Nonequilibrium thermodynamics of highly charged ion plasmas

G. Faussurier,[1,*] R. M. More,[2] C. Blancard,[1] and T. Kato[2]

[1]*Département de Physique Théorique et Appliquée, CEA/DAM Ile-de-France, B.P. 12-F-91680 Bruyères-le-Châtel, France*
[2]*National Institute for Fusion Science, Oroshi-cho, Toki, Gifu 509-5292, Japan*

Thermodynamics of irreversible processes is applied to study the interaction of matter and radiation field in nonlocal thermodynamic equilibrium. The rate of entropy production of matter and radiation field, in contact with a free electron reservoir in local thermodynamic equilibrium, is obtained using the conjugate variables of the state variables. When approximating the electronic configuration populations by an effective Boltzmann law, the corresponding effective temperature is determined by minimizing the rate of entropy production at fixed electronic density, electronic temperature, and radiation field. Numerical results and comparisons with recent experiment for photoionized iron plasma are presented and discussed.

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I. INTRODUCTION

In laboratory plasma physics or in astrophysics, plasmas containing highly charged ions exist in many ionization and excitation states and for various thermodynamic conditions. For instance, the properties of hot dense matter in stellar interiors or dense plasmas produced by short-pulse laser interaction with solid-density target are usually studied assuming local thermodynamic equilibrium (LTE). On the other hand, low-density plasmas in solar corona or in tokamak machines require nonequilibrium kinetic models. Between these two extremes, laser-produced plasmas, pinches, or divertor plasmas involve intermediate conditions combining high-density, a significant radiation environment, and non-LTE (NLTE) excited-state populations [1–3].

Despite the important role radiation has played in many parts of astrophysics and laboratory plasma physics in describing populations of atomic and molecular systems and heat transfer, there is still a considerable need for fundamental research in the area of nonequilibrium thermodynamics [3]. Radiation cannot reach equilibrium by itself but requires interaction with matter to do so; this is due to the linear nature of the electrodynamic equations or wave equations [4]. Such a problem is not encountered with matter because collisions between ions and electrons are sufficient to achieve thermalization under, for instance, the driving influence of a reservoir at a given temperature. In fact, collisions between particles can always be reduced to some exchange of virtual photons at the most fundamental level for the ordinary energy scale considered in laboratory or stellar plasma physics. It is clear that understanding irreversible phenomena of radiation requires the study of the macroscopic behavior of radiation and matter as a single system, and in particular, the irreversible thermodynamics of matter in interaction with radiation.

There are some circonstances where a consistent description of matter and radiation is not so crucial. This is the case when one pays more attention to atomic physics than to ra-

diative transfer. Radiation field, defined by its set of brightness temperatures, may be assumed to be given from outside and only acts as an external system upon the atomic system. Indeed, various situations may be faced with. When for example, radiation field intensity is so small that it does not influence matter properties, or when radiation field intensity is not negligible but is emitted spontaneously and can escape freely from the system under consideration without being (re)absorbed, the plasma is said to be optically thin. Another extreme situation is encountered when the photon mean free path is so short that the photons are reabsorbed nearly immediately after having been emitted. We face what is called a thick plasma. From the atomic viewpoint, radiation can be considered as an external reservoir. Like the free electron degrees of freedom, we can simply integrate out or trace over the external unwanted degrees of freedom. This makes sense when we focus on the statistical description of matter under the influence of radiation and electron reservoirs.

The theoretical framework of treating nonequilibrium radiation as a nonequilibrium photon gas interacting with nonequilibrium matter is still in infancy, especially when we go farther and farther away from equilibrium and when we look for computational and tractable expressions to compare to experiment. Here, we study the consequences of treating on the same level and in a self-consistent way radiation and matter, i.e., of coupling atomic kinetic and radiative transfer equations [2,3] using general principles of nonequilibrium thermodynamics [5–12]. In Sec. II, we consider the atomic system in contact with the constant environment represented by two external reservoirs, i.e., the free electron heat bath in thermodynamic equilibrium and the radiation field out of thermodynamic equilibrium. We give then an explicit expression of the corresponding rate of entropy production. Finally, we present a method to determine the effective temperature law (or Boltzmann law) that the atomic processes tend to establish in NLTE steady state, i.e., a decreasing-exponential law versus energy for the total atomic populations of the configurations [13–16]. We propose to determine this effective temperature law by minimizing the rate of entropy production for matter and radiation field out of thermodynamic equilibrium in contact with the constant environment represented by the free electron reservoir at given electronic tem-

*Corresponding author: gerald.faussurier@cea.fr

perature and electronic density. In Sec. III, we employ a collisional-radiative equilibrium (CRE) model between detailed configurations [16] in NLTE steady-state conditions to calculate the charge-state distributions of photoionized iron plasmas far from LTE. Comparisons with recent experiment are presented and discussed. Section IV is the conclusion. Mathematical details and additional developments are given in the Appendix.

II. THERMODYNAMICS OF IRREVERSIBLE PROCESSES

A. Kinetic and radiative transfer equations

Let us consider a plasma made of single element ions with particle density N_{at}, free electrons with electronic density N_e, and nonpolarized radiation field with specific intensity I_ν. The overall system of ions and electrons is supposed to be neutral and locally homogeneous with mass density ρ. For simplicity, the free electron gas is considered to be a reservoir in thermodynamic equilibrium at electronic temperature T_e and chemical potential μ_e. Free electrons are assumed to be nondegenerate. The relationship between N_e and μ_e is obtained using the well-known Maxwellian velocity distribution for the electron gas. However, ions and photons may be in LTE or NLTE with either steady-state or transient evolution. We assume that radiation can be depicted as an ideal Bose gas described by Bose-Einstein statistics and the plasma as an ideal gas in classical approximation described by Maxwell-Boltzmann statistics. All interactions are treated as small perturbations which induce transitions between eigenstates of the photons and of the plasma particles, i.e., ions or atoms. Our system may thus be described by the specific intensity I_ν of the radiation field and the local atomic populations or particle densities N_i, with energies E_i, degeneracies or statistical weights W_i, and electron populations Q_i. I_ν depends on photon frequency ν, as well as space coordinates, i.e., radius and angle.

