



Computational Fluid Radiative Dynamics of The Galileo Jupiter Entry at 47.5 km/s

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Dedicated to my mother, who always supported me when times got tough.

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Resumo

A 7 de Dezembro de 1995, a sonda Galileo iniciou uma entrada atmosférica em Júpiter a uma velocidade relativa de 47.4 km s^{-1} . Contudo, análise dos dados recolhidos em voo revela uma grande disparidade no perfil de recessão da camada protectora do veículo (TPS) face ao esperado, particularmente no *shoulder* da sonda. Este trabalho procura explicar as diferenças observadas, através de diversos estudos de sensibilidade realizados a 180 km de altitude. O modelo de transporte Wilke/Blottner/Eucken revela novamente ser impreciso a temperaturas acima dos 5,000 K. No caso da Galileo, isto traduz-se num choque mais fino e um pico de temperaturas superior em comparação com o modelo Gupta/Yos. A radiação proveniente de He e H₂ foi estudada usando uma elevada resolução espectral, sendo responsável por um aumento de 10% dos fluxos radiativos no ponto de estagnação. Se os efeitos de aquecimento do escoamento a montante forem abrangidos, a excitação dos estados internos do H₂ provoca emissão de radiação antes da sua dissociação, aumentando este valor para 209%. Este resultado destaca a importância da radiação devido a H₂ na recessão da Galileo e em futuras missões a Gigantes Gasosos. A inclusão de H₂ em condições de desequilíbrio térmico reduziu a radiação em 25% face aos valores de equilíbrio, contrariamente ao previsto no passado. A absorção promovida pelos produtos de ablação revela potencial para neutralizar a emissão de H₂ a montante, mas torna-se fundamental a correcta modelação da temperatura da camada ablativa. Finalmente, os modelos *tangent-slab* e *ray-tracing* diferem menos de 13%.

Palavras-chave: Hipersónico, Galileo, Não-Equilíbrio, Radiação, Aerotermodinâmica

Abstract

On December 7th, 1995, the Galileo descent probe entered Jupiter’s atmosphere at a relative velocity of 47.4 km s⁻¹. Data collected during flight revealed an unforeseen recession profile: while the stagnation region had been significantly oversized, the shoulder almost completely ablated. In an attempt to understand why numerical predictions diverge from the flight data, several sensitivity studies were performed at the 180 km altitude point. The inaccuracy of the Wilke/Blottner/Eucken model at temperatures above 5,000 K was again confirmed. When applied to Galileo’s entry, it predicts a narrower shock with higher peak temperatures compared to the Gupta/Yos model. The effects of He and H₂ line-by-line radiation were studied. Inclusion of these systems increased the radiative heating by 10% at the stagnation point, even when precursor heating is unaccounted for. Otherwise, the internal excitation of H₂ due to absorption of radiation originating from the highly emitting shock layer promotes H₂ emission before dissociation occurs at the shock, resulting in 209% higher radiative heat fluxes. This result emphasizes the importance of H₂ radiation, not only on the recession experienced by Galileo, but also for future entries in Gas Giants. Accordingly, thermal non-equilibrium resulted in 25% lower radiative heating when compared to an equilibrium solution, contrary to previous investigations that neglected H₂. Ablation product absorption was shown to counteract precursor heating of H₂, but the ablation layer temperature must be accurately predicted using a material-response code coupled to the flowfield. Finally, the tangent-slab and ray-tracing models agreed to within 13%.

Keywords: Hypersonics, Galileo, Non-Equilibrium, Radiation, Aerothermodynamics

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Nomenclature

Physical Constants

π	Pi number	3.141593 [-]
$\tilde{\phi}$	Golder ratio	$\frac{(1+\sqrt{5})}{2}$ [-]
c	Speed of light	299,792,458 [m s ⁻¹]
e	Elementary charge	1.602177×10^{-34} [C] or 4.803204×10^{-10} [statC]
h	Planck's constant	$6.6260702 \times 10^{-34}$ [J s]
k_B	Boltzmann's constant	1.380649×10^{-23} [J K ⁻¹]
N_A	Avogadro's constant	6.022140×10^{23} [mol ⁻¹]
$\mathcal{R}$	Universal gas constant	8.134459 [J mol ⁻¹ K ⁻¹]

Greek symbols

α_r	Coefficient for reaction r in Arrhenius equation [-]
$\alpha_{s,l}$	Coefficient in Gupta/Yos formulation for interaction (s,l) [-]
β	Coefficients entering Pirani's phenomenological potential approach [-]
$\Delta\bar{\nu}$	Wavenumber interval [cm ⁻¹]
$\Delta\lambda_{\text{SB},0}$	Reference Stark FWHM for transition [m]
$\Delta\lambda_{\text{SB}}$	Stark FWHM for transition [m]
$\Delta_{s,l}^{(1)}$	First collision term [m s]
$\Delta_{s,l}^{(2)}$	Second collision term [m s]
η	Kinematic viscosity coefficient [m ² s ⁻¹]
ε_J	Energy level [-]
ε	Particle energy [J]
ε_{tr}	Translational particle energy [J]

ε_{rot}	Rotational particle energy [J]
ε_{vib}	Vibrational particle energy [J]
ε_{exc}	Electronic excitation particle energy [J]
ε_0	Zero-point particle energy [J]
ε_{tot}	Total particle energy [J]
γ	Specific heat ratio [-]
κ_ν	Spectral absorption coefficient [$\text{m}^{-1} \text{Hz}^{-1}$] or [$\text{m}^{-1} \text{cm}^{-1}$] ¹
λ	Second viscosity coefficient [Pa s] or electromagnetic radiation wavelength [m]
λ_D	Debye shielding length [m]
μ	Dynamic viscosity coefficient [Pa s]
$\nu_{s,r}''$	Stoichiometric coefficient associated with product s of reaction r [-]
$\nu_{s,r}'$	Stoichiometric coefficient associated with reactant s for reaction r [-]
ν	Electromagnetic radiation frequency [Hz]
$\bar{\nu}$	Electromagnetic radiation wavenumber [cm^{-1}]
ν_s	Fundamental vibration frequency of species s [s^{-1}]
$\dot{\Omega}$	Energy-exchange source term [W m^{-3}]
$\dot{\Omega}_k$	Energy-exchange source term associated with thermal energy mode k [W m^{-3}]
$\dot{\Omega}_{\text{V-T}}$	Vibration-translation energy-exchange source term [W m^{-3}]
$\Omega_{s,l}^{(m,n)*}$	Reduced collision integral (m, n) for interaction (s, l) [-]
$\Omega_{s,l}^{(m,n)}$	Collision integral (m, n) for interaction (s, l) [$\text{m}^3 \text{s}^{-1}$]
$\bar{\Omega}_{sl}^{(m,n)}$	Average collision cross-section (m, n) for interaction (s, l) employed by Gupta <i>et al.</i> [m^2]
$\sigma^2 \Omega_{s,l}^{(m,n)*}$	Collision cross-section (m, n) for interaction (s, l) [m^2]
ϕ	Coefficient used in Wilke's mixing rules [-] or azimuthal angle [rad]
ϕ_{ul}	Spectral distribution function [Hz^{-1}]
φ_0	Well depth in Pirani's phenomenological potential approach [meV]
ρ	Mass density [kg m^{-3}]

¹Spectral coefficients can be defined in several units. In this work, frequency units (ν) and wavenumber units ($\bar{\nu}$) are used, in which cases the corresponding units are multiplied by Hz^{-1} or $(\text{cm}^{-1})^{-1} = \text{cm}$, respectively.

σ	Collision-limiting cross-section (Park's correction) or rigid sphere collision diameter [m ²]
$[\boldsymbol{\tau}]$	Viscous stress tensor [kg m ⁻¹ s ⁻²]
τ_e	Characteristic time for energy exchanges [s]
τ_f	Characteristic flow time [s]
$\tau_{\bar{\nu}}$	Optical thickness to radiation of wavenumber $\bar{\nu}$ [-]
τ_{vib}	Vibrational relaxation time [s]
τ_{ν}	Optical thickness to radiation of frequency ν [-]
θ	Zenith angle [rad]
ξ_1	Coefficient entering Pirani's phenomenological potential approach [-]
ξ_2	Coefficient entering Pirani's phenomenological potential approach [-]

Operators

$[\mathbf{I}]$	Identity matrix	δ_{ij}
$\cdot$	Dot product between two vectors	
∇	Nabla operator	
$\otimes$	Outer product between two vectors	

Roman symbols

$\bar{a}_i$	Coefficients for CCS curve-fits following Pirani's potential [-]
a	Coefficient in Wright <i>et al.</i> 's curve-fit for charged-species CCS ratio B^* [-]
A_s	Coefficient for species s in Gupta/Yos formulation [m s kg ⁻¹ or m K W ⁻¹]
a_{av}	Coefficient in Gupta/Yos formulation [m s kg ⁻¹ or m K W ⁻¹]
a_i	Coefficients for neutral-neutral and neutral-ion interactions in Bruno <i>et al.</i> 's CCS curve-fits [-]
$A_{s,l}^{\mu}$	Coefficient for viscosity for interaction (s, l) in Gupta/Yos formulation [m s kg ⁻¹]
$a_{s,l}^{\mu}$	Coefficient for viscosity for interaction (s, l) in Gupta/Yos formulation [m s kg ⁻¹]
$A_{s,l}^k$	Coefficient for thermal conductivity for interaction (s, l) in Gupta/Yos formulation [m K W ⁻¹]
$a_{s,l}^k$	Coefficient for thermal conductivity for interaction (s, l) in Gupta/Yos formulation [m K W ⁻¹]
A_{s-c}^{MW}	Coefficient for Millikan-White correlation [K ^{$\frac{1}{3}$}]
A_{ul}	Einstein coefficient for spontaneous emission [s ⁻¹]

AB	General molecular species [-]
A	General atomic species [-]
b	Coefficient in Wright <i>et al.</i> 's curve-fit for charged-species CCS ratio B^* [-]
B_{lu}	Einstein coefficient for absorption [$\text{m}^2 \text{J}^{-1} \text{s}^{-1}$]
$B_{s,l}^*$	Third collision term for interaction (s, l) [-]
B_{s-c}^{MW}	Coefficient for Millikan-White correlation [$\text{K}^{-\frac{1}{3}}$]
B_{ul}	Einstein coefficient for induced emission [$\text{m}^2 \text{J}^{-1} \text{s}^{-1}$]
B	General atomic species [-]
$\bar{c}_j$	Coefficients entering Pirani's phenomenological potential approach [-]
c	Mass fraction or coefficient in Wright <i>et al.</i> 's curve-fit for charged-species CCS ratio B^* [-]
C_m	Coefficient in Wright <i>et al.</i> 's curve-fit for charged-species CCSs [-]
c_m	Coefficient in Wright <i>et al.</i> 's curve-fit for charged-species CCSs [-]
C_p	Total specific heat at constant pressure [$\text{J kg}^{-1} \text{K}^{-1}$]
C_p^f	Frozen component of specific heat at constant pressure [$\text{J kg}^{-1} \text{K}^{-1}$]
C_p^r	Reactive component of specific heat at constant pressure [$\text{J kg}^{-1} \text{K}^{-1}$]
C_r	Coefficient for reaction r in Arrhenius equation [$\text{mol m}^{-3} \text{s}^{-1} \text{K}^{-\alpha_r}$]
C_v	Total specific heat at constant volume [$\text{J kg}^{-1} \text{K}^{-1}$]
C_v^f	Frozen component of specific heat at constant volume [$\text{J kg}^{-1} \text{K}^{-1}$]
C_v^r	Reactive component of specific heat at constant volume [$\text{J kg}^{-1} \text{K}^{-1}$]
$d\Omega$	Infinitesimal solid angle [sr]
dA	Infinitesimal area [m^2]
D	Global mass diffusion coefficient [$\text{m}^2 \text{s}^{-1}$]
D_m	Coefficient in Wright <i>et al.</i> 's curve-fit for charged-species CCSs [-]
D_s	Species mass diffusion coefficient [$\text{m}^2 \text{s}^{-1}$]
d_i	Coefficients for charge-exchange corrections in Bruno <i>et al.</i> 's CCS curve-fits [-]
$D_{s,l}$	Binary mass diffusion coefficient for pair of species (s, l) [$\text{m}^2 \text{s}^{-1}$]
$\mathcal{E}_n$	Exponential integral of order n [-]
E	Total internal energy or energy [J]

E_{ion}	Ionization energy [J]
E_{u}	Energy of an upper state [J]
E_f	Activation energy for the forward reaction in Arrhenius equation [J]
e	Total specific internal energy [J kg^{-1}] or elementary charge [C]
e_k	Specific internal energy associated with thermal energy mode k [J kg^{-1}]
e_{tr}	Translational specific internal energy [J kg^{-1}]
e_{rot}	Rotational specific internal energy [J kg^{-1}]
e_{vib}	Vibrational specific internal energy [J kg^{-1}]
e_{exc}	Electronic excitation specific internal energy [J kg^{-1}]
e_0	Zero-point specific internal energy [J kg^{-1}]
G	Gibbs free energy per mole of mixture [J mol^{-1}]
g	Energy level degeneracy [-]
g_i	Coefficients for neutral-electron interactions in Bruno <i>et al.</i> 's CCS curve-fits [-]
h	Total specific enthalpy [J kg^{-1}]
h_k	Specific enthalpy associated with thermal energy mode k [J kg^{-1}]
h_{tr}	Translational specific enthalpy [J kg^{-1}]
h_{rot}	Rotational specific enthalpy [J kg^{-1}]
h_{vib}	Vibrational specific enthalpy [J kg^{-1}]
h_{exc}	Electronic excitation specific enthalpy [J kg^{-1}]
$(\Delta h_f)^\circ$	Formation enthalpy [J kg^{-1}]
$\mathbf{i}$	Cartesian basis vector (1, 0, 0) [-]
$I^{\theta, \phi}$	Directional radiative intensity [$\text{W m}^{-2} \text{sr}^{-1}$]
$I_{\nu, b}^+$	Spectral blackbody radiative intensity emitted by the body [$\text{W m}^{-2} \text{Hz}^{-1}$] or [$\text{W m}^{-2} \text{cm}$]
I_ν	Spectral radiative intensity [$\text{W m}^{-2} \text{Hz}^{-1}$] or [$\text{W m}^{-2} \text{cm}$]
I_ν^+	Upstream-directed spectral radiative intensity [$\text{W m}^{-2} \text{Hz}^{-1}$] or [$\text{W m}^{-2} \text{cm}$]
I_ν^-	Wall-directed spectral radiative intensity [$\text{W m}^{-2} \text{Hz}^{-1}$] or [$\text{W m}^{-2} \text{cm}$]
$I_\nu^{\theta, \phi}$	Spectral directional radiative intensity [$\text{W m}^{-2} \text{sr}^{-1} \text{Hz}^{-1}$] or [$\text{W m}^{-2} \text{sr}^{-1} \text{cm}$]
I_ν^θ	Spectral zenithal radiative intensity [$\text{W m}^{-2} \text{rad}^{-1} \text{Hz}^{-1}$] or [$\text{W m}^{-2} \text{rad}^{-1} \text{cm}$]

$I_{p,\nu}^{\text{in}}$	Spectral radiative intensity entering cell intersection p [$\text{W m}^{-2} \text{sr}^{-1} \text{Hz}^{-1}$] or [$\text{W m}^{-2} \text{sr}^{-1} \text{cm}$]
$I_{p,\nu}^{\text{out}}$	Spectral radiative intensity exiting cell intersection p [$\text{W m}^{-2} \text{sr}^{-1} \text{Hz}^{-1}$] or [$\text{W m}^{-2} \text{sr}^{-1} \text{cm}$]
$\mathbf{J}$	Mass diffusion flux vector [$\text{kg m}^{-2} \text{s}^{-1}$]
$\mathbf{j}$	Cartesian basis vector $(0, 1, 0)$ [-]
J	Energy level index [-]
j_ν	Spectral emission coefficient [$\text{W m}^{-3} \text{sr}^{-1} \text{Hz}^{-1}$] or [$\text{W m}^{-3} \text{sr}^{-1} \text{cm}$]
$\mathbf{k}$	Cartesian basis vector $(0, 0, 1)$ [-]
k_b	Backward reaction rate coefficient [$\text{mol m}^{-3} \text{s}^{-1}$]
K_c	Equilibrium constant based on concentrations [-]
k_f	Forward reaction rate coefficient [$\text{mol m}^{-3} \text{s}^{-1}$]
k_{neq}	Reaction rate coefficient corrected for thermal non-equilibrium [$\text{mol m}^{-3} \text{s}^{-1}$]
k	Total thermal conductivity coefficient [$\text{W m}^{-1} \text{K}^{-1}$]
k_k	Thermal conductivity coefficient associated with thermal mode k [$\text{W m}^{-1} \text{K}^{-1}$]
k_{tr}	Translational contribution to the thermal conductivity coefficient [$\text{W m}^{-1} \text{K}^{-1}$]
k_{rot}	Rotational contribution to the thermal conductivity coefficient [$\text{W m}^{-1} \text{K}^{-1}$]
k_{vib}	Vibrational contribution to the thermal conductivity coefficient [$\text{W m}^{-1} \text{K}^{-1}$]
k_{exc}	Electronic excitation contribution to the thermal conductivity coefficient [$\text{W m}^{-1} \text{K}^{-1}$]
L	Ray length [m]
Le	Lewis number [-]
$\mathcal{M}$	Molar mass [kg mol^{-1}]
M	Total mass [kg]
m	Particle mass [kg] or exponent used in expression for Stark FWHM of a transition [-]
M	General colliding species or number of cells in tangential direction [-]
Ma	Mach number [-]
$\mathbf{n}$	Normal direction vector [-]
$\mathcal{N}$	Number of moles [mol]
N	Total number density [particles m^{-3}] or number of cells in normal direction [-]
n	Number of particles or exponent used in expression for Stark FWHM of a transition [-]

N_s	Total number of species [-] or species' number density [particles m ⁻³]
$N_{\bar{\nu}}$	Number of wavenumber intervals [-]
N_{FL}	Number of points in Fibonacci Lattice [-]
N_{mol}	Number of molecular species [-]
n_u	Main quantum number of the upper state [-]
N_c	Number of colliding species [-]
N_J^*	Boltzmann population distribution function (thermodynamic equilibrium) [-]
N_r	Number of rays in ray-tracing directional integration [-]
p	Pressure [Pa]
p_s	Partial pressure due to species s [Pa]
$\mathbf{q}_c$	Conduction heat flux vector [W m ⁻²]
$\mathbf{q}_{\text{rad}}$	Radiative heat flux vector [W m ⁻²]
$\mathbf{q}$	Heat flux vector [W m ⁻²]
Q	Partition function [-]
q	Exponent in generalized Park model for non-equilibrium chemical kinetics [-]
q^-	Wall-directed radiative heat flux [W/m ²]
$q^{\theta,\phi}$	Directional radiative heat flux [W m ⁻² sr ⁻¹]
$q_{0,\nu}$	Spectral radiative heating (at wall) [W m ⁻² Hz ⁻¹] or [W m ⁻² cm]
q_{rad}	Magnitude of radiative heat flux vector [W m ⁻²]
q_{ν}	Spectral radiative heat flux [W m ⁻² Hz ⁻¹] or [W m ⁻² cm]
q_{ν}^+	Upstream-directed spectral radiative heat flux [W m ⁻² Hz ⁻¹] or [W m ⁻² cm]
q_{ν}^-	Wall-directed spectral radiative heat flux [W m ⁻² Hz ⁻¹] or [W m ⁻² cm]
$q_{\nu}^{\theta,\phi}$	Spectral directional radiative heat flux [W m ⁻² sr ⁻¹ Hz ⁻¹] or [W m ⁻² sr ⁻¹ cm]
R	Specific gas constant [J mol ⁻¹ K ⁻¹]
r_e	Equilibrium distance in Pirani's phenomenological potential approach [Å]
R_n	Nose radius [m]
$\mathbf{s}$	Arbitrary direction vector [-]
s	Coordinate normal to body wall [-] or distance along body wall [m]

$s^{(i)}$	Normal distance to wall at cell-center i in tangent-slab computational implementation [m]
s'	Coordinate between upstream boundary and a point in the computational domain at an angle θ [-]
Sc	Schmidt number [-]
t	Time [s]
$T_{\bar{\nu}}$	Spectral transmittance coefficient [-]
T	Temperature [K]
T_k	Temperature associated with thermal energy mode k [K]
T_{tr}	Translational temperature [K]
T_{rot}	Rotational temperature [K]
T_{vib}	Vibrational temperature [K]
T_{el}	Translational temperature of electrons [K]
T_{exc}	Electronic excitation temperature [K]
$T_{\text{tr-rot}}$	Translational-rotational temperature [K]
T_{ve}	Vibrational-electronic-electron temperature [K]
T_{e}	Electron-electronic excitation temperature [K]
T_{v}	Vibrational temperature [K]
T_{c}	General controlling temperature [K]
$T_{f,c}$	Forward rate-controlling temperature in Arrhenius equation [K]
T^*	Reduced temperature in Wright <i>et al.</i> 's curve-fits for charged-species CCSs [-]
$\mathbf{V}$	Velocity vector [m s^{-1}]
v	Velocity magnitude [m s^{-1}]
V	Volume [m^3]
$\dot{w}$	Mass source term [$\text{kg m}^{-3} \text{s}^{-1}$]
w_r	Weight associated with a given ray r [-]
x	Mole fraction [-]
$x_{2\text{D}}$	Transformed coordinate x in two-dimensional domain [m]
$x_{3\text{D}}$	Coordinate x in three-dimensional domain [m]

$[X]$	Species concentration $[\text{mol m}^{-3}]$
X'	Reactant [-]
X''	Product of reaction [-]
$\bar{y}_{2D}$	Transformed coordinate y in two-dimensional domain [m]
y_{3D}	Coordinate y in three-dimensional domain [m]
Z	Correction factor for non-equilibrium reaction rates [-]
z	Normal distance between wall and a point in the computational domain [m]
z'	Distance between upstream boundary and a point in computational domain at angle θ [m]
z_{3D}	Coordinate z in three-dimensional domain [m]
z_{∞}	Normal distance between wall and upstream computational boundary [m]

Subscripts

A	Avogadro
av	Averaged value
B	Boltzmann
c	Colliding species index
ch-ex	Charge-exchange contribution
e^-	Free electron
e	Electron-electronic modes considered thermalized
el	Electron's translational mode contribution or elastic contribution
exc	Electronic excitation mode contribution
k	Thermal mode index
l	Lower energy level
mol	Molecular species
$\bar{\nu}$	Quantity measured in wavenumber units
ν	Quantity measured in frequency units
neq	Non-equilibrium condition
r	Reaction index or ray index
rad	Radiative term

rot	Rotational mode contribution
<i>s</i>	Species index
tr – rot	Translational-rotational modes considered thermalized
tot	Total contribution
tr	Translational mode contribution
u	Upper energy level
v	Vibrational mode considered separately
V-T	Vibration-Translation energy exchange
ve	Vibrational-electronic modes considered thermalized
vib	Vibrational mode contribution

Superscripts

*	Equilibrium or excited condition
MW	Millikan-White
T	Transpose matrix

Acronyms

ARAD	Analog Resistance Ablation Detector
CCS	Collision Cross-Section
CFD	Computational Fluid Dynamics
DPLR	Data Parallel Line Relaxation
EAST	Electric Arc Shock Tube
FWHM	Full Width at Half Maximum
HARA	Hypersonic Air Radiation Algorithm
HTGR	High Temperature Gas Radiation database
IPFN	Instituto de Plasmas e Fusão Nuclear
LAURA	Langley Aerothermodynamic Upwind Relaxation Algorithm
NASA	National Aeronautics and Space Administration
OOP	Object-Oriented Programming
RMS	Root Mean Square

SB	Stark Broadening
SPARK	Software Package for Aerothermodynamics, Radiation and Kinetics
SPARK LbL	Software Package for Aerothermodynamics, Radiation and Kinetics Line-by-Line
TPS	Thermal Protection System
VSL	Viscous Shock Layer
VUV	Vacuum Ultra-Violet

Glossary

Ablation	Ablation in the context of spacecraft refers to the erosion of material from its surface by processes such as spallation, sublimation and vaporization.
Boltzmann Distribution	The Boltzmann distribution describes the distribution of energy within a system of particles under thermodynamic equilibrium.
CFD	Computational Fluid Dynamics is a branch of fluid mechanics that uses numerical methods and algorithms to solve problems that involve fluid flows.
Fortran	Fortran is a compiled programming language suited for high-performance scientific computing.
Hypersonic	A flight regime generally above Mach 5 characterized by the strong presence of high-temperature effects.
NASA9	A set of coefficients compiled by Gordon and McBride at NASA for calculating thermodynamic properties of individual species (specific heats, enthalpy and entropy) using polynomial curve-fit expressions.
OOP	Object-Oriented Programming is a programming paradigm that relies on the concept of objects, entities that encapsulate data and the functions that operate on that data. A hierarchical structure emerges as a result of objects being able to inherit certain attributes from one another.
Shock Tube	A shock tube is a device intended for studying high temperature compressible flows by inducing the propagation of a shock wave through a tube and analyzing the ensuing flow.

Spallation	Spallation is an erosive process that results in the ejection of small fragments of material due to impact or stress.
Stark Broadening (SB)	Line broadening in spectroscopy is the spreading of absorption or emission lines across a greater wavelength range. Stark broadening, in particular, results from the effects of external electric fields induced by charged particles in plasma flows. The energy associated with an electronic transition may increase or decrease if the electric field is oriented in such a way (relative to the bound electrons) so as to strengthen or weaken the electronic bond, respectively. In turn, this causes a frequency shift according to Planck's relation, ultimately leading to a broadened line.
State-to-State	State-to-State is an approach in the field of chemical kinetics that regards the internal energy levels of the chemical species as independent pseudo species.
Sublimation	Sublimation is a phase transition of a substance directly from its solid to its gaseous form, without it becoming liquid in the process.
TPS	A vehicle's TPS (Thermal Protection System) is a protective layer of material designed to either directly reduce the heat fluxes by using low catalycity surface materials (reusable TPS), or to promote material ablation in a controlled manner, thus cooling the surface and leading to the creation of an ablation layer that protects the surface.

CHAPTER 1

Introduction

“... the heritage of mankind is not the Earth, but the entire universe ... ”

Pierre Boulle, *Garden on the Moon* (1999)

1.1 Hypersonic Flight - An Overview

Hypersonic flight, typically defined as the flow regime where $Ma > 5$, has experienced significant development in the 20th century, mainly driven in its early stages by military interests on ballistic missile applications. In this flight regime, the so-called high-temperature effects become important. These phenomena include dissociation and ionization of chemical species, non-equilibrium thermo-chemistry and radiative emission due to atomic and molecular de-excitation, to state a few. Under these conditions, the Mach number loses its usefulness, and one is better off speaking in terms of flight velocity instead [1].

As a spacecraft enters a planet's atmosphere from its hyperbolic trajectory, its velocity is typically above 2 km s^{-1} and may reach up to 50 km s^{-1} , as was the case for Galileo, depending on the planet's gravitational pull. As the vehicle's speed is higher than that of sound itself, a strong shock wave forms upstream of the spacecraft's forebody, converting most of its kinetic energy into thermal energy, which is deposited in the atmosphere along its path. Blunt-body designs are typically preferred since the resulting detached bow-shocks are stronger and dissipate more energy. However, this also means the spacecraft will be engulfed in a high-temperature gaseous environment and will be experiencing extreme heating, coming mostly from two contributions: convective heating from direct interaction between the vehicle's surface and the gas particles, and radiative heating from absorption of electromagnetic radiation emitted in the high-temperature shock layer. A thermal protection system (TPS) is therefore a requirement to ensure the spacecraft's survival upon entry. Both reusable and ablative TPS exist, although the former is limited to mild aerothermal conditions. The shape of the TPS varies from spherical sections (Apollo-era) to sphere-cones (Galileo probe), and its nose-bluntness can be shown to significantly affect the heat transfer to the vehicle. While higher nose-bluntness (higher nose radius) decreases convective heat fluxes, the opposite is true for radiative fluxes, ultimately leading to a mission-based compromise.

The extreme temperatures present in the shock layer, imposed by the strong shock wave that forms upstream of the spacecraft, are sufficiently high to excite the typically dormant internal energy modes of the particles composing the gas (vibrational and electronic excitation modes, particularly), making

them more easily accessible reservoirs for thermal energy storage. These excitation processes occur mainly through inter-particle collisions, relaxing the translational energy mode¹ in favor of exciting the internal ones. Molecules quickly store large amounts of vibrational energy, until inter-nuclear bonds are overcome and dissociation takes place. In the meantime, bound electrons are also brought to excited configurations as a result of collisions, and the gas starts to emit electromagnetic radiation as the electrons spontaneously decay to less energetic states [2]. Similar to dissociation, the bound electron may even escape the parent nuclei's attraction, provided a sufficiently energetic collision occurs, leading to ionization.

Additionally, the characteristic flow times under such high speeds are typically close to those characterizing both chemical reactions and the collisional processes described in the previous paragraph. In simpler terms, this means that the time it takes for the flow to adapt to the extreme post-shock conditions on a microscopic level is comparable to the time spent by the particles in the vicinity of the vehicle, meaning this *relaxation* occurs as the particle traverses the flow region of interest. The species composing the flow are chemically reacting, trying to attain a minimized energy configuration (equilibrium), and their internal energy states are populated according to non-Boltzmann distributions. Under such conditions, the flow is said to be in thermo-chemical non-equilibrium. Clearly, this non-equilibrium must be somehow modeled in order to accurately solve the mass, momentum and energy equations.

The effects of some of these phenomena are represented in Figure 1.1, which illustrates the flowfield surrounding the Galileo probe as seen from its reference frame. As the particles approach the shock wave, precursor heating promoted by radiation emitted from the hot shock layer induces pre-photo-ionization and pre-photo-dissociation, an effect which is often neglected. Across the shock, translational, rotational and vibrational excitation is significant, leading to dissociation. Electronic excitation eventually leads to ionization and electron-ion pairs are produced. A thermal equilibrium region is eventually established once the relaxation promoted by collisions is sufficient to induce internal Boltzmann distributions. Additionally, the shock layer itself is a source/sink for electromagnetic radiation, resulting in non-adiabatic energy transfer at light speed. As the plasma is swept into the high-density boundary layer, the temperature drops and some recombination occurs. Despite this, the heating environment is still severe enough to result in TPS erosion, forming an ablation layer of carbonaceous species over the surface.

The Achille's heel of hypersonic flight is the difficulty in obtaining ground-based experimental data. Besides being expensive, wind tunnel and shock tube facilities cannot simulate free flight conditions. Hence, scientists rely on reliable extrapolation of ground-based data to flight conditions with support of numerical models, which are of crucial importance to bridge the gap between the two. The present work aims at using these numerical tools to shed some light on the flight conditions experienced by the Galileo probe during entry in Jupiter's atmosphere, on December 1995.

1.2 The Galileo Mission

Jupiter is one of the most remarkable planets in our Solar System. Aside from its large size, Jupiter has 53 confirmed moons, the most important of which are Callisto, Europa, Ganymede and Io. The Galileo

¹The conventional temperature of a gas is a direct measure of its translational energy.

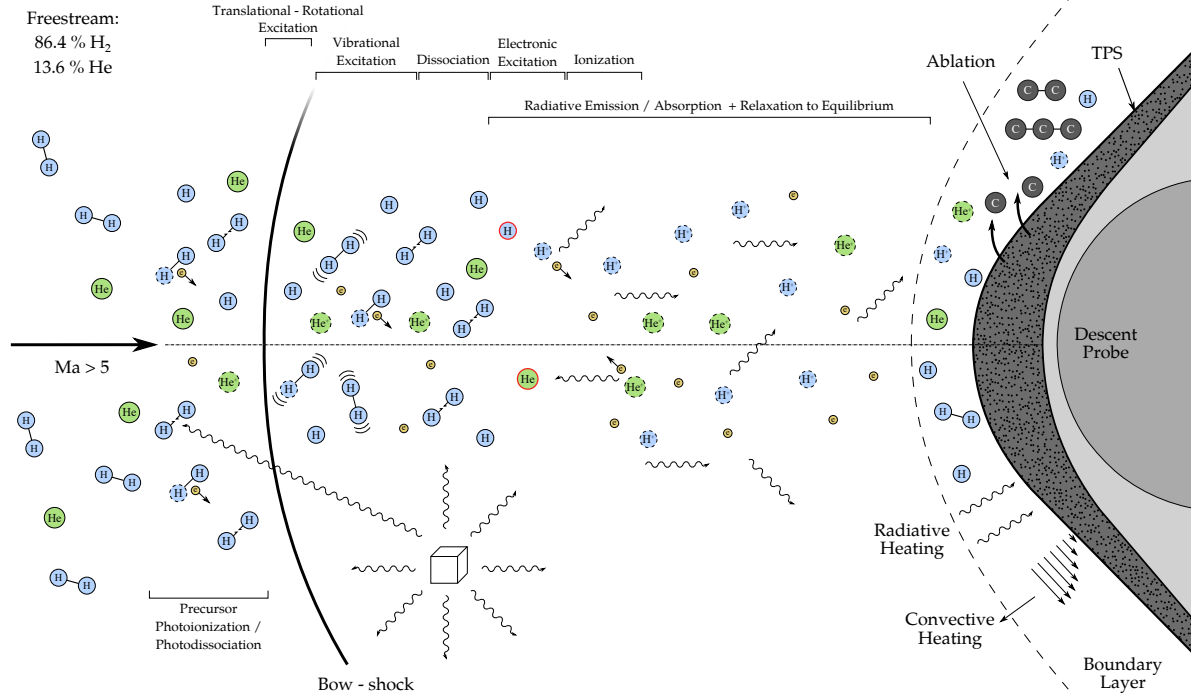


Figure 1.1: Illustration of high-temperature effects in Galileo's reference frame.

mission was devised to help understand the formation of the Solar System, by studying the giant planet's atmospheric composition, structure and its moons.

To accomplish this, the Galileo orbiter was sent aboard the cargo bay of Space Shuttle Atlantis on October 18, 1989, carrying a descent probe designed to penetrate the Jovian atmosphere with a set of scientific instruments. After a six year orbit through the Solar System, the probe separated from the orbiter about 150 days before encountering the sensible atmosphere of Jupiter and, on December 7, 1995, it officially began its descent at a relative velocity of 47.4 km s^{-1} . During a 30 second period, the probe decelerated from Mach 50 to under Mach 1, having reached a maximum deceleration of 250 g, while experiencing peak heating rates exceeding 300 MW m^{-2} [3, 4]. This extreme entry environment led to a total forebody ablation of over 80 kg, almost half the probe's TPS initial mass [4, 5]. The heating environment experienced by the probe during its descent remains, until today, one of the most severe ever encountered by a planetary entry capsule.

The sphere-cone geometry of the probe's TPS is shown in Figure 1.2. The 339 kg probe was equipped with 10 ablation sensors (ARAD, A_{1-10}) and four resistance thermometers (T_{1-4}) for collecting data during entry. After sufficient deceleration, the probe released its parachute, detached its heat shields, and began a 58 minute descent while gathering scientific data on the atmosphere's composition, location and structure of the clouds and the local radiative field. The collected data was successfully sent to the spacecraft overhead and then transmitted back to Earth. The probe ultimately melted and vaporized, due to the intense atmospheric pressure at lower altitudes.

Although the mission was a success, the post-flight data analysis revealed how close the entry probe's TPS came to completely ablate near the shoulder [8]. Despite the efforts undertaken during pre-flight mission preparation to simulate the flowfield around the vehicle, the predictions have since been confirmed

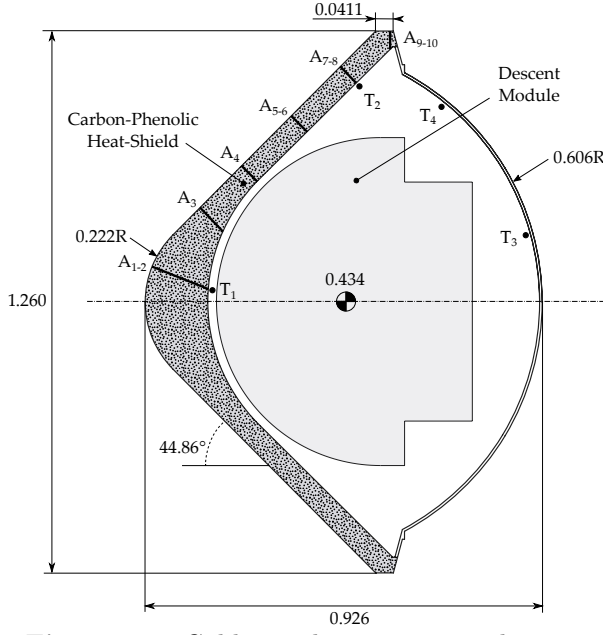


Figure 1.2: Galileo probe geometry and sensor locations.

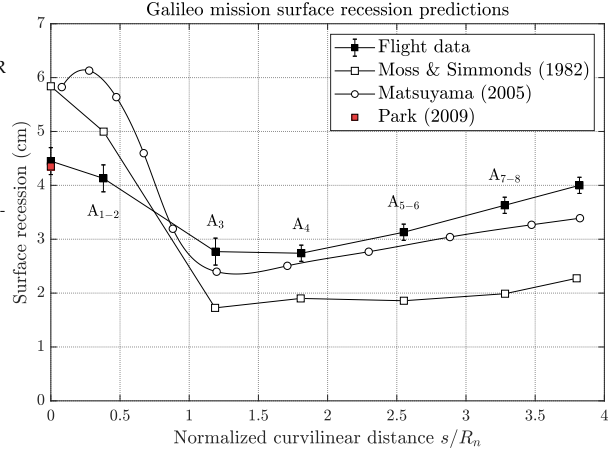


Figure 1.3: Predicted heat shield recession comparison [4, 6, 7].

to present large discrepancies with flight data, mainly when it comes to the predicted recession of the heat shield. This has spurred a revival of research aimed at understanding the causes for these disparities, while at the same time increasing the confidence on future predictions regarding TPS sizing. This will allow scientists and engineers to redirect part of the heat shield's mass into scientific equipment, increasing the available payload and cost-effectiveness of future missions.

1.2.1 Mission Preparation and Flight Data Treatment

Numerical simulations have been an essential tool for the predictions involving the Galileo mission, due to the limitations in providing ground-based experimental simulations on the extreme heating environment experienced by the probe. This meant that most of the mission preparation relied on numerical results, for which data on H_2 –He mixtures had to be provided. The typical way of studying the thermo-chemical non-equilibrium processes occurring under such high-temperature conditions is to examine the time history of the radiation emitted by the gas behind a generated shock-wave, for which specialized facilities exist around the world.

Two sets of ground-based experiments conducted independently have previously studied the chemical kinetics of H_2 –He mixtures. In 1972, Leibowitz performed electric arc driven shock tube experiments on such mixtures, having explored shock velocities ranging from 13 to 20 km s^{-1} [9]. Similar experiments were conducted by Livingston and Poon in 1976 with shock velocities between 26 and 46 km s^{-1} [10]. Both studies assessed the ionization relaxation processes between atomic hydrogen and electrons in the high-temperature shock layer downstream of the shock-wave, and recommended expressions for the chemical kinetic rates in agreement with the experimental measurements were provided[11]. These old experiments are still used today for the validation of theoretical models, emphasizing the value attributed to experimental ground testing.

More recently, shock tube experiments conducted in the Electric Arc Shock Tube (EAST) at the NASA Ames Research Center investigated the shock speed range from 20 to 30 km s⁻¹ [12]. A sudden increase in radiance for speeds above 25 km s⁻¹ was observed to coincide with an increase in electron density and effective electronic temperature, which gradually build up over the width of the shock. As a result, planetary entries to Uranus or Saturn, where entry velocities shouldn't exceed 27 ~ 28 km s⁻¹, are not expected to sustain severe radiative heating compared to convective heating. However, the same cannot be said about entry in Jupiter, where relative velocities reach around 46 km s⁻¹.

Using the valuable data collected in the older experiments, several pre-flight numerical predictions were obtained. Moss and Simmonds performed extensive simulations during the mission preparation phase [6, 13–15]. These ranged from Viscous Shock Layer (VSL) [1] to Navier-Stokes solutions, studying the effects of distinct physico-chemical processes taking place, such as turbulence, ablation, spallation and wall reflectivity, all under the assumption of chemical equilibrium. Tiwari and Szema also studied the role of thermo-chemical non-equilibrium and precursor heating in Galileo's entry [16], having found a significant increase in both convective and radiative heating relative to an equilibrium solution. The influence of precursor heating is enhanced due to non-equilibrium conditions, and radiative heat fluxes at the stagnation point were found to increase by 10% when this phenomenon was modeled.

After the mission's success, the flight data regarding the heat shield ablation and temperature captured by the sensors during descent was analyzed by Milos *et al.* [4]. The actual heat shield recession along the wall is shown in Figure 1.3, where a comparison is also provided on the numerical recession predicted by other authors. Moss and Simmonds' pre-flight predictions highlight the classical trend observed for the Galileo mission: the nose recession is largely overpredicted, while the opposite is true in the frustum region. This trend translates the heat fluxes experienced by the probe's surface, which lead to ablation, spallation and sublimation of the probe's TPS.

1.2.2 Numerical Reproduction of Flight Data

Since the publication of the data gathered by Galileo, several authors have tried to numerically replicate the descent probe's heat shield recession.

Among the first to have done so, Matsuyama *et al.* performed coupled radiative transfer simulations assuming thermo-chemical equilibrium, while assessing the influence of a tangent-slab approximation against an accurate ray-tracing approach for radiative transfer calculations [17]. Given the reduced computational resources back in 2002, a multi-band model containing just 570 important wavelengths was employed in the spectral radiation calculation, indeed a small sample when compared to a detailed line-by-line computation. Nevertheless, the ray-tracing approach was found to predict a 10% lower stagnation point radiative heating when compared to the tangent-slab approach.

In 2005, the same authors studied the effects of turbulence coupled with the injection of ablation products near the wall [7], using a modified version of the Baldwin-Lomax turbulence model proposed by Park [18]. This time, a tangent-slab analysis was conducted using 4,781 wavelengths in the range 750 to 15,000 Å. It was found that weaker absorption of radiation caused by increased turbulence-induced diffusion in the shoulder allows for a better prediction of the recession in this region, as their results attest

in Figure 1.3.

Subsequently, Furudate *et al.* studied the effects of thermo-chemical non-equilibrium using Euler’s equations and the tangent-slab approximation for radiation [19]. By using an improved model for the kinetic rates of atomic hydrogen ionization proposed by Park [20], it was found that non-equilibrium effects could reduce the predicted radiative heat fluxes in the stagnation region by as much as 10%. However, the same study predicted post-shock temperatures as high as 50,000 K, about 60 to 100% higher than those predicted by other authors, present work included.

Park also studied the effect of spallation in radiative absorption near the stagnation point under chemical equilibrium conditions [21]. Radiation calculations were performed using 10,001 wavelengths, accounting for detailed radiative systems from carbonaceous species resulting from spallation of the heat shield. Comparison of the uniform slab result with a coarse ray-tracing approach resulted in differences lower than 1%. However, Park only considered nine lines of sight in the ray-tracing approach, which, as will be shown, is a rather low number and may have misled the author into concluding both methods provide similar results. Nonetheless, Park reported good agreement with the flight data on the stagnation region recession (see Figure 1.3), provided the effects of spallation and inclusion of vacuum ultraviolet (VUV) bands for C₂ and C₃ species were incorporated in the radiative analysis.

More recently, Reynier *et al.* compiled the state-of-the-art in the modeling of giant-planet atmospheres (H₂–He) for convective heating predictions, and reviewed previous attempts in simulating the Galileo entry [3, 22]. Additionally, three distinct models differing in chemical kinetics, thermodynamics and transport databases were developed and compared with previous calculations. The increasing level of detail provided by the improved databases, which are supported by state-to-state kinetic studies that have been subject to research in recent years, is shown to decrease the convective component of the wall heat fluxes by between 70% and 85% when compared to older estimates.

Table 1.1 summarizes the past numerical predictions regarding Galileo’s entry in Jupiter. It should

Table 1.1: Summary of computational predictions found in the literature regarding Galileo’s entry.

Source	Radiation Modeling	Wall Location	Spectral Range (Å)	Radiative Systems	Trajectory Point Altitude (km)	Convective Heating (MW m ⁻²)	Radiative Heating (MW m ⁻²)
Moss, Simmonds [6] (1978)	TS	SP	NA	H, H ⁺ , H ₂ , e ⁻	184.50	80.00	40.00
					166.60	107.00	101.00
					132.20	150.00	446.00
					123.9	154.00	512.00
Matsuyama [17] (2002)	TS, Coupled	SP	500 – 15,000	H, H ⁺	184.50	83.00	64.00
					166.60	116.00	123.00
					132.20	189.00	360.00
					123.90	194.00	438.00
	TS, Coupled RT, Coupled	SP	500 – 15,000	H, H ⁺	114.10	185.00	452.60 407.60
Matsuyama (2005) [7]	TS, Coupled	SP	750 – 15,000	H, H ⁺ , C, C ₂ , C ₃ , O, O ₂ , CO	130.00	NA	242.00
Park [21] (2009)	TS	SP	400 – 24,000	H, C, C ⁺ , C ₂ , C ₃	190.00	4.18	20.31
					170.00	2.28	37.07
					130.00	1.38	146.80
Reynier [3] (2018)	-	-	-	-	180.00	105.00	-
					130.00	255.00	-
					180.00	14.70	-
					130.00	81.60	-
					180.00	18.90	-
NA: Not Available TS: Tangent-Slab SP: Stagnation Point RT: Ray-Tracing -: Not Applicable							

be noted that all previous studies which take into account the radiation field only considered radiative mechanisms from H (and H^+) when it comes to the atmospheric species present in the flowfield². The effect of He lines and H_2 bands, for example, remains unaccounted for, even though their presence in the mixture is not negligible. Moreover, the true three-dimensional character of radiative transport is rarely included, and modeling of transport properties has, until now, relied on Wilke’s mixing rules, despite their poor accuracy at high temperatures. Furthermore, thermo-chemical equilibrium is often assumed. While thermal equilibrium may be a good approximation at the lower altitudes, where the atmospheric density is sufficiently high to rapidly induce equilibrium, chemical non-equilibrium is still present throughout the flowfield. This is the case for the higher altitude trajectory point focused in the present work, where both processes are in strong non-equilibrium. Hence, a thorough study of these effects is still lacking for understanding the unresolved mysteries regarding the Galileo entry.

