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Population densities and partition functions of partially ionized ideal and non-ideal multi-component plasma mixtures in P–T phase space

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Abstract. In most practical situations, for multi-component non-ideal complex plasma mixtures in pressure–temperature (P–T) phase space, the problem of solving the system of coupled nonlinear Saha equations subjected to the constraints of electro-neutrality and conservation of nuclei is found to be effectively a one-dimensional nonlinear problem, i.e. solving a *single* transcendental equation. Computation of ionization stages and partition functions in the P–T phase space is particularly important for non-ideal plasmas generated in devices in which pressure is a reliably measurable parameter while it is difficult to measure the number density of heavy particles. The methodology and algorithm presented herein are based on deriving an equivalent single transcendental equation, for which the solution is eminently trivial. The algorithm takes into account different practical models for non-ideality corrections (lowering of ionization potentials, truncation of partition functions and a corrected equation of state). The ease and efficiency of the introduced algorithm allows, with significant simplicity, the computations of population densities of all plasma species (ionized and excited) up to maximum ionization states equal to the atomic numbers of the involved elements with minimal computational work. It also considers an extensive database of energy levels of the excited states. The algorithm presented herein is analytically known to be safe, fast and efficient. It shows no numerical instabilities, no convergence problems and no accuracy limitations or lack of change problems, which have been reported in the literature. A couple of non-trivial problems are worked out and presented herein showing the effectiveness of the present methodology. For completeness, a criterion for the validity of the assumption of local thermodynamic equilibrium (LTE) is applied to the results from the sample problems, showing the regions of the pressure–temperature phase space over which the assumption is valid.

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1. Introduction

An accurate description of thermodynamic, optical and transport properties of various substances over a wide region of the pressure–temperature (P–T) phase space is of fundamental as well as practical interest. Of great importance to many applied problems is the case of high-temperature, partially ionized gas mixtures (plasma mixtures). Nowadays a great number of plasma mixtures have come into extensive use in a variety of industrial and engineering applications. Reliable information about thermodynamic, transport and radiative properties of complex plasma mixtures over a wide range of temperatures and pressures is required for the solution of many scientific and technological problems arising in industrial plasma engineering, and high-energy density physics. However, a quantitative investigation of these properties necessitates information concerning the detailed population densities of plasma species at specified temperature and pressure. Population densities of plasma components (neutrals and charged) in the ground and excited states are required for the calculation of the plasma equation of state, internal energy, entropy, enthalpy, sound speed, specific heats, adiabatic exponent, as well as transport properties such as electric conductivity, viscosity, thermal conductivity, opacities and ion stopping power. Shielding gases for laser and plasma arc welding [1], gas mixture discharges in thermal plasma processing [2], gas mixtures used for X-ray emission and other purposes in small plasma focus experiments [3, 4], plasmas generated from polyethylene and Lexan polycarbonates in the source section of electrothermal-chemical plasma guns [5–7], dense plasma lasers, as well as plasma mixtures generated in the chamber of inertial fusion energy (IFE) reactors from the molten salts Flibe and Flinabe or any other proposed compound liquid wall material [8, 9] are examples of plasma mixtures for which computing the detailed plasma composition is required for the development, functioning and optimization of these devices and technologies. In regimes where the assumption of Local Thermodynamic Equilibrium (LTE) is applicable, the populations of atoms and their ionization products (ions and electrons) obey the Saha equation [10]. If the lowering of ionization potentials due to non-ideal effects [11–14] is taken into account, the Saha equation (for a single chemical plasma species) can be written as

$$\frac{n_{r+1}n_{\mathrm{e}}}{n_r} = 2\frac{U_{r+1}}{U_r}\left[\frac{2\pi m_{\mathrm{e}}K_{\mathrm{B}}T}{h^2}\right]^{3/2}\exp\left(-\frac{I_r^{\mathrm{eff}}}{K_{\mathrm{B}}T}\right) \quad r = 0, 1, \ldots, (Z-1), \tag{1}$$

where n_{e} is the number density of free electrons, n_r is the number density of all r-fold ionized atoms, U_r is the state-dependent partition function of r-fold ionized atoms, m_{e} is the mass of an electron, h is Planck's constant, and $I_r^{\mathrm{eff}} = I_r - \Delta I_r$ is the effective ionization energy for the ionization process $r \rightarrow (r+1)$, ΔI_r is the lowering of the ionization potential. The set of Saha equations (1) can be derived from thermodynamic principles through the minimization of the free energy. The derivation of this set of equations from the minimization of the free energy ensures consistency of the population densities calculated using this set of equations with all thermodynamic properties derived from the same free energy function. Different forms of the free energy functions will be directly reflected in the non-ideality corrections to the Saha equations. The system of Saha equations (1), subjected to the constraints of electro-neutrality,

$$\sum_{i=1}^{Z} i n_i = n_\mathrm{e} \tag{2}$$

and conservation of nuclei (constant number of heavy particles, n_h) in the ionization and recombination processes,

$$\sum_{r=0}^{Z} n_r = n_\mathrm{h} \tag{3}$$

is a closed system which is sufficient for the calculation of the composition of a plasma generated from a single chemical species. However, plasmas generated from compound materials or from mixtures of gases are thought to be more complex than plasmas generated from a single chemical species. For these complex plasmas, the equations for different chemical species are linked (at least) through the electron number density and the common temperature.

The case of an ideal mixture of two monatomic gases has been treated in [1] where a new technique by Trayner and Glowacki [15] has been used to solve the equations. However, accuracy limitations (lack-of-change problems) of the algorithm used and concerns about numerical stability were reported [1, 15]. Numerical stability concerns and problems were even reported for the simplest case of solving a single Saha equation (with unity as the maximum ionization state) coupled to an energy equation when a Newton–Raphson technique was used [16]. In the present work, we clear the complexity of this problem and introduce a simple, safe and stable, fast and accurate solution to this problem. The method depends on the reduction of the set of nonlinear equations into a simple form (an equivalent single transcendental equation), showing that the problem *for most cases* is effectively a one-dimensional nonlinear problem which requires minimal numerical work to be solved.

