

Average-ion level-population correlations in off-equilibrium plasmas

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We present techniques to calculate statistical distributions in time-dependent off-equilibrium atomic physics. Starting from the master equation, a first method assumes a Gaussian distribution and deduces the time evolution of the means and correlations. Alternatively, the discrete probability distribution is written as the product of the known statistical factor with the exponential of an unknown function. This function of the electronic populations can then be fitted using a second-order polynomial. Another method sets up a continuous version of the master equation, then expands the probability around the most probable configuration. It is remarkable that the obtained equation set is the same as in the Gaussian approximation of the first method. A major property of all these models is that they recover the probability distribution of thermodynamical equilibrium, when external conditions make it possible. Numerical tests on a two-level system are presented.

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I. INTRODUCTION

Simulations of laboratory and astrophysical plasmas need absorption and emission spectra of highly charged ions in many different conditions. Among the atomic physics models, we can separate those that use a discrete description of matter from those that use a continuous one. The former are consistent with the quantum reality of matter, but they are often difficult to use, due to the enormous number of states that should be taken into account. Much simplification is needed, and this is usually done by means of a continuous model such as an average ion [1–5], which calculates mean values. As for two-electron correlations, well-established methods [6–9] are used when thermodynamical equilibrium (LTE) prevails, but little has been done to tackle them out of equilibrium [6]; this is the problem we want to address.

The models that describe time-dependent off-equilibrium statistics rely on the master equation (see [10], for instance). This equation describes the evolution of the statistical distribution of probabilities under the action of microscopic processes. In this paper we present several attempts to obtain from the master equation a practical description of the statistics of plasmas off-equilibrium. A first method assumes a Gaussian distribution of probabilities and deduces the time evolution of the mean values and correlations of populations. A second one, extending the expression valid at thermodynamic equilibrium (LTE), writes the probability of a configuration $\{n\}$ as

$$\mathcal{P}(\{n\}, t) = W(\{n\}) \exp[-A(\{n\}, t)],$$

where $W(\{n\})$ is the known statistical factor, and $A(\{n\}, t)$ is a function to be determined. Assuming that this function of the populations is a second-order polynomial, we get the time evolution of the coefficients of this polynomial from the master equation. A third method constructs a continuous version of the master equation, and the solution is developed

around the most probable one. It is quite remarkable that the obtained equations are the same as in the Gaussian approximation.

The paper is organized as follows. The formulation of the master equation in the framework of an exact discrete statistics is recalled in Sec. II. In Sec. III, the Gaussian approximation is made. In Sec. IV, we present the aforementioned discrete approximation. The continuous model, which can be used either as such, or to find a discrete statistics, is described in Sec. V. In Sec. VI, the time evolution generated by the three models is compared numerically on two-level systems. Section VII is the conclusion.

II. MASTER EQUATION

Consider an atom having N electronic levels with integer degeneracies D_i . A configuration $\{n\}$ is defined as a set of integer occupation numbers of these levels n_1, n_2, \dots, n_N (also called populations). In addition to these N bound levels, there is a continuum of free electrons denoted c .

The evolution of the probability distribution $\mathcal{P}(\{n\}, t)$ of the various configurations is driven by the master equation [10,11]

$$\frac{\partial}{\partial t} \mathcal{P}(\{n\}) = \sum_{\{m\}} \mathcal{P}(\{m\}) R_{\{m\} \rightarrow \{n\}} - \mathcal{P}(\{n\}) \sum_{\{m\}} R_{\{n\} \rightarrow \{m\}},$$

where $R_{\{m\} \rightarrow \{n\}}$ is the rate of transitions from a configuration to another one. Physically, the transitions arise from interactions with external sources (such as collisions with free particles, absorption or emission of light).

Here we only consider one-particle transitions: bound-bound transitions $i \rightarrow j$, ionizations $i \rightarrow c$, and recombinations $c \rightarrow i$. The rate of transitions between configurations can then be written in terms of transition rates between levels:

$$R_{\{m\} \rightarrow \{n\}} = \sum_{i=1}^N \sum_{j=1}^N \left(\prod_{k \neq i,j} \delta_{m_k, n_k} \right) \delta_{m_i, n_i-1} \delta_{m_j, n_j+1} T_{j \rightarrow i}(\{m\}, t) + \sum_{i=1}^N \left(\prod_{k \neq i} \delta_{m_k, n_k} \right) [\delta_{m_i, n_i-1} T_{c \rightarrow i}(\{m\}, t) + \delta_{m_i, n_i+1} T_{i \rightarrow c}(\{m\}, t)].$$

Following an established usage, we write the rates $T(\{n\})$ as functions of the *initial* configuration of the transition. An obvious convention is $T_{i \rightarrow i} \equiv 0$.

The number of electrons n_i in the departure level and the number of holes ($D_j - n_j$) in the arrival level can be factored out to recall that there is no transition $j \rightarrow i$ starting from an empty level j , or going to a full level i :

$$T_{i \rightarrow j}(\{n\}, t) \equiv n_i (D_j - n_j) \tau_{i \rightarrow j}(\{n\}, t),$$

$$T_{i \rightarrow c}(\{n\}, t) \equiv n_i \tau_{i \rightarrow c}(\{n\}, t), \quad T_{c \rightarrow i}(\{n\}, t) \equiv (D_i - n_i) \tau_{c \rightarrow i}(\{n\}, t). \quad (1)$$

The reduced rates $\tau_{i \rightarrow j}$, $\tau_{i \rightarrow c}$, and $\tau_{c \rightarrow i}$ generally depend both on populations and on time.

The master equation is then

$$\frac{\partial}{\partial t} \mathcal{P}(\{n\}) = \sum_{i,j} \mathcal{P}(\{m_1\}) T_{j \rightarrow i}(\{m_1\}) + \sum_i \mathcal{P}(\{m_2\}) T_{c \rightarrow i}(\{m_2\}) + \sum_i \mathcal{P}(\{m_3\}) T_{i \rightarrow c}(\{m_3\}) - \mathcal{P}(\{n\}) \left[\sum_{i,j} T_{j \rightarrow i}(\{n\}) + \sum_i T_{c \rightarrow i}(\{n\}) + \sum_i T_{i \rightarrow c}(\{n\}) \right], \quad (2)$$

where the initial configurations of the transitions are carefully distinguished:

$$\{n\} = (n_{k \neq i,j}, n_i, n_j), \quad \{m_1\} = (n_{k \neq i,j}, n_i - 1, n_j + 1),$$

$$\{m_2\} = (n_{k \neq i}, n_i - 1), \quad \{m_3\} = (n_{k \neq i}, n_i + 1).$$

Thermodynamical equilibrium

The total energy $E(\{n\})$ is a function of the configuration. For instance, the screened-hydrogenic model [8,12] assumes it is a third-order polynomial. Quantum-mechanical models of the atom lead to second-order polynomials in the populations [13,14], with coefficients depending on a reference configuration.

When the external sources responsible for the transitions are in thermodynamical equilibrium at temperature T and chemical potential μ , the reduced rates verify the microreversibility relations

$$\tau_{i \rightarrow j}(\{n\}) \exp \left[-\frac{1}{T} E(\{n\}) \right] = \tau_{j \rightarrow i}(\{m_1\}) \exp \left[-\frac{1}{T} E(\{m_1\}) \right],$$

$$\tau_{i \rightarrow c}(\{n\}) \exp \left[-\frac{1}{T} E(\{n\}) \right] = \tau_{c \rightarrow i}(\{m_2\}) \exp \left[-\frac{E(\{m_2\}) - \mu}{T} \right]. \quad (3)$$

On each side of these equalities is a rate, with the initial configuration of the transition, and the energy of that con-

figuration. Such microreversibility relations exist for each kind of rate (detailed balance principle), each pair of levels, and each configuration.

