Low-temperature plasmas with nonequilibrium ionization

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Low-temperature plasmas are frequently not in thermodynamic equilibrium. External fields, the emission of radiation, gradients of various physical properties, and the finite rates of various processes can all prevent the attainment of equilibrium. In nonequilibrium conditions the ionization state, the distribution of atomic excited states, and the electron energy distribution all become complicated functions of the factors responsible for the deviation from equilibrium. Since the components of the plasma—the electrons, atoms, and ions—are strongly coupled, a departure from equilibrium in one component causes departure in the others. The criteria for a deviation from local thermodyamic equilibrium are given. A study is made of plasmas far from equilibrium, in which the electron density is not described by the Saha equation, the atoms do not have a Boltzmann energy-level distribution, and the electrons do not have a Maxwellian energy distribution. A steady-state nonequilibrium plasma and time-dependent relaxation phenomena are studied. The theory is compared with the extensive experimental data available.

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CONTENTS

1. INTRODUCTION

The state of an equilibrium plasma can be characterized completely by the thermodynamic variables, e.g., the pressure and the temperature. The plasma composition, the particle velocities, and the populations of excited levels all follow from simple thermodynamic relations: the Saha equation and the Maxwell and Boltzmann distributions. In practice, however, a complete thermodynamic equilibrium is exceedingly rare. Among the factors which can prevent equilibrium are external fields, radiation losses, gradients in various physical properties, and the finite rates of various physical and chemical processes. Collisional processes, on the other hand, which redistribute the energy and momentum of the particles, tend to move the system toward equilibrium. The net result is a compromise of some sort: a system which is nonequilibrium overall but possibly at equilibrium with respect to certain degrees of freedom. States of this sort cannot be described by a single temperature. The simplest nonequilibrium state of a plasma, for example, the so-called two-temperature plasma, is characterized by both an electron temperature and a heavy-particle temperature. The degree of ionization, the distribution of atoms with respect to energy levels, and the electron velocity distribution are all determined in this case by the electron temperature. The deviation from equilibrium, however, frequently leads to more complicated distributions and to a more complicated equations for the degree of ionization, such that the system could not be described correctly by any single temperature. A deviation from ionizational equilibrium affects chiefly certain macroscopic properties of the plasma, and such plasmas are accordingly referred to as "plasmas with nonequilibrium ionization."

A review of the literature shows that much effort has been devoted to establishing simple criteria for determining whether a plasma is in equilibrium.[1,2] In recent years, in contrast, much progress has been made in the study of very nonequilibrium plasmas. There are two motivations for this work: Plasmas with nonequilibrium ionization are produced in many plasma

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devices of various types, and effects of general physical interest occur in nonequilibrium plasmas.

Let us consider, for example, the situations which arise when an external electric field is applied to a plasma originally in equilibrium. The field rapidly heats the electron gas, and the degree of ionization usually lags behind the values which would correspond to the rising electron temperature. The Boltzmann distribution and possibly the Maxwell distribution may not hold. Various states may be reached, depending on radiation and charged particles losses. If both are slight, a two-temperature plasma is produced, but if either emission or charged-particle losses are intense the result is a steady-state "underionized" plasma, in which all three distributions (Saha, Boltzmann, and Maxwell) may be modified.

As the electric field decays, a different group of nonequilibrium states arises. The degree of ionization falls more slowly than the rapidly dropping temperature, and a recombining plasma appears. As it cools, this plasma gradually converts into an unionized gas.

We emphasize that these deviations from equilibrium in the various degrees of freedom are generally interrelated. Thus a factor which can cause a deviation from equilibrium for one degree of freedom can indirectly cause a deviation for some other degree of freedom. For example, the line emission from a plasma may cause not only a nonequilibrium distribution in excited states but also a nonequilibrium degree of ionization and a disruption of the Maxwell distribution.

To find a systematic description of nonequilibrium plasmas we must use the methods of physical kinetics, and the problem is quite complicated in general. To a large extent, these difficulties stem from the fact that the atoms have many energy levels. In a nonequilibrium plasma there are actually dozens of neutral components which are converting back and forth into each other and which differ in ionization energy, the cross sections for various processes, and other physical characteristics. There are complications of the same sort for the ions, but not as extreme. In these circumstances it is advantageous to study the most typical deviations from nonequilibrium, to identify states which are partially at equilibrium, etc. This approach dramatically simplifies the description of the plasma, making it far easier to understand and interpret the various events.

The present review is devoted primarily to atomic low-temperature plasmas with nonequilibrium ionization, although molecular components will be taken into account in certain places. The review covers plasmas of very different compositions, charge densities from 10^{10} to 10^{17} cm^{-3}, temperatures from 10^3 to 10^5 °K, and typical dimensions from a fraction of a centimeter to several meters. These are the pertinent parameters for the development of devices which use low-temperature plasmas.

This review cannot of course cover all the important and interesting questions which arise in the study of low-temperature nonequilibrium plasmas. For a discussion of these other topics the reader is referred to other reviews and monographs.[3-7]

2. CONDITIONS FOR NONEQUILIBRIUM IONIZATION

A study of any plasma generally begins with the following questions: Is the electron temperature the same as the heavy-particle temperature? What is the distribution of atoms with respect to excited states? What is the degree of ionization? Do the electrons have a Maxwell distribution? The answers to these questions give us definite information about the state of the plasma and also point out appropriate ways for pursuing the study of the plasma properties. The literature accordingly reflects a considerable effort to find inequalities characterizing various types of deviations from equilibrium. Spatially nonuniform plasmas are extremely common, for these local criteria determine the conditions under which a distribution is in equilibrium with respect to local values of the thermodynamic properties. Obviously, these local equilibrium criteria may be satisfied in one part of the plasma but not in another. The most familiar criteria in the literature are those which determine whether the atoms satisfy a Boltzmann distribution with respect to excited levels, depending on the local value of the electron temperature. Other criteria are less familiar but frequently crucial. Let us examine the various criteria for a local thermodynamic equilibrium.

A. Condition for a hot-electron plasma

The electron gas reaches a temperature higher than that of the other particles in an external electric field because the energy exchange between the electrons and the heavy particles is inefficient. The fraction of the energy transferred is small, equal to twice the mass ratio, $\delta = 2m/M$, so the electron temperature T_e becomes higher than the heavy-particle temperature.

The experimental data[8] in Fig. 1 demonstrate how the electron temperature T_e exceeds the gas temperature T in the plasma of an atmospheric-pressure arc. In certain other situations, the heavy particles may reach a higher temperature: $T > T_e$. This is the case, for example, behind a strong shock front, where the gas is heated as the front passes, but there is a delay in the ionization and thus in the heating of the resulting electrons, which occurs at the same time as the ionization.

In an atomic gas in an external electric field, because of the small value of δ, the electron temperature T_e becomes higher than the gas temperature at a com-

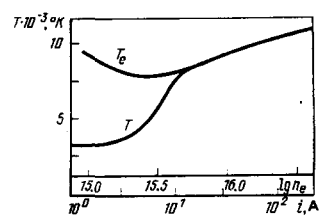

FIG. 1. Variation of the temperatures T_e and T with the current i (or the electron density n_e) in the plasma of an argon arc with a 5% H_2 admixture.[8]

paratively low field $\mathscr{E}$. Let us use electron energy balance to estimate the field $\mathscr{E}$ required. In the simplest case, Joule heating $\sigma\mathscr{E}^2$ (σ is the electrical conductivity of the plasma) is offset by the energy lost through elastic collisions:

$$\sigma\mathscr{E}^2 = \delta n_e \nu (T_e - T) \qquad \sigma = \frac{e^2 n_e}{m\nu}; \tag{2.1}$$

where ν is the frequency of elastic collisions. In a weakly ionized plasma we would have $\nu = n_a \sigma_{ea} v$, where n_a is the atomic number density, σ_{ea} is the elastic electron-atom cross section, and v is the average electron velocity. Then

$$\frac{T_e - T}{T} = \left(\frac{\mathscr{E}}{n_a} \frac{e}{\sigma_{ea} T \sqrt{\delta}}\right)^2. \tag{2.2}$$

In cold hydrogen ($T = 300$ °K), a small temperature difference $(T_e - T)/T \approx 0.1$ arises even in a field $\mathscr{E}/n_a \approx 3 \cdot 10^{-19} V \cdot \text{cm}^2$. As the degree of ionization increases, electron-ion collisions must also be taken into account. The corresponding cross section is

$$\sigma_{ei} = 2\pi \frac{e^4}{T^2} \lambda,$$

where λ is the Coulomb logarithm. This cross section is quite large (at $T = 3000$ °K, for example, $\sigma_{ei} = 3 \cdot 10^{11}$ cm^2), so that electron-ion collisions are important in the electron energy balance even at comparatively low ionization levels, $\sim 10^{-4} - 10^{-3}$.

