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Effects of nonequilibrium plasmas on atomic reaction rates

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The influence of electron-density fluctuations on atomic reaction rates is studied in a hydrogen model plasma. We show that the effective ionization rates are found to be extremely sensitive to deviations of the electron density from the local thermal equilibrium (LTE) distribution, while the effective recombination rates are relatively stable against such fluctuations. This sensitivity has serious implications on plasma modeling and diagnostics, and could be employed to test the LTE assumption in an evolving plasma.

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The importance of plasma density and field effects on atomic reaction rates is known to plasma modelers. Thus, the plasma effects manifest themselves, for example, as pressure broadening of spectral lines emitted by atoms and ions inside plasmas [1–3], and shift the population density [4–6] of excited states of the plasma ions and of different charge states. In modeling plasmas, it is customarily assumed that a local thermodynamic equilibrium (LTE) exists for the continuum electrons and ions contained in a small sample volume located inside plasmas, with the total number of electrons and ions held fixed. However, experimentally the electron distributions are often found [7–9] to be non-Maxwellian, due to various external perturbations, such as electron-beam injection, ion-beam heating, and electron emission at the container surface exposed to ion bombardment. Low-temperature rf discharge plasmas in a cavity, high-temperature fusion plasmas with external beam injection, and laser-driven plasmas are some additional examples of nonequilibrium plasmas. Previous analyses did not focus on how sensitive the final solutions of the rate equations were to the excited-state population and ionization degrees to the electron density, i.e., to the non-LTE electron distribution.

We present here a detailed study of this non-LTE problem using the simple hydrogen plasma as testing system. It is shown that the effective rates can be seriously affected by the non-Maxwellian electron distribution, especially the collisional ionization rates. The relative population densities P_p for states p are changed, often severely, as they are the solutions of the rate equations that contain these modified rates. The sensitivity should also dictate the accuracy requirement on some of the (collisional) rates which are to be calculated theoretically for plasma diagnostic and modeling purposes. The validity of the LTE assumption routinely employed may be tested using this sensitivity.

The hydrogen plasma is described by the rate equations for the normalized population density $P_p(t)$ as [4],

$$P_p=[n_c n_i/n_p^E]\alpha_p - n_c S_p P_p \ , \tag{1}$$

where P_p of state p of hydrogen is normalized with respect to the Saha equilibrium value n_p^E, as $P_p \equiv n_p/n_p^E$. n_c, n_i, and n_p are the densities of the continuum electrons, proton ions, and hydrogens in state p, respectively, all in units of cm^{-3}. The α_p and S_p, both in units of cm^3/sec, are the effective collisional radiative and ionization rates, respectively. They are, in turn, defined in terms of the elementary reaction rates, as described by Bates and co-workers [4] and in Ref. [10]. Specifically, if one assumes the LTE for the plasma electrons, the collisional excitation rates K_{pq} for the transition $p \to q$ for example are defined as

$$K_{pq}=\langle v_p \sigma_{pq}\rangle_{\text{MX}}=\int dv\, f_{\text{MX}}(v,T) v \sigma_{pq} \ , \tag{2}$$

where f_{MX} is the Maxwellian distribution with temperature T. The radiative recombination, collisional ionization, etc., are similarly defined.

It is the purpose of this paper to examine the sensitivity of these rates on the electron distribution f, and to show that some of the effective rates derived from the modified set of rate equations are strongly dependent on the electron density distribution f; the collisional radiative ionization rate S_1 for the ground state in (1) will be shown to be especially sensitive to the electron temperature T. Thus, we assume in the following that the nonequilibrium electron distribution is expressed in the double Maxwellian form [8],

$$f=f_a\mu_a+f_b\mu_b \ , \tag{3}$$

where f_a and f_b are themselves Maxwellian, with temperatures T_a and T_b, respectively, and $\mu_a+\mu_b=1$. We have $n_a=\mu_a n_c$, $n_b=\mu_b n_c$, with $n_a+n_b=n_c$. For a nonequilibrium plasma, alternate forms such as $f' \propto \exp[-(v_x^2/2T_x+v_y^2/2T_y+v_z^2/2T_z)]$ have also been used, but in the following we adopt the simpler quasiequilibrium form (3). All the rates used below are modified using (3) and approach the simple Maxwellian form in the limit $\mu_b \to 0$, for example,

$$K_{pq}=\mu_a K_{pq}^a+\mu_b K_{pq}^b \ , \tag{4}$$

etc.