If these relations hold, the LTE distribution

$$\mathcal{P}(\{n\}) = \frac{1}{Z} \left(\prod_i \frac{D_i!}{n_i! (D_i - n_i)!} \right) \exp \left\{ -\frac{1}{T} \left[E(\{n\}) - \mu \sum_i n_i \right] \right\}, \quad (4)$$

where the statistical weight (equal to the degeneracy of the configuration) is factored out, and where Z is a normalization factor, is a steady-state solution of the master equation (2).

Evolution of average populations and correlations

Let us now consider the evolution equation for the average populations

$$\langle n_i \rangle = \sum_{\{n\}} \mathcal{P}(\{n\}, t) n_i.$$

The notation $\langle X \rangle$ means the statistical average of the quantity $X(\{n\})$:

$$\langle X \rangle = \sum_{\{n\}} \mathcal{P}(\{n\}, t) X(\{n\}).$$

From Eq. (2), we obtain

$$\frac{d}{dt} \langle n_i \rangle = \langle V_i \rangle, \quad (5)$$

where

$$\begin{aligned}
V_i &\equiv T_{c \rightarrow i} - T_{i \rightarrow c} + \sum_j (T_{j \rightarrow i} - T_{i \rightarrow j}) & \frac{d}{dt} \bar{n}_i &\approx \bar{V}_i, \\
&\equiv (D_i - n_i) \tau_{c \rightarrow i} - n_i \tau_{i \rightarrow c} + \sum_j [n_j (D_i - n_i) \tau_{j \rightarrow i} \\
&\quad - n_i (D_j - n_j) \tau_{i \rightarrow j}]. \tag{6}
\end{aligned}$$

So far, this equation has been the best justification for the non-LTE average-ion methods [4]. In an off-equilibrium average-ion calculation, the transition rates $T_{i \rightarrow j}$ are functions of the populations n_i considered as continuous variables. A first approximation consists of using ‘‘average’’ rates $\bar{T}_{i \rightarrow j}$, independent of the configurations, calculated, for example, by using average populations. For any function $X(\{n\})$ of the populations, we now denote by \bar{X} its value at the average configuration: $\bar{X} \equiv X(\{\bar{n}\})$, $\bar{n}_i \equiv \langle n_i \rangle$. The evolution equation (5) can then be recast as

which is the set of equations actually solved in the non-LTE average-ion codes [4,5,15]. The electroneutrality of the plasma is ensured by the constraint $\sum_i \langle n_i \rangle + Z^* = Z$, where Z is the nuclear charge, and where Z^* can be calculated analytically [5,9,16].

Equation (2) also yields

$$\frac{d}{dt} \langle n_i n_j \rangle = \langle n_i V_j + n_j V_i + B_{ij} \rangle, \tag{8}$$

where

$$\begin{aligned}
B_{ij} &\equiv -T_{i \rightarrow j} - T_{j \rightarrow i} + \delta_{ij} \left[T_{c \rightarrow i} + T_{i \rightarrow c} + \sum_k (T_{i \rightarrow k} + T_{k \rightarrow i}) \right] \\
&\equiv -n_i (D_j - n_j) \tau_{i \rightarrow j} - n_j (D_i - n_i) \tau_{j \rightarrow i} + \delta_{ij} \left\{ (D_i - n_i) \tau_{c \rightarrow i} + n_i \tau_{i \rightarrow c} + \sum_k [n_i (D_k - n_k) \tau_{i \rightarrow k} + n_k (D_i - n_i) \tau_{k \rightarrow i}] \right\}. \tag{9}
\end{aligned}$$

Linearizing the continuous rates around the average populations

$$T(\{n\}) \approx \bar{T} + \sum_i \frac{\partial \bar{T}}{\partial n_i} (n_i - \langle n_i \rangle),$$

Mirone *et al.* [17] get an equation for the time evolution of the correlation or covariance matrix

$$\Xi_{ij} \equiv \langle (n_i - \langle n_i \rangle)(n_j - \langle n_j \rangle) \rangle = \langle n_i n_j \rangle - \langle n_i \rangle \langle n_j \rangle,$$

which we write in the form

$$\frac{d}{dt} \Xi_{ij} \approx \sum_k \frac{\partial \bar{V}_j}{\partial n_k} \Xi_{ki} + \sum_k \frac{\partial \bar{V}_i}{\partial n_k} \Xi_{kj} + \bar{B}_{ij}. \tag{10}$$

Linearizing the transition rates around the average configuration thus yields a somewhat simple set of equations (7) and (10) that must be solved self-consistently. Equation (10) being decoupled from Eq. (7), it can be solved afterwards; being linear in the unknowns Ξ , it is relatively easy to solve. However, a linear approximation of the rates may seem questionable, if only because bound-bound rates (1) have a built-in second-order factor: $T_{i \rightarrow j} \equiv n_i (D_i - n_j) \tau_{i \rightarrow j}$. But, if rates were developed to second order, the time evolution of the average would depend on correlations, which in turn would depend on higher-order correlations. Such situations are known to be difficult.

III. GAUSSIAN PROBABILITY

Equation (2) is too general to be practical for highly charged ion plasmas. We therefore assume continuous occupation numbers $\{n\}$ instead of integer values, a ‘‘large numbers hypothesis,’’ and we neglect orbital relaxations. We can then rewrite Eq. (2) as

$$\begin{aligned}
\frac{\partial}{\partial t} \mathcal{P}(\{n\}) &\approx \sum_{i,j} \mathcal{P}(\{m_1\}) T_{j \rightarrow i}(\{n\}) \\
&\quad + \sum_i \mathcal{P}(\{m_2\}) T_{c \rightarrow i}(\{n\}) \\
&\quad + \sum_i \mathcal{P}(\{m_3\}) T_{i \rightarrow c}(\{n\}) - \mathcal{P}(\{n\}) \\
&\quad \times \left[\sum_{i,j} T_{j \rightarrow i}(\{n\}) + \sum_i T_{c \rightarrow i}(\{n\}) \right. \\
&\quad \left. + \sum_i T_{i \rightarrow c}(\{n\}) \right]. \tag{11}
\end{aligned}$$

We now propose a heuristic argument to find an approximate solution to this equation. Writing

$$\mathcal{P}(\{m_\alpha\}, t) = \exp[-\mathcal{S}(\{m_\alpha\}, t)], \quad 1 \leq \alpha \leq 3,$$

a Taylor expansion of $\mathcal{P}(\{m_\alpha\}, t)$ in the occupation numbers around a reference configuration is performed. At the level of approximation required here, we retain the first order for

$\mathcal{S}(\{m_\alpha\}, t)$, or equivalently the second order in $\mathcal{P}(\{m_\alpha\}, t)$ while neglecting any second derivative of $\mathcal{S}(\{m_\alpha\}, t)$ with respect to populations. The motivation of these assumptions is the compatibility with LTE, which will appear clearly later. For the applications we have in mind, and following previous work [8,9,18], we consider a Gaussian approximation:

$$\mathcal{P}(\{n\}, t) = \exp\left[-\frac{1}{2} \sum_{i,j} \Delta n_i(t) \omega_{ij}(t) \Delta n_j(t)\right],$$

where $\Delta n_i(t) = n_i - \hat{n}_i(t)$. The reference populations $\hat{n}_i(t) \simeq \langle n_i \rangle$ are still unknown but near the average ones. The time-dependent symmetric matrix $[\omega_{ij}(t)]$ is an estimate of the electron correlations: $(\omega^{-1})_{ij}(t) \approx \langle \Delta n_i(t) \Delta n_j(t) \rangle \approx \Xi_{ij}$.