Inelastic collisions can be taken into account by estimating the energy radiated by the plasma and the energy carried off by charged particles which diffuse to the plasma boundaries.

The radiative energy loss is governed by radiative transitions between various states:

$$S_R = \sum_{k,n} n_k A^*_{kn} (E_k - E_n), \tag{2.3}$$

where n_k is the population of level k, A^*_{kn} is the effective probability for the radiative transition $k \to n$, and $E_k - E_n$ is the energy of the emitted photon. For an upper estimate of S_R, we can replace n_k by n^0_k, the Boltzmann population at T_e.

Just what do we mean by "effective probability for the radiative transition?" If we replace A^*_{kn} by A_{kn}, where A_{kn} is the probability for a spontaneous transition, we would be taking into account only the radiative transitions $k \to n$ (this is the thin-slab approximation). Under real conditions, radiative transitions $n \to k$ can also occur, because of the absorption of the radiation emitted from adjacent regions. This effect can partially or even completely offset spontaneous emission. The theory for radiative transport of excitation takes this effect into account through the introduction of the quantity Θ_{kn}, the probability for the escape of a photon from the plasma.[9-11] As a result we have $A^*_{kn} = A_{kn}\Theta_{kn}$. For Θ_{kn} we have the following simple but quite accurate equations:

$$\frac{1}{\Theta} = 4k_0 R \sqrt{\pi \ln (k_0 R)}$$

for a Doppler-broadened line or

$$\frac{1}{\Theta} = 3\sqrt{\pi k_0 R}$$

for a dispersion-broadened line. Here $k_0 R$ is the optical density for the center of the line; the absorption coefficient k_0 depends on the nature of the line broadening; and R is the linear dimension of the plasma.

Let us estimate the radiative energy loss of an inert-gas plasma with a small admixture of a readily ionized alkali metal. The inert gas is responsible for the elastic loss $S_{ei} = \delta n_e \nu (T_e - T)$ and broadens the lines of the metal atoms, thereby determining Θ_{kn}. The alkali metal vapor furnishes the electrons and radiates primarily in its own doublet. Then we can restrict the calculation of S_R in (2.3) to a single term, equal to $n^0_2 A^*_{21}(E_1 - E_2)$, where E_2 is the binding energy of the first excited level, and $k = 2$. Then the behavior of $\Delta_R = S_R/S_{ei}$ as a function of T_e is basically described by

$$\Delta_R \sim \frac{n^0_2 (E_1 - E_2)}{n^0_e (T_e - T)} \sim e^{(2E_2 - E_1)/2T_e} \frac{E_1 - E_2}{T_e - T}.$$

Since we have $2E_2 - E_1 > 0$ for alkali metals, the radiative energy loss is never important at high T_e. Numerical calculations show that for an argon pressure $p = 1$ atm, a temperature $T = 2000$ °K, and a relative potassium concentration of 10^{-3} the characteristic value of T_e corresponding to $\Delta_R = 1$ is ~3000 °K for $R = 10$ cm (Ref. 12).

If the situation is far from equilibrium, it is a more complicated matter to calculate the energy loss due to inelastic processes (this would include the radiative energy loss S_R). This loss causes a close relationship between the nonequilibrium values of T_e and the atomic distributions with respect to excited levels, which will be discussed in Section 3 below.

To find a rough estimate of the energy loss from diffusion of charged plasma particles to the boundaries, we introduce a diffusion scale time. Then

$$S_D = E_1 \frac{n_e}{\tau_D},$$

where E_1 is the ionization energy, $\tau_D = R^2/gD$, D is the ambipolar diffusion coefficient, and g is a numerical factor which depends on the plasma configuration.

Experiments on the inelastic energy loss due to radiation and ambipolar diffusion are reported in Refs. 13 and 14. The results show that there is a certain parameter range in which this loss is negligible, but this range is limited.

The inelastic loss can be extremely high in a plasma containing a molecular component, because the thresholds for the excitation of rotational and vibrational levels are low. If the vibrational and rotational temperatures (T_v and T_r) are approximately equal to the gas temperature (T), this type of loss can be incorporated in the criterion for a hot-electron plasma by introducing a quantity δ_{eff}. The values of δ_{eff} can be much larger than $\delta = 2m/M$. Let us examine some simple equations, which also hold when $T_v, T_r \neq T$.

In a plasma with homonuclear molecules, e.g., nitrogen, there is a substantial loss due to vibrational excitation,[15] S_v:

$$S_v = \hbar\omega n_m P_{01} (e^{\hbar\omega/T_v} - e^{\hbar\omega/T_e}) e^{-\hbar\omega/T_e} [e^{\hbar\omega/T_v} - 1]^{-1},$$

where $\hbar\omega$ is the vibrational quantum, and P_{01} is the ex-

citation rate. Ordinarily, we would have $P_{01} \approx 10^{-10} - 10^{-9}$ cm^3/sec. The electrons can be in equilibrium with the molecular vibrations. We can write a criterion for a temperature T_e higher than the temperature of the other particles, analogous to criterion (2.2):

$$\frac{T_e - T_v}{T_v} = \left(\frac{\mathscr{E}}{n_a}\frac{e}{\sigma_{ea}T_v}\right)^2 \frac{\sigma_{ea}\sqrt{T_v/M}}{P_{01}} \frac{T_v}{\hbar\omega}\frac{n_a}{n_m}(e^{\hbar\omega/T_v}-1). \quad (2.4)$$

Even if $n_a \gg n_m$, i.e., even if the molecules constitute only a small fraction of the total number of particles, the values of $\mathscr{E}/n_a$ required for a relatively high T_e increases substantially.

In a medium of polar molecules the predominant loss is that due to rotational excitation,

$$S_r = \hbar\omega_r n_e n_m \frac{4\pi}{3}\left(\frac{ed}{\hbar}\right)^2 \sqrt{\frac{m}{T_e}} \ln\left(\frac{T_e}{\hbar\omega_r}\right)(T_e - T_r); \quad (2.5)$$

here $\hbar\omega_r$ is the rotational quantum, and d is the dipole moment of the molecule. For a significant difference between the electron temperature and the rotational temperature, say $T_e = 2T_r$ in water vapor we would need an extremely high field, $\mathscr{E}/n_a = 3 \cdot 10^{-16} V \cdot \text{cm}^2$.

B. Condition for an equilibrium distribution with respect to excited states and for equilibrium ionization

The generation of charged particles by ionizing irradiation or the escape of these particles from the plasma directly affects the degree of ionization and indirectly affects the distribution with respect to excited states. The line emission affects the excited state populations and indirectly affects the degree of ionization. The reason for the mutual relationship is that excited atoms represent the primary source of electrons over a broad range of conditions (the ionization energy falls off toward the boundary of the discrete spectrum, while the cross section, in contrast, increases). Correspondingly, recombination occurs primarily to excited states.

Equilibrium conditions are easily derived by using a simplified kinetic model which incorporates only transitions between adjacent levels (the "single-quantum approximation"). It should be noted that when charged particles are produced in the plasma by external irradiation or when these particles escape from the plasma, the ionization and recombination do not cancel out. A flux thus arises in the energy space of the atom. For example, if charges diffuse to the plasma boundaries and are neutralized there, ionization will be faster than recombination in the plasma volume. The energy-space flux, j, is directed from the ground state toward the continuum.

