Statistical mechanics of highly charged ion plasmas in local thermodynamic equilibrium

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The screened-hydrogenic average-atom model is well suited to describe multicharged ion plasmas in local thermodynamic equilibrium (LTE) for in-line plasma physics calculations. Using general principles of statistical mechanics, this model is shown to be properly defined and thermodynamically consistent. The grand canonical partition function Z_G of the bound electrons is written as a multidimensional integral. Its saddle-point evaluation gives the intuitive average-atom equations. Using this formalism, a method for accounting the various ionization stages of a LTE plasma is proposed. It can be used to estimate the integer charge stage distribution in this type of medium from any average-atom model. Once the model is well established, simpler formulas, more suitable for fast computations, are derived in the framework of the classical theory of fluctuations. Numerical results are presented and discussed. [S1063-651X(97)12006-2]

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I. INTRODUCTION

Hot and dense matter is of great importance in astrophysics and plasma laboratory physics where thermodynamic conditions can be extremely diverse. The high temperature encountered in such systems is responsible for the large number of ion species that can be found simultaneously. The study of their spectroscopic properties and their interactions with other microscopic entities (atoms, electrons, ions, . . .) is complex but central in estimating macroscopic quantities including thermodynamic data (pressure and energy), transport coefficients (electrical and thermal conductivity), and optical absorption coefficients (opacities) required to perform accurate numerical simulations.

Only local thermodynamic equilibrium (LTE) plasmas are considered in this paper. In such media, the multiplicity of available excited states makes explicit configuration accounting difficult or computationally impracticable. Statistical approaches must then be used. The basic idea is to study the plasma using an ''average atom'' [1–5] which extends the Thomas-Fermi approach [6–11]. Its atomic structure is supposed to represent the average electron populations of the plasma for a temperature T and a density ρ. Results obtained with such a theory are very satisfying, but the thermodynamic consistency is sometimes questionable [12]. The Stewart and Pyatt formalism [13] is a typical example. These authors brought a correction to the description of the microscopic properties of ions embedded in a plasma to study the continuum lowering. Their formula is widely used in practical ionization and opacity calculations, but it is known to lead to thermodynamically inconsistent results at high density [14]. The implementation of a model with such a drawback in simulation codes may cause nonphysical changes in temperature for compressed matter [15]. Finally, the average-atom picture is too restrictive because it does not describe the various ionization stages whose spectral features can be seen on experimental photoabsorption spectra [16,17].

For laser-plasma simulations, Zimmerman and More [18,19] proposed a screened-hydrogenic average-atom model. Their formalism is well suited for in-line calculations of equation of state and opacity. Thermodynamic consistency is ensured by deriving it from a free energy but many questions still remain unclear. Since we are dealing with interacting electrons, what is the physical meaning of the fractional occupations of the bound orbitals defined by Fermi-Dirac statistics? What is the form of the one-electron shell energies that should be used? What is the role of correlations on orbital occupation numbers?

This paper proposes another scheme for the screened-hydrogenic average-atom model which is thermodynamically consistent and allows us to evaluate the fractional distribution of ion states. In Sec. II, the requirement of thermodynamic consistency for statistical mechanics of correlated electrons in the screening constant model is formulated. An integral representation of the grand canonical partition function Z_G for bound electrons is proposed. Its evaluation becomes possible using the standard saddle-point method. The saddle-point equations are found to be the coupled nonlinear Fermi-Dirac equations defining the fractional occupations of the bound orbitals of the screened-hydrogenic average-atom model. Closed forms for thermodynamic mean quantities such as mean occupancy, mean electronic energy, and population correlations between bound electrons are then derived. The fraction of any integer ion stage and its mean orbital occupancy can be evaluated from a simple modification of Z_G. This method can be applied to estimate the integer charge stage distribution in plasmas from any average-atom model. In Sec. III, an analytical approximation to Z_G is found using the classical theory of fluctuations. This expression allows fast computations of the mean value and standard deviation of any physical quantity which is an explicit function of the electron shell populations. In Sec. IV, the formalism is tested by comparison to theoretical results. The role of correlations on the variance of ionization is emphasized. The influence of temperature, density, maximum principal quantum number necessary to truncate the grand canonical partition function, and pressure ionization model on the population fractions of the various ionization states is studied.

II. FORMAL DEVELOPMENTS

A. The plasma model

Consider a one-component plasma as an ensemble of ion spheres of radius R_0 determined by the mass density ρ of the

plasma. Introducing the Avogadro number $\mathcal{N}$, the atomic particle density n_a, the atomic mass m_a, and the molar mass A of the element, we have the identities: $4/3\pi R_0^3 n_a = 1$, $n_a = \rho/m_a$, and $m_a = A/\mathcal{N}$, leading to $n_a = \rho\mathcal{N}/A$. We choose to describe in ion species embedded in a plasma by the knowledge of the electron occupancies of its K_{max} bound orbitals. Each orbital k ($1 \leq k \leq K_{max}$) has a degeneracy D_k^0 and an integer occupancy P_k. The superscript 0 means that we are dealing with the degeneracy of an isolated ion. The reason for this convention will appear clearly in discussing pressure ionization phenomena [18].

The usual and proper way to analyze the thermodynamic properties of equilibrium systems is to appeal to a partition function. Deriving standard thermodynamic quantities from it ensures thermodynamic consistency. Consider the system defined by the electrons of the K_{max} ion bound orbitals in the grand canonical ensemble. It is assumed that LTE is established among free electrons. Electron-electron bound-free interactions are neglected. Let $E[(P_k)]$ and $\mathcal{D}_{(P_k)}$ be, respectively, the energy and the statistical weight of an electronic configuration (P_k). Introducing the binomial coefficient

$$\binom{n}{p}\left[\binom{n}{p} = \frac{n!}{p!(n-p)!}\right],$$

$\mathcal{D}_{(P_k)}$ is equal to: $\mathcal{D}_{(P_k)} = \Pi_{k=1}^{K_{max}}\binom{D_k^0}{P_k}$. The grand canonical partition function Z_G of the system of interest is

$$Z_G = \sum_{(P_k)} \mathcal{D}_{(P_k)} e^{-\beta\left(E[(P_k)] - \mu \sum_{k=1}^{K_{max}} P_k\right)}. \tag{1}$$

In this expression, $\beta = 1/k_B T$ (k_B is Boltzmann constant and T the system temperature), μ is the chemical potential, whereas the sum $\Sigma_{(P_k)}$ runs over the set of all the configurations that can be constructed from the K_{max} orbitals. So $\Sigma_{(P_i)}$ means $\Sigma_{P_1=0}^{D_1^0} \cdots \Sigma_{P_k=0}^{D_k^0} \cdots \Sigma_{P_{K_{max}}=0}^{D_{K_{max}}^0}$. The grand potential Ω, the mean energy $\bar{E}$, and the mean bound electron number $\bar{N}$ can then be deduced from Z_G using the relations [20–22] $Z_G = e^{-\beta\Omega}$,

$$\bar{N} = -\left(\frac{\partial\Omega}{\partial\mu}\right)_{\rho,T}, \tag{2}$$

and

$$\bar{E} = \left[\frac{\partial(\beta\Omega)}{\partial\beta}\right]_{\rho,\mu} + \mu\bar{N}. \tag{3}$$

The thermodynamic limit is assumed, hence the use of the mass density ρ instead of the volume V of the system. Throughout this article, we will not mention the thermodynamic variables kept constant when partial derivatives are performed. The chemical potential μ is determined by requiring that the ion cell is neutral on the average. Introducing the nuclear charge Z of the element, the average ionization $\bar{Z}$, and the Fermi-Dirac function $F_\alpha(\eta)$ ($F_\alpha(\eta) = \int_0^\infty (x^\alpha/1 + e^{x-\eta})dx$), μ satisfies the equations ($\eta = \beta\mu$)

$$\bar{N} + \bar{Z} = Z$$

$$\bar{Z} = 4\pi \frac{A}{\rho\mathcal{N}}(\sqrt{2m/\beta h^2})^3 F_{1/2}(\eta). \tag{4}$$

In situations where the configuration energy $E[(P_k)]$ is a nonlinear function of the (P_k) (thus when we go beyond the ideal Fermi-Dirac gas), the main difficulty in this approach is the calculation of the partition function Z_G. A solution is to find an integral representation of Z_G. Its factorization becomes possible at the expense of the introduction of auxiliary variables. The saddle-point technique [23–26] gives the main contribution to the integral and thus, a good approximation of the exact value of Z_G. The corrective terms can then be taken into account by perturbation around the saddle point.

In the following, two expressions of $E[(P_k)]$ are considered. The first one is a quadratic form in the orbital populations. Mayer's formula [1,2] is chosen. It is adapted to any average-atom model when used in a second-order Taylor expansion in populations about some reference configuration [27]. The second one results from describing the atomic structure with the screened hydrogenic model (SHM) [19,28]. The partition function associated with the last form is proved to possess its own integral representation. Thus there is no need to develop $E[(P_k)]$ around some particular reference point. This fact is essential to prove that the screened-hydrogenic average-atom model (SHAAM), originally proposed by More and Zimmerman, is thermodynamically consistent.