Starting from Eq. (11) we can write $(\partial_i \equiv \partial / \partial n_i)$

$$\begin{aligned} \frac{\partial}{\partial t} \mathcal{P} = & \sum_{i,j} [\partial_j \mathcal{P} - \partial_i \mathcal{P} + \frac{1}{2} (\partial_{ii}^2 \mathcal{P} + \partial_{jj}^2 \mathcal{P} - 2 \partial_{ij}^2 \mathcal{P})] T_{j \rightarrow i}(\{n\}) \\ & + \sum_i [(-\partial_i \mathcal{P} + \frac{1}{2} \partial_{ii}^2 \mathcal{P}) T_{c \rightarrow i}(\{n\}) \\ & + (\partial_i \mathcal{P} + \frac{1}{2} \partial_{ii}^2 \mathcal{P}) T_{i \rightarrow c}(\{n\})]. \end{aligned}$$

Replacing the Gaussian estimate in this equation and using $\partial_{ij}^2 \mathcal{P} \approx \sum_{k,l} (\Delta n_k \omega_{ki}) (\Delta n_l \omega_{lj}) \mathcal{P}$, equations for the first and second order in Δn_k are obtained. The first order is

$$\sum_i \omega_{ki} \left(\frac{d}{dt} \hat{n}_i - \hat{V}_i \right) = 0, \quad (12)$$

where V_i has been defined in Eq. (6), and \hat{X} is a notation for $X(\{\hat{n}\})$. The second order yields

$$\begin{aligned} -\frac{d}{dt} \omega_{kl} = & \sum_i \frac{\partial \hat{V}_i}{\partial n_l} \omega_{ik} + \sum_i \frac{\partial \hat{V}_i}{\partial n_k} \omega_{il} \\ & + \sum_i (\widehat{T_{c \rightarrow i}} + \widehat{T_{i \rightarrow c}}) \omega_{ik} \omega_{il} \\ & + \sum_{i,j} \widehat{T_{j \rightarrow i}} (\omega_{ik} - \omega_{jk}) (\omega_{il} - \omega_{jl}). \quad (13) \end{aligned}$$

If the matrix ω is nonsingular, we find that the populations $\{\hat{n}\}$ satisfy the non-LTE average-atom equations [4,5,15], already seen as Eq. (7):

$$\frac{d}{dt} \hat{n}_i = \hat{V}_i. \quad (14)$$

The evolution equations (13) for (ω_{kl}) are nonlinear. However, it is the matrix C , inverse of ω , which is of physical interest since it gives an estimate of two-electron correlations. Extending the range of continuous occupancies to \mathbb{R}

(instead of $[0, D_i]$), the matrix C is the covariance matrix related to the Gaussian probability. The classical theory of fluctuations extends the Gaussian approximation to any function of the populations. The variance of a function $X(\{n\})$ is then

$$\sigma_X^2 = \sum_{i,j} \frac{\overline{\partial X}}{\partial n_i} C_{ij} \frac{\overline{\partial X}}{\partial n_j}.$$

Hence, the covariance matrix C is in fact more useful than its inverse ω .

Using the matrix identity

$$\frac{d}{dt} C_{i,j} = - \sum_{k,l} C_{ik} \left(\frac{d}{dt} \omega_{kl} \right) C_{lj},$$

we obtain the *linear* evolution equation

$$\frac{d}{dt} C_{ij} = \sum_k \frac{\partial \widehat{V}_i}{\partial n_k} C_{kj} + \sum_k \frac{\partial \widehat{V}_j}{\partial n_k} C_{ki} + \widehat{B}_{ij}, \quad (15)$$

identical in form to Eq. (10), where B_{ij} has been defined in Eq. (9). The Gaussian ansatz to the solution of the master equation thus leads to a set of equations (14), (15) having the same form as Eqs. (7) and (10).

The parameters of the Gaussian probability at LTE have been found to be [8,9,18]

$$\begin{aligned} \hat{n}_i &= \frac{D_i}{1 + \exp[(1/T)(\partial E / \partial n_i - \mu)]}, \\ \omega_{ij} &= \delta_{ij} \frac{D_i}{\hat{n}_i (D_i - \hat{n}_i)} + \frac{1}{T} \frac{\partial^2 E}{\partial n_i \partial n_j}. \end{aligned}$$

One can check that these are indeed solutions of Eqs. (14) and (13) when appropriate microreversibility relations are satisfied.

IV. APPROXIMATION OF A DISCRETE NON-LTE DISTRIBUTION

Principle

Taking the equilibrium distribution (4) as a model, we write the probability of a discrete configuration as

$$\mathcal{P}(\{n\}, t) = \left(\prod_i \frac{D_i}{n_i! (D_i - n_i)!} \right) \exp[-A(\{n\}, t)], \quad (16)$$

where the known statistical weight is factored out, and where $A(\{n\}, t)$ is a function of the populations and of time to be determined.

Using this form of $\mathcal{P}(\{n\})$ and the reduced rates (1), the master equation (2) becomes

$$\begin{aligned} -\frac{\partial A}{\partial t}(\{n\}) = & \sum_{i,j} n_i (D_j - n_j) \{ \tau_{j \rightarrow i}(\{m_1\}) \exp[A(\{n\}) - A(\{m_1\})] - \tau_{i \rightarrow j}(\{n\}) \} + \sum_i n_i \{ \tau_{c \rightarrow i}(\{m_2\}) \exp[A(\{n\}) \\ & - A(\{m_2\})] - \tau_{i \rightarrow c}(\{n\}) \} + \sum_i (D_i - n_i) \{ \tau_{i \rightarrow c}(\{m_3\}) \exp[A(\{n\}) - A(\{m_3\})] - \tau_{c \rightarrow i}(\{n\}) \}, \quad (17) \end{aligned}$$

where

$$\begin{aligned} A(\{n\}) - A(\{m_1\}) &= A(n_{k \neq i, j}, n_i, n_j) \\ &\quad - A(n_{k \neq i, j}, n_i - 1, n_j + 1), \\ A(\{n\}) - A(\{m_2\}) &= A(n_{k \neq i}, n_i) - A(n_{k \neq i}, n_i - 1), \\ A(\{n\}) - A(\{m_3\}) &= A(n_{k \neq i}, n_i) - A(n_{k \neq i}, n_i + 1) \end{aligned} \quad (18)$$

are finite differences of the function A of the integer populations $\{n\}$. This new form (17) of the master equation is mathematically equivalent to the original one (2).

We now perform an approximation. We assume that A is a second-order polynomial in the populations. The dynamics of the statistics is then described by the time dependence of the coefficients of this polynomial. Let us write A as

$$A(\{n\}, t) = A_0(t) + \sum_i a_i(t) n_i + \frac{1}{2} \sum_{i, j} b_{ij}(t) n_i n_j.$$

For each configuration, equation (17) is a linear relation satisfied by the $(N^2 + 3N + 2)/2$ unknowns $dA_0(t)/dt$, $da_i(t)/dt$, and $db_{ij}(t)/dt$. It is written as

$$\begin{aligned} \frac{dA_0}{dt} + \sum_i \frac{da_i}{dt} n_i + \frac{1}{2} \sum_{i, j} \frac{db_{ij}}{dt} n_i n_j &= \sum_{i, j} n_i (D_j - n_j) [\tau_{i \rightarrow j}(\{n\}) - \tau_{j \rightarrow i}(\{m_1\}) e^{A(\{n\}) - A(\{m_1\})}] + \sum_i n_i [\tau_{i \rightarrow c}(\{n\}) \\ &\quad - \tau_{c \rightarrow i}(\{m_2\}) e^{A(\{n\}) - A(\{m_2\})}] + \sum_i (D_i - n_i) [\tau_{c \rightarrow i}(\{n\}) \\ &\quad - \tau_{i \rightarrow c}(\{m_3\}) e^{A(\{n\}) - A(\{m_3\})}], \end{aligned} \quad (19)$$

where

$$\begin{aligned} A(\{n\}) - A(\{m_1\}) &= a_i - a_j + \frac{1}{2} (2b_{ij} - b_{ii} - b_{jj}) \\ &\quad + \sum_k (b_{ik} - b_{jk}) n_k, \\ A(\{n\}) - A(\{m_2\}) &= a_i - \frac{1}{2} b_{ii} + \sum_k b_{ik} n_k, \\ A(\{n\}) - A(\{m_3\}) &= -a_i - \frac{1}{2} b_{ii} - \sum_k b_{ik} n_k. \end{aligned} \quad (20)$$

