PHYSICAL REVIEW E VOLUME 50, NUMBER 5 NOVEMBER 1994

Saha equation for two-temperature plasmas: Theories, experimental evidence, and interpretation

J. A. M. van der Mullen, D. A. Benoy, F. H. A. G. Fey, and B. van der Sijde
Department of Physics, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

J. Vlček
Department of Physics, Institute of Mechanical and Electrical Engineering, 306, 14 Plzeň, Nejedleho Sady 14, Plzeň, Czech Republic

(Received 8 April 1994)

The following statement is investigated: *if electrons realize an equilibrium between ionization and recombination in a two-temperature radiationless plasma, then the Saha equation can be obtained by replacing the thermodynamic temperature by the electron temperature.* It is found that the statement is in general rather academic, but becomes realistic if it is confined to the higher excited states. These states are in so-called partial local Saha equilibrium (pLSE). The elementary mass action law (EMAL) is used to derive the Saha equation for pLSE conditions and the method is compared to a derivation based on the maximum entropy principle (MEP). This comparison reveals why the complicated two-temperature Saha variants as found in literature are incorrect and why the EMAL is much more suitable than the MEP to treat partial equilibria. Experimental evidence proves once more that the complicated two-temperature Saha equations are incorrect and that the statement is justified as long as we confine ourselves to the pLSE part of the system.

PACS number(s): 52.25.−b

I. INTRODUCTION

There is much confusion in literature on the Saha equation for two-temperature (2T) plasmas, i.e., plasmas for which electrons and heavy particles differ in temperature. This confusion originates from the fact that (modified) functions from equilibrium thermodynamics are used to describe this treacherous case of partial equilibrium; i.e., a situation with equilibrium and nonequilibrium aspects. The nonequilibrium aspect is the difference between the temperatures of electrons (T_e) and heavy particles (T_h) whereas equilibrium is present (1) in the Maxwellization between particles of equal mass and (2) in the electron-induced balance of ionization and three-particle recombination

$$e + A \leftrightarrow e + A^+ + e \ , \tag{1}$$

the so-called electron-induced (*e*-induced) Saha balance [1]. The class of plasmas of interest can be specified as follows: (1) it is a subclass of the electron excitation kinetics (EEK) plasmas for which *h*-induced excitation kinetics (charge and/or excitation transfer, molecular processes) are unimportant; (2) atomic (ionic) transitions are induced by free electron collisions solely, i.e., the influence of bound electron transitions (radiative decay) can be neglected; and (3) the plasma is composed of electrons $\{e\}$ and heavy particles $\{h\}$; the latter consists of atoms $\{a\}$ and singly charged ions $\{i\}$ of the same element. The excitation dominance of electrons $\{e\}$ over heavy particles $\{h\}$ (i.e., the first condition) puts a lower limit on the ionization degree. The second condition (the leak of radiation can be neglected: the plasma is radiationless) requires a large electron density n_e and/or a large opacity. We will not discuss the boundary criteria for this class of plasmas but investigate the Saha equation under the assumption that the relevant criteria are fulfilled.

Due to the dominance of the electron-induced transitions it is plausible that the number density $\eta_x(p)$ of a state p of a system x can be found by using the Boltzmann law in which the thermodynamic temperature is replaced by the translational electron temperature T_e, giving

$$\eta_x(p) = \frac{n_x(p)}{g_x(p)} = \frac{n_x}{G_x}\exp(-E^x_{1p}/kT_e) \ . \tag{2}$$

Here n_x is the density of atoms ($x=a$) or ions ($x=i$) and E^x_{1p} the excitation energy of the state p with respect to the ground state of the atomic or ionic system. In fact we might also take $x=e$, i.e., treat the free electron with its two spin states as a system. The sum of states of the system in question, given by

$$G_x = \sum_p g_x(p)\exp(-E^x_{1p}/kT_e) \ , \tag{3}$$

is related to the one-particle internal partition function by

$$\begin{aligned} Z_e^{\text{in}} &= G_e = g_e = 2 \ , \\ Z_a^{\text{in}} &= G_a \ , \\ Z_i^{\text{in}} &= G_i \exp(-I_1/kT_e) \end{aligned} \tag{4}$$

for the systems $\{e\}$, $\{a\}$, and $\{i\}$, respectively. In the last expression I_1 represents the ionization potential of the element in question. Equation (2) also expresses that the number density η of the state and the corresponding level n are interrelated by $\eta = n/g$ where g is the statistical weight of the level.

So far we dealt with densities on three scales, namely, systems, levels, and states. Section II will continue this series using for the microscopic scale the elementary occupation $\hat{\eta}_x(\alpha)$, the number of particles per state α of species x, a dimensionless quantity.

Following the same reasoning that leads to the Boltzmann equation we can get the Saha equation for a 2T EEK plasma by replacing the thermodynamic temperature by the electron temperature. This gives

$$\frac{n_a}{G_a} = \frac{n_e}{2}\frac{n_i}{G_i}\left[\frac{h^2}{2\pi m_e k T_e}\right]^{3/2} \exp(I_1/kT_e) \ . \qquad (5)$$

It is the aim of this article to find support for the simple reasoning given above which may be formulated as the following statement: if electrons realize an equilibrium between ionization and recombination in a 2T radiationless plasma then only the electron temperature will be important in the description of the atomic state distribution function (ASDF); the Saha and Boltzmann equations in a 2T plasma are obtained by replacing "the" temperature by the electron temperature. Support for this statement will be given by theoretical and experimental evidence.

Despite the reasonable degree of consensus on the Boltzmann equation [cf. Eq. (2)] different formulas can be found for the Saha equation in collisional-dominated 2T EEK plasmas. The discussion of the differences will be guided by writing the 2T Saha formula as

$$\frac{n_a}{G_a} = F(\gamma)\frac{n_e}{2}\frac{n_i}{G_i}\left[\frac{h^2}{2\pi m_e k T_e}\right]^{3/2} \exp(I_p/kT_e) \qquad (6)$$

so that the differences can be brought back to the factor $F(\gamma)$ which depends on the temperature ratio $\gamma = T_e/T_h$. It is the aim of this article to prove that for 2T radiationless plasmas $F(\gamma)=1$, that is, independent of the value of γ. By discussing the theoretical and experimental background of the various $F(\gamma)$ functions we automatically make a selection of the different Saha variants existing in literature. We will, e.g., exclude the work of Refs. [2,3] in which the presence of 2T plasmas in inductively coupled plasmas (ICP) is denied and the whole plasma (including the ASDF) is described by only one "thermodynamic temperature" of which the value as proposed for the ICP (2000 K) is much too low. On the other hand, there is the "generalized multithermal equilibrium (GMTE) model" [4] which claims that (under some conditions) even more than two temperatures are needed to describe the Saha equation. This multitemperature Saha variant also being excluded from discussion is obviously ruled out as well once the above statement is proved.

