Extension of Lighthill's gas model for multi-component air

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Abstract

Lighthill's well-known ideal dissociating gas model is still a fundamental part of analytical and engineering methods describing dissociation effects in high temperature hypersonic flow. But its availability only for a one-component gas limits its application in case of air more to qualitative than quantitative results. Therefore, a new gas model has been developed which yields the degree of dissociation in equilibrium flow for a five-component gas. Like Lighthill's model it is based on statistical mechanics and introduces a characteristic dissociation density. Compared to a complete solution for equilibrium air, its maximum deviation only amounts to 4 % for a temperature range up to 12 000 K.

Nomenclature

A = species A
B = species B
h = Planck constant, $h = 6.6256 \text{ x } 10^{-34}$ J · s
k = Boltzmann constant, $k = 1.38054 \text{ x } 10^{-23}$ J/K
M = total mass
m_a = mass of atom of species A
m_b = mass of atom of species B
N = number of atoms, molecules
N_A = total number of atoms species A
N_B = total number of atoms species B
Q = partition function
T = temperature
α_a = degree of dissociation of species A
α_b = degree of dissociation of species B
ϵ = relative deviation, $\epsilon = |\alpha - \alpha_{ref}|/\alpha_{ref}$
ρ = density
ρ_D = characteristic density of dissociation
Θ_D = characteristic temperature of dissociation
Θ_{rot} = characteristic temperature of rotation
Θ_{vib} = characteristic temperature of vibration
ω_i = mass fraction of species i

Subcripts

el = electronic excitation

Superscripts

a, aa = atoms, molecules of species A at temperature T
b, bb = atoms, molecules of species B at temperature T

1. Introduction

The reactive hypersonic flow around simple as well as complex vehicles is nowadays studied by sophisticated numerical simulations. In general, these include viscous effects as well as thermal and chemical relaxation processes at high temperatures. Numerous computational results in literature prove the high capability of computational fluid dynamics.

Nevertheless, to gain physical understanding of the main mechanism of reactive flows, simple gas models are required which may even allow to find solutions based on analytical methods. Furthermore, simple but sufficiently accurate gas models are necessary for engineering methods and relations to calculate main flow characteristics like stagnation point heat fluxes, shock stand-off distances etc. One of these methods to model the flow-chemistry interaction for high temperatures is the well-known ideal dissociating gas model of Lighthill [1]. It has been used in numerous papers [2,3,4] to study the effect of dissociation on various hypersonic flow phenomena. This model is based on a single species gas consisting of atoms and molecules. For equilibrium conditions it allows to determine the degree of dissociation α as function of the actual gas temperature and density. The derivation of this model makes use of statistical mechanics and a simplification which is valid in the temperature range from 1 000 K to 7 000 K.

Unfortunately, in hypersonics most interest is devoted to air mainly consisting of oxygen and nitrogen. The dissociation behaviour of these two species is quite different which leads to significant deviations when considering air as a single species gas. For example, oxygen dissociates in the temperature range between 2 000 K and 6 000 K, whereas significant nitrogen dissociation takes place from 4 000 K to about 8 000 K.

The aim of the present paper is to develop an extended ideal dissociation gas model which takes into account the two components oxygen and nitrogen of air. As Lighthill's model it is based on the description by statistical mechanics and suitable simplifications. It leads to analytical solutions for the degree of dissociation, the equation of state and other parameters of the thermodynamic state. A comparison with more accurate gas models for air shows a very good agreement with this in the following derived simple model.

2. Gas model and theoretical description

In the following three different gas models for air will be presented which are used to describe the equilibrium gas properties of air at high temperatures. The degree of complexity increases from one model to the other, but therewith also its accuracy.

2.1 Lighthill's ideal dissociating gas model

The detailed derivation of this well-known gas model is described in many papers and text books [5]. Therefore, in the following only a brief description of its main features is given.