Similarly, the Saha equilibrium density can be found which is consistent with (3) and (4), and at the same time satisfy (1) at high p. We have derived the following form of the quasiequilibrium Saha density ($k_B \equiv 1$):

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$$n_p^E = n_i n_c p^2 \left[\frac{h^2}{2\pi m_e} \right]^{3/2} [\mu_a / T_a^{3/2} + \mu_b / T_b^{3/2}]$$
$$\times \{ \mu_a \exp[I_p / T_a] K_{pc}^a + \mu_b \exp[I_p / T_b] K_{pc}^b \} / [\mu_a K_{pc}^a + \mu_b K_{pc}^b] , \quad (5)$$

which satisfies the requirement that the P's defined in terms of the equilibrium values (5) approach the proper limit $P_p \to 1$ for all $p > s$. In the limit $\mu_b \to 0$, n_p^E approach the usual single-temperature Saha values used in Refs. [4] and [10]. The parameter s depends on the density and temperature and must be determined [4,10] numerically by self-consistency; this property allows the truncation of the rate equations (1) to a finite set of coupled equations.

The modified rate equations for P_p, as normalized with the mixed Saha density (5), are given by

$$\dot{P}_p = -P_p [n_a k_p^a + n_b k_p^b + a_p] + \left[n_a \sum_{q \neq p} K_{qp}^a (n_q^E / n_p^E) + n_b \sum_{q \neq p} K_{qp}^b (n_q^E / n_p^E) \right] P_q + \sum_{q > p} (n_q^E / n_p^E) A_{qp} P_q + (n_i / n_p^E) [n_a^2 K_{cp}^a + n_b^2 K_{cp}^b] + (n_i / n_p^E) [n_a \beta_p^a + n_b \beta_p^b] , \quad (6)$$

where the various changes in the normalizations of the terms involved are important in satisfying the Saha equilibrium in the case of two temperature plasmas. We also used in (6) $k_p^a = K_{pc}^a + \sum_{q \neq p} K_{pq}^a$ and similarly for k_p^b and where K_{pq}^a are the collisional excitation rates for the transitions $p \to q$ caused by plasma electrons of the a type. $a_p = \sum_{q < p} A_{pq}$ where A_{pq} are the spontaneous radiative decay probabilities for the $p \to q$ transitions. K_{pc} are the direct collisional ionization rates for the transitions $p \to c$ caused by plasma electrons, with their inverse K_{cp} (the three-body recombination). Finally, β_p are the radiative recombination of continuum electrons to state p, $c \to p$. All these quantities are l averaged under the assumption of rapid redistribution of l levels within each principal quantum number p caused by rapid plasma particle perturbations [5].

The truncated system of equations (6) is relatively simple to solve, and the cutoff parameter s is usually small ($s < 25$) for the density and temperature ranges considered here. The effective rates are evaluated as functions of T_a, T_b, μ_b, and $n_c = n_a + n_b$. The equilibrium solution for the ground state $p = 1$ is obtained by setting first $\dot{P}_p = 0$ for all p in the range $s > p > 1$ and $\dot{P}_p = 1$ for $p \geq s$. From (6), we then have

$$\dot{P}_1 = -n_c S_1 P_1 + (n_c n_i / n_1^E) \alpha_1 , \quad (7)$$

where, as in previous work [4,10], we introduced the effective collisional ionization and recombination rates, S_1 and α_1, respectively, for the ground state. At the quasiequilibrium defined by (3), the ground-state relative population density is then given by

$$P_1^e = (n_i / n_1^E) \alpha_1 / S_1 , \quad (8a)$$

where the plasma electron density n_c is still held fixed and its distribution described by (3). The actual, unnormalized population densities are given by

$$n_p^e \equiv n_p^E p_p^e = n_i \alpha_p / S_p . \quad (8b)$$

Obviously, the strong dependence of S_p on the non-Maxwellian distribution of the plasma electrons found above is reflected on n_p^e which decreases rapidly with increasing T_b.

The analysis of the system described by (3) and (6) requires various reaction rates for $\mu_a = 1$ and $T = T_a$; the collisional ionization rates K_{pc}, the collisional excitation (and deexcitation) rates K_{pq}, the radiative recombination rates β_p, and the radiative decay probabilities A_{pq}. They are given, for example, in Ref. [10]. For later comparison, the rate equations (6) are first solved for the standard case $\mu_b = 0$, and the effective rates introduced in (7) evaluated [10].