The background of the models considered in this study leads to the following classification.

(1) The thermodynamic derivations. (a) The work of Ref. [5] is based on the criterion that the affinity (a derivative of the free energy) should be zero. This leads to a result which can be expressed as

$$F_{\text{pri}}(\gamma) = \left[\frac{n_a G_i}{n_i G_a}\right]^{1-1/\gamma} \ . \qquad (7)$$

According to this Saha variant, T_a plays an important role in the ASDF of plasmas with relatively low (or high) degrees of ionization.

(b) Using the minimum-of-free-energy principle a Saha equation was found by Refs. [6,7] which can be characterized by

$$F_{\text{pot}}(\gamma) = \left[\frac{n_a}{n_i}\right]^{1-1/\gamma} \ . \qquad (8)$$

Again the T_a is found to be important.

(c) Taking a "generalized" form of the free energy (a quantity with the dimension of entropy) it is found in Ref. [8] that T_h has no influence, i.e.,

$$F_1 = 1 \ . \qquad (9)$$

(2) Linear nonequilibrium thermodynamics. In Ref. [9] the working hypothesis is used that the entropy production should be minimal with the result that the influence of T_h is limited. Expressed as

$$F_{m/M}(\gamma) = 1 + O((\gamma-1)m_e/M) \qquad (10)$$

it states that the temperature ratio γ comes in via a term of order m_e/M. Consequently F differs only very slightly from unity.

(3) Nonlinear nonequilibrium thermodynamics based on the Zubarev formalism [10] by which again a limited role of T_h is found [cf. Eq. (10)].

(4) A kinetic derivation [1] based on the elementary mass action law (EMAL) derived from the principle of microscopic reversibility. This results in an ASDF which depends on T_e solely [cf. Eq. (9)].

Before discussing the various models in relation to the fundamental background (Sec. II) and the experimental evidence (Sec. III) some general statements should be made on the problem as such and the model classification as given above.

The ordering given, from equilibrium thermodynamics (1) to kinetic theory (4), is parallel to the route from a macroscopic (global) towards a microscopic (detailed) description. In spite of the differences they all have in common to deal with an academic (or idealized) situation in which a nonequilibrium aspect $T_e \neq T_h$ exists under the presence of full equilibrium on the level of Maxwellization and ionization recombination. However, to maintain the temperature difference, the electron gas $\{e\}$ must be matched between a relatively strong accelerating electric field and an effectively cooling heavy particle gas $\{h\}$. This needs a large value of the electric field strength E and a small degree of ionization α which drives $\{e\}$ towards a Druyvensteyn distribution and distorts the balances between inelastic (excitation and ionization) and superelastic (deexcitation, recombination) processes. The consequence is that full Maxwell and Saha equilibrium cannot exist. The question is how strong the impact of E and α on the ASDF is and if there are conditions under which the academic problem posed in this paper is realistic. To get an answer we should explore the kinetics more precisely, i.e., extrapolate the route (1)–(4) as given above in the direction of more microscopic details. This leads to a fifth category.

(5) The collisional radiative (CR) models. From the many studies in the framework of CR models we refer to the classification studies of Refs. [1,11,12] which in most cases are dedicated to the ASDF of EEK plasmas. Special attention deserves the extensive model of Ref. [13] which apart from the *e*-induced also contains the *h*-induced processes and the calculation of the electron energy distribution function (EEDF). Such an extensive model is ideal to demarcate the validity regime of our academic problem, provided all rate coefficients are known.

We are not going to discuss the CR models but will use their results as a guideline in the search for a realistic application for our academic problem.

From the CR studies it can be deduced that (1) for a vast range of E and α values only the tail (electron energy larger than the first excitation threshold E_{12}) of the EEDF and the transitions from the ground state to the first excited state or the ionization from the ground state are affected; (2) the bulk of the EEDF is Maxwellian so that excitation and ionization of highly excited states are not affected by the EEDF-tail distortion; and that (3) since the ionization cross section roughly scales with the square of the principal quantum number p, ionization from and recombination to an excited state occur more frequently for higher p values. This implies that the top of the system is less sensitive to equilibrium disturbing processes and that it is more realistic to use the Saha equation as a predictor for the relation between the density of highly excited atomic states and the ion ground state [i.e., $\eta(p)/\eta_+(1)$] rather than for the relation [cf. Eq. (6)] between the atomic and ionic (i.e., system) densities (i.e., n_a/n_i). This relation between state densities can be obtained using the Boltzmann equation, Eq. (2), $\eta(p)=(n_a/G_a)\exp(-E_{1p}/kT_e)$ for the atomic states, $\eta_+(1)=n_+/G_+$ for the ion ground state, and $\eta_e=n_e/2$ for the electrons. After substitution in Eq. (6) we get

$$\eta(p)=F(\gamma)\eta_e\eta_+(1)\left[\frac{h^2}{2\pi m_e kT_e}\right]^{1/2}\exp(I_p/kT_e)\ . \tag{11}$$

We will see that the models classified as the most macroscopic (i.e., under 1 and 2), deal with the determination of the ratio of the total atom (n_a) and total ion densities (n_i) as if the balance in Eq. (1) constantly transforms all the atoms irrespective of their excited state into the agglomerate of ions and vice versa. Obviously this is not a realistic picture of the actual ionization-recombination kinetics. It is better to use a theory which makes it possible to confine the Saha balance to the atomic top. The next section gives a theoretical treatment (classified under 4) which makes it easy to "isolate" the atomic top levels. The result is that our simple kinetic statement, i.e., that $F=1$, is justified. This type of partial equilibrium will be denoted (cf. [1]) by partial local Saha equilibrium (pLSE). Section III describes experimental techniques applied to inductively coupled plasmas in argon for which it will be proved that most of the atomic states are in pLSE while there is a significant difference between T_h and T_e. The experimental results also show that $F=1$ is justified while Eqs. (7) and (8) are wrong.