B. Integral representation of Z_G using Mayer's model

The total energy of an electronic configuration (P_k) is assumed to be written in the following form (in atomic units):

$$E = \sum_{k=1}^{K_{max}} P_k\left(E_k - \frac{V_{kk}}{2}\right) + \frac{1}{2} \sum_{k,k'=1}^{K_{max}} P_k P_{k'} V_{kk'}, \tag{5}$$

where $E_k = -Z^2/2n_k^2$ and $V_{kk'} = (Z\sigma_{kk'})/n_k^2$. The screening constants $(\sigma_{kk'})$ are independent of the configuration [28]. The electrostatic interaction matrix element potentials $(V_{kk'})$ in Eq. (5) prevent us from factorizing Z_G. Using the notation $P^T V P = \Sigma_{k,k'=1}^{K_{max}} P_k V_{kk'} P_{k'}$, where P^T is the line vector transposed from the column vector P whose components are the populations of the K_{max} orbitals, Z_G is equal to

$$Z_G = \sum_{(P_k)} \left[\prod_{k=1}^{K_{max}} \binom{D_k^0}{P_k} e^{-\beta(E_k-(V_{kk}/2)-\mu)P_k}\right] e^{-(\beta/2)P^T V P}. \tag{6}$$

Using a perturbative development with respect to βZ, Green [2] showed that one can obtain the expression of the mean occupancy $\bar{P}_k$ of orbital k to lowest order, as first proposed by Mayer, and correct it to first order. A set of nonlinear coupled equations has to be solved to find all the $(\bar{P}_k)$. The correction tends to offer a better description of the statistical mechanics of a LTE plasma that goes beyond the independent particle approximation ($\bar{P}_k = D_k^0/\{1 + \exp[\beta(E_k$

$-\mu)]\})$. Wilson [27] has found a simple method to obtain the Green's results without handling complex operators. We will extend it to the SHM.

Starting from Eq. (6), the key of the reduction of Z_G comes from the identity [23,29,30]

$$e^{-(1/2)P^T\beta VP} = \left(\frac{\det(V^{-1})}{(2\pi\beta)^{K_{\max}}} \right)^{1/2}$$

$$\times \int d^{K_{\max}}X e^{-([1/2]X^T[V^{-1}/\beta]X + iP^TX)}. \quad (7)$$

where $\int d^{K_{\max}}X$ means $\Pi_{k=1}^{K_{\max}}\int_{\mathbb{R}}dX_k$. Z_G becomes factorizable. Introducing the quantities

$$e_k = E_k - \frac{V_{kk}}{2} + \frac{iX_k}{\beta} - \mu, \quad (8)$$

$$e^{\beta\varphi_k} = \frac{1}{1+e^{\beta e_k}} = f_k, \quad (9)$$

$$[dX] = \frac{d^{K_{\max}}X}{\sqrt{\det(2\pi\beta V)}}, \quad (10)$$

$$S(X) = \frac{1}{2}X^T\frac{V^{-1}}{\beta^2}X + \sum_{k=1}^{K_{\max}} D_k^0(e_k + \varphi_k), \quad (11)$$

we find a closed form for Z_G

$$Z_G = \int [dX]e^{-\beta S(X)}. \quad (12)$$

The classical partition function of the ideal Fermi-Dirac gas is obtained if all the $(V_{kk'})$ vanish. Z_G is a continuous function with respect to the degeneracies (D_k^0). We can then forget the superscript 0. With this new writing, we can treat formally fractional degeneracies (D_k) and include, by analytic continuation, the reduction of each maximal occupancy due to plasma effects as proposed by Zimmerman and More [18]. This procedure is impossible if we stay with the original form (6) of Z_G. The electrostatic interactions among the electrons inside the atom do not disappear. They are taken into account by the term $\frac{1}{2}X^T(V^{-1}/\beta^2)X$ in Eq. (11). The interactions have been linearized using auxiliary integration variables.

The saddle-point method allows us to estimate Z_G. This procedure is justified by the fact that we are dealing with the partition function of a system at thermodynamic equilibrium. Only a group of configurations contribute significantly to the discrete sum (6). These configurations are those whose energy and orbital populations are close to the mean energy and mean occupancies of the system. We develop $S(X)$ in Eq. (11) around its minimum up to the second order

$$S(X) = S(X^0) + (X-X^0)^T\frac{\partial S}{\partial X}\bigg|_{X^0}$$

$$+\frac{1}{2}(X-X^0)^T\frac{\partial^2 S}{\partial X^2}\bigg|_{X^0}(X-X^0) + \cdots, \quad (13)$$

where X^0 satisfies the equation $(\partial S/\partial X)|_{X^0}=0$. Writing $\partial^2 S^0 = (\partial^2 S/\partial X^2)|_{X^0}$ and using the relation $1/\sqrt{\det(A)\det(B)}$ $=\exp(-\frac{1}{2}\text{Tr}[\ln(AB)])$, with $A=\beta V$, $B=\beta\partial^2 S^0$, and AB $=\Delta S^0$, we find a practical formula for Z_G. It is approximately given by $e^{-\beta\Omega^{\text{eff}}}$ with

$$\Omega^{\text{eff}} = S^0 + \frac{\text{Tr}[\ln(\Delta S^0)]}{2\beta}. \quad (14)$$

Ω^{eff} depends on β and μ. From Eqs. (5), (8), and (9) we find the average-atom equations

$$\overline{N}_k^0 = \frac{D_k}{1+e^{\beta e_k^0}}$$

$$e_k^0 = \frac{\partial E}{\partial P_k}\bigg|_{(\overline{N}_k^0)} - \mu. \quad (15)$$

To go beyond this average-atom model and the related independent electron description, the usual method is to express the configuration energy as a second-order Taylor expansion in occupation numbers about the average-atom configuration. The quadratic term incorporates relaxation effects and offers a better description of physics than the truncation of the Taylor expansion after the linear term. Moreover, as pointed out by Wilson [27], it gives an opportunity to estimate the thermodynamic mean quantities and correlations between orbital populations that neither an average-atom model nor brute force computation of (1) permit.

The last step is to give the expression of the effective grand potential Ω^{eff}. Combining Eqs. (8), (9), (11), and (15), we find

$$S(X^0) = E[(\overline{N}_k^0)] - \mu\sum_{k=1}^{K_{\max}} \overline{N}_k^0$$

$$+k_BT\sum_{k=1}^{K_{\max}} D_k[f_k^0\ln(f_k^0) + (1-f_k^0)\ln(1-f_k^0)].$$

$$(16)$$

$S(X^0)$ is the "classical" grand potential of the electrons of the $K_{\max}$ bound orbitals. We obtain the entropy of an ideal Fermi-Dirac gas with mean quantum state occupancies (f_k^0). The energy is deduced from the energy of an isolated ion by substituting the integer occupation numbers by the average-atom populations $(\overline{N}_k^0)$ defined by Eq. (15). Note that we must calculate the mean energy and the mean occupation numbers with the formulas (2) and (3) before identifying $E[(\overline{N}_k^0)]$ and $(\overline{N}_k^0)$ to the former thermodynamic quantities.

As mentioned by Wilson [27], these manipulations are more rigorous than those using the method of expansion in inverse temperature [2], or Stirling's approximation to the configuration degeneracy and the continuum approximation to perform discrete summations [31]. Finally we see that no reference configuration whose occupation numbers are given by an auxiliary average-atom model is needed. Our model is thermodynamically self-consistent and the average-atom configuration is defined by the saddle-point equations. This

fact will be of great importance in the case of the SHM. The correction to $S(X^0)$ is obtained using Eqs. (8), (9), and (11). Defining $\bar{\omega}_k^2 = [\bar{N}_k^0(D_k - \bar{N}_k^0)/D_k]$, we arrive at

$$(\beta V \beta \partial^2 S^0)_{kk'} = (\Delta S^0)_{kk'} = V_{kk'}\beta\bar{\omega}_k^2 + \delta_{kk'}. \qquad (17)$$

C. Integral representation of Z_G using the SHM

As in the SHM, an exact integral representation can be found for Z_G. The SHM configuration energy $E[(P_k)]$ expression is (in atomic units)

$$E[(P_k)] = -\sum_{k=1}^{K_{\max}} \frac{Z_k^2}{2n_k^2} P_k$$

$$Z_k = Z + \alpha_k - \sum_{k'=1}^{K_{\max}} \sigma_{kk'}P_{k'}. \qquad (18)$$

$(\sigma_{kk'})$ is a set of screening constants independent of the electronic configuration [19,28,32]. (α_k) are constants characteristic of a SHM. The partition function for such a model is

$$Z_G = \sum_{(P_k)} \prod_{k=1}^{K_{\max}} \binom{D_k^0}{P_k} e^{-\beta(-Z_k^2/2n_k^2 - \mu)P_k}. \qquad (19)$$

$E[(P_k)]$ is a cubic form in the occupation numbers, but a quadratic form in the screened hydrogenic charges (Z_k). So, the integral representation of Z_G is obtained in two steps

$$\prod_{k=1}^{K_{\max}} e^{\beta P_k Z_k^2/2n_k^2} = \frac{1}{\left(\prod_{k=1}^{K_{\max}} 2\pi \dfrac{\beta P_k}{n_k^2}\right)^{1/2}} \int d^{K_{\max}}X$$

$$\times \prod_{k=1}^{K_{\max}} e^{-([1/2]X_k^2[n_k^2/\beta P_k] + Z_k X_k)}$$

$$\prod_{k=1}^{K_{\max}} e^{-(1/2)X_k^2(n_k^2/\beta P_k)} = \frac{1}{\sqrt{\left(\prod_{k=1}^{K_{\max}} 2\pi \dfrac{n_k^2}{\beta P_k}\right)^{1/2}}} \int d^{K_{\max}}Y$$

$$\times \prod_{k=1}^{K_{\max}} e^{-([1/2]Y_k^2[\beta P_k/n_k^2] + iX_k Y_k)}. \qquad (20)$$

