ANALYSIS OF DIFFERENT APPROXIMATION LEVELS INTRODUCED IN THE DEVELOPMENTS FOR TRANSPORT COEFFICIENTS MODELS OF HIGH ENERGY AIR

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Abstract

Nomenclature

Symbol	Definition - CGS
D	Air mass diffusivity
R	Gas universal constant
T	Temperature in Kelvin
d	Mulecular diameter
k	Air thermal conductivity
r	Molecular distance
v	Velocity of flux
x	Position in direction flux perp.
μ	Air viscosity
c_i	Mass fraction i-specie
C_v	Specific heat at constant volume
C_p	Specific heat at constant pressure
D_m	Air self-diffusivity
D_i	Multicomponent diffusion coeff.
D_{ij}	Binary mass diffusivity
J_E	Energy flux
J_i	Mass flux
J_p	Impulse flux
k_i	Thermal conductivity
M_i	Molecular weigth
X_i	Molar fraction
a_{ki}	Fit coefficients for viscosity
b_{kij}	Fit coefficients for binary diffusivity
k_i	Thermal conductivity
ϵ	Interaction charactesristic energy
μ_i	Viscosity
Φ	Intermolecular potential
ρ	Density
$\Omega_{ii}(1,1)$	First Collision Integral
$\Omega_{ij}(2,2)$	Second Collision Integral

High energy air Transport Coefficients modelling is made either with semiempirical laws or following molecular theory of gases and liquids developments. Semiempirical models come from Sutherland's law for air viscosity. Instead, it is possible to develop different theoretical models using different approximation levels of the theory and different hypothesis on intermolecular potentials variations

The present work developed three models, the first is semiempirical, the other ones are theoretical. The results have been compared among themselves and in this manner it has been possible to investigate the temperature range in which the different modelling can be considered a critical effect. The present work evaluated the use of approximate sum rules to calculate air viscosity with respect to the use of theoretical exact sum rules use; this fact doesn't produce catastrophic effects.

Moreover , has been investigated the correction on binary diffusivity of the species ie pairs in air due to the presence of various components in mixture. We noted that is not important to introduce this kind of correction.

Introduction

When space vehicles reenter the atmosphere at hypersonic speed, high energies are developed in air surrounding the body. Energy transfer in different flow zones are very important. For this reason a correct modelling of Transport Properties is necessary to provide the thermal and

mechanical loads by CFD. We are speaking of temperatures higher than 1000 K.

In the complete flow equations there are the following quantities: air viscosity (μ), air thermal conductivity (k) and air mass diffusivity (D). They are a measure of the transfer respectively of impulse, thermal energy and mass in the different flow regions.

The viscosity for a specie is defined by the relationship:

$$j_p = \mu_i \cdot \frac{dv}{dx} \qquad (1)$$

The thermal conductivity for a specie is defined by the Fourier law:

$$J_E = k_i \cdot \frac{dT}{dx} \qquad (2)$$

The binary diffusivity for two species by the Fick law:

$$J = \rho \cdot D_{ij} \frac{dc_i}{dx} \qquad (3)$$

They suppose linear proportionality between the impulse, energy and mass flow with velocity gradients, temperature and mass concentration respectively. The quantities μ_i, k_i and D_{ij} naturally depend from temperature that is the measure of the gas molecules agitation, responsible for the trasport.

The air is a mixture of different species for which μ (air viscosity) and k (air conductivity) depend from μ_i and k_i respectively and from c_i (concentrations of different components in the gas mixture). The c_i depends from pressure and temperature and from the conditions in which the gas is considered : chemical equilibrium or chemical non-equilibrium.

For a mixture the multicomponent diffusion coefficients are defined:

$$J_i = \rho \cdot D_i \frac{dc_i}{dx} \qquad (4)$$

for a specie in the mixture.

The quantities μ, k and D_i are present in the Navier-Stokes equations for which a correct modelling with temperature variation is required.

Semiempirical and Teorethical models

At present, two kinds of approches to model Transport Coefficient variation with temperature are possible: the semiempirical one and the theoretical one.