Choosing $(N+1)(N+2)/2$ distinct configurations such that the set of linear equations [the left-hand-side of Eq. (19)] is nonsingular, evolution equations are obtained:

$$\frac{d}{dt} a_i = F_i, \quad \frac{d}{dt} b_{ij} = G_{ij}. \quad (21)$$

$A_0(t)$, which does not appear on the right-hand side of Eqs. (19), is kept for normalization.

The problem with this method is that the rates F_i and G_{ij} depend on the configurations that are chosen. We propose to choose the configurations among the most probable ones. To that aim, we first perform an average-atom calculation, which yields a noninteger reference configuration:

$$\widehat{n}_1 = \frac{D_i}{1 + \exp(\partial A / \partial n_i)}.$$

We then retain the integer configurations that are nearest neighbors to the reference one. Hence, we obtain a discrete

description of the statistics that uses a moderate number of dynamical quantities and still takes electronic correlations into account.

Thermodynamical equilibrium

When the external sources responsible for the transitions are in thermodynamical equilibrium, the reduced rates verify the microreversibility relations (3), and

$$A(\{n\}) = \frac{1}{T} \left[E(\{n\}) - \mu \sum_i n_i \right]$$

is a stationary solution of the master equation (17).

Using a Taylor expansion around the average configuration, limited at order two with respect to occupation numbers [7], the energy is written as

$$E(\{n\}) = E_0 + \sum_i U_i n_i + \frac{1}{2} \sum_{i, j} V_{ij} n_i n_j.$$

With

$$a_i = \frac{U_i - \mu}{T}, \quad b_{ij} = \frac{V_{ij}}{T}$$

the right-hand side in the set of equations (19) is equal to zero. Because this linear set is nonsingular (the configurations are chosen accordingly), the stability condition

$$\frac{d}{dt} A_0 = 0, \quad \frac{d}{dt} a_i = 0, \quad \frac{d}{dt} b_{ij} = 0,$$

is satisfied. The model is therefore compatible with thermodynamic equilibrium.

V. APPROXIMATION OF A CONTINUOUS NON-LTE DISTRIBUTION

We now construct a continuous model with noninteger populations. By ‘‘construct,’’ we mean ‘‘define the basic constituents’’ from which everything else will be deduced exactly. Thus, we consider a configuration $\{n\}$ defined by a set of noninteger populations n_1, n_2, \dots, n_N of the various electronic levels ($0 \leq n_i \leq D_i$).

The total energy $E(\{n\})$ of the ion is now a continuous function of the populations (a second- [2,7] or a third-order polynomial as in the screened-hydrogenic model [8,12]). The partial derivatives of $E(\{n\})$ with respect to populations are interpreted as the energies of the levels, and we denote them $E_i(\{n\})$:

$$E_i = \frac{\partial E}{\partial n_i}.$$

The energy of transitions $i \leftrightarrow c$ or $i \leftrightarrow j$ are defined from the level energies; they are derivatives of the total energy,

$$E_i = \frac{\partial E}{\partial n_i}, \quad E_i - E_j = \frac{\partial E}{\partial n_i} - \frac{\partial E}{\partial n_j},$$

instead of the finite differences of the discrete cases. To appreciate the approximation thus made, note that there is an exact correspondence at some intermediate ‘‘half-integer’’ points [19,20]:

$$\begin{aligned} -\frac{\partial A}{\partial t} = & \sum_{i,j} n_i(D_j - n_j) \left[\tau_{j \rightarrow i} \exp\left(\frac{\partial A}{\partial n_i} - \frac{\partial A}{\partial n_j}\right) - \tau_{i \rightarrow j} \right] + \sum_i n_i \left[\tau_{c \rightarrow i} \exp\left(\frac{\partial A}{\partial n_i}\right) - \tau_{i \rightarrow c} \right] \\ & + \sum_i (D_i - n_i) \left[\tau_{i \rightarrow c} \exp\left(-\frac{\partial A}{\partial n_i}\right) - \tau_{c \rightarrow i} \right]. \end{aligned} \quad (22)$$

The microreversibility compatible with this continuous model is an equality between *functions* of the continuous populations $\{n\}$:

$$\begin{aligned} \tau_{i \rightarrow j}(\{n\}) &= \tau_{j \rightarrow i}(\{n\}) \exp\left[\frac{E_i(\{n\}) - E_j(\{n\})}{T}\right], \\ \tau_{i \rightarrow c}(\{n\}) &= \tau_{c \rightarrow i}(\{n\}) \exp\left[\frac{E_i(\{n\}) - \mu}{T}\right]. \end{aligned} \quad (23)$$

To implement this definition of the continuous microreversibility, we must interpolate the rates of the discrete model, which are only defined in the intermediate ‘‘half-integer’’ configurations, and modify one of the rates if the total energy is not a polynomial of degree two.

The equality (23) between functions of the populations is satisfied when the external sources responsible for the transitions have reached thermodynamic equilibrium at a temperature T with a chemical potential μ . It is easily seen that the stationary solutions of the master equation (22) are then

$$\left(\frac{\partial E}{\partial n_i}\right)_{\{n_{k \neq i}, n_i - 1/2\}} = E(\{n_{k \neq i}, n_i\}) - E(\{n_{k \neq i}, n_i - 1\}),$$

$$\begin{aligned} \left(\frac{\partial E}{\partial n_i} - \frac{\partial E}{\partial n_j}\right)_{\{n_{k \neq i,j}, n_i - 1/2, n_j + 1/2\}} \\ = E(\{n_{k \neq i,j}, n_i\}) - E(\{n_{k \neq i,j}, n_i - 1, n_j + 1\}), \end{aligned}$$

if the total energy is a second-order polynomial of the populations.

Continuous version of the master equation

Unlike the standard LTE procedure used to define a continuous extension of a discrete statistical model (i.e., the mean-field approximation [7–9]), we proceed by defining a continuous extension of the master equation (17). This equation is ‘‘non-local’’ in the configuration space, since the rate of change at configuration $\{n\}$ depends on $N(N+1)$ neighbor configurations. It appears slightly simpler if the transition rates are indexed by the intermediate ‘‘half-integer’’ configurations: only then are the configurations that index the up-rate and the down-rate the same. Changing the finite differences of A into derivatives, writing all terms at the same configuration $\{n\}$ instead of the various ‘‘half-integer’’ neighbors, a ‘‘local’’ approximation to the master equation (17) is obtained:

$$\frac{\partial A}{\partial n_i} = \frac{E_i - \mu}{T}.$$

Thus, the microreversibility relations, extended to equalities (23) between functions of the populations, make the whole statistical distribution of fluctuations at equilibrium (4) a consequence of our continuous master equation (22). This very strong property (stronger than recovering the most probable configuration, for instance) is the best support for the off-equilibrium continuous model presented.