While it is a well-known fact that safety in obtaining convergence and numerical stability are critical for such a problem, it may be helpful to explain why accuracy and computational time are also of interest. In spite of the commonly known fact that better (e.g. more accurate) numerical techniques should replace worse techniques if they need the same or less computational effort, accuracy and computational time are of interest for some other reasons. First of all, no procedure will allow the computation of the populations of different species if their population does not exceed the accuracy of the procedure. Therefore, in a weakly ionized plasma, if the population of any species does not exceed the accuracy, the method fails. Secondly, the time derivative of the ionization state may also be required in many applications (see, for example, [17]). If the increment in time, dt, is small enough such that the change in the ionization is comparable to the accuracy, the derivative term may assume the opposite sign which may be catastrophic and seriously impose restrictions on the solution of the physical problem under consideration. Noting that the time derivative is just an example and the argument applies to the derivative with respect to any other parameter it becomes clear that accuracy may be crucial in calculating ionization equilibrium; and finally, calculating the ionization equilibrium of the plasma is not the ultimate goal. It is needed for the calculation of thermodynamic functions, transport and optical properties. In a typical simple self-consistent hydrodynamic simulation one needs to calculate the ionization equilibrium several million times. Time savings in the calculation of ionization equilibrium, however small, lead to a huge time saving in the overall time needed for the computations.

For these reasons, it is quite clear that improvements in terms of solution accuracy and computational time, in addition to safety in obtaining convergence and stability of the solution, are also valuable and needed.

2. A reduced formulation for plasma-mixtures in P–T phase space

Assuming that all chemical compounds and polyatomic molecules are fully dissociated excludes all chemical reactions except ionization and recombination and the plasma mixture in this case is effectively a mixture of inert gases. Hence, the plasma composition can be completely described by the set of nonlinear Saha equations with the constraints of conservation of electric charge and conservation of nuclei. Noting that diatomic molecules dissociate at several thousand degrees Celsius while, and because of the weaker bonds, polyatomic molecules begin dissociation at even lower temperatures [12], the above assumption can be considerably justified for plasmas of temperatures $\geqslant$1 eV. Denoting any chemical species in the mixture by the subscript j and using J to refer to the total number of the elemental species ($J = \sum j$), the requirement of a *constant number of heavy particles* (conservation of nuclei) gives

$$\sum_{r=0}^{Z_j} n_{r,j} = n_{\mathrm{h},j} \tag{i}$$

and

$$\sum_{j=1}^{J} n_{\mathrm{h},j} = n_{\mathrm{H}} \tag{ii}$$

where $n_{\mathrm{h},j}$ is the number density of heavy particles (nuclei) of elemental species j, n_{H} is the total number density of heavy particles of all elemental species in the mixture and Z_j is the atomic number (or the maximum allowed ionization stage) of elemental species j. Dividing (i) by n_{H} one obtains

$$\sum_{r=0}^{Z_j} \alpha_{r,j} = c_j \tag{4}$$

where $\alpha_{r,j} = n_{r,j}/n_{\mathrm{H}}$ and $c_j = n_{\mathrm{h},j}/n_{\mathrm{H}}$ are the molar fractions of the r-fold ionized ions of the elemental species j and the total molar fraction of the elemental species j, respectively. Summing over all elemental species (or equivalently dividing (ii) by n_{H}) yields

$$\sum_{j=1}^{J} c_j = 1. \tag{5}$$

Similarly, the condition of *quasi-neutrality* (conservation of electric charge) gives

$$\sum_{i=1}^{Z_j} i n_{i,j} = n_{\mathrm{e},j} \tag{iii}$$

with

$$\sum_{j=1}^{J} n_{\mathrm{e},j} = n_{\mathrm{e}} \tag{iv}$$

where $n_{i,j}$ is the number density of i-fold ionized ions of the elemental species $j, n_{\mathrm{e},j}$ is the number density of free electrons introduced to the system by ionizing the atoms/ions of the elemental species j and n_{e} is the total number density of free electrons. In principle, free electrons can take any energy and, they should be considered *indistinguishable*. Accordingly, the subscript j in the term $n_{\mathrm{e},j}$ must not be misread as a sort, or quality distinguisher, but rather as a quantity or share assigner for different sources of free electrons (elemental species). If one defines $P_{r,j} = n_{r,j}K_{\mathrm{B}}T/P$ and $P_{\mathrm{e}} = n_{\mathrm{e}}K_{\mathrm{B}}T/P$, where P is the plasma pressure, we can express the set of nonlinear Saha equations in terms of $P_{r,j}$, P_{e} and the pressure P and obtain the following recurrence relation:

$$P_{r+1,j} = \frac{P_{r,j}}{(P_{\mathrm{e}}P)}\eta_{r+1,j}(T, n_{\mathrm{e}}, \dots)$$

where

$$\eta_{r+1,j}(T, n_{\mathrm{e}}, \dots) = (K_{\mathrm{B}}T)\cdot 2\frac{U_{r+1}}{U_r}\left[\frac{2\pi m_{\mathrm{e}}K_{\mathrm{B}}T}{h^2}\right]^{3/2}\exp\left(-\frac{I_r^{\mathrm{eff}}}{K_{\mathrm{B}}T}\right) \tag{6}$$

where the Saha coefficients $\eta_{r+1,j}$ have been written in a general form to account for any possible formulae for the lowering of ionization potentials. For ideal plasmas, the Saha coefficients are functions of temperature only.

Multiplying (iii) by $K_{\mathrm{B}}T/P$ and using the recurrence relation (6) one obtains

$$P_{0,j} = \frac{P_{\mathrm{e},j}}{\sum_{i=1}^{Z_j}(i/(P_{\mathrm{e}}P)^i)\prod_{m=1}^{i}\eta_{m,j}(T, n_{\mathrm{e}}, \dots)} \tag{7}$$

where $P_{\mathrm{e},j} = n_{\mathrm{e},j}K_{\mathrm{B}}T/P$.

