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Frequency-fluctuation model for line-shape calculations in plasma spectroscopy

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A model is developed that permits the calculation of the radiation emitted by complex or highly charged ions in a plasma. The model is based on the usual separation of the plasma-emitter interaction into the homogeneous broadening effects of the fast electrons and the inhomogeneous broadening arising from slow ions. For plasma conditions where the ion motion can be neglected, the spectrum is the usual static line shape. To account for ion dynamics, the frequency-fluctuation model is introduced by decomposing the line shape of each radiative transition into a sum of radiative channels that are associated with the smallest observable inhomogeneities that form the static profile. The fluctuations of the ion microfield, the ion dynamics effect, is modeled by an exchange process between the static radiative channels. This results in both a smoothing and an overall coalescence of the radiative channels and depends strongly on an averaged characteristic fluctuation rate associated with the dynamics of the interaction of the local plasma microfield with the ion. This rate is formally related to the double-time field-field correlation function behavior. This stochastic model of the observed frequency fluctuations permits fast and accurate calculations of the emitted spectral profiles, including ion dynamics emitted by complex ions in a wide range of plasma conditions.

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I. INTRODUCTION

The emitted radiation is usually the only observable physical quantity available to obtain information on the underlying physical processes that are involved in line formation in plasmas. The information contained in the spectrum is related to both the atomic physics of the ionic emitters and to the plasma physics of the environment. This physical content is the reason that a great deal of work has, in the past, been devoted to the effort to model the physical processes associated with the electromagnetic radiation emitted from various plasma environments. In addition, plasma spectroscopy constitutes the main diagnostic tool for a wide range of plasma conditions, such as gas discharges, stellar atmospheres, or the hot, dense, and laser-produced plasmas of inertial confinement fusion (ICF). The conditions found in these plasmas mean that the line-shape model, to be presented here, must describe the spectra emitted from plasmas with electron densities which range over more than ten orders of magnitude and temperatures up to a few keV.

The developments which follow are intended to be especially useful when a Stark-broadened impurity ion spectrum is used for plasma diagnostic purposes. This line-shape computation, in hot, dense plasma conditions, can be difficult and lengthy. This is because the spectra of interest are not limited to the simplest hydrogenlike or heliumlike ionic lines, but include also lines radiated by complex, three or more electron ions. An order-of-magnitude estimate for the number of components involved in a typical calculation can be found from the following considerations. A calculation of one radiative transition may, typically, far exceed 20 states in the lower and 50 in the upper subspace connected by this transition. In addition, typically 50, or more, ion microfield values are required to reasonably describe the probability distribution of the random plasma ion microfield perturbation. Therefore, the resulting basis can involve more than 50 000 states. Conventional theoretical spectroscopic approaches that are commonly used to generate the line shapes of complex ions, would give rise to calculations so large that, in practice, they cannot be used for predicting their spectra. Thus given the fact that a number of approximations are necessary to obtain a solution for even the simplest systems, a robust model capable of describing complex spectra emitted from a wide range of plasma conditions is needed. The formulation of such a model is the subject of this work. As will be shown, this model, rather than leading to a formal analytical method drastically limited to the simplest systems, will permit practical spectral intensity calculations of an arbitrarily complex ion perturbed by very general plasma environments.

All line-shape calculations must deal more or less

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directly with the problem of converting macroscopic physics into a solvable N-body problem. One of the most common methods has been to transform the problem into one of resolving a stochastic evolution equation [1]. The underlying hypothesis that yields such an equation is the requirement that the emitter motion, or, more generally, the emitter degrees of freedom, are not strongly coupled to the local perturbing microfield. Such an assumption is generally valid in the case of weakly coupled plasmas where the interaction can be considered as a stochastic external perturbation of the quantum emitter system. For this purpose, the dynamical behavior of the ion-plasma interaction can be replaced by the stochastic fluctuations of the local perturbing plasma microfield. The weak-coupling assumption involved in the use of a stochastic equation generally assumes that the plasma coupling parameter Γ, the ratio of the ionic potential to thermal energy, be smaller than 1. For the plasma spectroscopy model developed in the following, however, it is required only that the features in the line shapes arising from collective charge motion be negligible relative to those due to the chaotic thermal motion. In this case the stochastic behavior of the local microfields is not driven by large charge-density oscillations and the microfield correlation functions can be expected to describe a nonoscillatory damping behavior that is sufficiently well represented by one or more decreasing exponential functions.

In Sec. II the theoretical background of traditional line-shape calculations will be reviewed. Next, in Sec. III the frequency-fluctuation method of modeling the emitted radiation is developed following essentially a classical idea involving spectral frequency fluctuations introduced by Kubo [2], but with more traditional ideas of line-shape theory incorporated. Here, the concept of modeling the microscopic ion perturbations with a Markovian fluctuation of the observable spectral components is formulated. This frequency-fluctuation mixing is extended to formulate a model for including the ion dynamics effect in Stark-broadening calculations. The model is based upon a statistical analysis of the static profile that allows a reduction of the amount of data required before the frequency-fluctutation mixing is applied.

In Sec. IV, the two main methods commonly used to include the ion dynamics effect are reviewed. In the first method, the model microfield method (MMM), the field fluctuations generated by the ion motion are assumed to be a Markovian modulation that reproduces the main statistical features known from statistical mechanics studies [3–7]. The other method is based on a molecular dynamics (MD) simulation of the movement of the plasma ions that produce the local microfield perturbing the emitter [8]. These more traditional methods to account for ion dynamics are discussed in order to clarify their relationship to the frequency-fluctuation model.

Finally, in Sec. V, several results, calculated using the frequency-fluctuation method, are presented and compared to the spectra produced by a molecular-dynamics simulation. This comparison illustrates the excellent agreement found between the proposed model and an ideal experiment, represented by the simulation.