The combination of these two integrals is ill defined because of the terms $Z_k X_k$ in the first identity. It is due to the sign of the energy. As Z_G is analytic in the screened hydrogenic charges (Z_k), the minus sign is absorbed doing the transformation [23,26,30]: $Z_k \to iZ_k$. Formally, it is equivalent to proceeding on the (Z_k) or on the screening constants $(\sigma_{kk'})$. This last manipulation is justified by the fact that these coefficients are homogeneous functions of degree one in the screened hydrogenic charges [33]. At the end of the calculation, the original real variables are recovered by making the inverse analytic continuation

$$Z_k \to -iZ_k$$

$$\sigma_{kk'} \to -i\sigma_{kk'}. \qquad (21)$$

$$\alpha_k \to -i\alpha_k$$

Z_G becomes $Z_G = \Sigma_{(P_k)} \Pi_{k=1}^{K_{\max}} \binom{D_k^0}{P_k} e^{-\beta([Z_k^2/2n_k^2] - \mu)P_k}$, which can be rewritten using Eqs. (20) as

$$Z_G = \sum_{(P_k)} \prod_{k=1}^{K_{\max}} \binom{D_k^0}{P_k} \frac{1}{2\pi} \int dX_k dY_k$$

$$\times e^{-([Y_k^2 \beta P_k/2n_k^2] + iX_k Y_k + iX_k Z_k - \beta\mu P_k)}. \qquad (22)$$

Let (χ_k) and the $K_{\max}$-dimensional vectors $\hat{Z}$ and $\hat{\alpha}$ be, respectively, $\chi_k = \Sigma_{k'=1}^{K_{\max}} \sigma_{k'k}X_{k'}$, $\hat{Z} = (Z,\ldots,Z)$, and $\hat{\alpha} = (\alpha,\ldots,\alpha)$. The right term can be factorized with the result

$$Z_G = \frac{1}{(2\pi)^{K_{\max}}} \int d^{K_{\max}}X d^{K_{\max}}Y e^{-iX^T(Y + \hat{Z} + \hat{\alpha})}$$

$$\times \prod_{k=1}^{K_{\max}} [1 + e^{-\beta(Y_k^2/2n_k^2 - i\chi_k/\beta - \mu)}]^{D_k^0}. \qquad (23)$$

The auxiliary variable number has been doubled due to the chosen energy form (18). The interaction linearization is ensured by the $iX^T Z$ term. The one-electron part (kinetic energy–potential energy due to the attraction of the nucleus) $Y_k^2/(2n_k^2)$ is separated from the electron-electron interaction part, $-i(\chi_k/\beta)$. The electronic configuration (P_k) has been replaced by a physically less transparent configuration (X_k, Y_k). For the same reasons given earlier, the superscript 0 of the degeneracies is deleted. Note that an integral representation of Z_G can be found with any term of the form $P_k Z_k^q$, where q is an even integer.

Before estimating Z_G, it is convenient to change the scale: $X_k \to ZX_k/\beta$ and $Y_k \to Y_k/Z$. Introducing ($k = 1,\ldots,K_{\max}$) $\mathbb{I}_k = 1$, $e_k = (Z^2 Y_k^2)/(2n_k^2) - i(\chi_k/Z) - \mu$, $e^{\beta\varphi_k} = 1/(1 + e^{\beta e_k})$, and

$$U_k = X_k, \quad k = 1,\ldots,K_{\max}$$

$$U_k = Y_k, \quad k = K_{\max} + 1,\ldots,2K_{\max}$$

$$[dU] = \frac{d^{K_{\max}}X d^{K_{\max}}Y}{(2\pi/\beta)^{K_{\max}}}$$

$$S(U) = iX^T\left(Y + \mathbb{I} + \frac{\alpha}{Z}\right) + \sum_{k=1}^{K_{\max}} D_k(e_k + \varphi_k), \qquad (24)$$

Z_G reads $Z_G = \int[dU]e^{-\beta S(U)}$. The saddle-point method is used to evaluate it. We find that $Z_G \approx e^{-\beta\Omega^{\text{eff}}}$ with U^0 satisfying $(\partial S/\partial U)|U^0 = 0$, $(\partial^2 S/\partial U^2)|U^0 = \Delta S^0$, and

$$\Omega^{\text{eff}} = S(U^0) + \frac{\text{Tr}[\ln(\Delta S^0)]}{2\beta}. \qquad (25)$$

Neglecting the electrostatic interactions between bound and free electrons, elementary algebraic manipulations show that

TABLE I. Coefficients of the matrix ΔS^0 for the SHM.

$\left.\dfrac{\partial^2 S}{\partial X_k \partial X_{k'}}\right|_0$	$\dfrac{\beta}{Z^2} \displaystyle\sum_{k''=1}^{K_{\max}} \sigma_{kk''}\sigma_{k'k''}\bar{\omega}_{k''}^2$
$\left.\dfrac{\partial^2 S}{\partial X_k \partial Y_{k'}}\right|_0$	$i\left(\delta_{kk'} - \dfrac{\beta Z_{k'}^0 \sigma_{kk'}}{n_{k'}^2}\,\bar{\omega}_{k'}^2\right)$
$\left.\dfrac{\partial^2 S}{\partial Y_k \partial Y_{k'}}\right|_0$	$\dfrac{Z^2 \delta_{kk'}}{n_k^2}\left(\bar{N}_k^0 - \dfrac{\beta Z_k^{0^2}}{n_k^2}\,\bar{\omega}_k^2\right)$

the variables $(\bar{N}_k^0)$, more relevant than (X_k^0, Y_k^0), are solutions of a system of nonlinear coupled equations which are precisely the screened-hydrogenic average-atom equations proposed by More and Zimmerman [15,18]

$$Z_k = Z + \alpha_k - \sum_{k=1}^{K_{\max}} \sigma_{kk'} P_{k'}$$

$$E[(P_k)] = \sum_{k=1}^{K_{\max}} \frac{Z_k^2}{2n_k^2}\, P_k$$

$$e_k^0 = \left.\frac{\partial E}{\partial P_k}\right|_{(\bar{N}_k^0)} - \mu$$

$$\bar{N}_k^0 = \frac{D_k}{1 + e^{\beta e_k^0}}. \tag{26}$$

Going back to the real axis to calculate the true physical quantities just changes the energy sign. As all formulas stay formally the same, the inverse analytic continuation will be omitted. The saddle-point equation interpretation is clear. The one-electron energies, which appear in the Fermi-Dirac factors, are the derivatives of the configuration energy [Eq. (18)]. The same result is obtained in Mayer's case. This point is crucial to ensure the thermodynamic consistency of the model. More generally, equations $(\partial S/\partial U)|_{U^0} = 0$ which determine the saddle point U^0 are known to be the mean-field equations [25,34]. Straightforward manipulations show that $S(U^0)$, appearing in the effective grand potential Ω^{eff}, is the grand potential corresponding to the free energy originally proposed by Zimmerman and More

$$S(U^0) = \sum_{k=1}^{K_{\max}} \left(\frac{Z_k^{0^2}}{n_k^2}\,\bar{N}_k^0 - \mu \bar{N}_k^0\right)$$
$$+ k_B T \sum_{k=1}^{K_{\max}} D_k \{f_k^0 \ln(f_k^0) + (1-f_k^0)\ln[(1-f_k^0)]\}. \tag{27}$$

We recognize the energy [Eq. (18)] calculated with the populations $(\bar{N}_k^0)$ and the entropy of an ideal Fermi-Dirac gas [$f_k^0 = 1/(1 + e^{\beta e_k^0})$, Eq. (26)]. The ΔS^0 matrix coefficients are given in Table I.

D. Evaluation of thermodynamic quantities

To calculate the mean occupancy, mean energy, mean orbital populations, and orbital occupation correlations, we must differentiate the grand potential with respect to μ and β. We therefore need to know the expressions of $\partial \bar{N}_k^0/\partial \mu$ and of $\partial \bar{N}_k^0/\partial \beta$. It is worth introducing the two matrices $(\omega_{kk'})$ and $(V_{kk'})$. The matrix V is deduced from the configuration energy by performing second derivatives with respect to populations ($V_{kk'} = \partial^2 E/[\partial P_k \partial P_{k'}]$). The notation $V_{kk'}^0$ means that $V_{kk'}$ is calculated with the average-atom configuration ($\bar{N}_k^0$). The matrix ω is constructed from V and $(\bar{N}_k^0)$

$$\omega_{kk'} = \beta V_{kk'}^0 + \frac{\delta_{kk'}}{\bar{\omega}_k^2}$$

$$\bar{\omega}_k^2 = \frac{\bar{N}_k^0(D_k - \bar{N}_k^0)}{D_k}. \tag{28}$$

These notations apply both to Mayer's model and to the SHM. In Mayer's case, V is identical to the electrostatic interaction matrix [28], as underlined by the notation. Using Eqs. (15) or (26), it can be shown that

$$\frac{\partial \bar{N}_k^0}{\partial \mu} = \beta \sum_{k'=1}^{K_{\max}} (\omega^{-1})_{kk'}$$

$$\frac{\partial \bar{N}_k^0}{\partial \beta} = \sum_{k'=1}^{K_{\max}} (\omega^{-1})_{kk'} e_{k'}^0. \tag{29}$$

With the chosen conventions, the system of equations (29) can be used for either the model is (Mayer or SHM). We now calculate mean occupancy, mean energy, orbital occupation numbers, and correlations. We have to differentiate the effective potential Ω^{eff} with respect to μ. The first part S^0 gives $\partial S^0/\partial \mu = -\Sigma_{k=1}^{K_{\max}} \bar{N}_k^0$. In order to treat the second correction to Ω^{eff}, we have to consider a symmetric, definite, and positive matrix $X(t)$ function of a parameter t. From $d/dt \operatorname{Tr}\{\ln[X(t)]\} = \operatorname{Tr}[X^{-1}(dX/dt)(t)]$ and by using Eqs. (2), (14), (25), (28), and (29), we find a closed form for $\bar{N}$

$$\nabla_k = \frac{\partial}{\partial \bar{N}_k^0}$$

$$\delta_{\bar{N}} = -\frac{1}{2} \sum_{k,k'=1}^{K_{\max}} (\omega^{-1})_{kk'}\, \operatorname{Tr}[(\Delta S^0)^{-1}\nabla_k \Delta S^0]$$

$$\bar{N} = \sum_{k=1}^{K_{\max}} \bar{N}_k^0 + \delta_{\bar{N}}. \tag{30}$$

The only difference between the two models will be in the calculation of the coefficients of the matrix ΔS^0 [Eq. (17) for Mayer's model and Table I for the SHM]. The expression of

TABLE II. Gradient of ΔS^0 with respect to average-atom populations ($\bar{N}^0_\lambda$) for the Mayer's model and the SHM.