Replacing, in Eq. (16), the entropy term due to the configurations (i.e., the product of combinatorial factors) by its usual continuous counterpart

$$S(\{n\}) = - \sum_i \left[n_i \ln\left(\frac{n_i}{D_i}\right) + (D_i - n_i) \ln\left(\frac{D_i - n_i}{D_i}\right) \right],$$

we write the probability of a noninteger configuration as

$$\mathcal{P}(\{n\}, t) = \frac{1}{\mathcal{Z}(t)} \exp[-\Phi(\{n\}, t)],$$

where

$$\Phi(\{n\}, t) = -S(\{n\}) + A(\{n\}, t)$$

is a kind of free energy, and where the partition function $\mathcal{Z}(t)$ is the normalization factor. From Eq. (22), and using the definitions (1), we deduce an equivalent master equation for Φ :

$$\begin{aligned} -\frac{\partial\Phi}{\partial t} &= \sum_{i,j} \left[T_{j \rightarrow i} \exp\left(\frac{\partial\Phi}{\partial n_i} - \frac{\partial\Phi}{\partial n_j}\right) - T_{i \rightarrow j} \right] \\ &+ \sum_i T_{c \rightarrow i} \left[\exp\left(\frac{\partial\Phi}{\partial n_i}\right) - 1 \right] \\ &+ \sum_i T_{i \rightarrow c} \left[\exp\left(-\frac{\partial\Phi}{\partial n_i}\right) - 1 \right]. \end{aligned} \quad (24)$$

Kinetics of the most probable populations

The most probable populations \hat{n}_i are solutions to the set of equations

$$\frac{\partial\Phi}{\partial n_i} = \ln\left(\frac{n_i}{D_i - n_i}\right) + \frac{\partial A}{\partial n_i} = 0. \quad (25)$$

We assume here that Φ has a true and unique minimum; other cases are beyond the scope of this paper. For any function $X(\{n\})$ of the populations, we now denote \hat{X} its value at the most probable configuration: $\hat{X} \equiv X(\{\hat{n}\})$.

The time evolution of \hat{X} is obtained by taking a total time derivative ‘‘following the motion’’:

$$\frac{d}{dt} \hat{X} = \frac{\partial \hat{X}}{\partial t} + \sum_i \frac{\partial \hat{X}}{\partial n_i} \frac{d}{dt} \hat{n}_i.$$

Applied to $\hat{X} = \widehat{\partial\Phi/\partial n_j}$, which is constantly zero, this reads

$$0 = \frac{d}{dt} \left(\frac{\widehat{\partial\Phi}}{\partial n_j} \right) = \frac{\partial}{\partial t} \frac{\widehat{\partial\Phi}}{\partial n_j} + \sum_i \left(\frac{\widehat{\partial^2\Phi}}{\partial n_i \partial n_j} \right) \frac{d}{dt} \hat{n}_i.$$

These relations form a set of linear equations satisfied by the unknowns $d\hat{n}_i/dt$, with matrix $\omega_{ij} \equiv \partial^2\Phi/\partial\hat{n}_i\partial n_j$. The partial derivatives of the master equation (24), calculated at the most probable configuration, are found to be

$$\frac{\widehat{\partial^2\Phi}}{\partial t \partial n_j} = -\sum_i \omega_{ij} \hat{V}_i,$$

where V_i has been defined in Eq. (6). The function $\Phi(\{n\})$ being minimum at $\{\hat{n}\}$, the matrix of its second-order deriva-

tives is positive definite in that point, so that the solution of the linear system $\sum_i \omega_{ij} [(d/dt)\hat{n}_i - \hat{V}_j] = 0$ is zero, and the evolution equation is just Eq. (14). The kinetics (14) of the most probable configuration is thus an exact consequence of the master equation (24). The equations of the *most probable* ion (14) have the same form as the usual *average-ion* equations (7).

As a particular case of thermodynamic equilibrium (preceding section), the most probable populations, obtained from Eqs. (25), are given by the Fermi-Dirac formulas:

$$\hat{n}_i = \frac{D_i}{1 + \exp[(\hat{E}_i - \mu)/T]}.$$

Statistics near the most probable configuration

We now consider the second derivatives of the master equation (24), which are related to correlations. Following the same lines that were detailed in the previous subsection, we calculate the second derivatives $(\partial/\partial t)\partial^2\Phi/\partial n_i\partial n_j$ of the master equation (24), then the total time derivatives $(d/dt)\partial^2\Phi/\partial n_i\partial n_j$. Once evaluated at the most probable configuration, we find that the equation for the symmetric matrix $\omega_{ij} \equiv \partial^2\Phi/\partial\hat{n}_i\partial n_j$ has exactly the relatively simple form (13).

The time-evolution equations (13), as well as the kinetics (14), are thus exact consequences of the continuous master equation (24). A nontrivial property is then easily obtained: if the rates satisfy the continuous microreversibility relations (23), then

$$\omega_{ij} = \delta_{ij} \frac{D_i}{\hat{n}_i(D_i - \hat{n}_i)} + \frac{1}{T} \frac{\partial^2 E}{\partial n_i \partial n_j},$$

which is the LTE result, i.e., the matrix of second derivatives of $\Phi(\{n\}) = -S(\{n\}) + (1/T)[E(\{n\}) - \mu\sum_i n_i]$, is a stationary solution of equations (13).

Because $\Phi(\{n\})$ is minimum in configuration $\{\hat{n}\}$, the matrix ω of its second derivatives is positive-definite in that point, so that it can be inverted. The evolution equation for the inverse matrix $C = \omega^{-1}$ is of course the *linear* evolution equation (15).

If we limit the development of Φ around its minimum to second order, then

$$\Phi(\{n\}, t) \simeq \frac{1}{2} \sum_{i,j} [n_i - \hat{n}_i(t)] \omega_{ij}(t) [n_j - \hat{n}_j(t)].$$

If, moreover, we boldly extend the variation domain of the populations to \mathbb{R}^N , we can write the probability of the configuration $\{n\}$ in the continuous model as

$$\mathcal{P}(\{n\}, t) = \left(\frac{\det(\omega)}{(2\pi)^N} \right)^{1/2} \exp\left\{ -\frac{1}{2} \sum_{i,j} [n_i - \hat{n}_i(t)] \omega_{ij}(t) [n_j - \hat{n}_j(t)] \right\},$$

which is the Gaussian approximation of Sec. III.

A different way to calculate probabilities is to subtract first the continuous entropy $S(\{n\})$ from $\Phi(\{n\}, t)$ to get an approximate quadratic expression for the function $A(\{n\}, t)$:

$$A(\{n\}, t) \simeq \frac{1}{2} \sum_{i,j} [n_i - \widehat{n}_i(t)] \left\{ \omega_{ij}(t) - \delta_{ij} \frac{D_i}{\widehat{n}_i(t)[D_i - \widehat{n}_i(t)]} \right\} [n_j - \widehat{n}_j(t)] + \sum_i [n_i - \widehat{n}_i(t)] \ln \left[\frac{D_i - \widehat{n}_i(t)}{\widehat{n}_i(t)} \right]$$

plus a constant term, and then use it in the discrete statistic formula (16), as in Sec. IV.

VI. NUMERICAL TESTS

Two-level system

When the number of configurations allows it, the exact calculation using the master equation (2) can be performed. This provides a benchmark to test the various models. Going to the simplest case, we test our models on a two-level system with a total number of electrons constant and equal to $n_1 + n_2 = n_{\text{tot}}$.