II. THEORETICAL BACKGROUND

The various theoretical approaches developed for the spectroscopy of Stark-broadened lines emitted from plasmas are all related to different approximate solutions of an N-particle problem. For plasmas the particular N-body system to be considered consists of the active emitting ions, which are usually taken to be distinct from the plasma ions and electrons. The plasma ions and electrons produce local electric fields that interact with the emitter and modify the radiated spectra. This plasma-emitter system is usually modeled by partitioning it into an active radiating system and a perturbing bath. The bath is taken to be the electric fields produced by the plasma particles, and the emitting ion then interacts with this bath through the Stark effect. The bath has, in general, a rapidly fluctuating field component produced by the electrons and a slowly fluctuating field component arising from the slowly moving plasma ions. The electron component can be removed from the bath through an impact approximation which results in the addition of a homogeneous damping and shift term to the emitter Hamiltonian H_0. The remaining ion microfield produces a splitting of the radiated lines into Stark components and is generally known only through its principal statistical properties. As will be seen, this knowledge is generally sufficient to predict line shapes.

The common starting point for the calculation of a line shape begins with the dipole autocorrelation function $C(t)$ related to the radiation intensity through the Fourier transform

$$I(\omega)=\frac{1}{\pi}\mathrm{Re}\int_0^\infty e^{i\omega t}C(t)dt \ , \tag{1}$$

where, in Liouville space notation, $C(t)$ is given by the trace,

$$C(t)=\langle\langle \mathbf{d}^* | U(t) | \cdot \mathbf{d}\rho_0 \rangle\rangle \ . \tag{2}$$

Here, $\mathbf{d}$ and ρ_0 are, respectively, the dipole and the equilibrium density matrix operator for the given finite quantum system. The average evolution operator $U(t)$ for the quantum emitter system can be found from the solution of a stochastic Liouville equation (SLE) of the form [1]

$$\frac{dU_f(t)}{dt}=i(L_0+l_f)U_f(t) \ , \qquad U_f(0)=1 \ . \tag{3}$$

The Liouville operator L_0 used in the above is a phenomenological operator, constructed from H_0 that describes the equilibrium emitter system behavior. It involves the transition energies of the free radiating system and also accounts for the electron broadening mechanism. As was indicated above, the electrons contribute to homogeneous broadening and their effect is described by a non-Hermitian collisional operator that was included in H_0 and which contributes to the decorrelation of the radiating dipole [9].

The time-dependent Liouville perturbation operator l_f, in the above, connects the quantum emitter system to the external ion electric field "f" where f is one of the possible microfield perturbation histories produced by the varying configuration of the perturbing ions in the plasma. When averaged, the ionic perturbation giving rise to the Stark splitting of the lines results in a broadening that, by analogy with Doppler broadening, is considered to be inhomogeneous. This ion field interaction is modeled with the time-dependent operator l_f that perturbs the emitter system, described by the operator L_0. These microfield perturbations are assumed to belong to a measurable functional space $\{F\}$ that provides a statistical method for the calculation of average quantities through the use of discrete weighted sums, or a more general integration process, with a given measure or probability density. The average evolution operator can be written,

$$U(t)=\langle U_f(t)\rangle_{f\in F} . \tag{4}$$

The formal resolution of the SLE of Eq. (3) can be obtained in principle with a two-step process. First, a solution to the equation for each of the field histories, and second, a sum, or integration, over the functional space. However, the quantum average in the trace of Eq. (2) works as a filter that reduces the information contained in $U(t)$, with the result that the line-shape problem becomes simpler than the resolution of the SLE. Since the final purpose is the calculation of line shapes, it is straightforward to develop methods that take advantage of this simplification.

In a few well-known cases, the SLE can be solved either exactly or to a good approximation. For example, an exact solution is obtained for the impact limit in which short and rare binary collisional events occur between emitters and perturbers and the mean time between collisions is much longer than the collision time. This type of approximation is used to describe the perturbation of the emitters by the electron collisions in the plasma. In the simplest approach, the impact theory, the collisions are assumed to be complete so that $U(t)$ becomes time independent and can be obtained by solving the SLE for each binary collision with an average taken over all the collision parameters. The electron interaction in this case is replaced by an averaged collisional operator and results in the homogeneous broadening and shifting of the lines.

The second common case in which the SLE can be solved exactly is the static limit where the perturbing ion microfields, acting on the emitters, are constant during the radiative process and are well characterized by a probability density. The resolution of the Liouville equation for each constant field is followed by an average of the corresponding evolution operator using the probability density of the electric microfields. In this case, the microfield average produces the inhomogeneous broadening and yields the usual static line shape.

These two limiting cases are the foundation of almost all theories of the shape of lines emitted from plasmas. In the usual formulation, they are combined so that a solution to the SLE is obtained in which the perturbing electrons are treated in the impact approximation and the ions are considered in the static limit. This is also the starting point for the model to be presented in the following section. However, for this model, we utilize a particular form [10,11] of the solution to the SLE that permits practical calculations to be performed for complex ionic emitters in a wide range of plasma conditions. The considerations which lead to this particular form of the solution to the SLE are based, first, on the fact that the electron impact, or homogeneous broadening, is well characterized by a frequency-independent collisional operator; and, then, second, to obtain the form required, the remaining average over the ion microfield values is performed by assuming a discrete set of perturbing ion microfield values f so that the mean evolution operator of Eq. (4) can be written

$$U(t)=\sum_f p_f e^{i(L_0+l_f)t} , \tag{5}$$

where p_f stands for the probability of the local-field state f. Thus, for each field value, the Fourier transform of Eq. (1) can be calculated in the f-dependent basis that makes the Liouville operators L_0+l_f diagonal,

$$I(\omega)=\frac{1}{\pi}\sum_f p_f \mathrm{Re}\int_0^\infty e^{i\omega t}\langle\langle \mathbf{d}^*|M_f^{-1}M_f e^{i(L_0+l_f)t} \times M_f^{-1}M_f|\cdot\mathbf{d}\rho_0\rangle\rangle dt . \tag{6}$$