II. THEORY

A. The elementary mass action law

As stated in the Introduction, it is merely academic to describe the ionization and recombination balance as a reaction between the atomic and ionic systems since it does not give a realistic description of the reaction kinetics. It is more appropriate to study the ionization and recombination balance from the atoms in level p to the ions in ground state 1 and vice versa. This is given by the reaction equation

$$e+A_p\leftrightarrow e+A^+(1)+e\ . \tag{12}$$

According to the mass action law the equilibrium state of the balance in Eq. (12) implies the following relation between the concentrations:

$$n_e n(p)K_{\rightarrow}=n_e^2 n_+(1)K_{\leftarrow}\ , \tag{13}$$

in which $K_{\rightarrow}$ and $K_{\leftarrow}$ are the reaction rate coefficients of the forward and backward processes. To extrapolate this route from systems to levels, i.e., from the macroscopic to the microscopic scale, we consider the equilibrium state of the Saha balance on the most elementary level where it describes how each particle changes from one particular initial to one particular final quantum state and vice versa. The elementary counterpart of Eq. (12) will then be given by

$$e_i(\epsilon_1)+A_p(\epsilon_2)\leftrightarrow e_i(\epsilon_3)+A_1^+(\epsilon_4)+e_j(\epsilon_5)\ , \tag{14}$$

while Eq. (13) transforms into (cf. [1])

$$\hat{\eta}_e(i,\epsilon_1)\hat{\eta}_A(p,\epsilon_2)=\hat{\eta}_e(i,\epsilon_3)\hat{\eta}_{A^+}(1,\epsilon_4)\hat{\eta}_e(j,\epsilon_5)\ . \tag{15}$$

Since the quantum state has a translational and an internal aspect we label the particles in Eqs. (14) and (15) with the translational energy ϵ and the internal state index i. On the elementary level the role of the densities is played by the elementary occupation $\hat{\eta}_x(i,\epsilon)$ which is defined as the number of particles x per state with internal index i and translation energy ϵ. Note that Eq. (15), the elementary mass action law applied to the Saha balance, does not contain rate coefficients. This is due to the principle of microscopic reversibility stating that the probability that a particle leaves a quantum state via a certain route equals that of the process in which the particle arrives at that quantum state via the reverse route. As a consequence the elementary counterpart of $K_{\rightarrow}$ can be eliminated against that of $K_{\leftarrow}$ which gives Eq. (15). More generally the EMAL is applicable to various types of reaction mechanisms and the classical variant can be formulated as follows: If an elementary balance equilibrates then the product of elementary occupations of the reactant equals that of the resultants. Note the conditional "if. . .then. . ." construction of this statement. It makes it possible to "isolate" the equilibrium part. In this particular situation it can be used to isolate the upper levels in pLSE, for which equilibrium disturbing processes (transport of particles and/or radiation) are relatively unimportant, from the lower lying levels which might be out of Saha equilibrium.

So far we only considered the Saha aspect of the partial equilibrium which via Eq. (15) interrelates elementary occupations of atoms, ions, and electrons. Another equilibrium property of the situation under study is that of the Maxwellization in $\{e\}$ and in $\{h\}$. This determines the $\hat{\eta}_x(i,\epsilon)$ in Eq. (15) which can be derived using the EMAL (cf. [1,14]) or can be obtained by dividing the number of particles per energy range by that of the translational states per energy range. The first quantity is given by the well-known Maxwell energy distribution function and the other one follows from elementary statistical mechanics. For particle x in internal state p we obtain

$$\hat{\eta}_x(p,\epsilon)=\eta_x(p)\mathcal{V}_{\mathrm{tr}}(m_x,T_x)\exp(-\epsilon/kT_x)\ , \tag{16}$$

where the elementary thermal de Broglie volume of the particle x,

$$\mathcal{V}_{\mathrm{tr}}(m_x,T_x)=\left[\frac{h^2}{2\pi m_x kT_x}\right]^{3/2}=\frac{V}{Z_x^{\mathrm{tr}}}\ , \tag{17}$$

an important character of the thermal translational distribution, is related to the translational partition function Z_x^{tr}. Another equilibrium aspect is that ions and atoms due to their equal mass have the same temperature and $\mathcal{V}_{\mathrm{tr}}$ value. (The small mass difference $m_a-m_i=m_e$ will generate an error in Saha's equation of order m_e/M. In a correct treatment we should use the reduced mass of the electron-ion system.) The nonequilibrium aspect comes in by the fact that $\{e\}$ and $\{h\}$ differ in temperature, i.e., $T_e\neq T_h$. The reason for this is that, due to the small mass ratio $m_e/M_h \ll 1$, the transfer of translational energy from $\{e\}$ to $\{h\}$ is not effective at all. However, the very same reason is responsible for the fact that the ionization energy of the atom (I_p) is supplied from the electron translational energy so that the following energy balances hold:

$$\begin{aligned}&I_p=\epsilon_1-\epsilon_3-\epsilon_5\ ,\\&\epsilon_2=\epsilon_4\ .\end{aligned} \tag{18}$$

[The equations (18) are only true within (a very good) approximation. The difference between $\Delta\epsilon=\epsilon_4-\epsilon_2$ is on the average on the order of $T_e(1-\gamma)m_e/M$. Taking this into account Eq. (9) will change into Eq. (10).] Substituting the expression Eq. (16) for each particle into Eq. (15) and using Eq. (18) we find

$$\eta(p)=\eta_e\eta_+(1)\left[\left[\frac{h^2}{2\pi m_e kT_e}\right]^{3/2}\right]\exp(I_p/kT_e)\ , \tag{19}$$

which is equivalent to Eq. (11) with $F=1$. Note that [under the assumption of Eq. (18)] (1) this method makes clear how the kinetics of $\{e\}$ is imposed on the ASDF of the atoms and ions, (2) the factor $\mathcal{V}_{\mathrm{tr}}$ between square brackets representing the elementary thermal de Broglie volume of the particle created in the ionization process (namely, the electron) depends on T_e solely, and that (3) each set of $\{\epsilon_i\}$ gives the same relation between the state density in the atomic top and the ion ground level [i.e., the same $\eta(p)/\eta_+(1)$ value].

B. Comments on the thermodynamic derivations

The theoretical proof that $F_1=1$ is (in good approximation) correct whereas F_{pri} and F_{pot} are wrong is twofold. First one should give a correct derivation of the Saha equation in a 2T plasma; second it must be demonstrated why the thermodynamic derivations leading to F_{pri} and F_{pot} are wrong. The first was done in the preceding subsection using the EMAL; the second will be done in this subsection.

Although the different works in the thermodynamic category (1) use different principles or thermodynamic functions to derive the Saha equation, all of these should be based on the second law, which states that the combination of a system with its surroundings strives to a maximum of entropy. Therefore we focus on the change in entropy due to the establishment of the Saha balance in a plasma which satisfies the conditions that (c1) both $\{e\}$ and $\{h\}$ are ideal Maxwellian gases each with their with their own constant temperature, (c2) the internal energy distribution of atoms and ions is prescribed by Eqs. (2) and (4), and (c3) the volume V of the plasma is constant; the only exchange of energy with the surroundings is that of heat exchange.