Employing statistical mechanics for equilibrium conditions it is possible to derive an expression for the degree of dissociation α of a single component gas consisting of atoms (a) and molecules (aa):

$$\frac{\alpha^2}{1-\alpha} = \left[m_a \left(\frac{\pi m_a \cdot k}{h^2} \right)^{3/2} \Theta_{rot} \sqrt{T} \left(1 - e^{-\Theta_{vib}/T} \right) \frac{(Q_{el}^a)^2}{Q_{el}^{aa}} \right] \frac{e^{-\Theta_D/T}}{\rho} \tag{1}$$

The degree of dissociation is defined as the ratio of the mass of dissociated components versus the total mass

$$\alpha = \frac{m_a \cdot N_a}{M} \tag{2}$$

with m_a being the mass of an atom, N_a the number of atoms and the total mass M. The degree of dissociation varies from zero (non-dissociated gas) to one (fully dissociated gas). Lighthill found that the expression in the square brackets of Eq. (1) only slightly varies with temperature in the interesting temperature range from 1 000 K to 7 000 K. Since this expression has the dimension of a density, he called this characteristic dissociation density ρ_D which is constant for the mentioned temperature range. Therewith, Eq. (1) simplifies to the well-known form:

$$\frac{\alpha^2}{1-\alpha} = \frac{\rho_d}{\rho} e^{-\Theta_D/T} \tag{3}$$

The values of ρ_D for oxygen and nitrogen have been approximated by Lighthill to 1.5 x 10^5 kg/m^3 and 1.3 x 10^5 kg/m^3, respectively. Whereas these values do not show a big difference, the characteristic dissociation temperatures Θ_D for oxygen and nitrogen significantly deviate from each other. The characteristic dissociation temperature for oxygen amounts to 59 500 K and for nitrogen to 113 000 K. This big difference does not allow to apply the simple Eq. (3) for air consisting of a mixture of oxygen and nitrogen. As it is well known, the different characteristics of the oxygen and nitrogen dissociation lead to a s-shaped curve of the degree of dissociation of air versus temperature. This behaviour cannot be described by Eq. (3). Therefore, in the following two more sophisticated gas models will be described which are based on Lighthill's ideal dissociating gas model. Especially the last model is capable to describe physically correct the complex dissociation behaviour of air.

2.2 Extension of Lighthill's gas model for a four-component gas

In the interesting flow regime of reentry into earth atmosphere the dominant chemical reactions are given by the oxygen and nitrogen dissociation. Therefore, in a first attempt the dissociation characteristics of air are modeled by a four component air model with the constituents O_2, O, N_2 and N according to the simple reactions in chemical equilibrium:

$$A_2 \rightleftharpoons A + A$$
$$B_2 \rightleftharpoons B + B$$

It is straightforward to show that in this case the mass action laws of each single component remain valid [5]:

$$\frac{(N^a)^2}{N^{aa}} = \frac{(Q^a)^2}{Q^{aa}} e^{-D_A/(kT)} \tag{4}$$

and

$$\frac{(N^b)^2}{N^{bb}} = \frac{(Q^b)^2}{Q^{bb}} e^{-D_B/(kT)} \tag{5}$$

Furthermore, molar conservation yields:

$$N^a + 2 \cdot N^{aa} = N_A \tag{6}$$
$$N^b + 2 \cdot N^{bb} = N_B \tag{7}$$

with the individual particle numbers N^a, N^b etc. and the total particle numbers N_A and N_B.

The total degree of dissociation is defined as:

$$\alpha = \frac{m_a N^a + m_b N^b}{M} = \alpha_a + \alpha_b \tag{8}$$

which is simply the sum of the individual degrees of dissociation. It is convenient to introduce the mass fractions of each species:

$$\omega_i = \frac{m_i \cdot N_i}{M} \tag{9}$$

with $i = a$, aa, b, bb, A and B.