1.3 Objectives

The present work aims at understanding the causes for the discrepancies mentioned in the previous section regarding the entry of Galileo in Jupiter’s atmosphere. Accordingly, a set of thorough sensitivity studies regarding the modeling of different phenomena that have been either neglected or poorly modeled in the past has been conducted. The purpose of these analyses is not to obtain an accurate estimate of the actual heating environment experienced by the probe during flight, since some important phenomena such as ablation, flowfield-radiation coupling and precursor heating have only been taken into account in an approximate decoupled fashion. Rather, the intention is to improve the understanding and assess the impact of the modeling of important physical processes in a controlled manner.

Specifically, the impact of the following physical processes/modeling strategies will be assessed: calculation of transport properties (viscosity, thermal conductivity and diffusion coefficients) using the traditional Wilke/Blottner/Eucken transport model or the Gupta/Yos model, more suited to high temperatures and ionization levels; thermo-chemical non-equilibrium effects; importance of modeling He and H_2 radiation; comparison of tangent-slab and ray-tracing approaches for the computation of radiative heat transfer. This is accomplished by first solving for the flowfield using the SPARK solver, after which the radiative field is computed using the SPARK Line-by-Line (SPARK LbL) radiative code as a post-processing step.

In the process, the capabilities of both codes have been extended and improved. First, the numerical module responsible for computing the transport properties of the gas in SPARK has been re-structured. In the past, only Earth’s atmosphere could be simulated using the Gupta/Yos transport model. However a database redesign using recently published collision cross-section (CCS) data now extends this capability to all planets in the Solar System. Furthermore, the radiative transfer module in SPARK LbL has been rebuilt from scratch using Fortran Object-Oriented Programming (OOP) techniques, allowing tangent-slab and ray-tracing computations to be performed much more efficiently when compared to the old Matlab routines implemented. This upgrade to both codes was deemed necessary so as to perform the desired

²Moss and Simmonds also include H_2 , but the equilibrium assumption used suppresses the effects it would otherwise have, as will be discussed.

sensitivity studies, while also providing an extension to the capabilities of both numerical libraries.

1.4 Thesis Outline

This dissertation is divided into five main chapters. The present Chapter 1 was intended to introduce the reader to the concept and challenges experienced during hypersonic flight. An introduction to the Galileo mission and an overview of the past works on its behalf were also presented.

In Chapter 2, the mathematical formulation used to model the complex phenomena occurring in the high-temperature shock layer is explored. This Chapter is divided into two main topics: flowfield and radiation modeling. Thermodynamic, kinetic and transport property calculations are detailed in the first, while the second deals with the radiative transfer equation and its solution strategies.

Chapter 3 bridges the gap between the theoretical treatment described in Chapter 2 and its practical implementation in the numerical codes used. An overview of the databases used to model Jupiter's atmosphere is presented, together with the numerical framework for transport in SPARK and the computational radiative transfer formulation in SPARK LbL, both implemented in the present work.

Finally, Chapter 4 presents and summarizes the results obtained. In Chapter 5 the main conclusions of the present work are drawn, and an overlook for future work regarding the Galileo mission is provided.

CHAPTER 2

Mathematical Formulation

This chapter presents the groundwork for understanding the high-temperature effects present in hypersonic flows. A fluid-dynamic description of the flow is exposed, following an introduction to radiative phenomena - another layer of complexity and uncertainty in the modeling of high-speed entry flows.

2.1 Fluid Dynamics of Hypersonic Flows

Here the fundamental models governing the simulation of hypersonic atmospheric flows are presented. The multi-species chemically reacting flow is modeled by neglecting intermolecular forces, present at the microscopic level, and assuming a continuum medium, allowing the use of the Navier-Stokes equations. These equations are presented in a form suitable for hypersonic flow in § 2.1.1.

The solution of the Navier-Stokes equations relies on the accurate modeling of several thermodynamic properties of the gas. Statistical thermodynamics is the classical theory developed for the fundamental understanding of these properties at a microscopic level. Several explicit formulas emerge from the theory allowing the calculation of thermodynamic properties previously known only from experiment. Furthermore, due to the violent nature of hypersonic flows, the microscopic collision times start to become noticeable when compared to a characteristic flow time, leading to non-equilibrium phenomena. These and other aspects regarding the thermodynamic properties of high temperature chemically reacting mixtures are presented in § 2.1.2 and detailed in Appendix A.

Furthermore, as a result of the high temperatures achieved in such flows, the energy involved in particle collisions is sufficient to break chemical bonds and induce chemical reactions, leading to chemical non-equilibrium. Proper modeling of these interactions is the subject of § 2.1.3, entitled after the discipline of chemical kinetics. Finally, transport phenomena is of the essence in Navier-Stokes' equations, and the accurate calculation of the transport properties of the flow is not a closed subject. Several models used to approximate these properties are discussed in § 2.1.4.

2.1.1 Governing Equations for Radiating Shock Layers

The compressible Navier-Stokes equations suitable for hypersonic flows are obtained by applying the equation of continuity to the conserved quantities of the flow, under the assumption of a continuum flow regime. These conserved quantities depend on the degree of thermo-chemical non-equilibrium considered,

but generally consist of the mass, momentum and energy of the mixture when thermo-chemical equilibrium is assumed. For planetary entry conditions, however, an accurate description of the flow requires the inclusion of non-equilibrium effects, both chemical and thermal. When chemical non-equilibrium is considered, mass conservation of each species must be enforced individually. In turn, under conditions of thermal non-equilibrium, each independent thermal mode's energy must be conserved.

The governing equations for hypersonic radiating shock layers are:

$$\frac{\partial(\rho c_s)}{\partial t} + \nabla \cdot (\rho c_s \mathbf{V}) = \nabla \cdot \mathbf{J}_s + \dot{w}_s \quad (2.1a)$$

$$\frac{\partial(\rho \mathbf{V})}{\partial t} + \nabla \cdot (\rho \mathbf{V} \otimes \mathbf{V}) = \nabla \cdot [\boldsymbol{\tau}] - \nabla p \quad (2.1b)$$

$$\frac{\partial(\rho e)}{\partial t} + \nabla \cdot (\rho \mathbf{V} e) = \nabla \cdot (\mathbf{V} \cdot [\boldsymbol{\tau}]) - \nabla \cdot (p \mathbf{V}) - \nabla \cdot \mathbf{q} , \quad (2.1c)$$

where the heat flux vector is defined as

$$\mathbf{q} = - \sum_k k_k \nabla T_k + \sum_s \mathbf{J}_s h_s + \mathbf{q}_{\text{rad}} . \quad (2.1d)$$

In addition to these equations, an additional energy conservation equation for each non-equilibrium thermal mode considered must be solved, that is

$$\frac{\partial(\rho e_k)}{\partial t} + \nabla \cdot (\rho \mathbf{V} h_k) = \nabla \cdot \left(-k_k \nabla T_k + \sum_s \mathbf{J}_s h_{s,k} \right) + \dot{\Omega}_k . \quad (2.1e)$$

In Eqs. 2.1a - 2.1e, ρ is the density, c_s is the species mass fraction, $\mathbf{V}$ is the flow velocity vector, $\mathbf{J}_s$ represents the mass diffusion flux vector, $\dot{w}_s$ is the source term for production/destruction of species s , $[\boldsymbol{\tau}]$ is the viscous stress tensor, p is the pressure, e is the specific internal energy of the mixture, k_k and T_k are the thermal conductivity and temperature associated with the thermal energy mode k , h_s is the species enthalpy, $\mathbf{q}_{\text{rad}}$ is the radiative heat flux vector and, finally, e_k and $\dot{\Omega}_k$ are the internal energy and energy-exchange source term associated with thermal energy mode k .

2.1.2 Thermodynamic Properties

The accuracy of the solution of the Navier-Stokes equations presented above will reflect the degree of uncertainty embodied in the thermodynamic properties assumed for the gas. In essence, a microscopic description of the gas is fundamental for the understanding of the thermal behavior of a chemically reacting mixture.

Statistical thermodynamics is the classical theory providing the tools for explicitly calculating the thermodynamic properties of a gas - internal energy, enthalpy, entropy, etc. The theory assumes the gas to be a collection of particles (atoms, molecules, ions and electrons), each of which carrying energy as it moves through the flow. This energy content is segregated into four energy modes, which may be thought of as different reservoirs for thermal energy. Depending on the particle type (atomic, molecular or electron), these can be: translational, rotational, vibrational and electronic energies¹. While atomic

¹The rotational, vibrational and electronic energy modes are commonly referred to as internal modes.

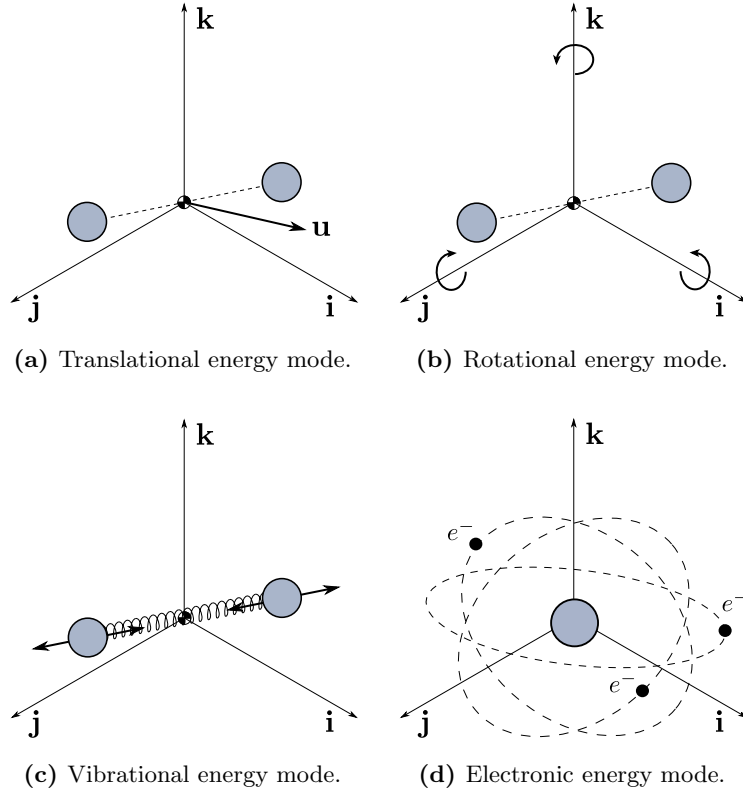


Figure 2.1: Representation of the different energy modes.

particles may only have translational and electronic energies, molecules can possess all forms of thermal energy due to the relative motion of its composing elements. Free electrons, on the other hand, only possess translational kinetic energy. Figure 2.1 illustrates the different energy modes associated to a given particle's energy level.

As a molecule or atom moves through space, its center of mass acts as a source of translational kinetic energy. Since each component of its velocity can attain any value, it is said to have three translational degrees of freedom. Similarly, a molecule's rotation in space can be decomposed into three Cartesian components, each amounting to some energy stored as rotational energy depending on the molecule's moments of inertia about the corresponding axis. Diatomic molecules, illustrated in Figure 2.1b, tend to possess a low moment of inertia about the internuclear axis, and thus only have two rotational degrees of freedom. Furthermore, the atoms of a molecule vibrate relative to an equilibrium position within the molecule. Depending on whether the molecule is diatomic or polyatomic, this vibrational motion can add one or more internal degrees of freedom to the system. Finally, the complex motion of the electrons orbiting the atoms or molecules adds yet another energy storage mode, though the concept of thermal degrees of freedom is not useful in this case.

Hence, in general, the total energy of a particle can be decomposed as²

$$\varepsilon_{\text{tot}} = \varepsilon_{\text{tr}} + \varepsilon_{\text{rot}} + \varepsilon_{\text{vib}} + \varepsilon_{\text{exc}} + \varepsilon_0, \quad (2.2)$$

²This decomposition is a result of extending the Born-Oppenheimer approximation, which states that the electronic motion can be separated from that of the nucleus, to all energy modes. As a result, its energy contributions can be considered as separate components.

where ε_k corresponds to the contributions from different energy modes and ε_0 is the zero-point energy of the species. In a mixture, each energy level - which can be degenerate³ - is populated with a certain number of particles. The population distribution across all energy levels associated with an equilibrium mixture - the Boltzmann distribution N_J^* - is the one that maximizes the entropy of the system. From a macroscopic viewpoint, the internal energy of a single-species equilibrium system is obtained by adding the contributions of all energy levels over the population distribution, that is,

$$E = \sum_J \varepsilon_J N_J^*(\varepsilon_J). \quad (2.3)$$

Each of these energy modes is quantized, and the classical theory of statistical thermodynamics provides an explicit means to calculate each energy mode ε_k . Since the population distribution N_J^* itself depends on the energy levels ε_J , the sum (2.3) is not easily evaluated. However, the contributions from the different energy modes can be separated, so that the total internal energy of a single species per unit mass is given by⁴

$$e_s = e_{\text{tr},s} + e_{\text{rot},s} + e_{\text{vib},s} + e_{\text{exc},s} + e_{0,s} . \quad (2.4)$$

The mathematical formulation for the energy stored in each energy mode e_k is provided in Appendix A, along with relevant thermodynamic relations relating internal energy, enthalpy and specific heats.

Thermal Non-Equilibrium

If the internal energy of each species in a gas mixture is distributed over its energy levels according to a Boltzmann distribution, then the gas is in thermal equilibrium. In this case, all thermal energy modes are associated to a single temperature, that is $T_{k,s} = T$ and Eq. 2.1e does not enter the formulation. However, this is typically not the case where large gradients in the flow exist. In general, each chemical species composing the gas can have each of its internal energy modes excited differently, and equilibrium is only reached after energy exchanges (through collisions and radiative mechanisms) take place at the microscopic level.

These energy exchanges can be modeled by the use of relaxation times. If the relaxation times of energy-exchange processes τ_e are larger than a characteristic flow time τ_f , some regions in the flow are expected to be in thermal non-equilibrium. Assuming the gas is in thermal equilibrium is equivalent to stating that $\tau_e = 0$ everywhere. While some flow regions are properly modeled by this assumption, others are not, as is the case for the region behind a strong shock wave.

This is where multi-temperature models come into play. Each non-equilibrium energy mode is explicitly defined through a distinct energy equation, and the gas mixture is described by multiple temperatures T_k . It is worth noting that associated to each temperature T_k is a different thermal conductivity k_k , thus allowing a mixture to be uniquely defined by a number of thermal conductivities greater than one. A global energy equation and an additional energy equation for each non-equilibrium energy mode are then solved

³Degeneracy is a consequence of the possibility of having the same energy level with different microscopic arrangements (states).

⁴Since the energy equation requires the computation of *changes* in energy, rather than *absolute* energy values, the quantity $e_{0,s}$ is usually replaced with the heat of formation of the species $(\Delta h_f)_s^\circ$.

for the global and non-equilibrium temperatures, respectively. The energy exchanges occurring between the different energy modes are accounted for by a source term $\dot{\Omega}_k$ appearing in each non-equilibrium energy equation. These are discussed in more detail below.

Table 2.1 summarizes the most often used multi-temperature models in hypersonic flows. The two-temperature (2T) model assumes the translational mode of the heavy particles to be in equilibrium with the rotational mode of the molecules at a single translational-rotational temperature $T_{\text{tr-rot}}$. This is generally a good assumption by virtue of the two modes requiring few collisions to achieve equilibrium. Due to the significant difference in mass, the translational energy of the electrons is typically much different from that of the heavy particles. Furthermore, as the interaction of free electrons with both the molecules' vibrational mode and the electrons bounded to the different particles is usually very efficient, it is often assumed that the three energy modes are in equilibrium at the vibrational-electronic-electron temperature T_{ve} . This model was first proposed by Park [23] and has been extensively used in the past.

An extension of this model is the 3T model, which separately considers the non-equilibrium between the free electrons' translational mode and the heavy particles' vibrational mode, introducing a third non-equilibrium temperature T_{el} . Alternatively, one may consider the electronic mode to be in equilibrium with the free electrons' translation, thus defining the different non-equilibrium temperatures as indicated in the fourth row of Table 2.1. The next level of complexity would be to consider each species' vibrational energy mode to be individually in thermal non-equilibrium at $T_{\text{v},s}$, resulting in a total of $(1 + N_s)$ additional non-equilibrium energy equations.

The state-of-the-art when it comes to non-equilibrium modeling is to consider each internal energy level as an individual pseudo-species, in the so-called state-to-state models. This allows capturing non-Boltzmann distributions within a given thermal energy mode, provided detailed state-specific chemical kinetic models are employed [24, 25]. This discipline is still under development today and its details are beyond the scope of this work.

The amount of multi-temperature models that can be defined is only limited to the extent of the physical relevance that the different models may have. In addition to the increased computational effort, the main limiting factor to the number of non-equilibrium temperatures considered is the availability of data required by the relaxation models.

Table 2.1: List of commonly employed multi-temperature models in hypersonic flows.

Model	Energy Mode (Particle Type)				
	Translational (e^-)	Rotational (Heavy)	Rotational (Molecules)	Vibrational (Molecules)	Electronic (Heavy)
Equilibrium	T	T	T	T	T
2T Model	T_{ve}	$T_{\text{tr-rot}}$	$T_{\text{tr-rot}}$	T_{ve}	T_{ve}
3T Model	T_{el}	$T_{\text{tr-rot}}$	$T_{\text{tr-rot}}$	T_{ve}	T_{ve}
	T_e	$T_{\text{tr-rot}}$	$T_{\text{tr-rot}}$	T_v	T_e
$(2 + N_s)$T Model	T_e	$T_{\text{tr-rot}}$	$T_{\text{tr-rot}}$	$T_{\text{v},s}$	T_e

Energy-Exchange Processes

When thermal non-equilibrium is considered, the interaction between the different energy modes of colliding species must be properly modeled in order to account for the energy exchanges that can occur between distinct thermal modes. Another way to put this is how to properly model the energy source term $\dot{\Omega}_k$ appearing in Eq. 2.1e. Several energy-exchange processes can occur depending on how the thermal energy partitioning is modeled, with the most common ones being vibration-translation (V-T), vibration-vibration (V-V) and vibration-electronic (V-E).

Regarding V-T energy exchanges, which must be considered when relying on the 2T model, the rate of vibrational energy exchange for molecular species s due to translational exchange with a series of colliding species c is modeled via the Landau-Teller formula

$$\left(\frac{de_{\text{vib}}}{dt} \right)_{\text{V-T},s} = \frac{e_{\text{vib},s}^* - e_{\text{vib},s}}{(\tau_{\text{vib},s})_{\text{V-T}}} , \quad (2.5)$$

where $(\tau_{\text{vib},s})_{\text{V-T}}$ is the net vibrational relaxation time between species s and all other species c , defined as

$$(\tau_{\text{vib},s})_{\text{V-T}} = \left[\sum_{c=1}^{N_c} \frac{x_c}{(\tau_{\text{vib},s-c})_{\text{V-T}}} \right]^{-1} \quad (2.6)$$

following the formulation presented by Thivet *et al.* [26], where x_c is the species mole fraction. The vibrational energy of species s in equilibrium, $e_{\text{vib},s}^*$, may be obtained from the formulation given in Appendix A. The vibration-translation source term $\dot{\Omega}_{\text{V-T}}$ is obtained after multiplying Eq. 2.5 by the species' density and summing over all molecules, leading to

$$\dot{\Omega}_{\text{V-T}} = \sum_{s=1}^{N_{\text{mol}}} \rho_s \frac{e_{\text{vib},s}^* - e_{\text{vib},s}}{(\tau_{\text{vib},s})_{\text{V-T}}} . \quad (2.7)$$

Finally, the vibration-translation relaxation times $(\tau_{\text{vib},s-c})_{\text{V-T}}$ are calculated using the empirical Millikan-White correlation, typically adjusted using Park's high-temperature correction [27]

$$(\tau_{\text{vib},s-c})_{\text{V-T}}^{\text{MW}} = \left(\frac{p}{101325} \right)^{-1} \exp \left(A_{s-c}^{\text{MW}} \left(T^{-\frac{1}{3}} - B_{s-c}^{\text{MW}} \right) - 18.42 \right) + \left(N_s \sigma_s \sqrt{\frac{8k_B T}{\pi m_s}} \right)^{-1} , \quad (2.8)$$

where A_{s-c}^{MW} and B_{s-c}^{MW} are Millikan-White's coefficients for collision $s - c$, N_s is the number density for species s , σ_s the collision-limiting cross section for species s , k_B is Boltzmann's constant and m_s is the particle mass of species s .

For additional details on other energy-exchange processes typical of hypersonic flow applications, one may consult [2, 23].

2.1.3 Chemical Kinetics

When a gas is in chemical equilibrium, its composition may only change in space due to temperature gradients, since the equilibrium composition is temperature-dependent. At low temperatures, this is

typically a good approximation, since chemical reactions are practically deactivated and the equilibrium composition is mostly constant. In such cases, the composition of the mixture may be obtained at a given temperature by minimization of the Gibbs free energy, which is mathematically equivalent to requiring that

$$\sum_s \nu_{s,r} G_s = 0 , \quad (2.9)$$

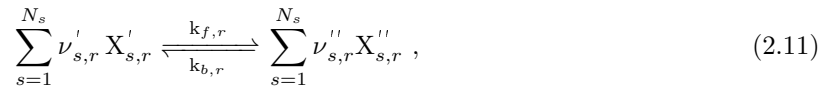
where ν_s is the stoichiometric coefficient associated to a given chemical reaction r containing species s , and G_s is its Gibbs free energy per mole of mixture. As mentioned in the introduction to this chapter, hypersonic flows are generally in chemical non-equilibrium due to the very low occupational times of the flow in the vicinity of the spacecraft. As a result, equilibrium in the flow may only be achieved long after the body has left a particular portion of gas. Contrary to the equilibrium case, the chemical composition will not only change due to temperature gradients, but also due to the fact that chemical reactions to restore equilibrium are taking place at a finite rate.

This added difficulty of high-temperature flows clarifies the need to employ chemical-kinetic models. The composition of the flow at a given point is uniquely specified by the set of unknowns c_s representing the species' mass fractions. The additional N_s equations are obtained by requiring mass conservation of each species individually, which is translated to Eq. 2.1a in the Navier-Stokes equations. Since the total mass is conserved, one can instead opt to solve the global continuity equation, given by

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{V}) = 0 , \quad (2.10)$$

in place of Eq. 2.1a for one particular species, thus keeping the number of equations equal to N_s , as required.

To obtain an expression for the source term, the chemical reactions taking place within the flow must be modeled. A general chemical reaction r may be written as



where $\nu'_{s,r}$ and $\nu''_{s,r}$ represent the stoichiometric coefficients for the reactants ($X'_{s,r}$) and products ($X''_{s,r}$), respectively, and $k_{f,r}$ and $k_{b,r}$ are the forward and backward reaction rate constants. Empirical results from experimental data have consistently shown that the net rate of formation of a species s involved in an elementary reaction r may be modeled through

$$\left\{ \frac{d[X_s]}{dt} \right\}_r = (\nu''_{s,r} - \nu'_{s,r}) \left\{ k_{f,r} \prod_s [X_s]^{\nu'_{s,r}} - k_{b,r} \prod_s [X_s]^{\nu''_{s,r}} \right\} , \quad (2.12)$$

where the bracket notation indicates concentrations (moles of species s per unit volume). Eq. 2.12 basically expresses the net rate for production of species s through reaction r as a balance between the forward and backward reactions. Although methods from kinetic theory exist for the theoretical estimation of the chemical rate constants, such results are avoided due to their large uncertainty. Instead, empirical results

are generally correlated through an Arrhenius equation of the form

$$k_{f,r} = C_r T_{f,c}^{\alpha_r} \exp\left(-\frac{E_{f,r}}{k_B T_{f,c}}\right), \quad (2.13)$$

where C_r , α_r and $E_{f,r}$ are model constants found experimentally and $T_{f,c}$ is the rate-controlling temperature of the forward reaction. To avoid introducing unnecessary uncertainty in the results, the relation

$$\frac{k_{f,r}}{k_{b,r}} = K_{c,r} \quad (2.14)$$

is employed to calculate the backward rate constant, using the equilibrium constant for concentrations K_c that can be accurately calculated from statistical thermodynamics. After summing Eq. 2.12 over all elementary reactions r involving species s , the mass source term present in Eq. 2.1a is simply

$$\dot{w}_s = \mathcal{M}_s \frac{d[X_s]}{dt}. \quad (2.15)$$

When thermal non-equilibrium is considered, the chemical reaction rate coefficients computed using Eqs. 2.13 or 2.14 must take into consideration which thermal reservoirs contribute to a given reaction energy. Although more detailed models take this into account by correcting the equilibrium rates computed using Eq. 2.13 by a correction factor Z , which depends upon the non-equilibrium temperatures considered, through

$$k_{\text{neq}} = Z(T_{\text{tr}}, T_{\text{rot}}, T_{\text{vib},1}, \dots, T_{\text{vib},N_s}, T_{\text{exc}}, T_{\text{el}}) k^*(T), \quad (2.16)$$

these fall out of the scope of this work. Some examples include the Marrone-Treanor, Knab and the Macheret-Fridman models [28]. Instead, a simpler approach is to modify $T_{f,c}$ appearing in Eq. 2.13 to a rate-controlling temperature that is more physically meaningful for a given reaction. As an example, consider the heavy-particle impact dissociation reaction of a molecule AB and its inverse recombination in the form



Park [23] proposes a rate-controlling temperature for such reactions based on a geometric average temperature between the translational and vibrational temperatures of the colliding particles, that is,

$$T_c = \sqrt{T_{\text{tr},\text{M}} T_{\text{vib},\text{AB}}}. \quad (2.18)$$

The idea behind this model is that the reaction dissociation energy is obtained in approximately equal proportions from the vibrational mode of the dissociating molecule and the translational mode of the colliding particle. A generalization of this approach considers instead

$$T_c = T_{\text{tr},\text{M}}^q T_{\text{vib},\text{AB}}^{1-q}, \quad (2.19)$$

which has been shown to produce improved results when compared with the simpler geometric average given by Eq. 2.18, provided an appropriate coefficient q is used [29].

2.1.4 Transport Properties

The conservation equations defined in § 2.1.1 consider the mass, momentum and energy fluxes due to concentration, velocity and temperature gradients, respectively. These dissipative fluxes model the natural transport of mass, momentum and energy due to the chaotic collisional character of the gas particles at a microscopic level. They appear explicitly in the Navier-Stokes equations through the mass diffusion flux vector $\mathbf{J}_s$, the viscous stress tensor $[\boldsymbol{\tau}]$ and the conduction heat flux associated with thermal mode k , $\mathbf{q}_{c,k} = k_k \nabla T_k$.

Several models exist to deal with the calculation of these properties. They are generally defined as functions of the corresponding transport coefficients and a given gradient, depending on which physical quantity is being transported. A summary of the models used to describe the dissipative fluxes and the corresponding transport coefficients required to define them is given in Table 2.2. These coefficients define the response of the gas to gradients in concentration, velocity and temperature, thus being fundamental to accurately capture the flow behavior, especially across a shock wave or near a wall, where large gradients are known to occur. Additionally, each thermal mode is seen to contribute differently to the global thermal conductivity of the mixture, which is calculated by summing the contributions due to the different modes.

Table 2.2: Dissipative flux definitions, corresponding models employed and transport coefficients required as part of their definitions. Transport coefficients: D_s - mass diffusion coefficient of species s , μ - dynamic viscosity coefficient and k_k - thermal conductivity associated with thermal mode k .

Dissipative Flux	Symbol	Model	Mathematical Definition	Transport Coefficient	SI Units	Gradient
Mass Diffusion	$\mathbf{J}_s$	Fick's Law	$\mathbf{J}_s = \rho D_s \nabla c_s$	D_s	$\text{m}^2 \text{s}^{-1}$	∇c_s
Momentum Diffusion	$[\boldsymbol{\tau}]$	Newtonian Fluid ^a	$[\boldsymbol{\tau}] = \mu \left(\nabla \mathbf{V} + (\nabla \mathbf{V})^T \right) - \frac{3}{2} \mu (\nabla \mathbf{V}) [\mathbf{I}]$	μ	$\text{kg m}^{-1} \text{s}^{-1}$	$\nabla \mathbf{V}$
Heat Conduction	$\mathbf{q}_{c,k}$	Fourier's Law	$\mathbf{q}_{c,k} = k_k \nabla T_k$	k_k	$\text{J m}^{-1} \text{s}^{-1} \text{K}^{-1}$	∇T_k

^a Stokes' Hypothesis is also considered as part of the model, that is, the dynamic and second viscosity coefficients are related through $\lambda + \frac{2}{3}\mu = 0$.

In light of the multi-component, possibly multi-temperature model outlined in the previous sections, it is therefore necessary to find expressions for the species mass diffusion coefficients D_s , the mixture's dynamic viscosity coefficient μ and the modal thermal conductivities k_k , in the presence of a partially ionized flowfield. Under translational equilibrium conditions, the Boltzmann equation may be solved to obtain these bulk transport properties. One such solution, the classical Chapman-Enskog solution, approximates the Boltzmann equation using a Sonine polynomial expansion [2, 30]. The resulting series is known to converge rapidly, and typically only the first order terms are retained. In the first Chapman-Enskog approximation, the viscosity and translational component of thermal conductivity for the mixture

can be calculated from the general system of equations expressed by [31]

$$[\mu \text{ or } k_{\text{tr}}]_{\text{mix}} = - \frac{\begin{vmatrix} A_{11} & \cdot & \cdot & \cdot & A_{1N_s} & | & x_1 \\ \cdot & \cdot & & & \cdot & | & \cdot \\ \cdot & & \cdot & & \cdot & | & \cdot \\ \cdot & & & \cdot & \cdot & | & \cdot \\ A_{N_s 1} & \cdot & \cdot & \cdot & A_{N_s N_s} & | & x_{N_s} \\ - & - & - & - & - & - & - \\ x_1 & \cdot & \cdot & \cdot & x_{N_s} & | & 0 \end{vmatrix}}{|A_{sl}|}, \quad (2.20)$$

where the coefficients A_{sl} are complicated functions of certain binary interaction parameters, namely, the classical collision integrals $\Omega_{s,l}^{(m,n)}$, which define the strength of the interaction between the pair of species (s, l) . Also note that different formulas apply to the coefficients A_{sl} for viscosity and translational thermal conductivity. Hence, the problem of calculating the transport coefficients for a given mixture consists of: 1) the determination of the collision integrals $\Omega_{s,l}^{(m,n)}$ for all possible interactions (s, l) and 2) the solution of the Chapman-Enskog system of equations. While important development has been occurring in recent years concerning the availability of reliable collision integral data for several species, the second matter still poses a significant challenge computationally. Therefore, several alternatives that try to find a compromise between efficiency and accuracy have been proposed [32, 33].

The common practice employed in hypersonic applications is to use mixture rules that approximate the Chapman-Enskog solution, usually valid for weakly ionized gases. In this work, three mixture rules were compared, namely, the Wilke/Blottner/Eucken model and the Gupta/Yos model, with two distinct levels of approximation for the latter. While Wilke's model is attractive due to its simplicity and easy implementation, requiring a relatively small amount of input data, it is also known to be the least accurate [2]. Despite being described as a last-resort method [32], it is still the most used model when it comes to hypersonic flow modeling. The Gupta/Yos model, on the other hand, relies on a large library of inter-species collision cross-section data as input, which is sometimes unavailable and difficult to obtain. In addition, its implementation is less straightforward and usually considered to be more computationally expensive, although the results obtained by Palmer *et al.* show otherwise [32]. The different models for transport will now be described.

2.1.4.1 Wilke/Blottner/Eucken Model

This model for computing multi-component gas mixtures' transport properties was proposed by Wilke and consists in the application of kinetic theory to the first order Chapman-Enskog solution [34]. This approximation assumes that all binary interactions have the same (hard-sphere) cross-section [32]. Reasonable results can be obtained using this approximation, provided temperatures do not exceed about 10,000 K and ionization levels are kept low.

The mixture's viscosity and thermal conductivity associated with each thermal mode may be obtained from the contributions of all species by a weighted sum on the individual species' contributions by applying

Wilke's semi-empirical mixing rule

$$\mu = \sum_s \frac{x_s \mu_s}{\phi_s} \quad , \text{ and } \quad k_k = \sum_s \frac{x_s k_{k_s}}{\phi_s} \quad , \quad (2.21)$$

where x_s is the species' molar fraction and ϕ_s is a coefficient dependent on all possible interactions between species s and l , and on the molar mass $\mathcal{M}$ of the interacting species:

$$\phi_s = \sum_l x_l \left[1 + \left(\frac{\mu_s}{\mu_l} \right)^{\frac{1}{2}} \left(\frac{\mathcal{M}_l}{\mathcal{M}_s} \right)^{\frac{1}{4}} \right]^2 \left[8 \left(1 + \frac{\mathcal{M}_s}{\mathcal{M}_l} \right) \right]^{-\frac{1}{2}} . \quad (2.22)$$

Blottner's model [35] is used to compute individual species' viscosities through a relation of the form

$$\mu_s(T) = 0.1 \exp \left[(A_s \ln T + B_s) \ln T + C_s \right] , \quad (2.23)$$

where T is the species' translational temperature and the A , B and C coefficients are curve-fit for each species individually. Moreover, the generalized Eucken's relation [33] is employed to evaluate the species' thermal conductivity associated with each thermal mode, assuming a unit Schmidt number⁵. This assumption leads to the following contributions from each thermal energy mode:

$$k_{\text{tr},s} = \frac{5}{2} \mu_s C_{v_{\text{tr},s}} \quad (2.24a)$$

$$k_{\text{rot},s} = \mu_s C_{v_{\text{rot},s}} \quad , \text{ for } s \in \{\text{Molecular Species}\} \quad (2.24b)$$

$$k_{\text{vib},s} = \mu_s C_{v_{\text{vib},s}} \quad , \text{ for } s \in \{\text{Molecular Species}\} \quad (2.24c)$$

$$k_{\text{exc},s} = \mu_s C_{v_{\text{exc},s}} \quad , \text{ for } s \notin \{\text{Electron}\} . \quad (2.24d)$$

Note that all species (atoms, molecules, and electrons) contribute to the mixture's translational thermal conductivity. On the other hand, only molecules possess rotational and vibrational energy, thus being the only contributors to the mixture's rotational and vibrational thermal conductivities. Finally, all species except electrons presumably possess electrons in their orbitals, thus contributing to the mixture's electronic excitation thermal conductivity. In Eqs. 2.24, $C_{v_{k,s}}$ is the specific heat at constant volume, defined in Appendix A. Also, the contributions of different species to the thermal conductivity associated to a given thermal mode through Eq. 2.21 depend on the multi-temperature model considered, if thermal non-equilibrium is assumed.

Finally, the mass diffusion coefficient is assumed equal among all species and is calculated using

$$D_s = D = \frac{\text{Le } k}{\rho C_p} , \quad (2.25)$$

assuming a Lewis number⁶ of $\text{Le} = 0.39$, equal to the one used by Reynier *et al.* [3]. In Eq. 2.25, k and C_p are the mixture's total thermal conductivity and specific heat at constant pressure, respectively.

⁵The Schmidt number is a dimensionless number defined as the ratio of momentum to mass diffusivity, that is, $\text{Sc} = \frac{\eta}{D}$, where η is the kinematic viscosity. The notation η was used to avoid confusion with the frequency ν .

⁶The Lewis number is a similarity parameter of the flow, defining the ratio of energy transport due to mass diffusion relative to thermal conduction.

2.1.4.2 Gupta/Yos Model

The commonly known Gupta/Yos model, employed by Gupta *et al.* [31], is based on a simplification of the Chapman-Enskog solution first proposed by Yos [36]. While the formulas obtained by Yos take into account the effect of the non-diagonal terms of matrix A_{sl} in Eq. 2.20, additional approximations are usually employed on the nature of these terms, either completely neglecting them or using an empirical constant instead. This was the case for the previous Gupta/Yos model available in SPARK [37]. The result of considering the transfer of momentum or energy by collisions between species through the non-diagonal elements of A_{sl} is to reduce the overall conductivity of the mixture below the value which it would have if such transfer processes were neglected [31].

Thus, in order to quantify the practical implications of this approximation, both models were implemented and compared in the present work in the context of H_2 –He mixtures. The more accurate model proposed by Yos will from now on be referred to as the 2nd Order Model, despite relying on the same first order Chapman-Enskog approximation, while the more common one will be called 1st Order Model.

In both models, the transport coefficients appear as functions of the collision terms $\Delta_{s,l}^{(1)}$ and $\Delta_{s,l}^{(2)}$, defined as

$$\Delta_{s,l}^{(1)} = \frac{8}{3} \left[\frac{2\mathcal{M}_s\mathcal{M}_l}{\pi\mathcal{R} T_c (\mathcal{M}_s + \mathcal{M}_l)} \right]^{\frac{1}{2}} \pi \left(\sigma^2 \Omega_{s,l}^{(1,1)*} \right) \quad (2.26)$$

$$\Delta_{s,l}^{(2)} = \frac{16}{5} \left[\frac{2\mathcal{M}_s\mathcal{M}_l}{\pi\mathcal{R} T_c (\mathcal{M}_s + \mathcal{M}_l)} \right]^{\frac{1}{2}} \pi \left(\sigma^2 \Omega_{s,l}^{(2,2)*} \right) . \quad (2.27)$$

At this point, a note on the terminology used throughout this work is in order, due to the several notations encountered in the literature. The notation used by Bruno *et al.* [38, 39] was followed, where

- $\Omega_{s,l}^{(m,n)}$ represents the dimensional collision integrals in $m^3 s^{-1}$;
- $\Omega_{s,l}^{(m,n)*}$ represents the dimensionless reduced collision integrals;
- $\sigma^2 \Omega_{s,l}^{(m,n)*}$ represents the dimensional collision cross-sections in m^2 , where σ is the rigid sphere collision diameter.

Thus, the average collision cross-sections $\bar{\Omega}_{s,l}^{(m,n)}$ employed by Gupta *et al.* [31] are replaced in the present work by the collision cross-sections $\sigma^2 \Omega_{s,l}^{(m,n)*}$. The collision cross sections in general depend on a controlling temperature T_c , which is taken to be the electrons' translational temperature $T_{tr,e}$ if the interaction involves an electron, or the heavy species' translational temperature $T_{tr,s}$ otherwise.

The two models outlined in the introduction to this chapter vary in the formulas employed for the mixture's viscosity and translational component of the thermal conductivity, and will now be presented.

1st Order Model

In the 1st Order Model, the mixture's viscosity is computed using

$$\mu = \sum_s \frac{x_s m_s}{\sum_l x_l \Delta_{s,l}^{(2)}} , \quad (2.28)$$

whereas the translational component of thermal conductivity is given by

$$k_{\text{tr}} = \frac{15}{4} k_B \sum_s \frac{x_s}{\sum_l \alpha_{s,l} x_p \Delta_{s,l}^{(2)}} . \quad (2.29)$$

The coefficient $\alpha_{s,l}$ depends on the species molar masses, and is calculated according to

$$\alpha_{s,l} = 1 + \frac{\left(1 - \frac{\mathcal{M}_s}{\mathcal{M}_l}\right) \left[0.45 - 2.54 \left(\frac{\mathcal{M}_s}{\mathcal{M}_l}\right)\right]}{\left(1 + \frac{\mathcal{M}_s}{\mathcal{M}_l}\right)^2} . \quad (2.30)$$

2nd Order Model

The 2nd Order Model employs the formulas proposed by Yos [36], which are computationally more expensive. The viscosity and translational thermal conductivity of the mixture are computed using

$$[\mu \text{ or } k_{\text{tr}}] = \frac{\sum_s \frac{x_s}{A_s + a_{\text{av}}}}{1 - a_{\text{av}} \sum_s \frac{x_s}{A_s + a_{\text{av}}}} , \quad (2.31)$$

where a_{av} is an average of the non-diagonal matrix elements present Eq. 2.20, and is defined as

$$a_{\text{av}} = \frac{\sum_s \sum_l x_s x_l \left(\frac{1}{A_s} - \frac{1}{A_l}\right)^2 a_{s,l}}{\sum_s \sum_l x_s x_l \left(\frac{1}{A_s} - \frac{1}{A_l}\right)^2} . \quad (2.32)$$

The coefficients A_s or A_l are calculated from

$$A_i = \sum_j x_j A_{i,j} , \quad (2.33)$$

and the coefficients $A_{i,j}$ and $a_{i,j}$ are defined differently for the viscosity and thermal conductivity. On one hand, to compute the viscosity terms, one uses the relations

$$a_{s,l}^\mu = \frac{N_A}{(\mathcal{M}_s + \mathcal{M}_l)} \left[2\Delta_{s,l}^{(1)} - \Delta_{s,l}^{(2)} \right] \quad (2.34a)$$

$$A_{s,l}^\mu = \frac{N_A}{\mathcal{M}_s} \Delta_{s,l}^{(2)} , \quad (2.34b)$$

whereas the translational component of the mixture's thermal conductivity uses instead

$$a_{s,l}^k = \left(\frac{2}{15k_B} \right) \frac{\mathcal{M}_s \mathcal{M}_l}{(\mathcal{M}_s + \mathcal{M}_l)^2} \left\{ \left(\frac{33}{2} - \frac{18}{5} B_{s,l}^* \right) \Delta_{s,l}^{(1)} - 4\Delta_{s,l}^{(2)} \right\} \quad (2.35a)$$

$$A_{s,l}^k = \frac{2}{15k_B (\mathcal{M}_s + \mathcal{M}_l)^2} \left\{ 8\mathcal{M}_s \mathcal{M}_l \Delta_{s,l}^{(2)} + (\mathcal{M}_s - \mathcal{M}_l) \left[9\mathcal{M}_s - \frac{15}{2} \mathcal{M}_l + \frac{18}{5} B_{s,l}^* \mathcal{M}_l \right] \Delta_{s,l}^{(1)} \right\} . \quad (2.35b)$$

Finally, this approximation relies on the additional collision term $B_{s,l}^*$, which is a function of two new collision cross-sections, and is defined through

$$B_{s,l}^* = \frac{5 \left(\sigma^2 \Omega_{s,l}^{(1,2)*} \right) - 4 \left(\sigma^2 \Omega_{s,l}^{(1,3)*} \right)}{\left(\sigma^2 \Omega_{s,l}^{(1,1)*} \right)}. \quad (2.36)$$

The following formulas for computing the internal contributions to the thermal conductivity of the mixture, as well as the mass diffusion coefficients, are common to both models. The rotational contribution is calculated through

$$k_{\text{rot}} = \sum_{s \in \text{mol.}} \frac{x_s m_s C_{v_{\text{rot}},s}}{\sum_l x_l \Delta_{s,l}^{(1)}}, \quad (2.37a)$$

with similar relations applying for the vibrational and electronic excitation contributions:

$$k_{\text{vib}} = \sum_{s \in \text{mol.}} \frac{x_s m_s C_{v_{\text{vib}},s}}{\sum_l x_l \Delta_{s,l}^{(1)}} \quad (2.37b)$$

$$k_{\text{exc}} = \sum_{s \notin e^-} \frac{x_s m_s C_{v_{\text{el}},s}}{\sum_l x_l \Delta_{s,l}^{(1)}}. \quad (2.37c)$$

Finally, the mixture's total thermal conductivity in thermal equilibrium is the sum of all contributions, namely

$$k = k_{\text{tr}} + k_{\text{rot}} + k_{\text{vib}} + k_{\text{exc}}. \quad (2.38)$$

When thermal non-equilibrium is considered, each component k_k will depend on the contributions from the corresponding non-equilibrium species in Eqs. 2.37 according to the multi-temperature model used.

When it comes to the mass diffusion coefficients D_s , the approach is similar in both models. An average diffusion coefficient is computed from individual multi-component mass diffusion coefficients through

$$D_s = \frac{1 - x_s}{\sum_{s \neq l} \frac{x_l}{D_{s,l}}}, \quad (2.39)$$

where the binary mass diffusion coefficients are given for a pair of species (s, l) by

$$D_{s,l} = \frac{k_B T_c}{p \Delta_{s,l}^{(1)}}. \quad (2.40)$$

In Eq. 2.40, T_c is a controlling temperature obeying the same rules described before.

In the preceding formulas, N_A is Avogadro's number and k_B is Boltzmann's constant. The dimensional collision cross sections $\sigma^2 \Omega_{s,l}^{(m,n)*}$ are usually provided in the literature as a function of temperature. The way this data is provided varies widely, but can usually be split into tabular form [40] or coefficients for a specific curve-fit formula [38, 39]. Details regarding the sources used and implemented in this work for the calculation of transport properties are given in § 3.4.

2.2 Radiation in Hypersonic Flows

When gases reach a sufficiently high temperature, energy exchange in the form of emission and absorption of electromagnetic radiation starts to significantly affect the flowfield. Emission of thermal radiation occurs in part as a result of transitions from upper to lower internal energy levels of the atoms or molecules composing the gas, and in part due to transitions involving free electrons [30]. The opposite process occurs when incoming radiation is absorbed, resulting in internal excitation of the absorbing particle. These radiative energy exchanges appear as a source term in the energy equation (Eq. 2.1c), thus significantly modifying the flowfield. Furthermore, surfaces exposed to a radiating shock layer will experience a significant increase in heat flux caused by the added radiative contribution.

