Development of an open-source thermochemical code

Fundamentals and application to shock turbulence interaction problems in the hypersonic regime

Alberto Cuadra [a] , César Huete, & Marcos Vera
[a] acuadra@ing.uc3m.es

Grupo de Mecánica de Fluidos, Universidad Carlos III de Madrid

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Part I

Combustion Toolbox: A MATLAB-GUI based open-source tool for solving gaseous combustion problems

Motivation I

- Thermochemical codes have been a research field since 1960's.
- Applications to many common combustion systems:
  - TP: tail pipe of a car.
  - HP: combustion chamber.
  - SP: expansion through a nozzle.
  - HP and SP: rocket engines.
- Standard thermochemical codes:
  - NASA's CEA (U.S. release only).
  - CANTERA (steep learning curve - new users).

Objectives:

- Encapsulate the thermochemical code in a user-friendly GUI.
- Perform shock calculations at high temperatures (ideal plasmas).

Chemical equilibrium

State in which the concentrations of reactants and products do not have a tendency to change with time.

At constant temperature and pressure:

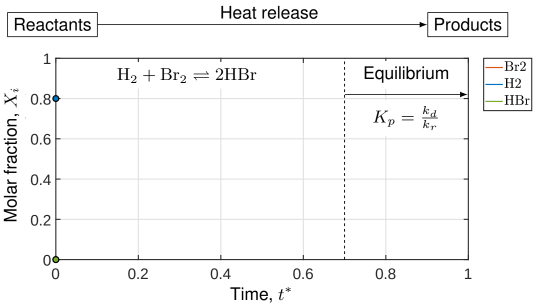
$$dg(T,p,\boldsymbol{n}) = \sum_{j=1}^{\mathrm{NS}} \mu_j(T,p)\,dn_j = 0,$$

with μ_j the chemical potential of the jth species, namely

$$\mu_j = \left(\frac{\partial g}{\partial n_j}\right)_{T,p,n_{k\neq j}}.$$

For ideal gases, this is the Gibbs free energy of the individual species (do not interact in a mixture).

- Extensive databases of thermochemical properties are required, e.g., NASA's database.



We have also a set of restrictions given by the mass balance:

$$h_i = \sum_{j=1}^{\mathrm{NS}} \underbrace{a_{ij} n_j}_{b_i} - b_i^\circ = 0 \quad \text{for } i = 1, \ldots, \text{NE}.$$

$$\underbrace{\begin{pmatrix} 0 & 2 & 1 \\ 2 & 0 & 1 \end{pmatrix}}_{A^T} \underbrace{\begin{pmatrix} n_{\mathrm{H}_2} \\ n_{\mathrm{Br}_2} \\ n_{\mathrm{HBr}} \end{pmatrix}}_{\boldsymbol{n}} - \underbrace{\begin{pmatrix} b_{\mathrm{Br}}^\circ \\ b_{\mathrm{H}}^\circ \end{pmatrix}}_{\boldsymbol{b}^\circ} = 0.$$

Chemical equilibrium

Constrained minimization with only equality constraints. Lagrange multipliers.

$$G(T,p,\boldsymbol{n},\boldsymbol{\lambda}) = g(T,p,\boldsymbol{n}) \pm \boldsymbol{\lambda}\left(h(T,p,\boldsymbol{n}) - C\right),$$

$$\nabla g(T,p,\boldsymbol{n}) = -\boldsymbol{\lambda}\nabla h(T,p,\boldsymbol{n}),$$

$$dG(T,p,\boldsymbol{n},\boldsymbol{\lambda}) = 0.$$

Many of the equations are not linear ⟶ Newton-Raphson method (NS + NE + 1 equations)

$$\Delta \ln n_j + \sum_{i=1}^{\text{NE}} a_{ij}\frac{\lambda_i}{RT} - \Delta \ln n = -\frac{\mu_j}{RT} \quad (j = 1,\dots,\text{NG}),$$

$$\sum_{i=1}^{\text{NE}} a_{ij}\frac{\lambda_i}{RT} = -\frac{\mu_j}{RT} \quad (j = \text{NG}+1,\dots,\text{NS}),$$