The elimination of the actual molecular particle numbers N^{aa} and N^{bb} by Eqs. (6) and (7) in the mass action laws leads to

$$\frac{\alpha_a^2}{\omega_A - \alpha_a} = \frac{\rho_{D,A_2}}{\rho} e^{-\Theta_{D,A_2}/T} \tag{10}$$
$$\frac{\alpha_b^2}{\omega_B - \alpha_b} = \frac{\rho_{D,B_2}}{\rho} e^{-\Theta_{D,B_2}/T} \tag{11}$$

where the characteristic dissociation densities are given by:

$$\rho_{D,A_2} = \frac{m_a}{2V} \frac{(Q^a)^2}{Q^{aa}} \tag{12}$$

and

$$\rho_{D,B_2} = \frac{m_b}{2V} \frac{(Q^b)^2}{Q^{bb}} \tag{13}$$

According to Eqs. (10) and (11) the degrees of dissociation can be written as:

$$\alpha_a = \frac{\rho_{D,A_2}}{2\rho}\, e^{-\Theta_{D,A_2}/T} \left[\sqrt{1 + 4\,\omega_A \frac{\rho}{\rho_{D,A_2}}\, e^{\Theta_{D,A_2}/T}} - 1 \right] \tag{14}$$

and

$$\alpha_b = \frac{\rho_{D,B_2}}{2\rho}\, e^{-\Theta_{D,B_2}/T} \left[\sqrt{1 + \omega_B \frac{\rho}{\rho_{D,B_2}}\, e^{\Theta_{D,B_2}/T}} - 1 \right] \tag{15}$$

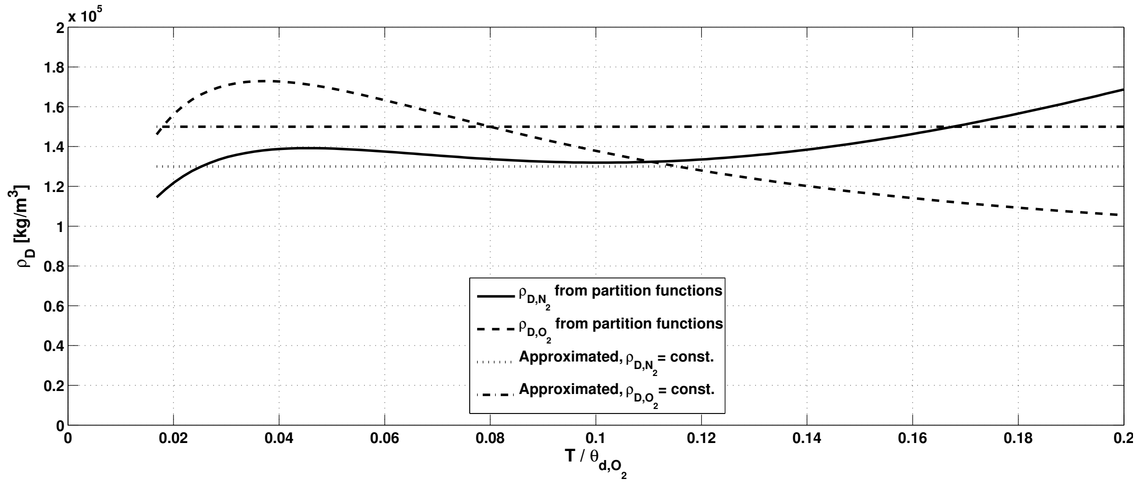

Figure 1: Dissociation density for O_2 and N_2 and approximated values by Lighthill

For a single component gas, i.e. $\omega_A = \omega_B = 1$, the equations reduce to Lighthill's original gas model. The characteristic dissociation densities have been computed according to Eqs. (12) and (13) for nitrogen and oxygen. The partition functions took into account translational, rotational, vibrational, electronic excitation and a finite dissociation energy. The achieved dissociation densities for O_2 and N_2 are shown in Fig. 1 for a temperature range from 1 200 K to 12 000 K. For comparison, also the constant approximated values according to Lighthill are given. For the temperature range considered by Lighthill the maximum deviation of the exact value from the approximated one amounts to 1.5 %.