This chapter briefly introduces the spectral emission and absorption coefficients required for the calculation of the radiative heating. In § 2.2.1, a distinction between discrete and continuum radiation is made. The Generalized Kirchhoff-Planck Law is introduced as a means to obtain the emission coefficient from knowledge of the absorption coefficient. Finally, the mathematical formulation describing radiation propagation through a non-scattering medium is presented in § 2.2.2, leading to an introduction of the classical radiative transfer equation.

2.2.1 Emission and Absorption Coefficients

As a consequence of the quantization of atomic and molecular energy levels, emission and absorption of radiative energy is also a quantized phenomenon. The particle theory of light describes radiation using photons, massless particles traveling at the speed of light, each carrying a *packet* of energy equal to

$$E = h\nu , \tag{2.41}$$

where h represents Planck's constant and ν is the frequency of the electromagnetic radiation associated with the photon. This is known as Planck's relation. Using this postulate, Planck formulated the theory describing the radiation field surrounding a black-body (a body in total thermodynamic equilibrium with its surroundings), showing that under such conditions the emission and absorption of radiation is perfectly balanced at every frequency. Conditions for radiative equilibrium, however, rarely occur in nature. Even air at room temperature does not emit radiative energy at the same rate it absorbs. This non-equilibrium is described by the radiative transfer equation, which requires knowledge on the emission and absorption coefficients at every point in the flowfield.

In a radiating ionized gas, three types of radiative mechanisms contribute to the bulk spectral coefficients, namely

1. Bound-bound transitions,
2. Bound-free transitions,
3. Free-free transitions.

Bound-bound radiative transitions occur between two quantized energy levels of an atom or molecule. As a result of energy level quantization, the spectrum of such transitions is sharply peaked at a specific frequency corresponding to the energy gap between the upper and lower energy levels, and the associated radiation is discrete. Furthermore, atomic bound-bound transitions occur between electronic states of the atom, while molecular bound-bound transitions take place between individual ro-vibronic⁷ states of the molecule. The resulting molecular emission and absorption spectra consist of systems composed of bands of lines corresponding to individual vibrational and electronic transition groups [2, 30, 41].

On the other hand, bound-free and free-free radiative transitions involve a free electron state. Accordingly, these transitions give rise to continuum radiation, since the free electron is allowed to take on any value of kinetic energy. Examples of bound-free mechanisms include photo-ionization, photo-dissociation and the inverse process photo-recombination, while free-free radiation (also known as Bremsstrahlung) occurs as a result of the acceleration/deceleration of a free electron upon interaction with an electric field.

Discrete radiation

Given this understanding of the fundamental sources of radiative energy, it is natural to describe emission and absorption coefficients as a function of the energy level populations of the atoms and molecules composing the gas. The so-called Einstein coefficients are introduced to represent the probability of certain bound-bound transitions occurring between two energy levels l (lower) and u (upper). A total of three Einstein coefficients exist, each corresponding to a distinct emission/absorption mechanism, namely, spontaneous emission A_{ul} , induced emission⁸ B_{ul} and absorption B_{lu} . The spectral emission and absorption coefficients for an atomic or molecular bound-bound transition with energy $h\nu_{ul}$ are, respectively,

$$j_{\nu,ul} = \frac{N_u h \nu_{ul}}{4\pi} A_{ul} \phi_{ul}(\nu) , \quad (2.42)$$

and

$$\kappa_{\nu,ul} = (N_l B_{lu} - N_u B_{ul}) h \nu_{ul} \phi_{ul}(\nu) , \quad (2.43)$$

where N_u and N_l are the number densities of the upper and lower energy levels, respectively, and $\phi_{ul}(\nu)$ is the spectral distribution function of the $u \rightleftharpoons l$ line transition. This line-shape factor describes the spectral distribution of the emission and absorption coefficients of a line transition. Although these transitions occur between quantized states with a definite energy gap (hence, a precise $h\nu_{ul}$), the corresponding spectral lines are never truly monochromatic; instead, they appear smeared over a finite frequency range due to various broadening mechanisms, including: natural line broadening, collision broadening, Doppler broadening, Stark broadening, Van der Waals broadening, etc. Detailed accounts of these processes are available in the literature [2, 42–44]. Moreover, the Principle of Detailed Balance

⁷A ro-vibronic state is a molecular configuration described by a set of rotational, vibrational and electronic quantum numbers.

⁸The presence of a radiation field increases the likelihood of emission occurring spontaneously.

[2, 30] relates the three Einstein coefficients, allowing the absorption coefficient to be expressed as

$$\kappa_{\nu,ul} = \left(N_l \frac{g_u}{g_l} - N_u \right) \frac{c^2}{8\pi h \nu_{ul}^3} A_{ul} h \nu_{ul} \phi(\nu) , \quad (2.44)$$

where g_l and g_u are the degeneracies of the lower and upper states, respectively. This principle also allows a relation between the emission and absorption coefficients to be drawn, meaning only one coefficient actually needs to be computed:

$$\frac{j_{\nu,ul}}{\kappa_{\nu,ul}} = \frac{2h\nu_{ul}^3}{c^2} \left(\frac{g_u N_l}{g_l N_u} - 1 \right)^{-1} . \quad (2.45)$$

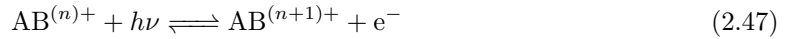
This relation is called the Generalized Kirchhoff-Planck Law.

Finally, the $N_{u,l}$ level populations may be determined assuming a Boltzmann distribution at one global temperature T or considering individual non-equilibrium temperatures T_{tr} , T_{int} ⁹. Alternatively, the populations may be determined considering a full state-to-state description or a simplified collisional-radiative model.

Continuum radiation

Examples of continuum radiation transitional processes include:

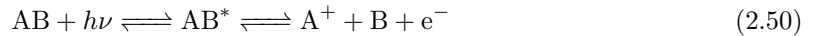
1. Photo-ionization / Radiative Recombination reactions:



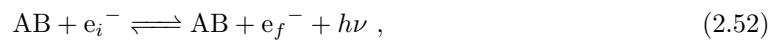
2. Photo-detachment / Photo-attachment reactions:



3. Photo-dissociation - Dissociative Photo-ionization / Radiative Association reactions:



4. Bremsstrahlung / Inverse Bremsstrahlung reactions¹⁰



⁹The subscript int here stands for the corresponding internal modes (rotational, vibrational and electronic excitation).

¹⁰Here e_i^- and e_f^- represent electrons with distinct initial (i) and final (f) velocities.

These reactions may include emission or absorption of a free electron. From energy conservation,

$$h\nu = E_{\text{ion}} + \frac{1}{2}mv_e^2, \quad (2.53)$$

where E_{ion} is the ionization energy of the atom or molecule. As a consequence, these radiative processes have an energy (thus, frequency) threshold below which they cannot occur, due to the limiting effect of the ionization energy. As such, their presence in the spectrum is limited to a higher frequency range.

The transition intensities for these processes are usually determined from computed or measured absorption cross-sections. The absorption coefficient is thus immediately calculated by taking into account the populations of the absorbing states, and the emission coefficient is obtained using Kirchhoff-Planck's Law.

While for processes 1-3 the expression for the absorption coefficient can be written as

$$\kappa_\nu(\nu) = \left[\sum_i N_i \sigma_i(\nu) \right] \left[1 - \exp\left(-\frac{h\nu}{k_B T_{\text{el}}}\right) \right], \quad (2.54)$$

provided the level-dependent $\sigma_i(\nu)$ spectral absorptions cross-sections are available, for free-free Bremsstrahlung transitions the absorption coefficient is written as

$$\kappa_\nu(\nu) = N N_e \sigma(\nu, T_{\text{el}}) \left[1 - \exp\left(-\frac{h\nu}{k_B T_{\text{el}}}\right) \right]. \quad (2.55)$$

In both cases the factor $\left[1 - \exp\left(-\frac{h\nu}{k_B T_{\text{el}}}\right) \right]$ allows for the subtraction of stimulated emission processes, yielding the net absorption coefficient.

2.2.2 Radiative Energy Transfer

2.2.2.1 Definitions

Consider an arbitrary direction $\mathbf{s}$ (defined in spherical coordinates by the azimuthal and zenith angles ϕ and θ , respectively) at a given point in a radiating flowfield. The spectral directional radiative intensity $I_\nu^{\theta,\phi}$ is defined as the radiative energy transferred in the $\mathbf{s}$ direction across a unit area perpendicular to $\mathbf{s}$, per unit frequency, per unit time, per unit solid angle. This geometrical interpretation of radiation is represented in Figure 2.2, along with the nomenclature used throughout this work. Referring again to Figure 2.2, the spectral radiative energy flux q_ν at a point P inside a radiating flowfield is defined as the energy per second crossing a unit area dA due to radiative intensity $I_\nu^{\theta,\phi}$ from all incoming directions at a given frequency ν . It is formally defined as

$$q_\nu = \int_{4\pi} I_\nu^{\theta,\phi} \mathbf{s} \cdot \mathbf{n} d\Omega = \int_{4\pi} I_\nu^{\theta,\phi} \cos \theta d\Omega = \int_0^{2\pi} \int_0^\pi I_\nu^{\theta,\phi} \cos \theta \sin \theta d\theta d\phi. \quad (2.56)$$

A similar expression describes the spectral surface radiative heating q_ν^- , which only takes into account the radiation coming from a hemisphere above the point under consideration on the surface, i.e., the integral in θ is taken between 0 and $\frac{\pi}{2}$. The magnitude of the total radiative heat flux vector $\mathbf{q}_{\text{rad}}$ requires

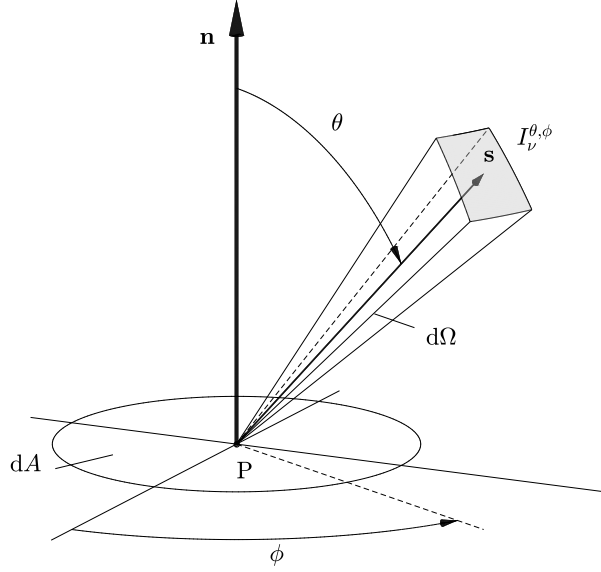


Figure 2.2: Geometric model for radiation.

integration of Eq. 2.56 over all frequencies, resulting in

$$q_{\text{rad}} = \int_0^\infty \int_\Omega q_\nu d\Omega d\nu. \quad (2.57)$$

While these quantities are useful to obtain fluxes at physical boundaries (such as the TPS in a spacecraft), inside the medium one needs to estimate the radiative source term appearing in the total energy equation (Eq. 2.1c), given by the negative divergence of the local radiative heat flux vector. This vector is obtained from Eq. 2.56 by removing the dot product with the surface normal $\mathbf{n}$, leading to

$$-\nabla \cdot \mathbf{q}_{\text{rad}} = -\nabla \cdot \int_0^\infty \int_{4\pi} I_\nu^{\theta,\phi} \mathbf{s} d\Omega d\nu. \quad (2.58)$$

2.2.2.2 Radiative Transfer Equation

The radiative transfer equation suitable for hypersonic applications [1, 30, 42] is given by

$$\mathbf{s} \cdot \nabla I_\nu^{\theta,\phi} = \frac{dI_\nu^{\theta,\phi}}{ds} = j_\nu - \kappa_\nu I_\nu^{\theta,\phi}, \quad (2.59)$$

where j_ν is the emission coefficient and κ_ν is the absorption coefficient. It represents the change in radiative intensity $I_\nu^{\theta,\phi}$ as a ray travels along a path $\mathbf{s}$ with direction specified by (θ, ϕ) through an emitting and absorbing gas. Introducing the relation $d\tau_\nu = \kappa_\nu ds$, Eq. 2.59 can be expressed as

$$\frac{dI_\nu^{\theta,\phi}}{d\tau_\nu} = \frac{j_\nu}{\kappa_\nu} - I_\nu^{\theta,\phi}, \quad (2.60)$$

where the optical thickness τ_ν is defined as

$$\tau_\nu(s) = \int_{s'=0}^{s'=s} \kappa_\nu ds'. \quad (2.61)$$

Assuming a solution of the form $I_\nu^{\theta,\phi} = c(\tau_\nu)e^{-\tau_\nu}$ and letting $\tau_\nu(0) = 0$, the solution to the radiative transfer equation at a distance L along a ray is expressed as

$$I_\nu^{\theta,\phi}(\tau_\nu(L)) = I_\nu^{\theta,\phi}(0)e^{-\tau_\nu(L)} + \int_0^{\tau_\nu(L)} \frac{j_\nu}{\kappa_\nu} e^{-(\tau_\nu(L)-\tau_\nu(s))} d\tau_\nu. \quad (2.62)$$

The physical meaning of each contribution to the local radiative intensity $I_\nu^{\theta,\phi}$ at each point should be kept in mind: while the first term represents the incoming intensity $I_\nu^{\theta,\phi}(0)$ attenuated by absorption between $s = 0$ and L (a form of Beer-Lambert's Law), the second term represents the emitted radiation at any point s between 0 and L , attenuated by absorption for the remainder of the integration path between s and L . Various models exist for the treatment of the radiation field, differing in the way Eq. 2.62 is approximated. The most commonly employed methods are:

1. Tangent-slab model
2. Ray-tracing model
3. Optically-thin model.

These models and their implementation in this work are described in detail in § 3.6. At this point it is useful to rewrite Eq. 2.58 in terms of the emission and absorption coefficients by introducing the radiative transfer equation, resulting in

$$-\nabla \cdot \mathbf{q}_{\text{rad}} = \int_0^\infty \int_{4\pi} \kappa_\nu I_\nu^{\theta,\phi} d\Omega d\nu - 4\pi \int_0^\infty j_\nu d\nu. \quad (2.63)$$

CHAPTER 3

Numerical Implementation

In this chapter, the numerical implementation of the mathematical models described in § 2 is described in detail, together with the databases used to support them.

First, the two numerical codes used to solve the flow and radiative fields in the present work are discussed. The thermodynamic database is defined in § 3.3, where the kinetic and thermal non-equilibrium models employed are described. The implementation of Bruno *et al.*'s collision cross-section database in SPARK is then detailed in § 3.4 in the context of the Gupta/Yos transport model, and the resulting transport properties are verified against several sources, including the commonly employed Wilke/Blottner/Eucken model. Finally, § 3.5 and § 3.6 describe and compare the radiative database in SPARK LbL with other sources, and outline the computational framework implemented in the present work to solve the radiative transfer equation using both the tangent-slab and ray-tracing approaches.

3.1 SPARK CFD Solver

SPARK - *Software Package for Aerothermodynamics, Radiation and Kinetics* - is a CFD code for the simulation of hypersonic non-equilibrium flows written in Fortran 03/08 under the object-oriented programming (OOP) paradigm. It was developed by Lopez *et al.* [45] and is maintained at the University of Illinois at Urbana-Champaign and IPFN (Instituto de Plasmas e Fusão Nuclear), a research unit of Instituto Superior Técnico. Unlike most scientific codes, which often neglect the maintainability and flexibility aspects of programming, SPARK is a highly modular and easily extendable code. By explicitly separating the physical models, numerical methods, geometry-manipulation tasks and organizational operations into distinct modules, integration and testing of new models and algorithms is straightforward.

SPARK is able to perform simulations in 0D (temporal relaxation), 1D (post-shock relaxation) or 2D (cylindrical or axisymmetric) geometries, using either Euler or Navier-Stokes compressible-flow formulations. Perfect and frozen gas assumptions can be selected, along with the more detailed chemically-reacting mixture employing chemical kinetic models. Furthermore, several multi-temperature models may be customized, allowing the simulation of user-defined thermal non-equilibrium conditions, typical phenomena of hypersonic re-entry flows. Finally, state-to-state models are also implemented in SPARK. From a numerical standpoint, a cell-centered time-dependent finite volume formulation is implemented, where the conservation equations are expressed in integral form over arbitrary quadrilateral cells. Regarding temporal

```

Type ,extends(Universal_Type)      :: Gas_Type
type(GasModel_Type)               :: Model
type(Mixture_Type)                :: Mixture
type(Transport_Type)              :: Transport
integer                           :: NSpeChe
<...>
contains
generic ,public :: Initialize      => InitializeGasFromInput, InitializeGasFromOptions
procedure ,private :: InitializeGasFromInput
procedure ,private :: InitializeGasFromOptions
generic ,public :: ComputeTransport => ComputeTransport_0d, ComputeTransport_1d
procedure ,private :: ComputeTransport_0d
procedure ,private :: ComputeTransport_1d
<...>
End Type

```

Figure 3.1: Illustration of data structure of the **Gas** object.

discretization, both implicit and explicit second-order schemes are available in SPARK. Convective fluxes are discretized using the second-order Harten-Yee scheme, and the minmod flux limiter is employed to avoid numerical oscillations.

The OOP structure of the code delineates the internal data handling and procedure definitions within it. Physical models or numerical methods are represented by objects, which define and interact with their own data and procedures. Encapsulation enables the creation of nested object structures that mimic the actual physical representation of a given concept. For example, a **Gas** object contains a **Mixture** object, which further encapsulates a set of **Chemical Species** objects, each with its own data structure. Thus, in a way, the physical representation of a given entity is directly translated into the programming language. Furthermore, type-bound procedures that can act on data can be defined for each object, thus allowing encapsulation of both data and procedures. This hierarchical structure is illustrated in Figure 3.1, which shows various objects of different type encapsulated within the **Gas** object, along with several type-bound procedures required to perform certain actions on the data.

3.2 SPARK Line-by-Line Code

SPARK Line-by-Line (SPARK LbL) is a line-by-line radiative solver maintained at IPFN that computes the frequency-dependent emission and absorption coefficients of a gas mixture in non-equilibrium. It is a libre code written in Matlab, although progress towards a Fortran version has started with this dissertation. While the code has been primarily developed for the simulation of low-pressure, high-temperature plasmas, characteristic of planetary atmospheric entry applications, it can also serve other applications such as combustion and low-temperature plasma radiation for medical treatments.

The structure of the code is illustrated in Figure 3.2. The code receives the number densities as well as the temperature associated with each thermal energy mode of each species, at a given computational cell. An input file is generated for every cell, also containing geometric information about its location and shape. This case-specific input file, along with an updated spectroscopic database containing species' electronic levels, level degeneracies, spectroscopic constants and other model parameters are fed to an excitation module responsible for the calculation of level populations. This data is then directed to the radiation module which handles the calculation of the spectral emission and absorption coefficients from appropriate quantum-mechanical models. The dashed box surrounding the radiative transfer module

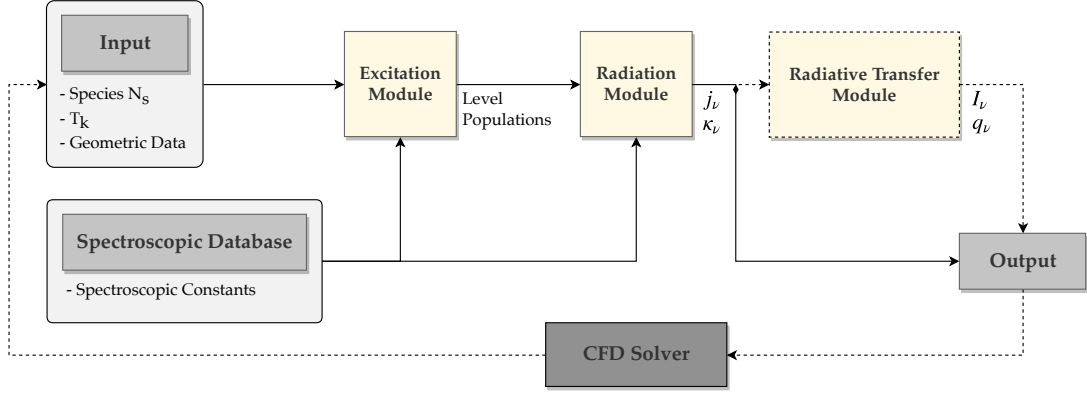


Figure 3.2: Structure of the SPARK LbL code.

indicates it is an optional post-processing tool. This is because the main application of the code is the simulation of local spectral properties of gases and plasmas to compare with experimentally obtained spectra from shock-tunnel measurements, for example, to validate the models implemented. However, it may be used in conjunction with a numerical CFD code (such as SPARK) to predict radiative heating fluxes in planetary atmospheric entry simulations, in which case the radiative transfer module is necessary to compute I_ν and q_ν . In the present work, this module was completely redesigned in Fortran under the OOP paradigm, as a step towards the future integration of SPARK LbL into the SPARK CFD code. For an in-depth description of the SPARK LbL code, see [44].

3.3 Thermodynamic Database Definition

The input data defining the thermodynamic properties of Jupiter’s atmospheric composition will now be reviewed. A seven species mixture was assumed in the present work, similar to the one employed by Reynier *et al.* [3] and several other post-flight works [7, 19, 46], composed of the following species:

$$\text{H} \quad \text{He} \quad \text{H}_2 \quad \text{H}^+ \quad \text{He}^+ \quad \text{H}_2^+ \quad \text{e}^-.$$

Throughout this work, Jupiter’s unperturbed atmosphere is assumed to consist of 86.4% H_2 and 13.6% He , in mole percent, as this was the value measured during the actual flight, as reported by Milos *et al.* [4]. The equilibrium composition of this mixture at 1 atm is presented in Figure 3.3 for temperatures ranging from 50 K to 50,000 K. Hydrogen dissociation is pronounced between 2,500 K and 6,650 K, and less than 0.1% molecular hydrogen is present above this temperature. Similarly, ionization of hydrogen atoms begins at around 7,000 K and reaches a plateau near 20,000 K, as indicated by the H^+ or e^- curves. These curves are coincident up to 20,000 K, revealing the relatively low presence of helium and molecular hydrogen ions below this point. In the meantime, helium ionization predominantly occurs above 17,500 K, leading to a 3.5% maximum helium ion mole fraction near 35,000 K. H_2^+ plays a minor role, reaching a maximum of about 0.00017% near 12,500 K. Nevertheless, it was considered in this study due to its presumed impact in the radiative analysis.

The calculation of species’ thermodynamic properties is discussed in detail in Appendix A. These

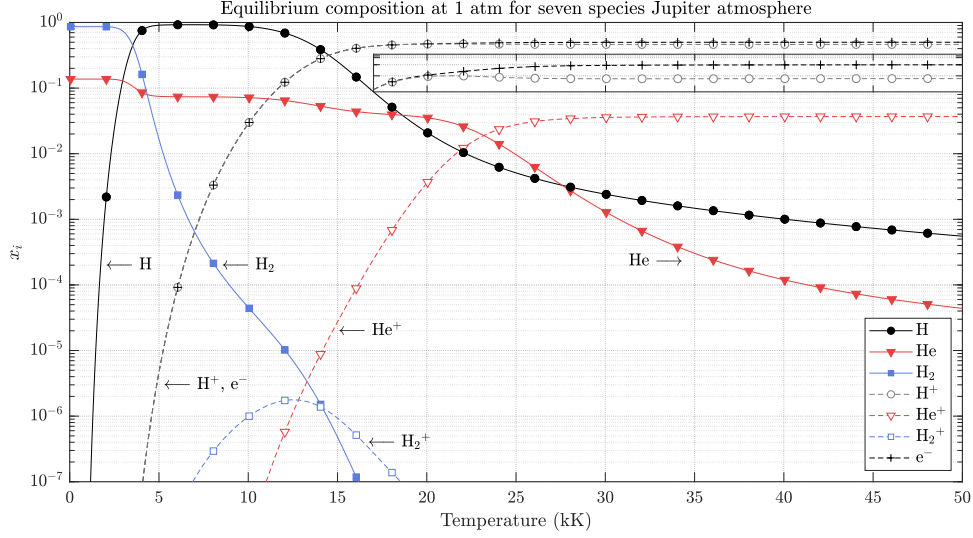


Figure 3.3: Equilibrium composition of Jupiter atmosphere mixture with $x_{\text{H}_2} = 0.864$ and $x_{\text{He}} = 0.136$.

computations can be performed either analytically at each timestep, by evaluating explicitly Eqs. A.15 to A.20 (Analytic model), or, more efficiently, by expressing these properties through simple curve-fits and evaluating those instead. The two most common sets of coefficients are the NASA9 [47] and Capitelli's [48, 49]. This option may be preferred if the resulting coefficients take into account more accurate models for the rotational/vibrational contributions, thus reducing the amount of computations if those were to be performed during runtime. However, these polynomial curve-fit expressions do not distinguish between the contributions of each internal mode, disallowing its use in conjunction with multi-temperature models. Still, both options are available in SPARK, which allowed for a comparison of transport properties calculated under each model in the present work (§ 3.4).

3.3.1 Chemical Kinetics Modeling

Several kinetic schemes regarding entry into giant planet atmospheres composed of H_2 –He mixtures can be found throughout the literature [3, 9, 16, 19]. All of these highlight the importance of properly modeling molecular hydrogen dissociation, as it is among the first processes taking place behind the shock wave [3]. Consequently, dissociating processes with H_2 , H, He, H^+ and e^- partners was considered. Atomic hydrogen and helium ionization processes are also critical to the proper modeling of the flow kinetics. Electron impact ionization of both atoms is considered in the present work, along with H- and He-impact ionization processes for atomic hydrogen. These considerations may be deduced from inspection of Figure 3.3, since these species coexist at a given temperature interval in significant percentages, and thus will considerably impact species' production rates from collisional processes. Finally, the associative ionization reaction resulting in the molecular hydrogen ion H_2^+ was modeled after Furudate [19, 46]. The kinetic model employed in the present work is summarized in Table 3.1.

A cautionary note is in order at this point. Upon gathering and comparing the data available in the literature regarding the Arrhenius coefficients entering Eq. 2.13, a discrepancy was found between the data reported by some authors. More specifically, Reynier *et al.* [3] uses the coefficients employed by

Table 3.1: Kinetic model employed in the present work with Arrhenius rate coefficients entering Eq. 2.13.

Reaction	Process	Arrhenius Rate Coefficients			Reference
		C_r ($\text{mol m}^{-3} \text{s}^{-1} \text{K}^{-\alpha_r}$)	α_r	$E_{f,r}/k_B$ (K)	
R1	$\text{H}_2 + \text{H} \longleftrightarrow \text{H} + \text{H} + \text{H}$	$8.347 \times 10^{+13}$	-1.0	$5.234 \times 10^{+04}$	[9]
R2	$\text{H}_2 + \text{He} \longleftrightarrow \text{H} + \text{H} + \text{He}$	$4.173 \times 10^{+12}$	-1.0	$5.234 \times 10^{+04}$	[9]
R3	$\text{H}_2 + \text{H}_2 \longleftrightarrow \text{H} + \text{H} + \text{H}_2$	$1.043 \times 10^{+13}$	-1.0	$5.234 \times 10^{+04}$	[9]
R4	$\text{H}_2 + \text{H}^+ \longleftrightarrow \text{H} + \text{H} + \text{H}^+$	$8.347 \times 10^{+13}$	-1.0	$5.234 \times 10^{+04}$	[9]
R5	$\text{H}_2 + \text{e}^- \longleftrightarrow \text{H} + \text{H} + \text{e}^-$	$8.347 \times 10^{+13}$	-1.0	$5.234 \times 10^{+04}$	[9]
R6	$\text{H} + \text{e}^- \longleftrightarrow \text{H}^+ + 2\text{e}^-$	$2.279 \times 10^{+05}$	0.5	$1.578 \times 10^{+05}$	[9]
R7	$\text{H} + \text{H} \longleftrightarrow \text{H}^+ + \text{e}^- + \text{H}$	$6.172 \times 10^{+02}$	0.5	$1.160 \times 10^{+05}$	[9]
R8	$\text{H} + \text{He} \longleftrightarrow \text{H}^+ + \text{e}^- + \text{He}$	$4.883 \times 10^{+02}$	0.5	$1.160 \times 10^{+05}$	[9]
R9	$\text{He} + \text{e}^- \longleftrightarrow \text{He}^+ + 2\text{e}^-$	$1.332 \times 10^{+05}$	0.5	$2.852 \times 10^{+05}$	[9]
R10	$\text{H}_2^+ + \text{e}^- \longleftrightarrow \text{H} + \text{H}$	$7.076 \times 10^{+08}$	-0.4	$0.000 \times 10^{+00}$	[19]

Tiwari and Szema [16] for reactions R6 – R9, which in turn were based on the work of Leibowitz and Kuo [9]. However, the C_r coefficients for those reactions originally published by Leibowitz were found to be two orders of magnitude lower than those used by the other authors. Since these rates are the ones recommended throughout the literature for H_2 –He mixtures [50], they were employed in the present work for all available reactions.

3.3.2 Thermal Non-Equilibrium Modeling

One important aspect regarding atmospheric entry to Jupiter is the modeling of thermal non-equilibrium, which has been previously studied by Furudate and Reynier *et al.* using a multi-temperature approach [3, 19]. This is in contrast to a state-to-state kinetic model, which instead of isolating a given thermal energy mode into a separate temperature *a priori*, would rather result in the knowledge of the possibly non-equilibrium populations of the species’ energy states, from which temperatures could be extracted. Such models for H_2 –He mixtures have recently been studied by Colonna *et al.* [51]. However, due to the large number of chemical variables considered, its application is still limited to 1D geometries. In an attempt to study its effects on more general scenarios, a multi-temperature kinetic model for Jupiter’s atmosphere had previously been derived from a similar state-to-state model by the same authors [52]. Reynier *et al.* investigated its application in the context of Galileo’s entry in Jupiter [3], and generally good agreement was found when compared to the classical kinetic model of Leibowitz and Kuo, except when it comes to the level of ionization, which was underpredicted by the latter¹. The classical model was retained in the present work due to its higher reliability and use amongst the community [50].

Excitation of the internal degrees of freedom and subsequent dissociation of H_2 are among the first processes occurring behind the strong shock wave. At high altitudes, where the atmosphere is thinnest and the density is low, collisions occur less frequently and thus the relaxation towards equilibrium takes longer. This translates into a larger non-equilibrium region, reaching as much as 1 cm, as well as a 10% decrease in radiative heating at the stagnation point, when compared to an equilibrium case, according to Furudate [19]. As the spacecraft loses altitude and atmospheric density increases, internal relaxation

¹The kinetic rates used by the author, however, place a question mark on the conclusions drawn.

processes occur at a faster rate, until eventually thermal equilibrium is reached throughout the shock layer. This was found to be approximately the case for the peak heating point in Galileo’s trajectory, according to both studies. As a result, the details of the internal relaxation processes are often neglected.

Thermal non-equilibrium effects were also subject to study in the present work. A 2T model was employed with a translational temperature T_{tr} shared by all species’ energy modes except for the vibrational mode of H_2 , which was modeled separately as T_{v,H_2} . Despite the attempts in considering a separate free-electron temperature, unidentified instability problems in the CFD solver, even in 0D and 1D simulations, prevented this refined treatment in a potential 3T model. Nonetheless, since the radiative transfer problem is decoupled from the flowfield in the present work, and due to the strong dependence of the radiative field on the electron temperature, it was assumed equal to T_{v,H_2} in the radiative analysis. This should provide a better approximation to the actual conditions when compared to considering $T_{\text{exc}} = T_{\text{tr}}$, since vibrational-electronic energy exchanges are significantly more efficient than translational-electronic energy exchanges. Finally, the vibration-translation relaxation times are calculated using Millikan-White’s correlation (Eq. 2.8), with the coefficients provided by Palmer *et al.* [50], presented in Table 3.2. Since only data is available for the collisions $\text{H}_2\text{--H}$, $\text{H}_2\text{--He}$ and $\text{H}_2\text{--H}_2$, the remaining ones with the corresponding ions were considered equal, as were the collisions involving H_2^+ and other species. Also, Park’s correction to Eq. 2.8 was not implemented in the present work, since Palmer *et al.* do not mention its application in the DPLR code at NASA.

Table 3.2: Millikan-White coefficients used in the present work [50].

Interaction	$\text{H}_2\text{--H}$	$\text{H}_2\text{--He}$	$\text{H}_2\text{--H}_2$	$\text{H}_2\text{--H}^+$	$\text{H}_2\text{--He}^+$	$\text{H}_2\text{--H}_2^+$	$\text{H}_2^+ - s_i$
A^{MW}	65.110	69.971	9.673				
B^{MW}	0.006821	0.004682	0.072500	$\text{H}_2\text{--H}$	$\text{H}_2\text{--He}$	$\text{H}_2\text{--H}_2$	$\text{H}_2 - s_i$

3.4 Transport Database Definition

One of the main accomplishments of the present work was the implementation of a new, re-structured transport module capable of handling the most up-to-date collision cross-section (CCS) databases available in the literature. Although developed in the context of an $\text{H}_2\text{--He}$ mixture, the integration of the improved module in SPARK now allows simulation of the several atmospheres present in the Solar System using the accurate Gupta/Yos model for transport, provided the relevant CCSs are available.

3.4.1 Numerical Implementation

The old transport implementation in SPARK allowed the calculation of transport properties using the Gupta/Yos model for air mixtures. It relied on outdated curve-fit expressions for air species’ CCSs published in 1989 by Gupta *et al.* [31]. Although the theory hasn’t changed, updated CCSs have since been published [38, 53, 54], primarily spurred by a team of several Italian investigators (M. Capitelli, D. Bruno and G. Colonna, to name a few).

Since curve-fit coefficients of the type published by Gupta *et al.* were not available for $\text{H}_2\text{--He}$ mixtures, it was necessary to implement a new database foundation into the **Transport** module in SPARK. The new implementation follows the OOP paradigm described in § 3.1, conforming to the code’s standards in terms of flexibility and efficiency. A significant improvement of the redesigned **Transport** module is the ability to easily define new formulas from which to compute the collision cross-sections $\sigma^2\Omega_{s,l}^{(m,n)*}$. This was a design requirement due to the varying nature of the curve-fit expressions found in the literature, which are simply analytic curve-fits on tabulated data points obtained from experiments or complex *ab initio* calculations.

The structure of the **Transport** module developed in the present work is illustrated in Figure 3.4. Both **Wilke/Blottner/Eucken Transport Strategy** and **Gupta/Yos Transport Strategy** objects contain a given **Mixing Rule Strategy**, based on the model selected by the user to compute the transport properties of the mixture. Furthermore, the **Mixing Rule Strategy** contained within the Gupta model has a **CCS Strategy** object containing an array of **CCS Interaction** objects and several mapping arrays to associate a given interaction (l, s) to the coefficients specified in the input files.

The structure is centered around the representation of different binary interactions through the **CCS Interaction** object. By exploiting Fortran’s OOP capabilities, one may assign a given interaction to one of the many inherited-type objects - which extend the abstract type **CCS Interaction** - available from a library, representing the set of curve-fit expressions available, as the code initializes. This is in direct contrast to an approach that would perform such selective tasks (assigning a certain **CCS Interaction** to be computed from a given curve-fit expression) during runtime, thus wasting significant computational resources performing pointless tests, compromising the efficiency of the code. In other words, it is much more efficient to assign a given expression to compute the collision cross section of the $A \longleftrightarrow B$ interaction as the code initializes, than it is to test if the interaction is $A \longleftrightarrow B$ at each iteration and then assign it

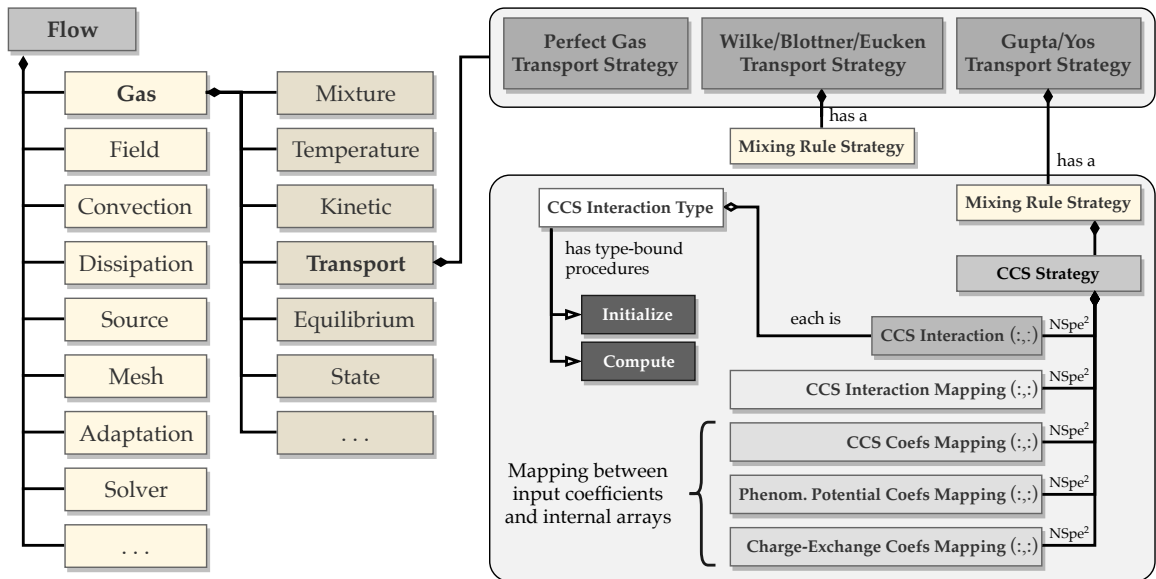


Figure 3.4: Illustration of the new internal structure of the **Transport** object. Both the Wilke/Blottner/Eucken and Gupta/Yos mixing rules were redesigned in a effort to improve the code’s efficiency and to allow a consistent integration of both models into a single **Transport** object.

to the corresponding expression. Finally, each `CCS Interaction` object has type-bound procedures that allow initialization and computation of a certain collision cross-section from its curve-fit expression and coefficients.

3.4.2 Database for H₂–He Mixtures

Wilke/Blottner/Eucken Model Database

One of the main advantages of the Wilke/Blottner/Eucken transport model is the easy implementation that comes as a result of the small amount of input data required to define each species' viscosity through Eq. 2.23. The Blottner coefficients used in the present work are those reported by Reynier *et al.* [3] and are presented in Table 3.3. These coefficients are said to have been obtained by curve-fitting Blottner's expression to the single-species viscosities obtained by Bruno *et al.*, who report accurate calculations of transport properties for Jupiter-atmosphere components using the second non-vanishing Chapman-Enskog approximation² [55] based on updated CCS data [38].

Table 3.3: Blottner coefficients used in the present work for a H₂–He mixture [3].

Species	A_s	B_s	C_s
H	4.7622453×10^{-2}	8.6627216×10^{-2}	$-1.1711139 \times 10^{+1}$
He	$-8.0783000 \times 10^{-3}$	8.2439000×10^{-1}	$-1.2968000 \times 10^{+1}$
H ₂	7.8201592×10^{-2}	$-4.4845798 \times 10^{-1}$	$-9.1570636 \times 10^{+0}$
H ⁺	$-8.8065896 \times 10^{-1}$	$1.9417680 \times 10^{+1}$	$-1.1630094 \times 10^{+2}$
He ⁺	1.3972250×10^{-1}	$-7.8183571 \times 10^{-1}$	$-1.5655289 \times 10^{+1}$
H ₂ ⁺	7.8201592×10^{-2}	$-4.4845798 \times 10^{-1}$	$-9.1570636 \times 10^{+0}$
e ⁻	$-8.8648824 \times 10^{-1}$	$1.9551323 \times 10^{+1}$	$-1.2078068 \times 10^{+2}$

Gupta/Yos Model Database

The Gupta/Yos transport model, on the other hand, requires knowledge of the CCSs of all possible pairs of species present in the mixture at a given time. This means that a total of $(N_s^2 + N_s)/2$ interactions have to be defined, for which different curve-fitting expressions may apply. Several options were made available to the `CCS Interaction` library mentioned above for the calculation of specific CCSs, namely:

1. Gupta *et al.*'s curve-fits for Earth-atmosphere components (N₂–O₂) [31]
2. Bruno *et al.*'s curve-fits for Jupiter-atmosphere components (H₂–He) [38, 39]
3. Bruno *et al.*'s curve-fit for Mars-atmosphere components (CO₂–N₂–Ar) [54]
4. Wright *et al.*'s screened Coulomb potential curve-fits for charged-species interactions [56, 57]
5. D'Angola *et al.*'s screened Coulomb potential curve-fits for charged-species interactions [55, 58]
6. Phenomenological approach based on Pirani's potential [55, 59]

²Equivalent to a second and third order approximation for viscosity and thermal conductivity, respectively.

The approach implemented in the present work follows that applied by Bruno *et al.* [38], albeit in the context of the Gupta/Yos mixing rules, which do not provide the same accuracy as their Chapman-Enskog approximation of higher order. In their report, a set of binary collision parameters for Jupiter-atmosphere components, valid between 50 K and 50,000 K, is provided. For heavy-particle interactions (referring to neutral-neutral and neutral-ion pairs), integration of the classical equation of motion using several interaction potentials was performed to obtain curve-fit coefficients for an expression of the form

$$\left[\left(\sigma^2 \Omega_{s,l}^{(m,n)*} \right)_{\text{el}} \right]_{\substack{\text{Neutral-Neutral} \\ \text{Neutral-Ion}}} = (a_1 + a_2 x) \frac{\exp \left[(x - a_3) / a_4 \right]}{\exp \left[(x - a_3) / a_4 \right] + \exp \left[(a_3 - x) / a_4 \right]} + a_5 \frac{\exp \left[(x - a_6) / a_7 \right]}{\exp \left[(x - a_6) / a_7 \right] + \exp \left[(a_6 - x) / a_7 \right]}, \quad (3.1)$$

where $x = \ln T$ and the coefficients $a_i \equiv a_i(s, l, m, n)$ are available in [38]. This formula only considers the elastic component of the collision integrals, neglecting the inelastic contribution to odd- m terms due to resonant charge transfer processes in interactions of the type atom/molecule-parent ion (in the present work, these are $\text{H}-\text{H}^+$, $\text{He}-\text{He}^+$ and H_2-H_2^+). Therefore, $(m = \text{odd}, n)$ collision cross-sections are corrected for charge-exchange according to

$$\sigma^2 \Omega_{s,l}^{(m,n)*} = \sqrt{\left(\sigma^2 \Omega_{s,l}^{(m,n)*} \right)_{\text{el}}^2 + \left(\sigma^2 \Omega_{s,l}^{(m,n)*} \right)_{\text{ch-ex}}^2} \quad \text{for } m = \text{odd}, \quad (3.2)$$

where the charge-exchange correction is given by

$$\left(\sigma^2 \Omega_{s,l}^{(m,n)*} \right)_{\text{ch-ex}} = d_1 + d_2 x + d_3 x^2, \quad (3.3)$$

and the coefficients $d_i \equiv d_i(s, l, n)$ are again provided in [38]. On the other hand, neutral-electron interactions are modeled through a different formula:

$$\left(\sigma^2 \Omega_{s,l}^{(m,n)*} \right)_{\text{Neutral-e}^-} = \frac{g_3 x^{g_5} \exp \left[(x - g_1) / g_2 \right]}{\exp \left[(x - g_1) / g_2 \right] + \exp \left[(g_1 - x) / g_2 \right]} + g_6 \exp \left[- \left(\frac{x - g_7}{g_8} \right)^2 \right] + g_4. \quad (3.4)$$

Fitting coefficients $g_i \equiv g_i(s, l, m, n)$ entering Eq. 3.4 are provided in [38] for neutral-electron interactions.

For certain heavy-particle interactions, not enough data is available to construct a set of coefficients for Eq. 3.1. Bruno *et al.* consequently implemented a phenomenological approach based on Pirani's potential [55]. This approach allows the direct evaluation of collision integrals for unknown collisional systems in terms of fundamental physical properties of the involved interacting partners [38]. This has already been verified to produce good results for collisional systems relevant to Earth's and Mars' atmospheres [59].

The CCS for interactions following this approach is calculated using

$$\left(\sigma^2 \Omega_{s,l}^{(m,n)*}\right)_{\text{el}} = \sigma_{s,l}^2 \exp \left\{ \left[\bar{a}_1 + \bar{a}_2 \bar{x} \right] \frac{\exp \left[(\bar{x} - \bar{a}_3) / \bar{a}_4 \right]}{\exp \left[(\bar{x} - \bar{a}_3) / \bar{a}_4 \right] + \exp \left[(\bar{a}_3 - \bar{x}) / \bar{a}_4 \right]} + \bar{a}_5 \frac{\exp \left[(\bar{x} - \bar{a}_6) / \bar{a}_7 \right]}{\exp \left[(\bar{x} - \bar{a}_6) / \bar{a}_7 \right] + \exp \left[(\bar{a}_6 - \bar{x}) / \bar{a}_7 \right]} \right\}, \quad (3.5)$$

where $\bar{x} = \ln \left(\frac{k_B T}{\varphi_{0,s,l}} \right)$ is now dimensionless and the coefficients $\bar{a}_i \equiv \bar{a}_i(\beta_{s,l}, \bar{c}^{(m,n)})$ are polynomial functions of $\beta_{s,l}$ of the form

$$\bar{a}_i = \sum_{j=0}^2 \bar{c}_j^{(m,n)} \beta_{s,l}^j. \quad (3.6)$$

The rigid sphere collision cross-section $\sigma_{s,l}^2$ entering Eq. 3.5 is calculated via

$$\sigma_{s,l}^2 = \left(\xi_1 \beta_{s,l}^{\xi_2} r_{e,s,l} \right)^2. \quad (3.7)$$

The Pirani potential parameters $\beta_{s,l}$, $\varphi_{0,s,l}$ and $r_{e,s,l}$ used in the present work are presented in Table 3.4. The remaining parameters $\bar{c}_j^{(m,n)}$ and ξ_i entering Eqs. 3.6 and 3.7 are provided in [55] for both neutral-neutral and neutral-ion interactions.

