

Governing equations for a hypersonic chemically reacting flow

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March 10, 2025

1 Preliminaries

In this summary, several assumptions will be made on the fluid to study hypersonic flows.

- Thermally Perfect : the fluid behavior can be described by the Equation of State (EOS) of an ideal gas:

$$p = \rho \times R \times T$$

where p is the fluid pressure, ρ the fluid density, T the fluid temperature and R the specific gas constant (with $R = 287.058 \text{ m}^2/\text{s}^2/\text{K}$)

- Calorically Imperfect : The specific heat capacities at constant volume (C_v) and at constant pressure (C_p) fluctuate with the fluid temperature.

$$C_v = C_v(T) \text{ \& } C_p = C_p(T)$$

In the case of a perfect gas, the latter is both thermally and calorically perfect. However, in hypersonic, the fluid can be thermally perfect but is calorically imperfect. We talk about "real gas".

Since the fluid is chemically reacting, we have to make other assumptions in order to take into account the modification of the fluid state linked to chemical reactions.

- Chemical nonequilibrium : the reaction states of the system aren't in balance, and fluid undergoes chemical changes.

$$\text{Damkholer number : } Da = \tau_F / \tau_C$$

where Da is the Damkholer number and indicates whether the fluid is in chemical equilibrium, τ_F is the characteristic bulk flow time, and τ_C is the time required for a chemical transformation to happen.

In the case of chemical nonequilibrium :

$$Da \simeq 1$$

- Thermal non equilibrium : A different temperature is used to describe each energy mode of the system. In hypersonic, four energy modes are used to describe the quantized energy levels of the fluid behind the shock:

1. the translational energy mode E_t , of translational temperature T_t
2. the rotational energy mode E_r , of rotational temperature T_r
3. the vibrational energy mode E_v , of vibrational temperature T_v
4. the electronic energy mode E_e , of electronic temperature T_e

However, the translational and rotational energy modes can be supposed in thermal equilibrium (they can be described by the same temperature) compared to the vibrational energy mode. Let's call the temperature linked to the translational-rotational mode T_{t-r} .

- Thermodynamic nonequilibrium : the fluid is in thermal nonequilibrium, or chemical nonequilibrium, or in thermal and chemical nonequilibrium. In the case of hypersonic chemically reacting flows, the system is supposed to be in chemical and thermal nonequilibrium. Hence, it is in thermodynamic nonequilibrium.

We will still suppose local thermodynamic equilibrium (LTE) in order to use Boltzmann's distribution of molecules to describe the particles' behavior behind the shock.

2 Nomenclature

Variables	Physical Meaning
γ	heat capacity ratio
ρ	density
ρ_s	density of the species s
T	temperature
T_{t-r}	translational-rotational temperature
T_v	vibrational temperature
T_e	electronic temperature

Table 1: Nomenclature Table

Variables	Physical Meaning
u_j	mass-averaged velocity
u	mass-averaged velocity in the direction x
v	mass-averaged velocity in the direction y
$u_{j,s}$	velocity of species s in the direction x_j
u_s	velocity of species s in the direction x
v_s	velocity of species s in the direction y
w_s	chemical source term
N	number of chemical species
p	total pressure
p_s	partial pressure linked to the species s
R	universal gas constant
M_s	molecular weight of the species s
E	total energy per unit volume
E_v	vibrational energy per unit volume
$E_{v,s}$	vibrational energy per unit volume of the species s
$E_{el,s}$	electronic energy per unit volume of the species s
E_e	free electron translational energy
$q_{v,x}$	vibrational energy heat conduction vector in the direction x
$q_{v,y}$	vibrational energy heat conduction vector in the direction y
$q_{t-r,x}$	translational-rotational energy heat conduction vector in the direction x
$q_{t-r,y}$	translational-rotational energy heat conduction vector in the direction y
h_s	the species s specific enthalpy
h_s^o	the species s standard specific enthalpy
e	electron
$e_{v,s}$	vibrational energy of the species s
$e_{el,s}$	electronic energy of the species s