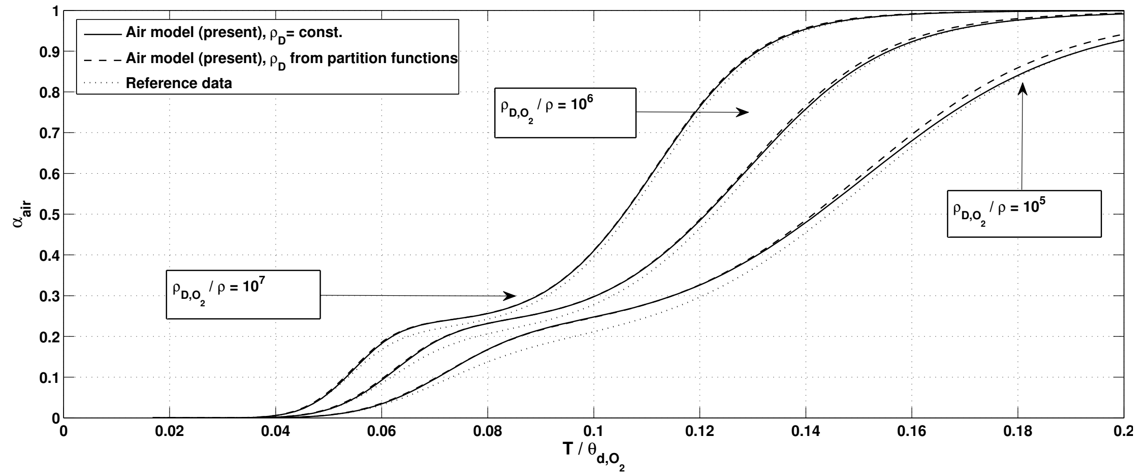

Figure 2: Degree of dissociation for four-component gas model and relative deviation to reference data

The evaluation of the degree of dissociation according to Eqs. (8), (14) and (15) yields the behaviour shown in Fig. 2. The data is compared with results from an in-house code for a five-component equilibrium air model which is based on statistical mechanics formulations employing partition functions. The results of this code can be considered as 'reference' or 'most accurate' data. In Fig. 3 also the relative deviation between both solutions is shown. The maximum deviation amounts to 22 % which is not acceptable for a sophisticated physical model. This deviation is caused by neglecting the formation of NO and its subsequent dissociation at higher temperatures.

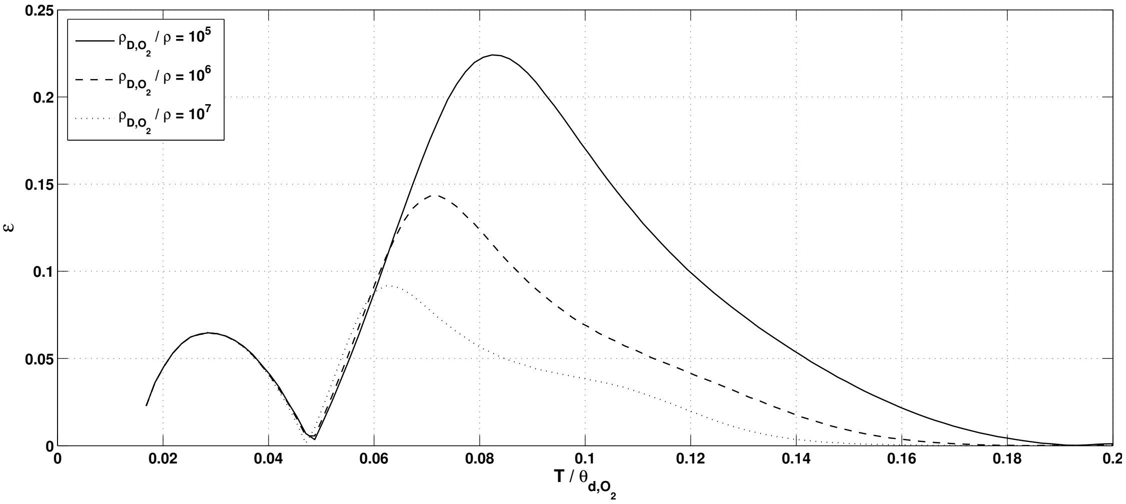

Figure 3: Relative deviation between four-component gas model and reference data, ρ_D = const.