One distinct feature in the case of a non-ideal plasma is the need to consider, in addition to the lowering of ionization energies, the non-ideality correction to the expression of the pressure, P, due to Coulombic corrections to the free energy. In general, P can be expressed as $P = n_{\mathrm{H}}(1 + Z_{\mathrm{av}})K_{\mathrm{B}}T + \Delta P$, where ΔP is the non-ideality correction to the plasma pressure. Performing similar steps with (i) one obtains the following expression for $P_{\mathrm{e},j}$;

$$c_j = \sum_{r=0}^{Z_j}\alpha_{r,j}$$

$$c_j\frac{n_{\mathrm{H}}K_{\mathrm{B}}T}{P} = \sum_{r=0}^{Z_j}\alpha_{r,j}\frac{n_{\mathrm{H}}K_{\mathrm{B}}T}{P}$$

$$\begin{aligned} &c_j(1 - P_{\mathrm{e}} - \Delta P/P) \\ &\quad = \sum_{r=0}^{Z_j}P_{r,j} = P_{0,j}\left(1 + \sum_{i=1}^{Z_j}\frac{\prod_{m=1}^{i}\eta_{m,j}(T, n_{\mathrm{e}}, \dots)}{(P_{\mathrm{e}}P)^i}\right) \qquad \text{(v)} \\ &\quad = P_{\mathrm{e},j}\left[\left(1 + \sum_{i=1}^{Z_j}\frac{\prod_{m=1}^{i}\eta_{m,j}(T, n_{\mathrm{e}}, \dots)}{(P_{\mathrm{e}}P)^i}\right)\Big/\sum_{i=1}^{Z_j}\frac{i}{(P_{\mathrm{e}}P)^i}\prod_{m=1}^{i}\eta_{m,j}(T, n_{\mathrm{e}}, \dots)\right] \end{aligned}$$

or

$$P_{\mathrm{e},j} = c_j(1 - P_\mathrm{e} - \Delta P/P) \times \left[\sum_{i=1}^{Z_j} \frac{i}{(P_\mathrm{e}P)^i} \prod_{m=1}^{i} \eta_{m,j}(T, n_\mathrm{e}, \dots) \Bigg/ \left(1 + \sum_{i=1}^{Z_j} \frac{\prod_{m=1}^{i} \eta_{m,j}(T, n_\mathrm{e}, \dots)}{(P_\mathrm{e}P)^i} \right) \right]. \tag{8}$$

Now, summing over all chemical species, we obtain the final transcendental equation needed to complete the system

$$P_\mathrm{e} = (1 - P_\mathrm{e} - \Delta P/P) \times \sum_{j=1}^{J} c_j \left[\sum_{i=1}^{Z_j} \frac{i}{(P_\mathrm{e}P)^i} \prod_{m=1}^{i} \eta_{m,j}(T, n_\mathrm{e}, \dots) \Bigg/ \left(1 + \sum_{i=1}^{Z_j} \frac{\prod_{m=1}^{i} \eta_{m,j}(T, n_\mathrm{e}, \dots)}{(P_\mathrm{e}P)^i} \right) \right]. \tag{9}$$

Equations (6)–(9) constitute a reduced formulation of the set of nonlinear Saha equations subjected to the condition of quasi-neutrality and the requirement of constant number of heavy particles. For the case of a pure single elemental species ($J = 1$), (9) and (8) become identical with $P_\mathrm{e} = P_{\mathrm{e},j}$.

The solution of the set of equations in its current form is very simple and can be performed safely and accurately with a minimum of computational work as shown in Sec. 4, below. Before discussing the method of solution of the newly derived reduced formulation, (6)–(9), one should recognize that the Saha coefficients $\eta_{m,j}$ include the state-dependent partition functions $U_{r,j}(P, T)$, it is essential, therefore, to start by investigating this term and discussing its computation.

3. Evaluation of the internal partition function

For a classical plasma in thermodynamic equilibrium, the population of excited levels in the atoms or ions of the plasma are determined by Boltzmann statistics. The population $n_{r,j,\zeta}$ of level ζ of the atom/ion r of the chemical element j relative to the total population $n_{r,j}$ of species r of that element j is given by

$$\frac{n_{r,j,\zeta}}{n_{r,j}} = \frac{g_{r,j,\zeta}}{U_{r,j}} \exp\left(-\frac{E_{r,j,\zeta}}{K_\mathrm{B}T} \right) \tag{10}$$

where $U_{r,j}$ is the sum over all states known as the total internal partition function. The total internal partition function is a dimensionless quantity, which for an isolated atom/ion can be formally evaluated according to the equation

$$U_{r,j} = \sum_{\zeta=1}^{\infty} g_{r,j,\zeta} \exp\left(-\frac{E_{r,j,\zeta}}{K_\mathrm{B}T} \right) \tag{11}$$

where $E_{r,j,\zeta}$ is the ζth excitation energy of species r of element j (counted from the ground state) and $g_{r,j,\zeta} = 2J_{r,j,\zeta} + 1$ is its statistical weight (degeneracy) where $J_{r,j,\zeta}$ is the total angular momentum. In the calculation of the internal partition function, all equilibrium populations (ground/excited states) have to be included. For an isolated (free) atom/ion, $U_{r,j}$ diverges and finite values are obtained only when interactions with the environment are accounted for in order to truncate the sum. Recalling that in a plasma environment, the ionization energies are reduced such that excitation states with very high ζ do not exist, and the partition function actually converges. The summation in (11) is thus limited to a maximum of $\zeta = \zeta^*$, which corresponds to a maximum energy $E_{r,j,\zeta*}$. In the computations of the partition function the summation is performed over all the available spectroscopic data [18] for the excitation energies and terminated at energy level $E_{r,j,\zeta*}$, which is related to the effective ionization energy, $I^{\text{eff}}_{r,j}$, by the relation $E_{r,j,\zeta*} \leqslant I^{\text{eff}}_{r,j} = I_{r,j} - \Delta I_{r,j}$. Thus the partition function is a function of T and $\Delta I(P,T)$ just like the exponential term of the Saha coefficients. This means that the solution technique of the Saha equations is not affected by the dependence of the partition function on the state as it does not introduce any new variables other than those already existing in the exponential term of the Saha coefficients.

4. Method of solution

The method of solution of the set of equations (6)–(9) depends on the formulae used for the lowering of ionization potentials, $\Delta I_{r,j}$ and the non-ideality correction to the pressure, ΔP. Practically, one can face the following cases.

(a) *An ideal plasma* with no lowering of ionization potential and no pressure correction term. In such a case, the Saha coefficients, η, are functions of the temperature only and (9) is a transcendental equation in P_{e}, the solution of which is eminently simple. Many software packages include solvers for transcendental equations or algorithms for finding the zeros of a function. In addition, efficient algorithms that use a combination of bisection, secant and inverse quadratic interpolation methods can also be used [19]. For cases in which one is only interested in determining P_{e} or equivalently $n_{\text{e}} = P_{\text{e}}P/K_{\text{B}}T$, the solution of the transcendental (9) will suffice. However, if the interest extends to the determination of the detailed composition of different elemental species and different ionization stages, simple direct back-substitution into (8), (7) and (6) will be required to determine the detailed composition. The algorithm is simply articulated in the following steps.