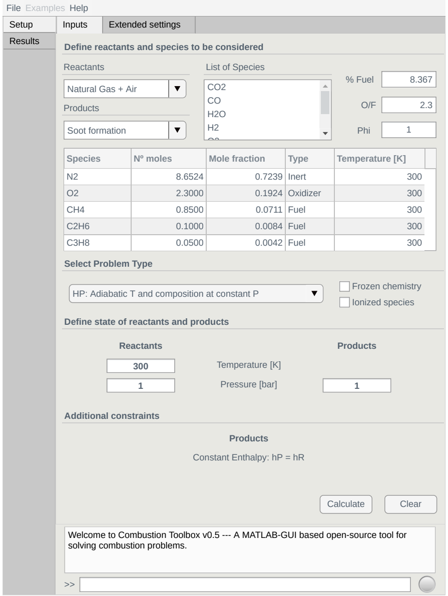
$$\sum_{j=1}^{\text{NG}} a_{ij} n_j \Delta \ln n_j + \sum_{j=\text{NG}+1}^{\text{NS}} a_{ij}\Delta n_j = b_i^{\circ} - b_i \quad (i = 1,\dots,\text{NE}),$$

$$\sum_{j=1}^{\text{NG}} n_j \Delta \ln n_j - n\Delta \ln n = n - \sum_{j=1}^{\text{NG}} n_j.$$

Combustion Toolbox

Main features

- Robust kernel based on Lagrange multipliers.
- Calculation of equilibrium properties of ideal plasmas.
- Up-to-date thermodynamic data (NASA’s 9-coefficient polynomial fit).
- Computation of standard chemical equilibrium problems.
- Shock calculations:
  - pre-shock and post-shock states,
  - incident or reflected shocks,
  - Chapman-Jouguet detonations and overdriven detonations, ...
- Operation through command line and GUI.
- Screen and .xls file format output.



Define reactants and species to be considered

Reactants: Natural Gas + Air

Products: Soot formation

List of Species: CO2, CO, H2O, H2

% Fuel: 8.367

O/F: 2.3

Phi: 1

Species	Nº moles	Mole fraction	Type	Temperature [K]
N2	8.6524	0.7239	Inert	300
O2	2.3000	0.1924	Oxidizer	300
CH4	0.8500	0.0711	Fuel	300
C2H6	0.1000	0.0084	Fuel	300
C3H8	0.0500	0.0042	Fuel	300

Select Problem Type

HP: Adiabatic T and composition at constant P

☐ Frozen chemistry

☐ Ionized species

Define state of reactants and products

Reactants		Products
300	Temperature [K]	
1	Pressure [bar]	1

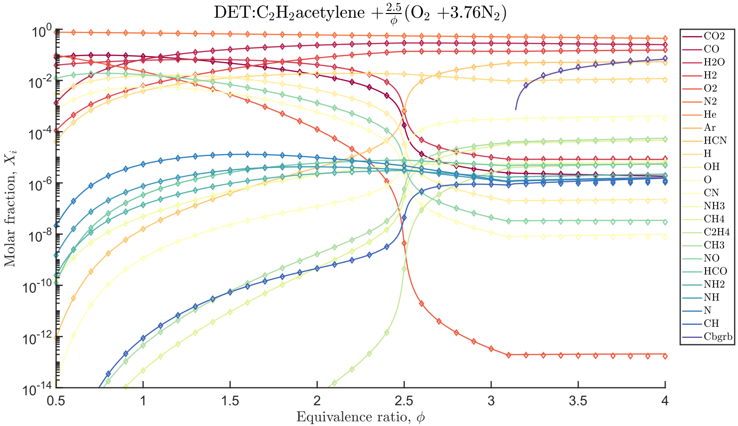
Additional constraints

Products

Constant Enthalpy: hP = hR

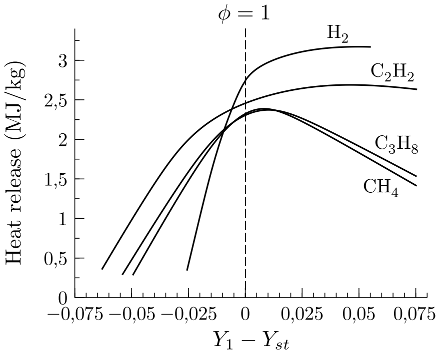
Welcome to Combustion Toolbox v0.5 --- A MATLAB-GUI based open-source tool for solving combustion problems.