In the most general case, the equations of hydrodynamics, radiative transfer, and atomic physics form a complex set of coupled, nonlinear, and nonlocal equations with boundary conditions and constraints [1,2,17]. To simplify this work, we do not consider transport terms for matter, i.e., we neglect macroscopic matter velocities, and the mass density ρ is taken to be constant. However, we will explicitly keep the transport terms for radiation. This approximation is consistent, for instance, with solar atmosphere physics, where all of the energy flowing though the atmosphere is carried out by radiation. We do not consider heat transport through conduction or convection. We are aware that this must reveal sometimes quite restrictive for laser-plasma physics. Yet, once clarified the coupling between radiation field and matter and the thermodynamic analysis of this system, all the restrictive hypothesis can be abandoned one after the other. If needed, the model can be refined since much more is known about heat transfer and nonequilibrium thermodynamics for matter [6].

The time evolution of atomic populations is called the rate or master equation. The general form of the rate equation has been known for a while [2,3,18,19]. However, its deduction from first principles, i.e., starting from quantum Liouville

equation and density matrix formalism, and taking into account interaction of the atomic system with free electron, radiation field, and ion environments seems still to be firmly established, to our knowledge. This is especially true for many electron atoms in complex environments such as dense plasmas [20–22]. In a compact notation, the rate equation reads

$$\frac{dN_j}{dt} = \sum_k T_{jk} N_k, \qquad (1)$$

where T_{jk} is a short-hand notation for the total transition rate between level k to level j. The total number of levels is assumed to be finite and equal to n_{max}. Note that the order of subscripts has been chosen to be consistent with a matrix notation. For simplicity, we will limit our description of atomic physics to electronic configuration notion. Extension to finer description, such as level notion [14], or to rougher approximation, such as superlevel [23] or superconfiguration [24], is possible. Processes taken into account may be collisional and radiative, i.e., electron collisional excitation and ionization and their inverse processes (collisional deexcitation and three-body recombination), photoexcitation and photoionization and their inverse processes (photodeexcitation and spontaneous decay, photorecombination and radiative recombination). Autoionization and its inverse process (dielectronic capture) are taken into account and considered as collisional processes. Since free electrons are assumed to be in LTE, these latter rates are related by detailed balance, like the direct and inverse electron collisional rates. The matrix T in Eq. (1) depends on the environment variables T_e, N_e, and I_ν.

In Eq. (1), we can separate the diagonal terms in the rate equation (1) by writing

$$\frac{dN_i}{dt} = \sum_{j \neq i} T_{ij} N_j + \left(-\sum_{j \neq i} T_{ji} \right) N_i. \qquad (2)$$

For the diagonal terms of the rate matrix T_{jk}, it is thus natural to consider

$$T_{jj} = -\sum_{j \neq k} T_{kj}. \qquad (3)$$

Generally, we have

$$T_{jk} \geq 0 \quad \forall \, k \neq j,$$

$$T_{jj} < 0 \quad \forall \, j. \qquad (4)$$

The matrix T_{jk} is real but not necessarily symmetric.

The rate equation defined by Eqs. (1), (3), and (4) has many interesting mathematical properties. The most important ones are simple consequences of its proper and very special structure [25]. Indeed, if we sum the whole elements of each column, the result is 0, from which we get

$$\sum_i \frac{dN_i}{dt} = 0. \qquad (5)$$

This is the condition of total number conservation,

$$\sum_i N_i = N_{at}, \qquad (6)$$

where N_{at} is a strictly positive constant. The matrix T_{jk} is singular, or equivalently, has one eigenvalue equal to zero. This is true for the time-dependent or time-independent matrix T_{jk}. Let us now suppose that the local environment is constant, i.e., the rate coefficients are constant in time, and that every state is connected to every other state, either directly or through intermediate states. Then the solution of equation

$$\sum_j T_{ij} N_j^0 = 0 \qquad (7)$$

is shown [25] to be positive and unique when one positive normalization condition such as Eq. (6) is provided. In other words, the zero eigenvalue is nondegenerate and has one and only one eigenvector N_i^0. Physically, this means that the rate equation has a unique steady-state N_i^{SS} with

$$N_i^{SS} = N_i^0 \geqslant 0 \qquad \forall\, i, \qquad (8)$$

with positive initial populations leading to positive steady-state populations [25].

The transfer equation for radiation reads [2]

$$\frac{1}{c}\frac{dI_\nu}{dt} = \frac{1}{c}\frac{\partial I_\nu}{\partial t} + \frac{\partial I_\nu}{\partial s} = \rho\kappa_\nu(S_\nu - I_\nu) + \rho_\nu(\bar{I}_\nu - I_\nu), \qquad (9)$$

where s is the coordinate along the direction of propagation, κ_ν is the spectral opacity corrected for stimulated emission, S_ν is the source function, ρ_ν is the coefficient of isotropic scattering, and $\bar{I}_\nu$ is the specific intensity averaged over the complete sphere. Denoting $\vec{\mu}$ and $d\omega$ the spatial direction and the infinitesimal solid angle element, respectively,

$$\bar{I}_\nu = \frac{1}{4\pi}\int d\omega I_\nu \qquad (10)$$

and

$$\frac{\partial I_\nu}{\partial s} = \vec{\mu}\cdot\vec{\nabla}I_\nu. \qquad (11)$$

The explicit expressions of the short-hand notation T_{jk} in Eq. (1) and of the term $\rho\kappa_\nu(S_\nu - I_\nu)$ in Eq. (9) are given in the Appendix.

B. Rate of entropy production

In practice, the NLTE situation is delicate because we do not know any *a priori* expression for the ion populations N_i. Even assuming a constant environment, one needs to consider, very often, a large rate matrix to obtain the steady-state ion populations [26].

In the NLTE steady-state situation, the determination of the N_i^{SS} is the key point of the whole problem. Once known, one can calculate average ionizations, emissivities, and opacities both for hydrosimulations and diagnostics. Any robust method to estimate accurately and quickly the steady-state ion populations is of great interest. This really makes

sense when the rate equations (1), (3), and (4) cannot be solved due to the huge number of atomic levels or atomic configurations to handle.

According to nonequilibrium thermodynamics, the steady state near LTE is constrained by rigourous general requirements of energy conservation, by the stability criterium, by Onsager relations, and by a variational principle, i.e., the Prigogine theorem of minimum entropy production [5,6]. This theorem says that the stationary states are also states of minimum entropy production compatible with the external constraints that prevent the system from reaching thermodynamic equilibrium [5,6]. In the present situation, the rate of entropy production σ of the system made of ions and radiation field in a constant environment represented by the free electron reservoir in thermodynamic equilibrium is minimum for the correct steady-state populations N_i^{SS} in the linear range near thermodynamic equilibrium [10,27,28]. The Prigogine theorem of minimum entropy production is the fundamental theorem of the thermodynamics of irreversible processes.

