p \rangle\), is obtained from the filtered equation of state, \(\langle p \rangle = \langle \rho \rangle \langle RT \rangle_L\) where \(\langle RT \rangle_L\) is obtained from the energy equation. A zero derivative boundary conditions are imposed for the scalar values at the outlet and lateral boundaries. The MC part involves solution of the SDEs, governing the En-FDF transport, using a Lagrangian MC method. In this method, the En-FDF is represented by an ensemble of \(N_p\) number of particles, which carry information pertaining to the En-FDF variables, i.e. positions \(X_i^{(n)}(t)\), velocities \(U_i^{(n)}(t)\), scalars \(\phi_\alpha^{(n)}(t)\), frequency \(\omega^{(n)}(t)\) and entropy \(s^{(n)}(t)\) \((n = 1, \ldots, N_p)\). This information is updated via temporal integration of the modeled SDEs using the Euler-Maruyamma discretization [117] which is consistent with Itô-Gikhman calculus. To understand the operational procedures of the hybrid FD/MC configuration, the elements of the computation are shown, for a two-dimensional domain in Fig. (2.1).

The MC particles are distributed randomly and are free to move anywhere within the domain. The statistical information, e.g. filtered values, at any point is obtained by considering an ensemble of particles residing within an ensemble domain centered around the point. For a fixed number of particles in the computational domain, large ensemble domain size decreases statistical error, but increases the spatial resolution error. The latter causes excessive diffusion. For a fixed ensemble domain size, small number of particles diminishes the reliability
of the statistics. For reliable statistics with minimal numerical dispersion, it is desired to minimize the size of the ensemble domain and maximize the number of MC particles [103]. In this way, the ensemble statistics approach the desired filtered values [72],

\[
\langle a \rangle_E \equiv \frac{1}{N_E} \sum_{n \in \Delta_E} a^{(n)} \xrightarrow{\Delta_E \to 0} \langle a \rangle \quad \text{and} \quad \tau_E (a, b) \equiv \frac{1}{N_E} \sum_{n \in \Delta_E} \left( a^{(n)} - \langle a \rangle_E \right) \left( b^{(n)} - \langle b \rangle_E \right) \xrightarrow{\Delta_E \to 0} \tau (a, b) \quad (2.65)
\]

where \( a^{(n)} \) and \( b^{(n)} \) denotes the information carried by \( n^{th} \) MC particle pertaining to transport variable \( a \) and \( b \), respectively. \( \Delta_E \) is the ensemble domain size as shown in Fig. (2.1); \( \langle a \rangle_E \) and \( \tau_E (a, b) \) are first and second moment statistics obtained on ensemble domain which in the limit \( N_E \to \infty, \Delta_E \to 0 \) approach \( \langle a \rangle \) and \( \tau (a, b) \), respectively. The boundary conditions for the Monte Carlo simulation require no special treatment. Particles are free to leave the computational domain as guided by the SDEs. As particles exit the domain at a periodic boundary, another particle enter the domain from the corresponding side. The transfer of information from grid points to MC particles is done by interpolation; and that from particles to grid points is handled by ensemble averaging as described above. To reduce the computational cost, a procedure involving the use of non-uniform weights for the particles [78, 80, 87] is also considered. In this implementation, the MC particles cover the computational domain uniformly but carry a weight \( w^{(n)} \) that is proportional to the filtered density. This numerical treatment is somewhat analogous to grid compression in FD schemes. In practice, the particles evolve according to the discrete weighted filtered density function. It can be shown that the sum of weights within the ensemble domain corresponds to filtered fluid density at any instant, i.e.

\[
\langle \rho \rangle \approx \frac{\Delta m}{\Delta^3_E} \sum_{n=1}^{N_E} w^{(n)} \quad (2.66)
\]

where \( \Delta m \) is the mass of a particle with unit weight and \( \Delta^3_E \) is the volume of ensemble domain. The Favre-filtered values are constructed from the weighted average by [72, 78, 80, 87, 103]

\[
\langle Q(x, t) \rangle_L \approx \frac{\sum_{n=1}^{N_E} w^{(n)} Q^{(n)} \rho^{(n)}}{\sum_{n=1}^{N_E} w^{(n)}} \quad (2.67)
\]

Note that Eqs. (2.66), (2.67) are approximate due to the statistical errors associate with finite ensemble domain size and particle number density. The approximation in these equations are exact in the limit \( \Delta_E \to 0 \) and the number of particles inside ensemble domain become infinite. Equation (2.66) implies that the filtered fluid density is directly proportional to the
sum of the weights in the ensemble domain. With uniform weights

\[ \langle \rho \rangle \approx \frac{\Delta m}{\Delta E} N_E \]  \hspace{1cm} (2.68)

\[ \langle Q(x, t) \rangle_L \approx \sum_{n=1}^{N_E} Q \]  \hspace{1cm} (2.69)

Therefore, with uniform weights, the particle number density decreases significantly in regions of high temperature. The implementation of variable weights allows the increase of the particle number density without a need to increase the number density outside the reaction zone.

### 2.7 Temporal mixing layer simulation

The En-FDF is applied to a non-reacting three-dimensional temporally developing mixing layer involving transport of passive scalars and entropy. Simulations provide detailed assessment of the En-FDF prediction. In these simulation, the comprehensive form of En-FDF methodology is employed and the predictions are validated against the data generated by DNS of the same layer. The temporal mixing layer consists of two parallel streams traveling in opposite streamwise directions at the same speeds (Fig. (2.2)). The flow configuration is parameterized similar to that considered by \[118\] and indicated in table 2.1. The reference length \( L_o \) is defined as the half initial vorticity thickness. The reference velocity \( U_o \) is half the velocity difference across the layer and the reference temperature is \( T_o = 298 K \). The Reynolds number based on these values is \( Re = 50 \). The heat capacity ratio is \( k = 1.4 \). In the following, \( x, y \) and \( z \) denote the streamwise, the cross-stream, and the spanwise coordinate directions, respectively. The velocity components along these directions are denoted by \( u, v \) and \( w \), respectively. We consider a cubic box, \( 0 \leq x \leq L, \ -L/2 \leq y \leq L/2, \ 0 \leq z \leq L \) where \( L = L_v/L_o \) and \( L_v \) is specified such that \( L_v = 2^{N_v} \lambda_u \), where \( N_v \) is the desired number of successive vortex pairings and \( \lambda_u \) is the wavelength of the most unstable mode corresponding to the mean streamwise velocity profile imposed at the initial time.

The filtered (normalized) streamwise velocity, density and mixture fraction \( \xi \) fields are initialized using hyperbolic tangent profiles with free-stream conditions as: \( \langle u \rangle_L = 1, \langle \rho \rangle = 0.5 \) and \( \langle \xi \rangle_L = 1 \) on the top and \( \langle u \rangle_L = -1, \langle \rho \rangle = 1 \) and \( \langle \xi \rangle_L = 0 \) on the bottom. With the uniform initial pressure field, the initial filtered temperature is set equal to inverse of \( \langle \rho \rangle \) according to the ideal-gas equation of state. The top and bottom streams carry \( H_2 \) and \( F_2 \), respectively. The flow involves (non-reacting) mixing of these species. Thus, the mass fractions and the enthalpy are fully determined by the mixture fraction, \( \phi \equiv \phi(\xi) \). The evolution of mixture fraction is described by

\[ d\xi^+ = -C_\phi \Omega (\xi^+ - \langle \xi \rangle_L) \, dt, \]  \hspace{1cm} (2.70)
where $\xi^+$ is the stochastic representation of mixture fraction. To assess the En-FDF predictions, DNS of the same layer is conducted. LES and DNS simulations are performed on $33^3$ and $193^3$ grid points, respectively. The LES filter size is twice as large as grid spacing in each direction. For comparison, the DNS data is filtered via a top-hat filter. The periodic boundary condition is used in the streamwise and spanwise directions and zero-derivative boundary condition is employed at cross-stream boundaries. The initial number of particles per grid point is 320 and the ensemble domain size is set equal to half the grid spacing in each direction. Initialization of the MC particles and their treatment at the boundaries are consistent with the FD initial and boundary conditions.

Table 2.1. Temporal mixing layer: summary of simulation parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Re$</td>
<td>Reynolds number</td>
<td>50</td>
</tr>
<tr>
<td>$Le$</td>
<td>Lewis number</td>
<td>1.0</td>
</tr>
<tr>
<td>$Sc$</td>
<td>Schmidt number</td>
<td>1.0</td>
</tr>
<tr>
<td>$Pr$</td>
<td>Prandtl number</td>
<td>1.0</td>
</tr>
<tr>
<td>$Sc_t$</td>
<td>SGS Schmidt number</td>
<td>1.0</td>
</tr>
<tr>
<td>$Pr_t$</td>
<td>SGS Prandtl number</td>
<td>1.0</td>
</tr>
<tr>
<td>$C_0$</td>
<td>Stochastic model parameter</td>
<td>2.1</td>
</tr>
<tr>
<td>$C_\phi$</td>
<td>LMSE model coefficient</td>
<td>1.0</td>
</tr>
<tr>
<td>$T_0$</td>
<td>Reference temperature (K)</td>
<td>298</td>
</tr>
<tr>
<td>$k$</td>
<td>Heat capacity ratio</td>
<td>1.4</td>
</tr>
</tbody>
</table>

2.7.1 Validation via DNS data

Figure (2.3) shows the instantaneous filtered entropy fields predicted by the En-FDF and DNS. As illustrated, the large scale coherent structures predicted by the En-FDF resemble those obtained from the DNS. This is an indication of the accuracy of the En-FDF. Further appraisal is made by comparing its Reynolds-averaged statistics. These are constructed from the instantaneous data by spatial averaging over the homogeneous (streamwise and spanwise) directions and hence, they vary only in the cross-stream direction. The mean quantities are denoted by an overbar. Figure (2.4) shows the close agreement of the Reynolds-averaged
filtered entropy predicted by En-FDF and DNS. This figure also exhibits the consistency of En-FDF as the FD and the MC solvers yield practically indistinguishable predictions. The filtered entropy is obtained from the MC solver by ensemble averaging. The FD prediction is obtained by solving Eq. (2.56) directly with the entropy generation source term and the SGS entropy flux obtained from the MC solver. This consistency check gives a useful assessment of the accuracy of both solvers, similar to previous FD studies \cite{72,78,80,86–88}.