	$\dfrac{\partial \bar{\omega}^2_k}{\partial \bar{N}^0_\lambda}$	$\delta_{\lambda k}\left(1 - \dfrac{2\bar{N}^0_\lambda}{D_\lambda}\right)$
Mayer	$\dfrac{\partial (\Delta S^0)_{kk'}}{\partial \bar{N}^0_\lambda}$	$\delta_{\lambda k}\left(1 - \dfrac{2\bar{N}^0_\lambda}{D_\lambda}\right)\beta V_{kk'}$
MHE	$\dfrac{\partial}{\partial \bar{N}^0_\lambda}\left[\dfrac{\partial^2 S}{\partial X_k \partial X_{k'}}\Big|_0\right]$	$\dfrac{\beta}{Z^2}\sigma_{k\lambda}\sigma_{k'\lambda}\left(1 - \dfrac{2\bar{N}^0_\lambda}{D_\lambda}\right)$
	$\dfrac{\partial}{\partial \bar{N}^0_\lambda}\left[\dfrac{\partial^2 S}{\partial X_k \partial Y_{k'}}\Big|_0\right]$	$\dfrac{-i\beta\sigma_{kk'}}{n^2_{k'}}\left[Z^0_\lambda\left(1 - \dfrac{2\bar{N}^0_\lambda}{D_\lambda}\right) - \bar{\omega}^2_{k'}\sigma_{k'\lambda}\right]$
	$\dfrac{\partial}{\partial \bar{N}^0_\lambda}\left[\dfrac{\partial^2 S}{\partial Y_k \partial Y_{k'}}\Big|_0\right]$	$\dfrac{\beta Z^2 \delta_{kk'}}{n^2_k}\left[\dfrac{\delta_{k\lambda}}{\beta} - \dfrac{Z^{0^2}_k}{n^2_k}\left(1 - \dfrac{2\bar{N}^0_\lambda}{D_\lambda}\right) + \dfrac{2Z^0_k \bar{\omega}^2_k}{n^2_k}\sigma_{k\lambda}\right]$

its gradient $\nabla_k \Delta S^0$ for both models is in Table II. The calculation of the mean energy proceeds as above and we find

$$\bar{E} = E[(\bar{N}^0_k)] + \mu\delta_{\bar{N}} + \delta_{\bar{E}}$$

$$\delta_{\bar{E}} = \frac{1}{2}\sum_{k,k'=1}^{K_{\max}}(\omega^{-1})_{kk'}e^0_{k'}\mathrm{Tr}[(\Delta S^0)^{-1}\nabla_k \Delta S^0]. \quad (31)$$

The orbital occupation number and correlation are usually obtained by differentiation of a generating function [21,26,30] with respect to a source term. In our case, we may introduce a chemical potential μ_k for each orbital k. The quantities of interest are then obtained using

$$\bar{N}_k = -\frac{\partial \Omega}{\partial \mu_k}\Big|_{\mu_k=\mu}$$

$$\overline{\Delta N_k \Delta N_{k'}} = -\frac{1}{\beta}\frac{\partial^2 \Omega}{\partial \mu_k \partial \mu_{k'}}\Big|_{\mu_k=\mu_{k'}=\mu} \quad (32)$$

with the result

$$\bar{N}_k = \bar{N}^0_k + \delta_{\bar{N}_k}$$

$$\delta_{\bar{N}_k} = -\frac{1}{2}\sum_{k'=1}^{K_{\max}}(\omega^{-1})_{kk'}\mathrm{Tr}((\Delta S^0)^{-1}\nabla_{k'}\Delta S^0)$$

$$\overline{\Delta N_k \Delta N_{k'}} = (\omega^{-1})_{kk'} + \text{correction.} \quad (33)$$

The corrective term can be obtained by the same technique as above.

E. Integer charge stage splitting

The aim of this section is to compute the abundance of a particular integer charge state and to find its mean orbital population numbers from minor manipulations of the grand canonical partition function Z_G. If the electrostatic interactions among the bound electrons are neglected, one is dealing with an ideal Fermi-Dirac gas. The exact partition function Z_G of this system is known in closed form

$$Z_G = \sum_{(P_k)}\sum_{k=1}^{K_{\max}}\binom{D_k}{P_k}e^{-\beta(\epsilon_k-\mu)P_k} \quad (34)$$

which factorizes as $Z_G = \Pi_{k=1}^{K_{\max}}[1+e^{-\beta(\epsilon_k-\mu)}]^{D_k}$. In the present case, the internal partition function Z^N_G of an N-electron charge state is $Z^N_G = \Sigma_{(P_k),\Upsilon}\Sigma_{k=1}^{K_{\max}}\binom{D_k}{P_k}e^{-\beta(\epsilon_k-\mu)P_k}$. The symbol Υ indicates that the summation runs through those configurations that satisfy the constraint $\Sigma_{k=1}^{K_{\max}}P_k=N$. We now face the difficulties generated by this constraint which prevents the factorization of Z_G [20,22]. We recall that the difference between the canonical description and the grand canonical description are fluctuations of $\bar{N}$, which are forbidden in the canonical case. The factorization of the grand canonical partition function requires the use of a Lagrange multiplier μ, which is found *a posteriori* from the equation $\bar{N} = (1/Z_G)(\Sigma_{(P_k)}\Sigma_{k=1}^{K_{\max}}P_k\binom{D_k}{P_k}e^{-\beta(\epsilon_k-\mu)P_k})$. We now keep this same idea to deduce Z^N_G from Z_G. The trick is to employ the identity

$$\frac{1}{2i\pi}\int_{-i\pi+\alpha_0}^{i\pi+\alpha_0}dt\, e^{tN} = \delta_{N,0}, \quad (35)$$

where N is an integer, α_0 a real, and $\delta_{N,0}$ is Kronecker symbol. So, inserting this formula in Eq. (34), we find

$$Z^N_G = \frac{1}{2i\pi}\int_{-i\pi+\alpha_0}^{i\pi+\alpha_0}dt\, e^{tN}\prod_{k=1}^{K_{\max}}[1+e^{-t}e^{-\beta(\epsilon_k-\mu)}]^{D_k}. \quad (36)$$

To go from Z_G to Z^N_G, we substitute μ for $\mu - t/\beta$ and integrate the modified partition function $Z_G(t)$ for each value of N. In order to understand more precisely the signification of Eq. (36), we change the variable of integration introducing z: $z = e^{-t}$. In the complex plane, we find

$$Z_G^N = \frac{1}{2i\pi} \oint \frac{dz}{z^{N+1}} \prod_{k=1}^{K_{\max}} [1 + ze^{-\beta(\epsilon_k - \mu)}]^{D_k} \quad (37)$$

or

$$\mathcal{Z}_G(z) = \prod_{k=1}^{K_{\max}} [1 + ze^{-\beta(\epsilon_k - \mu)}]^{D_k}$$

$$Z_G^N = \frac{1}{N!} \left. \frac{d^N \mathcal{Z}_G}{dz^N} \right|_{z=0}. \quad (38)$$

This result is quite obvious because Z_G^N is a polynomial of degree N with respect to the quantities $[e^{-\beta(\epsilon_k - \mu)}]$. Z_G^N is the Nth-order term of the Taylor expansion of $\mathcal{Z}_G(z)$ around the origin. For Mayer's model or the SHM, we have for Z_G^N

$$Z_G^N = \frac{1}{2i\pi} \int_{i\pi - \alpha_0}^{i\pi + \alpha_0} dt\ e^{tN} e^{-\beta \Omega^{\mathrm{eff}}(t)}. \quad (39)$$

The fraction (percent) $\mathcal{F}_{(Z-N)}$ of N-electron species [charge state $(Z-N)$] is then straightforward to compute since

$$\mathcal{F}_{(Z-N)} = \frac{Z_G^N}{Z_G}. \quad (40)$$

In the same spirit we have direct access to the mean orbital population numbers of N-electron ions. It is a simple application of the general formula: $\overline{N}_k^N = (1/\beta Z_G^N)(\partial Z_G^N / \partial \mu_k)|_{\mu_k = \mu}$. For an ideal Fermi-Dirac gas, we obtain

$$\overline{N}_k^N = \frac{\frac{1}{2i\pi} \int_{i\pi - \alpha_0}^{i\pi + \alpha_0} dt\ e^{tN} \frac{D_k}{1 + e^t e^{\beta(\epsilon_k - \mu)}} \prod_{k=1}^{K_{\max}} [1 + e^{-t} e^{-\beta(\epsilon_k - \mu)}]^{D_k}}{Z_G^N} \quad (41)$$

and for any other case

$$\overline{N}_k^N = \frac{-\frac{1}{2i\pi} \int_{i\pi - \alpha_0}^{i\pi + \alpha_0} dt\ e^{tN} \frac{\partial \Omega^{\mathrm{eff}}}{\partial \mu_k} \bigg|_{\mu_k = \mu} e^{-\beta \Omega^{\mathrm{eff}}(t)}}{Z_G^N}. \quad (42)$$

Those integrals can be evaluated numerically or using the saddle-point method.