Table 2: Nomenclature Table

Variables	Physical Meaning
$\tau_{i,j}$	shear stress tensor
Y_s	mass fraction of the species s
$(C_p)_{t-r,s}$	translational-rotational energy specific heat at constant pressure of the species s
$(C_v)_{t-r,s}$	translational-rotational energy specific heat at constant volume of the species s
$(C_v)_{v,s}$	vibrational energy specific heat at constant volume of the species s
$(C_v)_{t,s}$	translational energy specific heat at constant volume of the species s
$(C_v)_{r,s}$	rotational energy specific heat at constant volume of the species s
x_s	mole fraction of the species s
$\tau_{v,s}$	vibration relaxation time of the species s
$< \tau_{MW,s} >$	Millikan-White correlation relaxation time of the species s
τ_{sr}	Landau-Teller relaxation time between collision pair of the species s and r
M_e	molecular weight of an electron
D_s	effective diffusion coefficient of the species s
μ	dynamic viscosity
μ_s	dynamic viscosity of the species s
η_{t-r}	translational-rotational thermal conductivity coefficient
$\tilde{\kappa}_{v,s}$	vibrational energy transport coefficient
κ	translational-rotational transport coefficient
$\Theta_{v,s}$	characteristic vibrational temperature of the species s
$\Theta_{el,s}^1$	state 1 characteristic electronic temperature of the species s
$g_{0,s}$	state 0 electronic degeneracy of the species s
$g_{1,s}$	state 1 electronic degeneracy of the species s
Le	Lewis number

Table 3: Nomenclature Table

$Q_{v,s}^{VT}$	translational-vibrational energy exchange rate of the species s
$Q_{v,s}^{chem}$	vibrational energy exchange rate in reactions of the species s
c_s	average molecular speed of the species s
N_s	number density of the colliding particles of the species s
σ_v	limiting collision cross-section
$\nu'_{s,\gamma}$	stoichiometric coefficients of the reactants in the reaction γ
$\nu''_{s,\gamma}$	stoichiometric coefficients of the products in the reaction γ
$k_{b,\gamma}$	kinematic reaction rates for the backward reaction γ
$k_{f,\gamma}$	kinematic reaction rates for the forward reaction γ
$w_{s,\gamma}$	rate of gain/loss of a chemical species s in a reaction γ
N_γ	total number of reactions
$K_{eq,\gamma}$	equilibrium constant of the reaction γ
T_{cf}	forward reaction rate controlling temperature
T_{cb}	backward reaction rate controlling temperature
k_B	Boltzmann's constant
Na	Avogadro's number
$\pi\tilde{\Omega}_{sr}^{-(l,s)}$	collision cross-section between a particle of the species s and r
\tilde{E}_i	steady state electric field in the direction i
p_e	electron pression
Φ_s	Degree of ionization of the atomic species s
eZ_s	charge of the species s
N_s	species s number density
$(N_{s,atom})_0$	original number of the atomic species s
$\Theta_{I,s}$	characteristic ionization temperature of the atomic species s

Table 4: Nomenclature Table

3 Governing Equation

Chemically reacting nonequilibrium fluid :

$$\frac{\partial U}{\partial t} + \frac{\partial F}{\partial x} + \frac{\partial G}{\partial y} = W \quad (1)$$

with :

$$U = (\rho_1, \rho_2, \dots, \rho_N, \rho u, \rho v, E_v, E)^T \quad (2)$$

$$F = \begin{bmatrix} \rho_1(u + u_1) \\ \rho_2(u + u_2) \\ \cdot \\ \cdot \\ \cdot \\ \rho_N(u + u_N) \\ \rho u^2 + p - \tau_{xx} \\ \rho uv - \tau_{xy} \\ E_v u + \sum_s u_s E_{v,s} + q_{v,x} \\ (E + p - \tau_{xx})u - \tau_{xy}v + q_{t-r,x} + q_{v,x} + \sum_s \rho_s h_s u_s \end{bmatrix} \quad (3)$$

$$G = \begin{bmatrix} \rho_1(v + v_1) \\ \rho_2(v + v_2) \\ \cdot \\ \cdot \\ \cdot \\ \rho_N(v + v_N) \\ \rho uv - \tau_{yx} \\ \rho v^2 + p - \tau_{yy} \\ E_v v + \sum_s v_s E_{v,s} + q_{v,y} \\ (E + p - \tau_{yy})v - \tau_{xy}u + q_{t-r,y} + q_{v,y} + \sum_s \rho_s h_s v_s \end{bmatrix} \quad (4)$$

$$W = \begin{bmatrix} w_1 \\ w_2 \\ \cdot \\ \cdot \\ \cdot \\ w_N \\ \sum_{s=1}^N eZ_s \times N_s \times \tilde{E}_x \\ \sum_{s=1}^N eZ_s \times N_s \times \tilde{E}_y \\ \sum_s Q_{v,s}^{VT} + \sum_s Q_{v,s}^{chem} \\ \sum_{s=1}^N eZ_s \times N_s \times \tilde{E}_x u + \sum_{s=1}^N eZ_s \times N_s \times \tilde{E}_y v \end{bmatrix} \quad (5)$$