To demonstrate the En-FDF prediction of the second order SGS moments, the SGS, the resolved and the total entropy flux in the streamwise direction are shown in Fig. (2.5). The resolved field is denoted by $R(u, s)$, with $R(u, s) = \left( \langle u \rangle_L - \langle u \rangle \right) \left( \langle s \rangle_L - \langle s \rangle \right)$; the total field is $r(u, s)$ with $r(u, s) = (u - \bar{u}) (s - \bar{s})$. In DNS, the total component is directly available, while in LES it is approximated by $r(u, s) \approx R(u, s) + \tau(u, s)$ \cite{118}. As shown, the streamwise entropy flux components are predicted reasonably well by the En-FDF. Similar agreements are obtained for other moments.

### 2.7.2 Analysis of entropy generation

The En-FDF is capable of accounting for individual filtered entropy generation terms. As displayed in Fig. (2.6), these terms are predicted accurately by the En-FDF. The entropy generation by heat conduction is dominant in this flow due to the large temperature difference across the layer. Consistent with Eq. (2.32), the effect of mass diffusion (Fig. (2.6b)) is smaller by a factor of $k/(k - 1) \approx 3.5$ and that of viscous dissipation (Fig. (2.6c)) is of two orders of magnitude smaller due to the low Mach number associated with this flow. All Reynolds-averaged entropy generation effects are dominant in the fully turbulent region, near the middle of the layer, where the rate of turbulent dissipation is the highest. Figure (2.7) shows the instantaneous contours of temperature at $t = 80$. The pairing of two neighboring rollers on a spanwise plane, along with the mushroom-like structures on a streamwise plane are visible. The intensity of turbulent mixing due to these structures is evident from contours of SGS mixing frequency in Fig. (2.8). Regions with large SGS mixing rate stretch from the core of the vortices to the braid regions, wherein sharp scalar gradients and large scalar dissipation exist. As a result, these regions are characterized by large entropy generation due to heat conduction and mass diffusion as demonstrated in Figs. (2.9), (2.10). The effect of viscous dissipation, in contrast, is more dominant within the vortices, where the rate of mixing is the highest; however, this effect is insignificant in this flow.
Figure 2.1. Ensemble averaging on three different domains. Black squares denote finite difference grid points and the blue circles are MC particles. Also shown are three different ensemble domains: (1) $\Delta_E = \Delta/2$, (2) $\Delta_E = \Delta$ and (3) $\Delta_E = 2 \times \Delta$
Figure 2.2. A schematic of the 3D temporally developing mixing layer.
Figure 2.3. Isosurface of instantaneous filtered entropy in temporal mixing layer simulations at $t = 80$, predicted by (a) En-FDF and (b) DNS.
Figure 2.4. Cross-stream variation of Reynolds-averaged filtered entropy obtained from temporal mixing layer simulations at $t = 80$. The solid line and (+) symbol denote the En-FDF predictions obtained from FD and MC solvers, respectively. The circles denote the filtered DNS data.
Figure 2.5. Cross-stream variation of Reynolds-averaged streamwise entropy flux components: (a) SGS, (b) resolved and (c) total obtained from temporal mixing layer simulations at $t = 80$. The solid lines denote the En-FDF results and the circles denote the filtered DNS data.
Figure 2.6. Cross-stream variation of Reynolds-averaged entropy generation by (a) heat conduction, (b) mass diffusion and (c) viscous dissipation obtained from temporal mixing layer simulations at $t = 80$. The solid lines denote the En-FDF results and the circles denote the filtered DNS data.
Figure 2.7. Instantaneous contours of temperature obtained from the En-FDF prediction of temporal mixing layer at $t = 80$ on planes: (a) $z = L$ and (b) $x = L$. 
Figure 2.8. Instantaneous contours of SGS mixing frequency obtained from the En-FDF prediction of temporal mixing layer at $t = 80$ on planes: (a) $z = L$ and (b) $x = L$. 
Figure 2.9. Instantaneous contours of entropy generation by (a) heat conduction, (b) mass diffusion and (c) viscous dissipation obtained from the En-FDF prediction of temporal mixing layer at $z = L$ and $t = 80$. 
Figure 2.10. Instantaneous contours of entropy generation by (a) heat conduction, (b) mass diffusion and (c) viscous dissipation obtained from the En-FDF prediction of temporal mixing layer at $x = L$ and $t = 80$. 
Chapter 3

MARGINAL ENTROPY FILTERED DENSITY FUNCTION

3.1 Introduction

In this chapter, marginal form of the En-FDF methodology is developed which is computationally more feasible for complex turbulent reacting flow simulations. The marginal En-FDF accounts for the joint SGS statistics of scalar and entropy fields. An overview of governing equations are provided. Subsequently, the marginal En-FDF is introduced to describe the unclosed entropy generation terms in the entropy transport equation. Following its mathematical definition, the “exact” marginal En-FDF transport equation is derived. The unclosed terms in this equation are modeled using an equivalent system of stochastic differential equations. Similar to En-FDF, a hybrid Eulerian/Lagrangian numerical solution procedure is developed. In the Eulerian part, the filtered transport equations are solved by finite-difference method. In the Lagrangian part, the solution of the modeled En-FDF transport equation is obtained by Monte Carlo method. The unclosed entropy generation statistics in the Eulerian part are obtained from the Monte Carlo solver. The En-FDF is used to predict a nonpremixed jet flame (Sandia Flame D) [119]. Our previous simulations of this flame have demonstrated the predictive capacity of earlier FDF formulations [73,84]. The objectives of the present study are to assess the accuracy of the En-FDF and to demonstrate its effectiveness for prediction and analysis of entropy generation in realistic turbulent flames.
3.2 Formulation

For a compressible, low Mach number, multicomponent flow involving \( N_s \) chemically reacting species, the starting equations are conservation laws of mass, momentum, energy (enthalpy) and mass fraction of chemical species \([120]\) as well as entropy transport equation \([47, 58]\).

\[
\frac{\partial \rho}{\partial t} + \frac{\partial \rho u_i}{\partial x_i} = 0 \tag{3.1}
\]

\[
\frac{\partial \rho u_i}{\partial t} + \frac{\partial \rho u_i u_j}{\partial x_j} = -\frac{\partial p}{\partial x_i} + \frac{\partial \tau_{ij}}{\partial x_j} \tag{3.2}
\]

\[
\frac{\partial \rho \phi_{\alpha}}{\partial t} + \frac{\partial \rho u_i \phi_{\alpha}}{\partial x_i} = -\frac{\partial J_i^\alpha}{\partial x_i} + \rho S_{\alpha} \tag{3.3}
\]

\[
\frac{\partial \rho s}{\partial t} + \frac{\partial \rho u_i s}{\partial x_i} = \frac{\partial}{\partial x_i} \left( \gamma \frac{\partial s}{\partial x_i} \right) + \frac{1}{T} \frac{\tau_{ij}}{\partial x_j} \frac{\partial u_i}{\partial x_j} + \frac{\gamma c_p}{T^2} \frac{\partial T}{\partial x_i} \frac{\partial T}{\partial x_i} + \sum_{\alpha=1}^{N_s} \gamma R_{\alpha} \frac{\partial \phi_{\alpha}}{\partial x_i} \frac{\partial X_{\alpha}}{\partial x_i} - \frac{\rho}{T} \sum_{\alpha=1}^{N_s} \mu_{\alpha} S_{\alpha} \tag{3.4}
\]

Considering the ideal gas equation of state

\[
p = \rho R_u T \sum_{\alpha=1}^{N_s} \frac{\phi_{\alpha}}{M_{\alpha}} = \rho RT \tag{3.5}
\]

these equations describe a closed set for transport of fluid density \( \rho(x,t) \), the velocity vector \( u_i(x,t) \), the pressure \( p(x,t) \), the specific enthalpy \( h(x,t) \), the mass fractions \( Y_{\alpha}(x,t) \) (\( \alpha = 1, \ldots, N_s \)) of chemical species and the specific entropy \( s(x,t) \). The scalar array \( \phi \) in Eq. (3.3) represents the species mass fraction \( \phi_{\alpha} \equiv Y_{\alpha} \), \( \alpha = 1, 2, \ldots, N_s \) and the enthalpy \( \phi_{N_s+1} \equiv h \) in a common form. In these equations, \( R_{\alpha}, X_{\alpha} \) and \( \mu_{\alpha} \) are gas constant, mole fraction and specific chemical potential of species \( \alpha \), respectively. \( R_u, R, T(x,t) \) and \( c_p \) denote the universal and mixture gas constants, temperature and the specific heat capacity at constant pressure of the mixture, respectively. \( J_i^\alpha \) is the flux of scalar \( \alpha \) in direction \( i \). We assume a Newtonian fluid with the molecular stress tensor,

\[
\tau_{ij} = \mu \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} - \frac{2}{3} \frac{\partial u_k}{\partial x_k} \delta_{ij} \right) \tag{3.6}
\]

Coefficient \( \mu \) denotes the molecular dynamic viscosity. The chemical reaction source term in Eq. (3.3) is the mass production rate of species \( \alpha \) per unit volume and unit time and is defined as the sum over all reactions in the mechanism,

\[
\rho S_{\alpha} = M_{\alpha} \dot{\omega}_{\alpha} \tag{3.7}
\]
where $\dot{\omega}_\alpha$ is the molar rate of production/destruction of species $\alpha$ due to chemical reaction. We employ Fourier’s law of heat conduction and Fick’s law of diffusion,

$$J_i^\alpha = -\gamma \frac{\partial \phi_\alpha}{\partial x_i}$$

(3.8)

where $\gamma$ denotes the molecular diffusivity coefficient for all the scalars.