III. APPROXIMATE DEVELOPMENTS USING THE CLASSICAL THEORY OF FLUCTUATIONS

The former developments are of limited practical interest for in-line calculations because we need to handle multidimensional integrals where the explicit orbital populations (P_k) are replaced with abstract variables. We could generalize this approach to calculate the thermodynamic mean of any physical quantity. The saddle-point method offers a valuable estimate of such integrals but finding the saddle point requires the time consuming solution of nonlinear coupled equations. An alternative is to use of a simplified version of the grand canonical probability density. The classical theory of fluctuations [22] is well suited in this case to tackle this problem. We just recall the principal steps which have been presented in detail elsewhere [28,31,35]. The first step is to replace the discrete summation (1) by a multidimensional integral. In doing so, the (P_k) are preferred to the aforementioned auxiliary variables. They are supposed to be real and take all possible values from $-\infty$ to $+\infty$. Starting from Eq. (1), writing the statistical weight of a configuration as e^{S/k_B}, and using Stirling's formula to compute each binomial factor we obtain $S = -k_B \sum_{k=1}^{K_{\max}} [P_k \ln(P_k/D_k) + (D_k - P_k)\ln([D_k - P_k]/D_k)]$ and

$$Z_G \propto \int d^{K_{\max}} P e^{-\beta\{E[(P_k)] - TS - \mu \sum_{k=1}^{K_{\max}} P_k\}}$$

$$= \int d^{K_{\max}} P e^{-\beta \Omega[(P_k)]}, \quad (43)$$

where $\propto$ means "up to a normalizing factor." The saddle point is then used to approximate the integral. Since Ω is the effective potential without the traditional corrective terms, it reaches precisely its minimum for the saddle-point determined by the average-atom equations $[\partial \Omega / \partial P_k|_{(\overline{N}_k^0)} = 0]$. As thermodynamic equilibrium is assumed, we just have to consider a second-order Taylor expansion of Ω. Let us introduce $\Delta P_k = P_k - \overline{N}_k^0$ and $\omega_{kk'} = \beta(\partial^2 \Omega)/(\partial P_k \partial P_{k'})|_{(\overline{N}_k^0)}$; elementary algebraic manipulations show that $\omega_{kk'} = (V_{kk'}/k_B T) + (\delta_{kk'}/\overline{\omega}_k^2)$ with $\overline{\omega}_k^2 = [\overline{N}_k^0(D_k - \overline{N}_k^0)/D_k]$. The symmetric, definite, positive matrix ω is identical to the previous one [Eq. (28)]. We deduce that the probability $d\mathcal{P}$ (normalized to unity) of an electronic configuration (P_k) reduces to

$$d\mathcal{P} = \left(\frac{\det(\omega)}{(2\pi)^{K_{\max}}} \right)^{1/2} d^{K_{\max}} \Delta P e^{-(1/2)\Delta P^T \omega \Delta P}. \quad (44)$$

Since the corrective terms in the effective grand potential have implicitly been neglected, the average-atom configuration ($\overline{N}_k^0$) is precisely equal to the mean orbital occupations ($\overline{N}_k$) and from now $\overline{N}_k^0 = \overline{N}_k = \overline{P}_k$. Equation (44) is of considerable interest for in-line calculations, especially in estimating the population distribution around their averages to improve the spectral opacity constructed with the average-atom configuration only. Introducing the correlation matrix C defined by $C_{kk'} = \overline{\Delta P_k \Delta P_k'}$, it is easy to show [22] that

$C_{kk'} = (\omega^{-1})_{kk'}$. The matrix ω is not diagonal with respect to the occupation numbers and we see clearly that the electrostatic interactions ($V_{kk'}$) induce correlations between them. Let us discuss the expression of the correlation matrix coefficients with respect to temperature. At high temperature, β tends to zero:

$$\omega_{kk'} \underset{k_B T \to \infty}{\approx} \frac{\delta_{kk'}}{\bar{\omega}_k^2} \to C_{kk'} \underset{k_B T \to \infty}{\approx} \delta_{kk'} \bar{\omega}_k^2.$$

Correlations then become negligible and we have an ideal Fermi-Dirac gas. On the contrary, correlations dominate at low temperature:

$$\omega_{kk'} \underset{k_B T \to 0}{\approx} \beta V_{kk'} \to C_{kk'} \underset{k_B T \to 0}{\approx} k_B T (V^{-1})_{kk'}.$$

Each coefficient of C varies linearly with $k_B T$ near absolute zero. Matter tends to freeze into the fundamental configuration at the chosen density. Finally, the correlation matrix coefficients depend explicitly on $(\bar{\omega}_k^2)$ and fluctuations are maximal for half-occupied orbitals.

This correlation matrix C plays a crucial role in calculating the fluctuations a physical quantity ζ around its thermodynamic mean $\bar{\zeta}$ [$\bar{\zeta} \approx \zeta(0)$]. Since thermodynamic equilibrium is assumed, these fluctuations are small [22] and the variance σ_ζ^2 of ζ can be found rapidly. Starting from

$$\zeta[(\Delta P_k)] = \zeta(0) + \sum_{k=1}^{K_{max}} \frac{\partial \zeta}{\partial \Delta P_k}\bigg|_0 \Delta P_k + \cdots$$

and $\sigma_\zeta^2 = \overline{[\zeta[(\Delta P_k)] - \zeta(0)]^2}$, σ_ζ^2 is approximately given by:

$$\sigma_\zeta^2 \approx \sum_{k,k'=1}^{K_{max}} \frac{\partial \zeta}{\partial \Delta P_k}\bigg|_0 \frac{\partial \zeta}{\partial \Delta P_{k'}}\bigg|_0 C_{kk'}.$$

For example, let us choose ζ to be the ionization: $\zeta = Z - \sum_{k=1}^{K_{max}} P_k$. $\zeta(0)$ is equal to $\bar{Z}$ and the ionization variance $\sigma_{\bar{Z}}^2$ to

$$\sigma_{\bar{Z}}^2 = \sum_{k,k'=1}^{K_{max}} C_{kk'}. \tag{45}$$

If we neglect correlations, which is justified at high temperature, we have an independent electron gas. Introducing $f_k = \bar{P}_k / D_k$, we then obtain the variance using the binomial distribution $\sigma_{\bar{Z}}^2 \approx \sum_{k=1}^{K_{max}} D_k f_k (1 - f_k)$.

In expression (44) of $d\mathcal{P}$, it is possible to reproduce the integer charge stage splitting. A very fast and simple evaluation of the detailed ionization stage accounting is possible. Moreover, the thermodynamic mean and the variance of any physical quantity can be computed with an explicit reference to a particular integer ion stage. The density $d\mathcal{P}$ is an approximation of the true density probability (or density matrix). In the evaluation of Z_G, the ion charges are between Z and $Z - \sum_{k=1}^{K_{max}} D_k$. It seems therefore natural to consider the new probability density $d\widetilde{\mathcal{P}}$

$$d\widetilde{\mathcal{P}} = \sum_{Z'} \frac{1}{\mathcal{Z}} d^{K_{max}} \Delta P e^{-(1/2)\Delta P^T \omega \Delta P} \delta\left(\sum_{k=1}^{K_{max}} \Delta P_k - \Delta Z'\right), \tag{46}$$

with $\sum_{k=1}^{K_{max}} P_k + Z' = Z$ and $\sum_{k=1}^{K_{max}} \bar{P}_k + \bar{Z} = Z$. To achieve that goal, a constraint is introduced in the partition function. The ion orbital populations are fractional but their sum is necessarily integer. $\Delta Z'$ means $\bar{Z} - Z'$. Normalizing $d\widetilde{\mathcal{P}}$ to unity and using the Fourier transformation of the Dirac distribution to reduce the Gaussian integral on the populations, $\mathcal{Z}$ is equal to

$$\mathcal{Z} = \sum_{Z'} \left(\frac{(2\pi)^{K_{max}}}{\det(\omega)}\right)^{1/2} \frac{e^{-1/2(\Delta Z'/\sigma_{\bar{Z}})^2}}{\sqrt{2\pi \sigma_{\bar{Z}}^2}}. \tag{47}$$

The ion fraction expression $\mathcal{F}_{Z'}$ of the charge state Z' is

$$\mathcal{F}_{Z'} = \frac{\mathcal{Z}^{Z'}}{\mathcal{Z}} = \frac{e^{-1/2(\Delta Z'/\sigma_{\bar{Z}})^2}}{\sum_{Z'} e^{-1/2(\Delta Z'/\sigma_{\bar{Z}})^2}}. \tag{48}$$

