EquilTheTA: a web-access tool for LTE plasma thermodynamics and transport properties

A. D'Angola[1,2], A. Laricchiuta[1], G. Colonna[1]

[1]*PLASMI Lab NANOTEC CNR, Bari, Italy*

[2]*Scuola di Ingegneria, Università della Basilicata, Potenza, Italy*

Introduction

EquilTheTA is a web-access tool to calculate thermodynamic and transport properties of complex plasmas in local thermodynamic equilibrium (LTE) in a wide pressure and temperature range. The code is composed by different modules: Statistical Thermodynamics, Equilibrium Solver, Transport Properties. The code is accessed through a friendly interface which includes the possibility of creating a plasma mixture starting from the species and of setting the thermodynamic conditions (pressure or density, temperature).

Statistical Thermodynamic module

The first step of equilibrium calculation is the determination of the partition functions of each species in the mixture, necessary to calculate the equilibrium constant of chemical reactions [1]. The partition functions of the species are expressed as the product of the translational and internal contributions

$$\mathscr{Q}_s = \mathscr{Q}_s^{tr} \mathscr{Q}_s^{int} \tag{1}$$

which is calculated directly from the internal levels of atomic and molecular species, or, if available, read from the internal database. For diatomic molecular species, also quasi–bound states are included. Particular attention is taken to calculate the atomic partition functions: a) the level set available from databases has been completed with the Ritz-Rydberg series; b) a self consistent cutoff, function of the particle, electron and ion densities, is used to limit the series. The latter introduces a dependence of $\mathscr{Q}_{int}$ on the plasma composition, therefore it should be updated during the equilibrium calculation [2]. Once the equilibrium composition has been determined, all internal thermodynamic properties

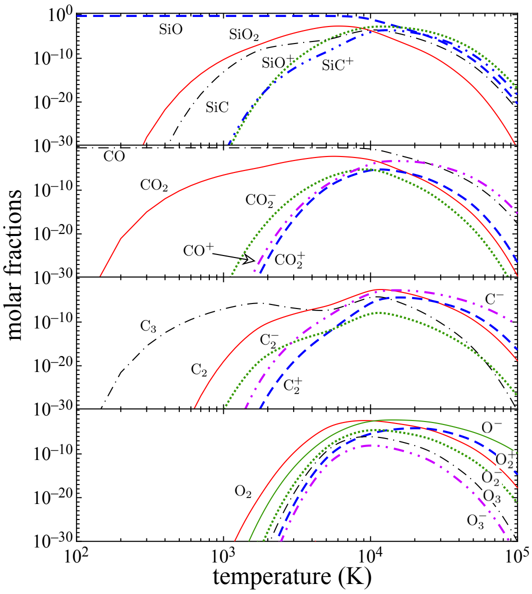

Figure 1: *Molar fractions of SiC + O_2.*

of the species are calculated. Virial and Debye-Hückel corrections are also considered, this last, depending on the gas composition and affecting the thermodynamic state of the plasma, are updated self-consistently during equilibrium composition. Then, all the mixture properties, including derivatives (specific heats, isentropic coefficient), are evaluated.

Chemical equilibrium module

The calculation of plasma chemical equilibrium composition has been widely investigated [3, 4]. EquilTheTA is based on a fast and stable hierarchical approach [5, 6], which consists in solving one equilibrium equation at a time, ordered on the *reaction distance*. The solver includes Debye–Hückel corrections, cutoff for atomic levels, consistently updated, and virial corrections. The hierarchical algorithm is based on the automatic determination of a shortcut reaction that produces in a single step the same advancement resulting from several steps.

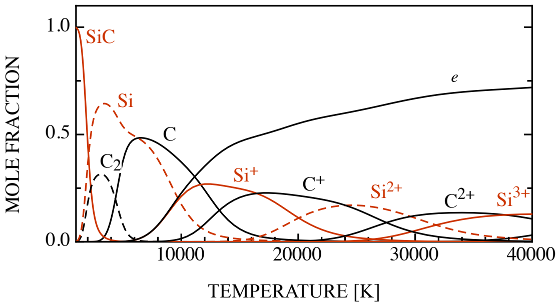

Figure 2: *Equilibrium composition of silicon carbide plasma at 1atm.*

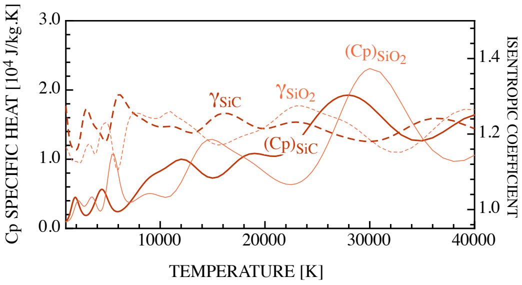

Figure 3: *Specfic heat (solid lines) and isentropic coefficients (dotted lines) for SiC and SiO_2.*

