

Hypersonic Thermochemical Non-Equilibrium Flow CFD Solver with Two-Temperature Model within OpenFOAM Framework

Mehmet Furkan Tunc* and Bayram Celik†
Istanbul Technical University, Istanbul, Turkey, 34144

After certain speed and rarefaction degree, fluid flow cannot be modeled with chemical and thermal equilibrium assumptions. Conventional Navier-Stokes equations must be updated with proper terms such as source terms and more than single temperature model. In this paper, new CFD solver within OpenFOAM framework which has the ability to handle thermochemical non-equilibrium flows is introduced.

I. Nomenclature

i (-)	=	equation number
j (-)	=	variable number
e (-)	=	electronic
v (-)	=	vibrational
ve (-)	=	vibrational-electronic
s (-)	=	specie
ρ (kg/m^3)	=	density
t (s)	=	time
u (m/s)	=	velocity vector
p (Pa)	=	pressure
τ (Pa)	=	shear stress tensor
E ($kg/(m^2 \cdot s^2)$)	=	total energy per unit volume
q ($W/m \cdot K$)	=	heat conduction vector
δ_{ij} (-)	=	Kronecker delta
\dot{w}_s ($kg/(m^3 \cdot s)$)	=	chemical source
$J_{s,j}$ ($mol/(m^2 \cdot s)$)	=	diffusion term
h_s ($kg/(m^2 \cdot s^2)$)	=	enthalpy of specie
Q ($kg/(m^3 \cdot s)$)	=	energy source

*Student Researcher, Aeronautical and Astronautical Sciences Department, Istanbul Technical University

†Prof., Aeronautical and Astronautical Sciences Department, Istanbul Technical University

II. Introduction

Equilibrium as flow-state description indicates the fact that macroscopic properties of the matter does not depend on time. In the case of non-equilibrium flow, another term that describes the necessary time to reach the equilibrium state again is defined as relaxation.

III. Theoretical Background

For a monatomic gas, dimensionless Knudsen number which determines rarefaction degree of the gas flow can be defined as:

$$Kn = \frac{\lambda}{L} \quad (1)$$

For monatomic gases, only translational motion of the gas can be taken into the account. For diatomic gases, there are also rotational and vibrational motions of the gas, thus different relaxation times for different motions are necessary to recognize. Fluid flow can be classified into two parts according to internal equilibrium of the flow. Equilibrium of the flow is related to the characteristic flow time which is tied to the rarefaction degree of the flow. Hence, nonequilibrium flow occurs when the gas flow is at a low density and/or involves very small length scales [1].

Non-equilibrium flow can be examined into two separate flows: chemical non-equilibrium, and thermochemical non-equilibrium. Depending on flow's equilibrium state, different governing equations are required.

A. Thermochemical Equilibrium Flow

Thermochemical equilibrium flow can be modeled with conventional Navier-Stokes equations as it can be seen in Eqs. (2) - (4) [1]:

$$\frac{\partial \rho}{\partial t} + \frac{\partial(\rho u_j)}{\partial x_j} = 0 \quad (2)$$

$$\frac{\partial(\rho u_i)}{\partial t} + \frac{\partial(\rho u_i u_j)}{\partial x_j} + \frac{\partial(p \delta_{ij})}{\partial x_j} - \frac{\partial \tau_{ij}}{\partial x_j} = 0 \quad (3)$$

$$\frac{\partial E}{\partial t} + \frac{\partial((E + p)u_j)}{\partial x_j} + \frac{\partial(\tau_{ij}u_i)}{\partial x_j} + \frac{\partial q_j}{\partial x_j} = 0 \quad (4)$$

Chemical reactions are independent of time and only depend on pressure and temperature. Thus, equations that govern the chemical composition of the mixture are independent of transportation equations. Chemical composition is required for calculating gas properties which will be employed in Navier-Stokes equations (Eqs. (2) - (4)). That means chemical composition governing equations and Navier-Stokes equations can be solved separately and sequentially[1].