(1) Solve the transcendental (9) for P_{e}.

(2) Substitute in (8) to determine $P_{\text{e},j}$ for the elements of interest.

(3) Substitute for P_{e}, and $P_{\text{e},j}$ in (7) to calculate $P_{0,j}$ for the elements of interest.

(4) Use the recurrence relation (6) to calculate all the $P_{r+1,j}$ of interest.

(5) The number density of any species r, j is simply recovered from $P_{r,j}$, where $n_{r,j} = P_{r,j}P/K_{\text{B}}T$.

(b) *Non-ideal plasma models* with expressions for the lowering of ionization potentials, $\Delta I_{r,j}$ and the pressure correction term, ΔP, that can be expressed explicitly in terms of P_{e} and other known quantities such as P, for example. In this case also, (9) is a transcendental equation in P_{e}. The method of solution is then identical to the case of ideal plasmas. Examples of such models for the lowering of ionization potentials can be found in the literature [13].

It may be appropriate at this stage to highlight some of the benefits and advantages gained (for these two cases) by recasting the equations into this reduced form. The solution of the problem, for these two cases, is reduced to the trivial problem of solving a single transcendental equation. Hereby, for these two cases, the problem of evaluating the plasma composition is shown to be effectively a one-dimensional nonlinear problem with only one independent variable that is, P_e (namely finding the root of a function). According to [19], 'Simultaneous solution of equations in N dimensions is much more difficult than finding roots in the one-dimensional case. The principal difference between one and many dimensions is that, in one dimension, it is possible to bracket or "trap" a root between bracketing values, and then hunt it down like a rabbit. In multi-dimensions, you can never be sure that the root is there at all until you have found it'. Furthermore, in principle, the zero of a transcendental equation can be determined to any degree of accuracy at the expense of the computational time (i.e. no accuracy limitations). Therefore, the accuracy of the computations of the detailed plasma composition will be dictated by the machine characteristics.

(c) *Non-ideal plasma models* where $\Delta I_{r,j}$, ΔP cannot be expressed explicitly in terms of P_{e} and known quantities but rather in terms of a common parameter (such as the Debye length, λ_{D}), which depends on the individual $P_{r,j}$. The model proposed by Griem [11] is an example of such a case. In this model the lowering of ionization potentials and the pressure correction term are derived consistently from the minimization of the free energy and are given by

$$\begin{aligned} \Delta I_{r,j} &= \frac{(r+1)e^2}{4\pi\varepsilon_0\lambda_{\mathrm{D}}}, \\ \Delta P &= -\frac{K_{\mathrm{B}}T}{24\pi\lambda_{\mathrm{D}}^3} \end{aligned} \tag{12}$$

with λ_{D} defined as

$$\lambda_{\mathrm{D}} = \left[\varepsilon_0 K_{\mathrm{B}}T/e^2\left(n_{\mathrm{e}} + \sum_{j=1}^{J}\sum_{r=0}^{Z_j} r^2 n_{r,j}\right)\right]^{1/2}. \tag{13}$$

A similar and widely used model, known as the *lambda approximation*, was proposed by Ebeling et al. [14]. The model introduced expressions for the lowering of ionization potentials and the pressure correction term. Although these corrections are derived consistently from the minimization of the free energy, the pressure correction term is represented only by the first three terms from a Taylor series. However, an exact closed form for this correction term is derived and is given below where the non-ideality corrections become

$$\Delta I_{r,j} = \frac{(r+1)e^2}{4\pi\varepsilon_0(\lambda_{\mathrm{D}} + a(T))},$$

and

$$\begin{aligned} \Delta P = -\frac{K_{\mathrm{B}}T}{24\pi\lambda_{\mathrm{D}}^3}\Bigg[&\tau(\kappa a(T)) - 9\frac{\ln(1+\kappa a(T))}{(\kappa a(T))^3} \\ &- \frac{3}{2(\kappa a(T))} + \frac{3}{(\kappa a(T))^2 + (\kappa a(T))^3} + \frac{6}{(\kappa a(T))^2}\Bigg] \end{aligned}$$

with $a(T) = \Lambda_{\mathrm{B}}/8$, $\kappa^{-1} = \lambda_{\mathrm{D}}$ and

$$\tau(\chi) = \frac{3}{\chi^3}\left[\ln(1+\chi) - \chi + \frac{\chi^2}{2}\right] \tag{14}$$

where $\Lambda_{\mathrm{B}} = h/\sqrt{2\pi m_{\mathrm{e}}K_{\mathrm{B}}T}$ is the de Broglie wavelength and λ_{D} is expressed as in (13).

With a bit of analysis and insight, the solution in this case can also be obtained with significant simplicity and to any desired accuracy. The fact that (9) can be easily and accurately solved for any specified value of $\lambda_{\rm D}$ makes it, effectively, equivalent to an algebraic expression of the form

$$P_{\rm e} = \bar{f}_1(\lambda_{\rm D}). \tag{15}$$

At the same time, the definition of $\lambda_{\rm D}$ in (13) can be rewritten as

$$\lambda_{\rm D} - f_2(P_{\rm e}) = 0$$

where

$$\begin{aligned} f_2(P_{\rm e}) &= \left[\varepsilon_0 K_{\rm B} T/e^2 \left(n_{\rm e} + \sum_{j=1}^{J} \sum_{r=0}^{Z_j} r^2 n_{r,j} \right)\right]^{1/2} \\ &= \frac{K_{\rm B} T}{\sqrt{P}} \left[\varepsilon_0/e^2 \left(P_{\rm e} + \sum_{j=1}^{J} \sum_{r=0}^{Z_j} r^2 P_{r,j}(P_{\rm e}) \right)\right]^{1/2}. \end{aligned} \tag{16}$$

Note that $P_{r,j}$ has been written in (16) as a function of $P_{\rm e}$ since if one knows $P_{\rm e}$, all $P_{r,j}$ can be calculated.