The simplicity of this model may seem too restrictive. There is really only one population, but also only one average population ($\langle n_1 \rangle + \langle n_2 \rangle = n_{\text{tot}}$), and one most-probable population ($\widehat{n}_1 + \widehat{n}_2 = n_{\text{tot}}$). Since $n_2 - \langle n_2 \rangle = -(n_1 - \langle n_1 \rangle)$, there is only one variance, which is also the correlation of the two populations:

$$\begin{aligned} \sigma^2 &= \langle (n_1 - \langle n_1 \rangle)^2 \rangle = \langle (n_2 - \langle n_2 \rangle)^2 \rangle \\ &= -\langle (n_1 - \langle n_1 \rangle)(n_2 - \langle n_2 \rangle) \rangle. \end{aligned}$$

As seen from the above equation, a system with a constant total number of particles is always correlated. Hence, the model is not suited to study independent electrons. In the atomic physics of plasmas, the total number of bound electrons is not fixed and, at high temperature, the equilibrium distribution of the electrons among the various levels is an uncorrelated binomial law. There is no such thing in the model considered, and this rules out the simplest results associated to the binomial distribution (the average is given by Fermi-Dirac formula, the variance is equal to $\langle n \rangle (D - \langle n \rangle) / D$, and they are equal to the most probable populations of the continuous model and to the variance of the Gaussian approximation).

Instead, at very high temperature, the system we consider follows a ‘‘hypergeometric’’ law ([21], formula 26.1.21) with an average and a variance exactly equal to

$$\langle n_1 \rangle = n_{\text{tot}} \frac{D_1}{D_1 + D_2}, \quad \sigma^2 = n_{\text{tot}} \frac{D_1 D_2}{(D_1 + D_2)^2} \frac{D_1 + D_2 - n_{\text{tot}}}{D_1 + D_2 - 1}.$$

Also, the most probable population observed at high temperature in the continuous model is equal to

$\widehat{n}_1 = n_{\text{tot}} D_1 / (D_1 + D_2)$, which is the same as the average. The variance calculated in the Gaussian approximation is

$$\begin{aligned} \widehat{\sigma}^2 &= \left(\frac{D_1}{\widehat{n}_1(D - \widehat{n}_1)} + \frac{D_2}{\widehat{n}_2(D - \widehat{n}_2)} \right)^{-1} \\ &= n_{\text{tot}} \frac{D_1 D_2 (D_1 + D_2 - n_{\text{tot}})}{(D_1 + D_2)^3}, \end{aligned}$$

which is smaller than the exact one by a factor $1 - 1/(D_1 + D_2)$.

Three calculations

We now compare the following calculations.

The *exact* one consists of integrating numerically the master equation (2) for all possible configurations. Thus, the probability of each configuration is obtained at each time step. The average $\langle n_1 \rangle$ and the correlation of the two populations C_{12} are then calculated afterwards by summing on all configurations.

The *discrete model* consists of integrating equations (21). The rates of change of the coefficients are calculated from a set of equations such as Eq. (19), written for a sufficient number of configurations. The development of $A(\{n\}, t)$,

$$A = A_0 + a_1 n_1 + a_2 n_2 + \frac{1}{2} b_{11} n_1^2 + \frac{1}{2} b_{22} n_2^2 + b_{12} n_1 n_2,$$

apparently depends on six coefficients. In fact, only three of them are relevant, since A can be written (up to an additive constant) as

$$A = [a_1 - a_2 + (b_{12} - b_{22}) n_{\text{tot}}] n_1 + \frac{1}{2} (b_{11} + b_{22} - 2b_{12}) n_1^2.$$

The set of equations to be solved is thus constructed using three distinct configurations. We chose the integer configuration that is the closest to the most probable one, and the two integer configurations that are the closest to this first one. The average and the variance are then calculated using the discrete probability (16).

In the *continuous model* (Secs. III and V) the evolution equation (14) for the most probable population of level 1,

$$\frac{d}{dt} \widehat{n}_1 = \widehat{V}_1 = \widehat{n}_2 (D_1 - \widehat{n}_1) \widehat{\tau}_{2 \rightarrow 1} - \widehat{n}_1 (D_1 - \widehat{n}_2) \widehat{\tau}_{1 \rightarrow 2},$$

and the only relevant equation in the set of equations (13),

$$\frac{d}{dt} (\omega_{11} + \omega_{22} - 2\omega_{12}) = 2 \left(\frac{\partial \widehat{V}_1}{\partial n_2} - \frac{\partial \widehat{V}_1}{\partial n_1} \right) (\omega_{11} + \omega_{22} - 2\omega_{12}) - [\widehat{n}_1 (D_2 - \widehat{n}_2) \widehat{\tau}_{1 \rightarrow 2} + \widehat{n}_2 (D_1 - \widehat{n}_1) \widehat{\tau}_{2 \rightarrow 1}] (\omega_{11} + \omega_{22} - 2\omega_{12})^2,$$

are integrated numerically. The quadratic approximation to the function $\Phi(\{n\}, t)$ is (up to an additive constant)

$$\Phi(\{n\}, t) \simeq \frac{1}{2} \omega_{11} (n_1 - \widehat{n}_1)^2 + \frac{1}{2} \omega_{22} (n_2 - \widehat{n}_2)^2 + \omega_{12} (n_1 - \widehat{n}_1) (n_2 - \widehat{n}_2) = \frac{1}{2} (\omega_{11} + \omega_{22} - 2\omega_{12}) (n_1 - \widehat{n}_1)^2.$$

The variance in the *Gaussian approximation* is therefore $1/(\omega_{11} + \omega_{22} - 2\omega_{12})$.

To compare the continuous model with the two others, we translate its results into a discrete formalism. We first reconstruct $A(\{n\}, t)$ from $\Phi(\{n\}, t)$ by subtracting the continuous entropy:

$$A(\{n\}, t) \simeq (n_1 - \widehat{n}_1) \ln \left[\frac{\widehat{n}_2(D_1 - \widehat{n}_1)}{\widehat{n}_1(D_2 - \widehat{n}_2)} \right] + \frac{1}{2} \left[\omega_{11} + \omega_{22} - 2\omega_{12} - \frac{D_1}{\widehat{n}_1(D_1 - \widehat{n}_1)} - \frac{D_2}{\widehat{n}_2(D_2 - \widehat{n}_2)} \right] (n_1 - \widehat{n}_1)^2.$$

The average and the variance are then calculated using the discrete probability (16). We call this procedure the *continuous-discrete* model.

Parameters used

We use a quadratic total energy, which is necessary for the discrete model to reach equilibrium exactly:

$$E(\{n\}) = U_1 n_1 + U_2 n_2 + \frac{1}{2} (V_{11} n_1^2 + V_{22} n_2^2 + V_{12} n_1 n_2).$$

Due to the simplicity of the model, the only relevant parameters are $U_1 - U_2 + (V_{12} - V_{22})n_{\text{tot}}$ and $V_{11} + V_{22} - 2V_{12}$.

The system is defined by (i) the degeneracies of the two levels (D_1 and D_2) and (ii) the total number of electrons n_{tot} , which remains constant. The cases that we study are defined by (i) the initial distribution. We suppose that the initial distribution corresponds to a thermodynamic equilibrium related to an initial temperature T_i . (ii) The temperature T_f of the free electrons, which is also the final temperature. It will be kept constant throughout the simulation. (iii) The transition rates. We assume the form

$$\tau_{1 \rightarrow 2} = \frac{1}{\chi} \exp\left(-\frac{\chi}{T_f}\right), \quad \tau_{2 \rightarrow 1} = \frac{1}{\chi},$$

where $\chi = E_2 - E_1$ is the transition energy. This transition energy is obtained by finite difference for both the exact and the discrete model, and by derivative for the continuous model. We choose level 1 with the smallest energy, so that χ is a positive quantity. These transition rates are simplified forms for transitions induced by collisions with free electrons [22].

Since there is only one mechanism for the transitions (there are no radiative transitions, for example) it is useless to specify the energy unit, or a multiplicative factor for the rates. These constants would simply change the time unit.