2.3 Extension to a five-component gas model

Motivated by the results achieved with the four-component gas model, Lighthill's ideal dissociating gas model has been extended to a five-component air model. The aim of this is to reduce the error in the degree of dissociation. The five-component gas model covers the species: N_2, O_2, O, N and NO. The atom conservation equations are now given by:

$$N_A = N^a + 2N^{aa} + N^{ab} = const. \tag{16}$$

$$N_B = N^b + 2N^{bb} + N^{ab} = const. \tag{17}$$

and the mass conservation is expressed as:

$$M = m_a N_A + m_b N_B = const. \tag{18}$$

with the suffix A for oxygen and B for the nitrogen species. The definition of the degree of dissociation is unchanged according to Eq. (8). It has to be stated that for reasons of simplicity the formation and dissociation of the combined molecule AB has not been considered according to the Zel'dovich Neumann exchange reactions but simply by the reaction $A + B \rightleftharpoons AB$. This procedure is valid for equilibrium conditions. According to the derivation described above this leads to the mass action law for the new component:

$$N^{ab} = \frac{\alpha_a \alpha_b M^2}{m_a m_b} \, \frac{Q^{ab}}{Q^a Q^b} \, e^{\Theta_{D,AB}/T} \tag{19}$$

Two new characteristic dissociation densities can be defined describing the gas properties:

$$\rho_{D,AB} = \frac{m_a}{2V} \, \frac{Q^a Q^b}{Q^{ab}} \tag{20}$$

and

$$\rho_{D,BA} = \frac{m_b}{m_a} \cdot \rho_{D,AB} \tag{21}$$

with

$$\rho_{D,AB} = \frac{m_a}{2} \left(\frac{m_a m_b}{m_a + m_b} \right)^{3/2} \left(\frac{2\pi k}{h^2} \right)^{3/2} \Theta_{rot} \, \sqrt{T} \, \frac{1 - e^{-\Theta^{ab}_{vib}}/T}{1 - e^{-\Theta^{ab}_{d}}/T} \, \frac{Q^a_{el} \, Q^b_{el}}{Q^{ab}_{el}} \tag{22}$$

From the mass action laws for species A and B and with the help of Eq. (19), finally the following two equations are derived for the five-component gas model:

$$\alpha_a = \frac{\rho_{D,A_2}}{2\rho}\, e^{-\Theta_{D,A_2}/T}\left[\sqrt{\left(1+\frac{\alpha_b}{2}\,\frac{\rho}{\rho_{D,BA}}e^{\Theta_{D,AB}/T}\right)^2 + 4\,\omega_A\,\frac{\rho}{\rho_{D,A_2}}\,e^{\Theta_{D,A_2}/T}} - \frac{\alpha_b}{2}\,\frac{\rho}{\rho_{D,BA}}e^{\Theta_{D,AB}/T} - 1\right] \tag{23}$$

and

$$\alpha_b = \frac{\rho_{D,B_2}}{2\rho}\, e^{-\Theta_{D,B_2}/T}\left[\sqrt{\left(1+\frac{\alpha_a}{2}\,\frac{\rho}{\rho_{D,AB}}e^{\Theta_{D,AB}/T}\right)^2 + 4\,\omega_B\,\frac{\rho}{\rho_{D,B_2}}\,e^{\Theta_{D,B_2}/T}} - \frac{\alpha_a}{2}\,\frac{\rho}{\rho_{D,AB}}e^{\Theta_{D,AB}/T} - 1\right] \tag{24}$$