Table 3.4: Potential parameters entering the phenomenological approach [38].

Interaction	β	Well Depth φ_0 (meV)	Eq. Distance r_e (Å)
H-H ₂ ⁺	8.00	$7.3104 \times 10^{+1}$	2.769
He-H ₂	9.29	$1.8650 \times 10^{+0}$	3.189
He-H ₂ ⁺	9.73	$3.0664 \times 10^{+1}$	2.574
H ₂ -He ⁺	9.22	$1.7750 \times 10^{+2}$	2.223
H ₂ -H ₂ ⁺	8.97	$8.3283 \times 10^{+1}$	2.809

It should be mentioned at this point that implementation of the phenomenological approach database in SPARK brings advantages not limited to Jupiter's atmosphere. In fact, an exhaustive CCS database for Mars-atmosphere components has recently been published under the phenomenological approach framework [54], meaning the new feature of the code will reveal useful in simulating hypersonic entry in the Martian atmosphere using the accurate Gupta/Yos model for transport. Of course, this extends to any atmosphere since this approach only requires knowledge on certain fundamental properties of the interacting species, which are generally encountered in the literature³. This extension, however, requires verification. In the present work, the extension of the model to Jupiter's atmosphere was verified against CCS data published by Biolsi [60] and in the Russian literature by Sokolova [40].

Finally, regarding charged-species interactions (which include ion-ion, ion-electron and electron-electron pairs), the corresponding CCSs were obtained assuming a screened Coulomb potential, following the

³Namely, the polarizability, the charge and the number of electrons effective in polarization.

approach proposed by Wright *et al.* [56]. A description of the model is available in Appendix B, and will not be discussed here. A summary for the 28 binary interactions and the corresponding methods used to calculate their CCSs in the present work is provided in Table 3.5. Since the curve-fitting expressions vary with the type of the interacting species, several objects derived from the type **CCS Interaction** had to be constructed, each containing a different function from which to compute its collision cross-section.

Table 3.5: List of 28 interactions considered in the present work and corresponding models used for collision cross-section computations.

Interaction Type	Calculation Method	Interactions						Ref.
Neutral – Neutral Neutral – Ion	Bruno Curve-Fit (Eq. 3.1)	H–H H–He	H–H ₂ H–He ⁺	He–He He–H ⁺	He–H ₂ ⁺ H ₂ –H ₂	H ₂ –H ⁺	[38]	
	Bruno Curve-Fit (Eq. 3.1) + Charge-Exchange (Eq. 3.2)	H–H ⁺	He–He ⁺				[38]	
	Phenomenological (Eq. 3.5)	H–H ₂ ⁺	He–H ₂	He–H ₂ ⁺	H ₂ –He ⁺		[55]	
	Phenomenological (Eq. 3.5) + Charge-Exchange (Eq. 3.2)	H ₂ –H ₂ ⁺					[38, 55]	
Neutral – Electron	Bruno Curve-Fit (Eq. 3.4)	H–e [–]	He–e [–]	H ₂ –e [–]			[38]	
Charged-Particles	Wright’s Curve-Fit (Eq. B.3)	H ⁺ –H ⁺ H ⁺ –He ⁺	H ⁺ –H ₂ ⁺ He ⁺ –He ⁺	He ⁺ –H ₂ ⁺ H ₂ ⁺ –H ₂ ⁺	H ⁺ –e [–] He ⁺ –e [–]	H ₂ ⁺ –e [–] e [–] –e [–]	[56]	

Figure 3.5 presents a comparison of important collision cross-sections in H₂–He mixtures from several sources to verify those used in the present work. Biolsi [60] and Sokolova [40] present several CCSs dating from the 1970s in tabular form, valid for temperatures in the ranges 1,000 K - 25,000 K and 2,000 K - 30,000 K, respectively. Note that Biolsi’s data is only given at temperatures where the mole fractions of the interacting pair is significant, leading to an absence of data points in Figures 3.5b and 3.5d.

In Figure 3.5a the H–H interaction is seen to agree well among all sources considered, especially comparing Bruno’s and Biolsi’s data. Furthermore, all sources present agreeing values regarding the H–H⁺ interaction, shown in Figure 3.5b, provided the charge-exchange correction is applied to $\sigma^2\Omega_{H,H^+}^{(1,1)*}$. Moreover, Figures 3.5c to 3.5f support the use of the phenomenological approach in the context of Jupiter’s atmosphere, for interactions unavailable in Bruno’s paper. Fairly good agreement is seen regarding the H–H₂⁺ interaction in Figure 3.5c between the phenomenological approach and Sokolova’s data. On the other hand, He–H₂ and He–H₂⁺ phenomenological interactions present significant deviations from Biolsi’s and Sokolova’s data, as may be appreciated from Figures 3.5d and 3.5e. The use of the approach in these cases is justified, first, for consistency (since it was the approach employed by Bruno *et al.* [38], and was kept here to allow for later comparisons) and, most importantly, because the interacting species always coexist in negligible amounts inside the shock layer, meaning their effect on the mixture’s transport properties will be negligible. The same can be said regarding the H₂–He⁺ collision pair, for which data was unavailable in [40]. Finally, Figure 3.5f shows the H₂–H₂⁺ interaction. Good agreement is seen for $\sigma^2\Omega_{H_2,H_2^+}^{(1,1)*}$, again, provided the charge-exchange correction is applied. No data was found in the literature regarding $\sigma^2\Omega_{H_2,H_2^+}^{(2,2)*}$, which did not allow for a direct comparison. On the same note, regarding $\sigma^2\Omega_{s,l}^{(1,2)*}$ and $\sigma^2\Omega_{s,l}^{(1,3)*}$ collision cross-sections, the phenomenological approach could not be verified since no data was encountered in the literature. Despite this, it was applied in the present work.

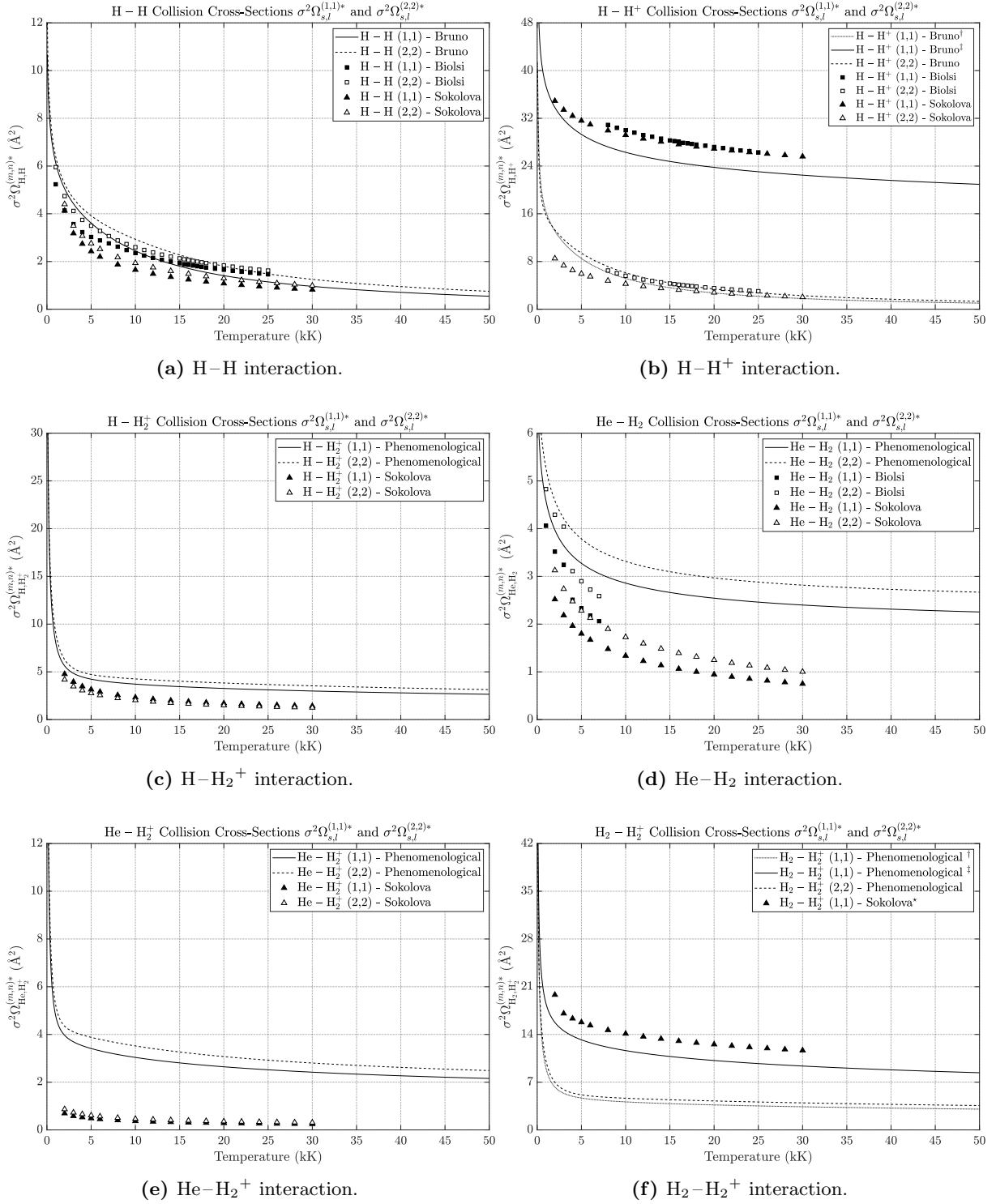


Figure 3.5: Comparison of collision cross-sections relevant to Jupiter's atmosphere among several sources [38–40, 55, 60].

[†] CCS before charge-exchange correction.

[‡] CCS after charge-exchange correction.

* No data was found regarding H₂ – H₂⁺ (2,2).

Transport Properties Verification

The global mixture transport properties obtained using the approaches outlined in the previous section will now be compared with several sources, namely: Biolsi's Jupiter-atmosphere transport property analysis

[61], Reynier *et al.*'s seven species Bari Model⁴ [3], Bruno *et al.*'s detailed calculations using a higher-order Chapman-Enskog approximation [38, 39], and a calculation of transport properties using NASA's Chemical Equilibrium with Applications (CEA) code [62]. A small difference regarding the presumed compositions of the unperturbed H_2 –He mixture among these sources should be noted. While Biolsi's and Bruno *et al.*'s data consider $x_{\text{H}_2} = 0.89$ and $x_{\text{He}} = 0.11$ (mole fractions), Reynier *et al.*'s and CEA's data corresponds to a composition of $x_{\text{H}_2} = 0.864$ and $x_{\text{He}} = 0.136$, similar to the one assumed to represent Jupiter's atmosphere in the present work.

All transport properties presented assume an equilibrium H_2 –He mixture at 1 atm. Bruno *et al.*'s calculations are considered the most accurate ones to date, so all comparisons will be made with respect to this data set. First, Figure 3.6 compares the viscosity of the mixture between all available sources. The Wilke/Blottner/Eucken model largely underpredicts the viscosity of the mixture between 5,000 K and 25,000 K, which is the temperature range of interest for the Galileo entry. On the contrary, the 1st Order Gupta/Yos model significantly overshoots the viscosity by 50% to 100% between 10,000 K and 25,000 K. When comparing Bruno's data with the 2nd Order Gupta/Yos calculation, a better agreement is found between 20,000 K and 25,000 K, but significant discrepancies still occur at lower temperatures, especially between 10,000 K and 20,000 K. Among all sources, Biolsi's data is seen to provide the best agreement with Bruno's detailed calculations.

Regarding thermal conductivity, results are presented in Figures 3.7 to 3.9. The translational contribution to the total thermal conductivity of both heavy-species and electrons are compared in Figure 3.7. The total translational thermal conductivity is presented in filled markers, allowing a comparison of the contributions due to electrons and heavy-species at different temperatures. Above 15,000 K, electrons become the main contributors to the translational component, despite their decreased mass, due to the large velocities they can acquire. Once again, a poor agreement is obtained for the Wilke/Blottner/Eucken model above 5,000 K. The large electron contribution of Bruno's data set is a result of considering a third-order Chapman-Enskog approximation for this species' translational thermal conductivity [55]. Additionally, the effect of considering the 2nd Order Gupta/Yos model over the 1st Order one is clearly seen. As predicted in § 2.1.4.2, the conductivity of the former model is decreased below that of the latter one. However, this results in a poorer agreement when compared to Bruno's data, especially above 10,000 K. Finally, Biolsi's data closely follows the tendency of the Gupta/Yos 1st Order model, as would be expected.

Figure 3.8 compares the internal contributions to the thermal conductivity of the mixture, resulting from the rotational, vibrational and electronic excitation thermal energy modes. Since these depend on the species' specific heats, the different thermodynamic databases mentioned in § 3.3 will result in different internal contributions. Hence, the Analytic database is compared to the polynomial databases provided by the NASA9 and Capitelli's curve-fits. Furthermore, the Gupta/Yos calculations are the same for the 1st and 2nd Order models, leading to the same curve in Figure 3.8. The Wilke/Blottner/Eucken model once again shows its inadequacy at higher temperatures, irrespective of the thermodynamic model used. The same may be said about the Gupta/Yos model under NASA9's thermodynamic database. Furthermore, a

⁴Assuming the Wilke/Blottner/Eucken model coefficients for H_2^+ to be equal to those presented for H_2 .

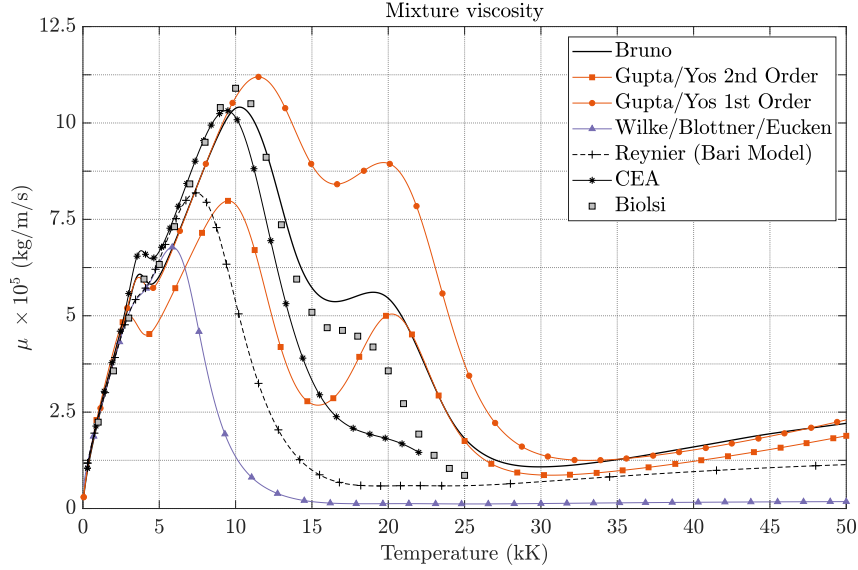


Figure 3.6: Viscosity coefficient of equilibrium Jupiter atmosphere at 1 atm.

fair agreement is obtained between Bruno’s data and the Gupta/Yos model under both the Analytic and Capitelli’s thermodynamic databases, with the latter providing a better accuracy, since it was the one used by Bruno *et al.* [38].

The total thermal conductivity resulting from these two contributions is presented in Figure 3.9. Similar considerations apply to those provided regarding the translational component, in light of the lower magnitude of the internal contribution. The two maxima observed in the CEA thermal conductivity result from considering the reactive component of the specific heats for the calculation of internal thermal conductivity contributions, which does not enter the remaining data sets. These spikes correspond to the dissociation of H_2 and ionization of H , respectively, and are seen to provide a significant contribution for the mixture’s thermal conductivity. As a result of the increased accuracy of the method employed by Bruno *et al.*, discrepancies respectively reach 50% and 75% at 25,000 K for the Gupta/Yos 1st and 2nd Order models employed in the present work. However, these high temperatures are only expected to exist in a small region after the shock, while the remaining shock layer is anticipated to remain between 5,000 K and 20,000 K, for which the agreement is substantially improved.

Finally, species’ mass diffusion coefficients are compared in Figure 3.10. The electron mass diffusion coefficient is not presented since it is not calculated explicitly in SPARK. Instead, the electron mass diffusion flux is computed at runtime to ensure flux neutrality and mass conservation through a modified Fick Model (see [37] for details). Bruno *et al.*’s data set did not provide mass diffusion coefficients [38], hence the comparison is made here considering Biolsi’s to be the most accurate. The Wilke/Blottner/Eucken model is seen to overpredict mass diffusion at temperatures below 10,000 K for all species except H_2 . On the other hand, fairly good agreement is encountered between Biolsi’s data and the Gupta/Yos models employed in the present work, further justifying its use over the Wilke/Blottner/Eucken model.

In summary, the Wilke/Blottner/Eucken transport model is seen to severely underpredict the transport properties of H_2 –He mixtures above 5,000 K. On the other hand, the Gupta/Yos models significantly improve the agreement with accurate calculations available in the literature. In the present work, the 2nd

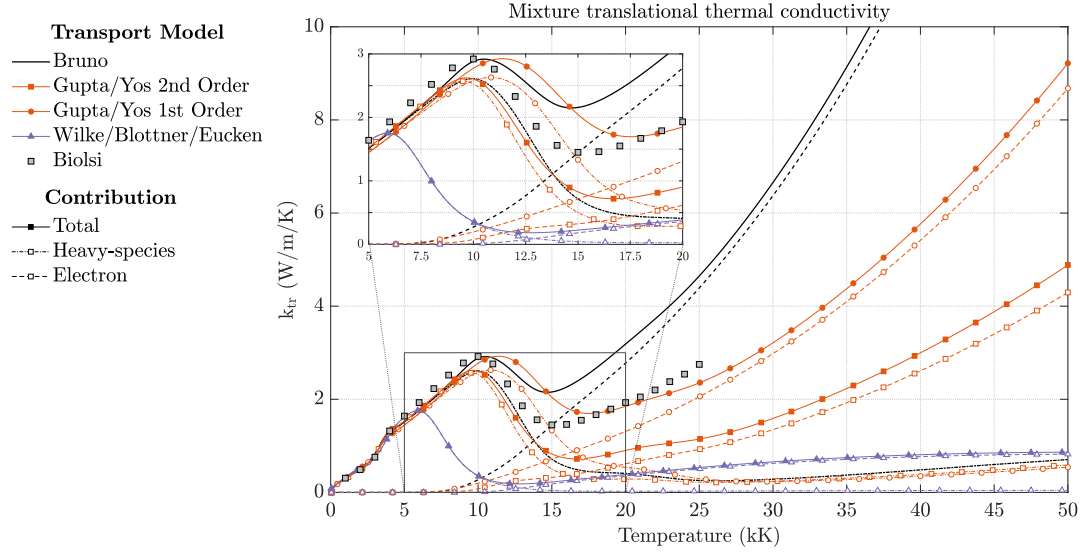


Figure 3.7: Translational thermal conductivity of equilibrium Jupiter atmosphere at 1 atm.

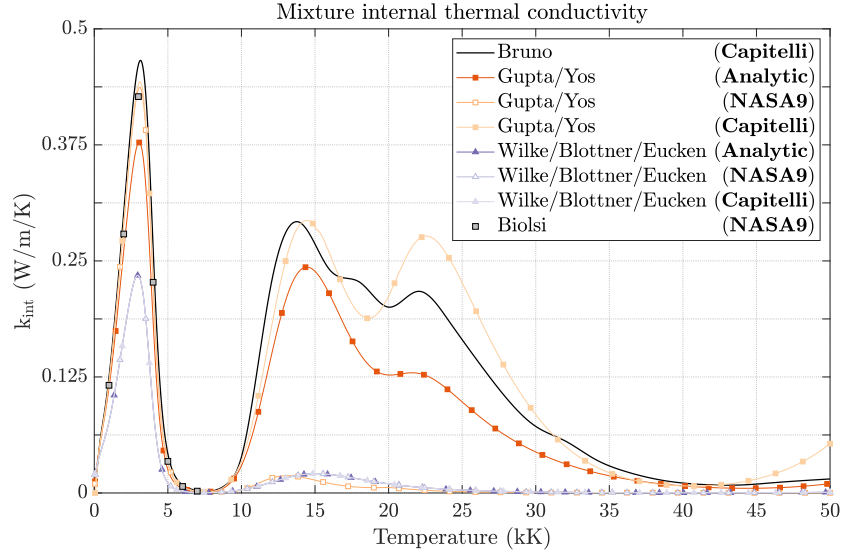


Figure 3.8: Internal thermal conductivity of equilibrium Jupiter atmosphere at 1 atm.

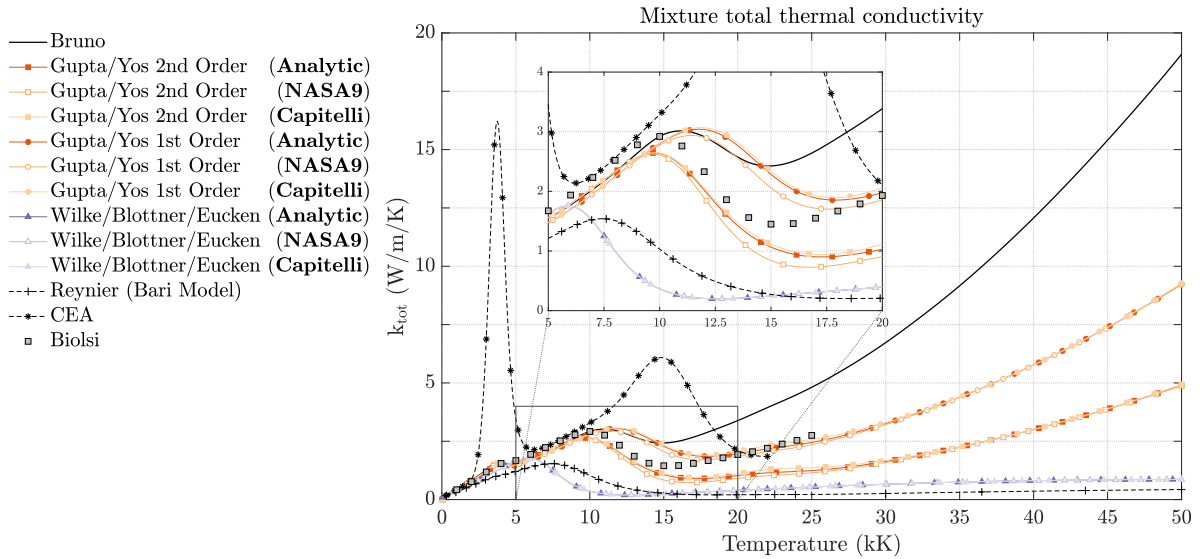


Figure 3.9: Total thermal conductivity of equilibrium Jupiter atmosphere at 1 atm.

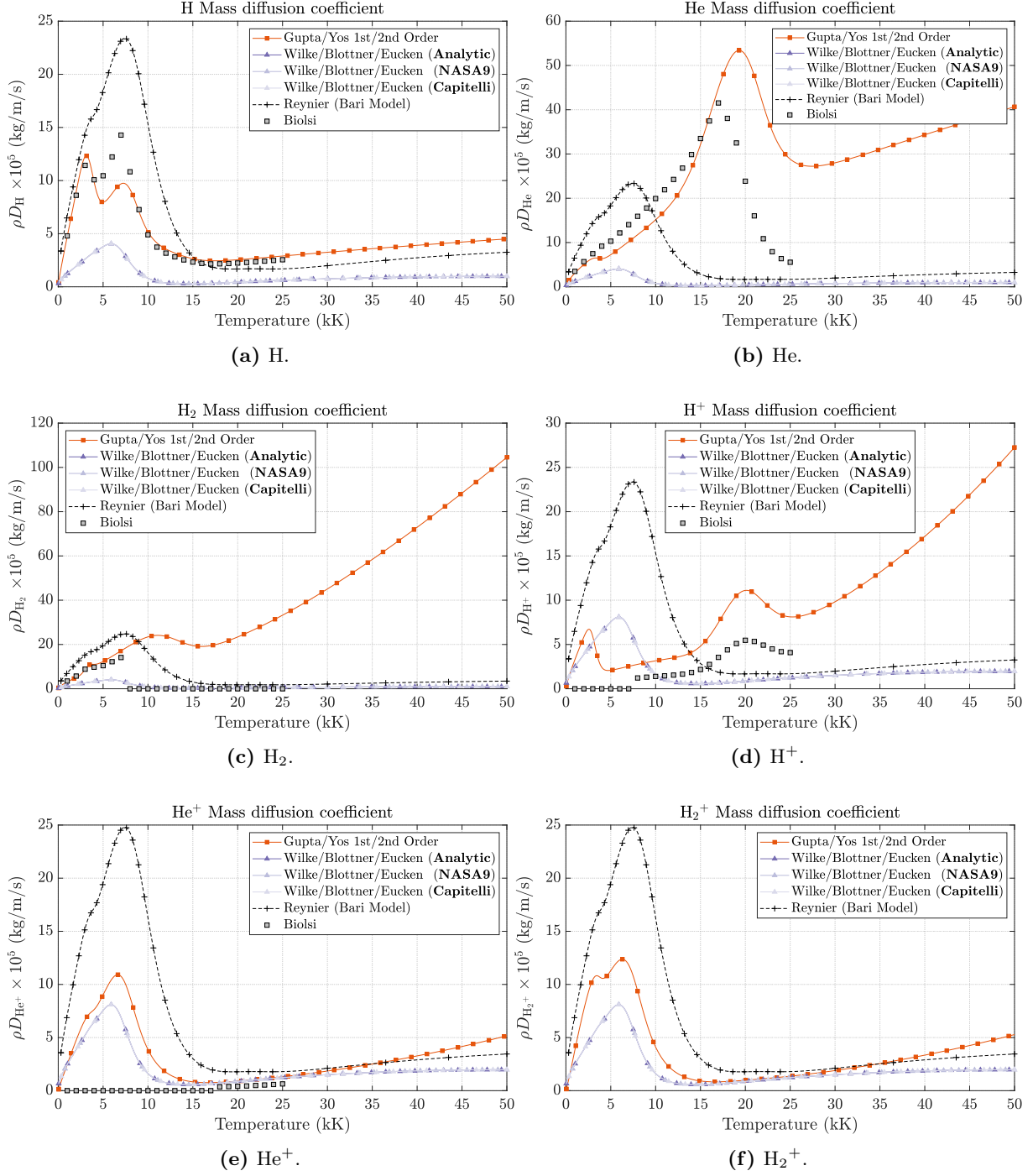


Figure 3.10: Species' mass diffusion coefficients for equilibrium Jupiter atmosphere at 1 atm. Note the multiplication by the mass density to provide the results in kg/m/s.

Order Gupta/Yos model was used in favor of the 1st Order one.

3.5 Radiative Database Description

The definition of a spectral database suited to the Galileo entry conditions has been carried out. Firstly, as the extremely high post-shock temperatures lead to a highly dissociated flow, great care must be exerted in defining a detailed set of atomic transitions, encompassing bound and continuum transitions. A considerable advantage of atomic radiation modeling is that the number of radiative transitions is moderate, and, accordingly, calculation times and spectral grid sizes will be moderate as well. Thus, the atomic spectral database accounts for as much radiative transitions as possible, regardless of their quantitative importance. For example, the contribution from bound transitions of He and He⁺ atoms may in general be neglected, since the first excited states lie respectively 20 eV and 40 eV above the ground state. This means these will not be considerably populated for the temperature range of interest if we assume a Boltzmann distribution for the internal levels. Nevertheless, these radiative systems have been accounted for the sake of completeness, as they have a negligible impact on calculation times and spectral grid sizes. All the atomic line data is issued from NIST [63].

Secondly, as the ionization degree of the flow is considerably high, great care must be exerted when modeling the broadening mechanisms for these atomic transitions, especially for what pertains to Stark broadening mechanisms. Two possibilities may be considered: either a general expression may be used, such as the one proposed by Johnston for N and O atomic transitions [64], or a reference FWHM (Full Width at Half Maximum) for each transition may be supplied and then scaled for the electronic temperature and density of the gas cell [65]. Since radiation from H atomic lines is key to the overall radiative fluxes, a literature review was carried out for the FWHM measured for the different H transitions, for a range of electronic temperatures and densities. Then, the data is fitted to the expression

$$\Delta\lambda_{\text{SB}}(N_{\text{e}^-}, T_{\text{e}}) = \Delta\lambda_{\text{SB},0} \left(\frac{T_{\text{e}}}{10,000} \right)^m \left(\frac{N_{\text{e}^-}}{10^{22}} \right)^n, \quad (3.8)$$

where $\Delta\lambda_{\text{SB},0}$ is the reference Stark FWHM for the transition. Whenever the m and n exponents are not supplied, $m = 2/3$ and $n = 1$ is assumed⁵.

The data used for the fit to Eq. 3.8 was retrieved from Griem [65] for the Lyman ($\alpha, \beta, \gamma, \delta$) and Balmer ($\alpha, \beta, \gamma, \delta$) transitions, Ref. [66] for the Paschen (α, β) transitions, Ref. [67] for the Paschen γ transition, Ref. [68] for the Brackett (α, β) transitions, and estimated for the Pfund α transition. From this data, a general semiempirical function for the missing transitions of hydrogenoid species was derived, similar to the one proposed by Johnston for air species:

$$\Delta\lambda_{\text{SB},0} = 1.72 \times 10^{-21} \times (E_{\text{ion}} - E_{\text{u}})^{2.5} \lambda^{1.7} n_{\text{u}}^{9.3}, \quad (3.9)$$

which is used whenever data is absent for specific transitions of hydrogenoid species. In Eq. 3.9, E_{ion} is the ionization energy, E_{u} is the upper state energy, n_{u} the main quantum number of the upper state and λ is the transition wavelength in Ångström.

⁵ $m = 2/3$ was found to better represent the T_{e} dependence than the value $m = 1/3$ proposed by Park for air species [64].

Besides the atomic transitions, H_2 transitions are also considered, in an effort to determine its impact using a line-by-line approach for the first time. This species is present to a certain extent in the shock-layer (before dissociation) and near the wall (due to recombination processes), and thus its effects on the radiative heating may be important. The Lyman ($B^1\Sigma_u^+ - X^1\Sigma_g^+$) and Werner ($C^1\Pi_u - X^1\Sigma_g^+$) VUV transitions are considered, which will be the more relevant in terms of emission, since the $B^1\Sigma_u^+$ and $C^1\Pi_u$ are the lowest excited states that may radiate towards the ground $X^1\Sigma_g^+$ state. The weaker Fulcher band was also included ($d^3\Pi_u - a^3\Sigma_g^+$). Additionally, the transitions $B'^1\Sigma_u^+ - X^1\Sigma_g^+$, $D^1\Pi_u - X^1\Sigma_g^+$, $B''B^1\Sigma_u^+ - X^1\Sigma_g^+$, and $D'^1\Pi_u - X^1\Sigma_g^+$ are also accounted for, since they are connected to the ground state $X^1\Sigma_g^+$. Although these will be weakly emissive transitions, due to the higher-lying states $B'^1\Sigma_u^+$, $D^1\Pi_u$, $B''B^1\Sigma_u^+$, $D'^1\Pi_u$ being sparsely populated, they will be strongly absorptive as the ground state $X^1\Sigma_g^+$ is strongly populated.

For the $X^1\Sigma_g^+$ level energies, the data proposed by Pachucki [69] is fitted to adequate Dunham and v -dependent constants, while for the $B^1\Sigma_u^+$ and $C^1\Pi_u$ states the same procedure is applied to the levels measured by Abgrall [70]. The Dunham coefficients for the high-lying states are retrieved from the Huber and Herzberg compilation [71]. Finally, the transition probabilities use the data compiled by Fantz [72].

This data set for discrete atomic and diatomic transitions has been complemented by a data set for continuum transitions (bound-free photo-dissociation/photo-ionization, and free-free bremsstrahlung), which was developed through an extensive literature review. Since continuum transitions lead to typically compact spectral grids, all possible transitions from all species are considered, regardless of how marginal these may be. A great majority of this data is issued from astrophysical plasma research, since H and He species make up for a majority of the Universe. Table 3.6 presents the entire spectral database that was utilized in the scope of this work.

The importance of each radiative system considered was assessed in different regions of the flowfield through the calculation of its volumetric emissive power⁶ using SPARK LbL's database at several temperatures between 100 K and 50,000 K. These results are presented in Figure 3.11, showing that

Table 3.6: Description of spectroscopic database used in the present work.

Species	Database	Model	Lines	Electronic Levels	Ref.	Species	System	Upper State - Lower State	Bands ($v'_{\max}, v''_{\max}$)	Ref.
Atomic Lines						Molecular Band Systems				
H	NIST	-	24	-	[63]	H ₂	Lyman	B ¹ Σ _u ⁺ – X ¹ Σ _g ⁺	(10,10)	[69, 70, 72]
He	NIST	-	152	-	[63]		Werner	C ¹ Π _u – X ¹ Σ _g ⁺	(10,10)	[69, 70, 72]
He ⁺	NIST	-	140	-	[63]		Fulcher	d ³ Π _u – a ³ Σ _g ⁺	(18,18)	[72, 73]
Atomic Photoionization							B' – X	B ¹ Σ _u ⁺ – X ¹ Σ _g ⁺	(8,10)	[71, 72, 74]
H	TOPBase	Level Q_a	-	55	[75]		D – X	D ¹ Π _u – X ¹ Σ _g ⁺	(10,10)	[71, 72, 74]
He	TOPBase	Level Q_a	-	53	[75]		B''B – X	B ¹ B ¹ Σ _u ⁺ – X ¹ Σ _g ⁺	(10,10)	[71, 72]
He ⁺	TOPBase	Level Q_a	-	55	[75]		D' – X	D ¹ Π _u – X ¹ Σ _g ⁺	(10,10)	[71, 72]
Atomic Photodetachment						Species	Database	Model	Lines	Ref.
H [−]						Molecular Photoionization				
He [−]						H ₂	-	Global Q_a	-	[79–81]
Bremsstrahlung						Molecular Photodissociation				
H	-	Global Q_a	-	-	[82]	H ₂	-	Global Q_a	-	[83, 84]
He	-	Global Q_a	-	-	[85]	H ₂ ⁺	-	Global Q_a	-	[83]
He ⁺	-	Global Q_a	-	-	[86]					
H ₂ [−]	-	Global Q_a	-	-	[87]					

⁶Obtained from integration of j_ν over the frequency spectrum and multiplied by the spherical area 4π .

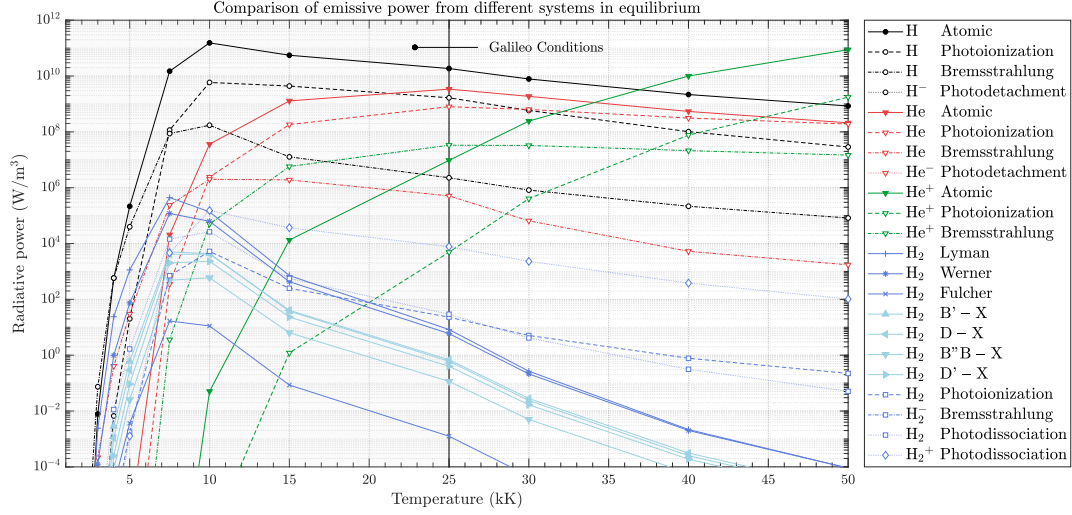
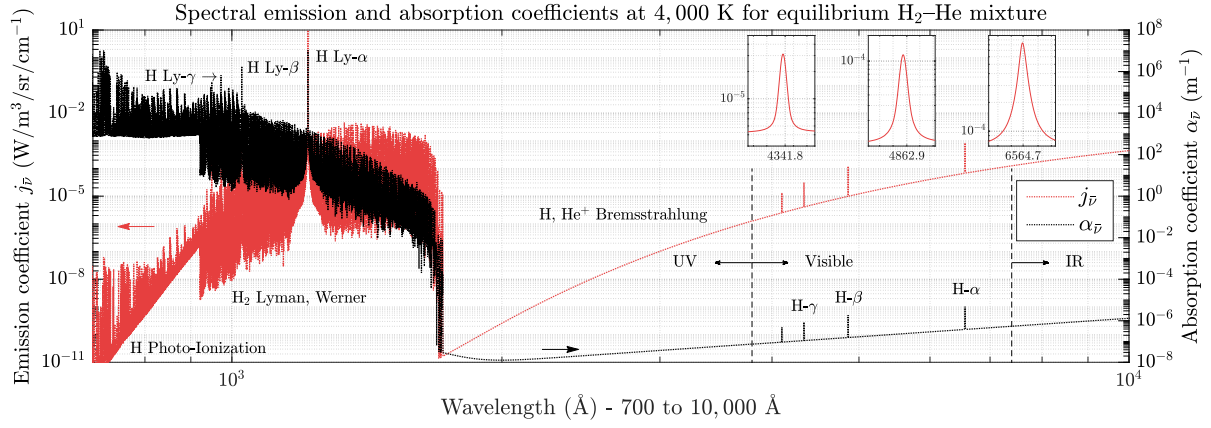


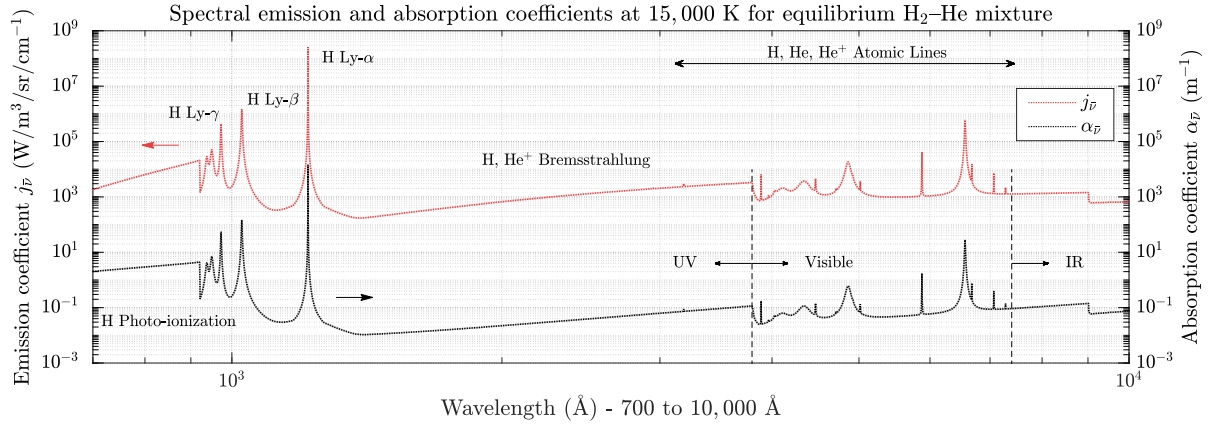
Figure 3.11: Emissive power of each radiative system as a function of temperature in equilibrium H_2 –He mixture.

atomic hydrogen dominates emission over the temperature range of interest for the Galileo entry, mostly due to the high-intensity atomic lines characteristic of this element. Furthermore, helium atomic and photo-ionization systems become important above 5,000 K, whereas the helium ion, despite its low presence in the mixture (around 3% mole fraction above 30,000 K), is seen to contribute significantly at higher temperatures. At low temperatures (below 5,000 K) practically all systems considered are equally important, while as one moves towards higher temperatures the diatomic H_2 and H_2^+ systems lose significance. This is a result of molecular hydrogen dissociation above 5,000 K.

Previous studies conducted on the simulation of the radiative environment surrounding the Galileo spacecraft have almost universally neglected radiation from molecular hydrogen, focusing mainly on atomic hydrogen [7, 17, 19, 21, 88]. The fact that molecular hydrogen systems become relevant at low temperatures raises the question of whether or not this assumption is reasonable, especially near the wall, where recombination takes place as a result of the lower-temperature equilibrium boundary-layer, accordingly increasing H_2 fractions in the process. To further illustrate this point, the spectral emission and absorption coefficients calculated using SPARK LbL at temperatures of 4,000 K and 15,000 K (corresponding to near-wall and shock-layer conditions, respectively) are shown in Figure 3.12. The main radiative systems are identified in both figures. The diatomic spectral bands corresponding to molecular hydrogen ro-vibronic transitions, observed in the ultraviolet (UV) region in Figure 3.12a, can have a filtering effect over the wall-ward radiative heating coming from the high-temperature shock-layer. That is, radiation that would otherwise reach the forebody of the spacecraft, will instead be absorbed by molecular hydrogen if the boundary-layer contains a significant fraction of this element. Thus, the presence of molecular hydrogen near the wall may result in a shielding effect from the radiation emitted elsewhere, provided the extra emission from the now excited H_2 systems is sufficiently low when compared to the absorbed radiation. Another possibility that may promote the opposing effect is the emission of radiation by H_2 from the shock location, just before the onset of dissociation, where large amounts of this species still exists and the temperature is rapidly increasing. Both possibilities were investigated in the present



(a) $T = 4,000$ K: diatomic H_2 systems highly active in UV region.



(b) $T = 15,000$ K: diatomic H_2 systems inactive.

Figure 3.12: Spectral emission and absorption coefficients for equilibrium H_2 –He mixture at different temperatures. Red - emission coefficient. Black - absorption coefficient.

work and will be analyzed in more detail in § 4.

Radiation Database Verification

The absorption coefficients obtained with SPARK LbL’s spectral database are now compared with those published by Perrin *et al.* using the HTGR database [89]. The comparison is performed considering an equilibrium H_2 –He mixture at 1 atm and initial molar composition in the ratio $H_2 : He = 89 : 11\%$. The spectral absorption coefficients resulting from both databases are presented in Figure 3.13 for 5,000 K and 20,000 K, again temperatures representative of the boundary and shock-layers, respectively.

Good agreement is seen between the two spectral databases, although a more pronounced Stark broadening of hydrogen atomic lines is observed in the HTGR database, especially at 20,000 K. As temperatures increase, the molecular absorption lines of H_2 present in the UV region are progressively overcome by atomic H Lyman absorption. At lower temperatures, such as in the 5,000 K case, these molecular absorption mechanisms are still very important, emphasizing the importance of H_2 ’s role in the radiative transfer process. Finally, the emission coefficient could not be compared against any other radiative database due to a lack of availability of this data for Gas Giant atmospheres. However, since they

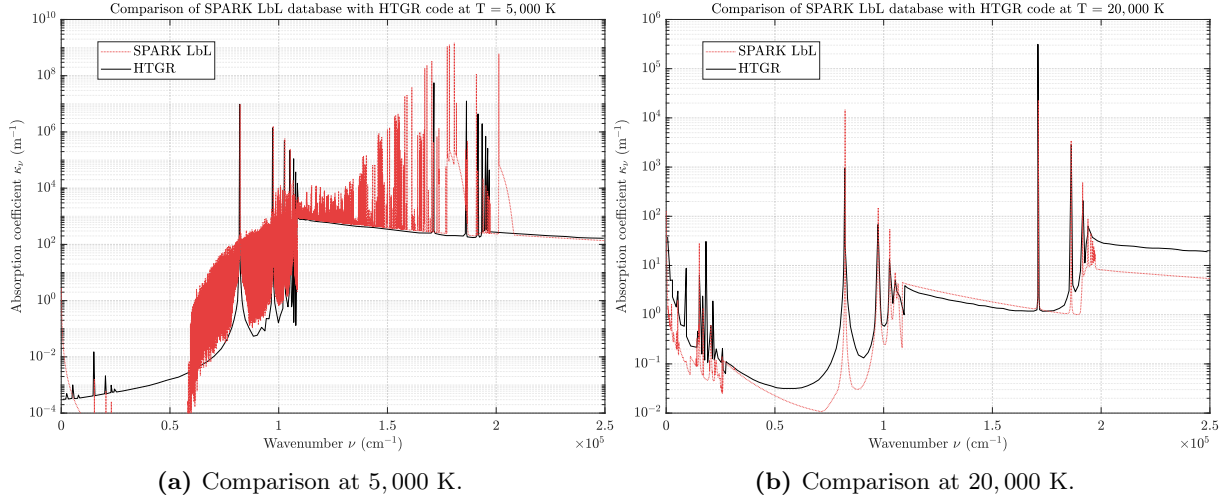


Figure 3.13: Comparison between SPARK LbL and HTGR’s spectral databases. Note that the detailed molecular absorption lines between 60,000 and 110,000 cm^{-1} couldn’t be manually retrieved from Perrin *et al.*’s paper [89], even though they are present.

are computed from the absorption coefficients through the Principle of Detailed Balance (or vice-versa), this means that both spectral quantities should present good agreement with HTGR’s database.