Results

Let us first stress that the averages and correlations calculated with both models are most of the time quite close to the exact quantities. In this section, we insist on the cases that showed significantly different behaviors. The sometimes large differences that we present should not be generalized.

An ordinary case is given, for instance, in Fig. 1:

$$U_1 = -10, \quad U_2 = 0, \quad V_{11} = V_{22} = 0, \quad V_{12} = 1,$$

$$D_1 = 6, \quad D_2 = 10, \quad n_{\text{tot}} = 8,$$

$$T_i = 2, \quad T_f = 200.$$

In that case, only the Gaussian approximation variance deviates from the exact result.

The results are more different in the following case (Fig. 2):

$$U_1 = -10, \quad U_2 = 0, \quad V_{11} = V_{22} = 0, \quad V_{12} = 1,$$

$$D_1 = D_2 = n_{\text{tot}} = 6,$$

$$T_i = 100, \quad T_f = 1.$$

The choice $D_1 = D_2 = n_{\text{tot}}$ makes level 1 full when level 2 is empty, which enhances the effect of transitions $n_2(D_1 - n_1)\tau_{2 \rightarrow 1}$. So does the rapid cooling ($T_i = 100, T_f = 1$). The probable populations are then markedly different from the averages when a level is almost full (or almost empty). The variance of the continuous model has difficulty following the evolution.

A case of rapid heating (Fig. 3),

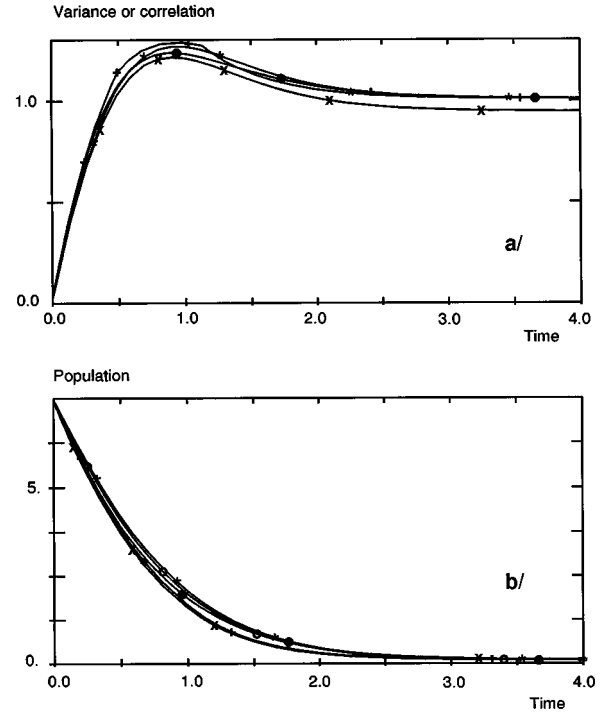


FIG. 1. Standard case. (a) Variance of the populations. ●: “exact” calculation; +: discrete model; *: continuous-discrete model; ×: Gaussian model. (b) Lower level population. ●: average population (“exact” calculation); +: average population (discrete model); *: average population (continuous-discrete model); ×: reference population of the discrete model; ○: most probable population (continuous model).

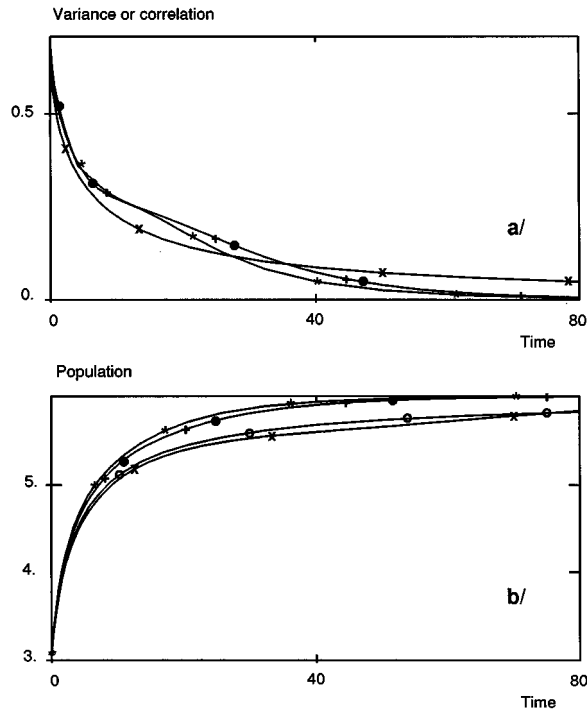


FIG. 2. Rapid cooling. (a) Variance of the populations. (b) Lower level population. Curve markers are as on Fig. 1.

$$U_1 = -10, \quad U_2 = 0, \quad V_{11} = V_{22} = V_{12} = 0,$$

$$D_1 = D_2 = n_{\text{tot}} = 6,$$

$$T_i = 2, \quad T_f = 200,$$

yields a discontinuity in the time derivative of the correlation calculated in the discrete model. The discontinuity occurs when the model changes the configurations it uses to construct the set of evolution equations.

The same case, with a still more brutal heating ($T_i = 1$, $T_f = 100$), shows a problem in the discrete distribution obtained from the continuous model (Fig. 4). The continuous model is of course continuous, but the modification introduced to resume a discrete statistics (subtract the continuous entropy and add the discrete one) has produced a probability distribution that has sometimes a second maximum. There is therefore the danger of extrapolating a quadratic approximation far from the reference configuration.

The last case we have retained (Fig. 5),

$$U_1 = -10, \quad U_2 = 0, \quad V_{11} = V_{22} = V_{12} = 0,$$

$$D_1 = D_2 = n_{\text{tot}} = 2,$$

$$T_i = 2, \quad T_f = 200,$$

shows that the models can handle correctly small degeneracies. It should be noted that with only three configurations the discrete model is exact in that case.

Let us recall once more that the variance in the Gaussian approximation would be much more accurate if the total number of electrons was allowed to fluctuate.

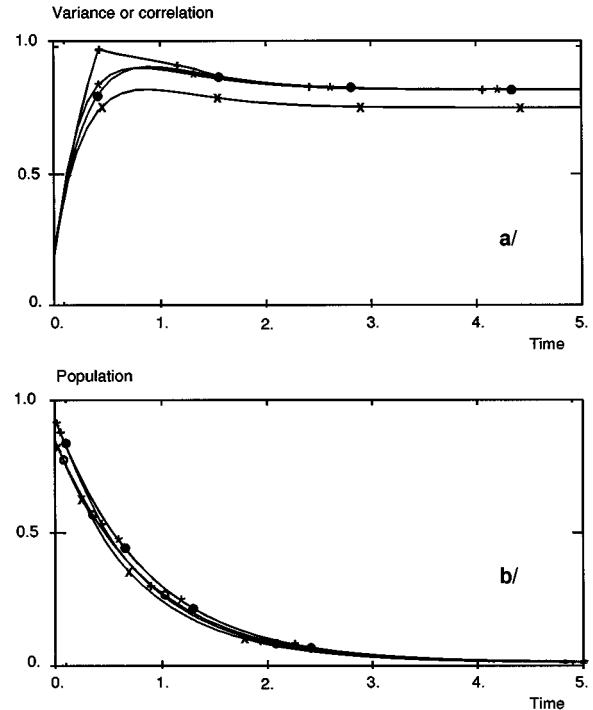


FIG. 3. Rapid heating. (a) Variance of the populations. (b) Lower level population. Curve markers are as in Fig. 1.