These are two implicit solutions for the degree of dissociation for a representative air gas model. An analytical explicit solution for α_a and α_b is quite tedious if that is possible at all. But a simple solution strategy is proposed which yields highly accurate values. In this case, Eqs. (23) and (24) are solved iteratively employing the degrees of dissociation of the four-component gas model as first guess values in the square roots of Eqs. (23) and (24). Since for the four-component gas model α_a and α_b can directly be determined from Eqs. (14) and (15), this procedure directly yields the degrees of dissociation for the five-component gas model. The results shown in the following have been achieved with only one iteration step, i.e. the degrees of dissociation at the right sides of Eqs. (23) and (24) have been approximated by those of the four-component gas model. The new characteristic dissociation densities $\rho_{D,AB}$ and $\rho_{D,BA}$ are still unknown in Eqs. (23) and (24). Their values have been computed according to Eqs. (21) and (22) for ON and NO and plotted versus temperature in Fig. 4.

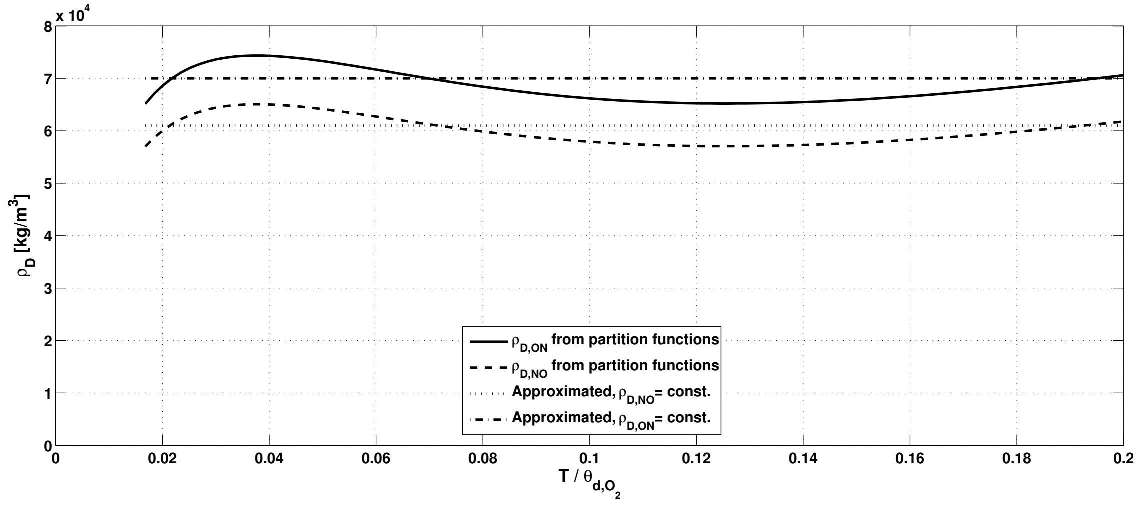

Figure 4: Characteristic dissociation densities $\rho_{D,ON}$ and $\rho_{D,NO}$

They show a weak temperature dependence which corresponding to Lighthill's ideal dissociating gas model can be approximated quite well by constant values with $\rho_{D,ON} \approx 7x10^4$ kg/m^3 and accordingly $\rho_{D,NO} \approx 6.1x10^4$ kg/m^3.

The results for the five-component air model are shown in Fig. 5 in comparison with reference data which are achieved with an in-house code employing a real gas model which is based on the equations of statistical mechanics and a thorough computation of the partition functions. Contrary to the four-component gas model now the s-shape behaviour visible for the degree of dissociation for the intermediate temperature regime is weaker yielding a better agreement to the reference data. This behaviour is caused by the formation of nitric oxyde at intermediate temperatures and its disappearance at even higher temperatures. This behaviour is missed in the four-component air model.