The semiempirical model developed in this work is based on air viscosity Sutherland's law [1]:

$$\mu = 1.462 \cdot 10^{-5} \frac{T^{\frac{1}{2}}}{1 + 112/T} \qquad (5)$$

proposed at the end of 19th century. Espresion (5) is in good agreement with experimental results at no high temperatures (< 1000 K) for which measurements are available.It permits us the calculation of even the air thermal conductivity and air mass self-diffusivity. In fact, there are two simple relationships that link k and D to μ, if molecular elastic collision is supposed:

$$k = \frac{15}{4} \cdot \frac{R}{M} \cdot \mu \cdot \left(\frac{4}{15} \cdot \frac{C_v}{R} + \frac{3}{5} \right) \qquad (6)$$

for the thermal conductivity and

$$D_m = \frac{1.4 \cdot k}{\rho \cdot C_p} \qquad (7)$$

for the mass diffusivity. Expression is the Eucken's law, that considers even the molecular vibrational freedom degrees.

The theoretical approch considers the intermolecular potential presence between the particles constituing the gas. This theoretical treatment has been made by Chapman and Cowling [2] and after has been completed by [3]. It is based on thermodynamic considerations associated with the classical mechanical laws describing the molecular collision in presence of central potentials.

For a i-specie holds the theoretical relationship

$$\mu_i = 26.693 \cdot 10^{-6} \cdot \frac{(M_i T)^{\frac{1}{2}}}{\Omega_{ii}(2,2)} \qquad (8)$$

for the viscosity, and

$$D_{ij} = 2.6280 \cdot 10^{-3} \cdot \frac{\left(T^3 \cdot \left(\frac{1}{M_i} + \frac{1}{M_j} \right) \right)^{\frac{1}{2}}}{p \cdot \Omega_{ij}(1,1)} \qquad (9)$$

for the binary diffusion between i-specie and j-specie. The quantities $\Omega_{ii}(2,2)$ and $\Omega_{ij}(1,1)$ are function of temperature. They are Collision Integrals and depend from intermolecular potentials between equal species (ii) and between different species (ij). They require great calculation efforts and are tabulated only for fixed temperatures. For thermal conductivity the theory is not able to give us a relationship similar to expressions (8) and (9) for which is possible only to use the expression(6).

The formulas (8) and (9) give us results only for a temperature discrete set and the Collision Integrals are tabulated in literature for different Intermolecular Potential shapes. In the following developments, the expressions (8) and (9)

have been approximated with relationships of this kind ([4] and [5]):

$$\mu_i = exp(a_{0i} + a_{1i} lnT + a_{2i} lnT^2 + a_{3i} lnT^3) \quad (10)$$

for i-specie viscosity and

$$D_{ij} = exp(b_{0i} + b_{1ij} lnT + b_{2ij} lnT^2 + b_{3ij} lnT^3) \quad (11)$$

for binary diffusivity between specie and j-specie.

Two theoretical models have been developed. The first one is indicated in the following developments so Lennard-Jones model and it considers between molecules an Intermolecular potential of this kind [7]:

$$\Phi = 4\epsilon \left(\left(\frac{d}{r} \right)^{12} - \left(\frac{d}{r} \right)^6 \right) \quad (12)$$

where d is the specie molecular diameter, ϵ the interaction characteristic energy, r the distance between the molecular centres. For interactions between different species, the potential is obtained so an average of potentials between equal species. This simplification impacts heavily on binary diffusion coefficients calculation.

The second theoretical model is indicated so Yun and Mason model and has been developed to investigate the effects of 'modern' intermolecular potential on Transport Coefficients. The Collision Integrals are tabulated on [6] and they come from semiempirical intermolecular potential fits of experimental data. Interactions between different species are considered. The Lennard-Jones model is much more simplified than the Yun and Mason one.

Single specie results : different models

Results for the main five species in the air (N_2, O_2, NO, N, O) has been obtained. Three models has been developed : semiempirical, Lennard-Jones and Yun-Mason. In refernce [8] are reported the fit coefficients of relationships (10) and (11) calculated for single specie viscosity and for specie pairs binary diffusivity. Figures 1 and 2 show viscosity of the five species calculated with Lennard-Jones and Yun-Mason models. The air Sutherland law behaviour is reported also.

The plots show very interesting behavior:

- Sutherland's law presents much lower values than other curves after 2000 K.