Let us give the explicit expression for the rate of entropy production of the system made of ions and radiation field in a constant environment represented by the free electron reservoir in thermodynamic equilibrium. The derivation is detailed in the Appendix. Using the Von Neuman definition of entropy [29], the rate and radiative transfer equations [2], and the notion of conjugate variables [11,30], the rate of entropy production σ can be written [27]

$$\begin{aligned}
\frac{\sigma}{k_B} = &\sum_{jk(\nu_0)} \frac{4\pi}{h}\int_0^\infty d\nu\, \frac{2h\nu^3}{c^2}\frac{\sigma_{jk}^\varepsilon(\nu)}{\nu}N_k[1 + f_\nu(\beta_r)]\mathcal{F}[X_k - X_j \\
&+ (\beta_e - \beta_r)h\nu - \beta_e(E_k - E_j) + \eta_e(Q_k - Q_j)] \\
&+ \sum_{jk(\nu_0)} C_{jk}N_k\mathcal{F}[X_k - X_j - \beta_e(E_k - E_j) + \eta_e(Q_k - Q_j)],
\end{aligned}$$
$$(12)$$

where h is the Planck constant, c is the speed of light, k_B is the Boltzmann constant, $\beta_r = 1/k_B T_r$ with T_r the radiation temperature, and $\eta_e = \mu_e/k_B T_e$. $X_i = -\ln(N_i/W_i) - 1$ is the conjugate variable of N_i with respect to the Von Neuman definition of entropy [11]. $\sigma_{jk}^\varepsilon(\nu)$ is the radiative emission cross section [31] related to the radiative absorption cross section $\sigma_{kj}^\kappa(\nu)$ by the microreversibility relation $\sigma_{jk}^\varepsilon(\nu) = \sigma_{kj}^\kappa(\nu) \times (W_j/W_k)e^{-\beta_e(h\nu - h\nu_0) + \eta_e(Q_j - Q_k)}$ [32]. C_{jk} is the total collisional rate between configurations k and j, i.e., collisional deexcitation for bound-bound transition and three-body recombination and autoionization for bound-free transition. $\Sigma_{jk(\nu_0)}$ means that we sum over a pair of configurations (j, k) with $E_k > E_j$ involving the frequency $\nu_0 = (E_k - E_j)/h$. $\mathcal{F}(x) = x(e^x - 1)$ and $f_\nu(x) = 1/(e^{xh\nu} - 1)$. The same function $\mathcal{F}(x)$ appears in the radiative and the collisional terms. $\mathcal{F}(x)$ is always positive and takes the zero value if and only if $x = 0$. In other words, $\sigma = 0$ if and only if free electrons, radiation field, and matter are in complete thermodynamic equilibrium between each other. In agreement with the second law of thermodynamics, the rate of entropy production is strictly

positive for irreversible processes and null for thermal equilibrium only.

We have established a very compact expression (12) for the rate of entropy production. After some algebra, it is also possible to rewrite Eq. (12) under a form that agrees more with the classical expression obtained in the framework of the thermodynamics of irreversible processes [5,6,27]. This equivalent and academic expression is a bilinear form, which consists of a sum of products of two factors. In each term, one of these factors is an energy flow, or flux. The other factor is a difference of "generalized thermodynamic" state variables: it plays the role of a generalized thermodynamic forces or affinities, for which a nonzero value causes a nonzero corresponding flux. These generalized thermodynamic state variables, which simply derive from the relevant conjugate variables, can be interpreted as "generalized" or "effective" temperatures. Each individual flux gives the net energy transfer per unit time between the two relevant systems at two different effective temperatures. The rate of entropy production is thus the resultant of all of these individual flux-times-affinity products. In the standard thermodynamics of irreversible processes, we need the postulate of the second law of thermodynamics to ensure that each individual flux-times-affinity product is positive, i.e., heat goes from hotter reservoir to colder reservoir at the microscopic scale. Here, we do not need the postulate of the second law of thermodynamics, because the positive sign of the rate of entropy production comes naturally from a combined and consistent use of microscopic theory and statiscal mechanics. In other words, the second law of thermodynamics appears to be a macroscopic effect of the law of quantum statistical mechanics [33]. Moreover, though we can express the rate of entropy production σ (12) in a strict and formal analogy with the classical formula for rate of entropy production obtained in the framework of the thermodynamics of irreversible processes, our work is not restricted to the neighborhood of thermodynamics equilibrium, i.e., to the domain of validity of the Gibbs' fundamental equation which is fundamental to establish the general rules of the thermodynamics of irreversible processes [5,6,27].

Once σ is known, we can consider first near-LTE conditions. Since the environment around the ion and radiation field subsystem is considered to be in LTE, the method consists in expanding the rate of entropy production σ, the rate equation, and the radiative transfer equation with respect to the deviations of the conjugate variables of interest from their LTE values. The Taylor expansion is performed at the lowest order, i.e., second order for the rate of entropy production and first order for the kinetic and radiative transfer equations. After some algebra, one can deduce from these Taylor expansions the Onsager relations [30,34], the Prigogine theorem of minimum entropy production and the Le Chatelier principle [5,6], or the response matrix properties [8,11]. Second, we can consider near-NLTE steady state conditions. This time, the environment around the ion subsystem is considered to be in NLTE steady state. This condition is obtained when the radiation field reservoir is perturbed from thermodynamic equilibrium by assuming some brigthness temperatures different from the electron thermal bath temperature. In this situation, the reference is not the LTE steady state but a NLTE steady state determined by the thermodynamic conditions of the free electron and radiation field reservoirs. The breakdown of LTE steady state leads for the ion subsystem to the violation of both the Onsager relations and invalidates the Prigogine theorem of minimum entropy production. However, the transition between near LTE conditions to far from LTE conditions is smooth and the steady state may differ only slightly from the state of minimum entropy production. Another way of expressing this point, though strictly valid near LTE, the Prigogine theorem of minimum entropy production may work indeed far from LTE [10,35].