3.6 Radiative Transfer Models Implementation

The computational framework used to solve the radiative transfer equation discussed in § 2.2.2.2 will now be presented. The three models mentioned earlier are described, along with the underlying approximations used to derive them. A brief comment on radiation-flowfield coupling will first be provided.

Radiative energy exchange is coupled to the Navier-Stokes equations through the presence of the negative divergence of the local radiative heat flux vector in the energy equation (Eq. 2.1c). The sometimes prohibitive computational cost associated with the calculation of this term means it is often neglected (leading to an uncoupled approach) or treated in a loosely-coupled manner, where the flow and radiation fields are considered separately. While the uncoupled approach fully neglects radiation-flowfield coupling, the loosely-coupled approach updates the radiative source term only once every few iterations with the radiative field stemming from the converged flow, until eventually global convergence is reached. Johnston *et al.* have recently shown that a coupled tangent-slab solution may be used in conjunction with a final ray-tracing iteration to provide radiative heating values within 1% accuracy in coupled flowfield-radiation simulations [90]. As radiation becomes important, the impact of this coupling may be significant: the divergence of the local radiative heat flux vector introduces an energy source/sink, leading to higher/lower temperatures at different locations in the flowfield that modify the chemical kinetics, ultimately changing the radiation field when compared to an uncoupled approach. Due to the prohibitive computational cost of this approach, the flow and radiation fields are solved in an uncoupled fashion in the present work. The correlation developed by Tauber and Wakefield specially for Galileo’s entry in Jupiter [91] was employed whenever appropriate in § 4, so as to account for the effects of radiation-flowfield coupling in an approximate manner.

The radiative transfer models mentioned earlier will now be presented.

Tangent-Slab Model

The tangent-slab model has been the most widely used approximation for radiative transfer in hypersonic flow applications, due to its simple implementation, reasonable accuracy and a relatively low computational cost with respect to other models. It is known to provide a 10-15% overprediction for the radiative heating around the stagnation region, but its accuracy decreases significantly towards the shoulder and afterbody regions, where up to 70% differences have been reported in previous studies when compared to the ray-tracing approach [92, 93]. This relatively good prediction near the stagnation region is to be expected, not only due to the small thickness of the shock layer, but also due to the gradual spatial variation of the flow properties. Near the shoulder and in the after-body regions, the flow fails to exhibit tangent-slab-like properties, and the accuracy of the approximation is accordingly compromised.

The fundamental assumption behind this approximation is that the variation of the flow properties along a line of sight normal to the body is considered to extend along an infinite slab tangent to the wall (hence the name) at any given point. This is equivalent to considering the flow properties only vary in the direction normal to the body. The concept is illustrated in Figure 3.14 when applied to the stagnation point of a flowfield. With this approximation, the dependency of the radiative field on the azimuthal direction is dropped, and the directional integration over the solid angle expressed by Eq. 2.56 may be performed analytically. The mathematical formulation of the tangent-slab approximation is derived in detail in Appendix C.

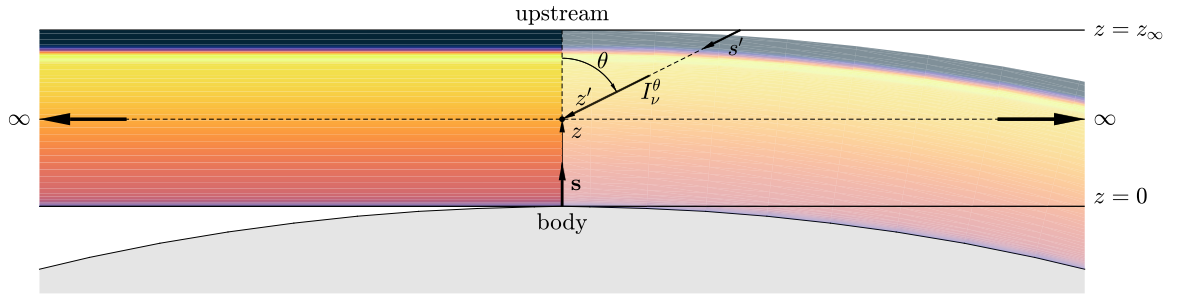


Figure 3.14: Tangent-slab approximation: the 2D flowfield profile (right) is approximated at a point by transferring the variation along the normal to that point into a slab tangent to the wall extending to infinity (left).

Regarding the computational implementation of the method, a structured mesh is assumed to discretize the flow domain throughout this work. The structured mesh is composed of quadrilateral cells distributed in the normal and tangential directions to the body, forming an $N \times M$ computational grid, where N and M are the number of cells in the normal and tangential directions, respectively. A single block of cells in the normal direction is used to represent the normal line-of-sight used in this approximation, taking advantage of the mesh orthogonality, thus avoiding the need to interpolate between cell centers and normal line-of-sight points.

The surface radiative heating experienced by a body emerged in a radiating shock layer under the tangent-slab approximation is given by evaluating Eq. C.5 at $z = 0$ and integrating over the frequency

spectrum, i.e.,

$$q^-(0) \equiv q_{\text{rad}} = 2\pi \int_0^\infty \int_0^{z_\infty} j_\nu \mathcal{E}_2[\tau_\nu(0, s)] ds d\nu. \quad (3.10)$$

In SPARK LbL, the spectral unit used for the emission and absorption coefficient is the wavenumber $\bar{\nu}$, defined in spectroscopy as the inverse of wavelength λ . Whenever wavenumber units are used, the spectral dependency is indicated with $\bar{\nu}$. The previous integral then reads

$$q_{\text{rad}} = 2\pi \int_0^\infty \int_0^{z_\infty} j_{\bar{\nu}} \mathcal{E}_2[\tau_{\bar{\nu}}(0, s)] ds d\bar{\nu}. \quad (3.11)$$

The two integrals are separated so that the spatial integration is performed at every frequency, that is,

$$q_{\text{rad}} = \int_0^\infty q_{\bar{\nu}}^-(0) d\bar{\nu} = \int_0^\infty q_{0, \bar{\nu}} d\bar{\nu}, \quad (3.12)$$

and the limits of integration are taken to capture the spectral regions that significantly contribute to the surface radiative heating. Using a trapezoidal rule, the approximation may be expressed as

$$q_{\text{rad}} \approx \sum_{k=1}^{N_{\bar{\nu}}} \frac{q_{0, \bar{\nu}_{(k-1)}} + q_{0, \bar{\nu}_{(k)}}}{2} \Delta \bar{\nu}_k, \quad (3.13)$$

where $N_{\bar{\nu}}$ is the number of wavenumber intervals considered and $\Delta \bar{\nu}_{(k)} = \bar{\nu}_k - \bar{\nu}_{(k-1)}$. A similar integration rule was employed for the spatial integration between 0 and z_∞ . The cell-centers were used as grid points for the trapezoidal rule, instead of the mesh face-centers, so as to avoid an unnecessary interpolation. Figure 3.15 illustrates the procedure. Evaluation of the integral requires knowledge of the integrand at the normal cell-block boundaries, as well as at the cell-centers. While the emission coefficient $j_{\bar{\nu}}$ is already known at the cell-centers from the line-by-line calculation, it is not known at the wall and upstream boundaries. Here, a linear extrapolation using the two closest inner points was employed. A test is then made on the extrapolated $j_{\bar{\nu}}$ to check for non-physical values, in which case $j_{\bar{\nu}} = 0$ is used instead. The discretization of the second term in the integrand of Eq. 3.10 is more involved, since it requires pre-computation of the optical thickness $\tau_{\bar{\nu}}$, which is itself subject to spatial integration. Again,

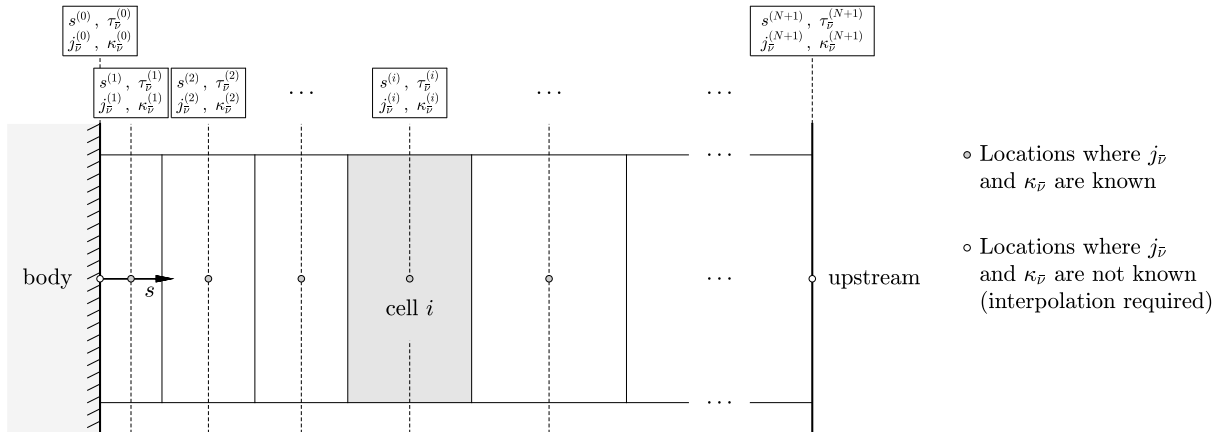


Figure 3.15: Computational implementation of the tangent-slab approximation along a single block of normal cells.

a trapezoidal rule is used to evaluate the optical thickness at a point $s^{(i)}$, resulting in

$$\tau_{\bar{\nu}_k} \left(0, s^{(i)} \right) = \tau_{\bar{\nu}_k}^{(i)} \approx \sum_{j=1}^i \frac{\kappa_{\bar{\nu}_k}^{(j-1)} + \kappa_{\bar{\nu}_k}^{(j)}}{2} \Delta s^{(j)}, \quad (3.14)$$

where $\Delta s^{(j)} = s^{(j)} - s^{(j-1)}$. Knowledge of the absorption coefficient $\kappa_{\bar{\nu}_k}$ is required at the normal cell-block boundaries, and a similar extrapolation is used as that described for the emission coefficient $j_{\bar{\nu}_k}$. Finally, the spatial integration in Eq. 3.10 may be written as

$$q_{0, \bar{\nu}_k} \approx \pi \sum_{i=1}^{N+1} \left\{ j_{\bar{\nu}_k}^{(i-1)} \mathcal{E}_2 \left[\tau_{\bar{\nu}_k}^{(i-1)} \right] + j_{\bar{\nu}_k}^{(i)} \mathcal{E}_2 \left[\tau_{\bar{\nu}_k}^{(i)} \right] \right\} \Delta s^{(i)}, \quad (3.15)$$

and the exponential integral of order 2 is approximated using the formula suggested by Johnston [94]:

$$\mathcal{E}_2(x) \approx 0.2653e^{-8.659x} + 0.7347e^{-1.624x}. \quad (3.16)$$

Due to the nature of the SPARK LbL code, a difficulty is encountered when evaluating Eqs. 3.14 and 3.15. The radiative code uses an adaptive wavenumber grid for the spectral coefficients for reducing the number of wavenumber points required to accurately define every radiative transition in the spectrum. Therefore, each cell will generally have a distinct spectral grid, since a variation in the flow properties will result in a corresponding variation in the contribution of different radiative transitions to the spectral emission and absorption coefficients. As a result, care must be taken when evaluating the sums in Eqs. 3.14 and 3.15, due to the varying vector-lengths where $j_{\bar{\nu}_k}^{(i)}$ and $\kappa_{\bar{\nu}_k}^{(i)}$ are stored during runtime.

To circumvent this problem, the algorithm for computing the sum in Eq. 3.15 was modified to follow the approach suggested by Lino da Silva [95]. Every time a new term of the sum is computed, the corresponding wavenumber grids of the two adjacent cells are compared, and the largest grid is selected. The spectral coefficients of the smallest grid are then linearly interpolated to the more refined grid, and the resulting vectors will now have the same length, meaning the individual term of the sum may be computed. This method is many times more efficient than comparing every spectral grid, obtaining the most refined one and then interpolating the spectral coefficients of the other cells to the most refined grid, since the comparison is only made between two adjacent cells.

Finally, the total radiative heating at a point along the surface is given by

$$q_{\text{rad}} \approx \sum_{k=1}^{N_{\bar{\nu}}} \frac{1}{2} \pi \left\{ \sum_{i=1}^{N+1} \left\{ j_{\bar{\nu}_{(k-1)}}^{(i-1)} \mathcal{E}_2 \left[\tau_{\bar{\nu}_{(k-1)}}^{(i-1)} \right] + j_{\bar{\nu}_{(k-1)}}^{(i)} \mathcal{E}_2 \left[\tau_{\bar{\nu}_{(k-1)}}^{(i)} \right] \right\} \Delta s^{(i)} \right. \\ \left. + \sum_{i=1}^{N+1} \left\{ j_{\bar{\nu}_k}^{(i-1)} \mathcal{E}_2 \left[\tau_{\bar{\nu}_k}^{(i-1)} \right] + j_{\bar{\nu}_k}^{(i)} \mathcal{E}_2 \left[\tau_{\bar{\nu}_k}^{(i)} \right] \right\} \Delta s^{(i)} \right\} \Delta \bar{\nu}^{(k)}. \quad (3.17)$$

Although the computation of the radiative source term is out of the scope of this work, it is briefly described for future reference given the framework already established for the tangent-slab approximation. Following the approach implemented in the coupled LAURA/HARA code framework [90], described in Appendix C, the two quantities that need to be computed at each normal cell-center are $q_{\bar{\nu}}^+(z)$ and $q_{\bar{\nu}}^-(z)$.

The wall-directed heat flux component may be computed in a similar fashion to that implemented for computing the surface radiative heat flux. However, since the lower limit of integration is no longer 0, the optical thickness is now computed between two points $s^{(p)}$ and $s^{(i)}$ (where $p < i$) as

$$\tau_{\bar{\nu}_k} \left(s^{(p)}, s^{(i)} \right) \equiv \tau_{\bar{\nu}_k}^{(p,i)} \approx \sum_{j=p+1}^i \frac{\kappa_{\bar{\nu}_k}^{(j-1)} + \kappa_{\bar{\nu}_k}^{(j)}}{2} \Delta s^{(j)}. \quad (3.18)$$

The wall-directed radiative heat flux at a point $s^{(p)}$ is then a generalization of equation 3.15, where the summation is no longer taken over all normal cells, but rather only includes the cells between $s^{(p)}$ and the upstream boundary, leading to

$$q_{(p),\bar{\nu}_k}^- \approx \pi \sum_{l=p+1}^{N+1} \left\{ j_{\bar{\nu}_k}^{(l-1)} \mathcal{E}_2 \left[\tau_{\bar{\nu}_k}^{(p,l-1)} \right] + j_{\bar{\nu}_k}^{(l)} \mathcal{E}_2 \left[\tau_{\bar{\nu}_k}^{(p,l)} \right] \right\} \Delta s^{(l)}. \quad (3.19)$$

Regarding the upstream-directed radiative flux $q_{\bar{\nu}}^+$, given by Eq. C.13 and repeated here for convenience,

$$q_{\bar{\nu}}^+(z) = 2\pi I_{\bar{\nu},b}^+ \mathcal{E}_3 [\tau_{\bar{\nu}}(0, z)] - 2\pi \int_0^z j_{\bar{\nu}} \mathcal{E}_2 [\tau_{\bar{\nu}}(s, z)] ds, \quad (C.13)$$

similar considerations apply, and at a point $s^{(p)}$ it is written as

$$q_{(p),\bar{\nu}_k}^+ \approx 2\pi I_{\bar{\nu},b}^+ \mathcal{E}_3 [\tau_{\bar{\nu}_k}^{(0,p)}] - \pi \sum_{i=1}^p \left\{ j_{\bar{\nu}_k}^{(i-1)} \mathcal{E}_2 [\tau_{\bar{\nu}_k}^{(i-1,p)}] + j_{\bar{\nu}_k}^{(i)} \mathcal{E}_2 [\tau_{\bar{\nu}_k}^{(i,p)}] \right\} \Delta s^{(i)}. \quad (3.20)$$

The third order exponential integral $\mathcal{E}_3(\tau_{\bar{\nu}_k})$ is again computed using an approximation suggested by Johnston [96]:

$$\mathcal{E}_3(x) \approx 0.4661e^{-1.447x} + 0.0339e^{-9.614x}. \quad (3.21)$$

Finally, using the computational framework illustrated in Figure 3.15, the spectral radiative source term

$$-(\nabla \cdot \mathbf{q}_{\text{rad}})_{\bar{\nu}} = -\frac{d(q_{\bar{\nu}}^+ + q_{\bar{\nu}}^-)}{dz} \quad (C.12)$$

at a point $s^{(p)}$ may be computed using, for instance, the central difference formula

$$-(\nabla \cdot \mathbf{q}_{\text{rad}})_{(p),\bar{\nu}} \approx -\frac{q_{(p+1),\bar{\nu}_k} - q_{(p-1),\bar{\nu}_k}}{s^{(p+1)} - s^{(p-1)}}, \quad (3.22)$$

which will still be essentially second order if the non-uniform grid is not expanding too rapidly.

Ray-Tracing Model

The use of the ray-tracing approach for the estimation of the surface radiative heating, required for TPS sizing, has been gaining widespread attention amongst the hypersonic community [2, 17, 90, 92, 93, 97], especially due to the tangent-slab's inability to produce accurate results near the shoulder and in the after-body region. However, its application to the calculation of the radiative source term has been significantly hindered by its computational cost. Even so, recently published work using this rigorous

approach already exists [2, 17, 90, 97].

Despite the increased complexity of the ray-tracing model, its mathematical foundation has already been established in § 2.2.2. The approach is based on the spatial integration of Eq. 2.62 along a given ray with direction $\mathbf{s}$ (referring back to Figure 2.2), between a point located inside the domain and a point located on its boundary, followed by a directional integration on all rays with different directions to obtain the radiative heating component or the radiative source term. The implementation of the ray-tracing model for the calculation of these terms in axisymmetric flows will now be described. For future reference, the implementation used by Potter [2] for the computation of the radiative source term is recommended.

The first step in setting up the computation for the surface radiative heating is the proper discretization of the hemisphere over which the directional integration will be conducted. For each surface point considered, the hemispherical domain described by $0^\circ < \phi < 360^\circ$ and $0^\circ < \theta < 90^\circ$ is approximated by a set of rays defined by distinct (θ, ϕ) coordinates (in axisymmetric flowfields, only ϕ values between 0° and 180° are required, provided the corresponding contributions are doubled to account for the symmetric ray). The simplest choice, one that is often (inadequately) implemented, would be to select a set of constant $\Delta\theta$ and $\Delta\phi$ values and subdivide the domain into equally spaced intervals, resulting in the angular mesh represented in Figure 3.16a. This approach is seen to cluster points near the poles of the spherical domain, which is inefficient in resolving the region near $\theta = 90^\circ$. Additionally, the Monte-Carlo-based integration technique that is used for the directional integration over the hemisphere in the present work would result in a poor estimation, since it largely depends on a uniform point sampling.

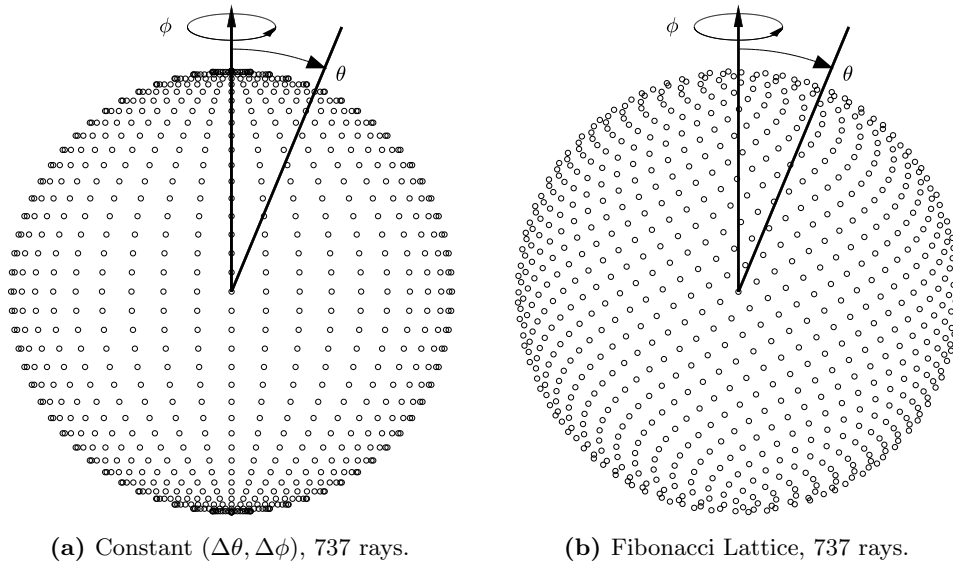


Figure 3.16: Point sampling comparison between the two approaches.

Since the problem of finding a uniform distribution of points on the surface of a sphere has no analytical solution, an alternative technique that was implemented in the present work relies on the so-called Fibonacci Lattice, which distributes points along a tightly wound generative spiral contained on the surface of the sphere [98]. The lattice points are generated as follows. Letting i range from $-N_{FL}$ to

N_{FL} , where N_{FL} is any natural number, the spherical coordinates of the i^{th} point are given in radians by

$$\begin{cases} \theta^{(i)} = \frac{\pi}{2} - \arcsin\left(\frac{2i}{2N_{\text{FL}} + 1}\right) \\ \phi^{(i)} = 2\pi i \left(\tilde{\phi}\right)^{-1}, \end{cases} \quad (3.23)$$

where $\tilde{\phi}$ is the golden ratio, defined as $\tilde{\phi} = \frac{(1+\sqrt{5})}{2}$. To have a line-of-sight perpendicular to the surface of the spacecraft at each wall point, the lattice resulting from Eq. 3.23 is rotated so that the ray corresponding to $i = 0$ sits directly above the local zenith. Furthermore, as aforementioned, only a quarter of the spherical domain is considered, meaning only points having $0^\circ < \phi^{(i)} < 180^\circ$ and $0^\circ < \theta^{(i)} < 90^\circ$ are kept. Finally, the symmetry at the stagnation point allows the directional integration to be taken over only a quarter of the hemisphere, again provided the corresponding rays are multiplied by a factor⁷ of 4. The spherical sampling of points using the Fibonacci Lattice is presented in Figure 3.16b, where the two approaches are compared. The improved uniformity provided by this distribution is evident when compared to the constant $(\Delta\theta, \Delta\phi)$ grid. Note that the Fibonacci Lattice achieves this through an internal spiral structure. Alternatively, random sampling Monte-Carlo methods may be superior in achieving uniformity, at the cost of a higher number of rays to ensure it.

When considering axisymmetric flows, the inherently three-dimensional ray-tracing radiative transfer problem may be solved in just two dimensions by taking advantage of their symmetric nature. Specifically, one may exploit the fact that any point (x, y, z) in the domain may be traced back to an equivalent point⁸ $(x, \bar{y}, 0)$ with the same flow properties [99]. The flowfield may thus still be solved in a two-dimensional mesh, since each ray in 3D space maps to its equivalent trajectory in the 2D plane where the CFD solution

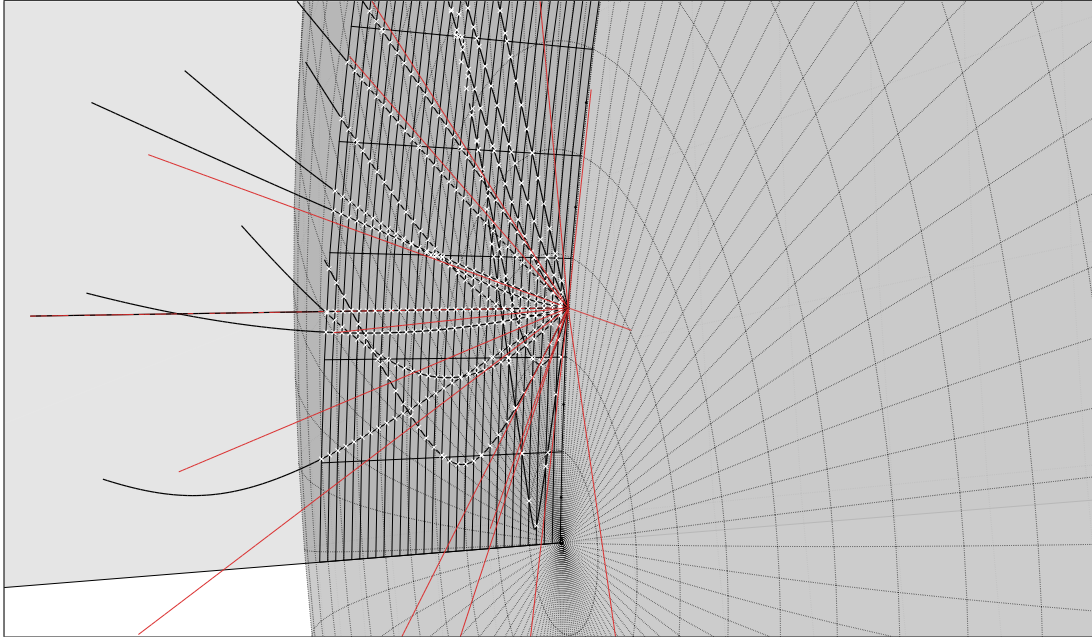


Figure 3.17: Mapping between 3D rays (red) and corresponding 2D projections (black).

⁷Note that the ray following the normal at each surface point only contributes once for the directional integration, irrespective of the slice of the spherical domain considered.

⁸Assuming x to be the symmetry axis.

is defined. This transformation is simply defined as

$$\begin{cases} x_{2D} = x_{3D} \\ \bar{y}_{2D} = \sqrt{y_{3D}^2 + z_{3D}^2} \end{cases} \quad (3.24)$$

and is illustrated in Figure 3.17. The three-dimensional rays are shown in red, departing from the same wall point, while the two-dimensional projections, in the same plane as the axisymmetric flowfield grid, are presented in black. The intersections between the rays and the grid divide the rays in several connected pieces, whose three-dimensional length, required for the spatial integration of the radiative transfer equation, is obtained in a straightforward manner from knowledge of the original ray's direction cosines. Also, note that this transformation causes the projected rays to curve in the 2D plane.

Once the directional discretization is set up and the trajectories of the rays through the flowfield are known, the emission and absorption coefficients need to be known along each line of sight. These depend on the flowfield temperatures and number densities, which are only defined on the CFD grid cell-centers. Thus, the accuracy of the radiative transfer algorithm will be subject to the way the cell-centered CFD solution is used by the radiative solver. The current option available in SPARK LbL is to feed the cell-centered temperatures and species' number densities to the radiative solver, which then outputs the corresponding spectral coefficients defined at the cell-centers. However, the rays' trajectories along which the spectral coefficients need to be known will generally not coincide with the grid cell-centers, meaning an approximate treatment must generally be employed.

The simplest option is to consider the emission and absorption coefficients constant along a given cell, inheriting the spectral values of the cell-center. However, this may potentially introduce large spatial integration errors in locations where the mesh is coarse, or if the integration is carried over lengthy rays, in which case the error accumulates with each cell. Another option is to assume a linear variation of the spectral coefficients between interpolating points, as suggested by Johnston *et al.* [90]. Both options were implemented in the radiative transfer module of the SPARK LbL solver in the present work, and will now be briefly described.

Option 1 - Constant Coefficient Approach

As aforementioned, this assumes the spectral coefficients along a given cell are constant and equal to their value at the cell-center. Several options then arise for solving the integral given by Eq. 2.62. One straightforward option is to march along a given ray through the cells it intersects and solve the integral cell-by-cell until the wall is reached. Consider a given ray r and an intersected cell along its path, identified by the normal and tangential indices (i, j) , respectively, as illustrated in Figure 3.18a. Assuming the spectral coefficients to be constant, solution of Eq. 2.62 along the cell results in

$$I_{p,\bar{\nu}}^{\text{out}} = I_{p,\bar{\nu}}^{\text{in}} e^{-\kappa_{\bar{\nu}}^{(i,j)} L_p} + \frac{j_{\bar{\nu}}^{(i,j)}}{\kappa_{\bar{\nu}}^{(i,j)}} \left[1 - e^{-\kappa_{\bar{\nu}}^{(i,j)} L_p} \right] , \quad (3.25)$$

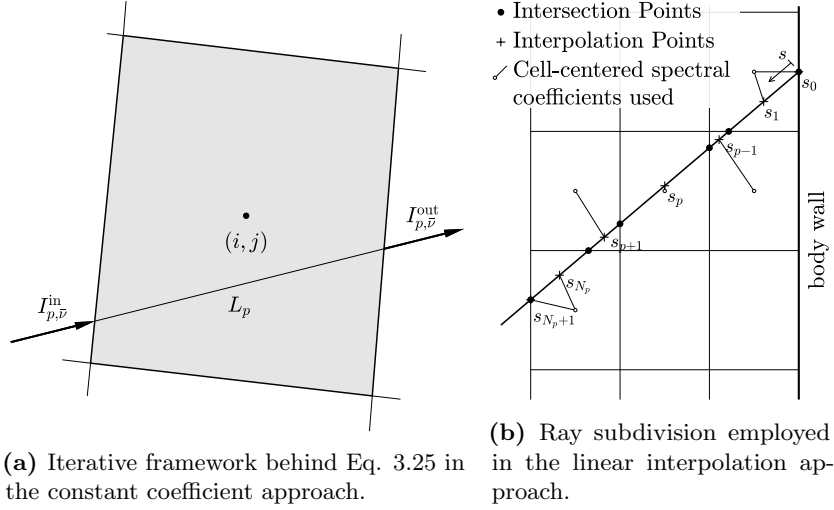


Figure 3.18: Geometric framework for the constant and linear ray-tracing approaches.

where $I_{p,\nu}^{\text{in}}$ and $I_{p,\nu}^{\text{out}}$ are the radiative intensities entering and leaving a given intersected cell, L_p is the three-dimensional length of the ray intersection with cell (i, j) and p is simply an index representing the cell intersection number for the given ray. The marching procedure starts at the upstream boundary with $I_{1,\nu}^{\text{in}} = 0$ and Eq. 3.25 is computed iteratively using the relation $I_{p,\nu}^{\text{in}} = I_{(p-1),\nu}^{\text{out}}$ until the wall is encountered. The problem described earlier for the tangent-slab approximation regarding the varying spectral grid is also met at this stage, and a similar interpolation technique was employed. The final computed value of $I_{p,\nu}^{\text{out}}$ will equal the spectral radiative intensity coming from the current direction at the wall position under consideration.

Option 2 - Linear Interpolation Approach

Another approach which should yield physically more accurate results is to assume for the spectral coefficients a linear variation between cells. However, as reported by Johnston *et al.*, this assumption for the absorption coefficient would result in an integral that may not be evaluated analytically, leading to a costly numerical integration [90]. The alternative suggested and implemented by the authors in the LAURA/HARA suite of codes at NASA is to consider a linear variation for the emission coefficient and a constant value for the absorption coefficient. In the present work, the constant value for κ_ν was assumed equal to the value at the cell-center.

Referring to Figure 3.18b, each ray is subdivided in segments, each delimited by interpolation points spread along the ray. These are the midpoints of the intersection between the ray's trajectory and the computational grid, and are labeled s_p according to the intersection number, where s is the three-dimensional distance traveled along the ray between the wall and the upstream boundary. Two additional interpolation points are defined at the ray extremities, namely s_0 and s_{N_p+1} , and the linear interpolation is performed between the interpolation points along a given ray. Hence, the spectral coefficients must be defined at each of these locations. Since these are only defined at the cell-centers, it was assumed that the spectral coefficients at a given interpolation point are equal to their value at the cell-center they belong to, as represented by the connections in Figure 3.18b.

With these assumptions, the radiative intensity of a given ray at the wall, $I_{\bar{\nu}}(s_0)$, is equal to

$$I_{\bar{\nu}}(s_0) = I_{\bar{\nu}}(s_{\max}) e^{-\tau_{\bar{\nu}}(s_{\max})} + \sum_{p=0}^{p_{\max}-1} \frac{a_p}{c_p^2} \left[(c_p s_p + 1) e^{-\tau_{\bar{\nu}}(s_p)} - (c_p s_{p+1} + 1) e^{-\tau_{\bar{\nu}}(s_{p+1})} \right] \\ + \sum_{p=0}^{p_{\max}-1} \frac{b_p}{c_p} \left[e^{-\tau_{\bar{\nu}}(s_p)} - e^{-\tau_{\bar{\nu}}(s_{p+1})} \right], \quad (3.26)$$

where the coefficients a_p and b_p define the linear variation of $j_{\bar{\nu}}$ between interpolation points and c_p is related to that assumed for the optical thickness [90]. Also, $s_{\max} = s_{N_p+1}$ and $p_{\max} = N_p + 1$. The details for the derivation and expressions for these coefficients are given in Appendix D.

Regardless of the option chosen for the spatial integration of the radiative transfer equation, Eqs. 3.25 or 3.26 must be solved for all rays defined previously when setting up the directional grid. Once this is done, the final step in obtaining the spectral surface radiative heating $q_{\bar{\nu}}^-$ is the integration over the hemisphere, similar to that defined in Eq. 2.56 with half the range in θ . However, a typical integration quadrature cannot be employed since the directional grid constructed from the Fibonacci Lattice is irregular in θ and ϕ . This complication may be avoided by using a Monte-Carlo integration technique, which is justified by the small number of variables and the large number of rays (samples). The spectral radiative heating at a given location at the wall is then simply

$$q_{\bar{\nu}}^- = V \frac{1}{N_r} \sum_{r=1}^{N_r} I_{\bar{\nu},r} \cos \theta_r = \left\{ \int_0^{2\pi} \int_0^{\frac{\pi}{2}} \sin \theta \, d\theta \, d\phi \right\} \frac{1}{N_r} \sum_{r=1}^{N_r} I_{\bar{\nu},r} \cos \theta_r = \frac{2\pi}{N_r} \sum_{r=1}^{N_r} I_{\bar{\nu},r} \cos \theta_r. \quad (3.27)$$

Here, N_r represents the total number of rays considered for a given wall point, and θ_r is the angle between the ray and the wall normal $\mathbf{n}$. As aforementioned, by taking advantage of the symmetry of the flow, only half the hemisphere is considered at each wall point, and a quarter at the stagnation point. Thus, each contribution to the final sum in Eq. 3.27 is multiplied by a weight w_r which may take the values 1, 2 or 4. Finally, the resulting $q_{\bar{\nu}}^-$ is integrated over the frequency spectrum to yield the surface radiative heating.

Optically-Thin Model

The two models previously described suffer from the considerable difficulty in the treatment of the spatial integration involving the absorption coefficient. Thus, a historically important simplification, embodied in the optically-thin model, is to neglect the absorption term in the original radiative transfer equation (Eq. 2.59), in which case it may be directly integrated to yield

$$I_{\bar{\nu}}^{\theta,\phi}(L) = I_{\bar{\nu}}^{\theta,\phi}(0) + \int_0^L j_{\bar{\nu}} \, ds. \quad (3.28)$$

However, as Figures 3.12a and 3.12b clearly show, there is significant emission in the VUV end of the spectrum, where absorption is significant. Hence, the optically-thin approximation will substantially overpredict the radiative heating in Galileo's entry, and was not considered further in the present work.

Results

This chapter follows the sequential order used for the numerical simulation framework established in the present work: the defined test matrix is discussed and a brief summary of the adopted models is given, followed by a general discussion on the numerical difficulties encountered and the corresponding strategies employed to overcome them; then, the main flowfield features are presented, the influence of transport models and thermal non-equilibrium is analyzed, and the sensitivity studies performed to better understand the main sources of radiative heating are discussed.

4.1 Problem Definition, Test Matrix and Models Used

The flowfield test matrix employed in the present work is given in Table 4.1. Simulations focused on the 180 km altitude trajectory point, where strong non-equilibrium conditions are expected. Reynier *et al.* further studied this trajectory point [3], allowing for qualitative comparisons to be drawn. The influence of the two transport models described in § 2.1.4 is assessed both in thermal equilibrium and non-equilibrium conditions for this altitude, by solving the Navier-Stokes equations assuming laminar flow and an axisymmetric flowfield with no angle of attack.

All simulations assume an isothermal, non-catalytic wall¹ at 3,000 K, as assumed by Reynier *et al.* [3]. According to the authors, a wall temperature of 4,000 K did not show significant differences. The thermodynamic, kinetic and energy-exchange models were discussed in § 3.3. Whenever thermal non-equilibrium was taken into account (2T cases in Table 4.1), the two-temperature model described in § 2.1.2 was used, considering all thermal energy levels to follow a Boltzmann distribution at temperature T_{tr} , while T_{v,H_2} governs that for H_2 's vibrational energy mode. Finally, Park's rate-controlling temperature

Table 4.1: Test matrix used in the present work [3, 4]. Times measured from 450 km altitude point.

Case	Altitude (km)	Time (s)	Velocity ($m s^{-1}$)	Temperature (K)	Pressure (Pa)
Wilke 1T Wilke 2T Gupta/Yos 1T Gupta/Yos 2T	180	42.06	46,674	161.9	27.5

¹The flowfield chemistry acts indifferent to the presence of the wall, and no chemical reactions are imposed.

model is applied to the dissociation reactions of H_2 according to Eq. 2.19, with $q = 0.7$.

4.2 Computational Framework and Strategy

The computational domain surrounding the Galileo probe is illustrated in Figure 4.1. The structured mesh shown consists of 72 cells aligned in the direction tangential to the body and 60 cells in the normal direction, amounting to 4,320 cells in total. A mesh convergence study was performed by increasing the latter from 30 to 75 in steps of 15 cells, with the value of 60 found to properly capture all flowfield features (see § 4.3.1). Two ARAD sensors, representative of mid-body and near-shoulder regions, are also shown, since sensitivity studies are later presented at these locations. The mesh was refined at strong-gradient regions, such as the shock and boundary layer that forms near the wall. The minimum cell height occurs near the stagnation point, at around 2.7×10^{-5} m.

The computational domain may be limited to the forebody flowfield around the capsule, since the measured TPS recession - and its prediction discrepancies - occur in this region. However, an extension of the computational domain to the expansion region passing the shoulder had to be performed. This was deemed necessary since the present work requires accurate ray-tracing simulations along the whole conical region. If the domain did not extend across the shoulder, the radiative fluxes at the last few wall points close to the shoulder would not be accurately computed using ray-tracing, since no flowfield solution would be available for half the hemisphere. However, this introduced significant challenges to the simulation of this flow, as the large expansion would reduce the pressure to near-vacuum values (similar to the free-stream ones), and the solution would become unstable, even though an implicit scheme was used for temporal discretization. On top of this, the extreme velocity and very small CFL numbers

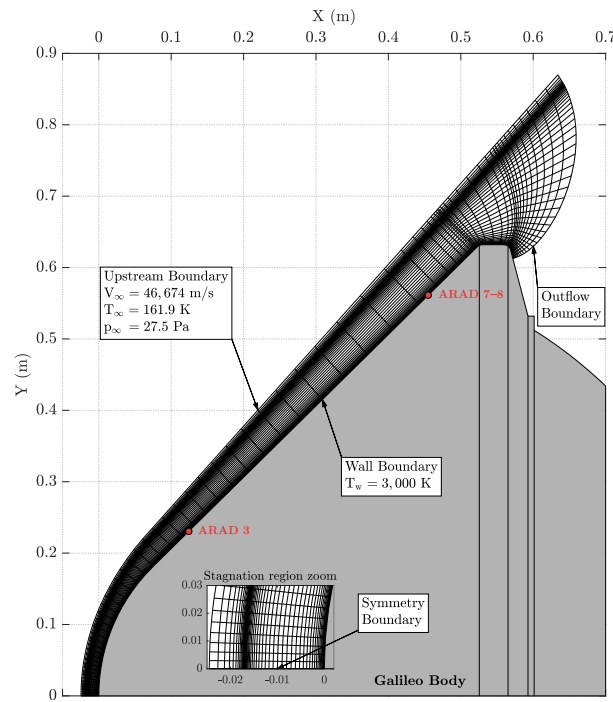


Figure 4.1: Computational domain, boundary conditions and 72×60 mesh used in the present work.

required to stabilize the numerical scheme (usually between 10^{-4} to 10^{-2} at the start, raised to 10^{-1} closer to convergence in some cases), meant that very small time steps were being used ($\mathcal{O}(10^{-12})$ s), and convergence took a long time, limiting the number of cases simulated in the present work. Furthermore, the solver could not handle a starting condition at $46,674 \text{ m s}^{-1}$. As a result, a strategy was developed to allow the solution to evolve. The simulation was initially started at 2 km s^{-1} , and the shock eventually detached from the surface and relaxed to a distance from the wall. Then, the velocity was increased to 10 km s^{-1} , and subsequent relaxation took place. Lastly, the final velocity of 46.674 km s^{-1} was enforced until convergence was attained.

4.3 Assessment of Discretization Convergence

4.3.1 Physical Domain: Mesh Convergence Study

As discussed in § 4.2, a total of 4 meshes were analyzed, varying in the number of cells in the direction normal to the wall (30, 45, 60, 75). Convergence for each separate mesh was assessed in two different ways, as the root mean square (RMS) of the residuals across all equations dropped below 10^{-4} : both the stagnation line temperature profile and the convective heat fluxes across the body were closely followed as the simulations progressed, providing local and global criteria for the convergence of the solution, respectively. After convergence was established for a given mesh, its radiative heat fluxes along the body were also calculated using the ray-tracing approach and the overall mesh convergence study was performed on the basis of comparing the convective, radiative and total heat fluxes across the different meshes.

The results of this comparison are presented in Figure 4.2. The case used for the convergence study was the *Gupta/Yos 1T* case. An overprediction of the convective heat fluxes is observed for the 72×30 mesh throughout the body wall, especially in the conical section of the probe, reaching a maximum difference of 18% near ARAD 7–8. A similar trend is obtained for the radiative heat fluxes, although a good agreement

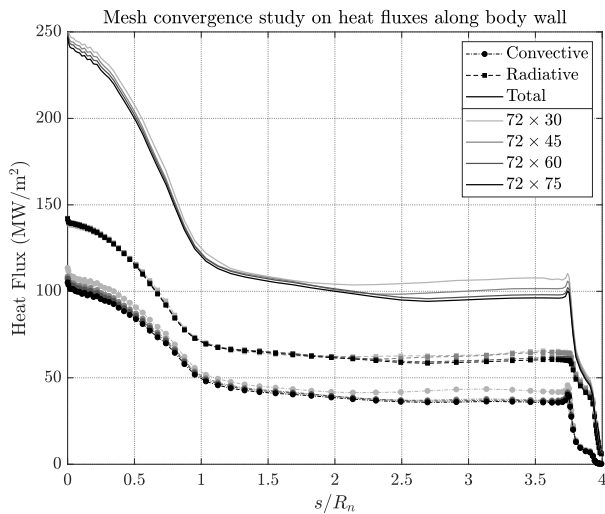


Figure 4.2: Convective, radiative and total heat fluxes indicating mesh convergence is obtained above the 72×60 mesh refinement.

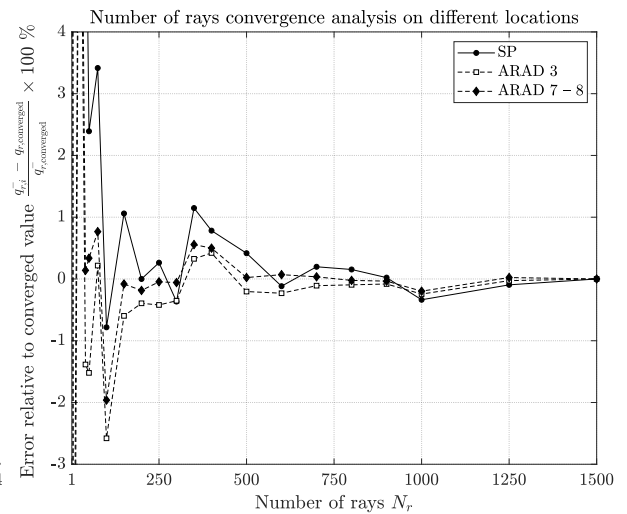


Figure 4.3: Ray-tracing radiative heat fluxes at three locations along the body: percentage error relative to converged value (1500 rays).

exists in the stagnation region. The total heat flux is seen to closely follow that of the finer meshes up until $s/R_n = 2$, where an overprediction of about 10% remains down to the shoulder. Similar considerations apply for the 72×45 mesh, albeit with smaller discrepancies. Finally, a small difference of about 1% is obtained between the 72×60 and 72×75 meshes. Thus, the least computationally expensive of the two was selected for subsequent studies.

4.3.2 Directional Domain: Ray Convergence Study

Similarly, when the ray-tracing approach is used to compute the radiative heat fluxes, one must select an appropriate number of rays to accurately capture the relevant directional variations of the flowfield, which also depend on the wall location under consideration. Hence, a convergence study on the number of rays discretizing the directional domain at different locations felt necessary. The results of this analysis are presented in Figure 4.3. Significant fluctuations occur at lower levels of directional discretization. For example, ARAD 3 presents a relative error below 1% at just 75 rays, which then increases to above 2% when using 100 rays. Similar behavior is observed at the other locations. This may lead one to assume directional convergence has been achieved, when actually the observed agreement is accidental and a result of fortuitous lines of sight selected by the ray-tracing algorithm.

As aforementioned, Park performed a very coarse comparison of ray-tracing and tangent-slab radiative heat fluxes at the stagnation region of the Galileo probe, using just 9 rays for the ray-tracing case [21]. One possible reason for this agreement is the fluctuating behavior described in the previous paragraph. Another possibility, more likely to have occurred, has to do with the consideration of ablation products to be present in the flowfield, significantly promoting radiation blockage and leading to an optically thick shock layer. Under such conditions, the stagnation point radiative heat fluxes are mainly a result of radiative transitions occurring in the direction normal to it, as this is the direction of least distance (hence, least absorption within the ablation layer) to the highly emitting shock. On a final note, the results show surprisingly good levels of accuracy at a relatively low number of rays (just 50 rays are sufficient to keep the accuracy to within 5% of the converged value). Thus, ray-tracing with a low number of rays can be an asset for performing fast but reliable radiative heating predictions for preliminary studies in the future.

