Numerical codes for the evaluation of thermodynamic properties are necessary tools not only for the characterization of high–pressure (LTE) plasmas but also for systems far from equilibrium, when the equilibrium constants are needed in relating direct and reverse processes through the detailed balance principle. Thermodynamic data represent also a relevant information for the calibration-free analysis applied to the emission spectra measured with the LIBS technique [1].

The theoretical framework to obtain accurate thermodynamic properties is the statistical physics: all the thermodynamic functions are derived from the internal partition functions of each species $s$ in the mixture, $Q_{s}^{\text{int}} = \sum g_{s,i}e^{-\varepsilon_{s,i}/kT}$, where $g_{s,i}$ and $\varepsilon_{s,i}$ are the statistical weight and the energy of the $i$-th level, respectively. Few tabulations do exist of the partition functions for both atomic and molecular species [2], however the temperature interval covered is not wide-enough for all the applications, this representing the main limit especially for neutral and ionized atoms, dominant species in the high-temperature region. For atomic species, partition functions depend on both temperature and composition, in fact the number of electronic levels that enter the summation is truncated, to avoid divergence, using a cutoff [3], whose value is mainly related to the electron density. As a consequence, the partition functions should be updated any time plasma composition changes, increasing the computational resources dedicated to thermodynamics. On the other hand, the calculation of the internal partition function for molecules, $Q_{s}^{\text{int}}$, though not affected by the divergence problem, is characterized by a high-computational-cost, due to the huge number of ro–vibrational levels for each electronic state to be accounted for. To simplify thermodynamic calculations, the single species properties are

![Figure 1: Internal contribution to energy normalized to RT, as a function of temperature for nitrogen and hydrogen in SbS and TLM calculated with self-consistent cutoff in air and Jupiter atmosphere respectively.](image-url)
usually stored as a piecewise polynomial fitting of the temperature [4]. This approach however cannot consider a variable cutoff of atomic species and therefore it is not suitable for high temperature calculations. In previous papers [5, 6] an alternative approach, the two–level model (TLM), has been proposed, calculating the atomic partition functions [5] in a simplified level scheme that considers the low-lying states and a fictitious level lumping all high-energy levels, whose energy and statistical weight are properly averaged, i.e. \( G_s = \sum_{i=0}^{i_{\text{max}}} g_s,i \) and \( \mathcal{E}_s = (\sum_{i=0}^{i_{\text{max}}} g_s,i \mathcal{E}_s,i) / G \). These quantities do not depend on the temperature, but only on the number of levels inserted in the summation, i.e. on the cutoff. In this case the partition function is calculated (in the first-order approximation) as \( \mathcal{Q}_s = \sum_{i=0}^{i_{\text{max}}} g_s,i e^{-\mathcal{E}_s,i/kT} + G_s e^{-\mathcal{E}_s/kT} \), while higher order corrections can be added to further reduce the errors. This scheme not only increases the code efficiency but allows a smoothing of the discontinuities observed in partition function temperature profile and introduced by the cut-off, due to its step-behavior when, increasing the temperature, a new level enter the summation (Mott’s effect [7]). The discontinuities are usually eliminated by considering a continuous weighting function of the cutoff for each level, ranging from 0 and 1 [8]. In the two–level model, fitting the lumped level properties \((G, E)\) as a function of the cutoff allows to use this data self-consistently, avoiding the discontinuity in \( \mathcal{Q}_s \) and also their amplified propagation to internal energy and specific heat, more pronounced in high-pressure regimes. Extending and completing the work done in Ref. [5], where the properties of different atomic species calculated with TLM the have been compared with the State-by-State (SbS) calculations changing the cutoff parametrically, a database of \( G_s \) and \( \mathcal{E}_s \) values, fitted as a function of the cutoff, has been created for a large number of atomic and atomic ion species and already implemented in the EquiTheTA tool [9]. This tool has been used to calculate the equilibrium composition of Earth (\( \text{N}_2[80\%] ; \text{O}_2[20\%] \)) and Jupiter (\( \text{H}_2[89\%] ; \text{He}[11\%] \)) atmospheres in wide temperature and pressure ranges. The results have been obtained adapting self-consistently the cutoff with the plasma composition, combining the Griem and Fermi criteria [3] and including non-ideal corrections to thermodynamic
quantities in Debye-Hückel approximation.

The behaviors described above can be observed in Fig. 1, where the internal contribution to internal energy of nitrogen and hydrogen atoms, calculated self–consistently with the cutoff in the relative mixtures have been reported for $P=1000$ bar, comparing the values obtained with SbS with those calculated using the TLM. For nitrogen the discontinuity are less pronounced because, being broken the $\ell, m$ degeneracy, the levels are more distributed in the energy scale. Similar behaviors are observed for all atomic species ( neutrals and ions) and for other thermodynamic properties. The discontinuities in single species properties are reflected on the mixture behaviors. In Fig. 2 the frozen, constant pressure, specific heat ($C_{pf}$) has been reported as a function of the temperature for the two mixtures, comparing results obtained with SbS and TLM approaches. The frozen specific heat is calculated simply summing the single species property weighted by the molar fractions $\chi_s$, i.e. $C_{pf} = \sum_s \chi_s (5/2 + C_{int, s})$. It should be noted that the jumps observed in Fig. 1 are present also in this case, while the TLM results are represented by a smooth function. If we consider the global, constant pressure specific heat, $C_p = \left( \frac{\partial U}{\partial T} \right)_P$ or constant volume specific heat $C_v = \left( \frac{\partial U}{\partial T} \right)_v$, we should notice that they can be expressed as the sum of the frozen and of the reactive contributions, this last depending on the temperature derivatives of species densities. The two terms in the specific heats are affected by the internal thermodynamic quantities in opposite way, resulting in a compensation between the different contributions, as can be observed in Fig. 3 where the constant pressure and constant volume specific heats for Earth atmosphere are reported. The TLM results present, also in this case, a smooth behavior, while the SbS curves show deviations, much smaller than that observed for the frozen specific heat (Fig. 2). These results can lead to the wrong conclusion that that contribution of internal states is negligible in the equilibrium calculation. In fact, the differences between TLM and SbS observed in the specific heats are amplified in the isentropic coefficient [10] (see Fig. 4). $\gamma = C_p/C_v$, especially for the air mixture. It should be noted that flow properties are strongly affected by $\gamma$. 
The TLM demonstrates to accurately reproduce the results obtained with the SbS approach, including in a simplified way the complex level information built for atomic species with the extension of level-series up to the ionization limits, to reduce significantly the computational cost (the efficiency is expected to be further improved once the lumped-level-database will be extended also to molecular species) and to cure the problems connected to the use of traditional self-consistent cutoff criteria.

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