In the single-quantum approximation, we can write the following equation for the steady state:

$$j = n_k w_{k,k+1} - n_{k+1}(w_{k+1,k} + A^*_{k+1,k}), \quad (2.6)$$

where $w_{k,k+1}$ and $w_{k+1,k}$ are the probabilities for the collisional transitions $k \rightleftarrows k+1$, and n_k and n_{k+1} are the level populations. To study the deviation from equilibrium it is convenient to introduce the relative population $y_k = n_k/n_k^0$, where n_k^0 is the equilibrium population of level k. Then using the relation between $w_{k,k+1}$ and $w_{k+1,k}$ which follows from the principle of detailed balance, we find

$$y_k - y_{k+1}\left(1 + \frac{A^*_{k+1,k}}{w_{k+1,k}}\right) = \frac{j}{n_k^0 w_{k,k+1}}. \quad (2.7)$$

Let us assume that the emission of radiation is the sole reason for a deviation from equilibrium. Then if we ignore external sources of excited atoms, e.g., the diffusion of excited atoms toward the plasma boundaries,[1)] the flux between any pair of levels vanishes ($j = 0$). Then from (2.7) we easily find the condition for the relative equilibrium of two adjacent levels ($y_k = y_{k+1}$):

$$\frac{A^*_{k+1,k}}{w_{k+1,k}} \ll 1. \quad (2.8)$$

The probabilities for radiative transitions fall off rapidly toward the boundary of the discrete spectrum, while the probabilities for collisional processes increase (the oscillator strength decreases $\sim k^{-3}$, while w increases $\sim k^4$). Then even at low electron densities there is always a group of upper levels which are at relative equilibrium with each other and simultaneously with the continuum. As n_e increases, this equilibrium-distribution region shifts downward, toward the ground state. If there is a level near the ground level for the given atom, the populations of these levels may be at equilibrium at relatively low values of n_e. Then condition (2.8) must be written for only a few levels, separated by the largest energy intervals.

Griem[1] has studied how the emission of radiation affects the distribution with respect to excited states in a hydrogen plasma. He assumed that the plasma volume was optically thin and that the electrons have a Maxwell distribution, and he used the Bethe-Born approximation for the cross sections for collisional transitions. He found the same condition as in (2.8), but in the form of an inequality, whose satisfaction guarantees an equilibrium between state k and the higher-lying states with-within an error of 10%:

$$n_e \geqslant 7.4 \cdot 10^{18} \frac{1}{k^{17/2}} \sqrt{\frac{T_e}{\text{Ry}}}\ (\text{cm}^{-3}). \quad (2.9)$$

Figure 2 shows the results calculated for n_e from Eq. (2.9) as a function of T_e. Also shown here are the corresponding results reported by Drawin,[2] who used slightly different cross sections.

Condition (2.8) and its modification in (2.9) were derived in the single-quantum approximation. To be rigorous, we would have to take all possible transitions into account. This approach would lead to a system of equations relating the populations of all the atomic energy levels. For given values of the electron density, the numerical solution of this system of equations leads to the excited state populations, so that it is possible to single out the levels which are at relative equilibrium. Figure 2 shows the values found for n_e in this manner; within 10%, these values lead to the relative equilibrium of the group of levels above the given lev-

[1)] This effect is usually negligible occurring only in the immediate vicinity of the boundaries. The corresponding condition is easily derived by comparing the scale times for diffusion and electron-impact decay. These questions are taken up in Subsection 2a.

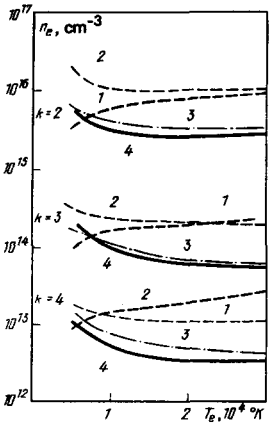

FIG. 2. The electron density which leads to equilibrium within a 10% error, plotted as a function of T_e for various states k. 1) According to Griem[1]; 2) according to Drawin[2]; 3) according to the criterion of the present paper; 4) numerical calculation.

el. The results differ noticeably from those of Griem and Drawin.

Condition (2.8) can be refined by using a modified diffusion approximation.[16] In this approximation, the motion of a bound electron among excited states is treated as a diffusion process in a discrete energy space. It is assumed that among the various w_{kn} the probabilities for single-quantum transitions, $w_{k,k+1}$, are predominant. Then effective transition probabilities $z_{k,k\pm1}$ are introduced; these effective probabilities reflect the probabilities $w_{k,k\pm1}$ exactly and the probabilities $w_{k,k\pm2}$, $w_{k,k\pm3}$, etc., approximately. As a result, the following equations are found for $z_{k,k+1}$:

$$z_{k,k+1}=n_e\frac{4\sqrt{2\pi}e^4\Lambda_k E_k}{(E_k-E_{k+1})(E_{k-1}-E_{k+1})\sqrt{mT_e}}\exp\left(-\frac{E_k-E_{k+1}}{T_e}\right). \quad (2.10)$$

In the particular case $k=1$,

$$z_{12}=n_e\frac{4\sqrt{2\pi}e^4\Lambda_1}{(E_1-E_2)\sqrt{mT_e}}\exp\left(-\frac{E_1-E_2}{T_e}\right). \quad (2.11)$$

The Λ_k reflect the particular structure features of the various atoms. They can be described by the universal curve in Fig. 3. The effective probabilities for the direct and inverse processes are related by

$$n_k^0 z_{k,k+1}=n_{k+1}^0 z_{k+1,k}.$$

If we use the effective transition probabilities in (2.8), and if we determine the critical values of n_e, we can improve the agreement with the results of the numerical solution of the balance equations (Fig. 2).

The curves in Fig. 2 hold for an optically thin plasma, $A_{kn}^*=A_{kn}$. Reabsorption moves the plasma toward equilibrium. The most stringent criterion, corresponding

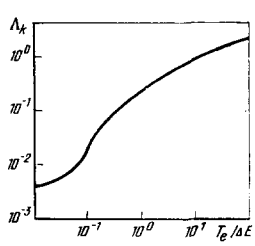

FIG. 3. Variation of Λ_k with $T_e/\Delta E_k(\Delta E_k=E_k-E_{k+1})$.

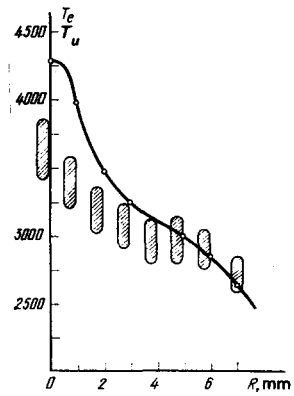

FIG. 4. Radial profiles of the electron temperature T_e (solid curve) and the temperature of the population of the potassium resonant level,[20] T_u. The hatched regions show the scatter in the experimental values of T_u.

to equilibrium with the ground state, becomes less stringent with decreasing Θ_{21}, which can be extremely small. The value of this factor, however, varies with the coordinates. Near the boundary, Θ may differ little from unity. In the central part of a sufficiently large volume, Θ can be much smaller than unity. In this case, the central part of the plasma is near equilibrium even if collisional processes are relatively inefficient.

The range over which the Boltzmann distribution holds was studied experimentally in Refs. 17 and 18. In the plasma of an inert gas with an admixture of readily ionized cesium, a local equilibrium obtains for electron densities $n_e \gtrsim 10^{14}$ cm^{-3}.

Radiative decay usually reduces the density of excited atoms, but a qualitatively different picture can arise if there are large temperature gradients in the plasma.

The radiation emitted from the hot parts of an arc and absorbed in the peripheral regions increases the density of excited atoms. Under certain conditions, the local density of excited atoms can be higher than the equilibrium value. This question was studied by Lagar'kov.[19] He introduced a factor Θ which has the same meaning as above for the hot regions but can become negative for cold regions. Negative values result when the density is above the local equilibrium value. Condition (2.8) becomes $A_{21}|\Theta_{21}|/w_{21}\ll 1$. Particular equations for these generalized quantities Θ are given in Ref. 19.