- The curves order is different for Lennard-Jones and Yun-Mason models. For example the atomic nitrogen curve is the curve with lowest values for Lennard-Jones model and is the curve with highest values for Yun-Mason model.

- The Yun and Mason model is coherent with physical expectation, because the curves N, O are similar , and the curves N_2, O_2 and NO are similar, being discriminating the molecular weight.

Consequently the three models show substantial differences between them, in particular for high temperatures.

Figure 3 shows the binary diffusivity of atomic oxygen in molecular oxygen and of atomic nitrogen in atomic nitrogen. The two images show the variations calculated with Lennard-Jones model and with Yun-Mason model. Fifteen figures of this kind has been obtained for all the specie pairs in air; only two are reported for brevity [5]. In general different behavior for different models has been observed. In particular for curves regarding atomic nitrogen have been observed catastrophic differences. This fact indicates Lennard-Jones model for nitrogen limitations in coherence with figures 1 and 2.

These comparisons show the strong sensibility of the Transport Properties to the use of different models for species in air at temperatures interesting for hypersonic problems.

Sum Rules

Air is approximatively a mixture of five gases, of which compositions vary with pressure and temperature. The air Transport Coefficients are calculated opportunely summing the single specie or single pair ones.

The mixture viscosity come from a sequence of analytical relationships very laborious to calculate. They are reported in [3] at pages 531 and 532. It is necessary to calculate determinants of 5x5 and 6x6 matrices and of the quantities A_{ij}^* defined by $\Omega(2,2)/\Omega(1,1)$ dependent from temperature, whose fits are reported in [5].

The Wilke law is reported in [9] and is an approximate semiempirical relationship to calculate mixture viscosity and it is at the moment the most used in literature. It, even if complex, can be implemented in CFD codes, without a catastrofic effort in terms of CPU time.

The air thermal conductivity is calculated from air viscosity using relationship (6).

The calculation of the five multicomponent diffusion coefficients for O, N, NO, N_2, O_2 in air is

made using simple semiempirical laws. The most used rule is the following [10] :

$$D_{im} = \frac{1 - c_i}{\sum_{j \neq k} \frac{X_j}{D_{jk}}}$$ (13)

The knowledge of gas specie concentrations, gas specie molar fractions and binary diffusivities is required.

The binary diffusivities in relationship (13) can not be calculated from the relationship (9), that holds for binary gas mixtures. It is necessary to correct relationship (9) considering the presence of various species in the mixture. The theory developed in [3] is able to give us correct formulas for D_{ij} of a multicomponent mixture and at page 541 there is a sequence of laborious relationships to calculate. Precisely it is reqired the knowledge of all the simple binary D_{ij}, of the molar fractons, of the molecular weigths and the calculation of the minors for a particular 6x6 matrix.

Air results : different models

The air viscosity and the five multicomponent diffusion coefficients have been calculated varying temperature; the approximate sum rules have been used, the Wilke law and the formula (13) respectively. The binary diffusivity was not correct for the presence of various species in the mixture. The air species concentrations has been calculated supposing chemical equilibrium and using the Park model([11] and [12]).

Figure 4 shows the results obtained for the three models : semiempirical, Lennard- Jones and Yun-Mason for air viscosity. The air chemical composition has been calculated for a pressure of 1 atm.

The three curves are superimposed until about 1000 K, where there are experimental results. After 4000 K the differences of the three models are very sensible in particular for the Yun-Mason model. We remember that after 8000 Kelvin the presence of free electrons, which we didn't consider, is important.

Figure 5 has two pictures. The first one is the air viscosity considering an air chemical composition 'frozen' at standard composition, the second one is the air viscosity considering an air chemical composition with oxygen and nitrogen completely dissociated. The three developed models are compared showing differences after 1000 K.

Figure 6 shows two calculated multicomponent diffusion. The Lennard-Jones and the Yun-Mason models are compared and it is possible to note sensible differences for high temperatures.

After the analysis in this section we can conclude that the different results for trasport prop-

erties for the three models for the air single species create sensible differences even for the air mixure properties.

Correct and approximate Sum Rules: effects on air

In this part of the work, the approximations introduced by semiempirical sum rules have been evaluated.