To examine the sensitivity of the rates and population density P_p on the distribution f, we choose two typical values for $\mu_b = 0.10$ and 0.01. As noted earlier, such magnitudes of mixing are quite common in many plasmas, for example, in low-temperature rf discharge plasmas. We also set $T_b > T_a$ with $\mu_a > \mu_b$; that is, the main component of the plasma is assumed to be in a lower temperature T_a. The opposite cases in which the dominant component is at higher temperature is less interesting. For illustration, we choose T_b to be $2T_a$, $4T_a$, and $8T_a$. Figure 1 shows the value of S_1 for $\mu_b = 0.10$, i.e., a 10%

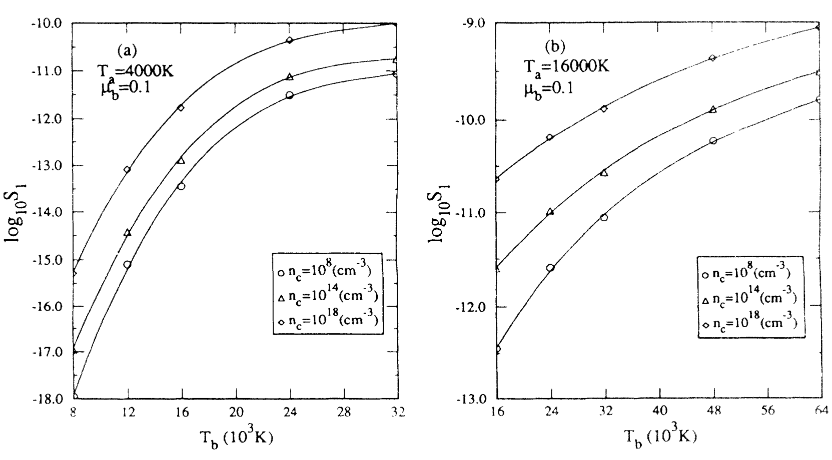

FIG. 1. The modified collisional ionization rates S_1 are given for the mixture with $\mu_b = 0.10$; (a) $T_a = 4000$ K and for three different densities; (b) $T_a = 16\,000$ K. The important feature is the strong T_b dependence of S_1, which shows the effect of non-LTE. The dependence of S_1 on the electron density at small T_b is not related to the non-LTE property.

mixture of the high-temperature component in the electron distribution for the total electron densities $n_c = 10^8$, 10^{14}, and 10^{18} cm^{-3}. Figure 1(a) gives S_1 for $T_a = 4000$ K and $T_b = 8\,000$ K, 16 000 K, while Fig. 1(b) contains the similar result at $T_a = 16\,000$ K. The extremely rapid change of S_1 as a function of T_b found here is apparently caused by the non-Maxwellian nature of f assumed in (3) and by the rapid variation of K_{pc}. This feature is the main result of this paper. The increase in the value of S_1 with increasing n_c in the limit $T_b \to T_a$ is equally dramatic, as discovered earlier by Bates and co-workers [4] and further discussed in Ref. [10], but this aspect of S_1 is not relevant to the nonequilibrium problem of interest here.

On the other hand, the collisional radiative recombination rates α_1 are found to be less sensitive to the mixed f than the collisional radiative ionization rates S_1. Figure 2 shows the values of collisional radiative recombination rates α_1 for the ground state $p = 1$ as a function of T_b, evaluated for the mixture $\mu_b = 0.10$ and for three different densities. The result is compared with the case $\mu_b = 0$; the n_c dependence of α_1 is not related to the effect of the distribution (3). Note the relative insensitivity of α_1 as compared to S_1 of Fig. 1; the change in α_1 with T_b describes the nonequilibrium effect, and in this case is at the level of 10–30 %.

Similarly, we present in Fig. 3 the variation of S_1 with T_b at $\mu_b = 0.01$ and for $T_a = 4000$ K, i.e., only a 1% mixture of the high-temperature components. Such a small perturbation in the distribution is usually difficult to detect in a transient plasma, but the present result shows that the ionization rates S are still very much affected at low T_a. The effect of the mixing (3) becomes less severe at high T_a, however, and to illustrate this we give in Table I more extensive results of the rates for the case $\mu_b = 0.01$.

The intensity of spectral lines emitted by plasmas depends on the excited-state population, which is, in turn, dictated by the effective collisional depopulation rates. The strong variation of S_p shows up in the final quasiequilibrium density n_p^e defined by (8a) as well as in the relative population density P_p^e. We present in Fig. 4 typical values of n_p^e (in cm^{-3}) for $p = 1$, 2, 3, as functions of T_b, all at $T_a = 4000$ K, $\mu_b = 0.10$, and $n_c = 10^{14}$ cm^{-3}. Note the generally rapid decrease in the density with increasing T_b. This is consistent with the result of Figs. 1 and 2, where the variation of S_1 and α_1 with T_b is demonstrated.