Here, M_f is the unitary matrix that diagonalizes the Liouville operators. This procedure leads to the desired result, which is that the above integral can now be written as a sum of rational fractions which are generalized Lorentzian spectral components of the line, i.e., the Stark spectral components,

$$I(\omega)=\sum_k \frac{c_k(\omega-f_k)+a_k g_k}{(\omega-f_k)^2+g_k^2} . \tag{7}$$

This form of the solution to the SLE will be used for the development of the calculational model in Sec. IV. Recall that this form is based on the impact electron and static ion approximations and is, therefore, formally equivalent to the standard formulation of plasma line-shape theory found, for example, in Ref. [10]. However, Eq. (7) has the added feature that it also permits the introduction of the concept of the Stark spectral component which will be important in the later formulation of the model. The Stark components are defined by two complex numbers, the generalized intensity a_k+ic_k and the generalized frequency $z_k=f_k+ig_k$. These components can be considered to contain a complete set of information for solving the line-shape problem. The imaginary parts that appear in both the frequency and the intensity are a result of the use of a non-Hermitian collisional operator to treat the electrons in L_0.

To establish a basis for the frequency-fluctuation model to be developed below, the physical meaning of the Stark components and their relationship to the physical information contained in the radiated spectra will be considered. The individual Stark components constitute the radiated spectrum whenever the static approximation is valid. However, since there can be unshifted Stark components, there is no one-to-one correspondence between the local microfield and the component frequency. In addition, from a spectroscopic point of view, if several Stark components appear at the same spectral position (or nearly the same position, within a fraction of their homogeneous width), they cannot be observationally distinguished. This means that the primitive Stark components of Eq. (7) should be considered as nonobservable objects and, therefore, will be replaced here with the concept of radiative channel which is the minimum inhomogeneity that is observed in the emitted radiation. The radiative channels represent the fundamental observable components of the static line shape. They are more precisely defined as the mean of a coarse-grained distribution of the Stark components. It is these observable objects that the ion microfield fluctuations affect. As will be discussed in detail later, these radiative channels represent, in some sense, a renormalization of the spectrum of the isolated ion dressed by the static plasma interaction. The model that is to be introduced in the next section is based on this concept.

The argument just given is the same as that found in the description of experiments involving two-photon sub-Doppler spectroscopy in which the homogeneous line is to be extracted from a Doppler broadened line. In these experiments, counterpropagating lasers detect a single velocity class (the projection over a given direction), i.e., a partial velocity average, not, as is sometimes stated, the contribution of atoms with the same velocity. As with the primitive Stark components, the exact velocities should be considered as unobservable objects. This is because, in general, no technique is available to unfold the contribution of different external static perturbations within the same homogeneous width, and, therefore, the objects that have a physical meaning are the result of some partial average over the indistinguishable primitive components.

This discussion concerning the observables of the system can be applied to simplify the introduction of ion dynamics effects into the line-shape calculation. For complex ionic spectra the large number of Stark components can become the limiting factor in calculations. As is usual in situations where a massive amount of data must be treated, a recourse to statistical methods is desirable. However, particular care must be taken to preserve the physical content when reducing the quantity of data involved in the calculation. Since the static line shape in this case results from the superposition of all the static Stark components, a reasonably coarse-grained distribution of these components will preserve this static spectral profile. Using a statistical algorithm to extract this coarse-grained distribution from the complete Stark component data results in a reduced set of equivalence classes that can be interpreted as the various radiative channels allowed for the radiation.

For intermediate cases, that is, when the ion interaction must be considered to have both static and impact contributions, the SLE must be solved for emitters perturbed by an electric microfield that fluctuates during the radiative process. This is referred to as the ion dynamics effect and becomes important when the perturbing ion microfield, and consequently the frequency radiated by the individual emitters, cannot be considered to be stationary during the radiation process. A number of approximate methods exist which have been formulated specifically to address this problem. The basic strategy of two of the most relevant methods developed for plasma line-shape calculations, the model microfield method (MMM), and the simulation method, is to treat directly the effect on the emitted spectrum of the stochastic fluctuations of the perturbing microfield. These methods will be reviewed in Sec. V, for a better understanding of the frequency-fluctuation model developed here. However, since we use a completely different approach, the previous methods will be discussed only for the purpose of displaying the utility of the technique to be adopted here. The principal advantage of the model is that these earlier methods for dealing with ion dynamics have only a formal relevance to the general problem of line-shape studies and can be used for practical calculations of plasma ionic line shapes only for the simplest quantum systems. Calculation for arbitrary complex ion emitters in a plasma is computationally impossible with these previous methods.

III. THE FREQUENCY-FLUCTUATION MODEL

First, we present an example due to Kubo [2] that will serve as a reference for our subsequent model calculation of the spectra of emitters subject to plasma perturbations which do not fall neatly into either the static or impact categories. A classical model of the emitted spectrum based on the fluctuations in frequency of the radiative channels is then introduced. Previous statistical treatments such as the MMM as well as the simulation model were based on a common strategy: an *a priori* stochastic field modeling followed by the solution of the SLE. The model we formulate will drastically change this point of view by using the fact that the field fluctuations induce fluctuations of the radiation intensity and of the radiation frequency through the evolution operator. This leads to the formulation of a method based on modeling the radiation fluctuations, so that a straightforward consideration of the stochastic properties of the observables, i.e., the radiated frequencies, can be used to model the ion dynamics effect on the line shape of a Stark-broadened transition. We defer to the following section the relationship between this frequency-fluctuation modeling and the physical quantity which is directly related to the ion dynamics, the microfield fluctuation.