The physical meaning of Eq. (48) is simply the quotient of the internal partition function $\mathcal{Z}^{Z'}$ of the charge state Z' by the total partition function $\mathcal{Z}$. The classical theory of fluctuations allows a fast evaluation of this term. It can be shown [28] that Eq. (48) is closely linked to the couple of Eqs. (39) and (40). This result is valid for the screened-hydrogenic average-atom model or any average-atom model where a second-order Taylor expansion in the occupation numbers is performed. The mean orbital populations ($\bar{P}_k^{Z'}$) for an integer charge state Z' can be computed as well. It is very important to remark that the positivity of these populations are not granted for ion stages far from the average atom. Similarly, the population of a nearly complete orbital k_0 can exceed the degeneracy D_{k_0}. By definition

$$\bar{P}_k = \sum_{Z'} \mathcal{F}_{Z'} \bar{P}_k^{Z'}$$

$$\bar{P}_k^{Z'} = \frac{1}{\mathcal{Z}^{Z'}} \int d^{K_{max}} \Delta P e^{-(1/2)\Delta P^T \omega \Delta P}$$

$$\times \delta\left(\sum_{k'=1}^{K_{max}} \Delta P_{k'} - \Delta Z'\right) P_k, \tag{49}$$

and we find after some basic calculations that

$$\bar{P}_k^{Z'} = \bar{P}_k + \frac{\Delta Z' \alpha_k}{\sigma_{\bar{Z}}^2} \tag{50}$$

with $\alpha_k = \sum_{k'=1}^{K_{max}} (\omega^{-1})_{kk'}$ [see Eq. (28)]. The computations are reasonably accurate for ion stages close to the average-atom charge. Note that the sum of ($\bar{P}_k^{Z'}$) is equal to the charge state ($Z - Z'$). The thermodynamic mean $\bar{\zeta}^{Z'}$ of a physical quantity ζ with respect to the integer ion stage Z' is given by the expression
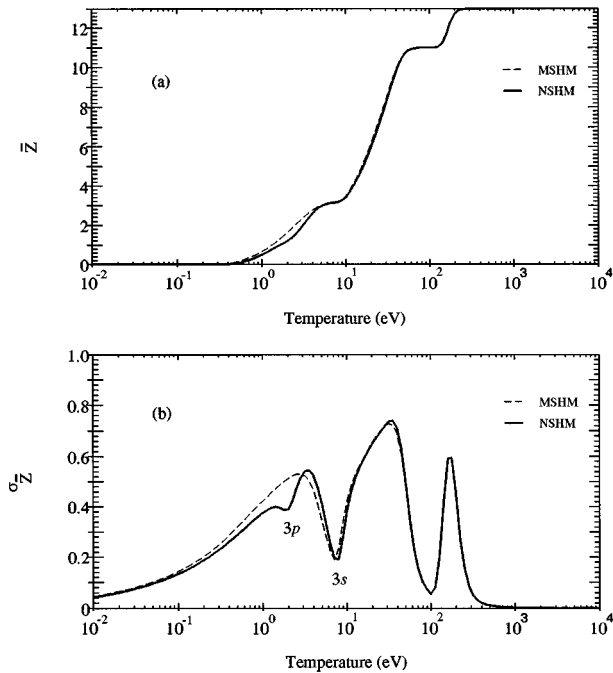
FIG. 1. Variations with temperature of the average ionization (a) and of the standard deviation (b) of an aluminum plasma, for a density equal to 10^{-4} g/cm^3. The MSHM and the NSHM (see text) are considered. In (b), the orbitals $3s$ and $3p$ are clearly distinct.

$$\overline{\zeta}^{Z'} = \overline{\zeta} + \sum_{k=1}^{K_{\max}} \left. \frac{\partial \zeta}{\partial P_k} \right|_0 \frac{\Delta Z' \alpha_k}{\sigma_Z^2}.$$

IV. NUMERICAL APPLICATIONS

To illustrate the usefulness of the formulas established above, we have chosen the screened-hydrogenic average atom to test some of them, and the classical theory of fluctuations to study statistical properties of LTE plasmas. We use the More's screened-hydrogenic model (MSHM) [19] degenerate with respect to the orbital quantum number l, and a new one (NSHM as new screened-hydrogenic model) [28] where l is explicitly considered. We restrict ourselves to the nonrelativistic regime. The pressure ionization model taking into account plasma effects is the version proposed by Zimmerman and More [18] with a_{ZM} and b_{ZM} equal, respectively, to 3 and 1 in order to match zero-temperature Thomas-Fermi ionization at high density ($\rho = \infty$) and solid density ($\rho = \rho_0$).

The first application of our method is the calculation of the average ionization of a LTE plasma. The fluctuations around average ionization $\overline{Z}$ are estimated, drawing the importance of correlations between orbital occupation numbers. The fast estimate of the integer charge stage distribution in a LTE plasma, which is a direct consequence of the generalization of the screened-hydrogenic average-atom model, has never been tackled to our knowledge, except through the standard Saha-Boltzmann equations, or methods resting on binomial manipulations [36,37]. The drawback of the first one is the inherent arbitrary selection of configurations to calculate the internal partition function of a particular ion stage and its problematic use at high density [15]. The dis-
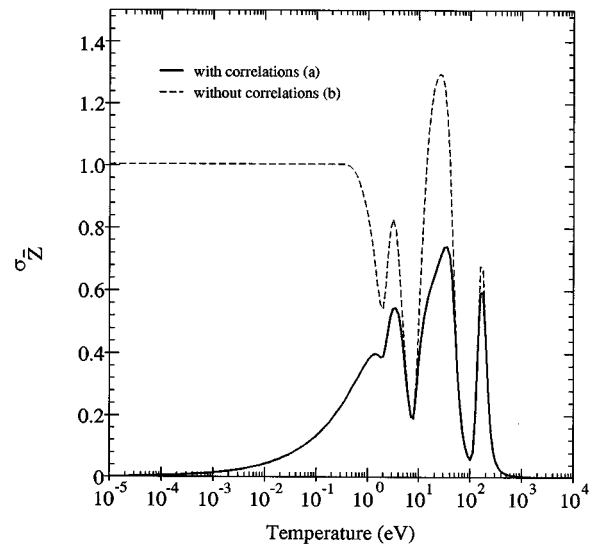

FIG. 2. Comparison between the standard deviation of ionization with (a) and without (b) correlations of an aluminum plasma as a function of temperature for a density of 10^{-4} g/cm^3.

advantage of the second one is the absence of correlations which can play an important role. We shall point out the influence of temperature, density, and principal quantum number when truncating the partition function on the fractions of the various ionization stages.

A. Average and fluctuation ionization

The variations of the average ionization $\overline{Z}$ and the standard deviation of ionization $\sigma_{\overline{Z}}$ with temperature of a LTE aluminum plasma are given in Fig. 1. A low density ($\rho = 10^{-4}$ g/cm^3) has been chosen in order to reduce pressure ionization and to show atomic effects that a model degenerate with respect to the orbital quantum number ignores. Both models give the same results as far as $\overline{Z}$ is concerned except near 2 eV [Fig. 1(a)]. The ionization plateau, only present on the NSHM curve, is due to the ionization of the $3p$ orbital. More's model is not able to predict it because $3s$ and $3p$ orbitals are not distinguished. This effect is far more visible in Fig. 1(b). When the temperature is not too low, each minimum of $\sigma_{\overline{Z}}$ means that a shell gets empty. So, on the NSHM curve, the plateaus near 2 eV and 6 eV correspond, respectively, to the $3p$ and $3s$ orbitals. At high temperature, both models give the same results. The energy splitting of orbitals with same principal quantum number is small compared to $k_B T$ so that these orbitals are populated according to their statistical weights. Since the electrostatic interactions between the electrons inside the atom become much less than $k_B T$, we have an independent particle gas in this temperature domain.

Ionization standard deviation gives valuable physical informations concerning the integer charge stage distribution around the average atom, and also on the occupancy orbital numbers. This point is quite clear when the correlation matrix ω expression is considered. To be more precise, let us look at Fig. 2 where (i) we have reproduced the NSHM curve (with correlations) of Fig. 1(b), (ii) we have included its uncorrelated counterpart (ω is diagonal). The temperature

TABLE III. Integer charge state distribution of an aluminum plasma ($T=40$ eV, $\rho=1.35\times10^{-2}$ g/cm^3) and an iron plasma ($T=25$ eV, $\rho=1.35\times10^{-2}$ g/cm^3). We have emboldened the dominant charge states.

	Aluminum	Iron
Average ionization ($\bar{Z}$)	7.036	7.227
Ionization standard deviation ($\sigma_{\bar{Z}}$)	0.849	0.888
Charge state	Fraction (%)	
4	7.87×10^{-2}	6.11×10^{-2}
5	2.65	1.94
6	**22.33**	**17.30**
7	**46.95**	**43.48**
8	**24.65**	**30.75**
9	3.23	6.12
10	0.11	0.34

domain ranges from very low temperatures 10^{-5} eV to 10^4 eV. At sufficiently high temperature, it is not surprising to see that the two curves are identical. The main differences are for intermediate and low temperatures. At zero temperature, the system lies in its ground state configuration at 10^{-4} g/cm^3. So, the absence of interactions between the electrons keeps $\sigma_{\bar{Z}}$ finite, except in situations where all the shells are either empty or full. Note that due to the pressure ionization model, $\sigma_{\bar{Z}}$ tends to 1.004 instead of $\sqrt{5/6}$ (0.913, one electron in the $3p$ orbital). $\sigma_{\bar{Z}}$ without correlations is always greater than $\sigma_{\bar{Z}}$ with correlations. The difference can exceed a factor 10. Neglecting correlations in the calculation of a thermodynamic average amounts to use a partition function in which the configuration energies are linearized with respect to populations around the average-atom configuration (or another reference point). Expansion up to second order in populations is required to introduce the electrostatic interac-

tion terms V_{ij} close to the average electrostatic interaction potentials between electrons. The correlations come from the V_{ij} which are positive since they represent the repulsive electrostatic interaction between electrons i and j. So, neglecting the V_{ij} amounts to underestimate the configuration energy and, hence, to overestimate each Boltzmann factor in the partition function. A far more important number of configurations around the average-atom configuration would then contribute and increase the dispersion around the reference point.

