

Numerical simulation of Vibrationally Active Ar-H2 Microwave Plasma

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Abstract: Microwave discharges have a wide range of applications, such as gas conversion, material processing and surface treatment; also they can provide an efficient way for dissociation of molecular gases as CO₂ and N₂O. Depending on the operating pressure and temperature, non-equilibrium conditions can be attained within the discharge, where electron temperature, vibrational temperature and translational temperature differ from each other. In this work we address the issue of simulating this non-equilibrium condition choosing as test case the Ar-H₂ plasma, which find applications for instance in chemical vapor deposition of diamond films or in nuclear fusion research for deuterium production.

Keywords: Vibrational Temperature, plasma, microwave.

1. Introduction

With the term “vibrational non equilibrium plasma” we refer in general to an ionized molecular gas where the condition $T_e \neq T_v \neq T$ is realized. The vibrational non equilibrium between the internal degrees of freedom of a molecule has been first studied by Landau and Teller [1] at the beginning of the century, and has been the subject of considerable attention since then. Much of the work has been devoted to the case $T_v < T$, which is realized typically downstream of shockwaves attached to reentry vehicles in the upper atmosphere, or in shock tube experiments [2].

From a chemical point of view the case $T_v > T$ is more interesting, since it results in catalytic promotion of chemical reactions with high energetic barriers; this phenomenon has been studied between 1970 and the 1990, mostly by Russian researchers [3,4], and in recent years, there has been a renowned interest on the topic, in order to address environmental and energetic issues.

It has been experimentally and numerically shown [5,6] that microwave plasma sources can provide efficient dissociation of molecular gases; microwave sources have been studied, for instance, for CO₂ splitting, H₂ plasmas for diamond film deposition and deuterium ion production; to our knowledge, however, numerical investigations accounting for the vibrational dynamic of the plasma, in the case $T_v > T$, have been restricted till now to global kinetic models.

In this work we simulate an Ar-H₂ gas subject to microwave heating in sub-atmospheric conditions, with a reduced kinetic dataset of reactions reported in Table[1]; from a mathematical point of view the problem can be solved coupling the Maxwell equations for the propagation of the electric field, together with the continuity, momentum and energy equations for the plasma-fluid in the Euler simplified form. For this purpose we use COMSOL Multiphysics with four modules coupled together: the plasma microwave module, the laminar flow module, one PDE module to solve the total energy equation and one PDE module to solve the vibrational energy equation. The catalytic effect of the supra thermal vibrational population, results in an enhancement of the rate of unimolecular dissociation (by a factor $\Phi(T, T_v)$, which is addressed with the Kuznetsov[7] model; in this situation the chemistry of the discharge is coupled to three temperatures solved by the model (i.e. T_e, T_v, T).

2. Model and governing equations

The reactor is composed by a rectangular slab where a mixture of gas Ar:H₂ enters the 2-dimensional domain at a velocity of 10 m/s (see Figure[1]). The mole fraction of the mixture is Ar:H₂ 9:1. A microwave guide irradiate the flowing gas with a TE mode beam at 2.45 GHz; the electron population is heated within the plasma by interaction with the electromagnetic

field, while power is transferred to the heavy species by electron collision reactions. Elastic collision and electron-rotational excitation (e-R) result in heating of the gas and increase of gas temperature; electron-vibrational excitation (e-V) results in pumping of energy into the vibrational reservoir of the H₂ molecules. Fast V-V resonant energy transfer between H₂ molecules results into the establishment of a Boltzmann distribution for the vibrational states at a temperature $T_v \geq T$.

The Comsol microwave plasma module solves the set of Maxwell equations in frequency domain in order to determine the power transferred to the electron population; the electron momentum equation is solved with the drift diffusion approximation, and a set of continuity equations are solved for each species in the discharge (Ar, Ar(4s), Ar⁺, H₂, H, H₂⁺, H₃⁺, e). The fluid flow field of the discharge is determined by coupling the laminar flow module with the inviscid and incompressible options.