C. Effective Boltzmann law

Near LTE, we know that the Boltzmann law is a good approximation for the electronic configuration populations. Following Fournier *et al.* [14] and Bauche *et al.* [15], Blancard *et al.* [16] have found that the configurations cluster in a limited number of groups by using CRE models between detailed configurations in NLTE conditions. All these works indicate that the atomic processes tend to establish an effective temperature law (or Boltzmann law), i.e., a decreasing-exponential law versus energy for the total atomic populations of the configurations.

We propose to use the Prigogigne theorem of minimum entropy production to derive the effective Boltzmann law near but also far from LTE. We make an ansatz for the conjugate variables in Eq. (12),

$$X_i^{eff} = [E_i - (\mu_e - \delta\mu_e)Q_i]/k_B T_{eff}. \tag{13}$$

These effective conjugate variables X_i^{eff} are written under a simple effective Boltzmann law. The particle density of configuration i can thus be written

$$N_i^{eff} = N_{at} \frac{W_i e^{X_i^{eff}}}{\sum_j W_j e^{X_j^{eff}}}. \tag{14}$$

T_{eff} is an effective temperature determined by minimizing the rate of entropy production (12) at constant T_e, N_e, and T_r. The corrective term $\delta\mu_e$ is introduced to ensure that

$$\sum_i Q_i N_i^{eff} = N_e \tag{15}$$

is satisfied. By construction, minimizing the rate of entropy production σ using Eqs. (13)–(15) should give a good estimate of the exact solution found solving the corresponding CRE model in the vicinity of thermodynamic equilibrium. The main issue concerns strong departure from LTE, i.e., when T_r is very different from T_e or when the radiation is far from being a Planckian or non-Planckian radiation field with many brightness temperatures $T_\nu \neq T_e$. In that case, the general expression (A40) for the rate of entropy production must be used instead of formula (12). In this document, we choose first one effective temperature T_{eff} to test our method. However, since this variational method is by construction flexible enough to deal with many effective temperatures for a given set of electronic configurations, we then consider one effective temperature per ionic stage.

III. NUMERICAL APPLICATIONS

In order to study the validity of combining the Prigogine theorem of minimum entropy production with the notion of effective Boltzmann law for electronic configuration, we consider the far from LTE photoionized iron plasma experiment of Foord *et al.* [36]. This experiment was performed at relatively low electronic density, i.e., $N_e = 2 \times 10^{19}$ cm^{-3}. The electron temperature T_e was estimated to be equal to 150 eV. The ambient radiation field was assumed to be a Planckian at a temperature $T_r = 165$ eV diluted by a geometrical factor that accounts for the fact that the plasma is only irradiated by the Planckian over a relatively small solid angle. The dilution factor is equal to 0.01. Using Eq. (A13) in the Appendix, this dilution factor is taken into account as a brightness temperature β_ν, i.e., $f_\nu(\beta_\nu) = 0.01 f_\nu(\beta_r)$. With the ansatz (13) for the electronic populations N_i^{eff} (14), the minimization of the rate of entropy production (A40) at fixed T_e, N_e, and radiation field is performed using a conjugate-gradient program [37]. In order to focus on the accuracy of the configuration populations N_i^{eff}, obtained by our variational method, compared to the configuration populations N_i, found by solving the CRE model, we compute the four first moments of the ionic and energy distributions, i.e.,

$$MQ_n = \frac{\sum_i (Q_i - \bar{Q})^n N_i}{\sum_i N_i}, \qquad (16)$$

and of the total energy distribution, i.e.,

$$ME_n = \frac{\sum_i (E_i - \bar{E})^n N_i}{\sum_i N_i}, \qquad (17)$$

where

$$\bar{Q} = \frac{\sum_i Q_i N_i}{\sum_i N_i} \qquad (18)$$

and

$$\bar{E} = \frac{\sum_i E_i N_i}{\sum_i N_i}. \qquad (19)$$

As usual, we consider rather the skewness $\lambda_Q = MQ_3/MQ_2^{3/2}$ ($\lambda_E = ME_3/ME_2^{3/2}$) and the kurtosis $\kappa_Q = MQ_4/MQ_2^2 - 3$ ($\kappa_E = ME_4/ME_2^2 - 3$) to check the deviation from a pure Gaussian distribution, for which the skewness and the kurtosis are zero [38].

In Fig. 1, we compare experimental data extracted from Ref. [36] to theoretical calculations. First, using the average-atom SCAALP model with ℓ-splitting and autoionization and dielectronic capture (AA) [39], we find an average charge state equal to 16.33 and a standard deviation equal to 0.52. The average charge state is close to the one predicted by the GALAXY code [31,36] and in good agreement with the experimental average charge state 16.1 ± 0.2. The charge state fraction of the dominant ion Fe^{16+} is underestimated compared to experimental results, whereas we overestimated the
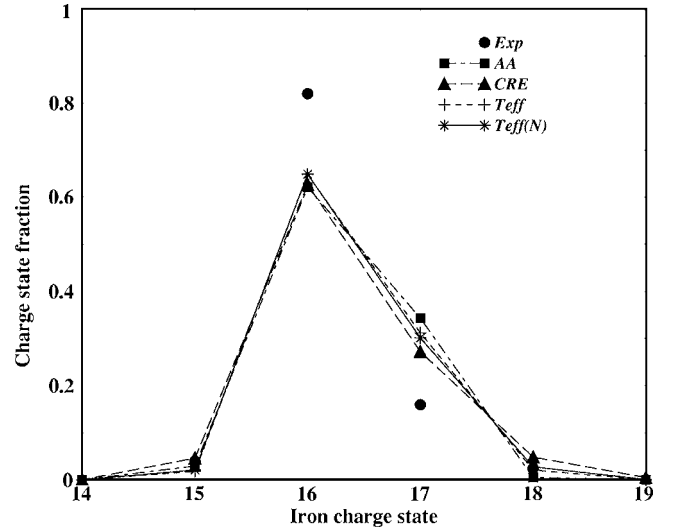

FIG. 1. Iron charge state distribution of a NLTE iron plasma at $T_e = 150$ eV, $N_e = 2 \times 10^{19}$ cm^{-3}, $T_r = 165$ eV, and a dilution factor equal to 0.01. We compare experimental results (Exp) [36] with theoretical calculations using an average-atom model (AA) [39], a CRE model [16], and combining the Prigogine theorem of minimum entropy production and the notion of effective Boltzmann law using one effective temperature (Teff) or one effective temperature per ionic charge-state [Teff(N)].