3.1 How to calculate p , ρ and h_s :

$$p = \sum_{s=1}^N p_s = \sum_{s=1, s \neq e}^N \frac{\rho_s R}{M_s} T_{t-r} + \rho_e \frac{R}{M_e} T_e$$

$$\rho = \sum_{s=1}^N \rho_s$$

$$h_s = \int_{T_{ref}}^T (C_p(T_{t-r}))_{t-r,s} dT_{t-r}$$

$$(C_p(T_{t-r}))_{t-r,s} = \begin{cases} \frac{5}{2} \frac{R}{M_s} & \text{if } s \text{ is an atom} \\ \frac{7}{2} \frac{R}{M_s} & \text{if } s \text{ is a molecule} \end{cases}$$

3.2 How to calculate the shear stress tensor $\tau_{i,j}$:

$$\tau_{ij} = \mu \left(\frac{\partial u_i}{\partial j} + \frac{\partial u_j}{\partial i} - \frac{2}{3} \frac{\partial u_k}{\partial k} \right) \text{ (shear stress tensor)}$$

$$\mu = \sum_s \left[\frac{x_s M_s}{Na \times (\sum_r x_r \Delta_{sr}^{(2)} T)} \right]$$

$$\Delta_{sr}^{(2)} = \frac{16}{5} \left(2 \times \frac{M_s M_r}{\pi R T (M_s + M_r)} \right)^{1/2} \times \pi \Omega_{sr}^{- (2,2)} \times 10^{-20}$$

$$\Omega_{sr}^{- (2,2)} = D(2, 2) \times T_{t-r}^{[(A_{(2,2)} \ln(T_{t-r}) + B_{(2,2)}) \ln(T_{t-r}) + C_{(2,2)}]} \text{ (Gupta)}$$

3.3 How to calculate q_{t-r, x_j} and q_{v, x_j} (1st method):

$$q_{t-r, x_j} = -\eta_{t-r} \frac{\partial T_{t-r}}{\partial x_j}$$

$$q_{v, x_j} = -\mu_s \frac{\partial e_{v, s}}{\partial x_j}$$

$$\eta_{t-r} = \frac{15}{4} \times K_B \times \left(\sum_s \frac{x_s}{\sum_r \alpha_{sr} x_r \Delta_{sr}^{(2)} (T_{t-r})} + \sum_{s \neq atoms} \frac{x_s}{\sum_r x_r \Delta_{sr}^{(1)} (T_{t-r})} \right)$$

$$\eta_{t-r} = \frac{15}{4} \times K_B \times \left(\sum_s \frac{x_s}{\sum_r \alpha_{sr} x_r \Delta_{sr}^{(2)} (T_{t-r})} + \sum_{s \neq atoms} \frac{x_s}{\sum_r x_r \Delta_{sr}^{(1)} (T_{t-r})} \right) \text{ (Gupta-Yos mixing Law)}$$

$$\eta_{t-r} = \frac{15}{4} \times K_B \times \left(\sum_s \frac{x_s}{\sum_r \alpha_{sr} x_r \Delta_{sr}^{(2)} (T)} + \sum_{s \neq atoms} \frac{x_s}{\sum_r x_r \Delta_{sr}^{(1)} (T)} \right)$$

$$\Delta_{sr}^{(1)} = \frac{8}{3} \left(2 \times \frac{M_s M_r}{\pi R T (M_s + M_r)} \right)^{1/2} \times \pi \Omega_{sr}^{- (1,1)} \times 10^{-20}$$

$$\Delta_{sr}^{(2)} = \frac{16}{5} \left(2 \times \frac{M_s M_r}{\pi R T (M_s + M_r)} \right)^{1/2} \times \pi \Omega_{sr}^{- (2,2)} \times 10^{-20}$$

$$\Omega_{sr}^{- (2,2)} = D(2, 2) \times T_{t-r}^{[(A_{(2,2)} \ln(T_{t-r}) + B_{(2,2)}) \ln(T_{t-r}) + C_{(2,2)}]} \text{ (Gupta)}$$

$$\bar{\Omega}_{sr}^{(1,1)} = D(1,1) \times T_{t-r}^{[(A_{(1,1)} \ln(T_{t-r}) + B_{(1,1)}) \ln(T_{t-r}) + C_{(1,1)}]} \text{ (Gupta)}$$

$$\alpha_{sr} = 1 + \frac{(1-M_s M_r)[0.45-2.54(M_s/M_r)]}{[1+M_s/M_r]^2}$$

$$\mu_s = 2.6693 \times 10^{(-6)} \times \frac{\pi \sqrt{M_s T_{t-r}}}{\pi \Omega_{ss}^{(2,2)}} \text{ (Hirschfelder model)}$$