Summarizing the results we obtained above, it has been shown that the collisional radiative ionization rates S_1 are extremely sensitive to the nonequilibrium electron distribution f. This sensitivity is caused mainly by the rapid variation with T of the corresponding collisional transition rates K_{pq} and K_{pc}. The rapid increase in S_p is reflected in the similarly rapid decrease in the population density n_p^e at quasiequilibrium. By contrast, the radiative rates A_{pq}, β_p, and α_1 are shown to be relatively insensitive to the variation in the non-Maxwellian distribution

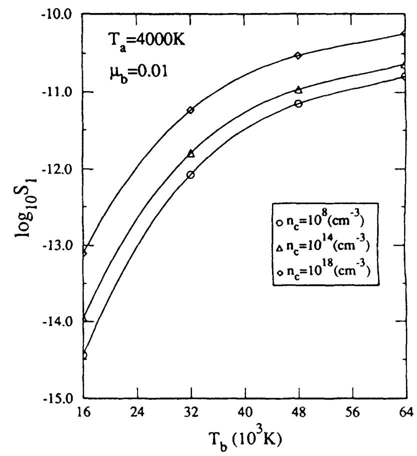

FIG. 3. The modified collisional ionization rates S_1 are presented for the mixture $\mu_b = 0.01$, at $T_a = 4000$ K. This is to be compared with Fig. 1(a) for the case $\mu_b = 0.10$, $T_a = 4000$ K.

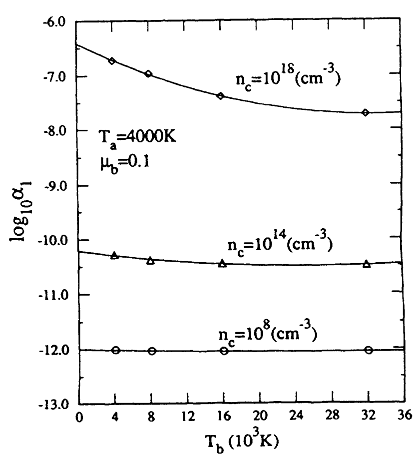

FIG. 2. The modified radiative capture rates α_1 are presented for the mixture $\mu_b = 0.10$. This is to be compared with Fig. 1. α_1 varies slowly with T_b and thus is insensitive to the non-LTE property of the electron distribution, especially at low densities. Sizable changes are seen at higher densities, however.

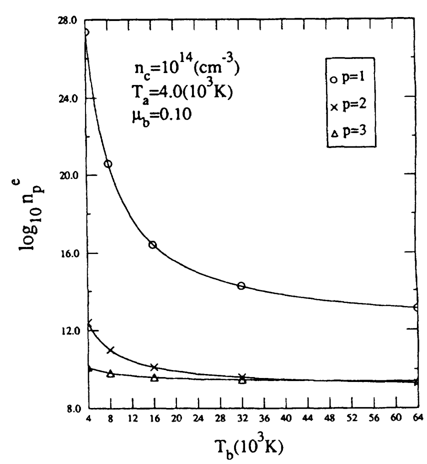

FIG. 4. The final quasiequilibrium density n_p^e is presented, in units of cm^{-3}, for the states $p = 1$, 2, 3, as functions of T_b of the mixture, and where $T_a = 4000$ K, $\mu_b = 0.10$, and $n_c = 10^{14}$ cm^{-3}. As defined by (8a), n_p^e decreases rapidly with increasing T_b, because of the variation of S_1. The result for $T_b < 8 \times 10^3$ K should be taken with caution.

TABLE I. The effective collisional ionization rates S_1 are presented for the double Maxwellian distribution f of (3) with a small mixture $\mu_b=0.01$. $T_a=4000-32\,000$ K, and the mixture temperature $T_b=2T_a 4T_a$, and $8T_a$. The single-temperature case with $\mu_b=0$ (α_1^B and S_1^B) is also listed for comparison. Note the rapid change in the rates with increasing T_b for low T_a, but less rapidly at higher T_a. The numbers in brackets denote multiplicative powers of ten.