B. Detailed ionization stage accounting

In this section, we study the estimate of the integer charge state distribution in the plasma. We first consider the influence of correlations and second the role of temperature and maximum principal quantum number, in the case of alumi-
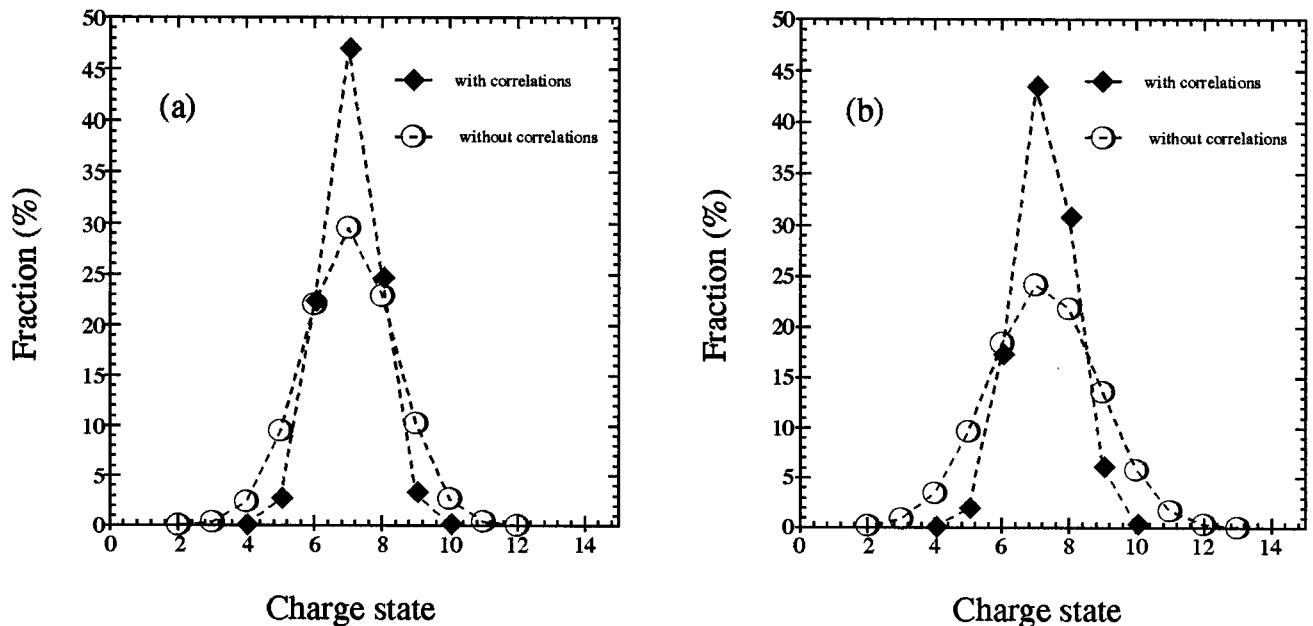

FIG. 3. Comparison of the integer charge state distributions with and without correlations for two plasmas (a) aluminum ($T=40$ eV, $\rho=1.35\times10^{-2}$ g/cm^3) and (b) iron ($T=25$ eV, $\rho=8.10\times10^{-3}$ g/cm^3).
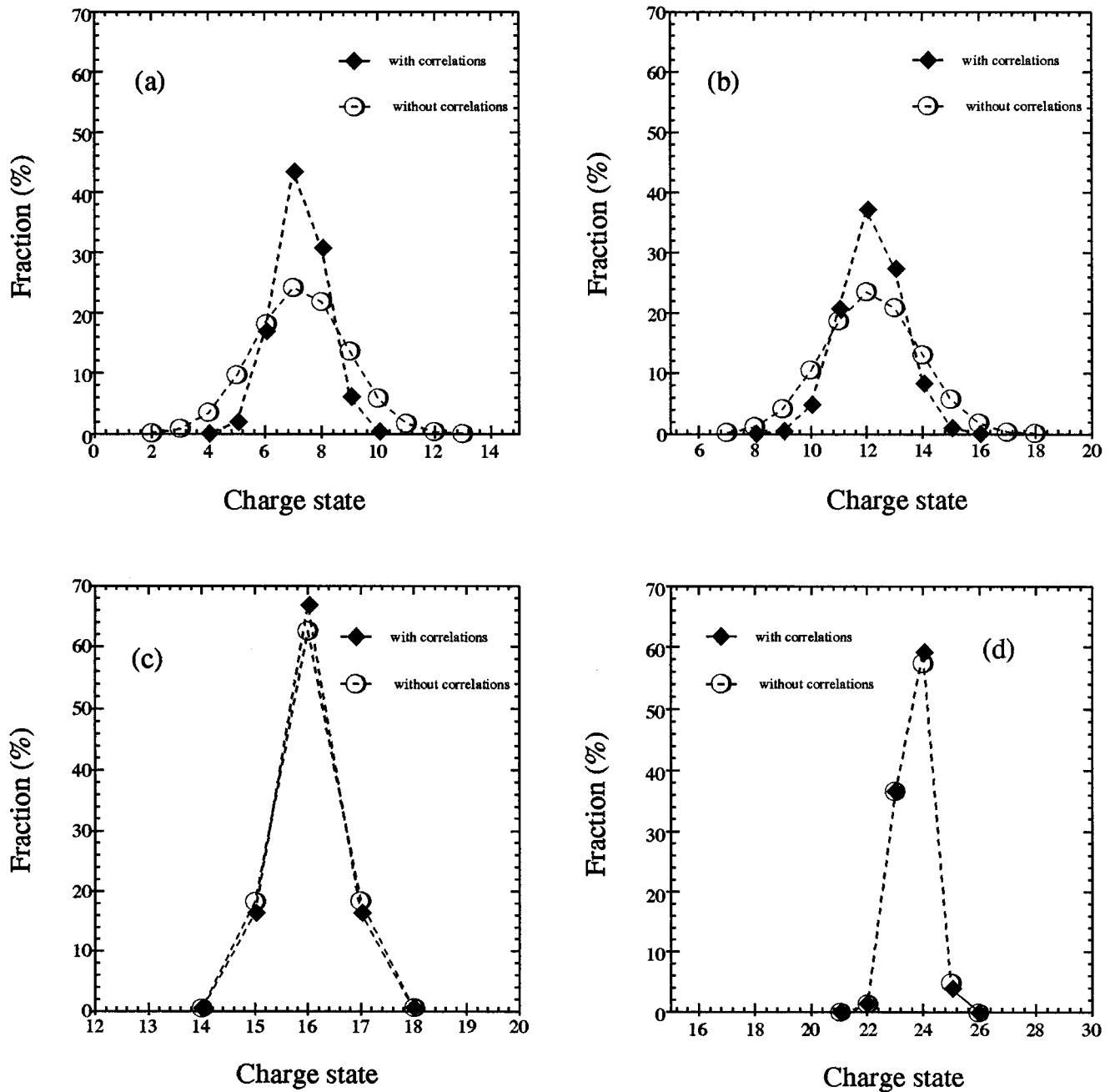
FIG. 4. Comparison of the integer charge state distributions with and without correlations for an iron plasma ($\rho = 8 \times 10^{-3}$ g/cm^3) for four temperatures 25 eV (a), 50 eV (b), 100 eV (c), and 300 eV (d).

num and iron. This gives us the opportunity to compare our formalism to more detailed calculations [38,39].

In Table III, the ion fractions estimated from Eq. (48) for two LTE plasmas of aluminum [17,39,40] ($T=40$ eV, $\rho = 1.35 \times 10^{-2}$ g/cm^3) and iron [41] ($T=25$ eV, $\rho = 8 \times 10^{-3}$ g/cm^3) are given. For the case considered, only a few charge states dominate in the plasma. In both cases, the distributions are quite similar and we find only three main ion species. In order to see the influence of correlations, we plot the former distributions where correlations are included together with the uncorrelated ones. The results are displayed in Fig. 3. As expected, the distributions without correlations have the largest variance. Due to the contributions of the

charge states in the wings, the dominant charge state fraction can be reduced by a factor two. This is understood in terms of ionization standard deviation. We recall the values of these for the aluminum and iron plasmas respectively: without correlations we find 1.351 and 1.634, and with correlations 0.849 and 0.888. So there is a factor of 2 between the two situations. The differences depend on the element and the thermodynamic conditions. In particular, an interesting phenomenon can be observed in the iron case. The initial density ($\rho = 8 \times 10^{-3}$ g/cm^3) is kept but three other temperatures are considered: 50 eV, 100 eV, and 300 eV. We add to these three examples the 25 eV plasma and plot them in Fig. 4. The curves with and without correlations tend to merge
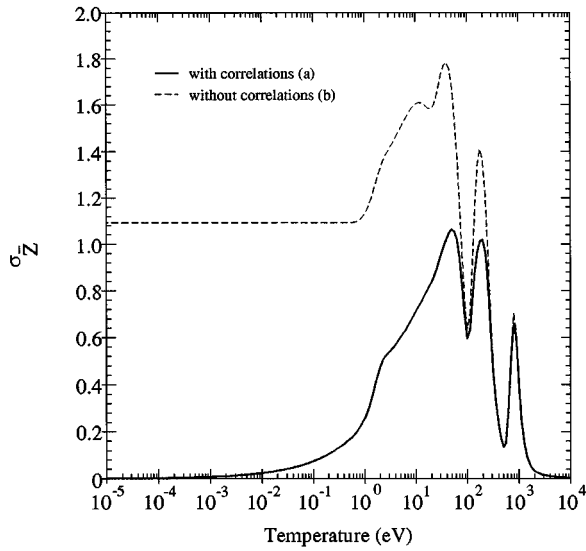
FIG. 5. Comparison of the ionization standard deviations with (a) and without (b) correlations of an iron plasma as a function of temperature ($\rho = 8 \times 10^{-3}$ g/cm^3).

FIG. 7. Integer charge state distribution of an aluminum plasma ($\rho = 1.35 \times 10^{-2}$ g/cm^3). We adopt the notations proper to atomic structure to label the different ion stages. For example, [F] is the fluorinelike charge state.

when the temperature is high enough. The calculations are equivalent at 100 eV because the M shell is just becoming empty. Examination of Fig. 5 is instructive enough. Even at 200 eV we are below the temperature edge because the L shell is half-empty and the standard deviations with and without correlations are notably different, explaining the deviations between the two curves of Fig. 6.