The LES spatial filtering operation is defined as [64, 106],

$$\langle Q(x, t) \rangle = \int_{-\infty}^{+\infty} Q(x', t) G(x', x) dx'$$

(3.9)

where $G$ denotes the filter function of width $\Delta$, and $\langle Q(x, t) \rangle$ represents the filtered value of the transport variable $Q(x, t)$. In reacting flows, it is more convenient to consider the Favre filtered variables, $\langle \rho Q(x, t) \rangle_L = \rho \langle Q \rangle_L$. We consider spatially invariant and localized filter functions,

$$G(x') = G(x' - x)$$

with characteristic filter size $\Delta$ and with the properties: $G(x) = G(-x)$, and $\int_{-\infty}^{+\infty} G(x) dx = 1$. We also consider a positive filter function for which all moments $\int_{-\infty}^{+\infty} x^m G(x) dx$ ($m \geq 0$) exist. The filtered form of conservation laws and entropy transport equation are

$$\frac{\partial <\rho>}{\partial t} + \frac{\partial <\rho >}{\partial x_i} = 0$$

(3.10)

$$\frac{\partial <\rho >}{\partial t} + \frac{\partial <\rho >}{\partial x_i} \frac{<u_j>}{<\rho >} = - \frac{\partial <\rho >}{\partial x_i} + \frac{\partial <\tau_{ij}>}{\partial x_j}$$

(3.11)

$$\frac{\partial <\phi_\alpha>}{\partial t} + \frac{\partial <\phi_\alpha>}{\partial x_i} \frac{<u_j>}{<\rho >} = \frac{\partial}{\partial x_i} \left( \gamma \frac{\partial <\phi_\alpha>}{\partial x_i} \right)$$

(3.12)

$$\frac{\partial <s>}{\partial t} + \frac{\partial <s>}{\partial x_i} \frac{<u_i>}{<\rho >} = \frac{\partial}{\partial x_i} \left( \gamma \frac{\partial <s>}{\partial x_i} \right) - \frac{\partial <\tau_{ij}>}{\partial x_i} + \frac{<1/T \tau_{ij}>}{<\rho >} + \frac{<\gamma c_p T \partial T / \partial x_i>}{<\rho >}$$

(3.13)

$$+ \sum_{\alpha=1}^{N_s} \left\{ \frac{\gamma R_\alpha}{X_\alpha} \frac{\partial \phi_\alpha}{\partial x_i} \frac{\partial X_\alpha}{\partial x_i} \right\} - \left\{ \frac{\rho}{T} \sum_{\alpha=1}^{N_s} \mu_\alpha S_\alpha \right\}$$

where $\tau(a, b) = <ab>_L - <a>_L <b>_L$ denotes the second order SGS moments. The last four terms in Eq. (3.13) denote the volumetric rate of entropy generation due to irreversible
processes [58]: viscous dissipation $S_{gv}$, heat conduction $S_{gh}$, mass diffusion $S_{gm}$ and chemical reaction $S_{gc}$,

$$
\langle S_{gv} \rangle \equiv \left\langle \frac{1}{T} \tau_{ij} \frac{\partial u_i}{\partial x_j} \right\rangle \quad (3.14a)
$$

$$
\langle S_{gh} \rangle \equiv \left\langle \frac{\gamma c_p}{T^2} \frac{\partial T}{\partial x_i} \frac{\partial T}{\partial x_i} \right\rangle \quad (3.14b)
$$

$$
\langle S_{gm} \rangle \equiv \left\langle \sum_{\alpha=1}^{N_s} \frac{\gamma R_\alpha}{X_\alpha} \frac{\partial X_\alpha}{\partial x_i} \frac{\partial \phi_\alpha}{\partial x_i} \right\rangle \quad (3.14c)
$$

$$
\langle S_{gc} \rangle \equiv -\left\langle \frac{\rho}{T} \sum_{\alpha=1}^{N_s} \mu_\alpha S_\alpha \right\rangle \quad (3.14d)
$$

All these terms as appear in Eq. (3.13) are unclosed. In addition, the filtered chemical reaction source term and all the second order SGS moments need to be closed. The latter include $\tau(u_i, u_j)$, $\tau(u_i, \phi_\alpha)$ and $\tau(u_i, s)$ which are modeled using the Modified Kinetic Energy Viscosity (MKEV) closure [73,86,87]. The closure of filtered entropy generation is provided by the marginal En-FDF, in which the effects of chemical reaction appear in closed forms.

### 3.3 Definition of Marginal En-FDF

To facilitate application of En-FDF to complex turbulent reacting flows, the marginal En-FDF is developed. This form of En-FDF, denoted by $F_{en}'(\hat{\phi}, \hat{s}; x, t)$, contains only the joint scalar-entropy statistics. The marginal En-FDF is defined as,

$$
F_{en}'(\hat{\phi}, \hat{s}; x, t) = \int_{-\infty}^{+\infty} \rho(x', t) \zeta(\hat{\phi}, \hat{s}; \phi(x', t), s(x', t)) G(x' - x) dx'
$$

wherein $\zeta(\hat{\phi}, \hat{s}; \phi, s)$ is the fine-grained density function defined as the product of Dirac delta functions $\delta$ for sample space variables included in marginal En-FDF, which are entropy and scalar,

$$
\zeta(\hat{\phi}, \hat{s}; \phi(x, t), s(x, t)) = \delta(\hat{s} - s(x, t)) \prod_{\alpha=1}^{N_s+1} \delta(\hat{\phi}_\alpha - \phi_\alpha(x, t))
$$

The sample space variables $\hat{\phi}$ and $\hat{s}$ correspond to scalar array and entropy, respectively. Alternatively, the marginal En-FDF can be defined by integrating En-FDF (Eq. (2.38)) over the velocity and frequency sample spaces,
The conditional filtered value of the variable \( Q(x, t) \) is defined by \([72, 78, 80]\),

\[
\langle Q(x, t) \mid \hat{\phi}, \hat{s} \rangle = \langle Q(x, t) \mid \phi(x, t) = \hat{\phi}, s(x, t) = \hat{s} \rangle
\equiv \int_{-\infty}^{+\infty} \rho(x', t) Q(x', t) \zeta \left[ \hat{\phi}, \hat{s} ; \phi(x', t), s(x', t) \right] G(x' - x) dx'
\]  

(3.18)

where \( \langle \mid \rangle \) denotes the “conditional” filtered values. Equation (3.18) has the following properties \([88]\),

\[
\langle \rho(x, t) \rangle \langle Q(x, t) \rangle = \int_{-\infty}^{+\infty} \langle Q(x, t) \mid \hat{\phi}, \hat{s} \rangle F'_{en}(\hat{\phi}, \hat{s}, x; t) d\hat{\phi} d\hat{s}
\]  

(3.19c)

which are similar to En-FDF properties (Eqs. (2.41a - 2.41c)). Following Eqs. (3.19), the filtered value of any function \( \tilde{Q} \left( \hat{\phi}, \hat{s} \right) \) defined by scalar and entropy, is obtained from the marginal En-FDF as,

\[
\langle \rho(x, t) \rangle \langle Q(x, t) \rangle_L = \int_{-\infty}^{+\infty} \tilde{Q} \left( \hat{\phi}, \hat{s} \right) F'_{en} \left( \hat{\phi}, \hat{s}, x; t \right) d\hat{\phi} d\hat{s}
\]  

(3.20)

### 3.4 Marginal En-FDF transport equations

The marginal En-FDF is governed by an exact transport equation \([72, 88]\). Differentiating Eq. (3.16) with respect to time yields,

\[
\frac{\partial \zeta}{\partial t} = \frac{\partial \zeta}{\partial s} \frac{\partial s}{\partial t} + \sum_{\alpha=1}^{N_s+1} \frac{\partial \zeta}{\partial \phi_\alpha} \frac{\partial \phi_\alpha}{\partial t}
\]

\[
= -\frac{\partial \zeta}{\partial \hat{s}} \frac{\partial \hat{s}}{\partial t} - \sum_{\alpha=1}^{N_s+1} \frac{\partial \zeta}{\partial \phi_\alpha} \frac{\partial \phi_\alpha}{\partial t}
\]