VII. CONCLUSION

We have presented two derivations of the same set of equations (14) and (13) or (15), able to describe atomic statistics off equilibrium in an average-ion model. The calculation of the most probable configuration, using Eq. (14) with Eq. (6), is what is already done by existing non-LTE average-ion codes [4,5,15,23]. The set of equations (13) or (15) with (9) for the matrix related to correlations is decoupled from the ‘‘average-ion’’ one, so that it can be solved afterwards. Equation (15), which gives an approximation of the covariance matrix, is linear, thus relatively easy to solve.

Equations (14) and (15) have the same form as Eqs. (7) and (10) for the ‘‘true’’ averages and covariance matrix, which are obtained directly from the master equation by linearizing the transition rates [17]. Note that the same general form of equations is known in different contexts such as linear Gaussian noise theory (see [24], Sec. 5). They can also be obtained from a Fokker-Planck model (see [10], Sec. VIII-6, and Appendix of the present paper).

In addition, a model has been set up that integrates the coefficients of a second-order polynomial of discrete populations, relying on a continuous model only to define a reference configuration.

A major achievement of these models is that they successfully reproduce the probability distribution of thermodynamic equilibrium, when external conditions make it possible. This property is stronger than obtaining either the average population or the most probable one, which is the result usually obtained with existing off-equilibrium average-ion models.

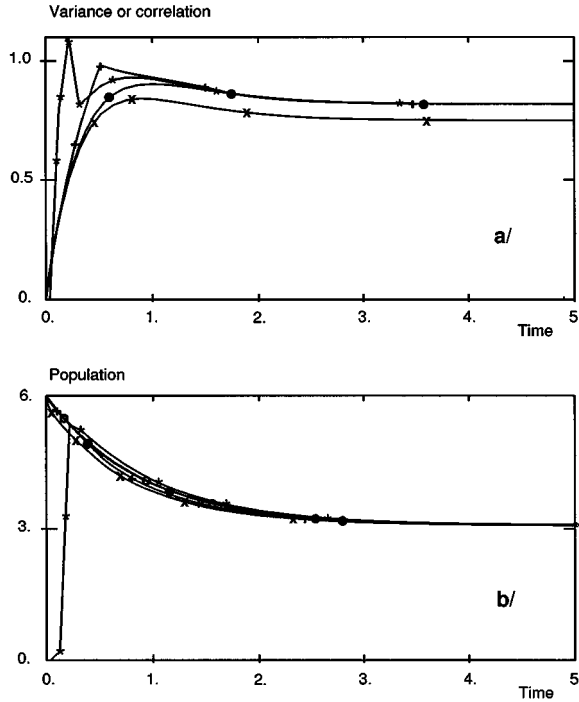


FIG. 4. Still more rapid heating; the continuous model fails. (a) Variance of the populations. (b) Lower level population. Curve markers are as in Fig. 1.

Numerical applications using two-level systems have shown a good agreement between our models and exact calculations. Certain dangers have been pointed out.

To give an idea of the progress expected from the proposed technique, we can recall the simplifications made in the existing non-LTE atomic physics codes. For instance, Limeil's nonequilibrium screened-hydrogenic average-ion model Nohel [23] (similar to Livermore's XSN [4]), assumes a Gaussian approximation with a matrix similar to its LTE form,

$$\omega_{ij} = \delta_{ij} \frac{D_i}{\hat{n}_i(D_i - \hat{n}_i)} + \frac{1}{T_e} \frac{\widehat{\partial^2 E}}{\partial n_i \partial n_j},$$

where T_e is the temperature of free electrons. The non-LTE model Radiom [25] often used in Limeil, relies on the concept of an "ionization temperature" T_Z ; it thus effectively uses a LTE-like approximation, with a different temperature. The non-LTE average-atom model of Rozsnyai [26] assumes also a LTE distribution of states at temperature T_Z . The use of an evolution equation to describe correlations should yield more reliable results than these rough approximations.

Moreover, dielectronic recombination and Auger effect can be included in our model, as any other transition rate can be. Although they are two-electron transitions, similar evolution equations can be derived. In particular, in the continuous model, uncoupled equations like (14) and (13) or (15) are obtained. Correlations are known to be particularly important in describing these two phenomena. The lack of a proper description of correlations has been a major difficulty in a statistical treatment of dielectronic recombination and

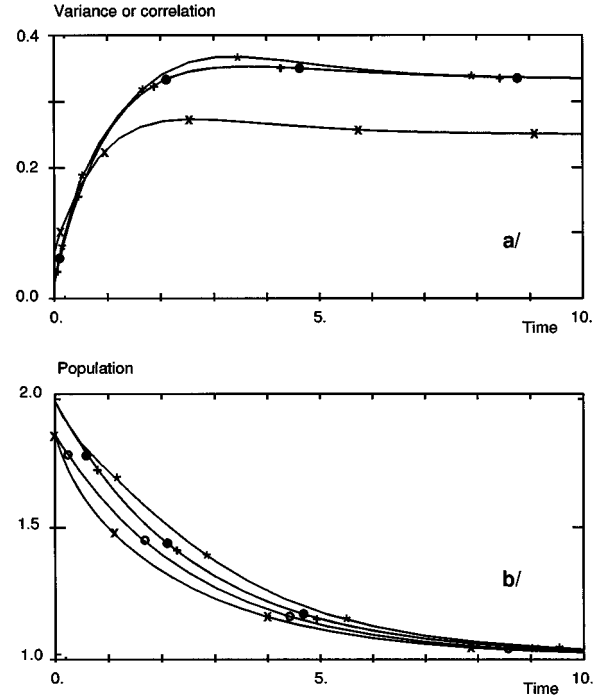


FIG. 5. Low degeneracy. (a) Variance of the populations. (b) Lower level population. Curve markers are as in Fig. 1.

autoionization [27]. Taking them into account would be a major step towards improving off-equilibrium atomic physics models.

APPENDIX: FOKKER-PLANCK EQUATION

The variation domain for the populations being extended to \mathbb{R}^N , let us consider the Fokker-Planck equation [10]

$$\frac{\partial}{\partial t} \mathcal{P}(\{n\}, t) = - \sum_i \frac{\partial}{\partial n_i} (V_i \mathcal{P}) + \frac{1}{2} \sum_{i,j} \frac{\partial^2}{\partial n_i \partial n_j} (B_{ij} \mathcal{P}).$$

The average of a function $X(\{n\})$ of the populations is defined as

$$\langle X \rangle = \int d^N n \mathcal{P}(\{n\}) X(\{n\}),$$

while its value at the average configuration is denoted $\bar{X} \equiv X(\{\bar{n}\})$, $n_i \equiv \langle n_i \rangle$. In particular, the evolution equations for the average populations $\langle n_i \rangle$, and for the correlations or covariances

$$\Xi_{i,j} \equiv \langle (n_i - \langle n_i \rangle)(n_j - \langle n_j \rangle) \rangle = \langle n_i n_j \rangle - \langle n_i \rangle \langle n_j \rangle,$$

are obtained after integration by parts. It is essential for this that the probability vanish at the border of the domain. The results are

$$\frac{d}{dt} \langle n_i \rangle = \langle V_i \rangle,$$

$$\frac{d}{dt} \Xi_{ij} = \langle V_i(n_j - \langle n_j \rangle) + V_j(n_i - \langle n_i \rangle) + B_{ij} \rangle,$$

which are identical in form to the corresponding equations (5) and (8) derived from the master equation.

After linearization of the functions V_i and B_{ij} around the average configuration, the approximations (7) and (10), or (14) and (15), are obtained [see [10], Chap. VIII, Eq. (6)–(9) for linear Fokker-Planck models].

However, the analogy should not be pushed too far, because the Fokker-Planck equation seems difficult to write down explicitly in our case: one would have to decide how to extend the transition rates $n_i(D_j - n_j)\tau_{i \rightarrow j}$ outside the domain $0 \leq n_k \leq D_k$.

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