4.4 Flowfield Features and Transport Model Influence

Two results obtained for the *Gupta/Yos 2T* case, showing the general features of the flowfield around Galileo at the 180 km altitude trajectory point, are presented in Figure 4.4. At the left, the Mach number contours near the stagnation region are shown². The subsonic flow rapidly accelerates to supersonic speeds along the spherical portion of the domain, and the sonic line attaches back to the body close to the start of the conical section of the probe. The flow is then mostly supersonic, except in the small region of the boundary layer near the wall, where viscous effects dominate. Figure 4.4b shows the temperature field

²A suggestion was given to the author by Markus Fertig at the 8th Radiation and High Temperature Gases workshop that took place in March 2019. If the sonic line re-attaches to the body before the shoulder (as is the case here) the shoulder expansion doesn't need to be modeled if one only cares for the forebody solution, and the conical region may simply be extended with no impact on the forebody flowfield. Unfortunately, there was no time to follow the suggestion in the present work, despite having the potential to solve part of the stability issues faced.

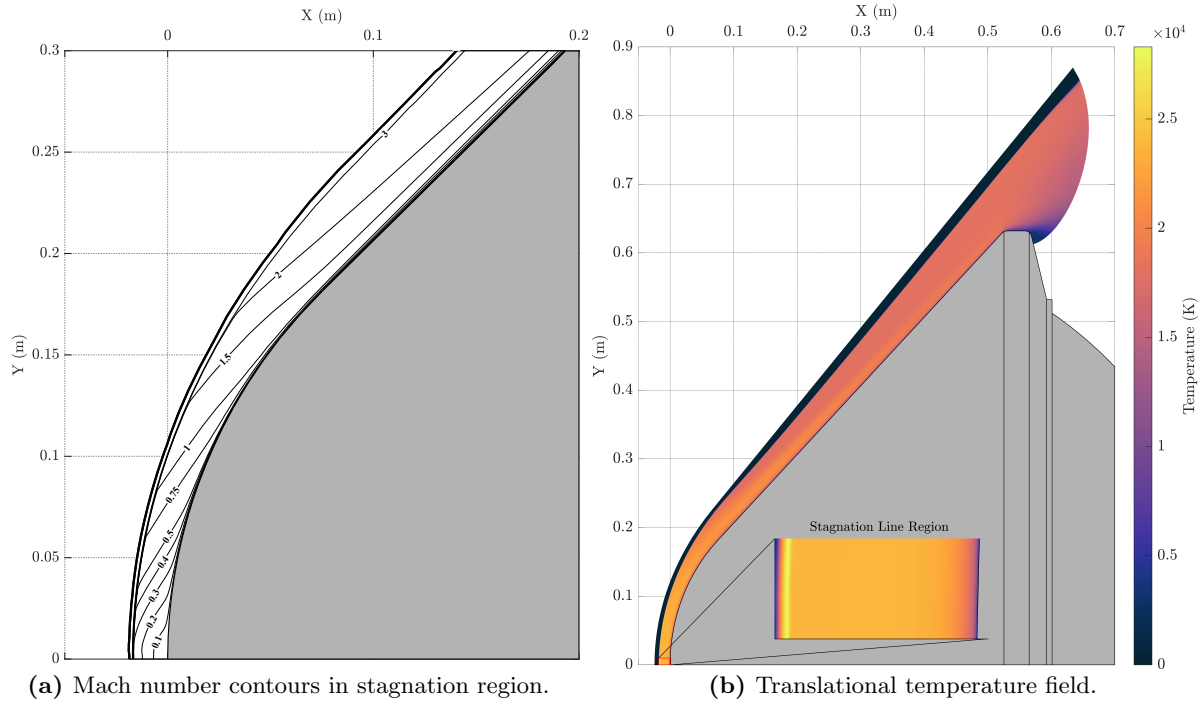


Figure 4.4: General features of *Gupta/Yos 2T* flowfield.

over the probe. The flow reaches a maximum temperature above 28,000 K at the stagnation line, near the shock. The refined mesh is able to capture the boundary layer gradients, and the predicted shock standoff distance is about 1.7 cm, higher than the 1.5 cm predicted by Reynier [3] at the same trajectory point.

The mole fraction fields of H and e^- are displayed in Figure 4.5. While atomic hydrogen is the biggest source of radiative heating experienced by the probe's TPS, the electron allows a direct assessment of the degree of ionization in the flow. Since the chemical composition is mainly governed by the kinetic model employed, both transport models produce similar results. Atomic hydrogen is the main species present in the shock layer, resulting from rapid H_2 dissociation after the shock, making up for more than 90% of the mixture's chemical composition. Electrons reach a maximum of about 3% in the rapid expansion after the shoulder, as a result of H ionization. This maximum is reached monotonically from the stagnation region towards the shoulder, along the thin boundary layer surrounding the probe. The maximum H mole fraction agrees with that predicted by Reynier *et al.* [3]. However, due to the different kinetic rates used, stronger ionization levels are predicted towards the boundary layer, reaching a maximum electron mole fraction of 0.28. This is mostly a result of H ionization, and thus the H mole fraction decreases towards the boundary layer, as opposed to that presented in Figure 4.5a.

Figure 4.6 presents the stagnation line temperatures obtained for the four cases considered, as well as a comparison with Reynier *et al.*'s results [3]. Regarding the Gupta/Yos cases, a 6% higher temperature peak is observed when thermal non-equilibrium is considered. Moreover, the non-equilibrium region extends for 3–4 mm after the shock, a value four times larger than the maximum of 1 mm reported by Park, where Leibowitz and Kuo's rates were used to estimate the non-equilibrium thickness for the Galileo case throughout its trajectory [21]. Despite this apparently small thickness of the non-equilibrium region, it will be important when considering radiation from H_2 , as will be discussed in § 4.5. After the two

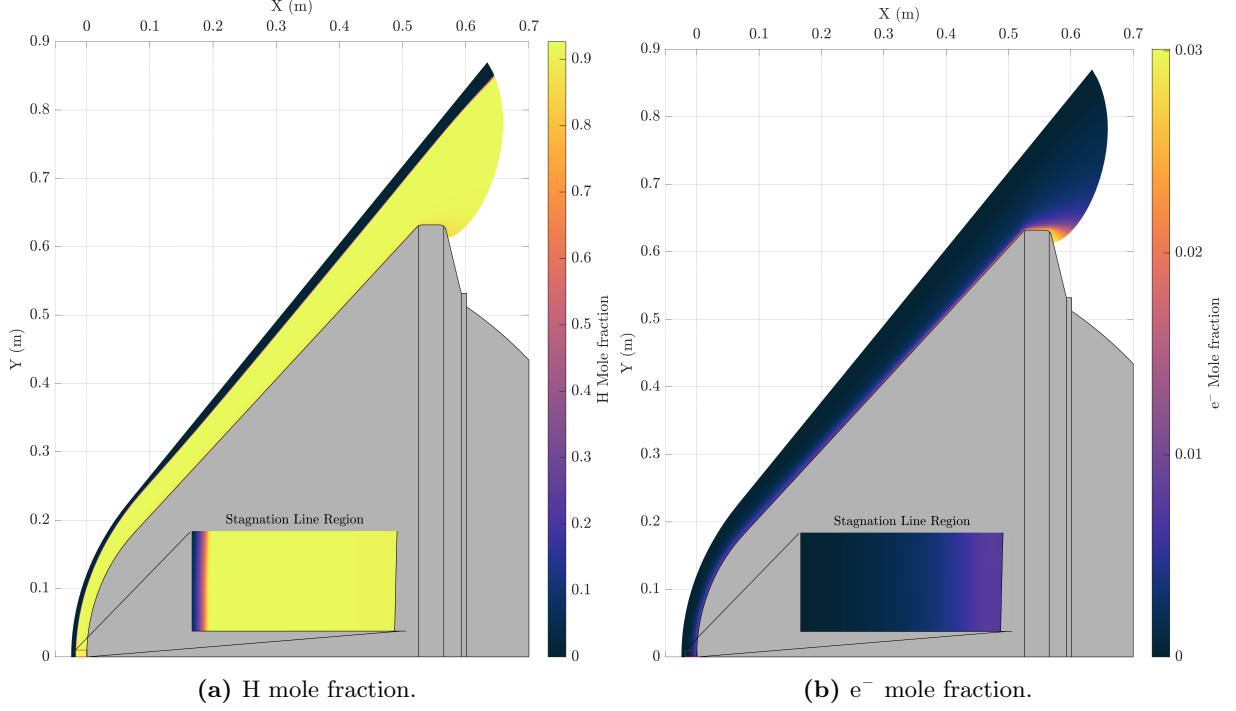


Figure 4.5: H and e^- mole fractions around Galileo.

temperatures thermalize, the remaining shock layer is essentially in thermal equilibrium, and both 1T and 2T solutions agree. Regarding the Wilke case, similar considerations apply between the 1T and 2T cases. Reynier *et al.*'s temperature profiles significantly differ from the ones obtained in the present work. The differing kinetic rates mentioned in § 3.3.1 are not the sole cause of the discrepancies, as those were used in a *Wilke 2T* case (not presented here) and the disagreement persisted. Thus, the most likely explanation is the use of different thermodynamic databases in both codes.

When comparing both transport models, several observations should be pointed out. First, the Wilke model predicts a peak temperature about 5% higher than Gupta/Yos. Additionally, the shock is thinner

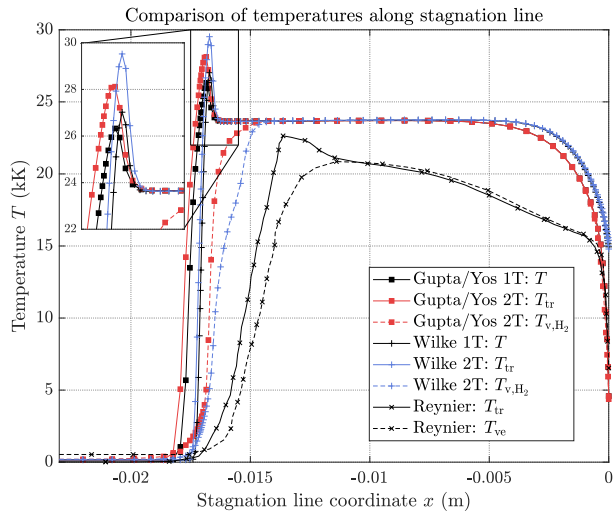


Figure 4.6: Comparison of stagnation line temperature profiles.

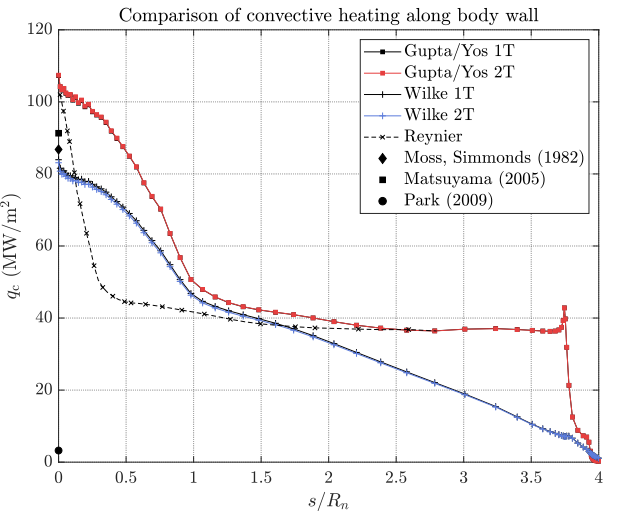


Figure 4.7: Comparison of convective heat fluxes along the body wall of Galileo's TPS.

and energy does not diffuse upstream to the extent observed in the latter, as revealed by the upstream temperature-increase delay between the two cases. This is a result of the larger thermal conductivity predicted by the more accurate model, allowing energy conduction at a faster rate away from the shock. The temperatures in the plateau are consistent among all cases considered. When it comes to the boundary layer in the Wilke cases, a difficulty was encountered. A temperature gap occurs at the wall and the boundary layer gradient is not perfectly captured. This issue had previously been encountered by Reynier *et al.*, and is simply a result of insufficient mesh refinement near the wall. However, the mesh that the author had to consider for obtaining a smooth near-wall flow resolution had a first-cell height of just 20 nm, which is too low for our solver to handle in a realistic time frame, since the time-step required to keep such a solution stable would be too low. Not even the increased mesh refinement provided by considering 90 cells normal to the wall in the Wilke cases was able to correctly predict the boundary layer gradients.

As a result of this inaccuracy, the convective heat fluxes presented in Figure 4.7 for the Wilke cases are underpredicted. Here, s/R_n represents the curvilinear distance along the body normalized by the nose-sphere radius. A good agreement is found between the Gupta/Yos cases and Reynier *et al.*'s prediction in the conical body section. However, in the spherical section following the stagnation point, the Gupta/Yos convective heat fluxes are larger by up to a factor of two. Again, different thermodynamic databases or the kinetic rates employed by the author could lead to these discrepancies. Regardless of the transport model employed, thermal non-equilibrium does not appear to have an impact over the equilibrium prediction, as would be expected. Finally, the local peak in convective heating observed near the shoulder is a result of the rapid expansion that, through the favorable pressure gradient that forms, reduces the boundary layer thickness across the shoulder curve, leading to larger temperature gradients and thus enhancing the heat transfer to the surface in this region. This increase contributes to higher TPS ablation in the shoulder corner, the lowest-thickness region after entry (with just 1 cm spare of TPS material), and may have played an important role in the recession experienced at this location. The convective heating at the stagnation point agrees reasonably well with the predictions of Moss and Simmonds [6] and Matsuyama [7]. The value reported by Park is significantly lower [21], presumably due to a combination of simplified models for the flowfield solution: VSL equations, Wilke's transport model and thermo-chemical equilibrium.

4.5 Sensitivity Studies on Radiative Heating

In this section, several sensitivity studies are presented in an attempt to assess the influence of different phenomena on the radiative heating experienced by the Galileo probe, one of the major uncertainties behind this historical event. The purpose here is not to attempt a good approximation to the actual heating environment encountered during flight, as that would require a flowfield solution coupled both to radiative and material-response solvers capable of accurately predicting the ablation of the TPS material. Instead, the aim is to understand the impact that different phenomena neglected in the past have in the radiative field, so that the assumptions used in previous predictions may be appraised. This way, future missions to Jupiter may benefit from a TPS design that is informed from improved pre-flight predictions. As the results of each sensitivity study are discussed, they can be readily compared in Table 4.2 (available

at the end of the chapter), which summarizes all the predictions obtained in the present work.

4.5.1 Transport Model Influence and Non-Equilibrium Effects

The radiative heating impacting the probe depends on the transport model by virtue of the different number density and temperature fields obtained. Figure 4.8 shows how the number densities predicted with each model compare along the stagnation line. Apart from small differences at the shock and boundary layer regions, the two are consistent. The observed discrepancies may be explained by the increased thermal conductivity and mass diffusivity of the Gupta/Yos model at the shock, and the inability to capture the boundary layer gradients with the Wilke model, respectively.

Both transport models are compared in terms of radiative heating along the body in Figure 4.9, using the conventional ray-tracing approach. Clearly, the overpredicted heat fluxes obtained with the Wilke model are consistent with the difficulty encountered at the boundary layer. The larger radiative heating is presumably a consequence of the unrealistically high temperatures obtained near the wall. However, the larger shock temperatures predicted by this model (due to the lower thermal conductivity) also contribute to the discrepancy observed between Wilke and Gupta/Yos formulations. Thus, it is difficult to conclude whether the overprediction is a result of the poor mesh refinement or a manifestation of the inaccuracy of the former model at high temperatures. Moreover, the results obtained with the Wilke transport model show a continuous increase in radiative heating towards the shoulder, as opposed to the slow decline predicted by the Gupta/Yos transport model. It is interesting to note that this trend conforms with the higher shoulder heat fluxes identified during post-flight data treatment, in spite of the inaccuracies of the model at higher temperatures.

Figure 4.9 also shows that the radiative heating is overpredicted by about 25% when equilibrium is assumed. The reason for this has to do with excess emission from H_2 systems arising from the shock location. This will be analyzed in more detail in the next section. The discrepancy is more pronounced at the stagnation point than at the shoulder, as a result of the higher temperatures. Because emission scales

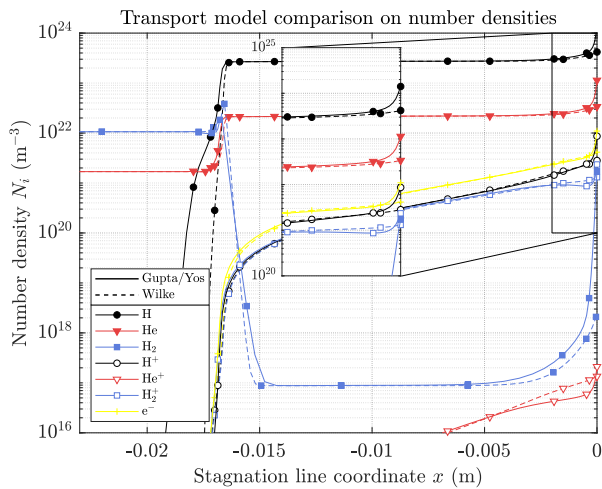


Figure 4.8: Number density comparison between Wilke and Gupta/Yos transport models.

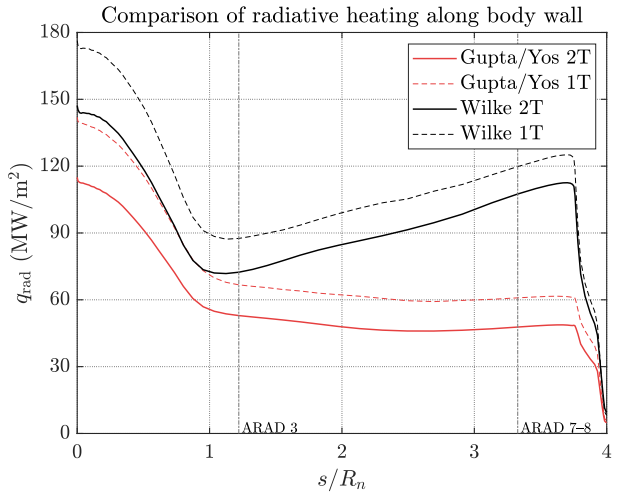


Figure 4.9: Influence of transport and non-equilibrium models on radiative heating.

with the fourth power of temperature, a 5% temperature increase can result in 20% higher radiative heat fluxes. Finally, similar values are obtained for convective and radiative heating along the body in the *Gupta/Yos 2T* case, indicating both contributions are equally as important at 180 km altitude.

4.5.2 He and H₂ Radiation

One of the main goals of the present work is to assess the influence of previously neglected radiative systems, namely, those resulting from He, He⁺ and H₂ excitation/de-excitation processes.

However, the effect of each individual system is difficult to quantify. By comparing the radiative heat fluxes that result from considering a set of systems to that resulting from a different set, one is able to effectively assess the impact of the systems not shared among the two sets, provided they have systems in common. This strategy was employed in the present work, and the results are presented in Figure 4.10. The tangent-slab approach was used at three different locations along the body, under thermal equilibrium and non-equilibrium conditions. Moving from the second to the last column, left to right, the radiative systems presented below are added to the analysis. For example, the second column considers only H, the third column adds He and He⁺ (so, H, He and He⁺ are considered), and so on. The last column corresponds to all systems, and the first one considers only atomic hydrogen transitions, while neglecting the Stark broadening (S.B.) of atomic lines. The percentages indicate the difference relative to the baseline, which corresponds to the prediction considering all radiative systems³.

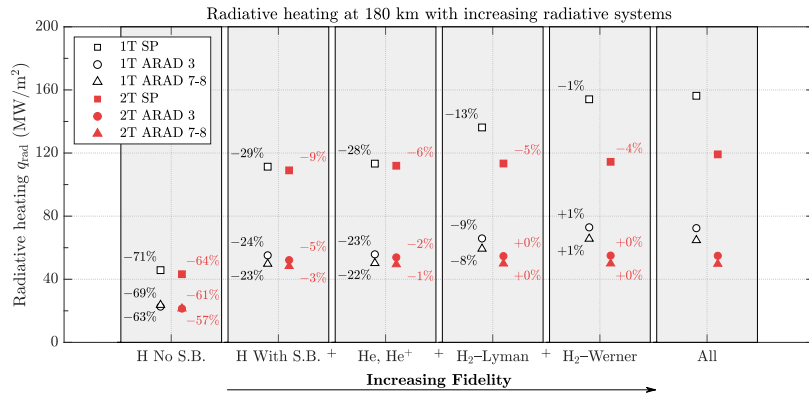


Figure 4.10: Analysis on the influence of different systems on the radiative heating.

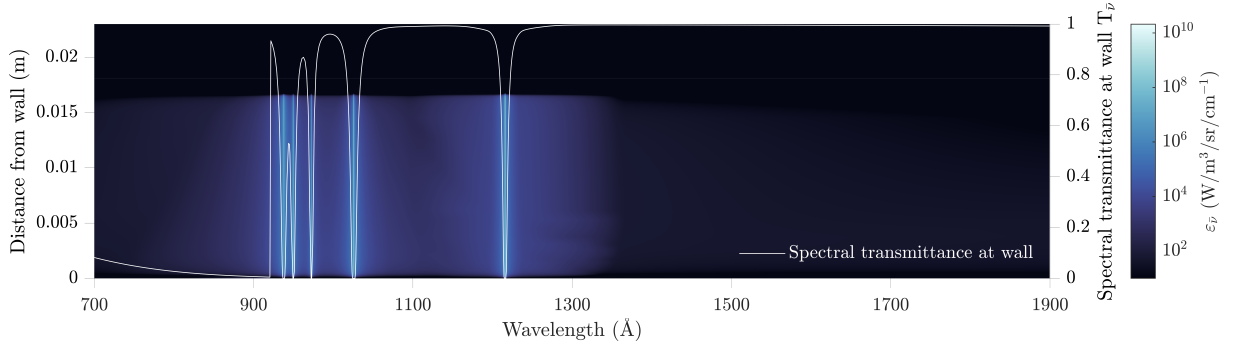
Clearly, Stark broadening of atomic H lines has a significant impact on the radiative heating experienced by the probe, as would be expected in such a highly ionized flow. The intense H lines are smeared, reducing the peak emission and absorption coefficients. The latter results in less self-absorption by the specific transition, significantly increasing wall heat fluxes. As a consequence, Stark broadening accounts for about 55% and 40% of the heat fluxes under thermal non-equilibrium and equilibrium conditions, respectively. When thermal equilibrium is considered (1T case), molecular hydrogen is seen to account for 22% to 28% of the total radiative heating at different locations along the body. Moreover, this contribution predominantly results from the H₂-Lyman system, although H₂-Werner is equally as important at the stagnation point. The effect of including other H₂ radiative systems is negligible, with less than 1%

³The last column adds the contributions from continuum, Fulcher and Rydberg H₂ systems to the analysis.

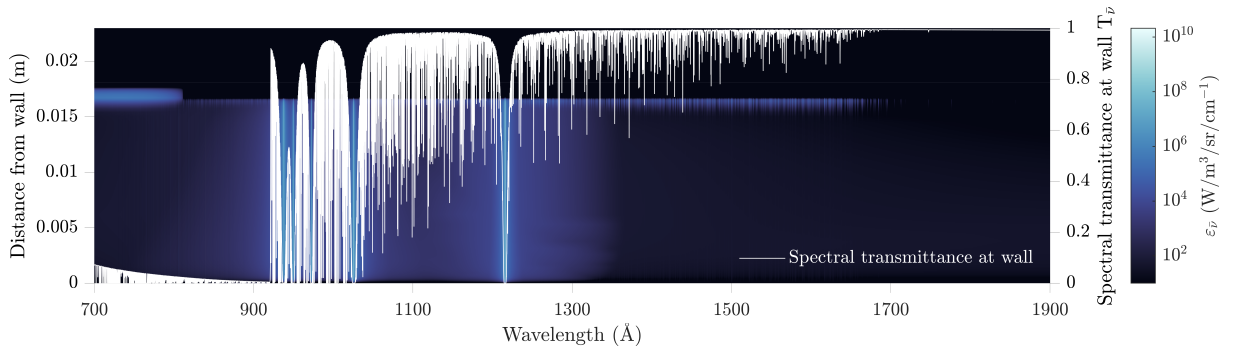
difference when compared to the baseline, as is the contribution due to He and He⁺ systems.

However, non-equilibrium conditions tell a different story. The 2T case shows a maximum difference of 9% between the radiative heating predicted with only H systems and that when considering all systems. This difference is primarily caused by inclusion of He and He⁺ systems, as well as those added in the last column resulting from H₂, particularly at the stagnation point. Nonetheless, the results point to a small increase in radiative heating due to He, He⁺ and H₂ systems under thermal non-equilibrium conditions.

To further investigate the source of H₂ radiation, the spectral emission coefficient at the stagnation point was mapped against the normal distance to the wall, using the 2T solution. The results are presented in Figure 4.11, where the bright spots correlate to stronger emission. The spectral transmittance of the shock layer to this radiation at the wall is also shown, calculated using $T_\nu = \exp\left(-\int_0^{z_\infty} \kappa_\nu(z) dz\right)$. This coefficient is a measure of the radiation that reaches the surface in the corresponding spectral location, meaning values closer to 1 indicate low absorption. Figure 4.11a shows the spectral emission map when considering only radiation from H systems. Atomic hydrogen emits significantly throughout the stagnation line, but the strong atomic lines are also highly absorbing, and the transmittance at these spectral locations is close to zero. However, it rapidly increases away from the peaks, resulting in the strong impact of Stark broadening mentioned earlier. Below, Figure 4.11b presents the same emission map when all systems are considered. There is an evident emission peak at the shock due to molecular hydrogen systems. More importantly, the remaining shock layer doesn't present any absorbing mechanisms capable of re-absorption between the shock and the wall in the spectral region ranging from 1,300 Å to 1,700 Å. Hence, radiation



(a) Only H radiative systems considered.



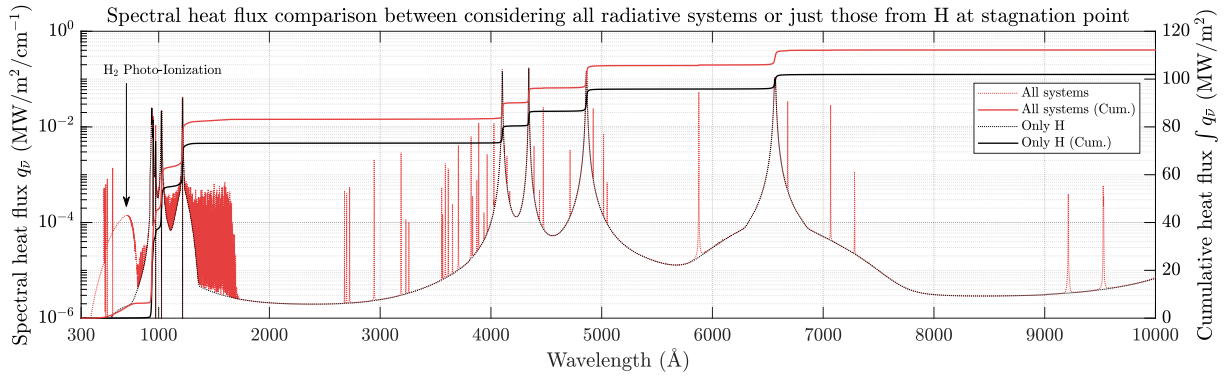
(b) All radiative systems considered.

Figure 4.11: Spectral emission maps at the stagnation point in VUV region (where H₂ systems are active) with spectral transmittance superimposed.

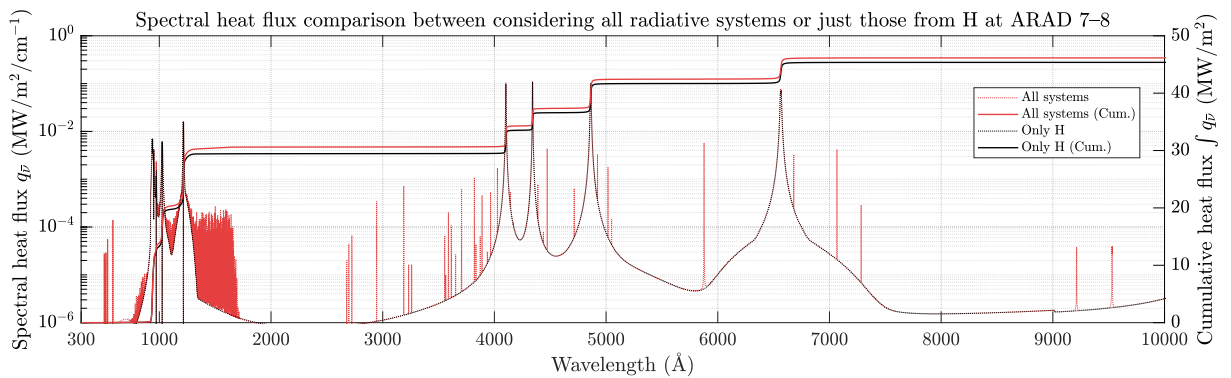
emitted at the shock due to H_2 internal excitation and subsequent de-excitation eventually reaches the wall, effectively contributing to the radiative heating. Finally, the presence of H_2 near the wall doesn't seem to noticeably increase absorption in this region (else, re-absorption near the wall would reduce the spectral transmittance in the spectral range mentioned before), thus refuting the idea introduced in § 3.5.

At the lower end of the spectrum, between 700 Å and 800 Å, Figure 4.11b indicates the presence of a strong continuum contribution, which was later identified to result from radiative H_2 recombination. To investigate which regions of the spectrum contribute most to the radiative heating, the spectral heat flux at the wall is shown in Figure 4.12 at the stagnation point and at ARAD 7–8, using the conventional ray-tracing approach applied to the *Gupta/Yos 2T* case. A comparison between the spectral fluxes obtained when considering only H systems and that resulting from all systems is presented, together with the cumulative heat flux after integration. A 9.5% increase in radiative heating when accounting for all systems is observed at the stagnation point, a difference that decreases to only about 1.7% at ARAD 7–8. This results essentially from the large H_2 photo-ionization contribution emitted at the shock, although a 1% to 2% share can also be attributed to H_2 –Lyman and H_2 –Werner bands. Overall, the strong atomic H lines are responsible for most of the radiation reaching the probe's surface in both locations, as indicated by the pronounced increase in the cumulative results when a line is integrated.

In summary, atomic hydrogen is the preeminent chemical species to consider for radiation, as other authors had previously assumed. Yet, they had also assumed thermal equilibrium conditions, which, when



(a) Stagnation point spectral radiative heat flux.



(b) ARAD 7–8 spectral radiative heat flux.

Figure 4.12: Spectral radiative heating when considering all systems or just atomic H systems.

combined with inclusion of H_2 systems, is seen to greatly increase the radiative heating due to strong emission at the shock. Only when the temperature non-equilibrium induced by the relaxation of the vibrational energy states of H_2 towards equilibrium is taken into account, does the emission lower to values similar to the ones predicted under thermal equilibrium conditions. Nevertheless, a 9.5% increase in radiative heating at the stagnation point may be attributed to inclusion of He, He^+ and H_2 systems, as indicated in Table 4.2.

4.5.3 Three-Dimensional Radiative Transfer Influence

Here, the influence of considering different models for radiative transfer through the flowfield is analyzed. Figure 4.13 shows the directional maps of radiation intensity and heat fluxes at the stagnation point and ARAD 7-8, where a comparison between the tangent-slab and ray-tracing results is presented. The two directional quantities are related through $q^{\theta,\phi} = I^{\theta,\phi} \cos \theta$, where θ is the angle between a given direction and that normal to the wall. The $\cos \theta$ term has a filtering effect on the directional variation of the radiative intensities $I^{\theta,\phi}$. In other words, the heat fluxes $q^{\theta,\phi}$ are only affected by spatial variations in $I^{\theta,\phi}$ to the extent allowed by this term. If these variations occur near the local zenith ($\cos \theta \rightarrow 1$), they are inherited by $q^{\theta,\phi}$, but if they occur at the periphery of the hemisphere ($\cos \theta \rightarrow 0$), then their contribution to $q^{\theta,\phi}$ is negligible. This is evident in Figure 4.13. In both the stagnation point and ARAD 7-8, the differences in $I^{\theta,\phi}$ between the ray-tracing and tangent-slab approaches are more noticeable at the periphery, where $\cos \theta \rightarrow 0$. In turn, this leads to a good agreement between the two approaches regarding

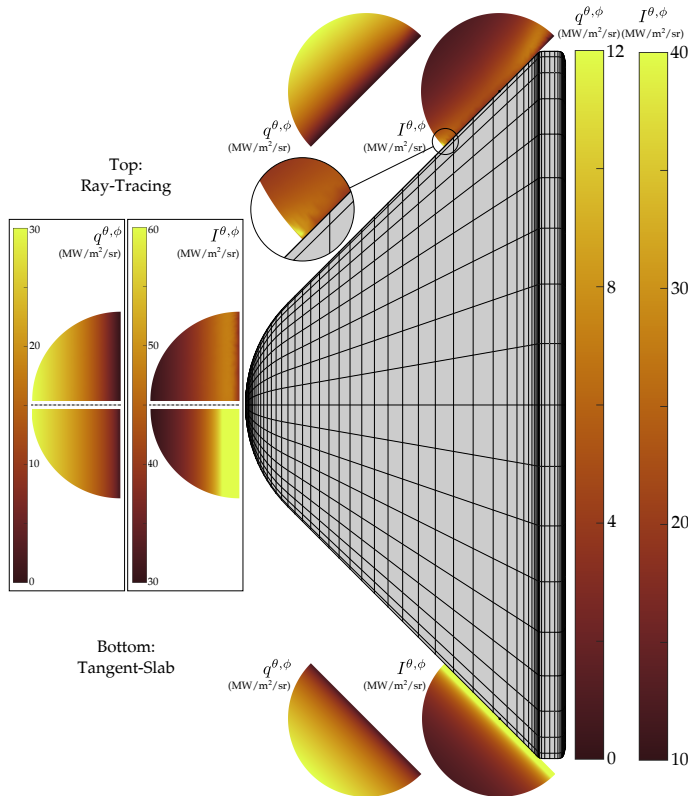


Figure 4.13: Map of directional radiative intensity and heat flux with tangent-slab and ray-tracing approaches.

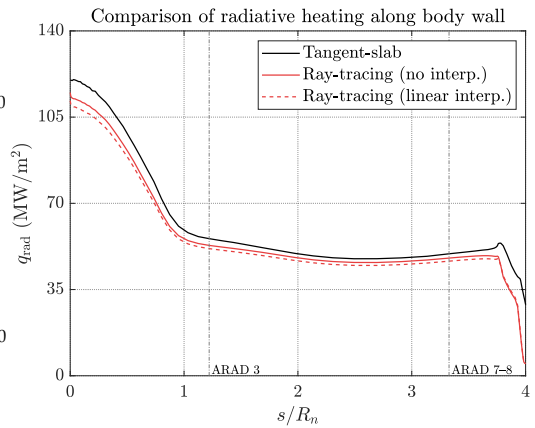


Figure 4.14: Influence of radiative transfer model on radiative heating along body.

$q^{\theta,\phi}$, which is ultimately responsible for radiative heating. At ARAD 7–8, the ray-tracing approach is able of capturing a stronger intensity from rays originating at the hottest region of the shock layer (as indicated by the circular inset), corresponding to the strong normal shock at the stagnation line, but its effect on $q^{\theta,\phi}$ is inconsequential. Due to the small shock layer thickness, the variations in flowfield properties around $\theta \sim 0^\circ$ are small, and the tangent-slab approach turns out to provide a good approximation.

This is further supported by comparing the radiative heat fluxes along the body for both models, as displayed in Figure 4.14. The tangent-slab approach overpredicts the heat fluxes by about 3% to 10% when compared to the constant coefficient ray-tracing, a difference that increases to about 6% to 13% when the comparison is performed against the more accurate linear interpolation ray-tracing model. A small discrepancy of around 3% between the two ray-tracing approaches is observed throughout the body wall. This is negligible given the fact that the linear interpolation approach takes twice the time of the conventional one. The tangent-slab model provides a very good initial estimate at a low computational cost when compared with the ray-tracing approach - a 10 minute simulation in contrast to a 1 day long one, when using the constant coefficient ray-tracing model with 500 rays.

Interestingly, the stagnation point results in Figure 4.13 reveal that the strongest intensity rays reaching the surface emerge from the periphery of the hemispherical domain, and not from the hottest region directly normal to the stagnation point. Although counter-intuitive, this results from a longer diagonal spatial integration path when $\theta \neq 0$, in which case the ray crosses a larger emitting portion of the shock. Obviously, the flowfield that follows is also absorbing radiation, but what Figure 4.13 indicates is that this balance tends to favor emission over radiation, eventually leading to a stronger radiative intensity.

4.5.4 Estimate of Precursor Heating Effects at Stagnation Point

For strongly radiating flowfields, the influence of radiation extends beyond the shock layer. While pressure waves travel through the flow at the local speed of sound relative to it, and cannot propagate upstream when it is supersonic, radiation in the form of electromagnetic waves propagates at the speed of light, and is thus able to affect the upstream flowfield. In particular, radiative absorption mechanisms in the *precursor* region eventually lead to photo-ionization and photo-dissociation, altering the chemical composition of the free-stream flow upstream of the shock (as illustrated in Figure 1.1). Additionally, several radiative transitions that do not lead to dissociation or ionization may occur, instead contributing to the excitation of the internal energy states of these particles [100]. In the context of a multi-temperature approach, this results in an increase in the internal temperatures modeling the non-equilibrium behavior.

The effects of precursor heating have been studied in preparation for the Galileo mission by Tiwari *et al.* [16]. Results for the stagnation point under non-equilibrium conditions showed that precursor heating would amount to 15% hydrogen becoming dissociated before even reaching the shock. Similarly, precursor photo-ionization was responsible for 0.8% H_2^+ in the same region. When compared to simulations where radiation to the precursor region is not modeled, both the translational and internal temperatures inside the shock layer increased by about 1%. In the upstream region, however, only the internal temperature increases due to internal excitation of the particles, since the density is too low for the energy relaxation terms to effectively exchange energy, which would allow the two temperatures to equilibrate. The results

obtained by Johnston *et al.* [100] for a Mars-return case support this 1% increase. Although this may seem insignificant, keep in mind that radiation scales with the fourth power of temperature, and Tiwari *et al.* report a 10.5% increase in radiative heat flux at the stagnation region due to these combined effects.

To estimate the impact of precursor heating at the stagnation point, in the context of the improved models applied in the present work to the Galileo case, its effects were superimposed to the *Gupta/Yos* $2T$ solution at the stagnation line. The corrections performed were as follows. Mass fractions of H_2 , H , H_2^+ and e^- were corrected at the upstream to approach the values reported by Tiwari *et al.* at the shock, using the following functional form, valid for $s > s_{\text{shock}}$:

$$c_i(s) = c_{i,\infty} \left[1 - \left(1 - \frac{c_{i,\text{shock}}}{c_{i,\infty}} \right) e^{-k(s-s_{\text{shock}})} \right], \quad i \in \{H, H_2^+, e^-\} \quad (4.1)$$

where s is the distance normal to the wall along the stagnation line, $c_{i,\infty}$ is the unperturbed atmosphere value, $c_{i,\text{shock}}$ is the value reported by Tiwari *et al.* at the shock location and k is a parameter adjusting the exponential variation approaching the shock. The resulting mass fraction for H_2 was imposed to keep $\sum c_i = 1$ across all species. To transition from this profile to the one actually computed by SPARK in the shock layer, a gluing function is applied for $s_{\text{shock}} - 2\Delta s < s < s_{\text{shock}}$ in the form $c_i = (1 - a)c_{i,\text{shock}} + ac_i^{\text{SPARK}}$, where $a = (s_{\text{shock}} - s)/2\Delta s$, so that no discontinuities occur, since the profile used in the shock layer is the one obtained in SPARK (that is, $c_i = c_i^{\text{SPARK}}$ for $s < s_{\text{shock}} - 2\Delta s$). The parameter Δs was tailored to ensure a smooth transition. Regarding the temperatures, a similar process was used to increase T_{v,H_2} in the upstream. Finally, both temperatures were increased by 1% in the shock layer, so as to simulate the increased values reported by other authors.

The mass fractions of H , H_2 , H_2^+ and e^- resulting from this approximate treatment are presented in Figure 4.15a, where a comparison is made with those before the corrections are applied. The corrected mass fractions now account for photo-dissociation and photo-ionization in the precursor region, through the processes $H_2 + h\nu \rightleftharpoons 2H$ and $H_2 + h\nu \rightleftharpoons H_2^+ + e^-$, which lead to the increase in H , H_2^+ and e^- mass fractions at the expense of H_2 . Figure 4.15b presents the temperature corrections applied at the

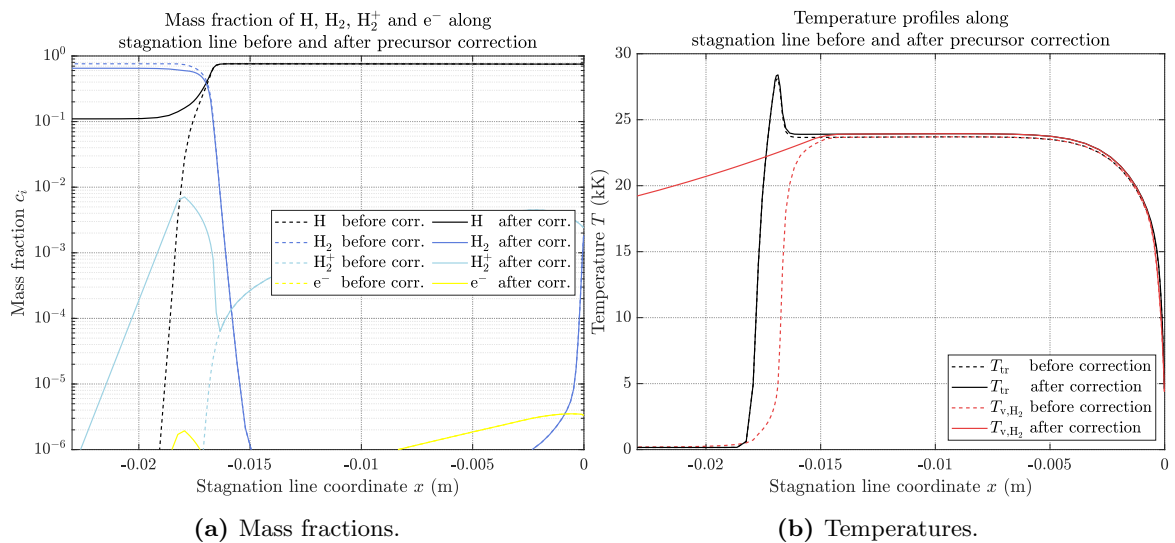


Figure 4.15: Stagnation line profiles before and after correction to account for precursor effects.

stagnation line, following the results reported by other authors on the temperature effects of precursor heating. Note that although T_{v,H_2} now starts increasing farther from the shock, leading to a corresponding increase in H_2 emission as previously discussed, the number density of H_2 is also significantly reduced, leading to an opposing effect. These stagnation line profiles were then fed to the SPARK LbL radiative solver, and the radiative heating at the stagnation point was obtained using the tangent-slab approach⁴.

To isolate the effects of precursor heating corrections, the spectral radiative heating obtained is compared to the one using the original tangent-slab model. The results revealed by Figure 4.16 are consistent with the discussion presented in § 4.5.2 regarding H_2 radiation originating from the high-temperature shock. As expected, the increased vibrational temperature of H_2 in the precursor region promotes de-excitation processes before dissociation takes place at the shock, resulting in a significant increase in the contribution of H_2 to the radiative heating reaching the wall. The total heat flux accounting for the precursor heating corrections is 355.6 MW m^{-2} , nearly a 200% increase relative to the original tangent-slab value. This is a much more pronounced increase compared to the 10.5% predicted by Tiwari *et al.* [16]. The most likely explanation to this discrepancy is their simplified treatment of H_2 radiation, which lacked the ability to consider its detailed line-by-line behavior. The thick lines in Figure 4.16 show that the corrected heat fluxes start diverging from the original ones as the spectral region where H_2 systems are active is integrated, indicating that most of the observed increase is due to the correction performed on T_{v,H_2} , rather than the 1% temperature increase imposed inside the shock layer. In fact, if the correction to T_{v,H_2} in the precursor region is removed, the increase in radiative heat fluxes is just 3%, thus confirming this observation. This suggests that H_2 radiation may have had a fundamental impact on the radiative heating experienced by Galileo, contrary to what has been assumed thus far.