The air viscosity has been calculated using the Wilke law for different pressure values in chemical equilibrium conditions. The variation with temperature is shown in figure 7. The pressure determines different concentrations values and different viscosity values. The pressure effect is not catastrophic on the results. In the same figure there is also the air viscosity at different pressure calculated using the correct relationships reported in [3]. The curve in this second graph doesn't differ substantially compared to the curve in the first graph. The figure 8 is the ratio between correct and approximate air viscosity for different pressure, showing that the use of the Wilke law is a very good approximation to calculate air viscosity.

Furthermore the fifteen binary diffusivity curves have been calculated using relationship (9) and has recalculated taking in account the presence of various species in the air mixture. All calculations has been made considering a pressure of 1 atm and the air mixture in chemical equilibrium conditions. The relationships in [3] has been used. The results for two pairs of species are shown in figure 9.

Moreover, the multicomponent diffusion coefficients of O_2, N_2, NO, N, O in air has been calculated with 'correct' binary diffusivities and using relationship (13). Figure 10 shows an example of the results.

Even for the air diffusion there are not substantial differences between the use of simple binary diffusivity or of 'correct' binary diffusivity.

In general the use of approximated sum rules for the air trasport properties calculations is correct.

Conclusions

The use of different approximation levels in the air trasport properties modelling has been evaluated.

For each specie in the air mixture the Trasport Coefficients variations with temperature has been calculated with three models : semiempirical, Lennard-Jones and Yun-Mason representing three approximation levels. We obtained sensible differences between the models when the temperature increases. At present the 'most correct'

model is considerad the Yun-Mason that is the most complex model.

The viscosity, thermal conductivity and multicomponent diffusion coefficients have been calculated for the air in chemical equilibrium, using the previous three models and approximated sum rules. The comparison of the obtained results indicated differences for the different models with increasing temperature.

The second part of the work investigated the 'goodness' in the use of an approximate sum rule for air viscosity and air thermal conductivity calculations (the Wilke's law). A comparison with results obteined by complex, but correct sum rules has been made. We didn't find great differencies in these comparisons. It is correct the use Wilke's law for calculations regarding air mixture.

Moreover the multicomponent diffusion coefficients has been calculated using binary diffusivities, corrected for the presence of various species in the mixture. These last five coefficients don't differ with respect to the coefficients calculated with simple binary diffusivity. This approximation can be made.

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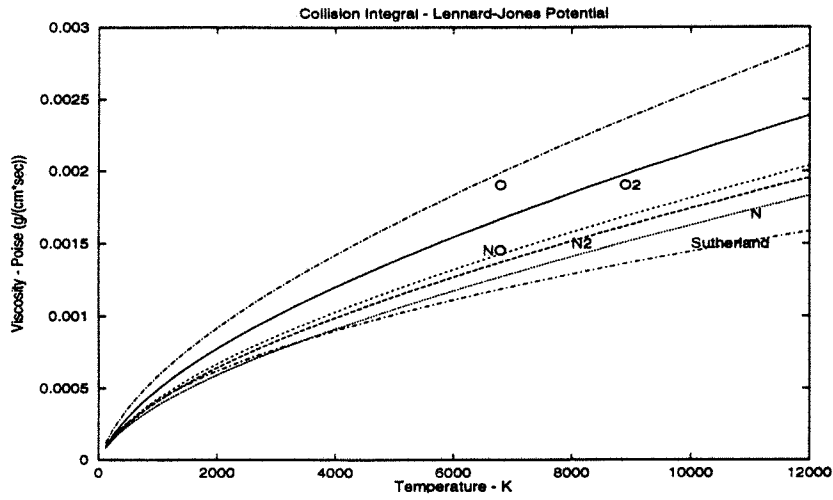
Figure 1: Viscosity for air species calculated by Lennard-Jones model and Sutherland law.
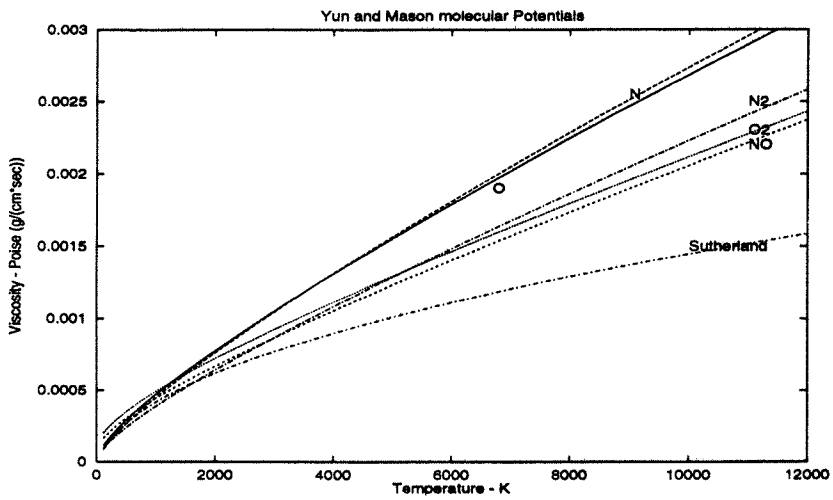