Now, upon substitution from (15) into (16) one obtains

$$\lambda_{\rm D} - f_2(\bar{f}_1(\lambda_{\rm D})) = 0 \tag{17}$$

which is a transcendental equation in $\lambda_{\rm D}$. The bar over f_1 refers to the numerical nature of the function f_1. From (17) one can see that even for case (c), in which $\Delta I_{r,j}$ and ΔP cannot be expressed explicitly in terms of $P_{\rm e}$ and known quantities but rather in terms of the common parameter, $\lambda_{\rm D}$, the present analysis shows that the problem of evaluating the plasma composition for a complex mixture is effectively a one-dimensional nonlinear problem (or simply finding the root of a function) with one independent variable, $\lambda_{\rm D}$. Therefore, even for such a case, the plasma composition can be determined with significant simplicity and to any desired accuracy. It is interesting to notice that solving (17) simultaneously gives the values of $\lambda_{\rm D}, P_{\rm e}, P_{{\rm e},j}$, $U_{j,r}$, $P_{j,r}$ and ΔP and therefore it represents the whole algorithm. Although (17) is solvable without any problem to the level of machine accuracy it may be important to note here that in cases in which one is willing to solve the equation to a lower accuracy it will be necessary in order for (17) to be fully satisfied to have the predetermined tolerance (relative error, ε) of the inner transcendental equation (9) be smaller than that of the outer transcendental equation (17).

In the following section a couple of non-trivial sample problems that represent this case are worked out in detail showing the simplicity and reliability of the present proposed algorithm.

A model in which the non-ideal plasma corrections $\Delta I_{r,j}$ can neither be expressed explicitly in terms of $P_{\rm e}$ and known quantities nor in terms of a common parameter that depends on the individual $P_{r,j}$ is not known to the author at the present time.

5. Sample problems

The current methodology has been applied to compute the composition of two complex plasma mixtures. In the first sample problem, the method has been used to calculate the ionization states of Teflon (C_2F_4) over a wide range of temperatures and pressures. While in the second problem, a hypothetical mixture of five elements representing ablation of Teflon in a helium–neon–argon atmosphere was considered. An arbitrary concentration of this mixture (He(0.3):C(0.1):F(0.2):Ne(0.2):Ar(0.2)) was chosen to work the second problem. Necessary atomic data and excitation and ionization energies have been taken from [18]. Comprehensive sets of energy levels (more than 2400 for C_2F_4 and 5500 for He/C/F/Ne/Ar) have been used in the computations of the partition functions. The model for non-ideality correction proposed by Ebeling et al. [14], which represents case (c) as shown above, is used to run these sample problems. For this case, all nonlinearities of the problem are reduced into the single transcendental equation (17) which can be solved with simplicity to machine accuracy for λ_{D}, $U_{r,j}$, P_{e}, $P_{j,r}$ and ΔP at the same time.

6. Results and discussion

Figures 1(a) and (b) show the temperature dependence of the quantities P_{e} and $\sum P_r$ in conjunction with the non-ideality correction term on the plasma pressure for 50 000 bar Teflon and (He(0.3)/C(0.1)/F(0.2)/Ne(0.2)/Ar(0.2)) plasmas, respectively. The total plasma pressure (unity) is the sum of three terms: 1, the ideal pressure of electrons, P_{e}; 2, the ideal pressure of ions including neutrals $\sum P_r$; and 3, the non-ideality correction term $\Delta P/P$. Although it does not have any mechanism to distribute the non-ideality correction among different species, the current picture of the pressure is very useful for the following reasons; (a) it allows the determination of the population densities without any problems (where densities can be simply recovered from these expressions as shown above); (b) it reduces to the ideal expressions as the degree of non-ideality is decreased with the terms P_{e} and P_r representing the relative partial pressures of these components.

The fact that these terms (P_{e} and P_r) reduce to the partial pressures in the ideal case gives some tolerability to use the same terminology for the non-ideal case while bearing in mind that these labels *relative partial pressures* for non-ideal plasmas should not be interpreted in the usual sense where the relative partial pressure is always less than unity. As shown in the figures, the sum of these three contributions or terms shows a value of unity, as expected, at all temperatures. As shown in the figures, the contribution of the non-ideality correction term assumes negative values with the result that the sum of total contributions of the terms P_{e} and P_r is greater than unity. With a non-ideal plasma equation of state such as that given above (14) and used to work these sample problems, the sum of the terms P_{e} and P_r or any of them or even the magnitude of the non-ideality correction may exceed unity. However, the three contributions should always satisfy the constraint that the sum of the three components should always be unity. In the rest of our discussion we will refer to these terms as the relative partial pressures of electrons and heavy particles with all of the above discussion kept in mind.

Figures 2(a) and 3(b) show the temperature dependence of the relative partial pressures of different ionic species in a 15 000 bar Teflon plasma and 40 000 bar He/C/F/Ne/Ar mixture plasma. As the temperature increases, the relative partial pressures of neutral species (C_0, F_0) for Teflon and (He_0, C_0, F_0, Ne_0 and Ar_0) for the He/C/F/Ne/Ar mixture decrease monotonically as a result of the progressive ionization. With further increases of temperature, higher ionized ionic species appear at the expense of lower-fold ionized species.