We first consider the entropy of the atoms $\{a\}$ which equals

$$S=k\ln P=-k\sum_{\alpha}N_\alpha\ln\hat{\eta}_a(\alpha)+kN\ , \tag{20}$$

where $N_\alpha=n_\alpha V$ is the number of particles in the discrete energy level E_α whereas $\hat{\eta}_a(\alpha)$ is the number of particles per state with energy E_α. Note that $E_\alpha=E_\alpha^{\mathrm{in}}+\epsilon_\alpha$ is an addition of the internal and translational energy. For atoms $E_\alpha^{\mathrm{in}}=E_{1p}$ (for the ions $E_\alpha^{\mathrm{in}}=E_{1p}+I_1$, i.e., the energy distance in the ion plus the ionization energy of the atom). The conditions (c1) and (c2) determine the value of the elementary occupation $\hat{\eta}_a(\alpha)$ which using Eqs. (2) and (16) inserted in Eq. (20) lead to

$$S_a(T_h,T_e)=\frac{U_a^{\mathrm{tr}}}{T_h}+\frac{U_a^{\mathrm{in}}}{T_e}+k\ln\frac{[Z_a^{\mathrm{in}}Z_a^{\mathrm{tr}}]^{N_a}}{N_a!}\ , \tag{21}$$

whereas $U_a^{\mathrm{in}}=\sum_\alpha N_\alpha E_\alpha^{\mathrm{in}}$ and $U_a^{\mathrm{tr}}=\sum_\alpha N_\alpha\epsilon_\alpha$. The same procedure can be applied to the gases $\{i\}$ and $\{e\}$. For $\{i\}$ this gives an expression $S_i(T_h,T_e)$ which is Eq. (21) in which all lower indices a are changed into i. The expression for the electron entropy $S_e(T_e)$ is Eq. (21) in which a is replaced by e, T_h by T_e, whereas the internal energy U_e^{in} is set to zero. This latter, being related to the equality $Z_e^{\mathrm{in}}=g_e=2$ [cf. Eq. (4)], is justified as long as the magnetic field strength is not too high. Since the entropy is an additive function we can write for the total entropy of the surroundings plus plasma

$$S_t = S_{\text{sur}} + S_a + S_i + S_e$$
$$= S_{\text{sur}} + \frac{U_a^{\text{tr}} + U_i^{\text{tr}}}{T_h} + \frac{U_e^{\text{tr}} + U_a^{\text{in}} + U_i^{\text{in}}}{T_e}$$
$$+ k \ln \left[\frac{[Z_a^{\text{in}} Z_a^{\text{tr}}]^{N_a} [Z_i^{\text{in}} Z_i^{\text{tr}}]^{N_i}]Z_e^{\text{in}} Z_e^{\text{tr}}]^{N_e}}{N_a! N_i! N_e!} \right] . \tag{22}$$

In the following we will prove that the change in the entropy ΔS_t as caused by ionization or recombination (i.e., Saha) processes is limited to a change in the last term, i.e.,

$$\Delta S_t = \Delta S_{\text{Saha}}$$
$$= k \Delta \ln \left[\frac{[Z_a^{\text{in}} Z_a^{\text{tr}}]^{N_a} [Z_i^{\text{in}} Z_i^{\text{tr}}]^{N_i} [Z_e^{\text{in}} Z_e^{\text{tr}}]^{N_e}}{N_a! N_i! N_e!} \right] , \tag{23}$$

provided (c1)–(c3) are fulfilled. The entropy, and thus its maximum value, associated with the Saha balance is determined by the particle distribution over the states a and i and not by the energy. To prove this we consider one particular recombination process in a plasma fulfilling conditions (c1)–(c3) but out of Saha equilibrium. More specifically we study the process in Eq. (14) towards the left. This process will not change the second term on the right-hand side of Eq. (22) since the sum of the translational energy of the heavy particles $U_a^{\text{tr}} + U_i^{\text{tr}}$ is not changed ($\epsilon_2 = \epsilon_4$). {The fact that this is an approximation [cf. Eq. (18)] implies that a certain (small) amount of energy (heat) is transferred from $\{e\}$ to $\{h\}$ during ionization. It is shown in [9] that this generates a deviation in the result in the order of $F_{m/M}$ [cf. Eq. (10)].} The recombination will also not change $U_e^{\text{tr}} + U_a^{\text{in}} + U_i^{\text{in}}$ due to the relation Eq. (18a). However, here we must be careful; the recombination process tends to increase the translational energy of the electron and thus T_e so that in order to fulfill conditions (c1) and (c2) the process must be accompanied by a process of heat exchange of the electron gas toward a "surrounding" thermodynamic bath of T_e. Therefore the first term will increase with the same amount as the decrease of the third term. Resumming, we may state that during recombination (or ionization) the second term on the right-hand side remains unaltered while changes in the first and third terms will compensate each other. This indeed implies that Saha processes will only affect the last term on the right-hand side of Eq. (22), i.e., justifying Eq. (23).

Now that we know that the maximum of entropy associated with the position of the Saha balance under the conditions (c1)–(c3) is determined by the maximum in S_{Saha} we have to search for that N_e, N_+, and N_a composition for which the small change $\Delta N_e = \Delta N_i = -\Delta N_a$ results in $\Delta S_{\text{Saha}} = 0$. This leads to the condition

$$\Delta S_{\text{Saha}} = \Delta N_e \left[\ln \frac{Z_e^{\text{in}} Z_e^{\text{tr}}}{N_e} + \ln \frac{Z_i^{\text{in}} Z_i^{\text{tr}}}{N_i} - \ln \frac{Z_a^{\text{in}} Z_a^{\text{tr}}}{N_a} \right] = 0 , \tag{24}$$

which is satisfied if

$$\frac{N_a}{N_i} = \frac{Z_a^{\text{in}}}{Z_i^{\text{in}}} \frac{N_e}{Z_e^{\text{in}} Z_e^{\text{tr}}} . \tag{25}$$

Using Eq. (4) for Z^{in}, Eq. (17) for Z^{tr} (note that $Z_a^{\text{tr}} = Z_i^{\text{tr}}$), and the relation $n = N/V$ it is found that Eq. (25) indeed is Eq. (6) for which $F = 1$.

The above sketch will be helpful in understanding the background of the procedure leading to F_{pot} and F_{pri}. In both cases thermodynamic principles are used which are derivatives of the second law, derivatives which are valid in full thermodynamic equilibrium but apparently misleading in a 2T situation.

The approach leading to F_{pot}, Eq. (8), uses the free energy which for a 1T and one-component system equals $F = U - TS$. The procedure followed in [6,7] can be sketched as follows: (1) the plasma is considered as being composed out of two subsystems, $\{e\}$ and $\{h\}$; (2) the internal energy of the atoms and ions contributes to the "energy" of the electrons; (3) the entropy associated with the internal distribution, i.e., $k \sum_s N_s \ln[Z_s^{\text{in}}]$ contributes to the entropy of $\{e\}$; and (4) the free energy is supposed to be an additive quantity so that under the conditions (c1)–(c3) the change in free energy gives

$$\Delta F = \Delta F_h + \Delta F_e$$
$$= \Delta N_e \left[T_e \ln \frac{Z_e^{\text{in}} Z_e^{\text{tr}}}{N_e} \frac{Z_i^{\text{in}}}{Z_a^{\text{in}}} + T_h \ln \frac{Z_i^{\text{tr}} N_a}{Z_a^{\text{tr}} N_i} \right] = 0 , \tag{26}$$

which is satisfied if

$$\left[\frac{N_a}{N_i} \right]^{T_h/T_e} = \frac{Z_a^{\text{in}}}{Z_i^{\text{in}}} \frac{N_e}{Z_e^{\text{in}} Z_e^{\text{tr}}} . \tag{27}$$

Using Eq. (4) for Z^{in} and Eq. (17) for Z^{tr} this leads to the Saha variant containing F_{pot}.