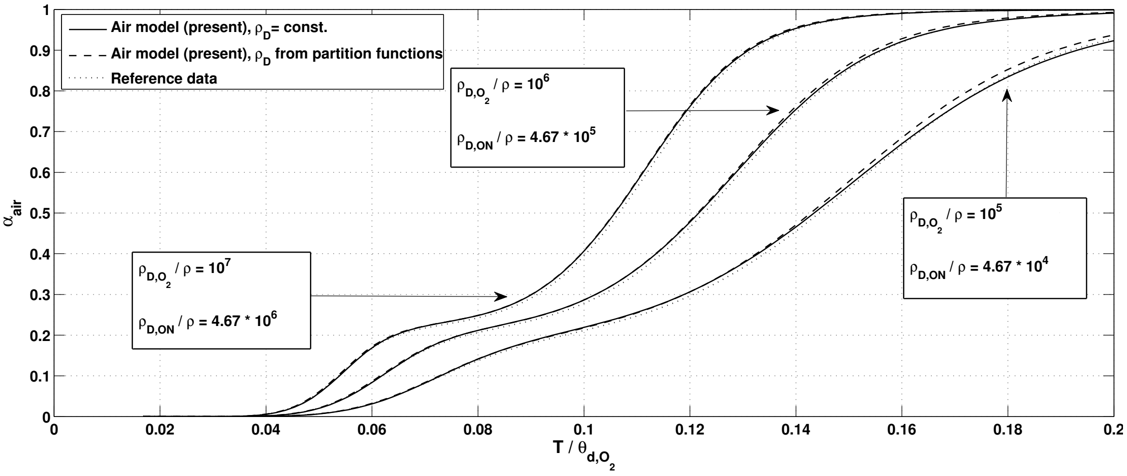

Figure 5: Degree of dissociation for five-component air model

With decreasing density for constant temperature, the degree of dissociation increases which is in agreement with Lighthill's ideal dissociating gas model. From Fig. 5 it is already obvious that there is a good agreement between the five-component gas model and the reference data. In case that the characteristic dissociation densities are calculated from Eqs. (12), (13), (21) and (22), i.e. their temperature dependence is taken into account as it is shown e.g. in Fig. 4, a maximum deviation of only about 3.5 % results between the five-component model and the reference data (see Fig. 6). Of course, in this case the calculation is a little cumbersome. The relative large errors for the low temperature regime are caused by the small dissociation degrees which in this regime are close to zero (see Fig. 5). This also explains the decrease of the relative error in this temperature regime with increasing temperature. The determination of the degree of dissociation becomes much less laborious if the characteristic dissociation densities are approximated as constant value as it was proposed by Lighthill. In this case, for the interesting temperature range the deviation between the five-component are model and the reference data is somehow little larger than for the previous case but not larger than 4 % (see Fig. 7). This impressively shows the validity of this simplification.

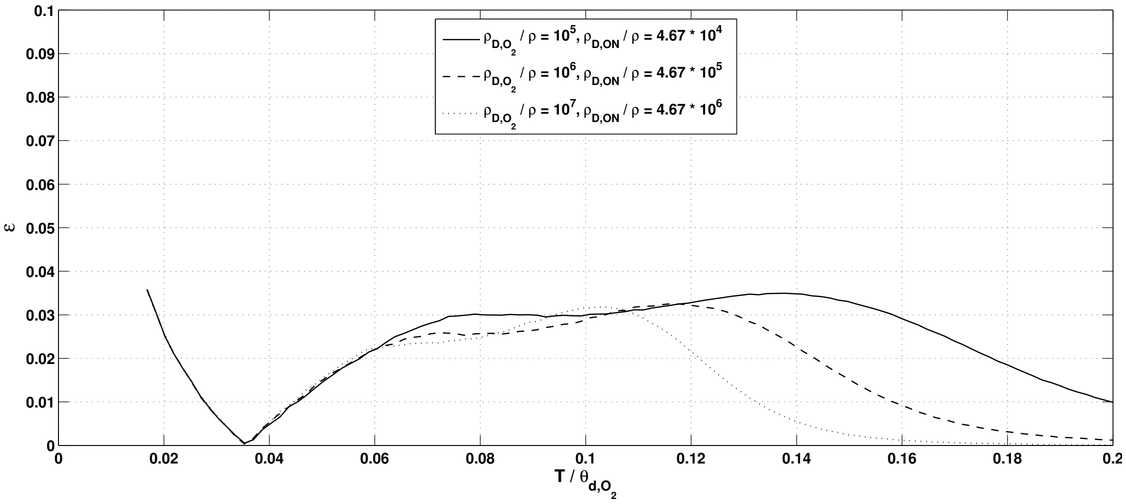

Figure 6: Relative deviation of the degree of dissociation for the five-component gas model to the reference data, characteristic densities of dissociation temperature dependent