The idea of calculating spectra with a simple frequency-fluctuation model of the radiating system has been introduced by Kubo [2]. The treatment is based on a Markovian model for the fluctuations of the emitted radiation frequency and contains concepts similar to those to be formulated here. It is especially relevant to understanding the behavior of the associated line shape. In this model, the fluctuation of the emitted frequency is taken to be caused by the complex perturbations to which the emitter is being subjected. Hypotheses about the process responsible for the frequency fluctuation are not necessary at this point. The simplest case is a system emitting two radiative components with frequencies ω_1 and ω_2 and equal intensities. The frequencies of these two lines are assumed to be exchanged, or mixed, by the Markovian process with a fluctuation rate ν, and the associated spectrum is given by the expression

$$I(\omega)=\frac{\nu(\omega_1-\omega_2)^2}{(\omega-\omega_1)^2(\omega-\omega_2)^2+\nu^2(\omega-\omega_m)^2}\ , \tag{8}$$

where $\omega_m=(\omega_1+\omega_2)/2$. This system can be seen to have two limits which depend on the fluctuation rate ν. For the static limit $\nu=0$ the spectrum consists of the two nonperturbed frequencies ω_1 and ω_2. Then, as the fluctuation rate, ν increases to infinity, these two lines broaden and coalesce towards the mean frequency ω_m.

This frequency-fluctuation model for the observable frequencies forms the basis of a practical method to account for the ion dynamics effect on a static Stark-broadened line shape. It is physically interesting because, instead of basing the calculations on speculations concerning nonobservable quantities like the fluctuating local microfield "seen" by an emitter as in microscopic theories, the frequency-fluctuation modeling is based on macroscopic physical quantities, i.e., the characteristics of the emitted radiation itself. In addition, as will be seen, this model permits rapid and accurate calculations of the spectra emitted by complex ions in hot dense plasmas.

The frequency-fluctuation model (FFM) generalizes the considerations leading to Eq. (8) in order to describe the frequency variation of the radiation emitted by ions in a plasma. The explicit steps necessary to extend the above calculation for the definition of the model are: first, define the component set to be mixed by the stochastic process; second, construct the Markov process through a consideration of the fluctuation rate for the chosen component set; and finally, give a prescription for the practical calculation of the line shape with an equation that is the generalization of Eq. (8).

The choice of a component set is based on the considerations concerning observable quantities which gave rise to the radiative channels. These radiative channels are defined by the mean of a coarse-grained distribution of the Stark components, which are obtained through a quantum-mechanical development in the static ion limit. The coarse-graining process is to be identified with a renormalization of the primitive information contained in the static profile. This gives rise to the first hypothesis of the FFM: the stochastic fluctuation of the static radiative channels represents the ion dynamic effect on the line shape. It is based on the assumption that the frequency fluctuation of the static frequencies is the physically observable result of the fluctuation of the ion microfield.

The next step, the construction of the Markov process, requires a discussion of the stochastic fluctuation process driving the frequency mixing. In principle, the channel fluctuation mechanism may not be Markovian. This is because the behavior of each channel formally can depend on the past behavior of all the others. Nevertheless, as this memory is completely unknown and, perhaps, irrelevant, its effect will be ignored and a stationary Markov process will be chosen. Assuming that the fluctuation mechanism of the static frequencies obeys a stationary Markov process driven by the field fluctuations is the second hypothesis used to define the frequency-fluctuation model.

Finally, the third step, the actual line-shape calculation, involves the method to be used to solve for the line shape. The choice of a particular Markov process cannot be unique, but must be selected in conjunction with this method. This will involve most of the approximations needed to complete the profile calculation and will also characterize the frequency-fluctuation mechanism. Unlike the microfield fluctuations, the frequency-fluctuation process necessarily ignores any field dependence of the transition rates involved in the definition of the Markov process. Therefore, the Markov frequency-fluctuation process is based on a unique fluctuation rate which is associated with the restrictions on the model. It is chosen here as the average rate of the fluctuations driven by the ion microfield and is obtained either from simulation, or from a simple model of the field-field correlations.

For complex ions, we consider n channels, characterized by their generalized complex frequencies and amplitudes, that fluctuate in accordance with a finite Markov process. The behavior with respect to the limits of the resulting profile will then be similar to that in the Kubo model. The static profile $\nu=0$ will be given by the sum of the channels, and is the static solution to the SLE. The opposite bound, the fast fluctuation limit $\nu\rightarrow\infty$ will have a single resonance which concentrates the entire set of radiative channels at the center of gravity of the original profile, as should arise with a very large ion dynamic effect. Thus, although the zero fluctuation limit is the same as the static limit, the infinite fluctuation limit is not the impact limit, as will be explained in more detail later.

This process is defined completely by two quantities, the instantaneous probability of states $p_1, p_2, \ldots, p_n$, and the transition rates between these states W_{ij} with $i,j=1,2,\ldots,n$. The transition probability matrix P is related to the matrix of transition rates W through

$$P=e^{-Wt}\ . \tag{9}$$

The transition rates to be used in the following are chosen to be proportional to the fluctuation rate ν and are defined by

$$W_{i,j}=\nu p_i\ \ (i\neq j),\quad W_{i,i}=-\nu(1-p_i)\ . \tag{10}$$

In the frequency-fluctuation model, the probabilities p_i are defined to be the normalized real part of the corresponding radiation channel intensity. The transition rates and the probabilities W and p satisfy the sum rules required by normalization and detailed balance:

$$\sum_i W_{i,j}=0,\quad \sum_j W_{i,j}p_j=0\ . \tag{11}$$

The quantities in Eqs. (9)–(11) define the stationary Markovian process that is the generalization to n channels of that used to produce the line profile of Eq. (8). The spectrum associated with the stochastic mixing of n radiation channels is now seen to be [12]

$$I(\omega)=\mathrm{Re}\sum_{i,j}(\omega-f+iW+i\gamma)^{-1}_{i,j}(a_i+ic_i)\ , \tag{12}$$

where the elements of the diagonal matrices f and γ are, respectively, f_i and g_i, the real and imaginary parts of the generalized frequencies z_i of the radiation channels.

The steps necessary to formulate the model have now been defined. That is, the component data set has been defined to be the static radiative channels and the fluctuation rate for the Markov process is defined by Eqs. (10) and (11) with a ν chosen to be that determined by the microfield fluctuation rate. Finally, the line shape is to be calculated with Eq. (12). This series of steps connects the N-body problem through the SLE to the final Markov model.