B. Chemical Non-equilibrium Flow

Thermochemical non-equilibrium can be solved with one-, two-, or three-temperatures models as it can be seen in Eqs. (5) - (10) [1]:

$$\frac{\partial \rho_s}{\partial t} + \frac{\partial}{\partial x_j}(\rho_s u_j + J_{s,j}) = \dot{\omega}_s \quad (5)$$

$$\frac{\partial}{\partial t}(\rho u_i) + \frac{\partial}{\partial x_j}(\rho u_i u_j + p \delta_{ij} - \tau_{ij}) = 0 \quad (6)$$

$$\frac{\partial E}{\partial t} + \frac{\partial}{\partial x_j} \left((E + p) u_j - \tau_{ij} u_i + q_j + \sum_{s=1}^{ns} J_{s,j} h_s \right) = 0 \quad (7)$$

$$\frac{\partial E_{ve}}{\partial t} + \frac{\partial}{\partial x_j} \left(E_{ve} u_j + q_{ve,j} + \sum_{s=1}^{ns} J_{s,j} h_{ve,s} \right) + p_e \frac{\partial u_j}{\partial x_j} = Q_{ve} \quad (8)$$

$$\frac{\partial E_v}{\partial t} + \frac{\partial}{\partial x_j} \left(E_v u_j + q_{v,j} + \sum_{s=1}^{ns} J_{s,j} h_{v,s} \right) = Q_v \quad (9)$$

$$\frac{\partial E_e}{\partial t} + \frac{\partial}{\partial x_j} \left((E_e + p_e) u_j + q_{e,j} + \sum_{s=1}^{ns} J_{s,j} h_{e,s} \right) - u_j \frac{\partial p_e}{\partial x_j} = Q_e \quad (10)$$

These equations are employed for:

- *One-Temperature Model*: Eqs. (5)-(7).
- *Two-Temperature Model*: Eqs. (5)-(8).
- *Three-Temperature Model*: Eqs. (5)-(7) and Eqs. (9)-(10).

1. Chemical Source Term

In Eq. (5), chemical source term ($\dot{\omega}_s$) represents the changes in the amount of a specie according to reactions that the specie participates or results from. $\dot{\omega}_s$ is given by Eq. (11):

$$\dot{\omega}_s = M_s \sum_{r_1}^{NR} (v''_{s,r} - v'_{s,r}) \left[k_{f,r} \prod_{n=1}^{NS} \left(\frac{\rho_n}{M_n} \right)^{v'_{n,r}} - k_{b,r} \prod_{n=1}^{NS} \left(\frac{\rho_n}{M_n} \right)^{v''_{n,r}} \right] \quad (11)$$

where 's' specifies which specie is taken into account for the source term calculation, 'r' specifies which reaction is currently processed, 'n' specifies which specie in 'r' reaction is being calculated.

In order to find $\dot{\omega}_s$ term, Eq. (11) requires forward (k_f) and backward (k_b) reaction rates which can be calculated with Arrhenius law:

$$k_f = A_f \times T_{c,f}^{B_f} \exp\left(-\frac{T_a}{T_{c,f}}\right) \quad (12)$$

where A_f is a pre-exponential factor, B_f is the temperature exponent, T_a is the temperature of activation derived from the activation energy, and $T_{c,f}$ is the controlling temperature of the forward reaction [1].

According to ParkTTv model, the controlling temperature of the forward dissociation reactions can be given by Eq. (13) [2]:

$$T_{c,f} = T_P = T_{tr}^{\alpha_P} \times T_v^{1-\alpha_P} \quad (13)$$

where $\alpha_P = 0.7$ is commonly accepted [3]. For backward dissociation reactions and exchange reactions, translational-rotational temperature T_{tr} is accepted as controlling temperature.

In Gupta [4] and Park [5] models, backward reaction rate is calculated as a function of forward reaction rate:

$$k_b = \frac{k_f}{K_{eq}} \quad (14)$$

where equilibrium constant K_{eq} is given by

1) according to Park:

$$K_{eq} = \exp(A_1/Z + A_2 + A_3 \ln Z + A_4 Z + A_5 Z^2) \quad (15)$$

where Z is:

$$Z = 10^4/T \quad (16)$$

and A_1, A_2, \dots, A_5 are taken from Park's reference work [5].