Figure 4 shows the radial profiles of the temperature T_e and the temperature of the population of the resonant level,[2)] T_u, for the experimental conditions of Ref. 20, where an arc was studied in argon with a potassium admixture at atmospheric pressure. For the central region we have the usual situation: Radiation losses reduce the density of excited atoms (in accordance with the value of Θ). We thus have $T_u<T_e$, so the level population is below the Boltzmann value. At the pe-

[2)] The temperature of the population of level k is determined from the formal equation $n_k/n_1=g_k/g_1\exp(-E_1-E_k)/T_u$. At equilibrium, we would have $T_u=T_e$.

riphery, the situation is different; here there is a tendency toward $T_u > T_e$.

How does the emission of radiation affect the degree of ionization? It was mentioned above that there are essentially always levels near the continuum which are at relative equilibrium with free electrons. The electrons in equilibrium with the upper excited levels may (along with these levels) not be at equilibrium with the ground state. We can find a quantitative measure of the deviation from equilibrium ionization by writing (2.7) for all the levels. Assuming $j = 0$ as before, we find a chain of equations, from which we easily find

$$y_1 = y_e^2 \Pi_1,$$

where

$$\Pi_1 = \left(1 + \frac{A_{21}^*}{w_{21}}\right)\left(1 + \frac{A_{32}^*}{w_{32}}\right)\cdots \qquad (2.12)$$

The last factor in (2.12) contains the ratio of the probabilities for radiative and three-body recombination, which takes into account the effect of radiation emitted in the continuum. This factor usually becomes equal to unity before the corresponding factors for transitions between levels near the continuum. For equilibrium ($y_1 \approx y_e^2$) we must obviously have $\Pi_1 \approx 1$ or

$$\Pi_1 - 1 \ll 1. \qquad (2.13)$$

In other words, we must have $A_{21}^*/w_{21} \ll 1, A_{32}^*/w_{32} \ll 1$, etc., in agreement with (2.8). In the modified diffusion approximation, $w_{k+1,k}$ should be replaced by $z_{k+1,k}$. In calculating Π_1 it is usually sufficient to take into account only a few factors, since $A_{k+1,k}^*/w_{k+1,k}$ falls off rapidly with increasing k, as mentioned above. We can determine the boundary between the group of upper levels which are in relative equilibrium and the other levels, which are moved away from equilibrium by the emission of radiation. The energy of the boundary level is found from

$$E_r = \left(\frac{n_e}{4.5 \cdot 10^{13}}\right)^{1/4} T_e^{-1/8} \text{ (eV)}, \qquad (2.14)$$

which will be derived in Subsection 3a below. In (2.14), E_r and T_e are in electron volts.

Let us now assume that free charges are being produced by irradiation or by the escape of charged particles from the interior of the plasma; then the flux is $j \neq 0$. In the steady state, writing the charged-particle balance, we find

$$j = n_e n_1 \beta - n_e^3 \alpha, \qquad (2.15)$$

where β and α are the coefficients for collisional-radiative ionization and for recombination. These coefficients are studied in detail in Ref. 16; at this point we simply note that each reflects the conditions for the emission of radiation. These coefficients are related by

$$\beta \Pi_1 = \alpha K_1, \qquad (2.16)$$

where K_1 is the ionizational-equilibrium constant, written for the ground state, $K_1 = (n_e^0)^2/n_1^0$. From (2.15) and (2.16) we find an estimate of the degree of ionization and a condition for proximity to ionizational equilibrium. The result is conveniently written in the two versions

$$\frac{y_1}{y_e^2} = \Pi_1 \left(1 + \frac{j}{n_e^3 \alpha}\right), \qquad (2.17)$$

$$\frac{y_1}{y_e^2} = \frac{\Pi_1}{1 - (j/n_1 n_e \beta)}. \qquad (2.18)$$

The flux j is easily estimated. If it is caused by irradiation, then it is determined by the radiation intensity. If, on the other hand, the diffusion of charges is the governing factor, then we have $j \approx n_e/\tau_D$, where τ_D is the diffusion scale time, which can be expressed in terms of the ambipolar diffusion coefficient. Then $j/n_e^3\alpha = 1/\tau_D n_e^2 \alpha$ is the raio of the recombination and diffusion scale times.

Gridneva and Kasabov[17] have studied an arc in argon with a cesium admixture (argon pressure $p \sim 0.1$ atm, $T_e \approx 3100$ °K, $n_{Cs} \approx 1.6 \cdot 10^{13}$ cm^{-3}, and $T \approx 1000$ °K). The cesium ionization coefficient under these conditions is $\beta \approx 2 \cdot 10^{-10}$ cm$^{-3} \cdot$ sec^{-1}. The ratio of the diffusion scale time $\tau_D^{-1} \approx 6D/R^2$ ($D_a \approx 300$ cm^2/sec, $R = 0.8$ cm) to the ionization time, $1/n_{Cs}\beta n_D = 0.9$ indicates that diffusion is important and that this mixture deviates from ionizational equilibrium.

The conditions for proximity to an ionizational equilibrium have been used to determine the plasma characteristics suitable for the working medium of closed-cycle MHD generators (an argon plasma with a potassium admixture). Figure 5, from Ref. 12, shows lines above which the Saha equation holds within 10%. Below the lines, the Saha equation and the two-temperature approximation break down. The deviation from ionizational equilibrium is affected by both radiation and the escape of particles to the wall. Diffusion is the primary reason for the deviation from equilibrium at low pressures, in small plasma volumes, and at low temperatures, $T_e < 2400$ °K. At higher temperatures, radiation losses become more important.

External factors affecting the electron density indirectly affect the excited state distribution. It follows from (2.7) that with $j \neq 0$ we have $y_k \neq y_{k+1}$, even if no radiation is emitted ($A_{k+1,k}^* \neq 0$). This is a completely plausible result, since for a flux j to exist in the en-

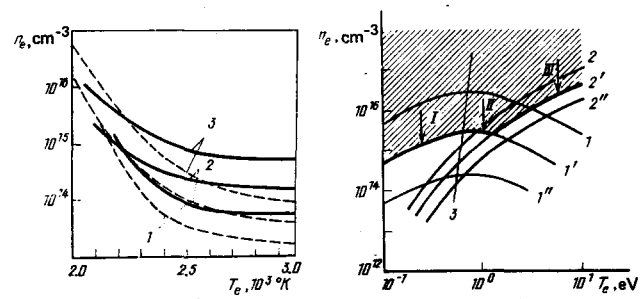

FIG. 5. a: Curves on the n_e, T_e plane which lead to satisfaction (within 10%) of the Saha equation.[12] Solid curves) Ar—K plasma; dashed) He—Cs plasma; 1) $p = 0.1$ atm, $R = 1$ cm; 2) $p = 1$, $R = 10$; 3) $p = 10$, $R = 10$. b: Region in which an equilibrium occurs in a hydrogen plasma. 1, 1′, 1″) Constant values of $A_{21}\Theta/z_{21} = 1$. 1) $\Theta = 1$; 1′) $\Theta = 0.1$; 1″) $\Theta = 0.01$; 2, 2′, 2″) constant values of $n_e^2 \alpha \tau_D = 1$; 2) $\tau_D = 10^{-4}$; 2′) $\tau_D = 10^{-3}$ sec; 2″) $\tau_D = 10^{-2}$ sec; 3) $c = 1$. The hatched region corresponds to an equilibrium plasma with $\Theta = 0.1$ and $\tau_D = 10^{-3}$ sec.

ergy space of the atom the state distribution must deviate from equilibrium. The quantity $n_k^0 w_{k,k+1}$ in the denominator on the right side of (2.7) is very sensitive to the position of level k. As k increases, n_k^0 decreases in accordance with a Boltzmann distribution; $w_{k,k+1}$ increases, at first slowly and then extremely rapidly. As a result, $n_k^0 w_{k,k+1}$ has a minimum. Small values of $n_k^0 w_{k,k+1}$ correspond to the largest values of the difference $y_k - y_{k+1}$, i.e., to the greatest deviations from equilibrium in the level distribution. This region forms a "bottleneck" impeding the flux j in the energy space of the atom.[31]

As shown below, the position of this bottleneck is related to the electron temperature and is approximately equal to $3T_e/2$. As T_e decreases, the bottleneck shifts toward highly excited states. At high values of T_e, it may be in the energy range between the ground and first excited states. Then the populations of all the excited states will correspond approximately to a relative equilibrium with a state in the continuum. In other words, the density of excited atoms will be given by the Saha equation with T_e. There is, however, no equilibrium between the ground and excited states. In this case we would say that the excited states form a "block."