n_c (cm^{-3})	T_s (K)	T_b (K)	α_1 (cm^3/s)	S_1 (cm^3/s)	α_1^B (cm^3/s)	S_1^B (cm^3/s)
1.0[+08]	4.0[+03]	3.2[+04]	9.6[−13]	8.5[−13]	9.7[−13]	8.8[−27]
1.0[+14]	4.0[+03]	3.2[+04]	4.9[−11]	1.6[−12]	5.2[−11]	2.2[−24]
1.0[+18]	4.0[+03]	3.2[+04]	1.4[−07]	5.8[−12]	1.9[−07]	7.9[−22]
1.0[+08]	4.0[+03]	1.6[+04]	9.6[−13]	3.6[−15]	9.7[−13]	8.8[−27]
1.0[+14]	4.0[+03]	1.6[+04]	4.9[−11]	1.1[−14]	5.2[−11]	2.2[−24]
1.0[+18]	4.0[+03]	1.6[+04]	1.6[−07]	7.8[−14]	1.9[−07]	7.9[−22]
1.0[+08]	4.0[+03]	8.0[+03]	9.6[−13]	1.1[−19]	9.7[−13]	8.8[−27]
1.0[+14]	4.0[+03]	8.0[+03]	5.0[−11]	9.5[−19]	5.2[−11]	2.2[−24]
1.0[+18]	4.0[+03]	8.0[+03]	1.8[−07]	2.6[−17]	1.9[−07]	7.9[−22]
1.0[+08]	8.0[+03]	6.4[+04]	5.3[−13]	1.6[−11]	5.3[−13]	1.1[−17]
1.0[+14]	8.0[+03]	6.4[+04]	5.1[−12]	2.7[−11]	5.2[−12]	2.3[−16]
1.0[+18]	8.0[+03]	6.4[+04]	2.2[−09]	7.9[−11]	2.5[−09]	1.1[−14]
1.0[+08]	8.0[+03]	3.2[+04]	5.3[−13]	8.5[−13]	5.3[−13]	1.1[−17]
1.0[+14]	8.0[+03]	3.2[+04]	5.1[−12]	2.0[−12]	5.2[−12]	2.3[−16]
1.0[+18]	8.0[+03]	3.2[+04]	2.3[−09]	1.0[−11]	2.5[−09]	1.1[−14]
1.0[+08]	8.0[+03]	1.6[+04]	5.3[−13]	3.6[−15]	5.3[−13]	1.1[−17]
1.0[+14]	8.0[+03]	1.6[+04]	5.1[−12]	1.7[−14]	5.2[−12]	2.3[−16]
1.0[+18]	8.0[+03]	1.6[+04]	2.4[−09]	2.1[−13]	2.5[−09]	1.1[−14]
1.0[+08]	1.6[+04]	6.4[+04]	3.0[−13]	1.6[−11]	3.1[−13]	3.6[−13]
1.0[+14]	1.6[+04]	6.4[+04]	1.0[−12]	3.2[−11]	1.0[−12]	2.5[−12]
1.0[+18]	1.6[+04]	6.4[+04]	9.3[−11]	1.1[−10]	9.7[−11]	2.3[−11]
1.0[+08]	1.6[+04]	3.2[+04]	3.0[−13]	1.2[−12]	3.1[−13]	3.6[−13]
1.0[+14]	1.6[+04]	3.2[+04]	1.0[−12]	4.9[−12]	1.0[−12]	2.5[−12]
1.0[+18]	1.6[+04]	3.2[+04]	9.5[−11]	3.4[−11]	9.7[−11]	2.3[−11]
1.0[+08]	3.2[+04]	6.4[+04]	1.8[−13]	1.0[−10]	1.8[−13]	8.5[−11]
1.0[+14]	3.2[+04]	6.4[+04]	3.2[−13]	3.2[−10]	3.2[−13]	2.9[−10]
1.0[+18]	3.2[+04]	6.4[+04]	1.2[−11]	1.2[−09]	1.2[−11]	1.1[−09]

f. Extreme caution should be exercised, therefore, in modeling plasmas and in generating the rates, by properly reflecting the sensitivity found in this report.

It is further suggested that the sensitivity of S_p and insensitivity of α_p may be used to examine the validity of LTE usually assumed in the modeling and rate calculation. Furthermore, we note that the present model does not maintain the total number of particles in a given volume as we change T_b for fixed T_a and n_c, and may result in excess overpopulation of the ground state at very low temperature.

The hydrogen plasma is the simplest system which can be used to study some of the critical characteristics of the plasma, without the complications of different charge states and multitude of resonant processes [11]. These latter problems are themselves very important for plasmas involving heavier elements and at high temperatures. Impurity ions in hydrogen plasmas are also of interest. They will the subject of future study [12–14].

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