IV. FIELD FLUCTUATION MODELS

There exists no straightforward relationship between methods based on the ion microfield fluctuations and those based on the frequency fluctuations, both methods necessarily involve the same basic physical framework. The first field fluctuation model that we consider for comparison with our frequency-fluctuation model, is the MMM, introduced by Frisch and Brissaud [3], for treating the ion dynamics. The assumptions contained in the MMM illustrate particularly well the requirements for a solution in the intermediate, nonstatic, nonimpact cases. This method, primarily developed for neutral emitters in plasmas, is purely analytical. It requires the history functions for the ion field to belong to a well-defined measurable stair-function space or, equivalently, it requires the time-dependent field fluctuations to obey a particular Markov process, the kangaroo process, that enables an exact resolution of the SLE. This Markov process is chosen in such a way that its static and dynamic properties match the static field distribution function and the field correlation function supposedly known from an independent plasma physics study. Thus, the MMM uses rather restrictive assumptions on the time-dependent field fluctuations in order to obtain a model for which an exact solution exists. Similar methods have been used in other fields, e.g., to treat problems related to spin fluctuations in solids [13].

The assumption that the functional space of perturbing ion microfield is restricted to stair-functions corresponds to the basic hypothesis that the electric field suddenly jumps from one field value to another according to precise rules, which for the MMM, is assumed to be the kangaroo process. This simple restriction permits the definition of a new basis that includes the microfield states. The relevant basis that generates a Liouville space $\mathbb{L}$ extended to the field states is denoted

$$|a,b,i\rangle\rangle \ . \tag{13}$$

In this extended space, the quantum operators act only on the atomic states a and b while the stochastic process is exclusively connected to the field states i belonging to a particular set F. This notation explicitly describes the evolution of a quantum system performing random jumps among states of the product space $\mathbb{L}\otimes\mathbb{F}$.

The mean evolution operator can now be written in terms of a partially averaged operator $U_{i,j}(t)$. This operator is averaged over all possible fields that occur between the two definite field states defined at times 0 and t. The mean evolution operator is then found as an average over initial states and a sum over the final states as

$$U(t)=\sum_{i,j} p_i U_{i,j}(t) \ . \tag{14}$$

In the case of a Markovian stochastic model of the field fluctuations, the problem is simplified because these partial averages can be expressed in terms of the evolution operators for constant fields, i.e., the evolution operators are restricted to one-field subspaces. Taking the frequency space transform of Eq. (14) and using the simple Poisson step process (PSP), where, unlike the kangaroo process, the fluctuation rate ν for the PSP is independent of the field states, the equation for the matrix U with elements $U_{i,j}(z)$ can be written [14]

$$U(z)=G(z)+i\nu pG(z)[1-i\nu\langle G(z)\rangle]^{-1}G(z) \ , \tag{15}$$

where

$$G_i(z)=\int_0^\infty e^{izt}e^{-i(L_0-l_i)t}dt \ . \tag{16}$$

Note that, for this example, the fluctuation rate ν in Eq. (15) is the ion microfield fluctuation rate. The evolution operator is easily calculated whenever the atomic systems are finite by inverting the complex non-Hermitian matrix

$$G_i(z)=(z-L_0-l_i)^{-1} \ , \tag{17}$$

or, equivalently, finding the eigenvalues and the eigenvectors of the matrix to be inverted

$$G_i(z)=M_i\begin{bmatrix}\ddots & & \\ & \dfrac{1}{z-z_{i_k}} & \\ & & \ddots\end{bmatrix}M_i^{-1} \ , \tag{18}$$

where M_i is the unitary matrix which transforms Eq. (17) into a diagonal form.

It can now be seen that, for a given stationary Markov process the z_{ik}, the M_i, and the microfield transition rate matrix are the necessary quantities required to obtain a solution of the SLE. This data set is seen to be equivalent to the one used for the definition of the static Stark components. It is assumed that the ion microfield fluctuation rate ν of Eq. (15) is the same as the frequency mixing rate ν in the frequency-fluctuation model of Eqs. (10) and (12). It can now be seen, that solutions of the SLE which assume Markovian fluctuations require the same data whether one considers the microscopic microfield fluctuations or the observable frequency fluctuations. However, it will be shown that the frequency-fluctuation model while containing all the fundamental information retains a calculational advantage and provides more accurate results. This latter point will be shown explicitly by comparison with simulation.

Molecular dynamics (MD) simulation is a second field fluctuation approach to the problem of including ion dynamics in line-shape calculations, relevant to the frequency-fluctuation model. The MD method is based on the numerical simulation of the ion microfield followed by an integration of the time-dependent evolution equation for the dipole operator [8,11]. Here, the solution obtained depends on the convergence of the simulation process. That is, the simulation process is stopped when the result reaches a definite neighborhood of the required solution. This convergence is directly checked on the dipole autocorrelation function, and is related to the line shape through Eq. (1). For the simulation method two steps are necessary. First, a reduced set of history functions is constructed with a molecular-dynamics algorithm that follows approximately 100 ions with mutual Coulomb interactions contained in a cubic box. This first step can be thought of as the construction of a function space reduced to N history functions each with an equal weight $1/N$. The SLE is then solved and averaged over the quantum states for each history. In this second step, the information contained in the evolution operator for a relevant time period is converted into the scalar function of Eq. (2). This, together with the relaxation mechanism, acts as a noise filter ensuring a fairly fast numerical convergence of the method. Results from simulation have been used as model laboratory experiments to compare with line shapes calculated by other methods or resulting from experiments [12].

V. DISCUSSION AND EXAMPLES

The frequency-fluctuation model has been developed primarily for plasma line-shape studies. In this field a number of sophisticated formal approaches have been discussed, e.g., the MMM [3–7] and the simulation method [8,11] that lead to calculations which are limited in practice to simple radiative systems. The main purpose of the present approach is to permit complex systems to be considered on the same level as those simpler systems. That is, to expand the field of plasma line-shape investigations so that rapid calculations involving multielectron ions present in hot dense plasmas can be considered. It should be emphasized, however, that this method is not restricted to studies involving plasma spectroscopy, but applies to any area where the decorrelation behavior of the bath fluctuations is well represented by an exponential damping. In addition, since the fluctuation rate is fundamental to the frequency-fluctuation model, it provides a simple and practical method to describe continuously the region between the static limit or, zero fluctuation rate, and the fast fluctuation limit in which the external perturbation vanishes.