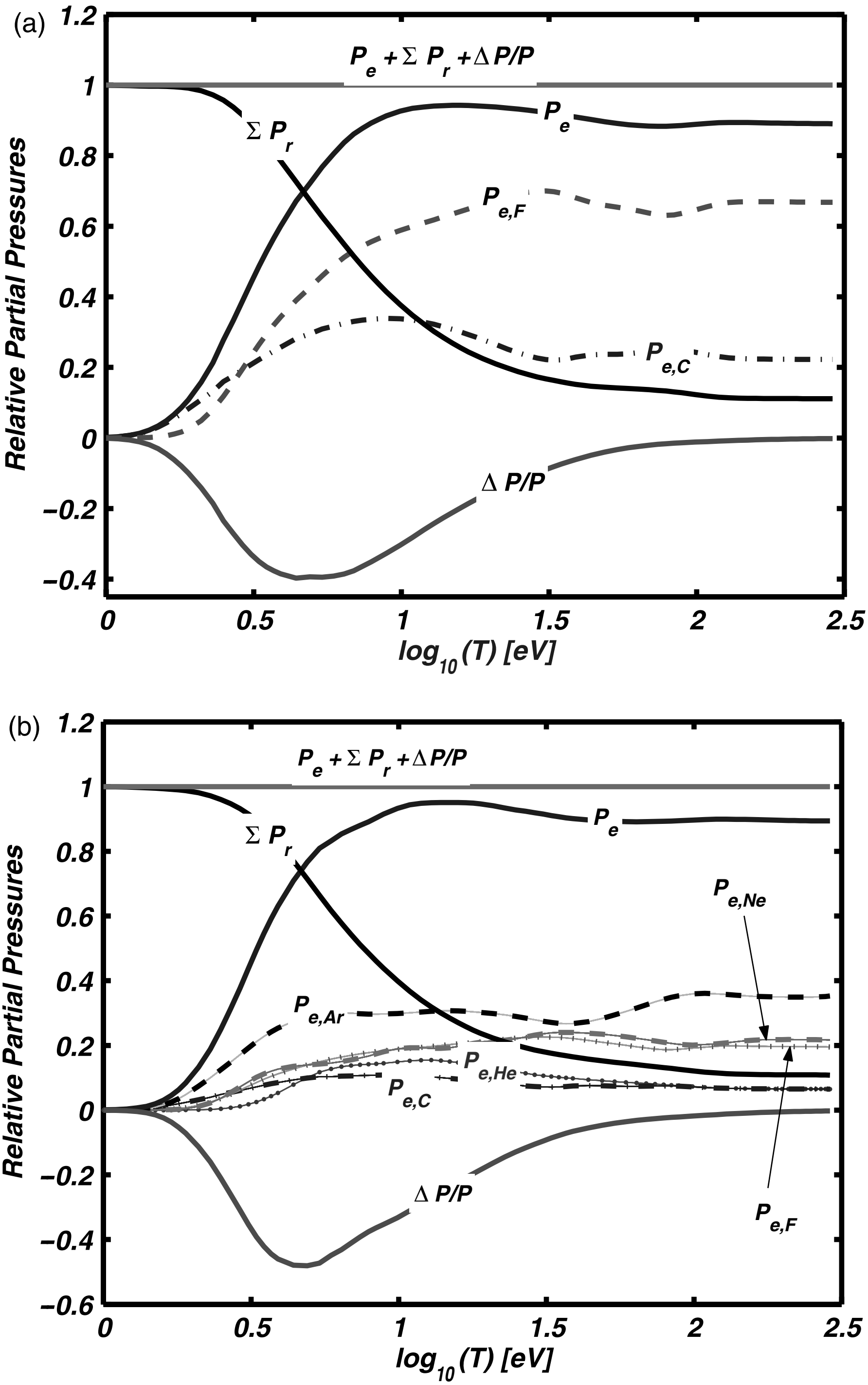

Figure 1. (a) Temperature dependence of the relative partial pressures of electrons and heavy particles of a Teflon plasma at 50 000 bar; (b) temperature dependence of the relative partial pressures of electrons and heavy particles of a He/C/F/N/Ar plasma at 50 000 bar.

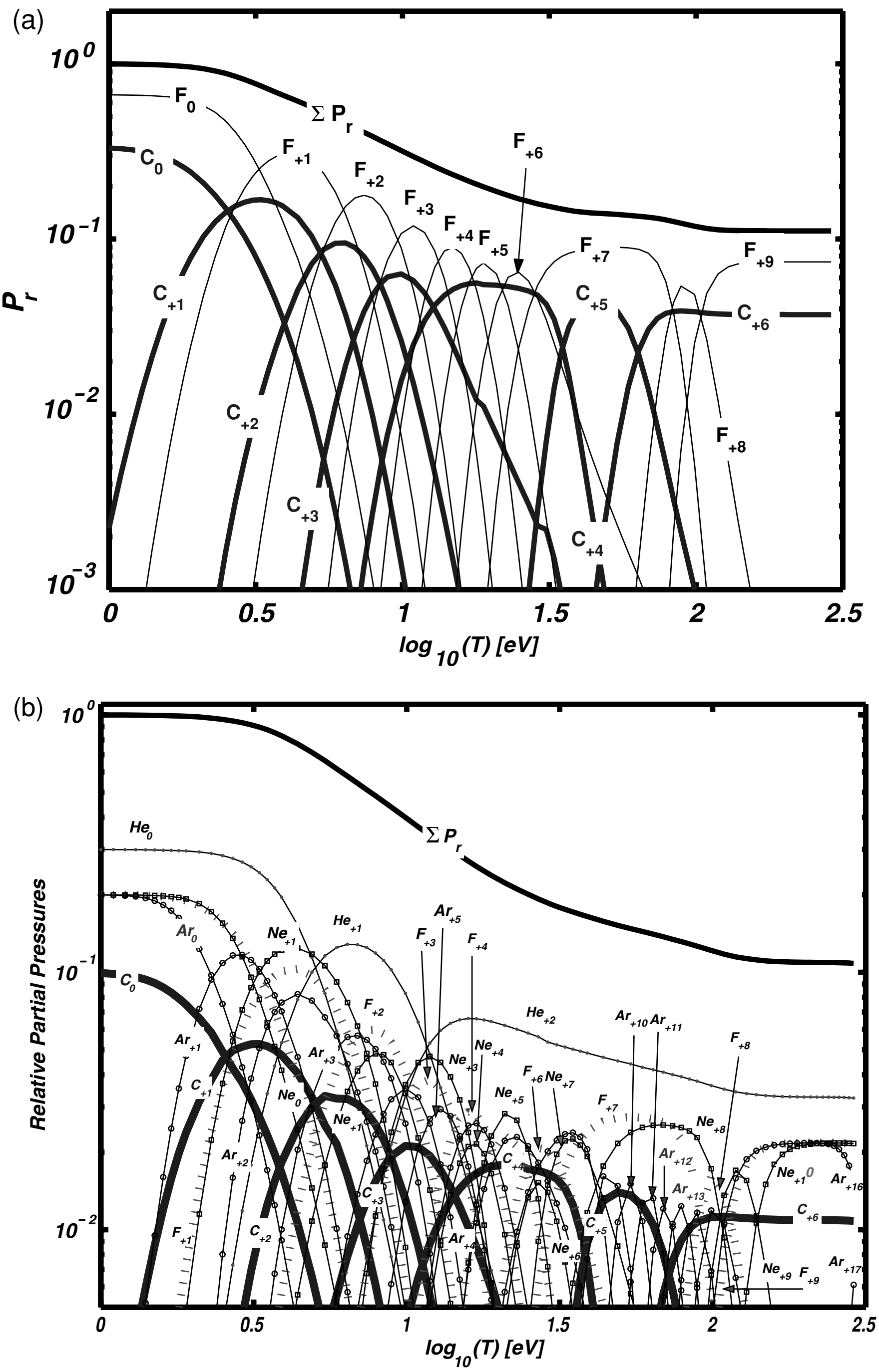

Figure 2. Temperature dependence of the relative partial pressures of individual ionic species in: (a) a 15 000 bar Teflon plasma and (b) a 40 000 bar He/C/F/Ne/Ar mixture plasma.