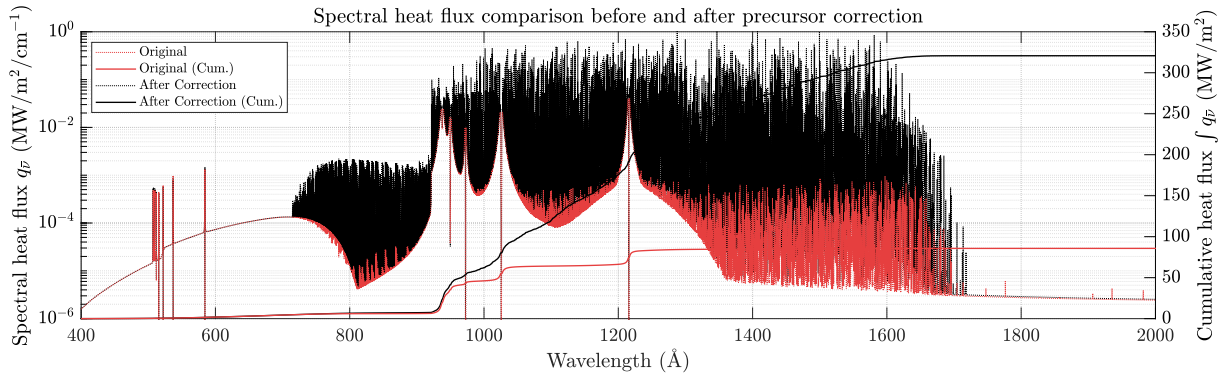


Figure 4.16: Influence of precursor effects in spectral heat flux between 400 Å and 2000 Å.

4.5.5 Influence of Ablation Products at Stagnation Point

In this section, the effects of ablation products injection in the stagnation line boundary layer are investigated. An approximate treatment is performed based on the work of Park [21], who studied ablation and spallation of C, C^+ , C_2 and C_3 in the stagnation region and its effects on the stagnation point radiative heating. The aim here is to understand the extent of radiative absorption in the ablation layer

⁴A ray-tracing approach would require these corrections to be applied throughout the flowfield, resulting in a significant extrapolation of the results reported in the literature for the stagnation line.

due to the presence of these contaminating species. More notably, the C_3 molecule is known to be a strong absorber in the VUV range, due to the Swings and VUV bands between 1,200 Å and 1,800 Å. Additionally, photo-ionization continua for C_2 and C_3 below 1,100 Å have been identified by Park to significantly reduce stagnation point heat fluxes [21]. In Park’s work, C_2 and C_3 radiative transitions are treated in an approximate way through temperature-dependent global absorption cross-sections. The same approach was employed here concerning C_3 transitions, using the same data as Park. However, for C_2 transitions a detailed line-by-line model was used. Transitions extending from the VUV to the visible range are considered, unlike Park who only accounts for VUV transitions and the C_2 Swan bands.

Regarding non-VUV transitions, the spectral data set from Lino da Silva [95, 101] already available in the SPARK LbL code was adopted. As for the VUV region, Park considers eight C_2 radiative systems in the VUV region, from which only three are reported observed in the literature [102], namely the Herzberg-F ($F^1\Pi_u - X^1\Sigma_g^+$), Herzberg-g ($g^3\Delta_g - a^3\Pi_u^+$) and Herzberg-f ($f^3\Sigma_g^- - a^3\Pi_u^+$). Accordingly, only these three VUV transitions for C_2 have been considered here. Spectroscopic constants for the higher-lying states are issued from Huber and Herzberg [71], whereas for lower states the compilation from Lino da Silva [95, 101] was adopted. Potential curves were refitted and the relevant vibrational wave functions were used alongside a constant electronic transition moment, estimated resorting to the data from Bruna [103] to yield the appropriate Einstein coefficients⁵. The temperatures in the boundary layer are still high enough to promote emission over absorption of some radiative systems, as may be the case of the C_2 Swan band in the visible range. Thus, although strong absorption in the VUV region may lead to reducing the impact of H and H_2 radiation, emission in other parts of the spectrum has the potential to neutralize this effect. A thorough accounting of these interactions is difficult and still lacking.

To account for the presence of carbonaceous species in the ablation layer in the absence of a material-response code, the mole fractions obtained by Park were used, and are presented in Figure 4.17. Hence, the analysis is limited to the species C, C^+ , C_2 and C_3 , since these are the only ones considered in the work of Park. The stagnation line profile of species mole fractions obtained with SPARK was kept for $s > 0.3$ cm, where s is the distance to the wall, and the same transition function used in § 4.5.4 was applied between $0.2 < s < 0.3$ cm to continuously join the two solutions. Again, care was taken to ensure $\sum x_i = 1$ throughout the stagnation line. The resulting mole fraction profiles are shown in Figure 4.18.

One important shortcoming of this approximation concerns the treatment of the boundary layer temperature. The injection of ablation species in the flowfield will reduce its temperature near the wall, and Park does not provide a temperature profile which could be used as a correction. Hence, two possible limiting cases were analyzed. One of them considers the injection has no effect on the flowfield temperatures, and thus the temperature profile obtained with SPARK is kept unchanged. Otherwise, one may assume that the ablation injection occurs at the wall temperature (3,000 K), and the flowfield does not affect their temperature. Since the high pressure in the boundary layer promotes thermal equilibrium conditions, the flowfield temperatures were corrected to 3,000 K for $s < 0.3$ cm in this case.

Both conditions are compared to the original tangent-slab solution using the *Gupta/Yos 2T* case in Figures 4.19a and 4.19b. In the lower temperature scenario (Figure 4.19a), the carbonaceous species at

⁵See Ref. [101], pp. 74 for a detailed description of this approach with the corresponding equations.

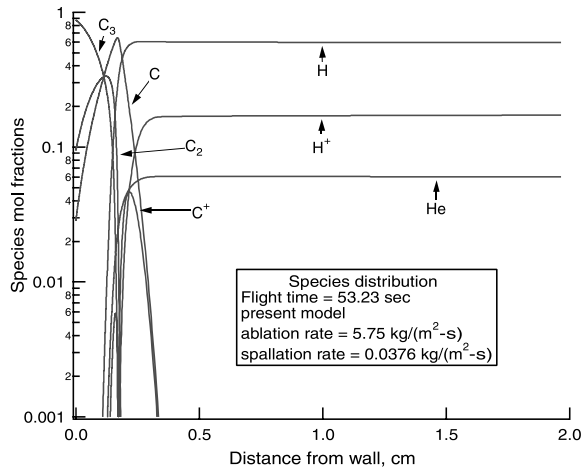


Figure 4.17: Mole fractions from Park [21].

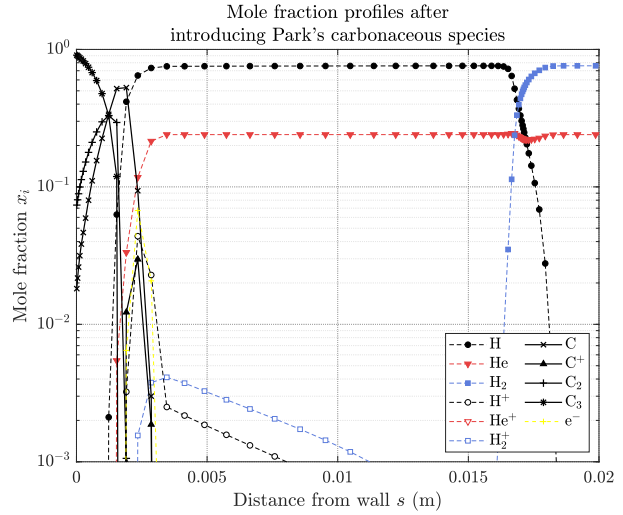


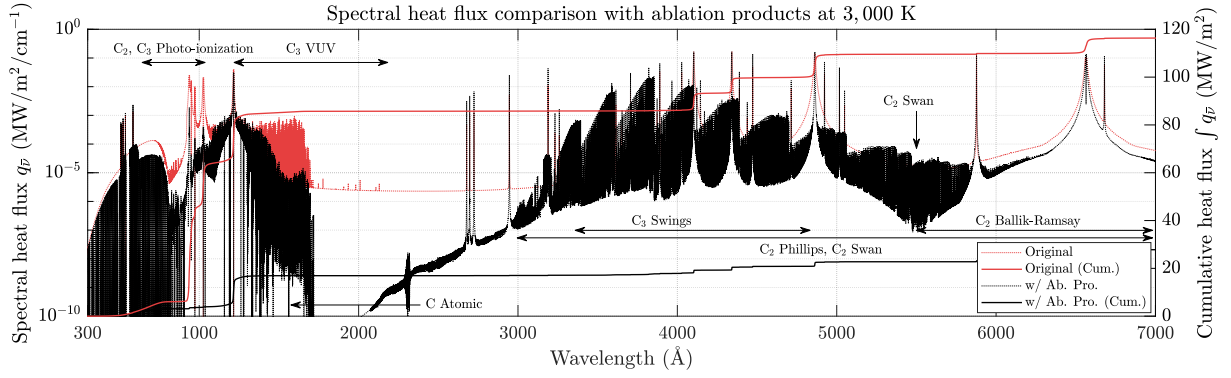
Figure 4.18: Corrected mole fractions.

3,000 K near the wall absorb 74.2% of the original radiation impacting the stagnation point, reducing the radiative heating to 29.7 MW m^{-2} . This significant decline is essentially a result of continuum absorption due to C_2 and C_3 photo-ionization, as well as the C_3 VUV band, all acting in the VUV region of the spectrum, which coincides with the domain of strongest emission due to atomic H lines and the H_2 band systems. Other C_2 band systems are important in the visible range, adding a layer of absorption but also providing millions of spectral de-excitation jumps that contribute to line emission, albeit with a negligible influence on the total heat flux at this temperature. As previously discussed, Park neglected several known radiative band systems. If only the systems used by the author are used in the present case, the radiative heating is 29 MW m^{-2} , close to the value predicted when all systems are accounted for, indicating a negligible effect for the remaining systems at 3,000 K.

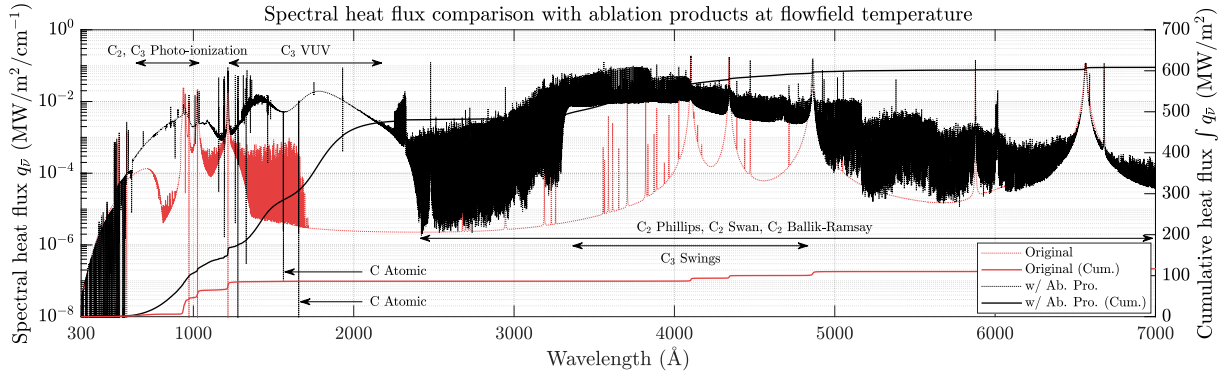
A very different picture is obtained for the other limiting case. If the ablation products had a negligible impact on the boundary layer temperature, then the carbonaceous species' temperatures would rapidly increase to 20,000 K at its boundary, and emission from these radiative systems would instead increase the radiative heating⁶. Figure 4.19b shows that C_2 and C_3 photo-ionization, together with C_3 VUV, now significantly increase the radiative heating over that experienced originally. The heat fluxes predicted under these conditions are 614.9 MW m^{-2} , a 435% increase over the case without ablation products injection. Furthermore, the previously unimportant band systems in the visible range now comprise about a quarter of this increase. If Park's systems are used under these conditions, the radiative heat fluxes decrease to 571.8 MW m^{-2} , indicating the systems neglected by the author may have an important contribution at higher temperatures. Although completely unrealistic, this scenario is at least able to provide an upper bound on the extra emission provided by the ablation products. Long before the 20,000 K temperature would be reached, dissociation of C_2 and C_3 would take place, decreasing their contributions substantially.

An additional comparison was performed taking into account the effects of ablation products injection with precursor heating. The optimistic case was assumed (boundary layer at 3,000 K), and the results

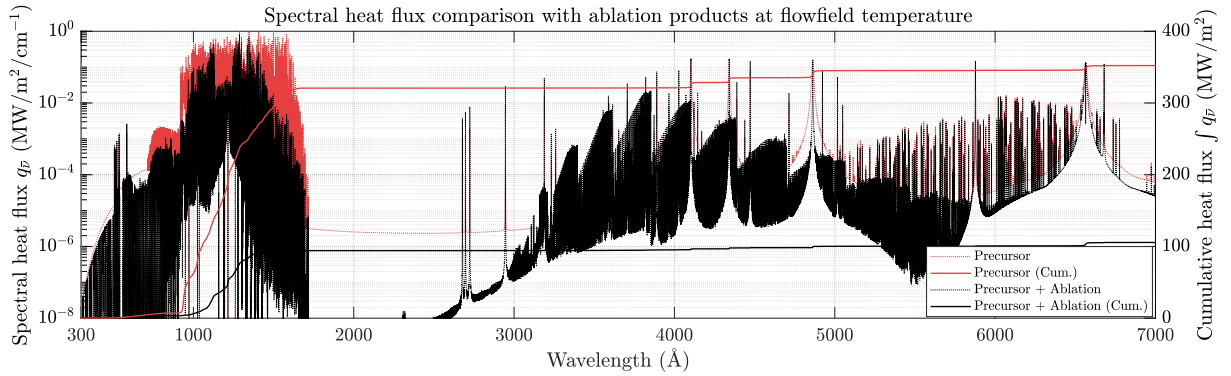
⁶Note that spallation is not being taken into account. This effect would result in an additional radiation blockage process, significantly lowering the surface radiative heating.



(a) Limiting case 1: ablation products and flowfield at 3,000 K for $s < 0.3$ cm.



(b) Limiting case 2: flowfield temperatures kept unchanged from SPARK.



(c) Precursor corrections with ablation products using limiting case 1 (3,000 K for $s < 0.3$ cm).

Figure 4.19: Spectral heat flux comparisons when ablation products are added to the radiative analysis.

are presented in Figure 4.19c. Not surprisingly, H_2 VUV radiation is severely hindered due to C_2 and C_3 photo-ionization and C_3 VUV. In the visible range, several band systems contribute to line emission, although with a negligible impact on the overall radiative heating. The presence of these systems in the background of the strong atomic H lines observed in red substantially reduces their contribution, and the total radiative heating is reduced to 107.5 MW m^{-2} , even lower than that originally predicted.

4.5.6 Empirical Correction for Flowfield-Radiation Coupling Effects

The so-called radiative cooling effect is caused by the inclusion of the divergence of the radiative heat flux in the energy equation. Radiative energy is “lost” to the free-stream flow, and the shock-layer

temperatures (in this, now, non-adiabatic flow) decrease as a result, leading to the term radiative cooling. The most widely used correlation for estimating the impact of radiative cooling on the radiative heating was actually developed by Tauber and Wakefield during pre-flight studies for the Galileo entry in Jupiter [91], as the severe radiative heating expected during flight was anticipated to be extremely sensitive to this coupling effect. The radiative heat fluxes are corrected according to

$$q_{\text{rad}}^{\text{TW}} = \frac{q_{\text{rad},0}}{1 + a\Gamma^{0.7}} , \quad (4.2)$$

where $q_{\text{rad},0}$ is the uncoupled radiative flux, a is a parameter depending on the atmosphere ($a = 3$ for Jupiter's case) and Γ depends on the free-stream flow properties according to $\Gamma = 4q_{\text{rad},0}/\rho_{\infty}V_{\infty}^3$. Correlations such as the Tauber-Wakefield, which depend on the local radiative heat flux, are known to underestimate the radiative cooling effect at downstream regions, due to its non-local character. Radiatively cooled gas at the strongly radiating stagnation region flows downstream and reduces the temperature, an effect that the correlation is unable to capture. Thus, the decrease in radiative heating expected after the correction is greater at the stagnation region than at the shoulder.

This is indeed observed in Figure 4.20. The decrease in radiative heating is significant all along the body, but more so in the stagnation region. Although the radiative heat fluxes predicted in the present work are higher than those predicted by previous authors, inclusion of radiative cooling effects, albeit in an approximate fashion, is shown to reduce these figures to values found in the literature. The results of Moss and Simmonds for the altitudes of 184.5 km (40 s) and 166.6 km (43 s) underpredict the heat fluxes at the spherical region of the probe, given that the trajectory point studied in the present work lies between the two. However, the opposite is true towards the shoulder. Several factors may have contributed to this disparity, the most important being the chemical equilibrium assumption employed and the Wilke transport model used. The stagnation point prediction is within the bounds reported by Matsuyama for the same altitudes, which were obtained using a coupled tangent-slab approach, but only considering H and H⁺ radiation and thermo-chemical equilibrium. Park's prediction, which properly treats ablation

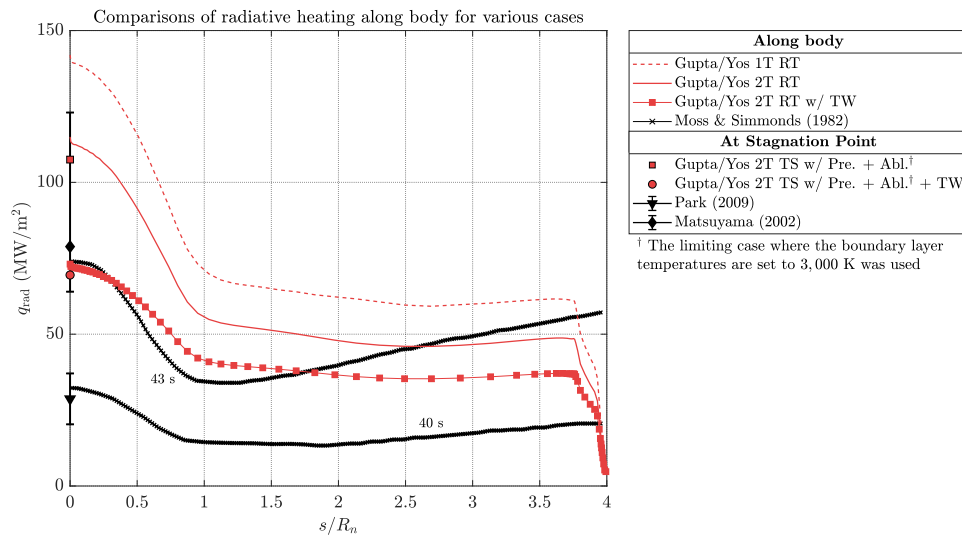


Figure 4.20: Comparison of radiative heat flux results along body wall with literature.

products injection, is significantly lower, but again an equilibrium assumption was used. It is difficult to provide a meaningful comparison with previous works on radiation, since these rely on a thermo-chemical equilibrium flowfield, a simplification that significantly departs from the chemical non-equilibrium actually present during flight. Thermal non-equilibrium also plays an important role, especially at higher altitudes such as in the case studied in the present work, due to H₂ emission at the shock.

Two additional points were included at the stagnation point in Figure 4.20. Both show how the combined effect of precursor heating and ablation product absorption almost cancel, provided the conservative case for the boundary layer temperatures is used. As a result, the radiative heating predicted originally for the *Gupta/Yos 2T* case is close to that with precursor and ablation injection corrections (square). The same applies to the results obtained after the Tauber-Wakefield correction is employed (circle).

The results obtained in the present work are summarized in Table 4.2. The convective heating results only vary for the first four rows, and thus these are the only ones presented. The radiative heating, on the other hand, was subject to extensive sensitivity studies, making up most of the table. Nonetheless, the influence of precursor heating and ablation products was only possible to study at the stagnation point.

Table 4.2: Summary of heat flux results obtained in the present work.

* This value corresponds to a percentage error relative to the *Gupta/Yos 2T RT All* case.

‡ Ablation products were considered using all systems at 3,000 K.

Case	Assess the Influence of	Convective Heat Fluxes MW m ⁻² / %*			Radiative Heat Fluxes MW m ⁻² / %*		
		SP	ARAD 3	ARAD 7-8	SP	ARAD 3	ARAD 7-8
Gupta /Yos 2T RT All	(Baseline)	107.4 / -	43.2 / -	36.5 / -	115.0 / -	52.9 / -	47.8 / -
Wilke 1T RT All	Transport modeling	83.9 / -21.9	40.9 / -5.3	10.5 / -71.2	176.4 / +53.4	87.6 / +65.6	119.8 / +151
Wilke 2T RT All	Transport modeling	84.0 / -21.8	40.6 / -6.0	7.3 / -80.0	147.2 / +28.0	72.4 / +36.9	107.5 / +125
Gupta/Yos 1T RT All	Non-equilibrium	107.3 / -0.1	43.1 / -0.2	36.6 / +0.3	142.0 / +23.5	66.7 / +26.1	60.9 / +27.4
Gupta/Yos 2T RT H-Only	He + H ₂ radiation	- / -	- / -	- / -	104.1 / -9.5	51.5 / -2.7	47.0 / -1.7
Gupta/Yos 2T TS All	3D radiative transfer	- / -	- / -	- / -	120.0 / +4.4	55.7 / +5.3	49.5 / +3.6
Gupta/Yos 2T RT Linear Interp.	Spatial integration approximation	- / -	- / -	- / -	111.7 / -2.9	51.6 / -2.5	46.5 / -2.7
Gupta/Yos 2T TS All + Pre.	Precursor heating	- / -	- / -	- / -	355.5 / +209	- / -	- / -
Gupta/Yos 2T TS All + Ab.	Ablation products	Park's systems, unchanged temperatures			571.8 / +397	- / -	- / -
		Park's systems, at 3,000 K			29.0 / -74.8		
		All systems, unchanged temperatures			614.9 / +435		
		All systems, at 3,000 K			29.7 / -74.2		
Gupta/Yos 2T TS All + Pre. + Ab.‡	Precursor heating Ablation products	- / -	- / -	- / -	107.5 / -6.5	- / -	- / -
Gupta/Yos 2T RT All + T-W	Radiative cooling	- / -	- / -	- / -	73.1 / -36.4	39.7 / -25.0	36.5 / -25.5
Gupta/Yos 2T TS All + Pre. + Ab.‡ + T-W	Precursor heating Ablation products Radiative cooling	- / -	- / -	- / -	69.5 / -39.6	- / -	- / -

All: All radiative systems considered H-Only: Only transitions from H are considered in the radiative analysis
RT: Ray-tracing TS: Tangent-slab Pre.: Precursor heating Ab.: Ablation products T-W: Tauber-Wakefield Correction

Conclusions

5.1 Achievements

In spite of the practical nature of this dissertation, a substantial amount of code development, testing and verification was necessary, so as to further the past Galileo entry predictions with improved models and accuracy. The transport properties module in SPARK was re-structured to integrate the current trend in CCS databases available in the literature, allowing the Gupta/Yos transport model to be applied to any atmosphere in the Solar System, whereas the previous design was hard-coded to Earth's. The new architecture supports user-defined CCS expressions, the general phenomenological approach, or a combination of the two for a given mixture. A comparison of the Wilke/Blottner/Eucken and Gupta/Yos transport models in the context of Jupiter's H_2 –He atmosphere confirmed the shortcomings of the former above 5,000 K, while the latter was observed to compare positively with other literature sources.

Moreover, the ray-tracing algorithm in SPARK LbL was re-built in Fortran using SPARK's OOP standard, allowing for an easier integration in the future and substantially improving its efficiency and versatility. The directional discretization scheme employed, based on the distribution provided by a Fibonacci Lattice, was shown to accurately predict radiative heat fluxes to within 5% differences of the converged value using just 50 rays, for Galileo's entry conditions.

Despite the boundary layer problem faced in the Wilke case, important differences between the two transport models may still be drawn, especially at the shock location. Due to its inability to accurately capture the mixture's thermal conductivity, the Wilke model not only predicts a higher maximum temperature at the shock, but also underestimates the shock thickness. Accordingly, energy diffuses away from the shock at a lower rate, resulting in a thinner, higher temperature shock. The higher thermal conductivity predicted with the Gupta/Yos model results in the convective heat fluxes exceeding 100 MW m^{-2} at the stagnation point. Over the conical region, this value drops about 60%. A similar trend is predicted for the radiative heating, meaning both contributions are equally as important. The Wilke model overestimates the radiative heat fluxes throughout the body, especially at the shoulder, but without a realistic boundary layer temperature profile it is difficult to estimate by how much.

No significant differences were observed in convective heating between the thermal equilibrium and non-equilibrium solutions. The radiative heating, on the other hand, significantly depends on the considered assumptions. Under thermal equilibrium conditions, the effects of H_2 radiation are important due to

strong emission at the shock, making up for more than 20% of the total radiative heat flux. Had previous investigators included H_2 in their radiation analyses, it is something they would've also experienced. However, since it originates from the shock, when thermal non-equilibrium is taken into account, the vibrational relaxation process significantly reduces H_2 emission, resulting in just a 6% difference at the stagnation point, a contribution that mainly stems from H_2 photo-ionization.

On the other hand, precursor heating effects are known to contribute to internal excitation before the shock, leading to an increase in T_{v,H_2} in this region. Given the origin of H_2 radiation previously discussed, the 209% increase in radiative heating predicted when accounting for these effects is of no surprise. Thus, the influence of H_2 radiation must be considered in future missions to Jupiter, together with an accurate modeling for the energy content of the upstream H_2 molecules due radiative absorption.

Regarding the approximate analysis conducted on the effect of ablation product injection, none of the cases considered may be said to accurately depict the actual flight conditions, which lie somewhere in between the two scenarios. However, it was shown that as the ablation products' temperatures increase due to thermal energy exchange with the flowfield, their absorption effectiveness in the VUV range may be counterbalanced by emission over the visible range. Although a 74% decrease in radiative heating is observed in the conservative case, the 435% increase predicted otherwise reveals the uncertainties one may expect to deal with if ablation product-flowfield energy exchanges are not accurately modeled.

The results of the combined precursor/ablation correction show that both effects tend to cancel at the stagnation point. However, Matsuyama previously showed that turbulence-induced diffusion of carbonaceous species at the shoulder leads to a decrease in the absorption capabilities of the ablation layer. This observation, combined with the precursor heating effects estimated in the present work, could arguably justify the inexplicably high recession rates experienced at the shoulder. A detailed study of this coupled interaction is required to validate this conjecture.

Finally, the analysis conducted on the effects of three-dimensional radiation modeling reveals a maximum 10% difference between the tangent-slab and ray-tracing approaches at the stagnation point. The spatial integration approach developed by Johnston *et al.* only shows a 3% difference compared to the conventional ray-tracing, which doesn't make up for the 100% higher associated computational cost.

5.2 Future Work

The results of this study brought new light into the Galileo entry problem, but also introduced new questions to be addressed in the future. The impact of H_2 radiation, when coupled to a material-response code capable of properly modeling the energy-exchange processes in the ablation layer, remains one of the biggest uncertainties (and challenges) at this point. The precursor region should also be coupled to the shock layer flowfield, so as to quantify its effects on the extra H_2 radiation reaching the shoulder and possibly explain the high recession rates experienced in this region. Finally, the Boltzmann distributions governing the population of internal energy levels should be replaced by general non-Boltzmann ones, which is especially important in the scope of radiative analyses. However, state-to-state kinetics still needs to mature, and the computing power needs to keep up with the ever-increasing demand.

Bibliography

- [1] J. D. Anderson. *Hypersonic and High-Temperature Gas Dynamics*. AIAA Education. AIAA, 2nd edition, 2006. doi: 10.2514/4.861956. URL: <https://doi.org/10.2514/4.861956>.
- [2] D. F. Potter. *Modelling of Radiating Shock Layers for Atmospheric Entry at Earth and Mars*. PhD thesis, University of Queensland, May 2011.
- [3] P. Reynier, G. D’Ammando, and D. Bruno. Modelling chemical kinetics and convective heating in giant planet entries. *Progress in Aerospace Sciences*, 96:1–22, 2018. doi: 10.1016/j.paerosci.2017.11.002. URL: <http://www.sciencedirect.com/science/article/pii/S0376042117300507>.
- [4] F. S. Milos, Y.-K. Chen, T. Squire, and R. Brewer. Analysis of Galileo probe heatshield ablation and temperature data. *Journal of Spacecraft and Rockets*, 36(3):298–306, 1999. doi: 10.2514/2.3465. URL: <https://doi.org/10.2514/2.3465>.
- [5] F. S. Milos. Galileo probe heat shield ablation experiment. *Journal of Spacecraft and Rockets*, 34(6):705–713, 1997. doi: 10.2514/2.3293. URL: <https://doi.org/10.2514/2.3293>.
- [6] J. Moss and A. Simmonds. Galileo probe forebody flowfield predictions during Jupiter entry. In *3rd Joint Thermophysics, Fluids, Plasma and Heat Transfer Conference*, page 874, 1982. doi: 10.2514/6.1982-874. URL: <https://doi.org/10.2514/6.1982-874>.
- [7] S. Matsuyama, N. Ohnishi, A. Sasoh, and K. Sawada. Numerical simulation of Galileo probe entry flowfield with radiation and ablation. *Journal of Thermophysics and Heat Transfer*, 19(1):28–35, 2005. doi: 10.2514/1.10264. URL: <https://doi.org/10.2514/1.10264>.
- [8] J. O. Arnold. Planetary entry probes 1953-2036: A technologist’s perspective. 10th International Planetary Probe Workshop, June 2013.
- [9] L. P. Leibowitz. Measurements of the structure of an ionizing shock wave in a hydrogen-helium mixture. *The Physics of Fluids*, 16(1):59–68, 1973. doi: 10.1063/1.1694174. URL: <https://doi.org/10.1063/1.1694174>.
- [10] F. R. Livingston and P. Y. Poon. Relaxation distance and equilibrium electron density measurements in hydrogen-helium plasmas. *AIAA Journal*, 14(9):1335–1337, 1976. doi: 10.2514/3.61466. URL: <https://doi.org/10.2514/3.61466>.
- [11] L. P. Leibowitz and T.-J. Kuo. Ionizational nonequilibrium heating during outer planetary entries. *AIAA Journal*, 14(9):1324–1329, 1976. doi: 10.2514/3.61465. URL: <https://doi.org/10.2514/3.61465>.
- [12] B. A. Cruden and D. W. Bogdanoff. Shock radiation tests for Saturn and Uranus entry probes. *Journal of Spacecraft and Rockets*, 54(6):1246–1257, 2017. doi: 10.2514/1.A33891. URL: <https://doi.org/10.2514/1.A33891>.

- [13] J. N. Moss. *A Study of the Aerothermal Entry Environment for the Galileo Probe*, pages 3–25. AIAA, 1980. doi: 10.2514/5.9781600865435.0003.0025. URL: <https://arc.aiaa.org/doi/abs/10.2514/5.9781600865435.0003.0025>.
- [14] J. N. Moss, J. J. Jones, and A. L. Simmonds. *Radiative Flux Penetration through a Blown Shock Layer for Jupiter Entry Conditions*, pages 22–41. AIAA, 1978. doi: 10.2514/5.9781600865381.0022.0041. URL: <https://arc.aiaa.org/doi/abs/10.2514/5.9781600865381.0022.0041>.
- [15] J. N. Moss, A. L. Simmonds, and E. C. Anderson. Turbulent radiating shock layers with coupled ablation injection. *Journal of Spacecraft and Rockets*, 17(3):177–183, 1980. doi: 10.2514/3.57726. URL: <https://doi.org/10.2514/3.57726>.
- [16] S. N. Tiwari and K. Y. Szema. Effects of precursor heating on chemical and radiative nonequilibrium viscous flow around a Jovian entry body. In *2nd Thermophysics and Heat Transfer Conference*, volume 64, May 1978. doi: 10.2514/6.1978-907. URL: <https://doi.org/10.2514/6.1978-907>.
- [17] S. Matsuyama, Y. Shimogonya, N. Ohnishi, K. Sawada, and A. Sasoh. Numerical simulation of Galileo probe entry flowfield with radiation. In *8th AIAA/ASME Joint Thermophysics and Heat Transfer Conference*, June 2002. ISBN 978-1-62410-118-2. doi: 10.2514/6.2002-2994. URL: <https://doi.org/10.2514/6.2002-2994>.
- [18] C. Park. Injection-induced turbulence in stagnation-point boundary layers. *AIAA Journal*, 22(2):219–225, 1984. doi: 10.2514/3.8371. URL: <https://arc.aiaa.org/doi/abs/10.2514/3.8371>.
- [19] M. Furudate, I.-S. Jeung, and S. Matsuyama. Nonequilibrium calculation of flowfield over Galileo probe. In *44th AIAA Aerospace Sciences Meeting and Exhibit*, volume 7, January 2006. ISBN 978-1-62410-039-0. doi: 10.2514/6.2006-383. URL: <https://doi.org/10.2514/6.2006-383>.
- [20] C. Park. *Effect of Lyman Radiation on Nonequilibrium Ionization of Atomic Hydrogen*, chapter 2277. AIAA, 2004. doi: 10.2514/6.2004-2277. URL: <https://arc.aiaa.org/doi/abs/10.2514/6.2004-2277>.
- [21] C. Park. Stagnation-region heating environment of the Galileo probe. *Journal of thermophysics and heat transfer*, 23(3):417–424, 2009. doi: 10.2514/1.38712. URL: <https://doi.org/10.2514/1.38712>.
- [22] P. Reynier. Numerical reconstruction of Galileo entry. In *5th International Workshop on Radiation and High Temperature Gases in Atmospheric Entry*, October 2012.
- [23] C. Park. *Nonequilibrium Hypersonic Aerothermodynamics*. John Wiley & Sons, 1989.
- [24] C. Garbacz Gomes. State-to-state models in hypersonic flows. Master’s thesis, Instituto Superior Técnico, September 2018.
- [25] B. Lopez, M. Lino Da Silva, V. Guerra, and J. Loureiro. Coupled hydrodynamic/state-specific high-temperature modeling of nitrogen vibrational excitation and dissociation. In *44th AIAA Thermophysics Conference*, page 3149, 2013. doi: 10.2514/6.2013-3149. URL: <https://arc.aiaa.org/doi/abs/10.2514/6.2013-3149>.
- [26] F. Thivet, M. Perrin, and S. Candel. A unified nonequilibrium model for hypersonic flows. *Physics of Fluids A: Fluid Dynamics*, 3(11):2799–2812, 1991. doi: 10.1063/1.858168. URL: <https://doi.org/10.1063/1.858168>.

- [27] C. Park. Review of chemical-kinetic problems of future NASA missions. I-Earth entries. *Journal of Thermophysics and Heat transfer*, 7(3):385–398, 1993. doi: 10.2514/3.431. URL: <https://doi.org/10.2514/3.431>.
- [28] M. L. Da Silva, V. Guerra, and J. Loureiro. Two-temperature models for nitrogen dissociation. *Chemical Physics*, 342(1-3):275–287, 2007. doi: 10.1016/j.chemphys.2007.10.010. URL: <https://doi.org/10.1016/j.chemphys.2007.10.010>.
- [29] M. L. Da Silva, V. Guerra, and J. Loureiro. Two-temperature models for nitrogen dissociation. *Chemical Physics*, 342(1-3):275–287, 2007. doi: 10.1016/j.chemphys.2007.10.010. URL: <https://doi.org/10.1016/j.chemphys.2007.10.010>.
- [30] W. G. Vincenti and C. H. Kruger. *Introduction to Physical Gas Dynamics*. John Wiley and Sons, 1st edition, 1965.
- [31] R. N. Gupta, J. M. Yos, R. A. Thompson, and K.-P. Lee. A review of reaction rates and thermodynamic and transport properties for an 11-species Air model for chemical and thermal nonequilibrium calculations to 30,000 K. Tech. Rep. NASA-RP-1232, NASA, August 1990. URL: <https://ntrs.nasa.gov/search.jsp?R=19900017748>.
- [32] G. E. Palmer and M. J. Wright. Comparison of methods to compute high-temperature gas viscosity. *Journal of Thermophysics and Heat Transfer*, 17(2):232–239, 2003. doi: 10.2514/2.6756. URL: <https://doi.org/10.2514/2.6756>.
- [33] G. Palmer and M. Wright. A comparison of methods to compute high-temperature gas thermal conductivity. In *36th AIAA Thermophysics Conference*, page 3913, 2003. doi: 10.2514/6.2003-3913. URL: <https://arc.aiaa.org/doi/abs/10.2514/6.2003-3913>.
- [34] C. Wilke. A viscosity equation for gas mixtures. *The Journal of Chemical Physics*, 18(4):517–519, 1950. doi: 10.1063/1.1747673. URL: <https://doi.org/10.1063/1.1747673>.
- [35] F. G. Blottner, M. Johnson, and M. Ellis. Chemically reacting viscous flow program for multi-component gas mixtures. Tech. Rep. SC-RR-70-754, Sandia Labs., Albuquerque, N. Mex., 1971. URL: <https://doi.org/10.2172/4658539>.
- [36] J. M. Yos. Approximate equations for the viscosity and translational thermal conductivity of gas mixtures. Tech. Rep. AVSSD-0112-67-RM, Avco Corporation, Wilmington, Massachusetts, 1967.
- [37] D. Dias Loureiro. High-temperature modeling of transport properties in hypersonic flows. Master’s thesis, Instituto Superior Técnico, September 2018.
- [38] D. Bruno, C. Catalfamo, M. Capitelli, G. Colonna, O. De Pascale, P. Diomede, C. Gorse, A. Laricchiuta, S. Longo, D. Giordano, et al. Transport properties of high-temperature Jupiter atmosphere components. *Physics of Plasmas*, 17(11):112315, 2010. doi: 10.1063/1.3495980. URL: <https://doi.org/10.1063/1.3495980>.
- [39] D. Bruno, C. Catalfamo, M. Capitelli, G. Colonna, P. Diomede, C. Gorse, A. Laricchiuta, S. Longo, F. Pirani, et al. Transport properties of high-temperature Jupiter-atmosphere components. Tech. Rep. STR-256, European Space Agency, 2008.

- [40] I. A. Sokolova. Collision integrals for components of high-temperature hydrogen-helium mixture. *Teplofizika Vysokikh Temperatur*, 15:734–743, July 1977. URL: <http://mi.mathnet.ru/tvt7135>. Original document in Russian.
- [41] Y. B. Zel'Dovich and Y. P. Raizer. *Physics of Shock Waves and High-Temperature Hydrodynamic Phenomena*, volume 1. Academic Press, 1966.
- [42] M. F. Modest. *Radiative Heat Transfer*. Academic Press, 2nd edition, 2003. doi: 10.1016/B978-0-12-503163-9.X5000-0. URL: <https://doi.org/10.1016/B978-0-12-503163-9.X5000-0>.
- [43] H. R. Griem. *Principles of Plasma Spectroscopy*. Cambridge Monographs on Plasma Physics. Cambridge University Press, 1997. doi: 10.1017/CBO9780511524578. URL: <https://doi.org/10.1017/CBO9780511524578>.
- [44] M. Lino da Silva, B. Lopez, and S. Espinho. *SPARTAN 2.6 User's Manual*, May 2016.
- [45] B. Lopez and M. Lino Da Silva. SPARK: a Software Package for Aerodynamics, Radiation and Kinetics. In *46th AIAA Thermophysics Conference*, page 4025, June 2016. doi: 10.2514/6.2016-4025. URL: <https://doi.org/10.2514/6.2016-4025>.
- [46] M. Furudate. Nonequilibrium calculation of high-temperature radiating H₂-He flowfield. *Journal of Thermophysics and Heat Transfer*, 23(4):651–659, 2009. doi: 10.2514/1.43961. URL: <https://doi.org/10.2514/1.43961>.
- [47] B. J. McBride, M. J. Zehe, and S. Gordon. NASA Glenn coefficients for calculating thermodynamic properties of individual species. Tech. Rep. NASA/TP-2002-211556, NASA, 2002.
- [48] D. Pagano, A. Casavola, L. D. Pietanza, G. Colonna, D. Giordano, and M. Capitelli. Thermodynamic properties of high-temperature Jupiter-atmosphere components. *Journal of Thermophysics and Heat Transfer*, 22(3):434–441, 2008. doi: 10.2514/1.34583. URL: <https://doi.org/10.2514/1.34583>.
- [49] D. Pagano, A. Casavola, L. Pietanza, M. Capitelli, G. Colonna, D. Giordano, and L. Marraffa. Internal partition functions and thermodynamic properties of high-temperature Jupiter-atmosphere species from 50 K to 50,000 K. Tech. Rep. STR-257, ESA, 2009.
- [50] G. Palmer, D. Prabhu, and B. A. Cruden. Aeroheating uncertainties in Uranus and Saturn entries by the Monte Carlo method. *Journal of Spacecraft and Rockets*, 51(3):801–814, 2014. doi: 10.2514/1.A32768. URL: <https://doi.org/10.2514/1.A32768>.
- [51] R. Celiberto, M. Capitelli, G. Colonna, G. D'Ammando, F. Esposito, R. Janev, V. Laporta, A. Laricchiuta, L. Pietanza, M. Rutigliano, et al. Elementary processes and kinetic modeling for hydrogen and helium plasmas. *Atoms*, 5(2):18, May 2017. doi: 10.3390/atoms5020018.
- [52] G. Colonna, D. D'Ambrosio, G. D'Ammando, L. Pietanza, and M. Capitelli. Multi-temperature model derived from state-to-state kinetics for hypersonic entry in Jupiter atmosphere. In *AIP Conference Proceedings*, volume 1628, pages 1162–1167. AIP, 2014. doi: 10.1063/1.4902724. URL: <https://aip.scitation.org/doi/abs/10.1063/1.4902724>.
- [53] M. Capitelli, C. Gorse, S. Longo, and D. Giordano. Collision integrals of high-temperature air species. *Journal of Thermophysics and Heat Transfer*, 14(2):259–268, 2000. doi: 10.2514/2.6517. URL: <https://doi.org/10.2514/2.6517>.

- [54] D. Bruno, M. Capitelli, C. Catalfamo, R. Celiberto, G. Colonna, P. Diomede, D. Giordano, C. Gorse, A. Laricchiuta, S. Longo, D. Pagano, and F. Pirani. Transport properties of high-temperature Mars-atmosphere components. Tech. Rep. STR-256, European Space Agency, 2008.
- [55] M. Capitelli, D. Bruno, and A. Laricchiuta. *Fundamental Aspects of Plasma Chemical Physics: Transport*, volume 74 of *Springer Series on Atomic, Optical, and Plasma Physics*. Springer, 01 2013. ISBN 978-1-4419-8172-1. doi: 10.1007/978-1-4419-8172-1. URL: <https://doi.org/10.1007/978-1-4419-8172-1>.
- [56] M. J. Wright, D. Bose, G. E. Palmer, and E. Levin. Recommended collision integrals for transport property computations part 1: Air species. *AIAA Journal*, 43(12):2558–2564, 2005. doi: 10.2514/1.16713. URL: <https://doi.org/10.2514/1.16713>.
- [57] J. R. Stallcop, H. Partridge, and E. Levin. Collision integrals for the interaction of the ions of nitrogen and oxygen in a plasma at high temperatures and pressures. *Physics of Fluids B: Plasma Physics*, 4(2):386–391, 1992. doi: 10.1063/1.860288. URL: <https://doi.org/10.1063/1.860288>.
- [58] A. D’Angola, G. Colonna, C. Gorse, and M. Capitelli. Thermodynamic and transport properties in equilibrium air plasmas in a wide pressure and temperature range. *The European Physical Journal D*, 46(1):129–150, 2008. doi: 10.1140/epjd/e2007-00305-4. URL: <https://doi.org/10.1140/epjd/e2007-00305-4>.
- [59] M. Capitelli, D. Cappelletti, G. Colonna, C. Gorse, A. Laricchiuta, G. Liuti, S. Longo, and F. Pirani. On the possibility of using model potentials for collision integral calculations of interest for planetary atmospheres. *Chemical Physics*, 338(1):62–68, 2007. ISSN 0301-0104. doi: 10.1016/j.chemphys.2007.07.036. URL: <http://www.sciencedirect.com/science/article/pii/S0301010407003217>.
- [60] L. Biolsi Jr. Transport properties in the atmosphere of Jupiter. Tech. Rep. NASA-CR-158094, NASA, 1978.
- [61] L. Biolsi. Transport properties in the Jovian atmosphere. *Journal of Geophysical Research: Space Physics*, 83(A3):1125–1131, 1978. doi: 10.1029/JA083iA03p01125. URL: <https://agupubs.onlinelibrary.wiley.com/doi/abs/10.1029/JA083iA03p01125>.
- [62] B. McBride and S. Gordon. Computer program for calculation of complex chemical equilibrium compositions and applications II. Users manual and program description. Tech. Rep. NASA-RP-1311, NASA, 1996.
- [63] A. Kramida, Y. Ralchenko, J. Reader, and N. A. Team. NIST Atomic Spectra Database (version 5.5.6). <https://physics.nist.gov/asd>, 2018. Accessed: 2018-05-10.
- [64] C. O. Johnston. *Nonequilibrium shock-layer radiative heating for Earth and Titan entry*. PhD thesis, Virginia Tech, 2006.
- [65] H. Griem. *Spectral Line Broadening by Plasmas*. Elsevier, 1st edition, 2012. ISBN 978-0-12-302850-1. URL: <https://www.elsevier.com/books/spectral-line-broadening-by-plasmas/griem/978-0-12-302850-1>.
- [66] A. Döhrn, P. Nowack, A. Könies, S. Günter, and V. Helbig. Stark broadening and shift of the first two Paschen lines of hydrogen. *Physical Review E*, 53(6):6389, June 1996. doi: 10.1103/PhysRevE.53.6389. URL: <https://link.aps.org/doi/10.1103/PhysRevE.53.6389>.