2) according to Gupta:

$$K_{eq} = \exp(A_1 Z^5 + A_2 Z^4 + A_3 Z^3 + A_4 Z^2 + A_5 Z + A_6) \quad (17)$$

where Z is:

$$Z = 10^4/T \quad (18)$$

and A_1, A_2, \dots, A_6 are taken from Gupta's reference work [4].

General process can be summarized explicitly as:

Algorithm 1 Chemical Source Term Calculation Algorithm

- 1: Select reaction
 - 2: Select chemistry model for reaction rate coefficients A_f, B_f, T_a (Park93, QK, Gupta)
 - 3: Calculate controlling temperature $T_{c,f}$
 - 4: Calculate forward reaction rate k_f using Eq. (12)
 - 5: Calculate equilibrium constant K_{eq}
 - 5.1 Select necessary coefficients and model from reference works (Park, Gupta)
 - 5.2 Calculate equilibrium constant K_{eq} using Eq. (15)
 - 6: Calculate backward reaction rate k_b using Eq. (14)
 - 7: Calculate species chemical source term
 - 7.1 Select density (ρ_s) and molecular weight (M_s)
 - 7.2 Select product stoichiometric ($v''_{s,r}$) and reactant stoichiometric ($v'_{s,r}$) coefficients according to selected reaction
 - 7.3 Calculate final value using Eq. (11)
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2. Diffusion Models

There are three diffusion models which can be employed to calculate mass diffusion.

Fick Diffusion Model: The mass diffusion flux is proportional to the gradient of the mass fraction:

$$J_{s \neq e, j} = -\rho D_s \frac{\partial Y_s}{\partial x_j} \quad (19)$$

where Y_s is the mass fraction of species s, and D_s is the effective diffusion coefficient of species s. For the electron mass diffusion flux:

$$J_{e, j} = -\frac{1}{q_e} \sum_{s \neq e} q_s J_{s, j} \quad (20)$$

where q_s is the charge per unit mass of species s.

Modified Fick Diffusion Model: To ensure that the sum of the mass diffusion fluxes is zero, Eq. (21) is proposed:

$$J_{s \neq e, j} = -\rho D_s \frac{\partial Y_s}{\partial x_j} - Y_s \sum_{r \neq e} \left(-\rho D_r \frac{\partial Y_r}{\partial x_j} \right) \quad (21)$$

Summation of Eq.(21) for all species is zero.

Stefan-Maxwell Model: It is derived by solving the mole fraction gradient as it can be seen in Eq. (22):

$$J_{s, j} = -\rho D_s \frac{\partial Y_s}{\partial x_j} + \frac{Y_s}{(1 - X_s)} D_s \sum_{r \neq s} \left(\rho \frac{M}{M_r} \frac{\partial Y_r}{\partial x_j} + \frac{M}{M_r} \frac{J_r}{D_{s, r}} \right) \quad (22)$$

Eq. (22) must be solved with iterative method.

Diffusion coefficient calculation is given below.

3. Thermodynamic Properties

Internal energies per unit mass can be written as following Eqs. (23) - (25):

$$e_t = \frac{3}{2} R_s T_{tr} \quad (23)$$

$$e_r = R_s T_{tr} \quad (24)$$

$$e_{v, s}(T) = R_s \left(\frac{\theta_{v, s}}{\exp(\theta_{v, s}/T) - 1} \right) \quad (25)$$

From Eqs. (23) - (25), specific heat constants under constant volume condition (C_v) can be written as in Eqs. (26) - (28):

$$C_{v,t,s} = \frac{3}{2}R_s \quad (26)$$

$$C_{v,t,s} = R_s \quad (27)$$

$$C_{v,t,s} = R_s \left(\frac{\theta_{v,s}/2T_{v,s}}{\sinh(\theta_{v,s}/2T_{v,s})} \right) \quad (28)$$