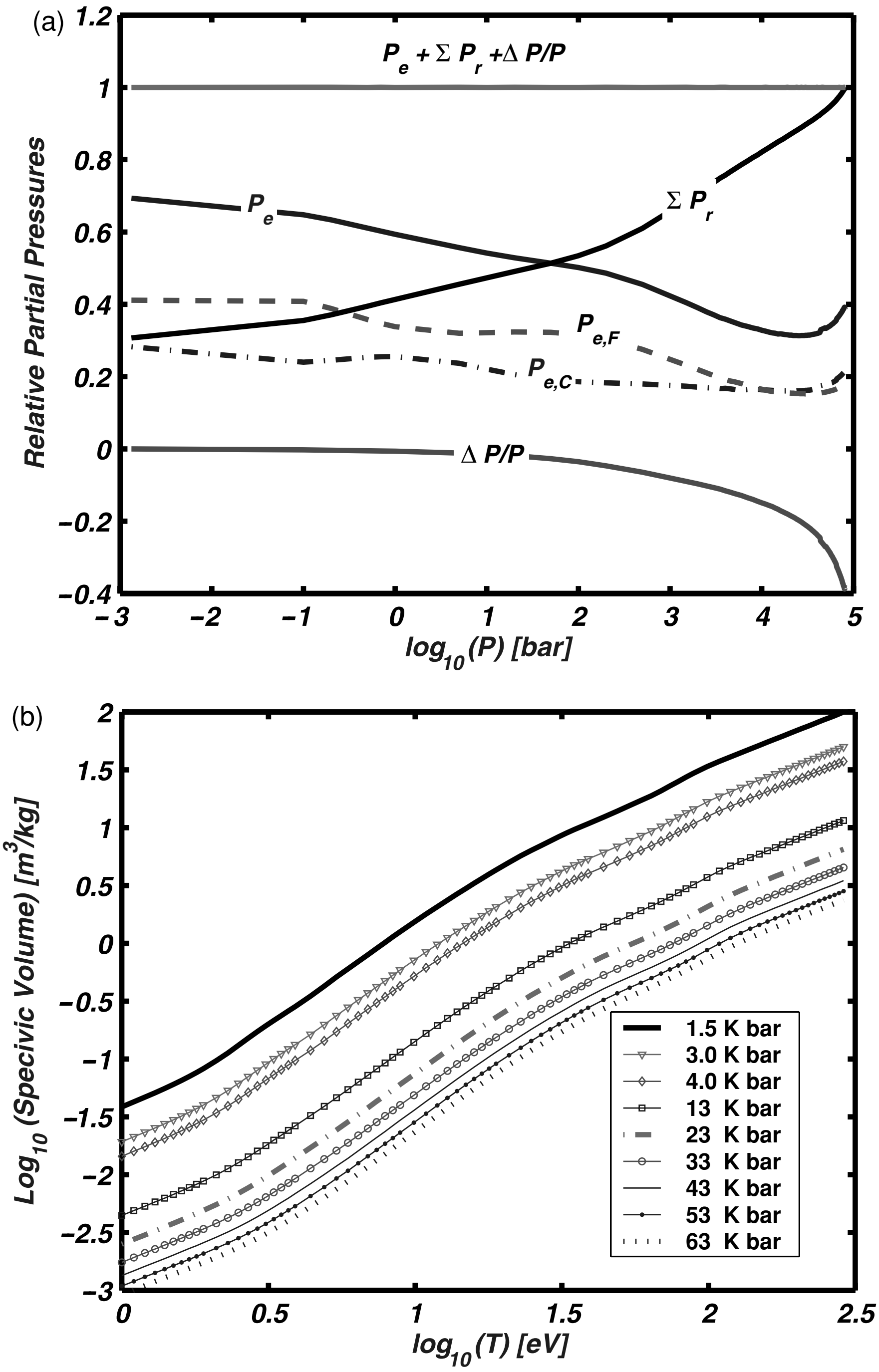

Figure 3. Pressure dependence of the relative partial pressures of electrons and heavy particles and the non-ideality correction term of a 2.7 eV Teflon plasma; (b) temperature dependence of the specific volume of Teflon plasma at different pressures.