In order to calculate the evolution of the vibrational temperature in the discharge, the vibrational energy equation, in its Euler form (inviscid) plus the incompressible condition, is added by means of the PDE module. The equation is[2]:

$$\frac{\partial e_v}{\partial t} + \nabla \cdot (e_v \mathbf{v}) = \frac{S_{n_{H_2}}}{n_{H_2}} e_v + S_{eV} - P_{VT} \quad (1)$$

Where e_v is the average vibrational energy in eV, $S_{n_{H_2}}$ is the net production/destruction of H₂ due to chemical reactions inside the reactor, S_{eV} is the energy input from e-V collisions and P_{VT} is the energy loss by relaxation to the translational degrees of freedom. The vibrational temperature is then calculated by the following relation:

$$T_v = \frac{h\nu}{k_b} \left[\log\left(\frac{h\nu}{q e_v} + 1\right) \right]^{-1} \quad (2)$$

The gas temperature is calculated from the solution of the total energy equation for the neutral species; ions in this case are neglected since they constitute a negligible fraction of the total particle density of the discharge.

Also in this case we adopt the simplified Euler form of the energy equation plus the incompressible condition; the equation is solved respect to the specific energy of the mixture, e_t

[J/kg] by implementation on an additional PDE module:

$$\frac{\partial e_t}{\partial t} + \nabla \cdot (e_t \mathbf{v}) = \frac{1}{\rho} (S_{eV} + S_{eR} + S_{el} + S_{eD}) \quad (3)$$

On the right hand side there is the energy input due to vibrational, rotational excitations and elastic collisions; S_{eD} is the energy liberated by electron impact dissociation of H₂. The temperature is calculated from the expression of the mixture specific energy from kinetic theory:

$$e_t = y_{H_2} \left(E_{v0} + \frac{e_v q}{M_{H_2}} + \frac{5}{2} R_{H_2} T \right) + \frac{3}{2} R_{Ar} T (y_{Ar s} + y_{Ar}) + y_H \left(\frac{3}{2} R_H T + h_0^H \right) \quad (4)$$

Where y and R are the mass fraction and gas constants, E_{v0} is the zero-point vibrational energy and h_0^H is the formation enthalpy of H.

2.1 Boundary conditions

The reactor geometry is reported in Figure[1]. For what concern the plasma module, the electron wall condition is applied on the lateral walls and the inlet section, while an electron outlet condition is applied on the outlet section; zero-potential condition is applied in all the boundaries. Outlet flux conditions are placed for all the species on the outlet section.

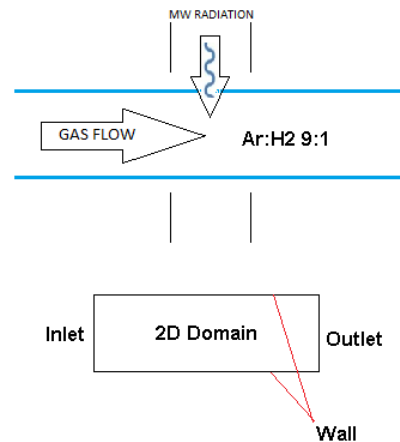


Figure 1: Schematic of the microwave reactor

Regarding the PDE modules that solves the vibrational energy and total energy equations, the zero flux condition is imposed on the lateral

walls of the slab; for the inlet and outlet section the following conditions are adopted:

Inlet:

$$\mathbf{n} \cdot (e_v \mathbf{v}) = -\mathbf{v}_{\text{in}} e_{v0}, \mathbf{n} \cdot (e_t \mathbf{v}) = -\mathbf{v}_{\text{in}} e_{t0}$$

Outlet:

$$\mathbf{n} \cdot (e_v \mathbf{v}) = -\mathbf{v}_{\text{out}} e_v, \mathbf{n} \cdot (e_t \mathbf{v}) = \mathbf{v}_{\text{out}} e_t$$

where e_{v0} and e_{t0} are calculated at the entering gas temperature T_0 .

2.2 Plasma-chemical reactions

A reduced reaction dataset is reported in Table[1].

Table 1: Ar-H2 model reactions dataset.