3.4 How to calculate q_{t-r,x_j} and q_{v,x_j} (2nd method):

$$q_{t-r,x_j} = -\kappa \frac{\partial T_{t-r}}{\partial x_j} \text{ (Fourier heat law)}$$

$q_{v,x_j} = -\tilde{\kappa}_{v,s} \frac{\partial e_{v,s}}{\partial x_j}$ (Fourier heat law). We use the vibrational energy gradients to get more robust results.

$$\tilde{\kappa}_{v,s} = \eta_v \mu_s \text{ (based on Eucken relation). Valid up to } 6 \times 10^3 \text{ K}$$

$$\kappa = \sum_s x_s \kappa_s$$

$$\kappa_s = \mu_s \left(\frac{5}{2} (C_v(T_{t-r}))_{t,s} + (C_v(T_{t-r}))_{r,s} \right) \text{ (Palmer and Wright for quantitative assessment)}$$

$$\eta_v = 1.2 \text{ (derived from kinetic theory).}$$

3.5 How to calculate \tilde{E}_i (steady state electric field):

$$\tilde{E}_i \simeq -\frac{1}{N_e} \times \frac{\partial p_e}{\partial x_i}$$

3.6 How to calculate N_e (total number of electrons):

$$N_e = N_{e,s} = \sum_{s,atoms} \Phi_s \times (N_{s,atom})_0$$

3.7 How to calculate Φ_s (degree of ionization of the atomic species s):

$$\frac{\Phi_s^2}{1-\Phi_s^2} = \frac{C_s \times T_{t-r}^{5/2}}{p} e^{-\Theta_{I,s}/T_{t-r}}$$

3.8 How to calculate $Q_{v,s}^{VT}$:

$$Q_{v,s}^{VT} = \rho_s \times \frac{e_{v,s}(T_{t-r}) - e_{v,s}(T_v)}{\tau_{v,s}} \quad (\text{Landau-Teller Formula})$$

$$e_{v,s}(T_v) = \begin{cases} 0 & \text{if } s \text{ is an atom} \\ \frac{\Theta_{v,s} R / M_s}{\exp(\Theta_{v,s} / T_v) - 1} & \text{if } s \text{ is a molecule} \end{cases}$$

$$(C_v(T_v))_{v,s} = \frac{\partial e_{v,s}}{\partial T_v} = \frac{R}{M_s} \left(\frac{\Theta_{v,s}}{T_v} \right)^2 \times \frac{\exp(\Theta_{v,s} / T_v)}{[\exp(\Theta_{v,s} / T_v) - 1]^2}$$

$$\tau_{v,s} = \langle \tau_{MW,s} \rangle + \tau_{c,s}$$

$$\langle \tau_{MW,s} \rangle = \frac{\sum_r x_r}{\sum_r (x_r / \tau_{sr})} \quad (\text{Millikan-White correlation})$$

$$P\tau_{sr} = \exp[A_{sr}(T_{t-r}^{-1/3} - 0.015m_{sr}^{1/4}) - 18.42]$$

$$A_{sr} = 1.16 \times 10^{-3} m_{sr}^{1/2} \Theta_{v,s}^{4/3}$$

$$m_{sr} = \frac{M_s \times M_r}{M_s + M_r}$$

$$\tau_{c,s} = \frac{1}{\sigma_s c_s n_s} \quad (\text{collision-limited relaxation time})$$