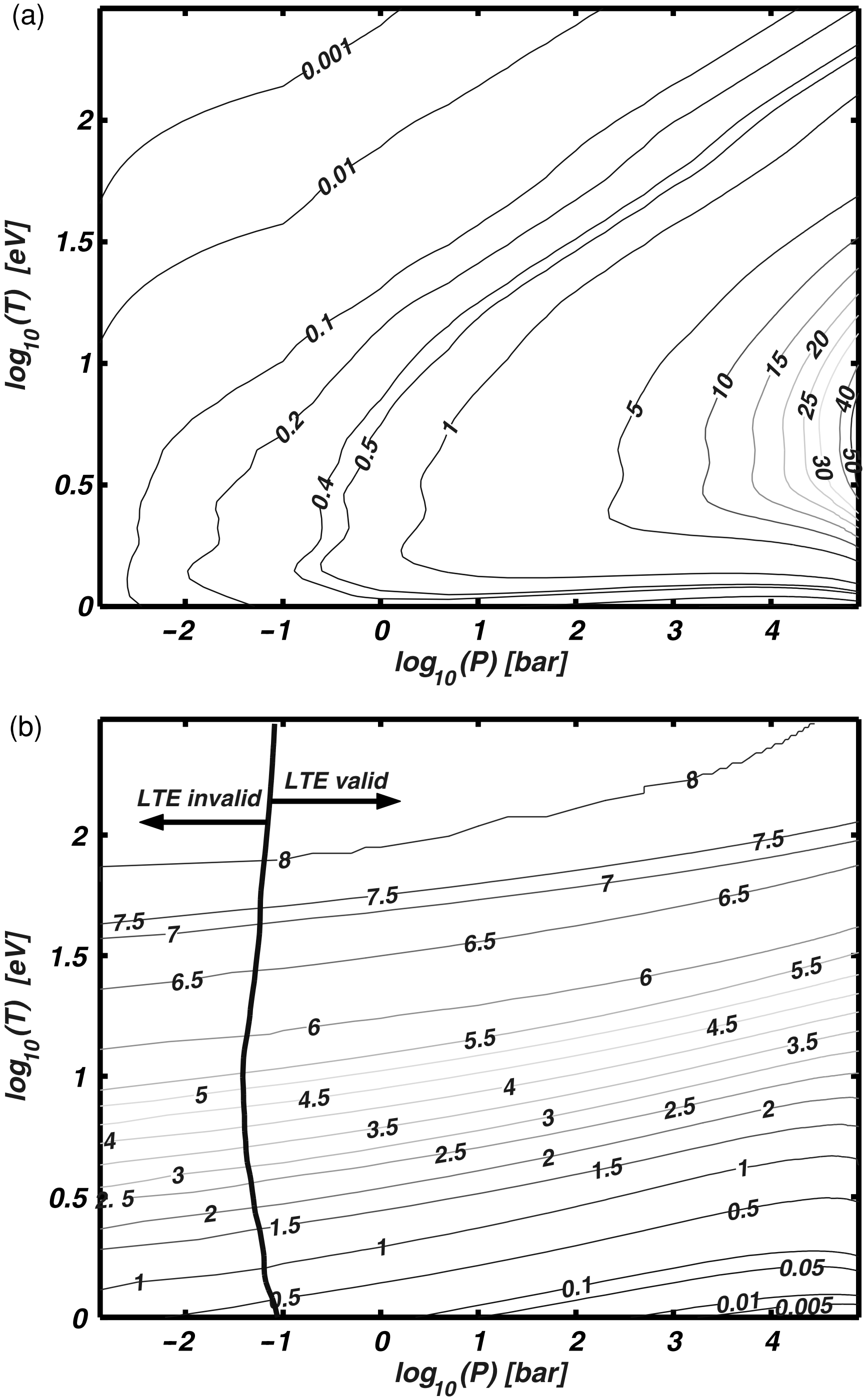

Figure 4. (a) Contours of the values of the non-ideality correction term to the pressure in a Teflon plasma over a wide range of temperatures and pressure and (b) contours of the average ionization state of Teflon over a wide range of temperatures and pressures and the LTE criterion.

Figure 3(a) shows the pressure dependence of the relative partial pressures of electrons, heavy particles and the non-ideality correction term of a 2.7 eV Teflon plasma. As expected the relative partial pressure of electrons (or electron density) decreases with increasing pressure because of the increase of the recombination rate. However, at very high pressure (high density too) it starts to increase with pressure again due to continuum lowering or what is known as a pressure ionization. In Fig. 3(b) the temperature dependence of the specific volume of Teflon plasma at different pressures is shown.

Figure 4(a) shows the contours of the values of the non-ideality correction term of the pressure in a Teflon plasma over a wide range of temperatures and pressure. As can be clearly seen in the figure, the magnitude of the non-ideality correction term increases with increasing pressure at the same temperature. An average nuclear charge can be approximately assigned to this plasma mixture and the critical (minimum) electron number density required for LTE can be determined as a function of temperature. The criterion given by Fujimoto and McWhirter [20] is adopted and applied for the present computations. For each pressure, a critical value for the average ionization state, Z_c, can be calculated by dividing the critical electron number density by the corresponding $n_H = P \sum_{r,j} P_{r,j}/K_B T$ and one can verify the validity of the LTE assumption by comparing both Z_{av} and Z_c as shown in Fig. 4(b). Figure 4(b) is a useful representation of the calculated ionization data where contours of Z_{av} are presented as functions of T and P. The logarithmic axes scales have been used to cover a wide range of temperatures and pressures. As shown in the figure the LTE assumption can be considered for Teflon plasmas with pressures >0.1 bar. Also from the figure one can see that at very high temperatures the average ionization state approaches its expected theoretical limiting value for a fully stripped plasma, i.e. $Z_{av} = (2/6) \times 6 + (4/6) \times 9 = 8$.

The results presented above have some interesting remarks that need some discussion. It is interesting to note that at very high temperature where the thermal energy of the plasma particles is much greater than the interaction potential, the plasma tends to be ideal with the result that the non-ideality correction terms vanish and the plasma becomes fully stripped at the same time. The limiting average ionization states for the mixtures are, therefore, 8 for Teflon and $(0.3) \times 2 + (0.1) \times 6 + (0.2) \times 9 + (0.2) \times 10 + (0.2) \times 18 = 8.6$ for the He/C/F/Ne/Ar mixture. The corresponding limiting relative partial pressures for electrons and heavy particles are, therefore, (8/9) and (1/9) for Teflon and (8.6/9.6) and (1/9.6) for He/C/F/Ne/Ar, respectively. These expected limiting values are in complete agreement with the results in the figures for Teflon, while for the He/C/F/Ne/Ar mixture the temperature range shown in the figure shows ionization states of argon up to Ar_{+16} only. The expected limiting partial pressures for He/C/F/Ne/Ar for the range of temperature shown is, therefore, (8.2/9.2) and (1/9.2) which is in complete agreement with Fig. 2(b).

Another interesting result can be seen in Figs 2(a) and (b) where, due to their helium-like stable configuration, the curves for C_{+4}, F_{+7}, Ne_{+8} and Ar_{+16} show wide distributions as a function of temperature.

7. Conclusion

The set of $1 + \sum_j Z_{\max,j}$ coupled nonlinear equations in $1 + \sum_j Z_{\max,j}$ unknowns resulting from the nonlinear Saha equations (derived from the minimization of the free energy function) supplemented by electro-neutrality and conservation of nuclei for complex plasma mixtures is reformulated into an equivalent reduced form, which showed that, for most practical cases, the problem is effectively a one-dimensional nonlinear problem (a single transcendental equation), the solution of which is trivial. Implementing this simple efficient methodology simplifies the problem and considerably reduces the computational effort needed to compute the detailed plasma composition for different cases. The method is analytically known to be safe, fast and efficient. It also shows no numerical instabilities, no convergence problems and no accuracy limitations or lack-of-change problems, which have been reported in the literature for other competitive techniques. Non-trivial sample problems have been worked in detail showing the value and usefulness of this method for applied and industrial plasma physicists. Finally, the present analysis and methodology strongly signifies the belief that computational success crucially depends on analysis and insight rather than numerics.

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