The derivation of F_{pri} is based on the principle that the affinity A should be zero. However, since $A = [\partial F / \partial n_e]_{T,V}$ there is no essential difference between $\Delta F = 0$ and $A = 0$. The relevant differences between the derivations behind F_{pri} and F_{pot} are (1) the entropy related to the internal distribution attributes to that of $\{h\}$ whereas (2) the Boltzmann equation is ruled by T_h instead of T_e. This leads to

$$\Delta F = \Delta F_h + \Delta F_e$$
$$= \Delta N_e \left[T_e \ln \frac{Z_e^{\text{in}} Z_e^{\text{tr}}}{N_e} + T_h \ln \frac{Z_i^{\text{in}} Z_i^{\text{tr}} N_a}{N_i Z_a^{\text{in}} Z_a^{\text{tr}}} \right] = 0 , \tag{28}$$

which is satisfied if

$$\left[\frac{N_a}{N_i} \right]^{T_h/T_e} = \left[\frac{Z_a^{\text{in}}}{Z_i^{\text{in}}} \right]^{T_h/T_e} \frac{N_e}{Z_e^{\text{in}} Z_e^{\text{tr}}} . \tag{29}$$

Realizing that the internal partition function in this approach is ruled by the heavy particle temperature we get after substitution of Eq. (4) for Z^{in} and Eq. (17) for Z^{tr} the Saha variant containing F_{pri}.

The derivations sketched above show that the difference between taking the minimum in free energy instead of the maximum in entropy essentially leads to "weighing" the entropies of the different components with the corresponding temperatures. This is by no means prescribed by the second law of thermodynamics so that no basis can be found for the factors F_{pri} and F_{pot}.

In order to offer an alternative thermodynamic approach comparable to that of those based on the minimum of free energy a function was introduced in [8] denoted by the generalized free energy and given by

$$\mathcal{F}=\sum_x \left[\frac{U_x}{T_x} - S_x \right] , \tag{30}$$

where the summation runs over the various subsystems. The demand that the generalized free energy of the plasma as a whole should be zero leads to the Saha variant with $F=1$. However, this quantity $\mathcal{F}$ has the dimension of entropy and essentially the demand is the same as that described above leading to Eq. (23) which is the maximum of entropy under the conditions (c1)–(c3). In that respect it is better to speak about the "free entropy" since, given the constraints (c1)–(c3), it is the only part of the entropy of the system plus surroundings which is free for striving to a maximum value.

C. The elementary mass action law versus the maximum entropy principle

It is useful to reflect on the differences between the two principles, the EMAL and the maximum entropy principle (MEP), i.e., the two bases of the Saha derivations given in the preceding subsections. A first comment is that they are essentially different. The EMAL, relating each elementary process to its corresponding inverse process (microscopic reversibility), has its roots in the ordering on the microscopic level. The MEP, on the other hand, dealing with the most probable distribution of particles over all possible states, is essentially based on the global features of the systems as a whole. In many studies it is even stated that the entropy can in principle only be dealt with if the whole universe is involved. It is useless to say that such an approach does not facilitate the treatment of partial equilibria, i.e., the situation in which some processes equilibrate while others do not.

A second note to be made is that almost any textbook on statistical mechanics uses the MEP to derive the distribution laws of statistical mechanics. However, it was shown in [1,14] that the EMAL can be used just as well and that the derivations are even more simple. Moreover, in his H theorem, Boltzmann used in principle the same method to show that in equilibrium the collision integral, the right-hand side of the Boltzmann transport equation, disappears. This integral vanishes since the product of the occupation of the reactants equals that of the resultants for any possible collision process (cf. the EMAL definition).

Finally we want to emphasize once more that the fact that the EMAL is related to balances on a detailed level makes it more suitable for the description of partial equilibria than the MEP. In this study it was used to isolate the top of atomic systems in pLSE but it can equally well be used to isolate the partial equilibrium between two levels coupled by an intense laser field or the Maxwellization in the bulk of the EEDF, etc. (cf. [1]).

It is not the aim of this paper to treat all these various partial equilibria. Nevertheless we want to give an example of the EMAL applied on the counterpart of the e-induced Saha balance (i.e., the balance under study), namely, the h-induced Saha balance of which the elementary variant reads

$$A_1(\epsilon_1)+A_p(\epsilon_2)\leftrightarrow A_1(\epsilon_3)+A_1^+(\epsilon_4)+e_j(\epsilon_5) , \tag{31}$$

where A_1 refers to an atom in the ground state. If this balance equilibrates we get the following relation between the elementary concentrations:

$$\hat{\eta}_A(1,\epsilon_1)\hat{\eta}_A(p,\epsilon_2)=\hat{\eta}_A(1,\epsilon_3)\hat{\eta}_{A^+}(1,\epsilon_4)\hat{\eta}_e(j,\epsilon_5) . \tag{32}$$

Substituting the expression Eq. (16) for each particle and using the energy conservation

$$\epsilon_1+\epsilon_2-\epsilon_3-\epsilon_4-\epsilon_5=I_p \tag{33}$$

we find

$$\eta(p)=\eta_e\eta_+(1)\left[\frac{h^2}{2\pi m_e kT_e}\right]^{3/2}\exp(I_p/kT_a) \times\exp[\epsilon_5(\gamma-1)/kT_e] . \tag{34}$$

This derivation shows that (1) a mixture of the kinetics of $\{e\}$ and $\{h\}$ is imposed on the ASDF of the atoms and ions, (2) the factor between square brackets, the thermal de Broglie volume $\mathcal{V}_{\text{tr}}$ of the $\{e\}$ depending on T_e solely, is still present, (3) but that the exponential factor is changed with respect to that in Eq. (19), and that (4) in contrast with Eq. (19) not each $\{\epsilon_i\}$ set gives the same relation between the state density in the atomic top and the ion ground state [i.e., the same $\eta(p)/\eta_+(1)$ value]; instead the density $\eta(p)$ created by this particular balance is determined by ϵ_5.

To get a global outcome one can determine the average value of $\eta(p)$. In this procedure we need ϵ_5 dependent rate coefficients for the various balances which provide the weighing factors for each corresponding $\eta(p)$ value. The outcome will be the same as that given by [15]. This hybrid procedure, in which the outcome of different elementary equilibria is averaged in a CR way, is comparable to the method given in [16]. Moreover, it is the essence of the treatment given in [10].