Fe^{17+} charge state fraction. Second, we perform CRE calculations based on the average subshell occupations and the electron covariance matrix elements given by the SCAALP model [16,39]. In this calculation, we consider ionic charge states between Fe^{14+} and Fe^{19+}. The following configurations have been retained: $1s^2[2s2p]^{q-n}[3\ell,4\ell',5\ell'']^{n+m}$, where $\ell = s,p,d$, $\ell' = s,p,d,f$, $\ell'' = s,p,d,f,g$. q (n) takes values between 5 and 8 (0 and 2). $m = 0$ except for Fe^{14+} and Fe^{19+}, in which $m = 1$ and $m = 2$, respectively. The chemical potential is optimized to have $N_e = 2 \times 10^{19}$ cm^{-3}. The CRE and SCAALP chemical potentials differ by less than 3%, indicating a pertinent selection of the set of electronic configurations. The CRE charge state distribution (CRE) is in better agreement with experimental data. In that case, the standard deviation is equal to 0.67. As for our approach of combining the Prigogine theorem of minimum entropy production with the notion of effective Boltzmann law for electronic configuration, the charge state distribution using one effective temperature (Teff) is intermediate between the AA and the CRE charge state distributions, whereas the charge state distribution using one effective temperature per ionic charge-state [Teff(N)] is in better agreement with experiment. The standard deviation of the Teff charge state distribution is equal to 0.552, i.e., close to the standard deviation of the AA charge state distribution. The standard deviation of the Teff(N) charge state distribution is equal to 0.571, i.e., closer to the standard deviation of the CRE charge state distribution than the Teff charge state distribution. We show in Table I the mean, standard deviation, skewness, and kurtosis of the ion distribution calculated from the CRE, Teff, and Teff(N) approaches, respectively. The ion distribution moments are dimensionless since ion populations are normalized to ion density N_a. In Fig. 1, the experimental charge state distribution

TABLE I. Moments of the ion distribution calculated by combining the Prigogine theorem of minimum entropy production and the notion of effective Boltzmann law using one effective temperature (Teff) or one effective temperature per ionic charge state [Teff(N)] and by solving the CRE model (CRE) for a NLTE iron plasma at T_e=150 eV, N_e=2×10^{19} cm^{-3}, T_r=165 eV, and a dilution factor equal to 0.01. The moments are dimensionless since ion populations are normalized to ion density N_a.

Moments	CRE	Teff	Teff(N)
Mean	9.66	9.66	9.66
Stand.dev.	0.668	0.552	0.571
Skewness	−0.866	−0.745	−0.807
Kurtosis	1.253	0.362	0.576

is clearly asymetric. Except AA calculation, which is restricted by the Gaussian hypothesis for the electronic correlation, other calculations predict also asymetric charge state distributions. It is well known that charge state distribution tends to be asymetric when the average number of bound electrons is in the vicinity of a shell closure. This behavior is related to the large change of ionization potential above and below the shell closure. In Table I, we can see that the Teff(N) values are closer to the CRE values than the Teff ones.

Another quantity of interest is the energy stored by electronic configurations. This internal energy is of prime interest for NLTE equation of state (EOS). Since our approach of combining the Prigogine theorem of minimum entropy production and the effective Boltzmann law is based on general principles of quantum statistical mechanics, our approach could be used to calculate NLTE EOS. In order to check this idea, we compare in Table II the mean, standard deviation, skewness, and kurtosis of the energy distribution calculated from the CRE, Teff, and Teff(N) approaches, respectively. Mean and standard deviation of the energy distribution are in Ry and skewness and kurtosis are dimensionless. The mean values predicted by all approaches are very close. The standard deviations and the skewness given by the CRE and Teff(N) are close too. The largest discrepancy concerns the kurtosis calculation. In this case far from LTE, using more

TABLE II. Moments of the energy distribution calculated by combining the Prigogine theorem of minimum entropy production and the notion of effective Boltzmann law using one effective temperature (Teff) or one effective temperature per ionic charge-state [Teff(N)] and by solving the CRE model (CRE) for a NLTE iron plasma at T_e=150 eV, N_e=2×10^{19} cm^{-3}, T_r=165 eV, and a dilution factor equal to 0.01. Mean and standard deviation are in Ry. Skewness and kurtosis are dimensionless.

Moments	CRE	Teff	Teff(N)
Mean	−2243.0	−2245.0	−2245.0
Stand.dev.	59.30	50.13	51.77
Skewness	1.477	1.076	1.172
Kurtosis	2.101	0.455	0.778

than one effective temperature leads to a sensitive improvement of the energy distribution description.

IV. CONCLUSION

We have applied the thermodynamics of irreversible processes to study interaction of matter and radiation field out of thermodynamic equilibrium. A compact and explicit expression for the rate of entropy production of matter and radiation field in a NLTE situation in contact with a free electron reservoir in LTE has been found using the conjugate variables of state variables. Assuming an effective Boltzmann law for electronic configurations, the corresponding effective temperature is determined using the Prigogine theorem of minimum entropy production. Comparisons between theoretical and experimental results for NLTE steady-state photoionized iron plasmas show that our approach, based on general principles of nonequilibrium thermodynamics, can be employed far from LTE. The effective temperature computation is fast and does not require any matrix manipulation. It could be implemented into atomic-physics packages based on average-atom models [39–43] for hydrocode simulations. The extension of our approach to superlevel [23] or STA [24] approaches, with or without the variational STA notion [44], is straigthforward. Indeed, it would be interesting to compare our method to the one proposed for computing superconfiguration temperatures [45,46] by calculating ionization balances and photoabsorption and photoemission spectra. Finally, we intend to improve the understanding of NLTE equation of states.

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APPENDIX: RATE OF ENTROPY PRODUCTION IN THE FRAMEWORK OF THE COLLISIONAL-RADIATIVE EQUILIBRIUM MODEL

In this Appendix, we derive the expression (12) of the rate of entropy production σ of the system made of ions and radiation field in a constant environment represented by the free electron reservoir in thermodynamic equilibrium.