Combustion Toolbox: results



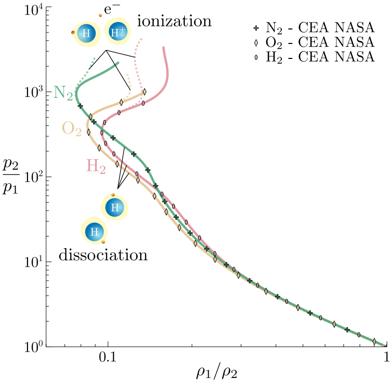
Combustion Toolbox: applications

Detonations



E.g., computation of the heat release.

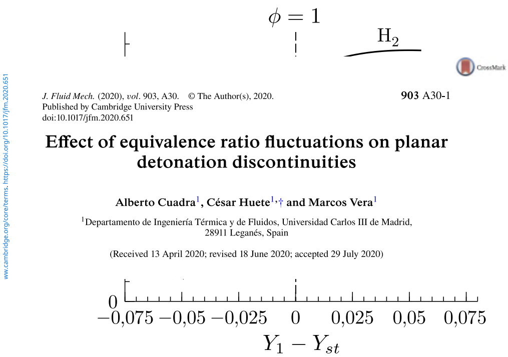
Strong Shocks



E.g., computation of the jump conditions.

Combustion Toolbox: applications

Detonations



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Effect of equivalence ratio fluctuations on planar detonation discontinuities

Alberto Cuadra[1], **César Huete**[1,†] **and Marcos Vera**[1]

[1]Departamento de Ingeniería Térmica y de Fluidos, Universidad Carlos III de Madrid, 28911 Leganés, Spain

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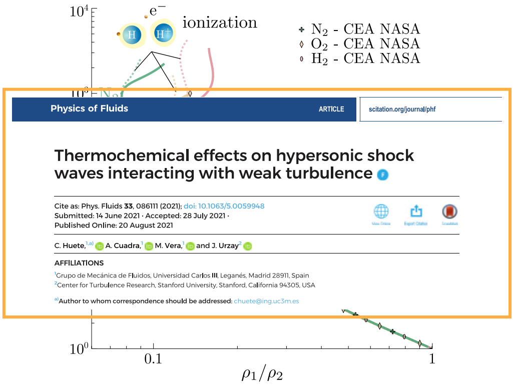
E.g., computation of the heat release.

Strong Shocks



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Thermochemical effects on hypersonic shock waves interacting with weak turbulence

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C. Huete,[1,a)] A. Cuadra,[1] M. Vera,[1] and J. Urzay[2]

AFFILIATIONS
[1]Grupo de Mecánica de Fluidos, Universidad Carlos III, Leganés, Madrid 28911, Spain
[2]Center for Turbulence Research, Stanford University, Stanford, California 94305, USA

[a)]Author to whom correspondence should be addressed: chuete@ing.uc3m.es

E.g., computation of the jump conditions.

Conclusion I

Key takeaways

- Combustion toolbox is an open-source tool for solving gaseous combustion problems under the ideal gases assumption. Allows to include ideal plasmas.
- The tool is equipped with an user-friendly GUI (standalone, no need MATLAB's license). A great complement for educational purposes.
- In it's transition to Python, 100% open-source.
- The plain code is ideal for more sophisticated tasks.
- The overall performance of the code is at level of other thermochemical equilibrium codes. Boost performance in shock calculations compared with Caltech's SD-Toolbox, which uses CANTERA as kernel.