$$\sigma_s = 10^{-20} \left(\frac{50000}{T_{t-r}} \right)^2$$

$$c_s = \sqrt{\frac{8RT_{t-r}}{\pi M_s}}$$

$$n_s = \frac{Na\rho Y_s}{M_s}$$

3.9 How to calculate $Q_{v,s}^{chem}$:

$$Q_{v,s}^{chem} = e_{v,s} w_s$$

$$w_s = M_s \times \sum_{\gamma}^{N_{\gamma}} w_{s,\gamma}$$

$$w_{s,\gamma} = (\nu''_{s,\gamma} - \nu'_{s,\gamma})(k_{f,\gamma} \prod_j^N \left(\frac{\rho_j}{M_j} \right)^{\nu'_{j,\gamma}} - k_{b,\gamma} \prod_j^N \left(\frac{\rho_j}{M_j} \right)^{\nu''_{j,\gamma}})$$

$$T_{cf} = T_{t-r}^{0.5} T_v^{0.5} \quad (\text{Two-temperature Park's model})$$

$$T_{cb} = T_{t-r} \quad (\text{Two-temperature Park's model})$$

$$k_{f,\gamma}(T_{cf}) = AT_{cf}^b \exp\left(\frac{-E_d/R}{T_{cf}}\right)$$

$$k_{b,\gamma}(T_{cb}) = \frac{k_{f,\gamma}(T_{cb})}{K_{eq,\gamma}(T_{cb})}$$

$$k_{b,\gamma}(T_{cb}) = \frac{k_{f,\gamma}(T_{cb})}{K_{eq,\gamma}(T_{cb})}$$

3.10 How to calculate E and $E_{v,s}$:

$$E = \sum_{s \neq e}^N E_{t-r,s} + \sum_{s \neq e}^N E_{v,s} + E_e + \sum_{s \neq e}^N E_{el,s} + \frac{1}{2} \rho u_i u_i + \sum_{s \neq e}^N \rho_s h_s^o$$

$$E_{t-r,s} = \rho_s (C_v)_{t-r,s} T_{t-r}$$

$$(C_v)_{t-r,s} = \begin{cases} \frac{3}{2} \frac{R}{M_s} & \text{if } s \text{ is an atom} \\ \frac{5}{2} \frac{R}{M_s} & \text{if } s \text{ is a molecule} \end{cases}$$

$$E_{v,s} = \rho_s e_{v,s} = \rho_s \frac{R}{M_s} \frac{\Theta_{v,s}}{\exp(\Theta_{v,s}/T_v) - 1}$$

$$E_e = \rho_e (C_v(T_e))_e T_e$$

$$C_v(T_e) = \frac{3}{2} \frac{R}{M_e}$$

$$h_s = (C_v)_{t-r,s} T_{t-r} + e_{v,s} + e_{el,s} + h_s^o + \frac{p_s}{\rho_s}$$

$$p_s = \rho_s \frac{R}{M_s} T_{t-r}$$

$$e_{v,s}(T_v) = \begin{cases} 0 & \text{if } s \text{ is an atom} \\ \frac{\Theta_{v,s} R / M_s}{\exp(\Theta_{v,s}/T_v) - 1} & \text{if } s \text{ is a molecule} \end{cases}$$

$$e_{el,s} = \frac{R}{M_s} \frac{(g_{1,s}/g_{0,s}) \exp(-\Theta_{1,s}^{el})}{1 + (g_{1,s}/g_{0,s}) \exp(-\Theta_{1,s}^{el})}$$

$$E_{el,s} = \rho_s \times e_{el,s}$$

3.11 How to calculate $\rho_s u_{j,s}$:

$$\rho_s u_{j,s} = -\rho D_s \frac{\partial Y_s}{\partial x_j} \text{ (Fick's law)}$$

3.12 How to calculate D_s (1st method):

$$D_s = \frac{1 - x_s}{\sum_{r \neq s} (x_r / D_{sr})}$$

$$D_{sr} = \frac{k_B \times T_{t-r}}{p \Delta_{sr}^{(1)}(T_{t-s})}$$

$$\Delta_{sr}^{(1)} = \frac{8}{3} \left(2 \times \frac{M_s M_r}{\pi R T (M_s + M_r)} \right)^{1/2} \times \pi \Omega_{sr}^{- (1,1)} \times 10^{-20}$$

$$\Omega_{sr}^{- (1,1)} = D(1,1) \times T_{t-r}^{[(A_{(1,1)} \ln(T_{t-r}) + B_{(1,1)}) \ln(T_{t-r}) + C_{(1,1)}]} \text{ (Gupta)}$$

3.13 How to calculate D_s (2nd method):

$$Le = \frac{\rho D_s C_p (T_{t-r})}{\kappa} \text{ (Lewis Number)}$$

$$Le = 1.4 \text{ for air}$$