C. Conditiion for nonMaxwellian distribution

Deviations from an equilibrium energy-level distribution of atoms correlate with deviations from an equilibrium electron energy distribution. Electrons lose energy in the course of excitation and ionization. If there is a Boltzmann distribution with respect to excited states, fast electron losses are offset by inverse processes, by detailed balance. If the system is not at equilibrium, there may be a nonequilibrium distribution. Deviations from a Maxwell distribution arise primarily in the tail of the electron energy distribution $f(\varepsilon)$ and peak at[3] $\varepsilon \geq E_1 - E_2$.

The frequency of the inelastic collisions experienced by an electron with an energy $\varepsilon = E_1 - E_2$ is $(n_1/n_e) z_{12}(\varepsilon = E_1 - E_2) = 4\pi e^4 \Lambda_1 n_1 / \sqrt{2m}\,(E_1 - E_2)^{3/2}$ (see Subsection 2b for more details). The corresponding frequency of elastic collisions, which tend to restore the Maxwell distribution, is $\nu_{ee}(\varepsilon = E_1 - E_2) = 2\pi e^4 \lambda n_e / \sqrt{2m(E_1 - E_2)}\, T_e$. For a Maxwell distribution to be maintained, the ratio of these frequencies must be small:

$$c = \frac{n_1 z_{12}}{n_e \nu_{ee}} = \frac{2n_1}{n_e} \frac{T_e}{E_1 - E_2} \frac{\Lambda_1}{\lambda} \ll 1. \qquad (2.19)$$

Under typical conditions, with $T_e \approx 1$ eV, the Coulomb logarithms for elastic and inelastic collisions are $\lambda \approx 10$ and $\Lambda_1 \approx 0.01 - 0.05$. Inequality (2.19) implies a Maxwell distribution when the degree of ionization is such that

$$\frac{n_e}{n_1} \geqslant 10^{-4} - 10^{-6}.$$

Cool and Zukoski,[32] for example, have studied the ionization of potassium for an original electron density $n_e = 5 \cdot 10^{-12}$ cm^{-3}, $n_1 = 1.4 \cdot 10^{16}$ cm^{-3}, and $T_e \approx 3000$ °K. Under these conditions, $c \approx 3$. As n_e increases, c decreases significantly.

If $c \gg 1$, the frequency of 1 – 2 collisions is given directly by the frequency of elastic collisions which move electrons from the subthreshold energy range $\varepsilon < E_1 - E_2$ to the region of the threshold, $\varepsilon = E_1 - E_2$. We thus have a modification of condition (2.8), which shows how the emission of radiation affects the plasma state. Specifically, this condition becomes more stringent,

$$\frac{A_{21}^* c}{z_{21}} \ll 1. \qquad (2.20)$$

In this condition, it is the square, rather than the first power, of the electron density which appears in the denominator.

At lower degrees of ionization, with $T_e \neq T$, a nonequilibrium distribution $f(\varepsilon)$ is caused by elastic collisions of electrons with atoms. We thus have the inequality

$$\frac{n_e}{n_1} \gg \frac{m}{M} \frac{\sigma_{ea}}{\sigma_{ee}}, \qquad (2.21)$$

where σ_{ea}/σ_{ee} is the ratio of the cross sections for electron-atom and electron-electron collisions when the electron energy is equal to ε. Inequality (2.21) usually holds for $n_e/n_1 \gtrsim 10^{-7} - 10^{-8}$.

The influence of strong external fields on $f(\varepsilon)$ has been studied, in Refs. 3 and 33, for example.

We have thus examined the basic conditions for a deviation from thermodynamic equilibrium in a plasma. In order to determine the roles played by the various factors responsible for a deviation from equilibrium, we show in Fig. 5, in a plot of n_e vs T_e, curves of constant values of $A_{21}\Theta_{21}/z_{21} = 1$ for a hydrogen plasma in equilibrium (as regards T_e). Curve 1 corresponds to $\Theta = 1$, while curves 1′ and 1″ correspond to $\Theta = 0.1$ and 0.01. The region above these lines evidently corresponds to a plasma in the two-temperature regime if there are no other factors to cause a deviation from it. Below the line $A_{21}\Theta_{21}/Z_{21} = 1$, the equilibrium is disrupted by the emission of radiation. Also shown in this figure are lines of constant $n_e^2 \alpha \tau_D = 1$ (curves 2, 2′, and 2″), which reflect the role of diffusion. For values of n_e and T_e below these curves, the equilibrium is disrupted by the diffusion of charged particles to the walls. Curves 2, 2′, and 2″ are plotted for $\tau_D = 10^{-4}, 10^{-3}, 10^{-2}$ sec, respectively. Finally, curve 3 determines where deviations from a Maxwell electron distribution, $c = 1$, can occur. To the left of curve 3 we have $c > 1$.

Then for $\tau_D = 10^{-3}$ sec and $\Theta = 0.1$, for example, the hatched region in Fig. 5b corresponds to a two-temperature plasma. If n_e is reduced, for example, along arrow I, the deviation from equilibrium is caused by the emission of radiation. In this case the distribution of atoms deviates from a Boltzmann distribution, and there is also a deviation from a Maxwell electron energy distribution. If we move along arrow II, i.e., at a higher value of T_e, the factor primarily responsible for the deviation from equilibrium is the same, but the electron energy distribution remains at equilibrium (for T_e). If we move along arrow III, the deviation from equilibrium is caused by the diffusion of charged particles to the plasma boundaries.

3. PLASMA IN A NONEQUILIBRIUM STATE OF IONIZATION

The criteria given in the preceding section do no more than state that there is a deviation from equilibrium. We turn now to the problem of finding a description of the nonequilibrium state.

A. Populations of the excited states

To analyze the distribution of atoms with respect to excited states it is convenient to examine how $\ln(n_k/g_k)$ varies with the binding energy, using curves drawn through the points which correspond to the real atomic levels. At equilibrium this curve would be a straight line with a slope depending on the temperature T_e (Fig. 6). This line can be continued into the region of continuum states by constructing $\ln[n(\varepsilon)/g(\varepsilon)]$, where $n(\varepsilon)$ is the density of electrons at energy ε, and $g(\varepsilon)$ is their statistical weight. Let us assume that for some reason the electron density in the plasma falls below the equilibrium value (at this point we will simply assume that the free electrons continue to be described by a Maxwell distribution). Then the part of the line in Fig. 6 corresponding to free electrons shifts downward. The distribution of atoms with respect to excited states becomes distorted, and it can no longer be described by a single temperature. We thus have an ionizational deviation from equilibrium, $y_e < y_1$.

When there is an electron excess, $y_e > y_1$, the deviation from equilibrium is associated with recombination, and the distribution of atoms with respect to excited states becomes deformed as shown in Fig. 6. We see from Fig. 6 that there is a certain group of states (II) which is far from equilibrium and within which there may be a quasi-Boltzmann distribution [$\ln(n_k/g_k)$ for these states conforms approximately to a straight line] with some temperature T_p. This temperature is not equal to the electron temperature; for recombination we would have $T_p > T_e$, while for ionization we would have $T_p < T_e$.

Figure 7 shows experimental values of the density of excited cesium atoms, found in Ref. 20 for various electron densities. Table I shows the basic characteristics of the cesium plasma under these conditions. In Ref. 22 the electron temperature was determined from the intensity of the recombination continuum.