- [67] T. Wujec, A. Jazgara, J. Halenka, and J. Musielok. Stark broadening of the hydrogen Paschen γ transition at electron densities of the order of cm. *The European Physical Journal D-Atomic, Molecular, Optical and Plasma Physics*, 23(3):405–408, 2003. doi: 10.1140/epjd/e2003-00084-x. URL: <https://link.springer.com/article/10.1140/epjd/e2003-00084-x>.
- [68] C. Stehlé and S. Fouquet. Hydrogen stark broadened Brackett lines. *International Journal of Spectroscopy*, 2010, 2009. doi: 10.1155/2010/506346. URL: <https://doi.org/10.1155/2010/506346>.
- [69] K. Pachucki and J. Komasa. Nonadiabatic corrections to rovibrational levels of H_2 . *The Journal of Chemical Physics*, 130(16):164113, 2009. doi: 10.1063/1.3114680. URL: <https://doi.org/10.1063/1.3114680>.
- [70] H. Abgrall, E. Roueff, F. Launay, J.-Y. Roncin, and J.-L. Subtil. The Lyman and Werner band systems of molecular hydrogen. *Journal of Molecular Spectroscopy*, 157(2):512–523, 1993. ISSN 0022-2852. doi: 10.1006/jmsp.1993.1040. URL: <http://www.sciencedirect.com/science/article/pii/S0022285283710404>.
- [71] K.-P. Huber and G. Herzberg. *Constants of Diatomic Molecules*. Van Nostrand Reinhold, New York, 1979. ISBN 978-1-4757-0963-6. doi: 10.1007/978-1-4757-0961-2. URL: <http://dx.doi.org/10.1007/978-1-4757-0961-2>.
- [72] U. Fantz and D. Wunderlich. Franck–Condon factors, transition probabilities and radiative lifetimes for hydrogen molecules and their isotopomers. Tech. Rep. INDC(NDS)-457, IAEA, 2004.
- [73] H. M. Crosswhite. *The hydrogen molecule wavelength tables of Gerhard Heinrich Dieke*. Wiley-Interscience, 1972.
- [74] D. Bailly, E. Salumbides, M. Vervloet, and W. Ubachs. Accurate level energies in the $EF^1\Sigma_g^+$, $GK^1\Sigma_g^+$, $H^1\Sigma_g^+$, $B^1\Sigma_u^+$, $C^1\Pi_u$, $B^1\Sigma_u^+$, $D^1\Pi_u$, $I^1\Pi_g$, $J^1\Delta_g$ states of H_2 . *Molecular physics*, 108(7-9):827–846, 2010. doi: 10.1080/00268970903413350. URL: <https://doi.org/10.1080/00268970903413350>.
- [75] TOPBase: Online Atomic Database. <http://cdsweb.u-strasbg.fr/topbase/topbase.html>, 2019. Accessed: 2019-03-10.
- [76] T. Ohmura and H. Ohmura. Electron-hydrogen scattering at low energies. *Physical Review*, 118(1):154–157, 1960. doi: 10.1103/PhysRev.118.154. URL: <https://doi.org/10.1103/PhysRev.118.154>.
- [77] A. M. Frolov. On the absorption of radiation by the negatively charged hydrogen ion. I. General theory and construction of the wave functions. *arXiv preprint arXiv:1110.3432*, 2011. URL: <https://arxiv.org/abs/1110.3432>.
- [78] C. Ramsbottom and K. Bell. Photodetachment cross sections for the $1s2s2p$ metastable state of the negative helium ion. *Journal of Physics B: Atomic, Molecular and Optical Physics*, 32(5):1315–1333, 1999. doi: 10.1088/0953-4075/32/5/021. URL: <https://doi.org/10.1088/0953-4075/32/5/021>.
- [79] J. A. R. Samson and G. N. Haddad. Total photoabsorption cross sections of H_2 from 18 to 113 eV. *J. Opt. Soc. Am. B*, 11(2):277–279, 1994. doi: 10.1364/JOSAB.11.000277. URL: <http://josab.osa.org/abstract.cfm?URI=josab-11-2-277>.
- [80] M. Yan, H. Sadeghpour, and A. Dalgarno. Photoionization cross sections of He and H_2 . *The Astrophysical Journal*, 496(2):1044–1050, 1998. doi: 10.1086/305420. URL: <https://doi.org/10.1086/305420>.

- [81] M. Yan, H. Sadeghpour, and A. Dalgarno. Erratum: Photoionization cross sections of He and H₂. *The Astrophysical Journal*, 559:1194, 2001. doi: 10.1086/322775. URL: <https://doi.org/10.1086%2F322775>.
- [82] W. F. Huebner and W. D. Barfield. *Opacity*. Astrophysics and Space Science Library. Springer, 2014. doi: 10.1007/978-1-4614-8797-5. URL: <https://doi.org/10.1007/978-1-4614-8797-5>.
- [83] A. Heays, A. Bosman, and E. van Dishoeck. Photodissociation and photoionisation of atoms and molecules of astrophysical interest. *Astronomy & Astrophysics*, 602:A105, 2017. doi: 10.1051/0004-6361/201628742. URL: <https://doi.org/10.1051/0004-6361/201628742>.
- [84] H. Abgrall, E. Roueff, and I. Drira. Total transition probability and spontaneous radiative dissociation of B, C, B' and D states of molecular hydrogen. *Astronomy and Astrophysics Supplement Series*, 141(2):297–300, 2000. doi: 10.1051/aas:2000121. URL: <https://doi.org/10.1051/aas:2000121>.
- [85] S. Geltman. Free-free radiation in electron-neutral atom collisions. *Journal of Quantitative Spectroscopy and Radiative Transfer*, 13(7):601–613, 1973. ISSN 0022-4073. doi: 10.1016/0022-4073(73)90019-8. URL: <http://www.sciencedirect.com/science/article/pii/0022407373900198>.
- [86] S. Chauveau. *Constitution de bases de données spectroscopiques relatives à un plasma d'air: application au calcul de transferts radiatifs*. PhD thesis, Châtenay-Malabry, Ecole centrale de Paris, 2001.
- [87] T. John. Neutral bremsstrahlung from molecular hydrogen and nitrogen. , 67:395–398, July 1978. URL: <http://articles.adsabs.harvard.edu/full/1978A%26A...67..395J>.
- [88] S. Matsuyama, Y. Shimogonya, N. Ohnishi, A. Sasoh, and K. Sawada. Multiband radiation model for simulation of Galileo probe entry flowfield. *Journal of thermophysics and heat transfer*, 20(3):611–614, 2006. doi: 10.2514/1.16432. URL: <https://doi.org/10.2514/1.16432>.
- [89] M. Perrin, G. Colonna, G. D’Ammando, L. Pietanza, P. Riviere, A. Soufani, and S. Surzhikov. Radiation models and radiation transfer in hypersonics. *The Open Plasma Physics Journal*, 7(1), 2014. doi: 10.2174/18765343014070101114. URL: <https://doi.org/10.2174/18765343014070101114>.
- [90] C. O. Johnston and A. Mazaheri. Impact of non-tangent-slab radiative transport on flowfield-radiation coupling. *Journal of Spacecraft and Rockets*, 55(4):899–913, 2018. doi: 10.2514/1.A34072. URL: <https://doi.org/10.2514/1.A34072>.
- [91] M. E. Tauber and R. M. Wakefield. Heating environment and protection during Jupiter entry. *Journal of Spacecraft and Rockets*, 8(6):630–636, 1971. doi: 10.2514/3.59703. URL: <https://doi.org/10.2514/3.59703>.
- [92] A. M. Brandis, B. A. Cruden, T. R. White, D. A. Saunders, and C. O. Johnston. Radiative heating on the after-body of Martian entry vehicles. In *45th AIAA Thermophysics Conference*, page 3111, 2015. doi: 10.2514/6.2015-3111. URL: <https://arc.aiaa.org/doi/abs/10.2514/6.2015-3111>.
- [93] C. O. Johnston and A. M. Brandis. Features of afterbody radiative heating for Earth entry. In *11th AIAA/ASME Joint Thermophysics and Heat Transfer Conference*, page 2675, 2014. doi: 10.2514/6.2014-2675. URL: <https://arc.aiaa.org/doi/abs/10.2514/6.2014-2675>.
- [94] C. O. Johnston. Influence of radiative absorption on non-Boltzmann modeling for Mars entry. *Journal of Thermophysics and Heat Transfer*, 28(4):795–799, 2014. doi: 10.2514/1.T4044. URL: <https://doi.org/10.2514/1.T4044>.

- [95] M. Lino da Silva. An adaptive line-by-line—statistical model for fast and accurate spectral simulations in low-pressure plasmas. *Journal of Quantitative Spectroscopy and Radiative Transfer*, 108(1):106–125, 2007. doi: 10.1016/j.jqsrt.2007.03.005. URL: <http://www.sciencedirect.com/science/article/pii/S0022407307001240>.
- [96] C. O. Johnston. Improved exponential integral approximation for tangent-slab radiation transport. *Journal of Thermophysics and Heat Transfer*, 24(3):659–661, 2010. doi: 10.2514/1.46197. URL: <https://doi.org/10.2514/1.46197>.
- [97] M. Lino Da Silva and J. Beck. Contribution of CO₂ IR radiation to Martian entries radiative wall fluxes. In *49th AIAA Aerospace Sciences Meeting including the New Horizons Forum and Aerospace Exposition*, page 135, January 2011. ISBN 978-1-60086-950-1. doi: 10.2514/6.2011-135. URL: <https://doi.org/10.2514/6.2011-135>.
- [98] Á. González. Measurement of areas on a sphere using Fibonacci and latitude–longitude lattices. *Mathematical Geosciences*, 42(1):49, 2010. doi: 10.1007/s11004-009-9257-x. URL: <https://doi.org/10.1007/s11004-009-9257-x>.
- [99] G. J. Elbert and P. Cinnella. Truly two-dimensional algorithms for radiative heat transfer calculations in reactive flows. *Computers & Fluids*, 24(5):523–552, June 1995. doi: 10.1016/0045-7930(95)00008-Z. URL: [https://doi.org/10.1016/0045-7930\(95\)00008-Z](https://doi.org/10.1016/0045-7930(95)00008-Z).
- [100] C. O. Johnston, P. A. Gnoffo, and A. Mazaheri. Influence of coupled radiation and ablation on the aerothermodynamic environment of planetary entry vehicles. In *Radiation and Gas-Surface Interaction Phenomena in High Speed Re-Entry*, May 2013. URL: <https://ntrs.nasa.gov/archive/nasa/casi.ntrs.nasa.gov/20130013722.pdf>.
- [101] M. L. Da Silva. *Simulation des propriétés radiatives du plasma entourant un véhicule traversant une atmosphère planétaire à vitesse hypersonique—application à la planète Mars*. PhD thesis, Université d’Orléans, 2004.
- [102] T. Furtenbacher, I. Szabó, A. G. Császár, P. F. Bernath, S. N. Yurchenko, and J. Tennyson. Experimental energy levels and partition function of the ¹²C₂ molecule. *The Astrophysical Journal Supplement Series*, 224(2):44, June 2016. doi: 10.3847/0067-0049/224/2/44. URL: <https://doi.org/10.3847/0067-0049/224/2/44>.
- [103] P. J. Bruna and F. Grein. Spectroscopy of the C₂ molecule: Valence and Rydberg states in the 7–10 eV region. An ab initio study. *Canadian Journal of Physics*, 79:653–671, February 2001. doi: 10.1139/p01-019. URL: <http://adsabs.harvard.edu/abs/2001CaJPh..79..653B>.
- [104] E. Mason, R. Munn, and F. J. Smith. Transport coefficients of ionized gases. *The Physics of fluids*, 10(8):1827–1832, 1967. doi: 10.1063/1.1762365. URL: <https://aip.scitation.org/doi/abs/10.1063/1.1762365>.

APPENDIX A

Thermodynamic Relations

This appendix provides the reader with some important results from statistical thermodynamics. A quick overview of the basic thermodynamic relations for a mixture of perfect gases is firstly given.

A.1 Definitions

Several variables can be used to define the composition of a given mixture of perfect gases. The three that are most commonly used are

- Number density: $N_s = \frac{n_s}{V}$ [particles m⁻³]
- Mass fraction: $c_s = \frac{M_s}{M}$
- Mole fraction: $x_s = \frac{\mathcal{N}_s}{\mathcal{N}}$,

where each variable is conveniently defined in Table A.1.

Variable	Name	Unit
Global	V Volume of mixture	m ³
	M Mass of mixture	kg
	$\mathcal{N}$ Number of moles of mixture	mol
Species	n_s Number of particles of species s	particles
	M_s Mass of species s	kg
	m_s Particle mass of species s	kg particle ⁻¹
	$\mathcal{N}_s$ Number of moles of species s	mol

Table A.1: List of global and species-specific composition variables commonly used to define the composition of a mixture.

Each of these variables obeys, respectively

$$\sum_s N_s = N \quad \sum_s c_s = 1 \quad \sum_s x_s = 1 , \tag{A.1}$$

where N is the global number density of the mixture. The number of particles and moles of a given species are related through Avogadro's constant N_A by

$$n_s = N_A \mathcal{N}_s , \quad (\text{A.2})$$

while the mass and number of moles of the same species are related through

$$\mathcal{M}_s = \frac{M_s}{\mathcal{N}_s} . \quad (\text{A.3})$$

Here, $\mathcal{M}_s$ is the molar mass for species s . Additionally, the mass density of species s and the global mass density for the mixture obey

$$\rho_s = N_s m_s \quad \text{and} \quad \rho = \sum_s \rho_s . \quad (\text{A.4})$$

Finally, the mixture's global molar mass $\mathcal{M}$ may be calculated through

$$\mathcal{M} = \sum_s x_s \mathcal{M}_s \quad \text{or} \quad \mathcal{M} = \sum_s \frac{1}{c_s / \mathcal{M}_s} , \quad \text{using} \quad c_s = x_s \left(\frac{\mathcal{M}_s}{\mathcal{M}} \right) . \quad (\text{A.5})$$

Dalton's Law of partial pressures relates the total pressure of the mixture to the partial pressure of each of its components through

$$p = \sum_s p_s . \quad (\text{A.6})$$

If each species is treated as an ideal gas, then each will behave according to an ideal gas law specific to that species, which can take several forms, namely

$$p_s V = M_s R_s T \quad \text{or} \quad p_s = \rho_s R_s T \quad \text{or} \quad p_s V = \mathcal{N}_s \mathcal{R} T , \quad (\text{A.7})$$

where R_s is the species' gas constant, related to the universal gas constant $\mathcal{R}$ and Boltzmann's constant k_B through

$$R_s = \frac{\mathcal{R}}{\mathcal{M}_s} = \frac{N_A k_B}{\mathcal{M}_s} . \quad (\text{A.8})$$

Furthermore, a global specific gas constant for the mixture can also be defined using

$$R = \sum_s c_s R_s . \quad (\text{A.9})$$

A.2 Internal Energy, Enthalpy and Specific Heats

The internal energy of the mixture of perfect gases is easily calculated from the internal energies of each of its components using the corresponding mass fractions, that is

$$e = \sum_s c_s e_s . \quad (\text{A.10})$$

As explained in § 2.1.2, several energy modes contribute to a species' internal energy. Thus, the internal energy contributions are separated according to Eq. 2.4, repeated here for convenience

$$e_s = e_{\text{tr},s} + e_{\text{rot},s} + e_{\text{vib},s} + e_{\text{exc},s} + e_{0,s} . \quad (\text{A.11})$$

Up until this point, only results from classical thermodynamics have been used. No explicit expressions would exist for each of these contributions if not for statistical thermodynamics, which uses a microscopic description of the gas. For a collection of quantum microstates in thermal equilibrium, the internal energy of a gas with specific gas constant R can be expressed in the context of statistical thermodynamics as

$$e = RT^2 \left(\frac{\partial \ln Q}{\partial T} \right)_v , \quad (\text{A.12})$$

where Q is the important partition function, defined as

$$Q = \sum_j g_j e^{-\varepsilon_j / k_B T} . \quad (\text{A.13})$$

In Eq. A.13, g_j represents the number of degenerate states of energy level j . Quantum mechanics shows that quantization also extends to molecular orientation. Consequently, a given energy level can result from different molecular orientations, leading to different quantum states. The number of states that coexist within a given energy level is called the degeneracy of that level.

Within the Born-Oppenheimer approximation of the separability of the internal energy modes¹, the total partition function may be decomposed into

$$\begin{aligned} Q &= \sum_i \sum_j \sum_n \sum_l g_i g_j g_n g_l \exp \left[-\frac{1}{k_B T} (\varepsilon_{i_{\text{tr}}} + \varepsilon_{j_{\text{rot}}} + \varepsilon_{n_{\text{vib}}} + \varepsilon_{l_{\text{exc}}}) \right] \\ &= \left[\sum_i g_i \exp \left(-\frac{\varepsilon_{i_{\text{tr}}}}{k_B T} \right) \right] \left[\sum_j g_j \exp \left(-\frac{\varepsilon_{j_{\text{rot}}}}{k_B T} \right) \right] \\ &\quad \times \left[\sum_n g_n \exp \left(-\frac{\varepsilon_{n_{\text{vib}}}}{k_B T} \right) \right] \left[\sum_l g_l \exp \left(-\frac{\varepsilon_{l_{\text{exc}}}}{k_B T} \right) \right] = Q_{\text{tr}} Q_{\text{rot}} Q_{\text{vib}} Q_{\text{exc}} . \end{aligned} \quad (\text{A.14})$$

Thus, the separation of the modes allows the total partition function to be factorized into its modal contributions, which enables the use of separate temperatures for each modal partition function when thermal non-equilibrium is considered. Each contribution depends on the corresponding mode's energy levels, which result from solving the appropriate Schrödinger equation.

For a single-species gas, the internal energy contributions that result from Eq. A.12 are given by²:

$$e_{\text{tr},s} = \frac{3}{2} R_s T \quad (\text{A.15a})$$

$$e_{\text{rot},s} = R_s T \quad (\text{A.15b})$$

¹Namely, the rotational, vibrational and electronic modes.

²The equations presented for the rotational and vibrational contributions assume a diatomic molecule modeled by a rigid dumbbell harmonic oscillator.

$$e_{\text{vib},s} = \frac{\frac{h\nu_s}{k_B T}}{\exp\left(\frac{h\nu_s}{k_B T}\right) - 1} R_s T \quad (\text{A.15c})$$

$$e_{\text{exc},s} = R_s T^2 \frac{\partial}{\partial T} \left\{ \ln \left[\sum_l g_{l,s} \exp\left(-\frac{\varepsilon_{l_{\text{exc}},s}}{k_B T}\right) \right] \right\}, \quad (\text{A.15d})$$

where h denotes Planck's constant and ν_s is the fundamental vibration frequency of the molecule. The electronic excitation contribution cannot be described by a simple explicit expression, having to rely on a sum over all achievable energy levels before ionization³.

The usual thermodynamic relation between internal energy and enthalpy may now be employed. The enthalpy of the mixture is simply

$$h = \sum_s c_s h_s, \quad \text{with} \quad h_s = e_s + \frac{p_s}{\rho_s} = e_s + R_s T. \quad (\text{A.16})$$

As a result, the enthalpy for a given species may be alternatively calculated as the sum of the contributions from different thermal modes, that is

$$h_s = h_{\text{tr},s} + h_{\text{rot},s} + h_{\text{vib},s} + h_{\text{exc},s} + (\Delta h_f)_s^\circ, \quad (\text{A.17})$$

where the formation enthalpy for the species $(\Delta h_f)_s^\circ$ was introduced. Each contribution can be computed using

$$h_{\text{tr},s} = e_{\text{tr},s} + R_s T, \quad h_{\text{rot},s} = e_{\text{rot},s}, \quad h_{\text{vib},s} = e_{\text{vib},s}, \quad h_{\text{exc},s} = e_{\text{exc},s}. \quad (\text{A.18})$$

The translational component is the only retaining the term $R_s T$ since it is the translational motion of the particles the one responsible for the existence of a pressure force.

Finally, the specific heats are defined by

$$C_v = \left(\frac{\partial e}{\partial T} \right)_v, \quad C_p = \left(\frac{\partial h}{\partial T} \right)_p. \quad (\text{A.19})$$

The specific heat equations provide an explanation to the loss of significance of the Mach number in hypersonic chemically reacting flows. Replacing the mixture's internal energy and enthalpy in terms of its components in these equations, they become,

$$C_v = \sum_s \left[e_s \frac{\partial c_s}{\partial T} + c_s \frac{\partial e_s}{\partial T} \right] = C_v^r + C_v^f \quad (\text{A.20a})$$

$$C_p = \sum_s \left[h_s \frac{\partial c_s}{\partial T} + c_s \frac{\partial h_s}{\partial T} \right] = C_p^r + C_p^f, \quad (\text{A.20b})$$

that is, they can be decomposed in a frozen and a reactive component. In chemically frozen flows, as is commonly the case for flight regimes where $\text{Ma} < 5$, the reactive terms are negligible. In reacting flows, on the other hand, these vary as the mixture's composition changes, and, in turn, will significantly alter

³In practice, a finite number of energy levels is used considering the magnitude of the corresponding contributions.

the specific heat ratio γ . Despite the fact that the sound speed does not have an explicit closed-form expression in chemically reacting flows, γ still enters the calculation. Hence, one may deduce that the sound speed in a chemically reacting flow depends largely on the mixture under consideration, whose composition varies with temperature, thus limiting the usefulness of the Mach number for this flight regime.

Thermal Non-Equilibrium

When thermal non-equilibrium is considered and a multi-temperature model is employed, it is necessary to separately define the contributions from different thermal energy modes to the internal energy and enthalpy, since these explicitly appear in the additional non-equilibrium energy equation (Eq. 2.1e). This is done in a straightforward manner by evaluating Eqs. A.15 using the corresponding temperature, that is

$$e_{\text{tr},s} = \frac{3}{2} R_s T_{\text{tr},s} \quad (\text{A.21a})$$

$$e_{\text{rot},s} = R_s T_{\text{rot},s} \quad (\text{A.21b})$$

$$e_{\text{vib},s} = \frac{\frac{h\nu_s}{k_B T_{\text{vib},s}}}{\exp\left(\frac{h\nu_s}{k_B T_{\text{vib},s}}\right) - 1} R_s T_{\text{vib},s} \quad (\text{A.21c})$$

$$e_{\text{exc},s} = R_s T_{\text{exc},s}^2 \frac{\partial}{\partial T_{\text{exc},s}} \left\{ \ln \left[\sum_l g_{l,s} \exp\left(-\frac{\varepsilon_{l,\text{exc},s}}{k_B T_{\text{exc},s}}\right) \right] \right\}. \quad (\text{A.21d})$$

Furthermore, relations A.16 - A.20 still apply, provided the correct temperature is used for each thermal mode contribution.

On a more curious note, if a low temperature gas is considered (for which the reactive contribution to the specific heats is zero and whose vibrational and electronic contributions to the internal energy are negligible), one may see from Eqs. A.19 and A.21a - A.21b that

$$C_{v_{\text{tr},s}} = \frac{3}{2} R_s \quad , \text{ and } \quad C_{p_{\text{tr},s}} = \frac{5}{2} R_s \quad (\text{A.22})$$

$$C_{v_{\text{rot},s}} = R_s \quad , \text{ and } \quad C_{p_{\text{rot},s}} = R_s. \quad (\text{A.23})$$

Under such conditions, both C_v and C_p are constant, and the specific heat ratio γ will assume the value $\gamma = C_p/C_v = \frac{7}{5} = 1.4$, which is the usual value employed in compressible thermodynamics for a calorically perfect diatomic gas. At low temperatures, the vibrational and electronic thermal modes cannot store a significant amount of energy because no energy is available to excite them, whereas the translational and rotational modes are already fully excited at room temperature, meaning they cannot possibly store any more energy.

APPENDIX B

Charged-Species CCSs

The 10 charged-species collision cross-section interactions used throughout this work follow the approach employed by Wright *et al.* [56]. Mason *et al.* have shown that under most circumstances these interactions may be accurately represented using an attractive or repulsive shielded Coulomb potential [104]. The classical transport collision integrals that result from the integration of this potential are only a function of the dimensionless reduced temperature, given by

$$T^* = \frac{\lambda_D}{e^2/k_B T_c} , \quad (\text{B.1})$$

where T_c is the controlling temperature, e is the elementary charge and λ_D is the Debye shielding length, defined as

$$\lambda_D = \sqrt{\frac{k_B T_c}{4\pi e^2 N_{e^-}}} . \quad (\text{B.2})$$

Using this approach, all charged-species CCSs are determined from the corresponding interaction type, namely, repulsive (ion-ion and electron-electron) or attractive (ion-electron). Wright *et al.* have taken the tabulated results from Mason and provided curve-fits for $\sigma^2\Omega_{s,l}^{(1,1)*}$ and $\sigma^2\Omega_{s,l}^{(2,2)*}$ under the form

$$\sigma^2\Omega_{s,l}^{(m,m)*} = 5.0 \times 10^{15} \left(\frac{\lambda_D}{T^*} \right) \ln \left\{ D_m T^* \left[1 - C_m e^{-c_m T^*} \right] + 1 \right\} , \quad (\text{B.3})$$

for which coefficients D_m , C_m and c_m are provided in Table B.1 for both repulsive and attractive interactions. Regarding higher-order CCSs, required for the 2nd Order Gupta/Yos transport model, the ratio B^* is instead given according to

$$B^* = a + b \exp \left(\left| \frac{\ln T^*}{c} \right| \right) , \quad (\text{B.4})$$

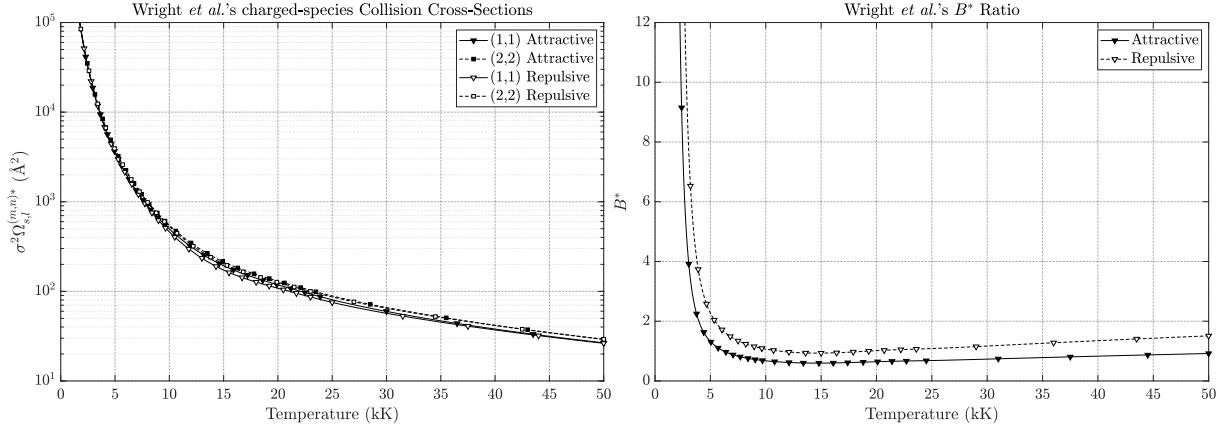
where the coefficients a , b and c are again available in Table B.1.

The resulting collision cross-sections are presented in Figure B.1. On the left, the CCS terms $\sigma^2\Omega_{s,l}^{(1,1)*}$ and $\sigma^2\Omega_{s,l}^{(2,2)*}$ for attractive and repulsive interactions are compared. Note the logarithmic scale, indicating these collision cross-sections tend to be several orders of magnitude higher than those involving neutral species, as seen in § 3.4.2. The variation of the collision term ratio B^* with temperature is illustrated on the right. While the repulsive ratio tends to stay relatively close to 1 throughout a significant

Table B.1: Wright's *et al* collision cross-section coefficients for charged-species interactions [56].

Collision Term	Attractive Potential			Repulsive Potential		
	D_m	C_m	c_n	D_m	C_m	c_n
$\sigma^2 \Omega_{s,l}^{(1,1)*}$	0.7840	-0.4760	0.0313	0.7650	0.1380	0.0106
$\sigma^2 \Omega_{s,l}^{(2,2)*}$	1.2620	-0.1460	0.0377	1.2350	0.1570	0.0274
Ratio	a	b	c	a	b	c
B^*	1.0355	0.2864	-4.4229	1.0322	0.4116	-3.1829

temperature range (between 7,500 K and 30,000 K), the attractive ratio is closer to 0.6 in the same interval. Additionally, both ratios tend to significantly higher values at low temperatures, although they have no effect on the overall transport properties since charged-species are generally negligible for these temperature ranges, when starting from a neutral mixture.



(a) Wright *et al.*'s charged-species collision cross-sections.

(b) Wright *et al.*'s charged-species B^* ratio.

Figure B.1: CCS terms calculated using Wright *et al.*'s curve-fits for attractive and repulsive interactions [56].

Tangent Slab Approximation

The mathematical formulation of the tangent-slab approximation is derived in this appendix. Although not implemented in the present work, the radiative source term is presented in the context of this approximation, so as to provide a future reference for the implementation of a loosely-coupled routine connecting SPARK and SPARK LbL.

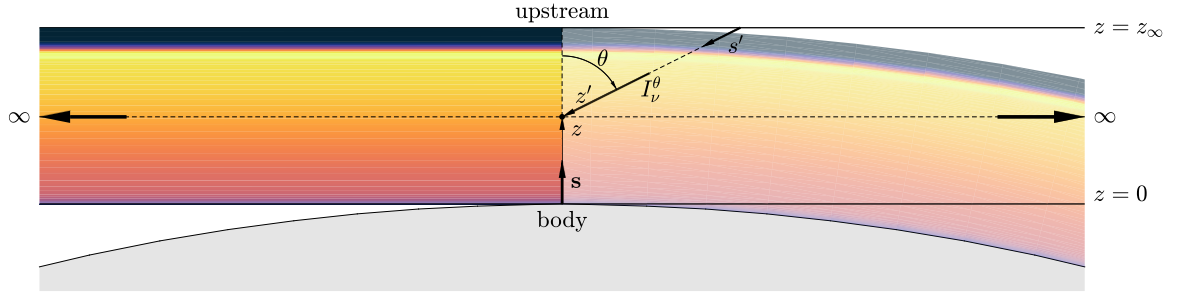


Figure C.1: Tangent-slab approximation: the 2D flowfield profile (right) is approximated at a point by transferring the variation along the normal to that point into a slab tangent to the wall extending to infinity (left).

Figure C.1 is repeated here for convenience. To begin with, Eq. 2.62 may be rewritten for a ray $I_\nu^{\theta, \phi}$ as

$$I_\nu(z', \theta) = I_\nu(z' = 0, \theta) e^{-\tau'_\nu(0, z')} + \int_0^{z'} j_\nu(s', \theta) e^{-\tau'_\nu(s', z')} ds', \quad (\text{C.1})$$

where the notation $\tau_\nu(s, z) = \tau_\nu(z) - \tau_\nu(s)$ was introduced. From Figure C.1, it is clear that $z' = (z_\infty - z) / \cos \theta$, where z is measured normal to the wall, along the direction $\mathbf{s}$. Let s express a distance measured along $\mathbf{s}$ such that $0 < s < z$, while s' denotes an equivalent distance measured along $\mathbf{s}'$ such that $0 < s' < z'$ (note that 0 here corresponds to a location on the upstream boundary and z' to the location defined by the horizontal dashed line in Figure C.1). Introducing this notation along with the change of variables in Eq. C.1, and noting the relations

$$\tau'_\nu(0, z') = \frac{1}{\cos \theta} \int_z^{z_\infty} \kappa_\nu ds = \frac{\tau_\nu(z, z_\infty)}{\cos \theta}, \quad (\text{C.2})$$

and

$$\tau'_\nu(s', z') = \frac{1}{\cos \theta} \int_z^s \kappa_\nu dt = \frac{\tau_\nu(z, s)}{\cos \theta}, \quad (\text{C.3})$$

it is possible to express the spectral radiative intensity at a distance z normal to the body and in the direction θ by¹:

$$I_\nu^-(z, \theta) = \frac{1}{\cos \theta} \int_z^{z_\infty} j_\nu e^{-\frac{\tau_\nu(z, s)}{\cos \theta}} ds, \quad \text{if } 0 \leq \theta < \frac{\pi}{2} \quad (\text{C.4a})$$

$$I_\nu^+(z, \theta) = I_{\nu, b}^+ e^{-\frac{\tau_\nu(0, z)}{\cos(\pi - \theta)}} + \frac{1}{\cos(\pi - \theta)} \int_0^z j_\nu e^{-\frac{\tau_\nu(s, z)}{\cos(\pi - \theta)}} ds, \quad \text{if } \frac{\pi}{2} \leq \theta \leq \pi. \quad (\text{C.4b})$$

It should be mentioned that the wall-directed spectral radiative intensity at the upstream boundary $I_\nu^-(z_\infty)$ is considered to be zero due to the presence of low-temperature gases. Also, $I_{\nu, b}^+$ represents the upstream-directed spectral radiative intensity at the body wall, usually approximated by Planck's Law using an emissivity ε_{wall} lower than unity. This term was not considered in the present work.

As noted in § 3.6, the benefit of this seemingly difficult treatment is that the directional integrations required to obtain both the radiative source term and the radiative heating contribution may be carried out analytically, thus lightening the computational loads of the model. The wall-directed spectral radiative energy flux is obtained by substituting Eq. C.4a in Eq. 2.56 with the corrected hemispherical integration limits, resulting in

$$\begin{aligned} q_\nu^-(z) &= \int_0^{2\pi} \int_0^{\frac{\pi}{2}} \int_z^{z_\infty} j_\nu e^{-\frac{\tau_\nu(z, s)}{\cos \theta}} ds \sin \theta d\theta d\phi \\ &= -2\pi \int_1^0 \int_z^{z_\infty} j_\nu e^{-\frac{\tau_\nu(z, s)}{\mu}} ds d\mu \\ &= 2\pi \int_z^{z_\infty} j_\nu \int_0^1 e^{-\frac{\tau_\nu(z, s)}{\mu}} d\mu ds \\ &= 2\pi \int_z^{z_\infty} j_\nu \mathcal{E}_2[\tau_\nu(z, s)] ds, \end{aligned} \quad (\text{C.5})$$

where a change of variable $\mu = \cos \theta \implies d\mu = -\sin \theta d\theta$ was introduced. Note that evaluation of Eq. C.5 at $z = 0$, followed by integration over the frequency spectrum, results in the tangent-slab prediction for the radiative heating. Also, the exponential integral of order n is defined by

$$\mathcal{E}_n(x) = \int_0^1 e^{-\frac{x}{\mu}} \mu^{n-2} d\mu \quad (\text{C.6})$$

and satisfies the relations $\mathcal{E}_n(0) = \frac{1}{n-1}$ and $\mathcal{E}'_n(x) = -\mathcal{E}_{n-1}(x)$. A similar development can be made for the radiative source term. The spectral radiative source term is obtained from Eq. 2.63 as

$$-(\nabla \cdot \mathbf{q}_{\text{rad}})_\nu = \int_{4\pi} \kappa_\nu I_\nu^{\theta, \phi} d\Omega - 4\pi j_\nu. \quad (\text{C.7})$$

¹For $\frac{\pi}{2} \leq \theta \leq \pi$ the previous relation between z' and z must be replaced by $z' = z / \cos(\pi - \theta)$.

Substituting Eqs. C.4a and C.4b in Eq. C.7 and carrying out the integration in ϕ results in

$$-(\nabla \cdot \mathbf{q}_{\text{rad}})_{\nu} = \underbrace{2\pi \int_0^{\frac{\pi}{2}} \kappa_{\nu} I_{\nu}^{-}(z, \theta) \sin \theta \, d\theta}_{(1)} + \underbrace{2\pi \int_{\frac{\pi}{2}}^{\pi} \kappa_{\nu} I_{\nu}^{+}(z, \theta) \sin \theta \, d\theta}_{(2)} - 4\pi j_{\nu}. \quad (\text{C.8})$$

Treating each term separately, and once again making use of the change of variables $\mu = \cos \theta \implies d\mu = -\sin \theta \, d\theta$, term (1) results in

$$\begin{aligned} (1) &= 2\pi \kappa_{\nu} \int_0^{\frac{\pi}{2}} \frac{1}{\cos \theta} \int_z^{z_{\infty}} j_{\nu} e^{-\frac{\tau_{\nu}(z,s)}{\cos \theta}} \, ds \sin \theta \, d\theta \\ &= -2\pi \kappa_{\nu} \int_z^{z_{\infty}} j_{\nu} \int_1^0 \frac{1}{\mu} e^{-\frac{\tau_{\nu}(z,s)}{\mu}} \, d\mu \, ds \\ &= 2\pi \kappa_{\nu} \int_z^{z_{\infty}} j_{\nu} \mathcal{E}_1[\tau_{\nu}(z, s)] \, ds, \end{aligned} \quad (\text{C.9})$$

while term (2) ends up being²

$$\begin{aligned} (2) &= 2\pi \kappa_{\nu} \int_{\frac{\pi}{2}}^{\pi} \left[I_{\nu,b}^{+} e^{-\frac{\tau_{\nu}(0,z)}{\cos(\pi-\theta)}} + \frac{1}{\cos(\pi-\theta)} \int_0^z j_{\nu} e^{-\frac{\tau_{\nu}(s,z)}{\cos(\pi-\theta)}} \, ds \right] \sin \theta \, d\theta \\ &= -2\pi \kappa_{\nu} I_{\nu,b}^{+} \int_0^{-1} e^{\frac{\tau_{\nu}(0,z)}{\mu'}} \, d\mu' + 2\pi \kappa_{\nu} \int_0^z j_{\nu} \int_0^{-1} \frac{1}{\mu'} e^{\frac{\tau_{\nu}(s,z)}{\mu'}} \, d\mu' \, ds \\ &= 2\pi \kappa_{\nu} I_{\nu,b}^{+} \int_0^1 e^{-\frac{\tau_{\nu}(0,z)}{\mu}} \, d\mu + 2\pi \kappa_{\nu} \int_0^z j_{\nu} \int_0^1 \frac{1}{\mu} e^{-\frac{\tau_{\nu}(s,z)}{\mu}} \, d\mu \, ds \\ &= 2\pi \kappa_{\nu} \left\{ I_{\nu,b}^{+} \mathcal{E}_2[\tau_{\nu}(0, z)] + \int_0^z j_{\nu} \mathcal{E}_1[\tau_{\nu}(s, z)] \, ds \right\}. \end{aligned} \quad (\text{C.10})$$

Finally, making use of the fact that $\mathcal{E}_1(\tau_{\nu}) = -\mathcal{E}_2'(\tau_{\nu})$, and grouping Eqs. C.9 and C.10 into Eq. C.8, the spectral radiative source term is written as

$$\begin{aligned} -(\nabla \cdot \mathbf{q}_{\text{rad}})_{\nu} &= -4\pi j_{\nu}(z) - 2\pi \kappa_{\nu} \left\{ \int_0^z j_{\nu}(z) \frac{d\mathcal{E}_2[\tau_{\nu}(s, z)]}{d\tau_{\nu}} \, ds \right. \\ &\quad \left. + \int_z^{z_{\infty}} j_{\nu}(z) \frac{d\mathcal{E}_2[\tau_{\nu}(z, s)]}{d\tau_{\nu}} \, ds - I_{\nu,b}^{+} \mathcal{E}_2(\tau_{\nu}(0, z)) \right\}. \end{aligned} \quad (\text{C.11})$$

An alternative means for computing the radiative source term is described in [90] as the approach implemented within the coupled LAURA/HARA code framework at NASA, and results from the fact that in the tangent-slab approach the radiative heat flux only varies in the direction normal to the wall. The divergence can thus be expressed as

$$-(\nabla \cdot \mathbf{q}_{\text{rad}})_{\nu} = -\frac{d(q_{\nu}^{+} + q_{\nu}^{-})}{dz}, \quad (\text{C.12})$$

²Here a second change of variables $\mu' = -\mu \implies d\mu' = -d\mu$ was necessary due to the term $\cos(\pi - \theta) = -\cos \theta$.

where the upstream-directed radiative flux q_ν^+ can be obtained similarly as

$$q_\nu^+(z) = 2\pi I_{\nu,b}^+ \mathcal{E}_3[\tau_\nu(0, z)] - 2\pi \int_0^z j_\nu \mathcal{E}_2[\tau_\nu(s, z)] \, ds . \quad (\text{C.13})$$

APPENDIX D

Ray-Tracing Linear Interpolation

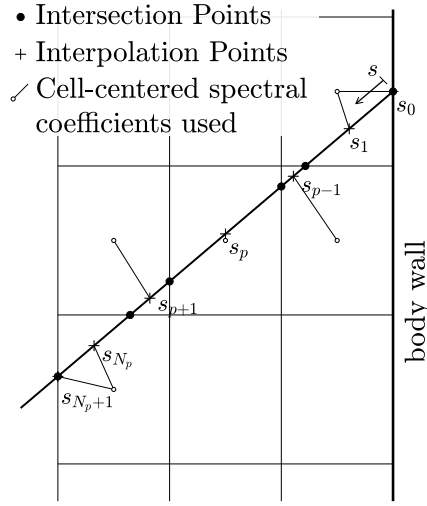


Figure D.1: Ray subdivision employed in the linear interpolation approach.

Figure 3.18b (repeated here for convenience) shows the reference frame employed in this derivation along with the discretized computational domain. By changing the coordinate frame in which Eq. 2.62 is expressed (from one starting at the upstream boundary following the ray's direction towards the wall, to a wall-centered reference frame with opposing direction, as illustrated in Figure D.1), the solution to the radiative transfer equation may be re-written as

$$I_{\bar{\nu}}^{\theta, \phi}(s_0) = I_{\bar{\nu}}^{\theta, \phi}(s_{\max}) e^{-\tau_{\bar{\nu}}(s_{\max})} + \int_{s_0}^{s_{\max}} j_{\bar{\nu}}(s') e^{-\tau_{\bar{\nu}}(s')} ds' . \quad (\text{D.1})$$

Within this approach, the final term in Eq. D.1 may be computed segment-by-segment through the sum

$$\int_{s_0}^{s_{\max}} j_{\bar{\nu}}(s') e^{-\tau_{\bar{\nu}}(s')} ds' = \sum_{p=0}^{p_{\max}-1} \int_{s_p}^{s_{p+1}} j_{\bar{\nu}}(s') e^{-\tau_{\bar{\nu}}(s')} ds' . \quad (\text{D.2})$$

As mentioned in § 3.6, the linear approach assumes a linear variation between nodes for the emission coefficient, that is

$$j_{\bar{\nu}}(s) = a_p s + b_p , \quad s_p \leq s \leq s_{p+1} , \quad (\text{D.3})$$

where the coefficients a_p and b_p are

$$a_p = \frac{j_{(p+1),\bar{\nu}} - j_{p,\bar{\nu}}}{s_{(p+1)} - s_p} \quad \text{and} \quad b_p = j_{p,\bar{\nu}} - \frac{j_{(p+1),\bar{\nu}} - j_{p,\bar{\nu}}}{s_{(p+1)} - s_p} s_p .$$

The emission coefficient at a certain intersected cell p will take on the value defined at the cell-center given by the indices (i, j) , namely $j_{\bar{\nu}}^{(i,j)}$. Since the absorption coefficient is considered constant along a given cell, this allows the optical thickness up to a node s_p to be expressed as the sum

$$\tau_{\bar{\nu}}(s_p) = \sum_{k=0}^{p-1} \kappa_{\bar{\nu},k} (s_{k+1} - s_k) , \quad (\text{D.4})$$

where, again, $\kappa_{\bar{\nu},k}$ is assigned the value at the corresponding intersected cell-center $\kappa_{\bar{\nu}}^{(i,j)}$. Additionally, the optical thickness itself is assumed to vary linearly across nodes in Eq. D.2 as

$$\tau_{\bar{\nu}}(s) = c_p s + d_p , \quad s_p \leq s \leq s_{p+1} , \quad (\text{D.5})$$

using $c_p = \kappa_{\bar{\nu}}^p$. The coefficient d_p can be defined using Eqs. D.4 and D.5, but does not need to be used. Substituting these expressions in Eq. D.2 leads to

$$\begin{aligned} & \sum_{p=0}^{p_{\max}-1} \int_{s_p}^{s_{p+1}} j_{\bar{\nu}}(s') e^{-\tau_{\bar{\nu}}(s')} ds' \\ &= \sum_{p=0}^{p_{\max}-1} \int_{s_p}^{s_{p+1}} (a_p s' + b_p) e^{-(c_p s' + d_p)} ds' \\ &= \sum_{p=0}^{p_{\max}-1} \left\{ \int_{s_p}^{s_{p+1}} a_p s' e^{-(c_p s' + d_p)} ds' + \int_{s_p}^{s_{p+1}} b_p e^{-(c_p s' + d_p)} ds' \right\} \\ &= \sum_{p=0}^{p_{\max}-1} \left\{ a_p e^{-d_p} \left[e^{-c_p s'} \left(\frac{-c_p s' - 1}{c_p^2} \right) \right]_{s_p}^{s_{p+1}} + b_p e^{-d_p} \left[-\frac{1}{c_p} e^{-c_p s'} \right]_{s_p}^{s_{p+1}} \right\} \\ &= \sum_{p=0}^{p_{\max}-1} \left\{ \frac{a_p}{c_p^2} [(c_p s_p + 1) e^{-c_p s_p} - (c_p s_{p+1} + 1) e^{-c_p s_{p+1}}] + \frac{b_p}{c_p} [e^{-c_p s_p} - e^{-c_p s_{p+1}}] \right\} e^{-d_p} \\ &= \sum_{p=0}^{p_{\max}-1} \left\{ \frac{a_p}{c_p^2} [(c_p s_p + 1) e^{-\tau_{\bar{\nu}}(s_p)} - (c_p s_{p+1} + 1) e^{-\tau_{\bar{\nu}}(s_{p+1})}] + \frac{b_p}{c_p} [e^{-\tau_{\bar{\nu}}(s_p)} - e^{-\tau_{\bar{\nu}}(s_{p+1})}] \right\} . \quad (\text{D.6}) \end{aligned}$$

Evaluating this sum for a given ray will result in its radiative intensity at the wall point under consideration, since the first term in Eq. D.1 is zero in the present work.