Finally, it should be noted that this method does not formally yield the impact limit. This limit is not a simple fluctuation rate limit, but rather corresponds to a particular regime of the external perturbation fluctuations. That is, since the FFM assumes that the effect of the perturbing ion microfield fluctuation is manifested as a fluctuation, at the same rate, of the observable radiative channels which compose the static line, then in the limit of an infinitely rapid ion microfield fluctuation, the effect of the perturbation disappears and the line components collapse to the center of gravity. This effect is the same as velocity narrowing where the rapid collisional mixing of velocity components causes a collapse of the Doppler line shape. Note that the no-fluctuation limit results in the static line shape, but the rapid fluctuation limit does not result in the ions contributing to the impact width of the transition, but rather in the complete disappearance of the ion microfield perturbation. This is because the fast fluctuation limit is not the same as the impact limit of short and rare binary collisional events. The modeling of collisions with a fluctuating microfield and a varying interaction parameter with an impact limit is possible [14], but could not be simply included in fluctuation of the radiative channels and is thus, not possible within the approximations of the FFM.

To perform a comparison with the frequency-fluctuation model, the hydrogenic argon Lyman-α transition, including fine structure, in a weakly coupled proton plasma, is now investigated. This choice is made for several reasons. First, this case has been frequently calculated with various theoretical line-shape methods [6,15], and therefore, reference profiles are available for comparison. In addition, the quantum system involved is simple enough so that a large number of time histories can be used in the MD simulations to minimize the noise. Finally, the Stark line shape investigated for different plasma density and temperature conditions can involve both a linear Stark effect for the red ($1S_{1/2}$-$2P_{1/2}$) and a quadratic Stark effect for the blue ($1S_{1/2}$-$2P_{3/2}$) component, which will be important in low-density cases. For higher densities these two components merge, so that another useful pattern for cross comparisons, the limit without fine structure, occurs. It should be emphasized that for the Lyman-α transition, the ion motion effect is nontrivial and is not simply accounted for by the common procedure of using a convolution process which broadens the line. It is therefore important to note, that in this case, the component mixing model permits ion dynamic effects to be included in a physical manner.

In the present context the MD simulations represent gedanken experiments, where essentially the same hypotheses are used as in the calculations with the frequency-fluctuation model. The simulation is based on a time-intensive step by step numerical integration of the multidimensional differential linear equations of motion for the plasma particles. The simulation results contain both noise, due to the finite sample size, and the equivalent of an apparatus function which arises from the finite number of time steps used. These are both smaller and better known than in experiments, but must be included for the comparisons. For a complete description of the simulation method see Ref. [8].

To make the comparison as rigorous as possible, the same static ion microfield distribution will be used for both methods. For the simulation calculation, this constraint is applied by using a sample history set with an initial field probability that is the same as the field distribution that produced the static Stark frequency component set for the frequency-fluctuation method. Further, the same atomic data, and the same homogeneous electron broadening mechanisms are used in the two methods, while the effects due to Doppler broadening are neglected to increase the sensitivity of the comparison. For the line-shape simulation, the temporal properties are accounted for through the normal evolution of the selected trajectories in the simulation, while in the frequency-fluctuation method the fluctuation rate is used. This rate, as explained above, can be obtained from the best exponential fit of the microfield time correlation function. An example of such a MD simulated electric field correlation function is shown in Fig. 1 with a typical stationary field distribution function. We point out that the fit is only required to provide a good representation of the decay of the $C_{EE}(t)$. Further, the fit to the field-field correlation function by the simple exponential shown in Fig. 1(b) indicates that the true field-field correlation function is indeed not a single exponential, but the single exponential approximation reproduces the decay—thus defining the fluctuation rate for this case. The variation of the fit to enhance agreement at early or late times is possible, but would not in any manner change the qualitative nature of the comparisons shown here.

Three cases have been considered, corresponding to electron densities $N_e=1.5\times10^{23}$ cm^{-3}, 1×10^{24} cm^{-3}, and 5×10^{24} cm^{-3}, all with the same electron temperature $T_e=10^7$ K. Figures 2–4 show the simulation result compared with the frequency-fluctuation model line shape convolved with the appropriate Gaussian apparatus function that, as explained above, accounts for the finite time used in the simulation. The corresponding static profiles are also presented for comparison to illustrate the contribution of the fluctuations to the line shape. These three cases are representative of the inhomogeneous Stark structures encountered in weakly coupled plasma spectroscopy. For the three cases, the good agreement of the