III. EXPERIMENTS

A. Characterization of the ICP

The inductively coupled plasma is a well known excitation source in spectrochemistry. It is an atmospheric flowing argon plasma in a quartz torch (Fig. 1) sustained by a radio frequent electromagnetic (EM) field (100 MHz) generated by a rf load coil. The argon flow consists of three parts: the outer flow (≈10 l/min) serves to avoid plasma-wall interaction, the intermediate flow (≈0.5 l/min) lifts the plasma, and the central flow (≈0.5 l/min) can be used for sample injection. The behavior of our

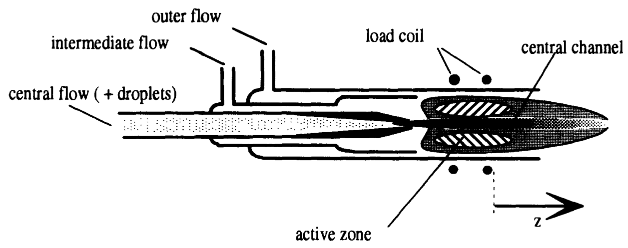

FIG. 1. A sketch of an inductively coupled plasma as used for spectrochemical applications. The active region where the energy coupling takes place and $\gamma = T_e/T_h > 1$ is located more or less in the load coil. Farther downstream the plasma is recombining.

plasma is studied by means of absolute line intensity (ALI) measurements, the power interruption (PI) technique, and H_β broadening (HB) determination. In some cases it is possible and fruitful to use experimental results obtained by other groups [17,18] although the plasma is somewhat different. Here we present only the basic principle of our experiments (ALI, PI, and HB). The full description containing the technical details can be found in [19,20]. In the case of ALI and PI the plasma radiation is focused on the entrance slit of a monochromator and detected by a photomultiplier. In the case of HB an optical multichannel analyzer was used in order to deduce the locally resolved line profile of H_β.

In the PI experiment we switch off the plasma generator for a short time (typically 100 μs) and study the response of line intensities in time with a resolution of 2 μs using a multichannel scalar. This information is especially interesting since the power interruption changes the plasma from a 2T into a 1T plasma.

In steady state the mechanism of energy transfer from the EM field to various species in the plasma occurs in three steps: the electrons gain energy from the EM field. Due to Ohmic heating this energy is transferred to the heavy particles which in their turn are cooled by the surroundings. This chain can be schematically presented as

$$RF \rightarrow \{e\} \rightarrow \{h\} \rightarrow \{\text{surrounding}\} \ . \tag{35}$$

The second link of this chain (i.e., Ohmic dissipation) is only possible if $T_e > T_h$ and due to the small mass ratio m_e/M, the factor $\gamma = T_e/T_h$ can differ significantly from unity. In order to show that the active plasma part is suitable to study the Saha equation under 2T conditions we give a brief summary of the plasma parameters of the active zone as found by the different techniques.

(1) The electron density as obtained via HB [19] is typically $n_e = 10^{21}\ \mathrm{m}^{-3}$.

(2) The T_e value of $T_e = 0.6-0.9$ eV as reported in [19] is obtained by combining ALI with HB measurements or by using the slope of the Boltzmann plot of the near continuum part of the argon spectrum [19,21]. These values are in reasonable agreement with each other and with the values as obtained by [17] using Thomson scattering.

(3) The T_h value can be obtained using Rayleigh scattering [17].

(4) Together with the T_e value this results in a value of $\gamma = T_e/T_h$ in the range of 1.2–1.4 which in its turn agrees with the γ value as reported in [18,20] using PI.

(5) Due to the relatively low n_e values the atmospheric pressure must be realized by argon atoms in the ground state which using the T_a value of typically 7500 K results in $n_a \approx 10^{24}\ \mathrm{m}^{-3}$. This implies that $n_e/n_a \approx 10^{-3}$.

Using the quantities summarized above it is found (taking $\gamma = 1.3$) that $F_{\mathrm{pot}} \approx 5$ whereas $F_{\mathrm{pri}} \approx 7$. The presence of these factors in Saha's equation must be easily traceable using ALI or PI measurements.

B. Absolute line intensities

One approach to testing the Saha variants is by applying Eq. (6) on the ionization degree of the plasma for that part of the plasma where 2T exists and the whole argon system is in local Saha equilibrium (LSE). This transition region must be somewhere between the active energy coupling region and the recombination zone. However, due to the uncertainty of T_e which enters into the various Saha equations via $\exp(I_1/kT_e)$ and due to the uncertainty about the Maxwellization of the EEDF tail, this exercise is doomed to be unsuccessful. Moreover, it is not easy to find the location of this LSE 2T region. Therefore it is better to investigate the upper part of the atomic system which is in pLSE. In [19,20] it was shown that apart from the ground state and first excited levels ($4s$ and $4p$ levels) the whole system is in pLSE for a considerable plasma region. Therefore it is possible to determine from the Boltzmann plot of highly excited states the value of η_∞, the value of $\eta(p)$ for p approaching the continuum. It was found in [19] that this η_∞ value only weakly depends on the position in the transition region between the active and recombining parts of the plasma.

By substitution of the experimentally determined local $n_e = n_i$ and T_e values it is found that depending on the position $\eta_\infty = 2\times10^{13}-4\times10^{13}\ \mathrm{m}^{-3}$. The ALI measurements giving η_∞ more or less directly lead within the error bars to the same values. The η_∞ value (ALI) is claimed to be better than 10%; the same precision applies to the n_e values obtained via the HB technique. Since F_{pot} and F_{pri} are typically 5 and 7, which if present would have been well detectable, we must conclude that these functions cannot be correct.

C. The power interruption technique

The power interruption technique, a powerful technique, provides insight into various processes in the plasma. The essence is that two basic decay phenomena, that of the T_e and n_e, are unraveled from each other due to difference in decay time. The method was introduced by [22] and applied on the ICP among others by [18,20]. A short break of the power input caused by switching off the plasma generator influences the energy balance, Eq. (35). Immediately after switching off the power supply the first link $RF \rightarrow \{e\}$ disappears, so that the electron temperature drops to the heavy particle temperature with a time constant which for our experiment is determined by the switching time of the generator being on the order of a few μs [20]. After this cooling period the electron density decreases due to recombination and/or outward diffusion of electrons occurring with a much longer time constant of about 200 μs. During all these processes the heavy particle temperature does not change significantly. After the power is switched on again the reverse processes occur and restore the steady state. We will concentrate on the response of the line intensities, i.e., excited state densities, on the cooling of the electrons $T_e \rightarrow T_h$ as caused by the switch off. The densities immediately after the cooling are denoted by an asterisk. The density of a level in PLSE (before and after cooling) will change from η^S_{2-T} into η^{S*}_{1-T} which, using Eq. (11), are interrelated by

$$\ln[\eta^{S*}(p)/\eta^S(p)] = -\ln F + \tfrac{3}{2}\ln\gamma + I_p(\gamma - 1)/kT_e \ . \tag{36}$$

If $F=1$ it is found that $\ln[\eta^{S*}(p)/\eta^S(p)] > 1$. This increase in intensity as a response on the cooling of the electron gas, which might be strange on first sight, can be understood by realizing that the balance, Eq. (12), shifts towards the left since the ionizing electron on the left-hand side is reduced in energy, which obstructs the endoergic process while the exoergic process of recombination keeps going on. This causes an increase in the density $n(p)$ of A_p.