Translational heat capacity at constant pressure and translational enthalpy can be given as following Eqs. (29) - (30):

$$C_{p,t,s} = C_{v,t,s} + R_s \quad (29)$$

$$h_{t,s} = C_{p,t,s}T_t \quad (30)$$

For different energy modes, total energy can be calculated as follows:

$$E = \frac{1}{2}\rho \sum_i u_i^2 + \sum_s E_{t,s} + \sum_s E_{r,s} + \sum_s E_{v,s} + \sum_s \rho_s h_s^0 \quad (31)$$

where

$$E_v = \sum_s \rho_s e_{v,s} \quad (32)$$

$$E_{tr} = E_t + E_r = \sum_s \rho_s e_{t,s} + \sum_s \rho_s e_{r,s} \quad (33)$$

which Eq. (31) becomes Eq. (34):

$$E = \frac{1}{2}\rho \sum_i u_i^2 + \sum_s \rho_s e_{t,s} + \sum_s \rho_s e_{r,s} + \sum_s \rho_s e_{v,s} + \sum_s \rho_s h_s^0 \quad (34)$$

where $\frac{1}{2}\rho \sum_i u_i^2$ is the total kinetic energy within mixture, $\sum_s \rho_s e_{t,s} + \sum_s \rho_s e_{r,s}$ is the total translational-rotational energy, $\sum_s \rho_s e_{v,s}$ is the total vibrational energy, and $\sum_s \rho_s h_s^0$ is the standard enthalpy of formation.

4. Transport Properties

In order to find viscosity, thermal conductivity, and diffusion coefficient each specie's property is calculated using empirical/semi-empirical formulas. After that, mixing rules helps to determine properties of the mixture.

Viscosity: τ_{ij} represents viscous stress tensor and given in Eq. (35) :

$$\tau_{ij} = \mu \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) - \frac{2}{3} \mu \frac{\partial u_k}{\partial x_k} \delta_{ij} \quad (35)$$

where Stokes' hypothesis assumed to be held. In that case, viscosity (μ) is needed for momentum equation. Viscosity can be calculated using two curve-fitting formulas Eqs. (36) - (37):

1) according to Blottner:

$$\mu_s = 0.1 \times \exp((A_B \ln(T) + B_B) \ln(T) + C_B) \quad (36)$$

2) according to Gupta:

$$\mu_s = 0.1 \times [\exp(C_G)] T^{A_G \ln(T) + B_G} \quad (37)$$

T is generally accepted as translational temperature.

Thermal Conductivity: q_j is the total heat conduction vector calculated with Fourier's law. For one-temperature model, it is given in Eq. (38):

$$q_j = -(\kappa_t + \kappa_r + \kappa_v) \frac{\partial T}{\partial x_j} = -\kappa \frac{\partial T}{\partial x_j} \quad (38)$$

For two-temperature model, q_j is given in Eq. (39):

$$q_j = -(\kappa_t + \kappa_r) \frac{\partial T_{tr}}{\partial x_j} - \kappa_v \frac{\partial T_v}{\partial x_j} = -\kappa_{tr} \frac{\partial T_{tr}}{\partial x_j} - \kappa_v \frac{\partial T_v}{\partial x_j} \quad (39)$$

In that case, thermal conductivities are required for heat conduction vector. κ and κ_{tr} is calculated using Eucken's relation which are Eqs. (40) - (41) although they can be calculated from collision integrals.

$$\kappa_{tr} = \mu_s \left(\frac{5}{2} c_{v,t,s} + c_{v,r,s} \right) \quad (40)$$

$$\kappa_v = \eta_v \mu_s \quad , \quad \eta_v = 1.2 \quad (41)$$

Eucken's relation only holds up until 6000 K.

Diffusion Coefficient: In order to calculate the effective diffusion coefficient (D_s), Eq. (42) is given for *constant Lewis number (CLN)* method. It is valid for one-temperature model:

$$D_s = D = \frac{\kappa Le}{\rho C_p} \quad (42)$$

For two- and three-temperature models:

$$D_s = D = \frac{\kappa_{tr} Le}{\rho C_p} \quad (43)$$

where Le is the Lewis number and generally set to 1.4.