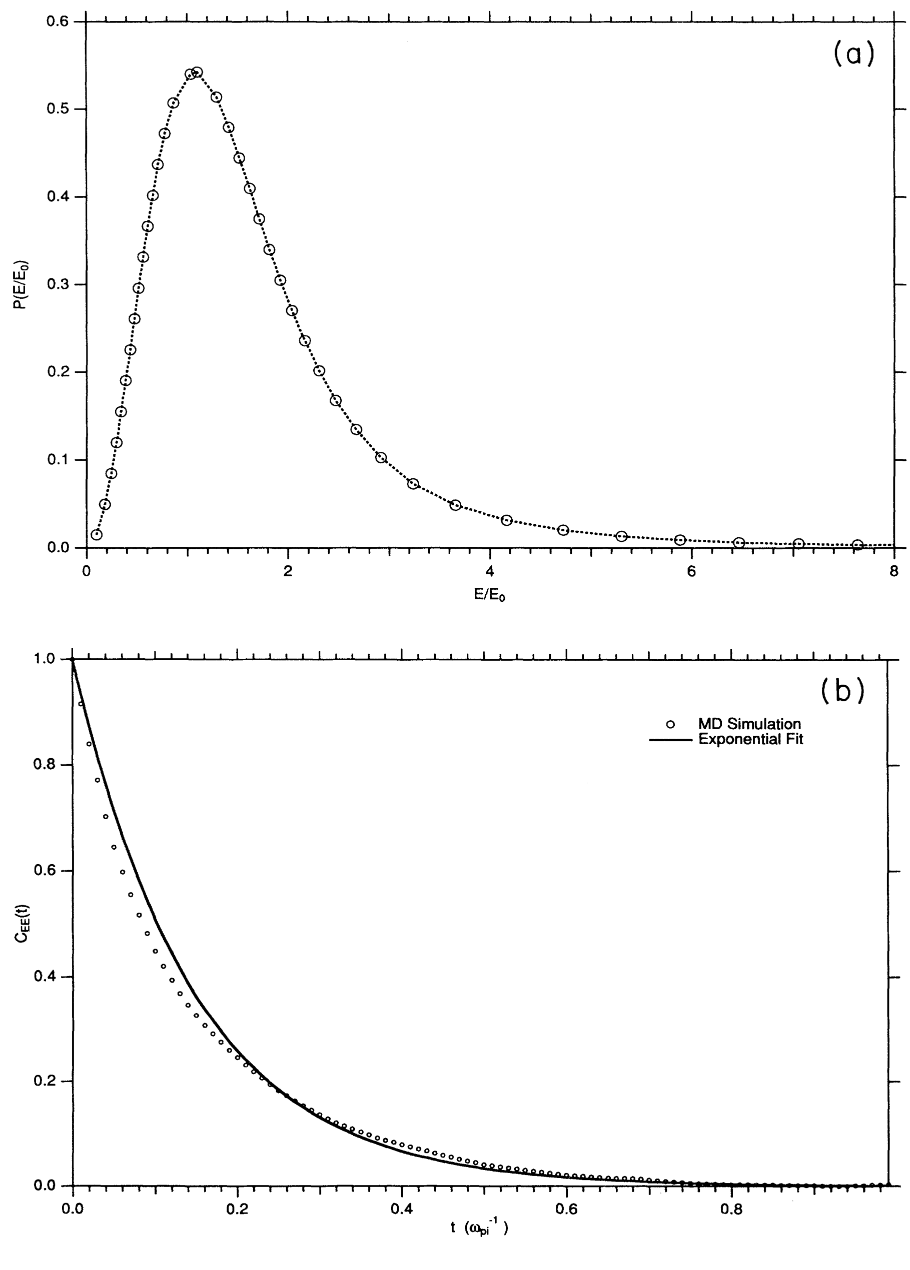

FIG. 1. The plasma statistical properties are given by both the static modulus field distribution (a) in mean field units, $E_0=2.61eN_e^{2/3}$ and the field-field correlation function (b). The later MD simulation result is in plasma frequency units (dark line) presented together with the exponential fit (dotted line) used in the case shown in Fig. 3.

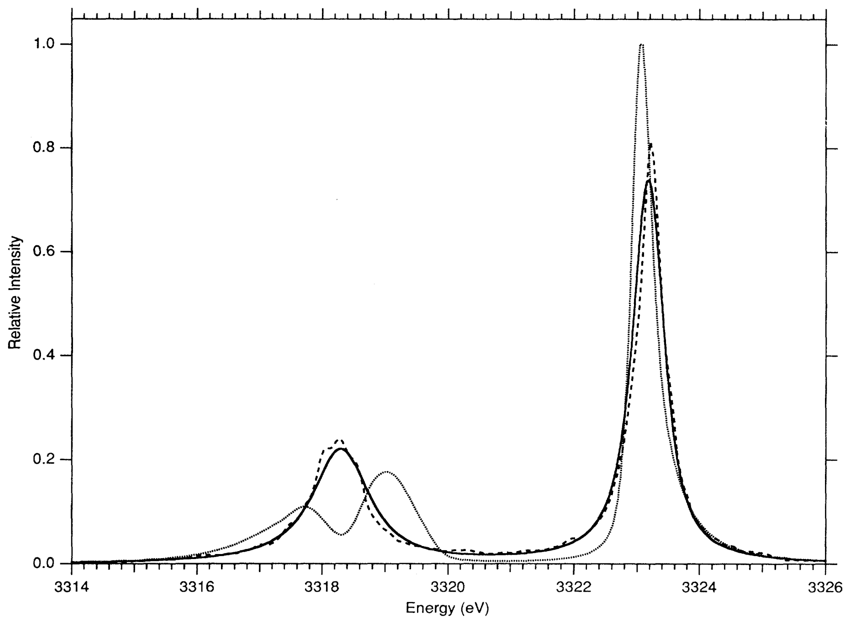

FIG. 2. The comparison of the Lyman-α transition, resulting from the MD simulation (dashed line) and from the frequency-fluctuation model (solid line), is shown for Ar^{17+} in a proton plasma. The static profile (dotted line) is also shown, for completeness. The conditions of electron density and temperature are, respectively, $Ne = 1.5\times 1023$ cm^{-3} and $T_e = 10^7$ K. The fine-structure effect is taken into account and an additional Gaussian width, $g = 0.15$ eV, is introduced in both the static and the model results. The red component shows a strong narrowing with respect to the static profile due to a large fluctuation rate, $\nu = 2.78$ eV. The model result matches well the simulated one in spite of the noise remaining in the simulation.

frequency-fluctuation model with the results provided by MD simulation indicates that the model can be used with confidence in place of other methods for more complex quantum systems in the analysis of plasma spectroscopy experiments.