Get the code

Cuadra, A. et al. (2022). Combustion Toolbox: A MATLAB-GUI based open-source tool for solving gaseous combustion problems. **Work in progress**.

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Part II

Thermochemical effects on hypersonic shock waves interacting with weak turbulence

In colaboration with Javier Urzay, Center for Turbulence Research, Stanford University.

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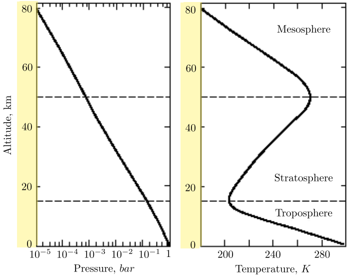
Motivation II



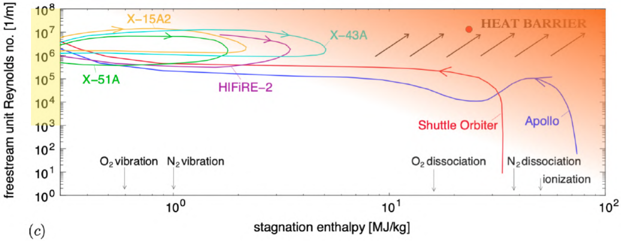
$$\frac{\Delta p}{p} \sim \frac{\Delta \rho}{\rho} = O(10^5), \quad \frac{\Delta T}{T} = O(1).$$

In hypersonic flight near the ground, the Reynolds number becomes large because of the comparatively larger densities

$$\frac{\Delta Re}{Re} = O(10^5).$$

Urzay, J., & Di Renzo, M. (2021). Annual Research Briefs, Center for Turbulence Research, 7-32.

Motivation II



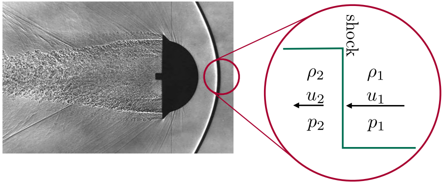
Urzay, J., & Di Renzo, M. (2021). Annual Research Briefs, Center for Turbulence Research, 7-32.

Hypersonic flight at low altitudes is characterized by:

- High free-stream Mach numbers $Ma \geq 5$
- High free-stream and post-shock unit Reynolds numbers $Re \sim 10^7 - 10^9$ m^{-1}
- High stagnation enthalpies $h_0 \sim 5 - 30$ MJ/kg
- Small mean free paths $\lambda \sim 0.1\ \mu$m

- large normal Mach numbers
- turbulent boundary layers
- much higher than the vibrational specific energies of O_2 and N_2
- short vibrational relaxation distances

Effects of dissociation and vibrational excitation on the mean post-shock quantities



Integral conservation equations accross shock waves in dissociating gases

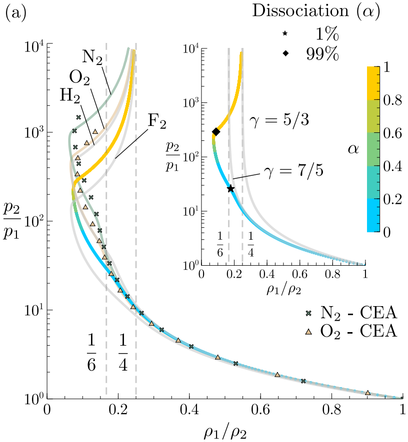
$$\rho_1 u_1 = \rho_2 u_2,$$

$$p_1 + \rho_1 u_1^2 = p_2 + \rho_2 u_2^2,$$

$$e_1 + p_1/\rho_1 + u_1^2/2 = e_2 + p_2/\rho_2 + u_2^2/2 + q_d,$$

Upstream flow is sufficiently cold to be approximated as

$$e_1 = (5/2) R_{g,\mathrm{A}_2} T_1, \quad p_1 = \rho_1 R_{g,\mathrm{A}_2} T_1.$$