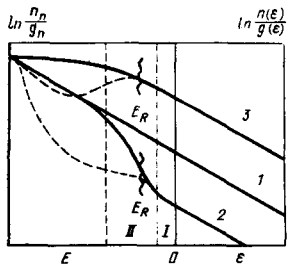

FIG. 6. Diagram showing the characteristic distributions of atoms with respect to excited states. 1) Equilibrium case (the slope of the line corresponds to T_e; 2) ionization; 3) recombination. The dashed curves reflect the influence of radiative processes. I) Group of excited states at relative equilibrium with the continuum; II) group of nonequilibrium states.

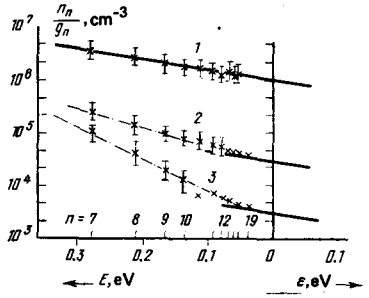

FIG. 7. Variation of the populations of the cesium F levels with the binding energy for various values of n_e (Ref. 22). 1) $n_e = 2.3 \cdot 10^{13}$ cm^{-3}; 2) $n_e = 4 \cdot 10^{12}$; 3) $n_e = 1.2 \cdot 10^{12}$. Crosses) Experimental data; solid lines) equilibrium according to the Saha equation with T_e; dot-dashed lines) distribution with T_p.

The solid lines are the equilibrium distributions associated with T_e; the dot-dashed lines are drawn through the experimental points and correspond to T_p. It can be seen from Fig. 7 that with $n_e = 2.3 \cdot 10^{13}$ cm^{-3} the excited states with $n = 7 - 19$ are in equilibrium with the continuum. As n_e decreases, T_e only charges slightly, according to Table I. Here T_p begins to be quite different from T_e, however, and the excited state populations do not conform to the straight line which corresponds to T_e. Here we are dealing with a level distribution of atoms which is characteristic of an ionizational deviation from equilibrium, with $T_e > T_p$ (curve 2 in Fig. 6).

The populations of excited states have been measured by many investigators; see Refs. 8, 17, and 22–30, for example.

In the theory, the level populations are determined from the system of balance kinetic equations written for each of the excited states; all possible elementary processes which populate or depopulate the given level are taken into account. Depending on the particular formulation of the problem, this system of equations may be supplemented with a kinetic equation for the electron distribution, a balance equation for the number of electrons, or energy-conservation equations.

Bates *et al.*[34-37] solved the system of kinetic equations for the population numerically assuming a given electron density, a given electron temperature, and a Maxwell energy distribution. Since their work, numerical methods have been widely adopted for solving the balance equations.[38-41]

The calculations of the excited-state populations carried out by various workers span an extremely broad range of electron temperatures and densities. These calculations are particularly valuable when accurate values are required for particular level populations. On the other hand, numerical methods have certain

TABLE I.

n_{Cs}, cm^{-3}	$n_e \cdot 10^{12}$, cm^{-3}	T_e, °K	T_p, °K
10^{13}	2.3	2320	2350
10^{13}	4.0	2270	1320
10^{13}	1.2	2380	730

limitations. For example, the results are in the form of tables. A more realistic formulation of the problem (which would, say, incorporate the relationships among the level distribution, the degree of ionization, and the electron energy distribution) would convert the balance equations into a nonlinear system. The shortcomings of the numerical methods become painfully clear when the plasma is simply one element of a composite system, and the description of the plasma state is only part of a more general problem. As a result, approximate analytic methods have been adopted widely on the basis of a variety of models which simplify the original system of equations (see the review in Ref. 16). The results found by the numerical methods can furnish a reliable test for various approximations.

The most successful approach has exploited the analogy between the motion of an electron among energy levels and the random walk of a Brownian particle. This "diffusion" approach has been pursued intensely beginning with papers by Belyaev, Budker, Pitaevskiĭ, Burevich, Smirnov, *et al.*[42-49] The analogy with diffusion becomes more obvious when we note that the transition probability of a bound electron in collisions with a free electron is proportional to $(E_k - E_n)^{-4}$, where E_k and E_n are the energies of the initial and final states, respectively. This implies that, averaged over several collisions, the energy of the electron changes by a comparatively small amount, and the system of balance kinetic equations can be replaced by a Fokker-Planck diffusion equation, whose solution gives the desired population distribution. Thus the energy spectrum is assumed to be continuous. This approach is evidently justified for highly excited states, for which the energy spectrum has closely spaced states. For the low-lying excited states, on the other hand, where the energy separations are large, this approach can hardly be used.

A theory combining the discreteness of real atomic energy levels and the basic principles of the diffusion approximation—the modified diffusion approximation—requires writing the diffusion equation in finite differences.[16] This approach has substantially extended the applicability of the diffusion method, making it useful for real plasmas of various compositions. This modified diffusion approximation can also incorporate radiative processes, and it ultimately yields analytic expressions for the ionization and recombination coefficients and the level populations.[16]

Results formally similar to those found through the modified diffusion approximation can be found by using the single-quantum approximation, discussed in Subsection 2b. We solve a chain of equations like (2.7), assuming that the boundary values y_1, y_e, and y^+ are known and that the flux j is constant. The result is conveniently written

$$j = \frac{(y_1/\Pi_1) - y_e y^+}{R_{1e}} = \frac{(y_2/\Pi_2) - y_e y^+}{R_{2e}} = \ldots = \frac{(y_k/\Pi_k) - y_e y^+}{R_{ke}}, \quad (3.1)$$

$$\frac{y_k}{\Pi_k} = \frac{(y_1/\Pi_1) R_{ke} + y_e y^+ R_{1k}}{R_{1e}}, \quad (3.2)$$

$$R_{k,k+1} = (n_k^2 w_{k,k+1} \Pi_k)^{-1}, \quad R_{ke} = \sum_{n \geqslant k} R_{n,n+1}, \quad R_{1e} = \sum_{k \geqslant 1} R_{k,k+1}. \quad (3.3)$$

The factors Π_k are defined by analogy with (2.12). The solution found in the modified diffusion approximation has the same form as (3.1)–(3.3), but $w_{k,k+1}$ should be replaced by $z_{k,k+1}$, and in the equation for Π_k in (2.12) we should replace $A^*_{k+1,k}$ by $\alpha^R_{k+1} = \sum_{n \geqslant k+1} \sum_{l<k} A^*_{nl}$ (Ref. 16).

The solution of system (2.7) written in the form in (3.1)–(3.3) can be interpreted by analogy with the current flow along a chain of series-connected resistances $R_{k,k+1}$ between junctions k and $k+1$ (Fig. 8). The potential of each junction corresponds to y_k/Π_k. The resistance between each pair of junctions n and m is $R_{nm} = \sum_{k=n}^{m-1} R_{k,k+1}$. The current in each circuit is equal to the potential difference between the extreme points, $y_1/\Pi_1 - y_e y^+$, divided by the total resistance $R_{1e} = R_{12} + R_{23} + \ldots$, as written in (3.1). Equation (3.2) determines the potential for an arbitrary junction k in terms of the potentials at the ends of the chain. The case $j = 0$ corresponds to equal potentials at all junctions:

$$\frac{y_1}{\Pi_1} = \frac{y_2}{\Pi_2} = \ldots = \frac{y_k}{\Pi_k} = \ldots = y_e y^+. \quad (3.4)$$

If $k < m$, then $\Pi_k \geqslant \Pi_m$. The flux is thus zero when the relative populations y_k fall off with increasing k. The overall distribution is not in equilibrium. Equilibrium obtains if all the factors Π_k are equal to unity, i.e., if radiative processes are suppressed by collisional processes. If $\Pi_k \gg 1$, excitation and ionization result from collisional processes, while the decay of excited states and recombination result primarily from radiative processes. A steady nonequilibrium state of this type is called a "coronal equilibrium."[50]

If, for some reason, $y_e y^+$ falls below the value determined by (3.4), a flux $j > 0$ appears; this corresponds to ionization conditions. Recombination conditions ($j < 0$) arise if $y_e y^+$ exceeds the value determined by (3.4), since the condition $y_e y^+ > y_1/\Pi_1$ is sufficient for recombination. At a sufficiently high value of Π_1, recombination can occur provided $y_e y^+ < y_1$, i.e., in a plasma which is underionized with respect to the equilibrium with T_e.