This system is made of the following three subsystems: ions, radiation field, and free electrons. Since these subsystems interact weakly between each other, the total local entropy $\mathcal{S}$ can be obtained by adding the entropies of the three subsystems [47]. From statistical mechanics, we know that the entropy of a system of independent particles depends on the nature of the particles [29,48]. If they are discernable, they form a classical ideal gas and obey the Maxwell-Boltzmann statistics. If they are indiscernable, they form either a Fermi gas and obey the Fermi-Dirac statistics, or a Bose gas and obey the Bose-Einstein statistics. A concise expression for the relevant entropy S_ε is

$$S_\varepsilon = -k_B \sum_i \left[p_i \ln(p_i) - (p_i + \varepsilon g_i)\ln(g_i + \varepsilon p_i) + \varepsilon g_i \ln(g_i) \right],$$
(A1)

where p_i and g_i are the population and degeneracy of state i and k_B is the Boltzmann constant. $\varepsilon = 0, -1, +1$ for Maxwell-Boltzmann, Fermi-Dirac, and Bose-Einstein statistics, respectively. One can check that both S_{+1} and S_{-1} give S_0 in the classical limit $p_i/g_i \ll 1$.

The total local entropy $\mathcal{S}$ for radiation field [47,49–51] and atomic populations [29] in contact with the free electron reservoir in thermodynamic equilibrium can thus be written as

$$\mathcal{S} = -k_B \sum_i S_i - k_B \int d\omega d\nu s_\nu + S_e,$$
(A2)

where

$$S_i = N_i \ln\left(\frac{N_i}{W_i}\right),$$
(A3)

and

$$s_\nu = \frac{2\nu^2}{c^3}\left\{ \left[\frac{c^2 I_\nu}{2h\nu^3}\right] \ln\left[\frac{c^2 I_\nu}{2h\nu^3}\right] - \left[1 + \frac{c^2 I_\nu}{2h\nu^3}\right] \ln\left[1 + \frac{c^2 I_\nu}{2h\nu^3}\right] \right\}.$$
(A4)

In Eq. (A2), $-k_B \sum_i S_i$, $-k_B \int d\omega d\nu s_\nu$, and S_e are the entropies of the ion subsystem, the radiation field subsystem, and the electron heat bath subsystem, respectively. $\mathcal{S}$ is understood to be given by unit volume. We have used the correspondance between the specific intensity I_ν and the number of photons per mode n_ν,

$$I_\nu = \frac{2h\nu^3}{c^2} n_\nu.$$
(A5)

The integration measure $2d\omega d\nu \nu^2/c^3$ is obtained replacing the finite summation about individual photon quantum states by an integral and assuming a nonpolarized radiation traveling at light speed c inside the medium along the spatial direction $\vec{\mu}$. In Eq. (A2), the explicit expressions for the entropies of the ion and radiation field subsystem are essential because these two subsystems are supposed to be in NLTE. Indeed, we do not really need the explicit expression of S_e because the free electron subsystem is assumed to be in LTE. We just have to keep in mind that S_e is a function of the state variables of the free electron subsystem, i.e., the energy density E_e and electronic density N_e. The S_e expression can easily be obtained from standard textbooks [29,48]. Moreover, since the free electrons are assumed to be nonrelativistic, nongenerate, and described by a Maxwell-Boltmann distribution, the equation of state of the free electron subsystem is simply the ideal gas equation of state.

In order to derive the expression of the total rate of entropy production σ_{tot}, we differentiate Eqs. (A2)–(A4) partially with respect to time. From the chain rule we find

$$\frac{\partial \mathcal{S}}{\partial t} = \sum_i \frac{\partial \mathcal{S}}{\partial N_i}\frac{dN_i}{dt} + \int d\omega d\nu \frac{\delta \mathcal{S}}{\delta I_\nu}\frac{\partial I_\nu}{\partial t} + \frac{\partial \mathcal{S}}{\partial E_e}\frac{dE_e}{dt} + \frac{\partial \mathcal{S}}{\partial N_e}\frac{dN_e}{dt}.$$
(A6)

Now, we introduce the conjugate variables with respect to the state variables [11,30].

For the ion subsystem,

$$\frac{\partial \mathcal{S}}{\partial N_i} = k_B X_i,$$
(A7)

where

$$X_i = -\ln\left(\frac{N_i}{W_i}\right) - 1,$$
(A8)

from Eq. (A3).

For the radiation field,

$$\frac{\delta \mathcal{S}}{\delta I_\nu} = \frac{k_B \beta_\nu}{c},$$
(A9)

where

$$\beta_\nu = \frac{1}{h\nu}\ln\left(1 + \frac{2h\nu^3}{c^2 I_\nu}\right),$$
(A10)

from Eq. (A4). h is the Planck constant and $\beta_\nu = 1/k_B T_\nu$, where T_ν defines by

$$\frac{1}{T_\nu} = c\frac{\partial s_\nu}{\partial I_\nu}$$
(A11)

is the brightness temperature [47]. Equation (A10) can be inverted to obtain the specific intensity as a function of the brightness temperature

$$I_\nu = \frac{2h\nu^3}{c^2}\frac{1}{e^{\beta_\nu h\nu} - 1}.$$
(A12)

Comparing Eq. (A5) and Eq. (A12), $1/(e^{\beta_\nu h\nu} - 1)$ is nothing but the number of photons per mode n_ν. There is a one-to-one map between n_ν and the brightness temperature β_ν, i.e., $n_\nu = f_\nu(\beta_\nu)$, where

$$f_\nu(x) \equiv \frac{1}{e^{xh\nu} - 1}$$
(A13)

is the Bose-Einstein distribution function.

For the free electron subsystem, since this susbsystem is in LTE [29,33,48], the conjugate variables of E_e and N_e are given by

$$\frac{\partial \mathcal{S}}{\partial E_e} = \frac{\partial S_e}{\partial E_e} = \frac{1}{T_e}$$
(A14)

and

$$\frac{\partial \mathcal{S}}{\partial N_e} = \frac{\partial S_e}{\partial N_e} = -\frac{\mu_e}{T_e},$$
(A15)

respectively.