5. Mixing Rules

Calculation of properties of each specie can be done separately. However, for the mixture, these individual properties are determined with *mixing rules*.

Wilke Mixing Rule: Wilke's mixing rule is given as in Eq. (44):

$$Q = \sum_s \frac{Q_s X_s}{\phi_s} \quad (44)$$

where Q is the quantity that belongs to the mixture, Q_s is the specie quantity, X_s is the mass fraction, and ϕ_s is the scaling factor which is given as:

$$\phi_s = X_s + \sum_{r \neq s} X_r \left[1 + \sqrt{\frac{\mu_s}{\mu_r}} \left(\frac{M_r}{M_s} \right)^{1/4} \right]^2 \left[\sqrt{8 \left(1 + \frac{M_s}{M_r} \right)} \right]^{-1} \quad (45)$$

It should be noted that Wilke's rule is only applicable to neutral gases and below 10000 K.

6. Energy Transfer Source Terms

There are three types of energy sources that should be taken into the account as it can be observed in Eq. (46):

$$Q_V = \sum_{s=mol.} Q_{s,V-T} + \sum_{s=mol.} Q_{s,V-V} + \sum_{s=mol.} Q_{s,C-V} \quad (46)$$

where Q_V is the total vibrational energy source term, $Q_{s,V-T}$ is the vibrational-translational energy source term, $Q_{s,V-V}$ is the vibrational-vibrational energy source term, and $Q_{s,C-V}$ is the chemical-vibrational energy source term. General calculation process can be seen in Algorithm 2.

Vibrational-Translational Energy Mode: For vibrational-translational energy mode, Millikan-White-Park model is employed. Classical Landau-Teller formulation is given as in Eq. (47):

$$Q_{s,V-T} = \rho_s \frac{e_{v,s}(T_t) - e_{v,s}(T_v)}{\tau_{s,V-T}} = \rho_s \frac{C_{V,v,s}(T_t - T_v)}{\tau_{s,V-T}} \quad (47)$$

Modified Landau-Teller equation is given as Eq. (48):

$$Q_{s,V-T} = \frac{T_t}{T_v} (T_t - T_v) \frac{C_{V,v,s} \rho_s}{\tau_{s,V-T}} \quad (48)$$

Relaxation time of the vibrational-translational energy mode for specie s is given by Eq. (49):

$$\tau_{s,V-T} = \frac{\sum_{r=mol} X_r}{\sum_{r=mol} \frac{X_r}{\tau_{s-r,V-T}}} \quad (49)$$

Vibrational-translational relaxation time between species s and r proposed by Millikan-White and corrected by Park is given as follows in Eq. (50):

$$\tau_{s-r,V-T} = \tau_{s-r,V-T}^{MW} + \tau_{s-r,V-T}^P \quad (50)$$

Millikan-White vibrational-translational relaxation time is given as in Eq. (51):

$$\tau_{s-r,V-T}^{MW} = \frac{1}{p} \exp \left[A_{s,r} \left(T_{tr}^{-1/3} - B_{s,r} \right) - 18.42 \right] \quad (51)$$

where coefficients $A_{s,r}$, $B_{s,r}$, and $\sigma_{s,r}$ are given as in Eqs. (52) - (54):

$$A_{s,r} = 1.16 \times 10^{-9/2} \sqrt{\frac{M_s M_r}{M_s + M_r}} \theta_{v,s}^{4/3}, \quad (52)$$

$$B_{s,r} = 0.015 \times 10^{-3/4} \left(\frac{M_s M_r}{M_s + M_r} \right)^{1/4}, \quad (53)$$

$$\sigma_{v,s} = \sigma'_{v,s} \left(\frac{50000}{T} \right)^2, \quad (54)$$

Park correction for vibrational-translational relaxation time is given as in Eq. (55):

$$\tau_{s-r,V-T}^P = \frac{1}{\bar{c}_s \sigma_{v,s} n_{s,r}} \quad (55)$$

where $\sigma'_{v,s}$ is typically given as $3 \times 10^{-21} \text{ m}^2$ for N_2 , O_2 , and NO , and \bar{c}_s is the average molecular speed given by Eq. (56):