VI. CONCLUSION

A fast calculational method has been presented that for the first time is capable of computing the spectral line profile emitted by an arbitrary ion immersed in plasmas of widely varying conditions. The calculation includes the effects of quasistatic ions, impact electrons and, most importantly, ion dynamics. The impact electrons contribute a non-Hermitian component to the plasma-radiator Hamiltonian, and to handle the large amount of data, which can arise for arbitrary atomic structures, a diagonalization procedure for this non-Hermitian Hamiltonian is employed. This diagonalization is performed under the assumption that the ion microfield does not fluctuate and results in a static line shape that is written as a sum of Stark components. This static limit calculation has been compared to experimental data for a number of complex ions in plasma conditions where ion dynamics was an unobservable effect, and the agreement found to be excellent [16]. The use of this method as a

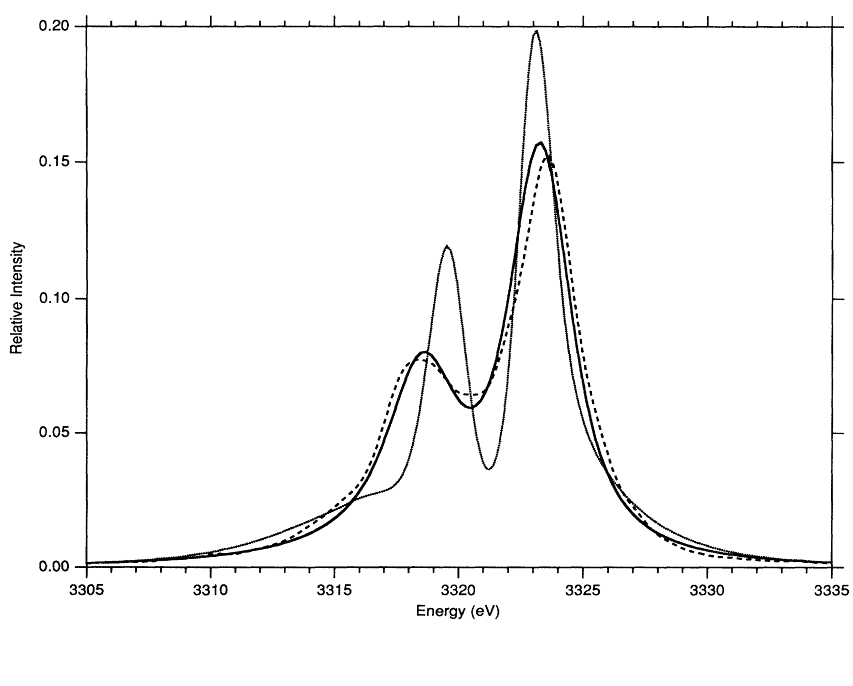

FIG. 3. The same as Fig. 2 for $N_e = 10^{24}$ cm^{-3} and $T_e = 10^7$ K. The additional Gaussian width and the fluctuation rate (see Fig. 2) used are, respectively, $g = 0.74$ eV and $n = 5.45$ eV.

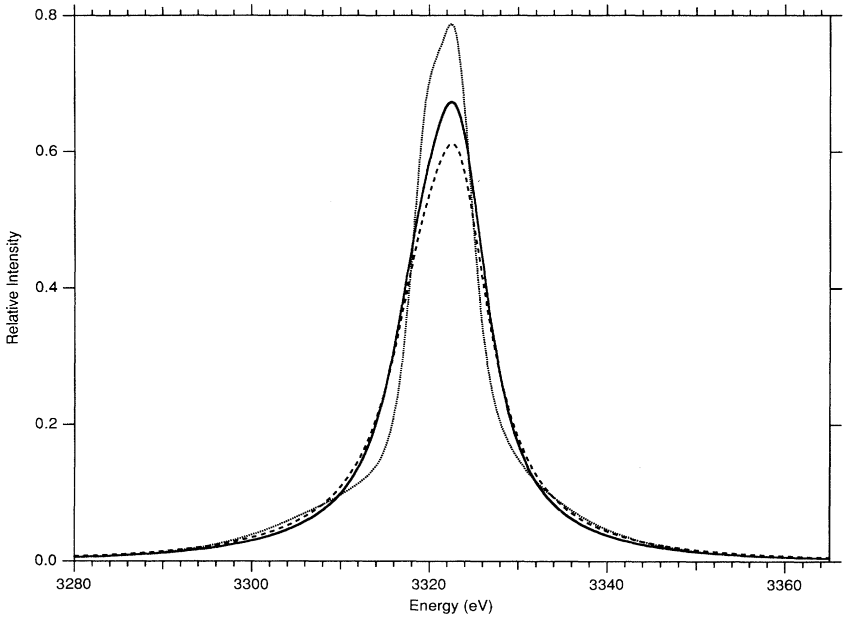

FIG. 4. The same as Fig. 3 for $N_e = 5\times10^{24}$ cm^{-3} and $T_e = 10^7$ K. The additional Gaussian width and the fluctuation rate used are, respectively, $g = 1.66$ eV and $\nu = 9.75$ eV.

plasma diagnostic tool is discussed in Ref. [17].

Using this representation of the static profile in terms of the Stark components, the amount of data required to describe the line shape can be reduced by coarse graining to obtain the observable radiative channels. The ion dynamics is then introduced through the frequency-fluctuation model. The physical basis for this model is found in the fact that a line shape originating from a radiative transition of an emitter embedded in a fluctuating electric field can also be considered to result from the Markovian mixing of the ensemble of inhomogeneous radiative channels that compose the static limit of the line shape. This mixing takes place at a fluctuation frequency taken to be the average microfield fluctuation rate, obtained from a simple model of the field-field decorrelation time.

As required, this model has the two expected limits: the static limit, when the fluctuation rate vanishes, and the fast fluctuation limit which corresponds to emitters unperturbed by the ions. We note that this fast fluctuation limit is not the ion impact limit. Using the same hypotheses, complete MD simulation and the frequency-fluctuation model have been compared for the same plasma conditions in the weakly coupled domain. These comparisons, based on the different profiles resulting from the two radiative transitions, $2P_{1/2}$-$1S_{1/2}$, $2P_{3/2}$-$1S_{1/2}$, show good agreement between the model and the simulation over a wide range of density. It is concluded that the frequency-fluctuation model accurately describes the shape of the lines emitted by complex ions in weakly coupled plasmas. Since this method gives rise to very fast calculations, it can replace the more usual, but slower and less practical, methods for more complex atomic transitions.

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