Combining Eq. (A6) with Eqs. (A7), (A9), (A14), and (A15), we obtain

$$\frac{\partial S}{\partial t} = \sum_i k_B X_i \frac{dN_i}{dt} + \int d\omega d\nu \frac{1}{T_\nu} \frac{1}{c} \frac{\partial I_\nu}{\partial t} + \frac{1}{T_e} \frac{dE_e}{dt} - \frac{\mu_e}{T_e} \frac{dN_e}{dt}.$$

$$(A16)$$

We now use the CRE rate equation (1),

$$\frac{dN_j}{dt} = \sum_k T_{jk} N_k, \qquad (A17)$$

and the equation of radiative transfer (9),

$$\frac{1}{c} \frac{dI_\nu}{dt} = \frac{1}{c} \frac{\partial I_\nu}{\partial t} + \frac{\partial I_\nu}{\partial s} = \rho \kappa_\nu (S_\nu - I_\nu) + \rho_\nu (\bar{I}_\nu - I_\nu). \quad (A18)$$

Inserting Eqs. (A17) and (9) inside Eq. (A16), we get

$$\frac{\partial S}{\partial t} = \sum_{ij} k_B X_i (T_{ij} N_j - T_{ji} N_i)$$

$$+ \int d\omega d\nu \frac{1}{T_\nu} \left[-\frac{\partial I_\nu}{\partial s} + \rho \kappa_\nu (S_\nu - I_\nu) + \rho_\nu (\bar{I}_\nu - I_\nu) \right]$$

$$+ \frac{1}{T_e} \frac{dE_e}{dt} - \frac{\mu_e}{T_e} \frac{dN_e}{dt}. \qquad (A19)$$

Using the chain rule (A11) between s_ν and I_ν, $\partial S/\partial t$ in Eq. (A19) is the sum of two terms. The first one, $-\int d\nu d\omega [\partial(c s_\nu)/\partial s]$, represents the transport of entropy by radiation field. The three-dimensional-space integration is classically converted into a surface integral and we obtain the flux of radiation entropy leaving the system through its surface. This term is related to boundary conditions. The second one is the rate of entropy change of the system due interaction between ions, radiation field, and free electron. This rate of entropy production σ_{tot} is defined as the time change of the entropy density due to collisions [27,28],

$$\sigma_{tot} = \sigma_{sr} + \sigma, \qquad (A20)$$

where

$$\sigma_{sr} = \int d\omega d\nu \frac{\rho_\nu}{T_\nu} (\bar{I}_\nu - I_\nu), \qquad (A21)$$

and

$$\sigma = \sum_{ij} k_B X_i (T_{ij} N_j - T_{ji} N_i) + \int d\omega d\nu \frac{1}{T_\nu} [\rho \kappa_\nu (S_\nu - I_\nu)]$$

$$+ \frac{1}{T_e} \frac{dE_e}{dt} - \frac{\mu_e}{T_e} \frac{dN_e}{dt}. \qquad (A22)$$

In Equation (A21), σ_{sr} is the rate of entropy production due to the scattering of radiation. It reads [27]

$$\sigma_{sr} = \int d\nu d\omega d\omega' \frac{\nu^2 \rho_\nu}{4\pi c^2} f_\nu [\beta_\nu(\omega')] \{ 1 + f_\nu [\beta_\nu(\omega)] \}$$

$$\times \mathcal{F}[\beta_\nu(\omega') h\nu - \beta_\nu(\omega) h\nu], \qquad (A23)$$

where $\beta_\nu(\omega) = 1/k_B T_\nu(\omega)$, $\beta_\nu(\omega') = 1/k_B T_\nu(\omega')$, and

$$\mathcal{F}(x) = x(e^x - 1). \qquad (A24)$$

By construction, σ_{sr} involves the radiation field only. In our case, this is rather the rate of entropy production σ in Eq. (A22) we are looking for, since it involves ions, radiation field, and free electron in a consistent way. Let us simplify σ in Eq. (A22). We can distinguish three contributions to σ. The first one, $\sum_{ij} k_B X_i (T_{ij} N_j - T_{ji} N_i)$, is the entropy produced inside the ion subsystem due to collisional and radiative transitions. The second one, $\int d\omega d\nu (1/T_\nu) [\rho \kappa_\nu (S_\nu - I_\nu)]$, is the entropy produced due to the interaction between the ion and radiation field subsystems. The last one, $(1/T_e)(dE_e/dt) - (\mu_e/T_e)(dN_e/dt)$, is the entropy produced due to the exchange of energy and electrons between the ion subsystem, the radiation field subsystem, and the electron heat bath. There is no entropy produced inside the radiation field subsystem because there is no photon-photon interaction at this energy scale. There is no entropy produced inside the electron heat bath because the free electron subsystem is in LTE. Clearly, the rates T_{jk} can be split between collisional rates C_{jk} and radiative rates R_{jk}, i.e., $T_{jk} = C_{jk} + R_{jk}$. The collisional rates obey the detailed balance principle

$$C_{jk} W_k e^{-\beta_e E_k + \eta_e Q_k} = C_{kj} W_j e^{-\beta_e E_j + \eta_e Q_j}, \qquad (A25)$$

where η_e is related to the chemical potential μ_e by $\eta_e = \mu_e/k_B T_e$. The radiative rate in absorption

$$R_{kj} = \frac{4\pi}{h} \int_0^\infty d\nu \frac{\sigma_{kj}^\kappa(\nu)}{\nu} \frac{2h\nu^3}{c^2} f_\nu(\beta_\nu) \qquad (A26)$$

and the one in emission

$$R_{jk} = \frac{4\pi}{h} \int_0^\infty d\nu \frac{\sigma_{kj}^\varepsilon(\nu)}{\nu} \frac{2h\nu^3}{c^2} [1 + f_\nu(\beta_\nu)], \qquad (A27)$$

where $\sigma_{kj}^\kappa(\nu)$ and $\sigma_{kj}^\varepsilon(\nu)$ are the absorption and emission cross sections [31], respectively. For the bound-bound transition,

$$\sigma_{kj}^\kappa(\nu) = \frac{\pi e^2}{mc} f_{kj} \Psi_{kj}^\kappa(\nu), \qquad (A28)$$

where e and m are the electron charge and the electron mass, respectively. f_{kj} is the absorption oscillator strength for the considered transition. f_{kj} is related to the corresponding emission oscillator strength by $f_{kj} W_j = f_{jk} W_k$. $\Psi_{kj}^\kappa(\nu)$ is the line profile in absorption for the considered transition. Since free electrons are assumed to be in local thermodynamic equilibrium at T_e, $\Psi_{kj}^\kappa(\nu)$ is related to the line profile in emission $\Psi_{jk}^\varepsilon(\nu)$ by

$$\Psi_{jk}^\varepsilon(\nu) = \Psi_{kj}^\kappa(\nu) e^{-\beta_e(h\nu - h\nu_0)}, \qquad (A29)$$

where

$$h\nu_0 = E_k - E_j. \qquad (A30)$$

The relation (A29) between line profiles in emission and absorption is essential for the source function to reduce to the Planck function over the entire line profile when radiation field and matter are in equilibrium with electron bath