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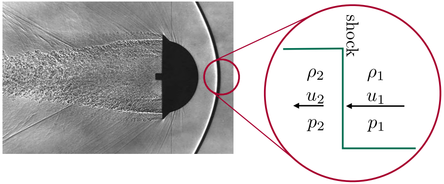
Effects of dissociation and vibrational excitation on the mean post-shock quantities



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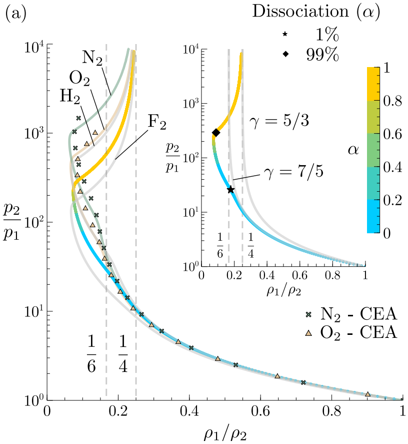
$$e_1 + p_1/\rho_1 + u_1^2/2 = e_2 + p_2/\rho_2 + u_2^2/2 + q_d,$$

$$p_2 = \rho_2 R_{g,\mathrm{A}_2} T_2 (1+\alpha), \quad q_d = \alpha R_{g,\mathrm{A}_2} \Theta_d,$$

$$e_2 = R_{g,\mathrm{A}_2} T_2 \left[3\alpha + (1-\alpha)\left(\frac{5}{2} + \frac{\Theta_v/T_2}{\mathrm{e}^{\Theta_v/T_2} - 1} \right) \right],$$

$$\frac{\alpha^2}{1-\alpha} = G m \Theta_r \left(\frac{\pi m k_B}{\hbar^2} \right)^{3/2} \frac{\sqrt{T_2}}{\rho_2} \mathrm{e}^{-\frac{\Theta_d}{T_2}} \left(1 - \mathrm{e}^{-\frac{\Theta_v}{T_2}} \right),$$



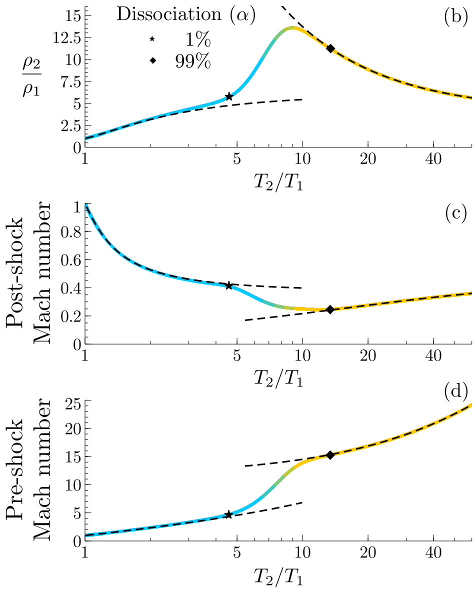
where α is the degree of dissociation, defined as the mass fraction of A atoms in the reaction $\mathrm{A}_2 \rightleftharpoons \mathrm{A} + \mathrm{A}$, that must be solved with the aid of the chemical equilibrium condition.

Effects of dissociation and vibrational excitation on the mean post-shock quantities

Endothermicity due to dissociation and vibrational excitation does the following:

- increases the mean post-shock density
- decreases the mean post-shock velocity
- decreases the mean post-shock Mach number
- decreases the mean post-shock temperature

Jump conditions



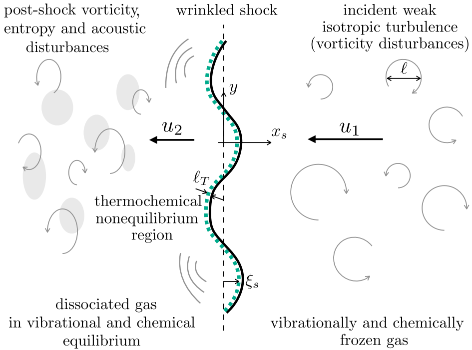
LIA of turbulence interacting with hypersonic shocks

Considering:

- turbulence is comprised of small fluctuations,
- Kovasznay decomposition into vortical, entropic and acoustic modes,

we can solve this problem analytically by using

- linearized Rankine-Hugoniot relations,
- linearized Euler equations in the post-shock gas.