$$\bar{c}_s = \sqrt{\frac{8RT}{\pi M_s}} \quad (56)$$

Chemical-Vibrational Energy Mode: Park proposed a chemical-vibrational energy model base on dissociation potential of the molecules with Eq. (57):

$$Q_{s,C-V} = \dot{w}_s \tilde{D}_s \quad (57)$$

where vibrational energy per unit mass of the diatomic molecule s is given by Eq. (58):

$$\tilde{D}_s = \alpha_s \epsilon_{d,s} \quad (58)$$

where $\epsilon_{d,s}$ is the dissociation energy/potential of molecule s , and α_s is a constant typically set as 0.3.

Vibrational-Vibrational Energy Mode: Knab gives his formulation of vibrational-vibrational energy source term as follows in Eq. (59) [6]:

$$Q_{m,V-V} = \sum_{l \neq m} N_A \sigma_{m,l} P_{m,l} \sqrt{\frac{8RT_{tr}}{\pi M_{m,l}}} \frac{\rho_l}{M_l} \rho_m \left(e_{v,m}(T_{tr}) \frac{e_{v,l}(T_{v,l})}{e_{v,l}(T_{tr})} - e_{v,m}(T_{v,m}) \right), \quad m, l \in N_m \quad (59)$$

where N_A is the Avogadro number, R is the universal gas constant, $P_{m,l}$ which is the value of assessed exchange probability constant recommended as 10^{-2} , and $\sigma_{m,l}$ is defined as the collision cross-section of the collision pair.

Summation of all energy source terms as in Eq. (46) gives required vibrational energy source term. General process can be summarized as:

Algorithm 2 Vibrational Energy Source Term Calculation Algorithm

- 1: Calculate vibrational-translational energy source term Q_{V-T}
 - 1.1 Calculate Millikan-White coefficients $A_{s,r}$ and $B_{s,r}$ by Eqs. (52) - (54)
 - 1.2 Calculate Millikan-White relaxation time $\tau_{s-r,V-T}^{MW}$ by Eq. (51)
 - 1.3 Calculate average molecular speed \bar{c}_s by Eq. (56)
 - 1.4 Calculate limited collision cross-section $\sigma_{v,s}$ by Eq. (54)
 - 1.5 Calculate number density of the collision pair n_{s-r}
 - 1.6 Calculate Park relaxation time $\tau_{s-r,V-T}^P$ by Eq. (55)
 - 1.7 Calculate total relaxation time $\tau_{s-r,V-T}$ by Eq. (50)
 - 1.8 Calculate average relaxation time $\tau_{s,V-T}$ by Eq. (49)
 - 1.9 Calculate vibrational-translational energy exchange $Q_{s,V-T}$ by Eq. (47) or by Eq. (48)
 - 2: Calculate chemical-vibrational energy source term Q_{C-V} by Eq. (57)
 - 2.1 Find chemical source term \dot{w}_s using Algorithm 1.
 - 2.2 Find dissociation energy D_s for specie s
 - 2.3 Calculate coefficient D'_s
 - 2.4 Calculate chemical-vibrational energy source term $Q_{s,C-V}$
 - 3: Calculate vibrational-vibrational energy source term Q_{V-V} by Eq. (59)
 - 3.1 Find M_s, ρ_s, ρ_n given $n \neq s$
 - 3.2 Calculate internal vibrational energy of specie s with T_{tr} using Eq. 25
 - 3.3 Calculate internal vibrational energy of specie s with T_v using Eq. 25
 - 3.4 Calculate internal vibrational energy of specie $n \neq s$ with T_{tr} using Eq. 25
 - 3.5 Calculate internal vibrational energy of specie $n \neq s$ with T_v using Eq. 25
 - 3.6 Calculate vibrational-vibrational energy source term $Q_{s,V-V}$
 - 4: Calculate total vibrational energy source term Q_V by Eq. (31)
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