(3.21)
Substitution for $\partial s/\partial t$ and $\partial \phi_\alpha/\partial t$ from transport Eqs. (3.4), (3.3) into Eq. (3.21) yields,

$$\frac{\partial \rho \zeta}{\partial t} + \frac{\partial \rho \zeta u_i}{\partial x_i} = -\frac{\partial}{\partial x_i} \left( \gamma \frac{\partial s}{\partial x_i} \right) - S_g \frac{\partial \zeta}{\partial s} + \sum_{\alpha=1}^{N_s+1} \frac{\partial J^\alpha_j}{\partial x_j} \frac{\partial \zeta}{\partial \hat{s} - \sum_{\alpha=1}^{N_s+1} \rho S_\alpha \frac{\partial \zeta}{\partial \hat{s}} + N_s \sum_{\alpha=1}^{N_s} \frac{\partial J^\alpha_j}{\partial x_j} \frac{\partial \zeta}{\partial \hat{s}}$$

(3.22)

Integrating Eq. (3.22) according to Eq. (3.15) produces the exact transport equation for the marginal En-FDF,

$$\frac{\partial F^\prime_{\text{en}}}{\partial t} + \frac{\partial}{\partial x_i} \left[ \langle u_i | \hat{\phi}, \hat{s} \rangle F^\prime_{\text{en}} \right] = -\sum_{\alpha=1}^{N_s+1} \frac{\partial}{\partial \hat{\phi}_\alpha} \left[ \langle \frac{1}{\rho} \partial \hat{\phi}_\alpha \left( \gamma \frac{\partial s}{\partial x_i} \right) | \hat{\phi}, \hat{s} \rangle F^\prime_{\text{en}} \right]$$

$$-\frac{\partial}{\partial \hat{s}} \left[ \langle \frac{1}{\rho} \sum_{\alpha=1}^{N_s} R_{\alpha} \frac{\partial \phi_\alpha}{\partial x_i} \frac{\partial X_\alpha}{\partial x_i} | \hat{\phi}, \hat{s} \rangle F^\prime_{\text{en}} \right] - \frac{\partial}{\partial \hat{s}} \left[ \langle \gamma \frac{c_p}{\rho T^2} \frac{\partial T}{\partial x_i} | \hat{\phi}, \hat{s} \rangle F^\prime_{\text{en}} \right]$$

$$-\sum_{\alpha=1}^{N_s} \frac{\partial}{\partial \hat{s}} \left[ S_\alpha \langle \hat{\phi} \rangle F^\prime_{\text{en}} \right] + \frac{\partial}{\partial \hat{s}} \left[ \frac{1}{T} \sum_{\alpha=1}^{N_s} \mu_\alpha S_\alpha \langle \hat{\phi} \rangle F^\prime_{\text{en}} \right]$$

(3.23)

Alternatively, Eq. (3.23) can be found by integrating Eq. (2.45) according to Eq. (3.17). Similar to Eq. (2.45), the effects of chemical reaction (the last two terms on the RHS of Eq. (3.23)) are in closed forms and all the terms involving conditional filtered values require closure.

### 3.4.1 Marginal En-FDF modeled transport equations

We consider the general diffusion process [107], given by the system of stochastic differential equations (SDEs),

$$d X^+_i = \left( \langle u_i \rangle_L + \frac{1}{\langle \rho \rangle} \frac{\partial (\gamma + \gamma_t)}{\partial x_i} \right) dt + \left( \sqrt{2 \langle \gamma + \gamma_t \rangle} \right) dW_i$$

(3.24a)

$$d \phi^+_\alpha = -C_\phi \Omega \left( \phi^+_\alpha - \langle \phi_\alpha \rangle_L \right) dt + S_\alpha \langle \phi^+ \rangle dt$$

(3.24b)

$$ds^+ = \frac{\epsilon_i}{T^+} dt + \frac{1}{T^+} \sum_{\alpha=1}^{N_s} \mu_\alpha^+ C_\phi \Omega \langle \phi^+_\alpha \rangle dt - \frac{1}{T^+} C_\phi \Omega \langle h^+ \rangle dt$$

(3.24c)
where $X_i^+$, $\phi^+_\alpha$ and $s^+$ are the stochastic representations of position, scalars and entropy respectively. $W_i$ denotes the Wiener-Lévy process [111, 112]. Similar to previous section, the marginal En-FDF is represented by a set of SDEs, which provides one-point, one-time description of the marginal En-FDF [72]. The set of SDEs include the linear mean square estimation (LMSE) [64] model. Comparing Eq. (3.24) with Eq. (2.46), it is noticed that the transport in physical space is described by a different SDE (Eq. (3.24a)) while same equations govern scalar (Eq. (3.24b)) and entropy (Eq. (3.24c)) variations. In this formulation, velocity and frequency fields must be obtained by other (non-FDF) means. In Eqs. (3.24), $C_\phi$ is the model parameter and $C_\phi = 8$ is set consistent with previous studies [73]. In this case, the mixing frequency is modeled as

$$\Omega = \frac{(\gamma + \gamma_t)}{(\rho)\Delta^2}$$

(3.25)

where $\gamma_t$ denotes the SGS diffusivity [86, 87].

The Fokker-Planck equation [114] for $F'_{en}(\hat{\phi}, \hat{s}, x; t)$ is the joint PDF of $X_i^+$, $\phi^+_\alpha$ and $s^+$ which evolves by the diffusion processes as given by Eqs. (3.24). The Fokker-Planck equation is the deterministic description of the processes described in the system of SDEs. The system of SDEs described in Eqs. (3.24) are selected in such a way that the resulting Fokker-Planck equation describes the modeled FDF transport equation [114]. So, the Fokker-Planck equation corresponding to the set of SDEs (Eqs. (3.24)) is the modeled transport equation for the marginal En-FDF,

$$\frac{\partial F'_{en}}{\partial t} + \frac{\partial (\langle u_i \rangle_L F'_{en})}{\partial x_i} = \frac{\partial}{\partial x_j} \left( (\gamma + \gamma_t) \frac{\partial (F'_{en}/(\rho))}{\partial x_j} \right)$$

$$+ C_\phi \Omega \frac{\partial}{\partial \phi_\alpha} \left[ \left( \hat{\phi}_\alpha - \langle \phi_\alpha \rangle_L \right) F'_{en} \right] - \frac{\epsilon_t}{T} \frac{\partial F'_{en}}{\partial \hat{s}}$$

$$- \frac{1}{T} \sum_{a=1}^{N_s} C_\phi \Omega \left[ \mu_\alpha \left( \hat{\phi}_\alpha - \langle \phi_\alpha \rangle_L \right) \right] \frac{\partial F'_{en}}{\partial \hat{s}} + \frac{1}{T} C_\phi \Omega \left[ \langle h - \langle h \rangle_L \rangle \right] \frac{\partial F'_{en}}{\partial \hat{s}}$$

(3.26)

$$- \sum_{a=1}^{N_s} \frac{\partial}{\partial \phi_\alpha} \left[ S_\alpha(\hat{\phi})F'_{en} \right] + \frac{1}{T} \sum_{a=1}^{N_s} \mu_\alpha S_\alpha(\hat{\phi}) \frac{\partial F'_{en}}{\partial \hat{s}}$$

From the computational standpoint, solution of the SDEs in Eqs. (3.24) is significantly easier than that of the modeled PDF transport Eq. (3.26). This most efficiently is handled via the Monte Carlo method which will be described in Section (3.5).

By comparing Eq. (3.26) with Eq. (3.23), it is evident that the exact and modeled marginal

39
En-FDF transport equations are statistically equivalent,

\[-\sum_{\alpha=1}^{N_s+1} \frac{\partial}{\partial \phi_\alpha} \left[ \left\langle \frac{1}{\rho} \frac{\partial}{\partial x_i} \left( \frac{\partial \phi_\alpha}{\partial x_i} \right) \right| \hat{u}, \hat{\phi}, \hat{\omega}, \bar{s} \right\rangle F'_{en} \right] \]

\[-\frac{\partial}{\partial \bar{s}} \left[ \left\langle \frac{1}{\rho} \frac{\partial}{\partial x_i} \left( \frac{\partial \bar{s}}{\partial x_i} \right) \right| \hat{u}, \hat{\phi}, \hat{\omega}, \bar{s} \right\rangle F'_{en} \right] \]

\[-\frac{\partial}{\partial \bar{s}} \left[ \left\langle \sum_{\alpha=1}^{N_s} R_{\alpha} \frac{\partial \phi_\alpha}{\partial x_i} \frac{\partial X_\alpha}{\partial x_i} \right| \hat{u}, \hat{\phi}, \hat{\omega}, \bar{s} \right\rangle F'_{en} \right] \]

\[-\frac{\partial}{\partial \bar{s}} \left[ \left\langle \frac{1}{\rho} T \frac{\partial}{\partial x_j} \left( \frac{\partial u_i}{\partial x_j} \right) \right| \hat{u}, \hat{\phi}, \hat{\omega}, \bar{s} \right\rangle F'_{en} \right] \]

\[= C_\phi \Omega \frac{\partial}{\partial \phi_\alpha} \left[ \left( \phi_\alpha - \langle \phi_\alpha \rangle_L \right) F'_{en} \right] - \frac{\epsilon_t}{T} \frac{\partial F'_{en}}{\partial \bar{s}} + \frac{1}{T} C_\phi \Omega \left[ \left( \langle h \rangle_L - \langle h \rangle \right) \frac{\partial F'_{en}}{\partial \bar{s}} \right] \]

\[-\sum_{\alpha=1}^{N_s} C_\phi \Omega \left[ \mu_\alpha \left( \phi_\alpha - \langle \phi_\alpha \rangle_L \right) \right] \frac{\partial F'_{en}}{\partial \bar{s}} \]

Equation (3.27) is implied closure for the marginal En-FDF which is obtained by comparing the Fokker-Planck equation (Eq. (3.26)) with exact transport equation (Eq. (3.23)).