Equations (3.1)–(3.3) can be used to calculate the excited state population during collisional and radiative processes for an energy spectrum with a discrete multilevel structure. Where necessary, several additional processes can be incorporated in the flux equation in (3.1): radiative recombination[16] and heavy-particle collisions. Some particular examples of this latter case are discussed in Section 5.

It can be seen from the structure of (3.1)–(3.3) that finding the populations reduces to a calculation of the resistance R and the factors Π. The resistance is the sum of the resistances of the various parts. The discreteness of the system is most important for transitions between low-lying atomic states, where the relative energy separations are comparatively large. For

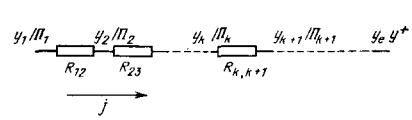

FIG. 8. Equivalent circuit.

highly excited states, there is more justification in transforming to an approximately continuous variation of the electron energy.

This transformation can be made by writing a differential analog of the finite-difference equation in (2.7). It can be shown that the solution of the resulting differential equation, with the boundary conditions $y(E)\big|_{E=E_1} = y_1$ and $y(E)\big|_{E\to 0} = y_e y^+$, can also be written in the form of Eqs. (3.1)–(3.3), but with the factors Π calculated from

$$\Pi_k = \Pi(E) = \exp\left[\int_0^E dE \frac{\alpha^R(E)}{B(E)}\right], \tag{3.5}$$

and with the resistance R calculated from

$$R_{km} = R(E_m, E_k) = \int_{E_m}^{E_k} \frac{dE}{n^0(E)B(E)\Pi(E)}, \quad E_m < E_k. \tag{3.6}$$

In (3.5) and (3.6), $n^0(E)$ is the equilibrium density of atoms per unit energy, $n^0(E) = n_k^0 dk/dE$; and

$$\frac{1}{2}B(E) = \frac{2\sqrt{2\pi}e^4 n_e E\Lambda}{\sqrt{mT_e}} \tag{3.7}$$

is the diffusion coefficient in energy space for a bound electron.[43] This coefficient is related to the effective probabilities $z_{k,k+1}$ by $z_{k,k+1}(E_k - E_{k+1})^2 \to \frac{1}{2}B(E_k)$ in the limit $E_k - E_{k+1}$, and $\alpha^R(E) = \alpha_k^R(dE/dk)$ is the probability for a change in the energy of the bound electron due to emission. Equations (3.5) and (3.6) can be used to derive simple equations for Π and R, which can in turn be used to establish important relations.

The role played by emission is reflected by the factors $\Pi(E)$. How do these factors vary with the energy? Calculations of $\alpha^R(E)$ for various elements show that this quantity can be approximated by the simple equation $\alpha^R(E) = (6-8)\cdot 10^{10}E^4/Ry^3$. Substituting this expression into (3.5), and using (3.7) for $B(E)$, we find

$$\Pi(E) = \exp\left(\frac{0.2E^4}{E_r^4}\right), \tag{3.8}$$

where the characteristic value E_r is determined by (2.14). If $E > E_r$, then $\Pi(E) \gg 1$, while if $E < E_r$ then $\Pi(E) \approx 1$.

When a flux is present, the population distribution depends on the resistance R. The contribution to the resistance from the energy interval dE is proportional to the integrand in (3.6). This function is not monotonic. Its maximum, determined from

$$\frac{3}{2} = \frac{E}{T_e} + \left(\frac{E}{E_r}\right)^4, \tag{3.9}$$

corresponds to a bottleneck: the energy interval which presents the greatest resistance to the current. If $E_r > 3T_e/2$, the second term on the right of (3.9) can be ignored, and the location of the bottleneck is determined from $E = 3T_e/2$ (Subsection 2b). When $T_e < E_r$, on the other hand, the bottleneck is at $E \approx E_r$.

For the part of the spectrum $E < E_r$ radiation is unimportant, and we have $\Pi(E) = 1$. Then $R(0, E) \approx \chi(0; E/T_e)$, where

$$\chi(x) = \frac{4}{3\sqrt{\pi}}\int_0^x t^{3/2}e^{-t}\,dt \tag{3.10}$$

is a function tabulated in Ref. 51. If $x \gg 1$ we have $\chi(x) = 1 - 4e^{-x}/3\sqrt{\pi}x^{3/2}$, while if $x \ll 1$ we have $x \ll 1\chi(x) \approx 8/15\sqrt{\pi}x^{5/2}$. Let us now assume that radiative processes have an important effect on the level populations when a flux is present. Clearly, these processes would usually couple the populations of different levels, retard ionization, and accelerate recombination. The dashed curve in Fig. 6 shows the possible behavior of the populations when radiative processes are taken into account. The position of the level E_r in (2.14) is important when we analyze the role played by radiation. If E_r is below the bottleneck, radiation does not affect its position, but in the opposite case the bottleneck actually moves upward and is determined by E_r. In these cases, the radiation significantly depopulates the highly excited states also. It can be seen from the structure of Eq. (3.6) that the factor $\Pi(E)$ exponentially "cuts out" the contribution of a state with $E > E_r$, so that we have $R(0, E) \approx R(0, E_r)$ for $E > E_r$. The resistances themselves in the region $E > E_r$ are exponentially small, and this region presents only a low resistance to the current, so that there is a negligible "potential drop" y/Π. The analysis here becomes similar to that for the case $y/\Pi = \text{const}$.

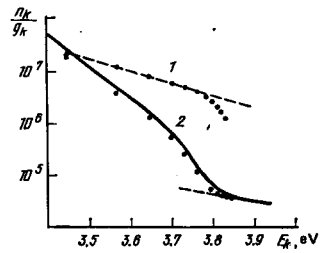

FIG. 9. Population distribution of the highly excited states of cesium atoms. The experimental points are from Ref. 29. 1) $n_e = 4.0\cdot 10^{13}$ cm^{-3}, $n_a = 1.1\cdot 10^{15}$ cm^{-3}, $T_e = 2250$ °K; 2) $n_e = 6.5\cdot 10^{12}$, $n_a = 1.2\cdot 10^{14}$ cm^{-3}, $T_e = 3850$ °K; dashed lines) distributions with T_e; solid curve) calculation according to the modified diffusion approximation for conditions 2.

The level distributions of the atoms predicted by the theory have been compared with experimental data for plasmas of various compositions over a broad range of conditions: $n_e \approx 10^{11} - 10^{17}$ cm^{-3}, $T_e \approx 1000 - 100\,000$ °K. The results obtained before 1975 are summarized in Ref. 53. Figure 9 illustrates the situation with a comparison of the calculated distributions and the results of recent cesium discharge experiments.[29]

The experimental points of group 1 in Fig. 9 were obtained for $n_e = 1.2\cdot 10^{14}$ cm^{-3} and correspond to an equilibrium plasma. In this case the quantity $\ln(n_k/g_k)$ conforms to a straight line with a slope determined by[3)] $T_e = 3850$ °K. At lower values of n_e there are deviations from equilibrium. For $n_e = 6.5\cdot 10^{12}$ cm^{-3} and $T_e = 3850$ °K, for example, the population distribution has the form typical of ionization: The highest levels are in equilibrium with the continuum, and the distribution has an inflection point near the bottleneck. Figure 9 shows the calculated curve.[4)] These calculations were

[3)] The deviation of $\ln(n_k/g_k)$ from a straight line for the highest levels is due to the experimental errors in the measurement of the intensities of the greatly broadened lines.[54]

[4)] This calculation was carried out by G. V. Naĭdis.

carried out using Eq. (3.2) and incorporate strong reabsorption of the resonant radiation. The calculated curve conforms well to the experimental curve.