If $F = F_{\text{pot}}$ or $F = F_{\text{pri}}$ and for $\gamma > 1$ thus larger than unity this upward cooling jump will be in competition with the disappearance of F. As far as we know it is not possible to explain this erroneous "thermodynamic" artifact by kinetic arguments.

Note that in all cases $\ln[\eta^*(p)/\eta(p)]$ has the same linear dependence on the ionization energy E_p of the level p [cf. Eq. (36)]. For given parameters T_e, T_h, n_e the difference lies in the value of $\ln[\eta^*(\infty)/\eta(\infty)]$, the extrapolated ratio for $I_p = 0$ which is determined by the value of F. Figure 2 shows a typical response of an argon line to the power interruption. In the upward jump at "power off" we clearly recognize the cooling jump ($T_e \rightarrow T_h$), which is followed by a relatively slow decrease due to the decay in the electron density. When the plasma generator is switched on again, opposite responses are visible. Eventually the plasma returns to its steady state.

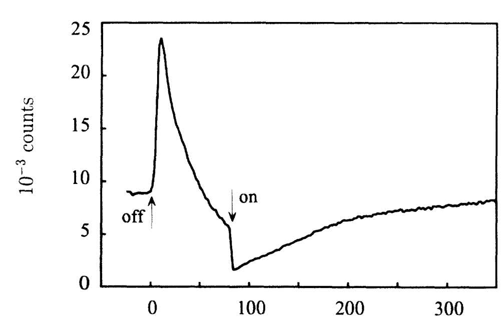

FIG. 2. A typical response, i.e., the intensity as a function of time, of the argon 6*d* level to the power interruption. At $t = 0$ ($t = 80\,\mu s$) the generator is switched off (on). The so-called cooling jump at $t = 0$ is plotted in Fig. 3 for several levels.

From this measurement we can easily determine the cooling ratio n^*/n as it equals the ratio of the peak intensity after switching to the steady state intensity. The measured values of $\ln[\eta^*(p)/\eta(p)]$ are plotted as a function of the I_p for several levels (Fig. 3). A linear relationship is found for the upper levels for which $I_p < 0.7$ eV. Extrapolating this line towards $I_p = 0$ gives $\ln[\eta^*(\infty)/\eta(\infty)] \approx 0.5$. Substituting this in Eq. (36) for the case $F=1$ gives $\gamma = 1.4$, which is in agreement with results obtained from Thomson and Rayleigh scattering as published in [17]. To obtain the γ values for the Saha variants corresponding to $F_{\text{pri}}(\gamma)$ and $F_{\text{pot}}(\gamma)$ (which are both γ dependent), we have to substitute Eqs. (7) and (8) into Eq. (36). For the case of F_{pri} we get for $I_p = 0$ the equation

$$\begin{aligned}\ln[\eta^{S*}(p)/\eta^S(p)] = {} & (1/\gamma - 1) \\ & \times[\ln(n_a/n_i) + \ln(G_i/G_a)] \\ & + \tfrac{3}{2}\ln\gamma \approx 0.5 \ ,\end{aligned} \tag{37}$$

which, taking $n_a/n_i = 10^3$ and $G_i/G_a = 6$, is fulfilled for $\gamma = 0.94$ whereas F_{pot} satisfies Eq. (37), in which $\ln(G_i/G_a)$ is omitted, provided $\gamma = 0.91$. Both results are in serious contradiction with reality.

First it implies that in the active zone $T_e < T_h$, which is impossible with respect to the chain given above Eq. (35) and the experimental values as published in [17]. Second, if nonetheless a value of $\gamma < 1$ could exist then according to Eq. (36) the slope in Fig. 3 should be negative, which is not the case. Therefore we must conclude once more that the Saha variants containing the F_{pot} or F_{pri} factors cannot be correct.

Returning to Fig. 3 we see that highly excited levels indeed follow a predicted slope but that the lower levels (e.g., level 4*p*) are not on this line. This implies that these levels are not in Saha equilibrium before and/or after the switch. Model calculations [1,23] have shown that the 4*p* levels under recombining ICP conditions are close (within 10%) to pLSE provided that $T_e > 0.5$ eV. Thus we may

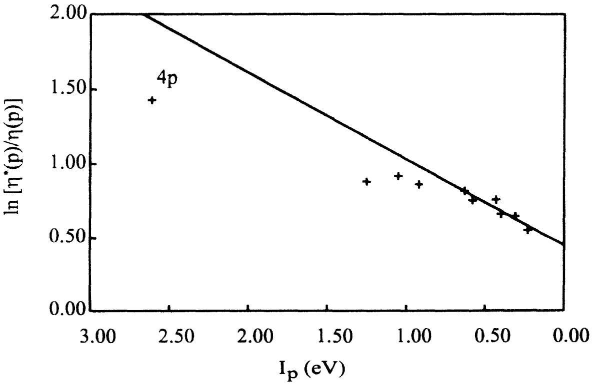

FIG. 3. The cooling jump [cf. Eq. (36)] for several levels as a function of the ionization energy of the level. The least squares fitting for levels in pLSE ($I_p < 0.7$ eV) gives for this condition $T_e = 0.65$ eV and $T_h = 0.48$ eV. Note that the lower levels show a systematic deviation which is explained in Fig. 4.

conclude that during the off period the $4p$ density is in a $T_e=T_h$ determined Saha equilibrium and that the deviation of $4p$ from the line in Fig. 3 must be due to the ionizing state of the ICP under standard conditions. The influence of the ionizing state on the ASDF can be studied using the excitation step flow, which reads

$$\begin{aligned} J(p,p+1) &= n_e n(p) K_{p,p+1} - n_e n(p+1) K_{p+1,p} \\ &= n_e \eta^S(p) g(p) K_{p,p+1} [b(p) - b(p-1)] , \end{aligned} \tag{38}$$

where the principle of detailed balancing is used together with the factor $b=\eta/\eta^S$ which expresses the deviation from Saha. This equation shows that above in the system where the value $g(p)K_{p,p+1}$ (scaling with p^6) is large, a small slope of the overpopulation $([b(p)-b(p-1)])$ generates a considerable stepwise flow. Lower in the system a steeper slope is needed to generate the same step flow. So, in an ionizing plasma where ionization is realized by stepwise processes it is evident that the lower levels are more easily disturbed than higher levels. It is also evident that the $\eta^S(p)$ sets a standard to this flow strength via Eq. (38). So even at large departure from pLSE it is useful to know the Saha value of the excited state densities. In Fig. 4 it is depicted how an ionizing system responds to the electron cooling. The jumps of lower levels are lower than the value predicted by the extrapolated Saha curve. In a future article we will use a time dependent CR model to study the behavior of the ASDF of the complete system, including the lower lying levels.