Figure 2: Viscosity for air species calculated by Yun and Mason model and Sutherland law.
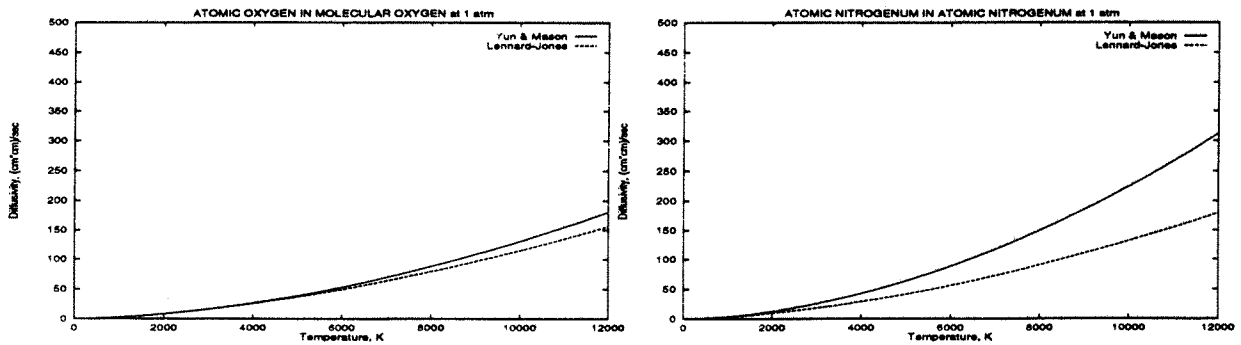

Figure 3: Binary mass diffusivity for Atomic oxygen in Molecular oxygen and for Atomic Nitrogen in Atomic Nitrogen - Different models comparisons.
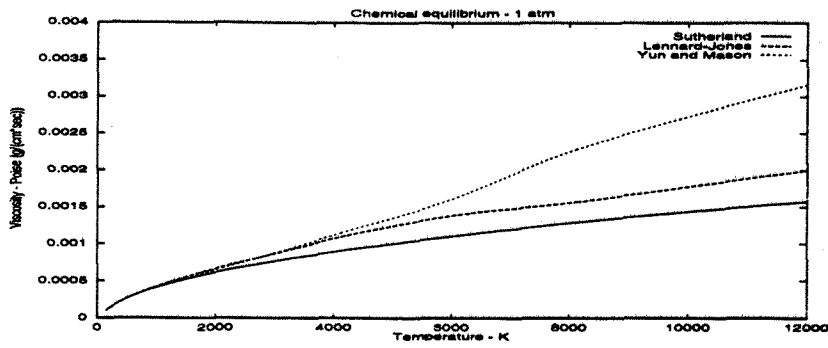
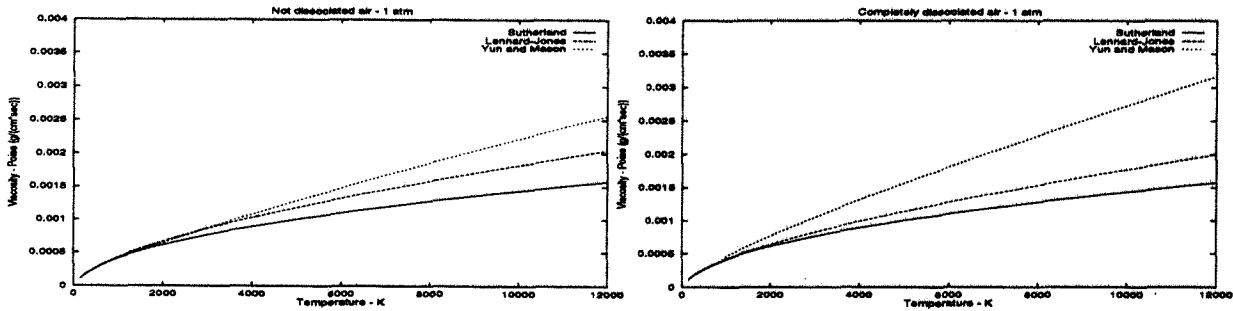Figure 4: Air viscosity in chemical equilibrium at 1 atm. Comparison between different models.