Limits of validity

Assumptions standard LIA:

(a) rms$(u_\ell) \ll a_1$ and a_2,

(b) $\xi_s \ll \ell$,

(c) $\ell / u_\ell \ll \ell^2 / \nu$.

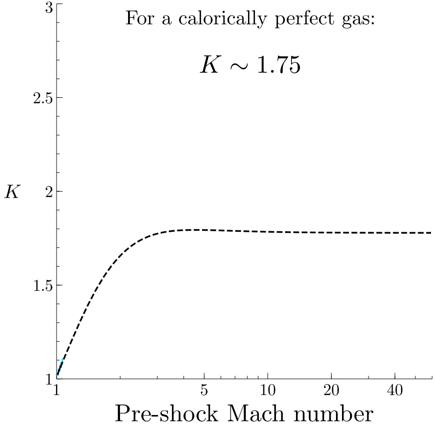
With thermochemical effects:

(d) $\ell_T \ll \ell$

For a given ℓ, this condition becomes increasingly more accurate as the altitude decreases.

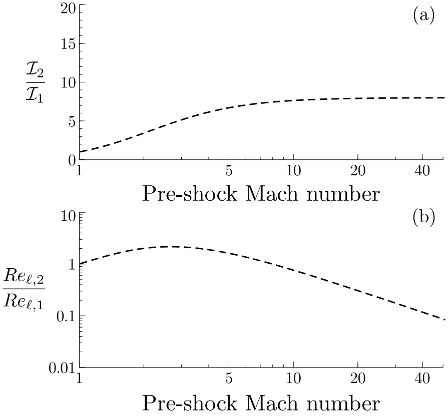
LIA of turbulence interacting with hypersonic shocks: Calorically Perfect Gas

Turbulent Kinetic Energy


For a calorically perfect gas:

$$K \sim 1.75$$

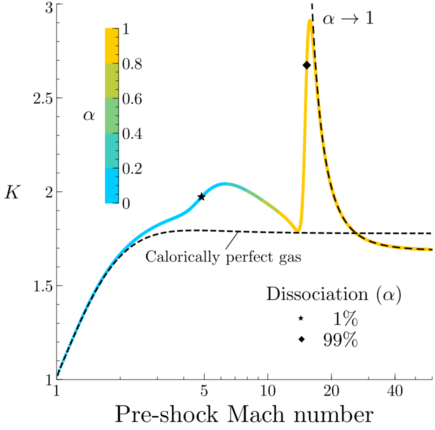
Turbulence intensity and Turbulent Reynolds number



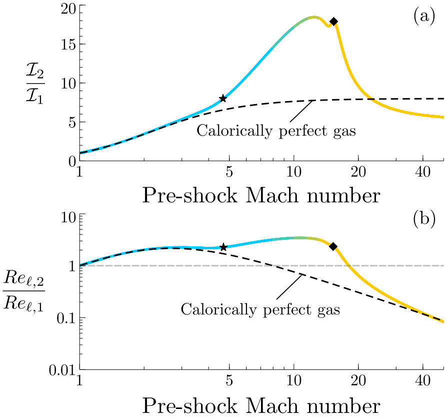
At hypervelocities $(Ma \gtrsim 10)$, the calorically perfect gas approximation predicts a saturation in the amplification of kinetic energy and turbulence intensity, along with a decrease in the turbulent Reynolds number accross the shock.