Before concluding this paper, we compare our model concerning the aluminum plasma to more elaborate calculations. From a detailed atomic physics data base, Abdallah and Clark [38] have computed the evolution of the integer charge state distribution of a LTE aluminum plasma with temperature from 20 eV to 100 eV ($\rho = 1.35 \times 10^{-2}$ g/cm^3). In Fig. 7

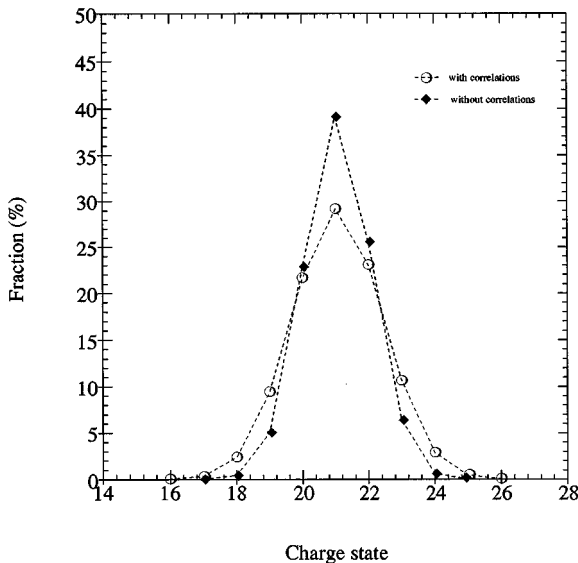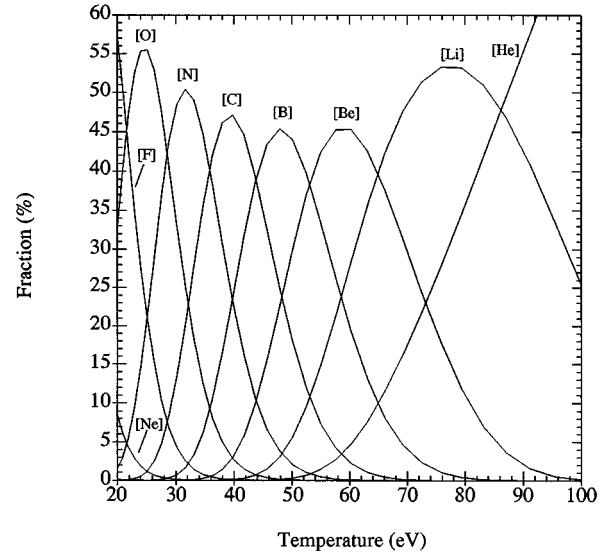FIG. 6. Comparison of the integer charge state distributions with and without correlations for an iron plasma ($T = 200$ eV, $\rho = 8 \times 10^{-3}$ g/cm^3).

our calculations are compared to Fig. 2 of Ref. [39]. At a given temperature, the NSHM predicts an ionization higher than that obtained by Kilcrease *et al.* [39]: the NSHM curve is shifted near the left by about 6 eV. Again in this model, the dispersion of the maxima is more pronounced than that in Ref. [39]. It is especially the case for the charge states near n shell closure ([He]- and [Li]-like ions for the K shell, [O]-, [F]-, and [Ne]-like ions for L shell). The uncertainty may arise from (i) the screening constants, (ii) the statistical method we used, (iii) the pressure ionization model, and (iv) the maximum quantum number n_{max} chosen to truncate the partition function. Since the calculations of Abdallah and Clark [38] did not account for pressure ionization, we performed a new set of calculations neglecting pressure ionization (so $a_{ZM} = b_{ZM} = 0$) and changing n_{max}. The results for the four cases are plotted in Fig. 8. We see that the integer charge state distribution depends strongly on n_{max}. When n_{max} increases, the excited configurations, due to their statistical weight, tend to play an increasingly important role, even the most improbable ones. They make the partition function diverge when n_{max} goes to infinity. This effect tends to flatten the arches. We note that the distribution of Kilcrease *et al.* lies between the graphs $n_{max} = 4$ and $n_{max} = 6$. With the ionization pressure model, the distribution is stable and independent of n_{max}. We know that this is the formulation which allows a physical truncation of the partition function, bound electrons going continuously into the continuum within a thermodynamically consistent average-atom model.

V. CONCLUSION AND PERSPECTIVES

The screened-hydrogenic average-atom model used to describe highly charged ions in LTE plasmas is well understood and thermodynamically consistent. The grand canonical internal partition function Z_G of the bound electrons has an exact integral representation when the total ion energy is expresed using the screened-hydrogenic model. Z_G is esti-
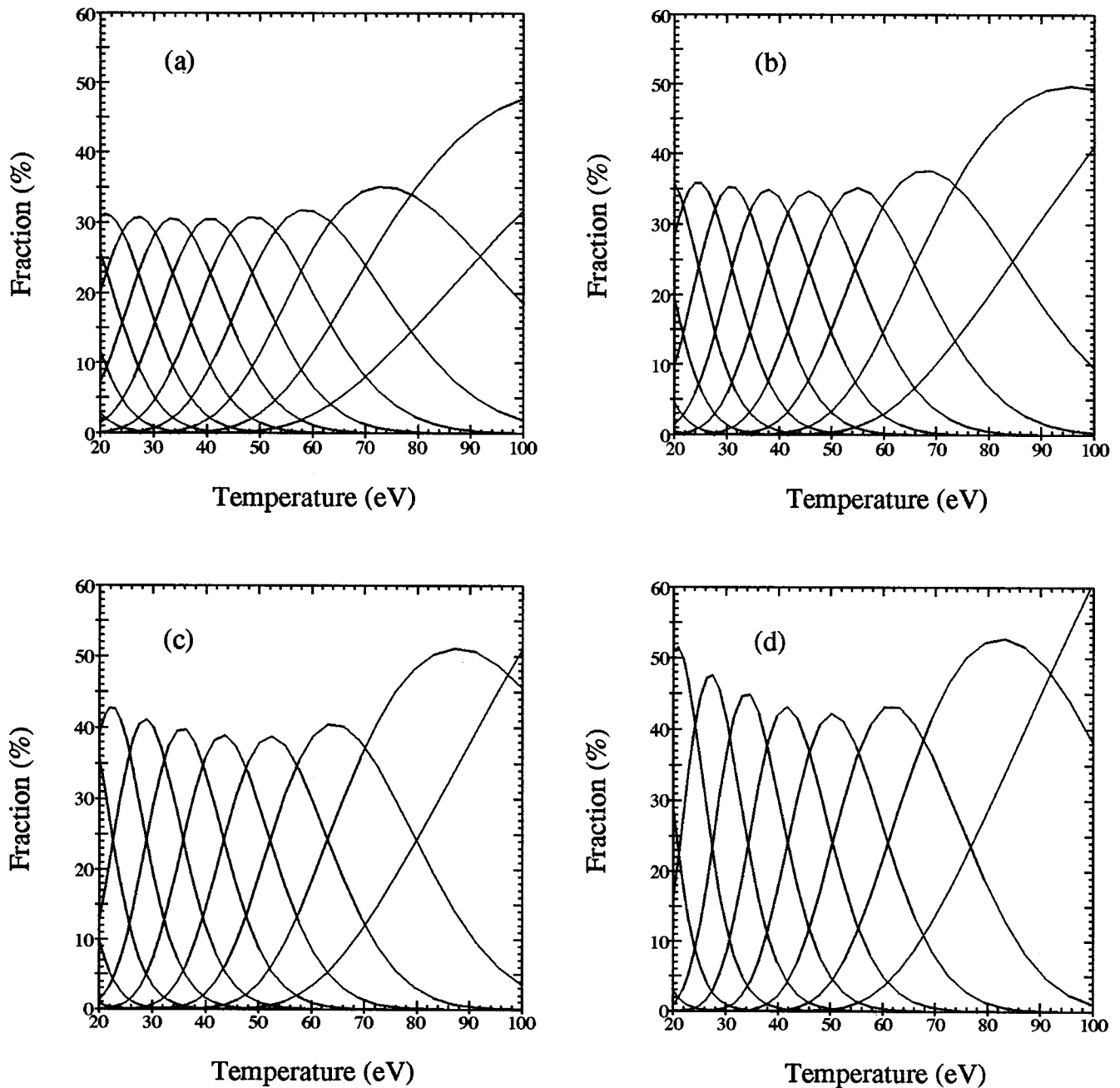
FIG. 8. Integer charge state distribution of an aluminum plasma ($\rho = 1.35 \times 10^{-2}$ g/cm^3). We vary the maximum principal quantum number n_{max}: (a) $n_{max} = 10$, (b) $n_{max} = 8$, (c) $n_{max} = 6$, and (d) $n_{max} = 4$.

mated with the saddle-point method. Straightforward differentiations with respect to the chemical potential μ and the inverse temperature β leads to the mean bound electron number and to the mean electronic energy. The equations which determine the saddle point are identical to the traditional set of nonlinear coupled equations dealing with average-atom populations ($\bar{P}_k$) and Fermi-Dirac statistics. To first order, the electron populations are equal to the thermodynamic mean orbital populations. A method, which can be extended to any average-atom model, for calculating the charge state

distribution from Z_G is proposed. The classical theory of fluctuations has been used in order to have more practical formulas for in-line calculations. The rapid estimate of the mean and variance of any physical quantity ζ, explicit function of the orbital occupation numbers, becomes possible. This formalism has been applied using More's screened hydrogenic model and the new screened-hydrogenic model.

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