Figure 5: Air viscosity 'frozen' at standard conditions and not completely dissociated at 1 atm - Different models comparisons.
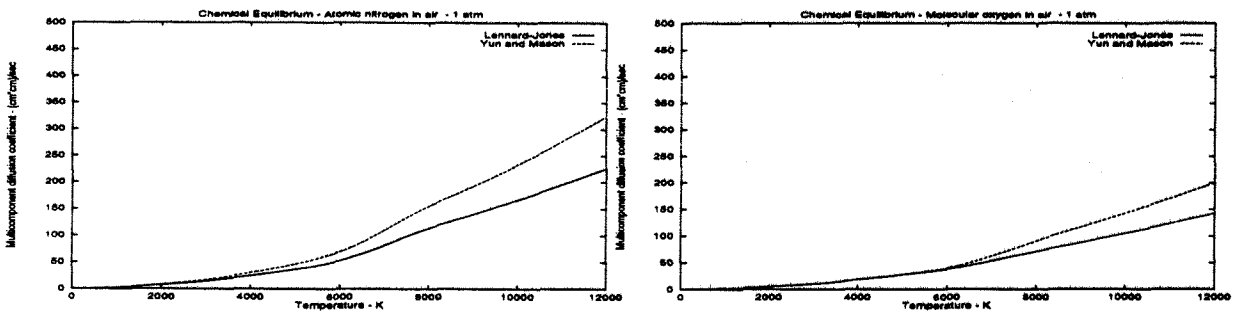
Figure 6: Multicomponent diffusion coefficients for Atomic nitrogen in Air and Molecular Oxygen in Air. Comparison between different models.
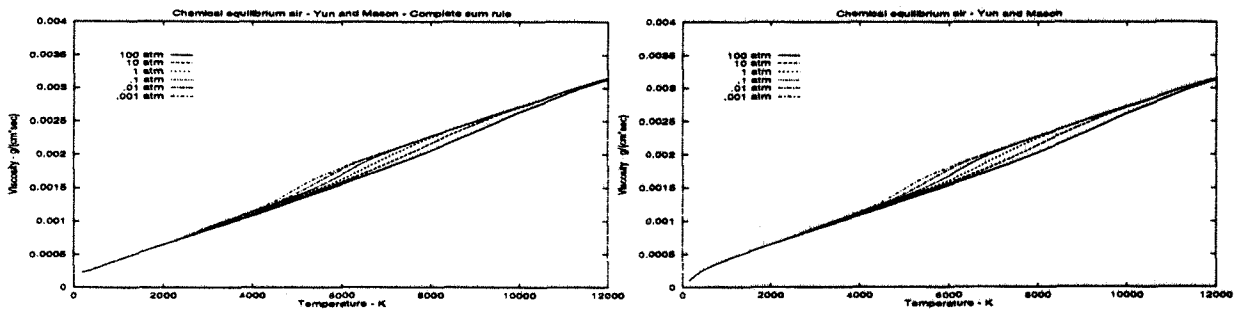