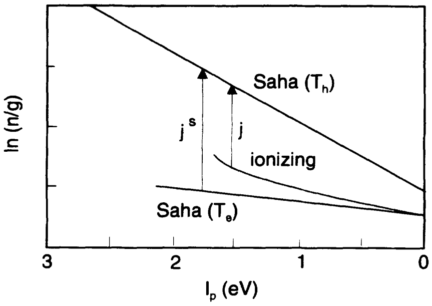

FIG. 4. A sketch of the atomic state distribution function for an ionizing system (dotted) compared to the corresponding Saha value for T_e [Saha (T_e)] and $T_h<T_e$ [Saha (T_h)] and the response to cooling. Since the lower levels are already overpopulated there is no need for a large cooling jump to reach Saha (T_h) at $t=0$ (the generator switch-off time). This explains why the lower levels (e.g., $4p$) are below the line in Fig. 3.

IV. DISCUSSION AND CONCLUSIONS

The situation of full ionization-recombination equilibrium and Maxwellization within the electron and heavy particle gases where the temperature inequality $T_e \neq T_h$ is present is suspected to be merely academic. Therefore one might conclude that it is useless to derive the Saha equilibrium for a two-temperature plasma. However, the experimental results obtained from an ICP show that it is still useful to talk about the Saha balance in a 2T plasma provided this concept is confined to the upper levels of an atomic system. These levels will reach the state of partial local Saha equilibrium (pLSE) much more easily than the atomic system as a whole. Moreover, even at large departures from ionization-recombination (i.e., Saha) equilibrium the Saha density provides a standard to which stepwise ionization can be related. We have shown that the elementary mass action law is suitable to "isolate" the pLSE and to find a correct but simple derivation of the Saha distribution law which despite the presence of the temperature inequality $T_e \neq T_h$ depends on T_e only. The Saha equation valid for levels in pLSE in a 2T plasma can be obtained by replacing the thermodynamic temperature by the electron temperature and by transforming the Saha formula from an interrelation between system densities to a relation between state densities. The 2T Saha density as found in literature [5,6] is ruled out by experimental evidence and a derivation based on the maximum entropy principle shows that the errors in [5,6] are generated by an incorrect generalization of the second law of thermodynamics. To describe the ASDF under a realistic plasma condition taking the various transport phenomena into account we need a full kinetic description which accounts for both radiative and collisional processes, i.e., a collisional radiative model.

ACKNOWLEDGMENTS

We want to thank M. C. M. van de Sanden and A. G. Peeters for fruitful discussions.

---

[1] J. A. M. van der Mullen, Phys. Rep. **191**, 109 (1990).
[2] H. B. Fanmin, J. J. Hurly, and F. R. Meeks, Appl. Spectrosc. **42**, 1181 (1988).
[3] F. R. Meeks, Spectrochim. Acta, Part B **48**, 1537 (1993).
[4] T. L. Eddy and A. Sedghinasab, IEEE Trans. Plasma Sci. **16**, 444 (1988).
[5] I. Prigogine, Bull. Cl. Sci. Acad. R. Belg. **26**, 53 (1940).
[6] A. V. Potapov, Teplofiz. Vys. Temp. **4**, 55 (1966) [High Temp. (USSR) **4**, 48 (1966)].
[7] H. G. Thiel, Wiss. Ber. AEG (Allg. Elektricitaets-Ges.)-Telefunken **44**, 123 (1971).
[8] M. C. M. van de Sanden, P. P. J. M. Schram, A. G. Peeters, J. A. M. van der Mullen, and G. M. W. Kroesen, Phys. Rev. A **40**, 5273 (1989).
[9] G. Ecker and W. Kroll, in *Proceedings of the Sixth International Conference on Phenomena in Ionized Gases, Paris,* 1964, edited by P. Hubert and E. Crémieu-Alcan (S.E.R.M.A., Paris, 1964), Vol. 1. p. 227.

ics of Non-Equilibrium Low-Temperature Plasmas (Consultants Bureau, New York, 1987).

[12] T. Fujimoto and R. W. P. McWhirter, Phys. Rev. A **42**, 6588 (1990).

[13] J. Vlček and V. Pelikán, J. Phys. D **23**, 526 (1990).

[14] L. Oster, Am. J. Phys. **38**, 754 (1970).

[15] C. B. Collins, Phys. Rev. **158**, 94 (1967).

[16] E. M. Dewan, Phys. Fluids **4**, 759 (1961).

[17] M. Huang and G. M. Hieftje, Spectrochim. Acta, Part B **44**, 291 (1989).

[18] G. P. Miller, Spectrochim. Acta, Part B **45**, 329 (1990).

[19] S. Nowak, J. A. M. van der Mullen, B. van der Sijde, and D. C. Schram, J. Quant. Spectrosc. Radiat. Transfer **41**, 177 (1989).

[20] F. H. A. G. Fey, ,W. W. Stoffels, J. A. M. van der Mullen, B. van der Sijde, and D. C. Schram, Spectrochim. Acta, Part B **46**, 885 (1991).

[21] B. van der Sijde and J. A. M. van der Mullen, J. Quant. Spectrosc. Radiat. Transfer **44**, 39 (1990).

[22] D. B. Gurevich and I. V. Podmoshenkii, Opt. Spektrosk. **15**, 587 (1963) [Opt. Spectrosc. (USSR) **15**, 319 (1963)].

[23] D. A. Benoy, J. A. M. van der Mullen, M. C. M. van de Sanden, B. van der Sijde, and D. C. Schram, J. Quant. Spectrosc. Radiat. Transfer **49**, 129 (1993).

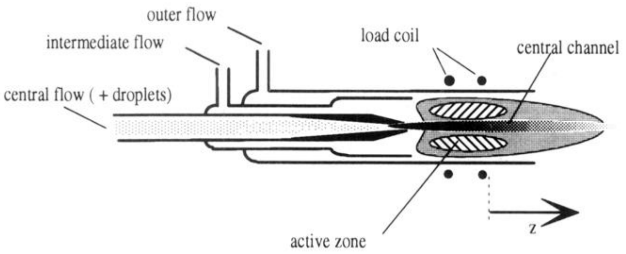

FIG. 1. A sketch of an inductively coupled plasma as used for spectrochemical applications. The active region where the energy coupling takes place and $\gamma = T_e / T_h > 1$ is located more or less in the load coil. Farther downstream the plasma is recombining.