In a system of N reactions, the jth reaction is

$$\sum_{i=1}^{Nr_j} Cr_{j,i} R_i^{(j)} \rightleftharpoons \sum_{i=1}^{Np_j} Cp_{j,i} P_i^{(j)} \tag{2}$$

where Nr_j and Np_j are the number of reactants $R_i^{(j)}$ and products $P_i^{(j)}$, where $Cr_{j,i}$ and $Cp_{j,i}$ are the stoichiometric coefficients (all positive) of the relevant species. The reaction quotient Π_j of reaction in Eq. (2) is defined as

$$\Pi_j = \frac{\Pi p_j}{\Pi r_j} \quad \text{where} \quad \Pi p_j = \prod_{i=1}^{Np_j} [P_i^{(j)}]^{Cp_{j,i}} \quad \text{and} \quad \Pi r_j = \prod_{i=1}^{Nr_j} [R_i^{(j)}]^{Cr_{j,i}} \tag{3}$$

being $[X_i]$ the species concentration of the generic i-th species. Using the mass action law, the equilibrium condition is given by

$$\Pi_j^{eq} = K_j^{eq} \Leftrightarrow \Pi p_j^{eq} = \Pi r_j^{eq} K_j^{eq} \tag{4}$$

The order of the chemical reactions is based on the definition of the reaction position ϑ_j (with respect to equilibrium), that is null at equilibrium, or alternately, it is shifted towards reactants ($>$0) or products ($<$0).

Two distances with different properties can be defined, as follows:

$$\vartheta_{1j} = K_j^{eq}\Pi r_j - \Pi p_j \qquad \vartheta_{2j} = \begin{cases} 1 - \frac{\Pi p_j}{K_j^{eq}\Pi r_j} & \text{if } \Pi p_j < K_j^{eq}\Pi r_j \\ \frac{K_j^{eq}\Pi r_j}{\Pi p_j} - 1 & \text{if } \Pi p_j > K_j^{eq}\Pi r_j \end{cases} \tag{5}$$

where ϑ_1 is adequate to find majority species, because it privileges reactions with higher equilibrium constant, and ϑ_2 is useful for refining the solution. Therefore both distances are used in EqulTheTA to improve the performances.

Shortcut reactions [6] are automatically added to speedup the convergence when a trap, i.e two reactions solved repetitively with a small advancement toward equilibrium.

As an example, Figure 1 shows molar fractions of molecules and atomic negative ions obtained in the case of a plasma of technological interest such as SiC+O_2 [7], which represents a complex chemical system. Moreover, Figures 2 and 3 show respectively the equilibrium composition and thermodynamic properties of the SiC and SiO_2 systems up to a temperature of 40 000 K, at atmospheric pressure.

Transport coefficients module

Transport coefficients are calculated by using high order approximations of the Chapman-Enskog method [8]. The first-order approximation of transport coefficients includes the calculation of $\Omega_{ij}^{(1,1)}$ and $\Omega_{ij}^{(2,2)}$, while $\Omega_{ij}^{(1,2)}$ and $\Omega_{ij}^{(1,3)}$ are required to extend the calculation to a second-order approximation. For the calculation of the electrical conductivity and of the electron contribution to the translational thermal conductivity, $\Omega_{ij}^{(1,4)}$, $\Omega_{ij}^{(1,5)}$, $\Omega_{ij}^{(2,3)}$ and $\Omega_{ij}^{(2,4)}$ for interactions between electrons and other particles (including e-e collisions) are also required. EquilTheTA provides these data for an extended species database. The viscosity coefficient is calculated using the first-order approximation considering negligible the contribution of the electrons. The total thermal conductivity of plasma is calculated as the sum

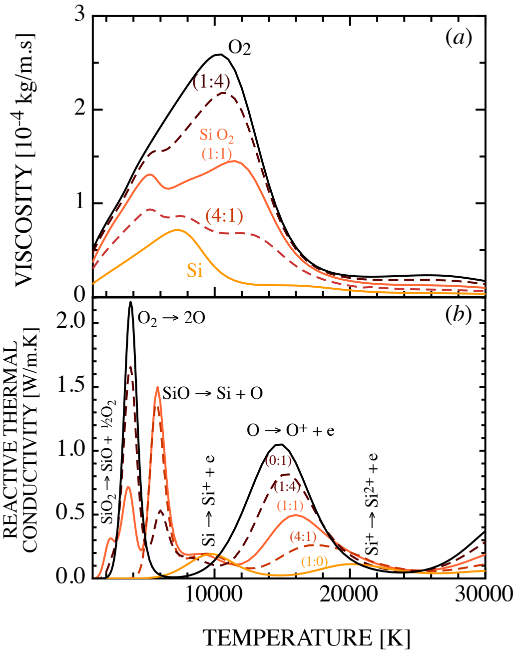

Figure 4: *Viscosity and reactive thermal conductivity, at 1 atm, for Si/O_2.*

the internal, the reactive and the translational contributions. The translational contribution is calculated considering a non-reacting plasma of spherical molecules without internal degrees of freedom and, as for the coefficient of viscosity, is considered as the sum of the heavy particles and the electron contributions. The Eucken [9] approximation and the Butler-Brokaw [10] equation have been used for internal and reactive thermal conductivities. Finally, the electric conductivity is calculated using the third approximation proposed by Devoto [11] to compute the ordinary diffusion coefficient neglecting the contribution of the ions to the current. Figure 4 shows the temperature profiles of viscosity and reactive thermal conductivity of Si/O_2 plasma, considering the parametric variation of the ratios Si/O_2, exhibiting a large sensitivity to the ratio of components. The peak structure of the total thermal conductivity mirrors the changes in the plasma composition associated to the onset of dissociation and ionization equilibria.

The stability of the calculation of transport properties requires to write a set of reactions in which all all the species are related to a basis composed by independent species with higher concentrations. Together with transport cross sections calculated from multi-potential approach [12], the database has been completed with the phenomenological approach [13].

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