LIA of turbulence interacting with hypersonic shocks: Vibrationally Excited, Dissociating Gas

Turbulent Kinetic Energy



Turbulence intensity and Turbulent Reynolds number

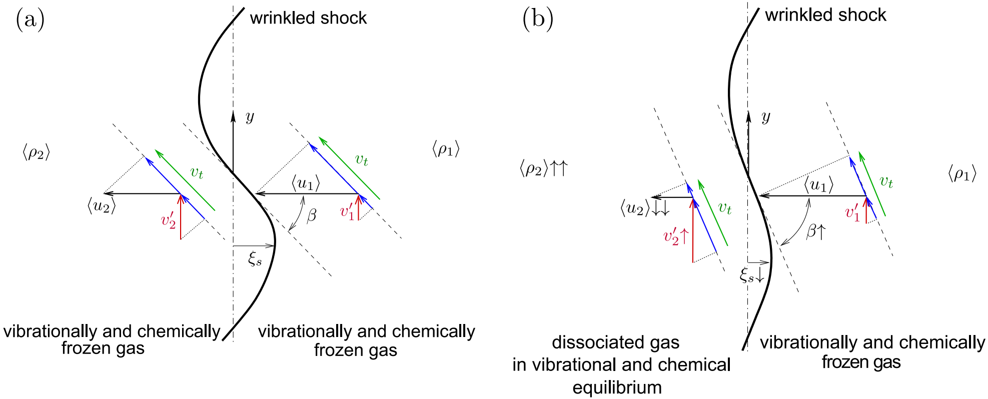


In contrast, the incorporation of dissociation and vibrational excitation predicts larger kinetic energy and turbulence intensity amplification rates, along with an increase in the turbulent Reynolds number accross the shock.

LIA mechanism of turbulence amplification across hypersonic shocks

Calorically perfect gas

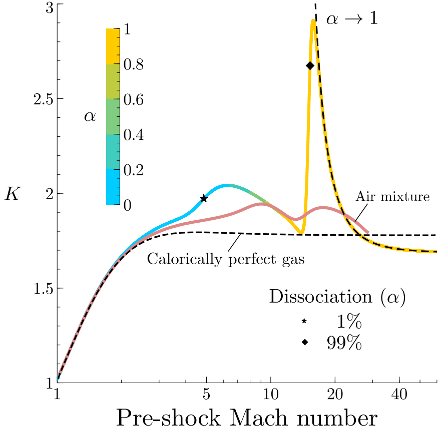
Vibrationally Excited, Dissociating Gas



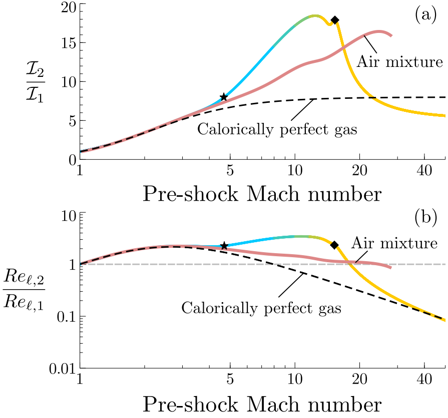
Conservation of tangential momentum dictates that the transverse velocity fluctuations should increase across the shock – these are larger at hypersonic velocities because of the associated larger post-shock densities induced by endothermic thermochemical effects.

Extension for real air mixture. **Preliminary results**

Turbulent Kinetic Energy



Turbulence intensity and Turbulent Reynolds number



In case of a real air mixture (recombination in multi-species gas and electronic excitation) there is a significant decrease of the peaks values of TKE. However, the qualitative picture remains intact.

Conclusions II

Key takeaways

- Significant departures from calorically perfect gas behaviour can be observed in the solution even at modest degrees of dissociation of 1%.
- The amplification of TKE doubles that observed in calorically perfect gases, with most of the content of TKE downstream in form of vortical modes.
- The turbulent Reynolds number is amplified across the shock at hypersonic Mach numbers in the presence of dissociation and vibrational excitation, as opposed to the attenuation observed in the calorically perfect case.
- Preliminary results show that real air mixture share qualitative results, but with lower amplitudes.

- **Thermochemical effects arising at hypersonic velocities appear to enhance turbulent fluctuations in the post-shock gas.**

Huete, C. et al. (2021). Thermochemical effects on hypersonic shock waves interacting with weak turbulence. Physics of Fluids, 33(8), 086111

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