Reaction	Reference
Elastic scattering	
$e + \text{Ar} \rightarrow e + \text{Ar}$	[8]
$e + \text{H}_2 \rightarrow e + \text{H}_2$	[9, 10]
Rotational and vibrational excitation	
$e + \text{H}_2 \rightarrow e + \text{H}_2(J_{0,2})$	[9, 10]
$e + \text{H}_2 \rightarrow e + \text{H}_2(J_{1,3})$	[9, 10]
$e + \text{H}_2 \rightarrow e + \text{H}_2(v1)$	[9, 10]
$e + \text{H}_2 \rightarrow e + \text{H}_2(v2)$	[9, 10]
$e + \text{H}_2 \rightarrow e + \text{H}_2(v3)$	[9, 10]
Excitation and dissociation	
$e + \text{Ar} \rightarrow e + \text{Ar}(4s)$	[8]
$e + \text{Ar}(4s) \rightarrow e + \text{Ar}$	[8]
$e + \text{H}_2 \rightarrow e + \text{H} + \text{H}$	[11]
Electron impact ionization	
$e + \text{Ar} \rightarrow e + \text{Ar}^+$	[8]
$e + \text{Ar}(4s) \rightarrow e + \text{Ar}^+$	[8]
$e + \text{H}_2 \rightarrow e + e + \text{H}_2^+$	
Electron-ion recombination	
$e + \text{H}_2^+ \rightarrow \text{H} + \text{H}$	[11]
$e + \text{H}_3^+ \rightarrow \text{H}_2 + \text{H}$	[11]
$e + \text{H}_3^+ \rightarrow \text{H} + \text{H} + \text{H}$	[12]
Charge exchange and neutral reactions	
$\text{H}_2 + \text{H}_2^+ \rightarrow \text{H}_3^+ + \text{H}$	[11]
$\text{Ar}(4s) + \text{Ar}(4s) \rightarrow \text{Ar} + e + \text{Ar}^+$	[13]
$\text{Ar}(4s) + \text{Ar} \rightarrow \text{Ar} + \text{Ar}$	[13]
$\text{H}_2 + \text{H}_2 \rightarrow \text{H}_2 + \text{H} + \text{H}$	[14]
$\text{H} + \text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}_2$	[14]
$\text{H}_2 + \text{H} \rightarrow \text{H} + \text{H} + \text{H}$	[14]
$\text{H} + \text{H} + \text{H} \rightarrow \text{H} + \text{H}_2$	[14]
$\text{Ar} + \text{H}_2 \rightarrow \text{Ar} + \text{H} + \text{H}$	[14]
$\text{H} + \text{H} + \text{Ar} \rightarrow \text{H}_2 + \text{Ar}$	[14]
Surface reactions	
	Recombination factor
$\text{Ar}^+ \rightarrow \text{Ar}$	$\gamma = 1$
$\text{Ar}(4s) \rightarrow \text{Ar}$	$\gamma = 1$
$\text{H}_3^+ \rightarrow \text{H}_2 + \text{H}$	$\gamma = 1$
$\text{H}_2^+ \rightarrow \text{H}_2$	$\gamma = 1$
$2\text{H} \rightarrow \text{H}_2$	$\gamma = 0.02$

Neutral gas phase reactions are expressed by the modified Arrhenius law:

$$K(T) = A \left(\frac{T}{300} \right)^n \exp\left(-\frac{E_a}{T}\right) \quad (5)$$

When the gas is in a non-equilibrium condition, the neutral gas phase reaction rate becomes function of the vibrational temperature also, and can be expressed as the product of $K(T)$ times a non-equilibrium factor $\Phi(T, T_v)$:

$$K(T, T_v) = \Phi(T, T_v) \cdot K(T) \quad (6)$$

$$\Phi(T, T_v) = \frac{1 - \exp\left(\frac{h\nu}{k_b T_v}\right)}{1 - \exp\left(\frac{h\nu}{k_b T}\right)} \exp\left[-E_G \left(\frac{1}{T} - \frac{1}{T_v}\right)\right] \quad (7)$$

Where the E_G characteristic energy is usually a function of gas composition and temperature, but is approximated in this work, following the suggestion in [7], as 65% of the dissociation energy. An example of the non-equilibrium factor is shown in Figure[2]. The non-equilibrium factor is applied to the following reactions:

1. $\text{H}_2 + \text{H}_2 \rightarrow \text{H} + \text{H} + \text{H}_2$
2. $\text{H}_2 + \text{H} \rightarrow \text{H} + \text{H} + \text{H}$
3. $\text{H}_2 + \text{Ar} \rightarrow \text{H} + \text{H} + \text{Ar}$

The reverse reactions depend only on the gas temperature [5].