3.4.2 Closure of unclosed terms in the marginal En-FDF

The transport equations for the filtered scalars and entropy are obtained by integration of Eq. (3.26) according to Eq. (3.19c),

\[\frac{\partial}{\partial t} \langle \rho \rangle_L \phi_\alpha + \frac{\partial}{\partial x_i} \langle \rho \rangle_L \frac{\partial \phi_\alpha}{\partial x_i} = \gamma \frac{\partial \phi_\alpha}{\partial x_i} \]

\[= -\frac{\partial}{\partial x_i} \langle \rho \rangle \tau (u_i, \phi_\alpha) + \langle \rho S_\alpha \rangle \]

\[\frac{\partial}{\partial t} \langle \rho \rangle s_L + \frac{\partial}{\partial x_i} \langle \rho \rangle L \frac{\partial s_L}{\partial x_i} = \frac{\partial}{\partial x_i} \left( \gamma \frac{\partial s_L}{\partial x_i} \right) - \frac{\partial}{\partial x_i} \langle \rho \rangle \tau (u_i, s) \]

\[= \langle \rho \rangle \epsilon_t \left( \frac{1}{T} \right)_L + \langle \rho \rangle C_\phi \Omega \left[ \sum_{\alpha=1}^{N_s} \tau (\phi_\alpha, \frac{g_\alpha}{T}) - \tau \left( h, \frac{1}{T} \right) \right] \]

\[+ \langle \rho \rangle C_\phi \Omega \sum_{\alpha=1}^{N_s} R_{\alpha} \tau (\phi_\alpha, \ln X_\alpha) - \left\langle \rho \right\rangle \frac{T}{\sum_{\alpha=1}^{N_s} \mu_\alpha S_\alpha} \]

It is clear that the transport equation for scalar implied by the model (Eqs. (3.28)) is consistent with the original LES equation (Eq. (3.12)). Comparing Eq. (3.29) with Eq. (3.13) reveals the En-FDF implied closure of the individual filtered entropy generation terms.
\[ \langle S_{gv} \rangle = \left\langle \frac{1}{T} \tau_{ij} \frac{\partial u_i}{\partial x_j} \right\rangle \approx \langle \rho \rangle \left\langle \frac{1}{T} \right\rangle \epsilon_t \] (3.30a)

\[ \langle S_{gh} \rangle = \left\langle \gamma \frac{c_p}{T^2} \frac{\partial T}{\partial x_i} \right\rangle \approx \langle \rho \rangle C_\phi \Omega \left[ \sum_{\alpha=1}^{N_s} \tau (\phi_\alpha, \frac{g_\alpha}{T}) - \tau (h, \frac{1}{T}) \right] \] (3.30b)

\[ \langle S_{gm} \rangle = \left\langle \sum_{\alpha=1}^{N_s} \gamma R_\alpha \frac{1}{X_\alpha} \frac{\partial \phi_\alpha}{\partial x_i} \frac{\partial X_\alpha}{\partial x_i} \right\rangle \approx \langle \rho \rangle C_\phi \Omega \sum_{\alpha=1}^{N_s} R_\alpha \tau (\phi_\alpha, \ln X_\alpha) \] (3.30c)

which is similar to closure for the En-FDF (Eqs. (2.57)). It is noted that in the marginal En-FDF formulation, the filtered entropy generation by chemical reaction \[ \langle S_{gc} \rangle = \left\langle \frac{\rho}{T} \sum_{\alpha=1}^{N_s} \mu_\alpha S_\alpha \right\rangle \] in Eq. (3.29) appears as closed.

The marginal En-FDF provides closure for unclosed entropy generation terms, as shown in Eqs. (3.30). However, other unclosed terms, i.e. the subgrid stress, subgrid species flux and subgrid entropy flux are modeled using conventional LES models. To describe the effect of second order SGS moments, we use the modified kinetic energy viscosity (MKEV) closure \[ \tau (u_i, u_j) = -2C_R \langle \rho \rangle \Delta \varepsilon^{1/2} \left( \langle S_{ij} \rangle_L - \frac{1}{3} \langle S_{kk} \rangle_L \delta_{ij} \right) + \frac{2}{3} C_I \langle \rho \rangle \varepsilon \delta_{ij} \] (3.31)

where \( \langle S_{ij} \rangle_L \) is the resolved strain rate tensor, \( \varepsilon = | \langle u_i^* \rangle_L \langle u_i^* \rangle_L - \langle \langle u_i^* \rangle_L \rangle_g \langle \langle u_i^* \rangle_L \rangle_g | \), \( u_i^* = u_i - U_i^* \) and \( U_i^* \) is a reference velocity in the \( x_i \) direction. In this work, the \( U_i^* \) is set to zero in the cross-stream and span-wise directions, and to the average of the high and low speed streams in the stream-wise direction at the inlet. The subscript \( g \) denotes a secondary filter level with characteristic filter width greater than the initial filter width (\( \Delta_g > \Delta \)). For the SGS scalar and entropy flux terms, a diffusion closure model

\[ \tau (u_i, \phi_\alpha) = -\gamma_t \frac{\partial \langle \phi_\alpha \rangle_L}{\partial x_i} \] (3.32)

\[ \tau (u_i, s) = -\gamma_t \frac{\partial \langle s \rangle_L}{\partial x_i} \] (3.33)

where the subgrid diffusivity is \( \gamma_t = \langle \rho \rangle \nu_t / S_{Cl} \). Typically the SGS Schmidt number \( (S_{Cl}) \) has the same value for all of the scalar variables. In this work, \( S_{Cl} = 0.75 \) is considered, which is equal to SGS Prandtl number. The subgrid eddy viscosity is expressed as

\[ \nu_t = C_R \Delta \varepsilon^{1/2} \] (3.34)

where \( C_R = 0.02 \), is considered consistent with previous work [73].
3.5 Numerical solution procedure

In marginal En-FDF, the system of Eqs. (3.10 - 3.12), (3.29) are solved along with corresponding system of SDEs (Eqs. (3.24)). Numerical solution is obtained by a hybrid finite difference (FD) - Monte Carlo (MC) procedure [86, 87, 122–124]. For simulations, the FDF is represented by an ensemble of \( N_p \) statistically identical MC particles. Each particle carries information pertaining to its position, \( X^{(n)}(t) \), scalar value, \( \phi^{(n)}(t) \), \( n = 1, \ldots, N_p \) and entropy, \( s^{(n)}(t) \), (Fig. (3.1)). This information is updated via temporal integration of the SDEs. The simplest way of performing this integration is via Euler-Maruyama approximation [117]. For example for Eq. (3.24a), we have

\[
X_i^n(t_{k+1}) = X_i^n(t_k) + (D_i^X(t_k))^n \Delta t + (B_{ij}^X(t_k))^n (\beta_j^X(t_k))^n \\
+ (F_{ij}^{X\phi}(t_k))^n (\beta_j^\phi(t_k))^n
\]

where \( D_i(t_k) = D_i(X^{(n)}(t_k), s^{(n)}(t_k), \phi^{(n)}(t_k); t_k), \ldots \), and \( \beta(t_k) \)'s are independent standardized Gaussian random variables. This scheme preserves the Itô character of the SDEs [110].

The computational domain is discretized on equally spaced finite difference grid points. These points are used for two purposes: (1) to identify the regions where the statistical information from the MC simulations are obtained, (2) to perform a set of complementary LES primarily by the FD methodology for assessing the consistency and convergence of the MC results.

Statistical information is obtained by considering an ensemble of \( N_E \) computational particles residing within an ensemble domain of characteristic length \( \Delta_E \) centered around each of the finite-difference grid points. This is illustrated schematically in Fig. (3.1). For reliable statistics with minimal numerical dispersion, it is desired to minimize the size of ensemble domain and maximize the number of the MC particles [103]. In this way, the ensemble statistics would tend to the desired filtered values,

\[
\langle a \rangle_E \equiv \frac{1}{N_E} \sum_{n \in \Delta_E} a^{(n)} \xrightarrow{N_E \to \infty, \Delta_E \to 0} \langle a \rangle \\
\tau_E(a, b) \equiv \frac{1}{N_E} \sum_{n \in \Delta_E} (a^{(n)} - \langle a \rangle_E)(b^{(n)} - \langle b \rangle_E) \xrightarrow{N_E \to \infty, \Delta_E \to 0} \tau(a, b)
\]

where \( a^{(n)} \) and \( b^{(n)} \) denotes the information carried by \( n^{th} \) MC particle pertaining to transport variable \( a \) and \( b \), respectively. \( \Delta_E \) is the ensemble domain size as shown in Fig. (3.1); \( \langle a \rangle_E \) and \( \tau_E(a, b) \) are first and second moment statistics obtained on ensemble domain which in the limit \( N_E \to \infty, \Delta_E \to 0 \) approach \( \langle a \rangle \) and \( \tau(a, b) \), respectively. The LES-FD solver is based on the compact parameter finite difference scheme [115,116]. This is a variant of the MacCormack scheme in which fourth-order compact differencing schemes are used to approximate the spatial derivatives, and second-order symmetric predictor-corrector sequence
is employed for time discretization. All of the finite difference operations are conducted on fixed grid points. The transfer of information from the grid points to the MC particles is accomplished via a second-order interpolation. The transfer of information from the particles to the grid points is accomplished via ensemble averaging as described above. The FD procedure determines the pressure field which is used in the MC solver. The FD also determines the filtered entropy and scalar fields. That is, there is a “redundancy” in the determination of the first filtered moments as both the FD and the MC procedures provides the solution of this field. This redundancy is actually very useful in monitoring the accuracy of the simulated results as shown in previous work [87]. Further discussions about the simulation methods are available in Refs. [86, 88, 122–124].