[2,32]. $\sigma_{kj}^{\kappa}(\nu)$ and $\Psi_{kj}^{\kappa}(\nu)$ can also be used to define the Einstein coefficient A_{kj} through the relation [52]

$$A_{kj}\Psi_{kj}^{\kappa}(\nu) = 4\pi\frac{2\nu^2}{c^2}\sigma_{kj}^{\kappa}(\nu). \tag{A31}$$

For the bound-free transition, introducing the differential oscillator strength $df_{kj}/d\nu$ in absorption, the associated bound-free cross section is given by

$$\sigma_{kj}^{\kappa}(\nu) = \frac{\pi e^2}{mc}\frac{df_{kj}}{d\nu} \tag{A32}$$

and the corresponding emission cross section reads

$$\sigma_{jk}^{\varepsilon}(\nu) = \sigma_{kj}^{\kappa}(\nu)\frac{W_j}{W_k}e^{-\beta_e(h\nu - h\nu_0) + \eta_e(Q_j - Q_k)}. \tag{A33}$$

Once the absorption cross section is known for either bound-bound or bound-free transitions, the term $\rho\kappa_\nu(S_\nu - I_\nu)$ in Eq. (A22) originating from the radiative transfer equation (9) reads

$$\rho\kappa_\nu(S_\nu - I_\nu) = \sum_{jk(\nu_0)}\left(\frac{2h\nu^3}{c^2}\sigma_{jk}^{\varepsilon}(\nu)N_k[1 + f_\nu(\beta_\nu)]\right.$$
$$\left. - \frac{2h\nu^3}{c^2}\sigma_{kj}^{\kappa}(\nu)N_j f_\nu(\beta_\nu)\right). \tag{A34}$$

The notation $jk(\nu_0)$ means that we sum over pairs of levels jk with $E_k > E_j$ and we use Eq. (A30).

On the one hand, the contribution dE_e/dt in Eq. (A22) reads

$$-\frac{dE_e}{dt} = \sum_{ij}E_i(C_{ij}N_j - C_{ji}N_i) + \sum_{jk(\nu_0)}\frac{4\pi}{h}\int_0^\infty d\nu(h\nu - h\nu_0)$$
$$\times\frac{2h\nu^3}{c^2}\left(\frac{\sigma_{jk}^{\varepsilon}(\nu)}{\nu}N_k[1 + f_\nu(\beta_\nu)] - \frac{\sigma_{kj}^{\kappa}(\nu)}{\nu}N_j f_\nu(\beta_\nu)\right) \tag{A35}$$

due to energy conservation. On the other hand, the contribution dN_e/dt in Eq. (A22) is given by

$$-\frac{dN_e}{dt} = \sum_{ij}Q_i(C_{ij}N_j - C_{ji}N_i) + \sum_{jk(\nu_0)}\frac{4\pi}{h}\int_0^\infty d\nu(Q_j - Q_k)$$
$$\times\frac{2h\nu^3}{c^2}\left(\frac{\sigma_{jk}^{\varepsilon}(\nu)}{\nu}N_k[1 + f_\nu(\beta_\nu)] - \frac{\sigma_{kj}^{\kappa}(\nu)}{\nu}N_j f_\nu(\beta_\nu)\right) \tag{A36}$$

due to particle number conservation. Let us reorganize the summation terms in Eqs. (A22), (A35), and (A36) under a form similar to what is encountered in Eq. (A34). In the former equations, the summation over the whole combination of indices ij can be recast under a summation over pairs of indices $jk(\nu_0)$, where the index k is the upper level and index j is the lower level $(E_k > E_j)$, and ν_0 is given by Eq. (A30). Thus we obtain obtain

$$\sum_{ij}\{\cdots\}_i(R_{ij}N_j - R_{ji}N_i) = \sum_{jk(\nu_0)}(\{\cdots\}_k - \{\cdots\}_j)(R_{kj}N_j - R_{jk}N_k) \tag{A37}$$

for the radiative rates, and

$$\sum_{ij}\{\cdots\}_i(C_{ij}N_j - R_{ji}N_i) = \sum_{jk(\nu_0)}(\{\cdots\}_k - \{\cdots\}_j)(C_{kj}N_j - C_{jk}N_k) \tag{A38}$$

for the collisional rates. In these expressions, $\{\cdots\}_i$ may be X_i, E_i, or Q_i. Combining Eqs. (A37), (A38), (A35), (A36), (A34), and (A22), we find that σ can be expressed as follows:

$$\frac{\sigma}{k_B} = \sum_{jk(\nu_0)}(C_{kj}N_j - C_{jk}N_k)[X_k - X_j - \beta_e(E_k - E_j)$$
$$+ \eta_e(Q_k - Q_j)] + \sum_{jk(\nu_0)}\frac{4\pi}{h}\int d\nu\left(\frac{2h\nu^3}{c^2}\sigma_{kj}^{\kappa}(\nu)N_j f_\nu(\beta_\nu)\right.$$
$$\left. - \frac{2h\nu^3}{c^2}\sigma_{jk}^{\varepsilon}(\nu)N_k[1 + f_\nu(\beta_\nu)]\right)[X_k - X_j + (\beta_e - \beta_\nu)h\nu$$
$$- \beta_e(E_k - E_j) + \eta_e(Q_k - Q_j)]. \tag{A39}$$

Finally, we factorize by $C_{jk}N_k$ and by $(2h\nu^3/c^2)\sigma_{jk}^{\varepsilon}(\nu)N_k[1 + f_\nu(\beta_\nu)]$ in the first and second terms of the sum in Eq. (A39), respectively. We then use Eqs. (A8), (A13), (A24), (A25), and (A28) to find a compact expression for σ,

$$\frac{\sigma}{k_B} = \sum_{jk(\nu_0)}\frac{4\pi}{h}\int_0^\infty d\nu\frac{2h\nu^3}{c^2}\frac{\sigma_{jk}^{\varepsilon}(\nu)}{\nu}N_k[1 + f_\nu(\beta_\nu)]\mathcal{F}[X_k - X_j$$
$$+ (\beta_e - \beta_\nu)h\nu - \beta_e(E_k - E_j) + \eta_e(Q_k - Q_j)]$$
$$+ \sum_{jk(\nu_0)}C_{jk}N_k\mathcal{F}[X_k - X_j - \beta_e(E_k - E_j) + \eta_e(Q_k - Q_j)], \tag{A40}$$

which is simply Eq. (12) when $\beta_\nu = \beta_r$.

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