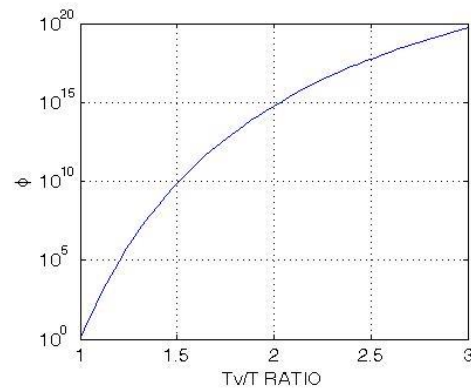


Figure 2: Non equilibrium factor versus T_v/T ratio for H2 at $T = 500\text{K}$.

3. Simulations and results

Simulations are carried at first with the gas entering the reactor at room temperature 300 K, and 1 Torr reactor pressure. In Figure[3] we report the electron density, the gas temperature and the vibrational temperature of H2 within the reactor.

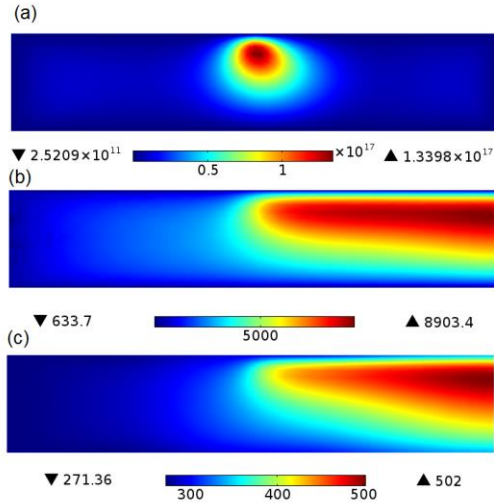


Figure 3: (a) n_e [m^3/s], (b) T_v [K], (c) T [K]

In this condition the H mass production corresponds to the 0.72% of the mass flow of H2 entering the reactor. The non-equilibrium factor raises the unimolecular dissociation rate by a factor spanning from 10^{24} to 10^{44} in the flow field; however, the thermal rate constant $K(T)$ for unimolecular dissociation, at 300 – 500 K, is so low that the vibrational catalysis doesn't affect the discharge, and the H production is mostly due to electron impact dissociation. The efficiency of conversion is calculated as follow:

$$\eta = \frac{\dot{m}_H h_0^H}{P_W} \quad (8)$$

Where P_W is the input electrical power, \dot{m}_H the mass flow of H exiting the reactor and h_0^H is the formation enthalpy of H.

Raising the temperature of the entering gas is beneficial for the thermal reaction rate, to an extent that, at a certain point, the vibrational catalysis becomes effective. Figure[4] shows the

electron density and the T_v/T ratio of a simulation where the gas is preheated and enters at a temperature of 1400 K; the entering region of the 2D domain has been elongated to have higher uniformity in the entrance region.

In this condition the H mass production corresponds to 10% of the mass flow of H2 entering the reactor; the H production from unimolecular decomposition is a factor 3 higher than electron impact dissociation. The efficiency is calculated as follow:

$$\eta = \frac{\dot{m}_H h_0^H}{P_W + h(1400)} \quad (9)$$

with $h(1400)$ the energy required to preheat the gas; the efficiency results 5%.

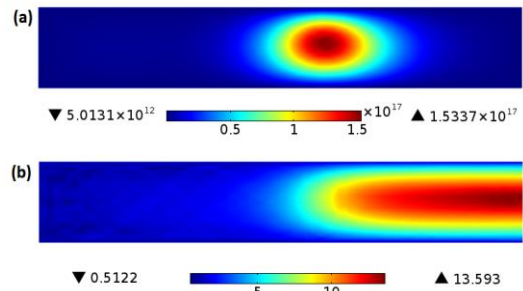


Figure 4: (a) n_e [m^3/s], (b) T_v/T ratio [K]

4. Conclusions

In this work we used COMSOL Multiphysics to simulate an Ar:H2 microwave plasma with inclusion of vibrational temperature evolution of the system and its effect on the chemistry of the discharge. Preliminary results are encouraging, simulations at 1 Torr and 1400 K entering gas temperature show that the effect of vibrational catalysis are comparable to electron impact dissociation; however further exploration of the parameter space (p_0 , T_0) is necessary in order to increase efficiency of the discharge. A more detailed kinetic model has to be included also in order to account for the formation of H⁻ negative ions by dissociative attachment, which is known to depend on the vibrational excitation state of the H2 molecule. Finally the complete

Kuznetsov model will have to be used instead of the approximated version used here.

5. References

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