The deviation of the equation of state and of the caloric equation to describe the internal energy and therewith the enthalpy of the gas is straightforward, but skipped at this place.

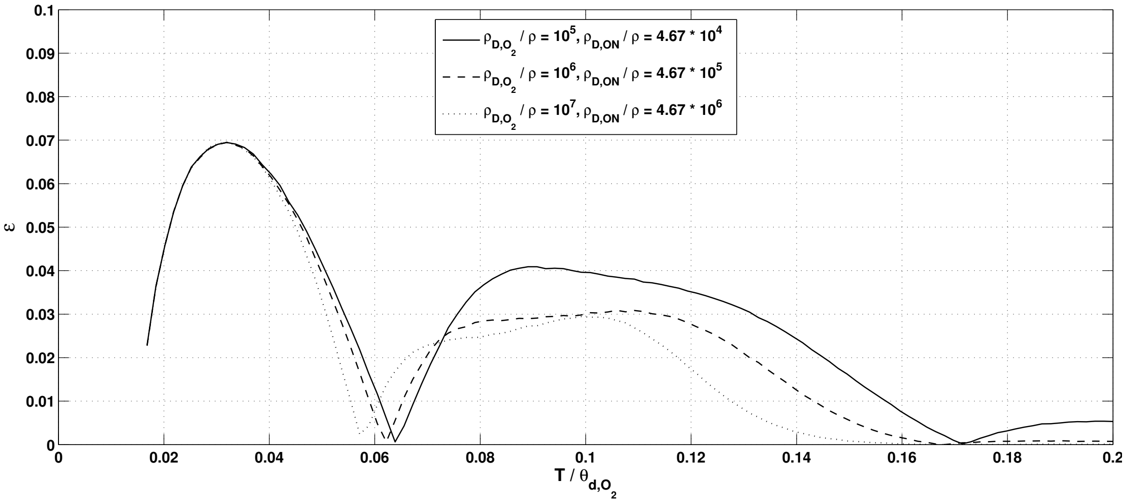

Figure 7: Relative deviation of the degree of dissociation for the five-component gas model to the reference data, constant characteristic densities of dissociation, $\rho_{D,O2} = 1.5x10^5$ kg/m^3, $\rho_{D,N2} = 1.3x10^5$ kg/m^3, $\rho_{D,ON} = 7.0x10^4$ kg/m^3

3. Conclusions

Despite the tremendous capabilities of today's numerical methods, simple analytical solutions of fundamental real gas phenomena are still necessary and worthwhile to be developed. These analytical models are useful to set up engineering relations and as part of more sophisticated models to describe more complex flow phenomena. Last but not least they are probably the most powerful tool to thoroughly analyze the physics of the considered phenomenon. For these reasons, Lighthill's ideal dissociating gas model is still in use for many fundamental studies. Its simplicity results from the limitation of considering only a one-component gas. This limits its accuracy especially for the interesting case of air with its different dissociation behaviour of oxygen and nitrogen.

In order to overcome these drawbacks, a five-component ideal dissociating gas model has been developed. Like Lighthill's model the present one introduces a characteristic dissociation density. It is shown that it is justified to approximate this value as a constant over the temperature range of interest which extends up to 12 000 K. Compared to an accurate equilibrium gas model, the maximum error of the new ideal dissociating gas model only amounts to 4 %. This is much better than Lighthill's model applying it for the case of air.

The application of this new gas model to determine not only the degree of dissociation but also the conditions of the thermal state and the gas enthalpy is straightforward.

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