Figure 7: Air viscosity at different pressures calculated with approximate and correct sum rules respectively.
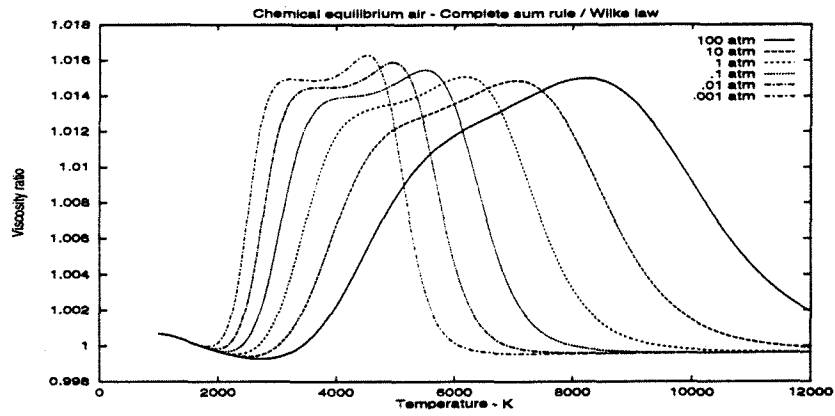
Figure 8: Air viscosity ratio between calculations made with approximate and correct sum rule at different pressures.
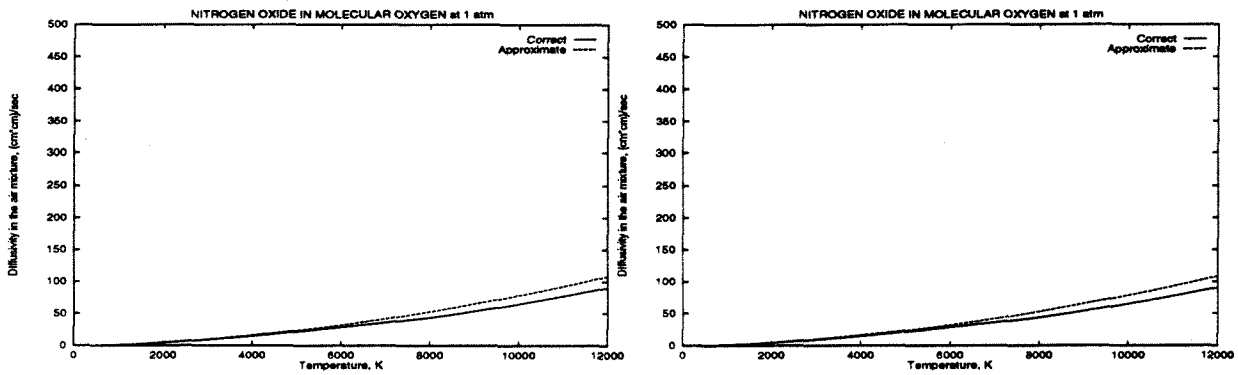

Figure 9: Binary diffusivity for atomic oxygen in atomic nitrogen and for nitrogen oxide in molecular oxygen. Comparison between correct and approximate calculations.
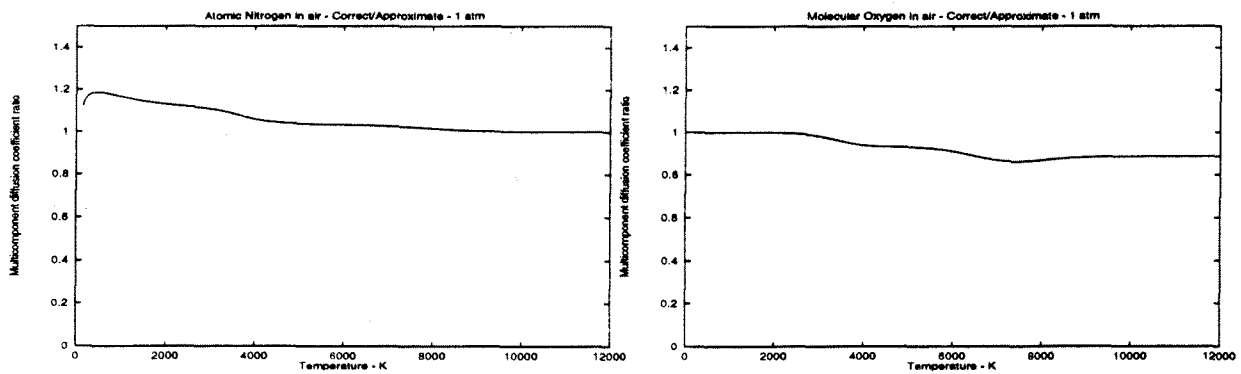

Figure 10: Multicomponent diffusion coefficients for atomic nitrogen in air and for molecular oxygen in air. Comparison between correct and approximate calculations.