3.6 Nonpremixed flame simulation

The marginal En-FDF is applied to the turbulent nonpremixed piloted methane jet flame (Sandia Flame D), studied in experiments of Sandia National Laboratories [119, 125]. The main objectives are to assess the En-FDF predictions against experimental data and to perform entropy generation analysis of a turbulent nonpremixed flame. Figure (3.2) shows a schematic of this flame. This flame has been the subject of many investigations [73, 83, 84, 126–131]. It consists of a main fuel jet with 25% methane and 75% dry air by volume. Such partial premixing reduces the formation of the soot precursors. The fuel nozzle is placed in a coflow of air, with the temperature \( T_c = 291 \) K, and the flame is stabilized by a substantial pilot. The pilot is a lean mixture of acetylene (\( \text{C}_2\text{H}_2 \)), hydrogen (\( \text{H}_2 \)), air, carbon dioxide (\( \text{CO}_2 \)) and nitrogen (\( \text{N}_2 \)) with the same equilibrium composition as the fuel jet and a temperature of 1880K. The pilot diameter is 18.2 mm. The energy release of the pilot is approximately 6% that of the main jet. The Reynolds number for the main jet is \( Re = 22,400 \) based on the nozzle diameter \( D = 7.2 \text{ mm} \) and the bulk jet velocity \( U_b = 49.6 \text{ m/s} \).

Since Sandia Flame D is close to equilibrium, with a single reaction zone occurring near the stoichiometric mixture fraction \( \xi_s = 0.351 \). The methane oxidation kinetics is considered along with the flamelet concept, in which the detailed kinetics of Gas Research Institute [132] is employed in a laminar, one-dimensional counterflow (opposed jet) flame [133]. The thermochemical variables are expressed as \( \phi \equiv \phi(\xi, a) \), where \( \xi \) is mixture fraction and \( a \) is the flame strain rate. The mixture fraction is carried as an additional passive scalar described as,

\[
d\xi^+ = -C_\phi \Omega \left( \xi^+ - \langle \xi \rangle_L \right) dt, \tag{3.37}
\]

where \( \xi^+ \) is the stochastic representation of mixture fraction. In near equilibrium flames, the strain rate can be assumed to be a constant, which is set as \( a = 100 \text{ s}^{-1} \), similar to the previous FDF predictions of this flame [73, 84].
The flow variables at the inflow are set similar to those in the experiment, including the inlet profiles of velocity and mixture fraction. The flow is excited by superimposing oscillating axisymmetric and helical perturbations at the inflow. The procedure is similar to that of [134], with the forcing amplitude set according to the experimentally measured turbulent intensity of the streamwise velocity at the inlet. Simulations are conducted on a 3D Cartesian mesh with uniform grid spacings along all coordinate directions. The Navier-Stokes characteristic boundary conditions [135] are used on all FD domain boundaries. The computational domain spans a region of $18D \times 10D \times 10D$ in the streamwise ($x$), and the two lateral ($y, z$) directions, respectively. The number of grid points are $91 \times 101 \times 101$ in the $x, y$ and $z$ directions, respectively. The filter size is set equal to $\Delta = 2^{\frac{1}{3}}\sqrt{\Delta x \Delta y \Delta z}$ where $\Delta x$, $\Delta y$ and $\Delta z$ denote grid spacing in the corresponding directions.

Construction of the filtered values from the MC solver is done on an ensemble domain with the size equal to the filter characteristic width. The particles are supplied at the inlet and are transported freely within the domain as prescribed by Eq. (3.24a). There are approximately 48 MC particles at each grid point participating in ensemble averaging. Per results of extensive previous studies, [72,78,80,86–88] this number is sufficient to yield an excellent statistical accuracy with minimal dispersion errors. In total, there are about 3.4 million MC particles within the domain at all times.

### 3.6.1 Validation via laboratory data

Figure (3.3) shows contours of the instantaneous filtered entropy obtained from the FD and the MC solvers. Similarity of the results indicates the consistency of the solvers in predicting the entropy field. This consistency is maintained at every instant throughout the simulation and is also observed for all other scalars. In this figure, the fuel nozzle is located at the centerline of the $x = 0$ plane, surrounded by the pilot which exhibits the highest temperature and entropy values. The region close to the nozzle is dominated by the molecular diffusion, and the flow resembles a laminar jet. Farther downstream, the growth of perturbations cause formation of large-scale coherent structures. The overall accuracy of the En-FDF predictions are assessed by comparing various statistics with the laboratory data; the experimental data for entropy statistics are constructed from the scalars instantaneous data. The En-FDF statistics are obtained by time-averaging the filtered fields during 7 flow through times. A total of 60,000 samples for each variable are averaged locally in this recording period. The notations $\overline{Q}$ and $RMS(Q)$ denote, respectively, the time-averaged mean and root mean square fields for a variable $Q$. Extensive validations of velocity and scalar variables against laboratory data are made in previous FDF studies of this flame [73,83,84]. Similar comparison is made here for the entropy statistics. In the following, the position, velocity, temperature and entropy are normalized by $D$, $U_b$, $T_c$ and $U_b^2/T_c$, respectively. As shown in Fig. (3.4), the radial ($r = \sqrt{z^2 + y^2}$) distributions of the time-averaged filtered entropy at $x/D = 7.5, 15$ are in good agreements with the data. Validation
of the entropy RMS value is shown in Fig. (3.5). The resolved RMS \( \left( R(s, s) \right)^{1/2} \), where \( R(s, s) = \left( \langle s \rangle_L - \langle s \rangle_L \right) \left( \langle s \rangle_L - \langle s \rangle_L \right) \), compare favorably with the data. The total RMS \( \left( r(s, s) \right)^{1/2} \), where \( r(s, s) \approx R(s, s) + \tau(s, s) \), shows higher values than the experimental data. This overprediction could be attributed to finite probe size in the experimental measurements and is also observed by [73] for mixture fraction and temperature fields.

3.6.2 Analysis of entropy generation

Figure (3.6) shows the instantaneous entropy generation contours superimposed on temperature iso-surfaces. The region close to the nozzle is dominated by the molecular diffusion, and the flow resembles a laminar jet. Farther downstream, the growth of perturbations causes formation of large-scale coherent structures. Figure (3.7) shows the instantaneous entropy generation contours superimposed on mixture fraction iso-surfaces. As evidenced in Figs. (3.6) and (3.7), near the nozzle the main cause of entropy generation is large gradients in the inner (jet/pilot) and the outer (pilot/coflow) shear layers. As the jet develops downstream, the entropy generation shows increased spread and peak values and entropy is produced due to turbulent mixing. Figure (3.8a) shows the instantaneous temperature on \( z = 0 \) plane. In this figure, the jet is discharged from the fuel nozzle centered at \( x = 0 \). The fuel jet is surrounded by a pilot which has the highest temperature values, as shown in Fig. (3.8a). The instantaneous contours of mixture fraction (Fig. (3.8b)) indicates local mixing of species as the turbulent jet evolves. The region close to the inlet shows a laminar-like behavior. Farther downstream, the growth of the turbulent jet is amplified by the formation of large-scale coherent vortices. The instantaneous structures of entropy generated in this turbulent flame due to processes described in Eqs. (3.14) are shown in Figs. (3.8c-e). The entropy production terms are non-dimensionalized with \( U_3^3 / (T_c D) \). The results for entropy generation by viscous dissipation is four orders of magnitudes smaller than other effects and not shown here. It is observed that the entropy generation by heat conduction and chemical reaction are dominant in this flame. Irreversibility due to mass diffusion is less important. These observations are consistent with previous studies [16,31,38].

Filtered entropy generation effects are further analyzed in conjunction with mixture fraction and temperature contours in Fig. (3.9). The entropy production due to heat conduction is shown in Fig. (3.9) along with superimposed instantaneous temperature contours. It is observed that peak values of local entropy generation occur in large temperature gradient regions. These are the inner (jet/pilot) shear layer near the nozzle and in between vortices in fully turbulent regions downstream. Figure (3.9b) illustrates the entropy generation by mass diffusion with overlaid mixture fraction contours. As depicted, the peak values coincide with dense concentration of mixture fraction contours near the flame zone. Similar structures are observed for the chemical reaction (Fig. (3.9c)). As anticipated, this irreversibility effect is dominant near the flame zone, which can be identified by large temperature values. The
mean entropy production at different axial locations (Fig. (3.10)) show that near the nozzle, all irreversibility effects exhibit peaks in the inner shear layer due to large velocity and scalar gradients. At downstream locations, the SGS dissipation associated with SGS mixing causes entropy production at different radial locations. For heat conduction, this mainly occurs near the centerline because of more rapid formation and convection of vortical structures. This effect also shows a secondary peak at $x = 15$ due to passage of vortices in the outer (pilot/coflow) shear layer. For mass diffusion and chemical reaction, similar entropy generation profiles are shown (Figs. (3.10b) and (3.10c)) with peaks located near the flame zones, as also observed in Fig. (3.9). It is useful to note that direct validation of these effects is not possible here since entropy production rate cannot be derived from the reported laboratory data. However, close agreement of filtered entropy with the data suggests that the source terms contributing to its generation are predicted accurately (according to Eq. (3.13)). Figure (3.11) exhibits comparisons of various entropy generation contributions at two axial locations. At $x = 5$, heat conduction in the inner shear layer is the main contributor to irreversibility, followed by chemical reaction whose influence is dominant in the pilot region (between the inner and outer shear layers). As the turbulent jet develops downstream, the irreversibility by heat conduction becomes more significant near the centerline, and that by mass diffusion and chemical reaction extend to farther radial locations. As a result, the total entropy generation peaks at the intersection of heat conduction and chemical reaction profiles at both axial locations. Again, it is noticed that the effect of mass diffusion is less significant and that of viscous dissipation (not shown) is negligible in this flame.

The effectiveness of the second law analysis in reducing irreversible losses is demonstrated by analyzing the sensitivity of entropy generation to inflow stream turbulence intensity as one of the configuration parameters. To control the turbulence intensity, the forcing amplitude of velocity perturbations in the lateral directions are multiplied with a constant factor. Simulations are conducted with several values of this factor, which correspond to $U'/u_{exp}' = 1.0, 1.014, 1.039, 1.087$, where $U' = (u_i'^2)_{tot}/2$, $u_i'$ is the velocity component perturbations specified at the inlet and $u_{exp}'$ is the axial velocity RMS value given by the experiment. Increasing the velocity perturbations at the inlet enhances the flapping excitation of the jet and causes generation of higher RMS values for velocity and scalar variables at downstream locations. This is evident in the resolved RMS of velocity ($R(u_i, u_i)$) and the total RMS of mixture fraction profiles as shown in Fig. (3.12). The corresponding entropy generation is depicted in Fig. (3.13). It is noticed that all entropy generation modes exhibit increased values with turbulent intensity. The heat conduction, mass diffusion and viscous dissipation components occur because of the dissipation associated with turbulent kinetic/scalar energy. These components become more dissipative as the turbulence intensifies, which is manifested as increase in production of entropy. The irreversibility by chemical reaction is due to high reaction rates and shows an increasing trend with turbulent mixing. A large increase is observed in the entropy generation by heat conduction near the centerline which is attributed to more rapid formation and
convection of vortical structures in this region. This mode also exhibits a secondary peak at farther radial locations caused by formation of coherent structures at the outer shear layer. The contribution of each entropy generation mode to the overall availability loss is obtained by integrating over the entire computational domain. The exergy destruction contributions are listed in Table 3.2 for various inflow velocity RMS values. The total exergy destruction indicates the loss of availability (work-producing capacity) of the fluid exiting the domain. The last column indicates the second law efficiency (as a measure of thermodynamic nonideality), defined as the ratio of available energy to exergy influx at the inlet

$$\eta_{II} = \left(1 - \frac{T_0 \langle S_g \rangle}{e_{xin}}\right) \times 100,$$

where $e_{xin}$ is the rate of specific exergy influx at the inlet, $\langle S_g \rangle$ is the mean filtered total entropy generation and $T_0 = 291 \, K$ is the dead state temperature. All entropy generation modes show increased values with higher turbulence intensity. As a result, the second law efficiency decreases significantly from 92.2\% to 79.8\%, which indicates that the availability of the outflowing fluid decreases due to increased irreversible losses with higher turbulence intensities.

Table 3.1. Sandia Flame D: summary of the LES simulation parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Re$</td>
<td>Reynolds number</td>
<td>22,400</td>
</tr>
<tr>
<td>$U_b$</td>
<td>Bulk jet velocity (m/s)</td>
<td>49.6</td>
</tr>
<tr>
<td>$D$</td>
<td>Jet diameter (mm)</td>
<td>7.2</td>
</tr>
<tr>
<td>$Le$</td>
<td>Lewis number</td>
<td>1</td>
</tr>
<tr>
<td>$Pr$</td>
<td>Prandtl number</td>
<td>0.75</td>
</tr>
<tr>
<td>$Sc$</td>
<td>Schmidt number</td>
<td>0.75</td>
</tr>
<tr>
<td>$Sc_t$</td>
<td>SGS Schmidt number</td>
<td>0.75</td>
</tr>
<tr>
<td>$C_I$</td>
<td>MKEV model parameter</td>
<td>0.0</td>
</tr>
<tr>
<td>$C_R$</td>
<td>MKEV model parameter</td>
<td>0.02</td>
</tr>
<tr>
<td>$C_\Omega$</td>
<td>SGS mixing frequency</td>
<td>8</td>
</tr>
<tr>
<td>$T_0$</td>
<td>Dead state temperature (K)</td>
<td>291</td>
</tr>
<tr>
<td>$T_c$</td>
<td>Coflow temperature (K)</td>
<td>291</td>
</tr>
</tbody>
</table>
Figure 3.1. Ensemble averaging on three different domains. Black squares denote finite difference grid points and the blue circles are MC particles. Also shown are three different ensemble domains: (1) $\Delta_E = \Delta/2$, (2) $\Delta_E = \Delta$ and (3) $\Delta_E = 2 \times \Delta$. 
Figure 3.2. Sandia Flame D configuration [125].
Figure 3.3. Instantaneous contours of filtered entropy in Sandia Flame D obtained from (a) MC and (b) FD solvers.
Figure 3.4. Radial variation of mean entropy in Sandia Flame D simulations at (a) $x = 7.5$ and (b) $x = 15$. The lines denote the En-FDF predictions. The circles denote the experimental data.
Figure 3.5. Radial variation of the RMS of entropy in Sandia Flame D simulations at (a) $x = 7.5$ and (b) $x = 15$. The solid and dashed lines denote the resolved and the total contributions, respectively. The circles denote the experimental data.
Figure 3.6. Instantaneous iso-surfaces of temperature (1700K, red; 1400K, yellow; 1100K, green) superimposed by contours of entropy generation (color bar) at different axial locations.
Figure 3.7. Instantaneous iso-surfaces of mixture fraction (0.3, red; 0.6, yellow; 0.9, blue) superimposed by contours of entropy generation (color bar) at different axial locations.
Figure 3.8. Instantaneous contours of: (a) temperature (K), (b) mixture fraction as well as contributions to entropy generation (non-dimensional) due to: (c) heat conduction, (d) mass diffusion and (e) chemical reaction, obtained from En-FDF simulations at $z = 0$ plane.
Figure 3.9. Instantaneous contours of entropy generation terms predicted by the En-FDF in Sandia Flame D simulations: (a) heat conduction (color) with temperature \([K]\) (black) contours, (b) mass diffusion (color) with mixture fraction (black) contours and (c) chemical reaction (color) with temperature \([K]\) (black) contours.
Figure 3.10. Radial variation of mean entropy generation rate due to: (a) heat conduction, (b) mass diffusion and (c) chemical reaction in the En-FDF prediction of Sandia Flame D at $x = 1 \ (\triangledown)$, $x = 5 \ (\square)$, $x = 10 \ (\Diamond)$ and $x = 15 \ (\cdot)$. 
Table 3.2. Effect of turbulent intensity on exergy loss (J/m³·s). The second law efficiency is \( \eta_{II} = \left( 1 - \frac{T_0 \langle S_g \rangle}{e_{xin}} \right) \times 100 \), where \( e_{xin} \) is the rate of exergy influx at the inlet and \( T_0 = 291 \) K is the dead state temperature.

<table>
<thead>
<tr>
<th>( U'/u'_{exp} )</th>
<th>( T_0 \langle S_{gH} \rangle )</th>
<th>( T_0 \langle S_{gM} \rangle )</th>
<th>( T_0 \langle S_{gV} \rangle )</th>
<th>( T_0 \langle S_{gC} \rangle )</th>
<th>( T_0 \langle S_g \rangle )</th>
<th>( \eta_{II} ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>762</td>
<td>172</td>
<td>0.0314</td>
<td>509</td>
<td>1443</td>
<td>92.2</td>
</tr>
<tr>
<td>1.014</td>
<td>1170</td>
<td>317</td>
<td>0.0616</td>
<td>1090</td>
<td>2577</td>
<td>86.0</td>
</tr>
<tr>
<td>1.039</td>
<td>1300</td>
<td>377</td>
<td>0.0579</td>
<td>1360</td>
<td>3037</td>
<td>83.6</td>
</tr>
<tr>
<td>1.087</td>
<td>1540</td>
<td>468</td>
<td>0.0815</td>
<td>1740</td>
<td>3748</td>
<td>79.8</td>
</tr>
</tbody>
</table>
Figure 3.11. Radial variation of mean entropy generation rate (dashed lines) and its individual terms: heat conduction ($\nabla$), mass diffusion ($\Box$) and chemical reaction ($-$) at (a) $x = 5$ and (b) $x = 15$ in the En-FDF prediction of Sandia Flame D.
Figure 3.12. Radial variation of total RMS of mixture fraction (left) and resolved RMS of velocity m/s (right) at $x/D = 10$. Symbols correspond to inflow stream velocity RMS, $U'/u'_{exp} = 1.0$ (○), 1.014 (▽), 1.039 (□) and 1.087 (×).
Figure 3.13. Radial variation of entropy generation modes at $x/D = 10$. Symbols correspond to inflow stream velocity RMS, $U'/u_{exp}' = 1.0$ (◦), 1.014 (∇), 1.039 (□) and 1.087 (∗).
Chapter 4

CONCLUSION AND SOME SUGGESTIONS FOR FUTURE WORK

Entropy generation in turbulent reacting flows is predicted and analyzed using large eddy simulation (LES). The entropy transport equation is considered in LES. This equation contains the unclosed entropy flux and filtered entropy generation terms due to: viscous dissipation, heat transfer, mass diffusion and chemical reaction. The subgrid scale (SGS) effects are taken into account by using the entropy filtered density function (En-FDF) methodology. The En-FDF in its most comprehensive formulation is essentially the probability density function of entropy, velocity, scalar and turbulent frequency within the SGS and accounts for all the unclosed filtered moments. A marginal form of the En-FDF, containing the scalar and entropy statistics, is also considered which provides closure entropy production terms as well as entropy, scalar statistics. Both formulations contain the chemical reaction effects in a closed form. The predictive capability of the methodology is assessed against experimental data and direct numerical simulation (DNS) predictions. For the former, the marginal En-FDF is used to simulate a turbulent nonpremixed jet flame (Sandia Flame D). For this case, the main objectives are to assess the En-FDF predictions against experimental data and to perform entropy generation analysis of a turbulent nonpremixed flame. The latter case deals with prediction of a turbulent temporal mixing layer involving transport of passive scalars. In this case, the objective is to validate the entropy generation terms from En-FDF model with those obtained by DNS. In both cases, close agreements of the En-FDF results with the data demonstrate the accuracy of the methodology. Entropy generation effects are predicted and analyzed. The contribution of heat conduction is shown to be significant in both cases. The turbulent jet flame exhibits areas with substantial entropy production due to chemical reaction. For this case, the effectiveness of this approach to identify and to reduce irreversible losses is demonstrated by analyzing the sensitivity of entropy generation with turbulent intensity at the inflow. It is observed that in both flows, entropy production
by mass diffusion is less significant and that of viscous dissipation is negligible.

In the following, some suggestions for future work are provided with brief descriptions:

- **Entropy generation by radiation:** In this work, the entropy transport equation was derived by neglecting the radiation effect in the energy transport. For sooting flames the effect of radiation in flame is important and should be considered in the entropy transport and the corresponding En-FDF formulation.

- **Entropy in compressible flows:** In this work, the formulation is presented for low speed flows. Therefore, the pressure variation is omitted. For high speed flows, pressure variation should be considered in the En-FDF formulation. Entropy transport and generation is of particular interest to compressible turbulence modeling [136] and arises in several applications such as turbulence-shock interactions [137], shock capturing [138] and noise prediction [139].

- **Thermodynamic optimization:** One of the important applications of this work is to improve the second law efficiency of engineering devices. In this work, the Sandia Flame D was considered to demonstrate the predictive capability of the novel methodology introduced in this work. This study can be applied to more complex flow configurations of practical interest such as combustors, heat exchanger, fuel cells, turbomachinery, etc. Flow parameters and operating conditions may be varied to design a system with optimum second law efficiency.

- **Entropy generation to describe dissipation:** For complex multi-species, non-isothermal flows, a more general description of dissipation, beyond that provided by viscosity, is useful to characterize turbulence. Such description is provided by entropy generation as it contains the full extent of dissipative effects in transport processes. This is particularly beneficial to understand the behavior of small scale turbulent motions [54].
Nomenclature

$C_I, C_R$ MKEV model parameters
$C_0, C_\phi, C_f, C_\Omega, C_\omega$ En-FDF model parameters
$c_p$ Specific heat at constant pressure
$c_{p\alpha}$ Specific heat at constant pressure for species $\alpha$
$c_v$ Specific heat at constant volume
$E_x$ Exergy
$E_{xD}$ Exergy destruction due to irreversible processes
$E_{xs}$ Exergy transfer due to heat, work and flow interaction
$e$ Specific internal energy of mixture
$D$ Jet flame diameter
$Da$ Damköhler number
$\mathcal{F}_{en}$ Entropy filtered density function
$\mathcal{F}'_{en}$ Marginal entropy filtered density function
$G$ LES filter function
$G_{ij}$ Generalized Langevin kernel
$g_\alpha$ Gibbs free energy of species $\alpha$
$h$ Total specific enthalpy
$h_\alpha$ Enthalpy of species $\alpha$
$h_\alpha^0$ Enthalpy of species $\alpha$ at reference temperature
$J_i^\alpha$ Scalar flux of scalar $\alpha$ in $i$ direction
$k_{bj}$ Rate coefficient of the backward reaction
$k_{fj}$ Rate coefficient of the forward reaction
$k_s$ Subgrid scale kinetic energy
$L_0$ Reference Length
$Le$ Lewis number
$M_\alpha$ Molecular mass of species $\alpha$
$Ma$ Mach number
$m$ Mass of gas mixture
$N_E$ Number of particles inside an ensemble domain
$N_p$ Total number of particles inside computational domain
$N_s$ Number of chemical species
$n_\alpha$ Number of moles of species $\alpha$
$Pr$ Prandtl number
$p$ Pressure
$q_i$ Heat flux
$R$ Mixture gas constant
$R_\alpha$ Gas constant of species $\alpha$
$R_u$ Universal gas constant
$Re$ Reynolds number
$r$ Radial coordinate, $r = \sqrt{z^2 + y^2}$
$S$ Extensive entropy
$Sc$ Schmidt number
$Sc_i$ SGS Schmidt number
$S_g$ Total entropy generation
$S_{gc}$ Entropy generation by chemical reaction
$S_{gh}$ Entropy generation by heat conduction
$S_{gm}$ Entropy generation by mass diffusion
$S_{gv}$ Entropy generation by viscous dissipation
$S_{ij}$ Strain rate tensor
$S_\alpha$ Chemical reaction source term for species $\alpha$
$s$ Specific entropy
$s_\alpha$ Entropy of pure species $\alpha$
$s_\alpha^0$ Partial entropy of species $\alpha$
$\hat{s}$ Sample space specific entropy
$T$ Temperature
$T_c$ Coflow temperature
$T_0$ Reference temperature
$t$ Time
$t_c$ Time scale associated with chemical reaction
$u_i$ Velocity component along $x_i$ coordinate
$u$ Velocity vector
$\hat{u}_i$ Sample space velocity
$\hat{u}$ Sample space velocity vector
$U_b$ Bulk jet velocity
$v$ Specific volume of mixture
$\mathcal{W}_j$ Rate of reaction $j$
$W_i$, $W_i'$ Wiener-Lévy processes
$w^{(n)}$ Weight of particle ($n$)
$Y_\alpha$ Mass fraction of species $\alpha$
$X_\alpha$ Mole fraction of chemical species $\alpha$
$x_i$ Coordinate in direction $i$
$x$ Coordinate vector
Greek Letters:
\( \gamma \) Molecular mass diffusivity
\( \gamma_t \) SGS diffusivity
\( \gamma_\alpha \) Molecular mass diffusivity of species \( \alpha \)
\( \Delta \) LES filter characteristic width
\( \Delta_E \) Characteristic length of an ensemble domain
\( \Delta m \) Mass of a particle with unit weight
\( \Delta x, \Delta y, \Delta z \) Grid spacing in corresponding directions
\( \delta \) Dirac delta function
\( \delta_{ij} \) Kronecker delta
\( \epsilon_t \) Total rate of turbulent dissipation
\( \Omega \) Subgrid scale mixing frequency
\( \omega \) Subgrid scale frequency
\( \hat{\omega} \) Sample space frequency
\( \dot{\omega}_\alpha \) Molar rate of production of species \( \alpha \)
\( \lambda \) Thermal conductivity
\( \mu \) Dynamic viscosity
\( \mu_\alpha \) Specific chemical potential of species \( \alpha \)
\( \nu \) Dynamic viscosity
\( \nu_t \) SGS eddy viscosity
\( \nu_{\alpha j}' \) Stoichiometric coefficient of forward reaction \( j \)
\( \nu_{\alpha j}'' \) Stoichiometric coefficient of backward reaction \( j \)
\( \xi \) Mixture fraction
\( \rho \) Fluid density
\( \tau_{ij} \) Viscous stress tensor
\( \tau(u_i, u_j) \) SGS stress tensor
\( \tau(u_i, \phi_\alpha) \) SGS scalar flux of species \( \alpha \)
\( \tau(u_i, s) \) SGS entropy flux
\( \phi_\alpha \) Scalar \( \alpha \)
\( \hat{\phi}_\alpha \) Sample space scalar \( \alpha \)
\( \phi \) Scalar array
\( \hat{\phi} \) Sample space scalar vector
\( \zeta \) Fine grained density

Symbols:
\( f^+ \) Stochastic process for variable \( f \)
\( f^* \) Non-dimensional value for variable \( f \)
\( \frac{\partial}{\partial t} \) Material derivative \( \left( \frac{\partial}{\partial t} = \frac{\partial}{\partial t} + u_i \frac{\partial}{\partial x_i} \right) \)
\( \langle \rangle \) LES filtered quantities
\( \langle \rangle_L \) LES Favre filtered quantities
\( \langle | \rangle \) Conditional filtered quantities
Abbreviations:
3D Three-dimensional
FD Finite difference
FDF Filtered density function
En-FDF Entropy filtered density function
GLM Generalized Langevin Model
LES Large eddy simulation
LMSE Linear mean square estimation
MC Monte Carlo
MKEV Modified kinetic energy viscosity
PDF Probability density function
RANS Reynolds averaged Navier-Stokes
SDE Stochastic differential equation
SGS Subgrid scale
VFDF Velocity filtered density function
Bibliography