With simple expressions for the resistances it is possible to derive an approximate equation for the distribution of excited atoms. For high electron densities, for example, all the factors Π are equal to unity, and the excitation kinetics is governed by collisions with electrons. Then substituting Eq. (3.6) for R into (3.2), using (3.10), and setting $\chi(E_1/T_e)\approx 1$, we find[52]

$$y_k = y_i\chi\left(\frac{E_k}{T_e}\right) + y_e y^+\left[1-\chi\left(\frac{E_k}{T_e}\right)\right]. \qquad (3.11)$$

It follows from (3.11) that a plot of y_k against E_k has an inflection point at the bottleneck $E = 3T_e/2$; states with $E < 3T_e/2$ tend toward equilibrium with the continuum, while states with $E > 3T_e/2$ tend toward equilibrium with the ground state.

The level distribution of atoms is an important characteristic of a nonequilibrium state; ignorance of this distribution rules out answers to several questions. The most important of these is the determination of the coefficients for stepwise ionization and recombination (see Subsection 3c below). The excited-atom distributions themselves determine the plasma emission in the spectral lines. This emission may be of interest for diagnostic purposes, and it can also be of independent interest. The plasma diagnostic methods which have been developed for equilibrium conditions cannot be applied directly to a nonequilibrium plasma. In certain parts of the spectrum, $\ln(n_k/g_k)$ may be approximately linear in energy even under nonequilibrium conditions, but the corresponding distribution temperature T_p may be very different from the electron temperature (see Table I).

Vorob'ev[52] has proposed a method for determining the electron temperature and density in a nonequilibrium plasma by measuring the populations of three excited states. His method is based on Eq. (3.11), which can be used to relate the populations of the three levels and to derive an equation from which T_e can be found numerically.

Vorob'ev's method[52] has been used in several experiments.[55-57] Figure 10 shows two excited-state distributions found in rf discharges in helium.[56] It turns out that Eq. (3.11) passes through the open circles at $T_e \approx 19\,000$ °K and through the filled circles at $T_e = 11\,000$°K. These temperatures are in reasonable agreement with the values of T_e found by other methods. The lines corresponding to the slope T_e are drawn into the continuum in Fig. 10 by continuing the function $\ln(n_k/g_k)$. We see that the atomic level distribution is not in equilibrium. The distribution temperature here is $T_p < T_e$.

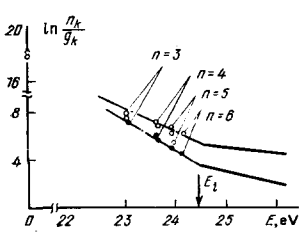

FIG. 10. Distribution of atoms with respect to excited states in helium according to the measurements of Ref. 56. Dot-dashed lines) Calculation from (3.11); solid lines) equilibrium according to the Saha equation with T_e.

The emission from a nonequilibrium plasma is of independent interest in many applications. For example, the intense emission from the ionizational-relaxation zone behind a strong shock in air can affect the gas ahead of the shock front and can affect the heating of the object whose motion causes the wave. In this emission the lines of the nitrogen atom are important.[58] There is much interest in plasma lasers which operate by means of a population inversion of excited atoms in a decaying plasma.[6] Vorob'ev,[53] for example, has studied the possibility of producing a population inversion by sending Ar and Xe plasmas through a Laval nozzle. To analyze the inversion problem we will use Eq. (3.2).

Under recombination conditions, we can ignore the first term on the right side of (3.2); then

$$\frac{n_n}{g_n} = n_e n^+ \frac{h^3}{(2\pi m T_e)^{3/2}} e^{E_n/T_e} \frac{1}{2\Sigma_i} \frac{R_{1n}\Pi_n}{R_{1e}}. \qquad (3.12)$$

In equilibrium, n_n/g_n increases with the binding energy E_n; under recombination conditions, with n_1/g_1 much lower than the equilibrium value, the function n_n/g_n may become nonmonotonic. Then for states with E_n above the maximum of this function the quantity n_n/g_n falls off with increasing binding energy; i.e., there is a population inversion.

Let us estimate the maximum of n_n/g_n. We assume conditions such that emission can be ignored ($\Pi = 1$), and we use Eq. (3.10) for R. In this case we can show that the maximum of n_n/g_n is determined by the condition

$$\chi(x_1) - \chi(x) - \frac{4}{3\sqrt{\pi}} x^{3/2} e^{-x} = 0. \qquad (3.13)$$

Figure 11 shows the results of a numerical solution of (3.13) as a plot of that fraction of levels which have a population inversion $(E_1 - E_m)/E_1$ against E_1/T_e, where E_m is the energy which satisfies (3.13). We see from this figure that at $E_1/T_e \gg 1$ we have $E_m \to E_1$; i.e., an inversion is possible only with respect to the ground state. The cases $E_1/T_e = 2-4$ are more favorable, with $(E_1 - E_m)/E_1 \sim 0.35$. These conditions can be met for elements with low ionization potentials or at high values of T_e. The conditions discussed in Ref. 60 for developing a recombination laser using a helium-hydrogen mixture ($T_e \approx 0.2$ eV, $E_1 = 24.6$ eV, $n_e \approx 2\cdot 10^{15}$

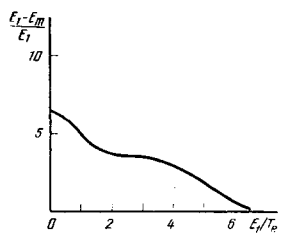

FIG. 11. Relative number of levels having population inversion $(E_1 - E_m)/E_1$ as a function of E_1/T_e during recombination.

cm^{-3}) do not lead to an absolute population inversion between the helium states with $n=2$ and $n=3$, as is pointed out by the authors themselves. This conclusion also follows from Fig. 11.

B. Electron energy distribution

In a nonequilibrium-ionization plasma, collisions of the second kind and recombination events do not offset excitation and ionization, so that inelastic electron-atom collisions can affect the electron energy distribution $f(\varepsilon)$. In turn, the deviation from equilibrium affects the rate of inelastic collisions. The problem arises of determining self-consistent nonequilibrium distributions of atoms with respect to levels and electron energy distributions. This problem was solved approximately in Ref. 61. Similar results were obtained somewhat later in Refs. 62 and 63, and numerical solutions were found in[5)] Refs. 64–66. Without attempting to cover all the questions which arise here, we would like to discuss how a nonequilibrium distribution $f(\varepsilon)$ affects the rates of inelastic processes, and we would like to determine the relationship between the nonequilibrium distributions n_k and $f(\varepsilon)$.

We write the Boltzmann equation in the simple form[3]

$$\frac{n_e}{\sqrt{\varepsilon}}\frac{\partial}{\partial\varepsilon}\left[\nu_{ee}(\varepsilon)\sqrt{\varepsilon}\,\varepsilon\left(f+T_e\frac{\partial f}{\partial\varepsilon}\right)\right]=S_{in}. \tag{3.14}$$

The electron-electron collision integral on the left side is written in the standard linearized form, $\nu_{ee}=2\pi e^4\lambda n_e(\sqrt{2m\varepsilon}\,\varepsilon)^{-1}$, where λ is the Coulomb logarithm. On the right side we have S_{in}, the inelastic-collision integral; the inelastic collisions cause a deviation of $f(\varepsilon)$ from a Maxwell distribution. The normalization condition is

$$\int_0^\infty f(\varepsilon)\sqrt{\varepsilon}\,d\varepsilon=1.$$

Transitions between excited states, $2\rightleftarrows3, 3\rightleftarrows4$, etc., have little effect on the inelastic-collision integral, because of the comparatively low populations of the upper levels. Let us consider the simplest and most important case, in which transitions between the ground and first excited levels dominate S_{in}. In this case S_{in} can be written

$$S_{in}=n_1z_{12}(\varepsilon)f(\varepsilon)-n_2z_{21}(\varepsilon-\Delta E_1)f(\varepsilon-\Delta E_1). \tag{3.15}$$

The first term corresponds to excitation events $z_{12}(\varepsilon)=4\pi e^4\Lambda_1n_e\times(2m\varepsilon)^{-1/2}\Delta E^{-1}$, where $\Delta E_1=E_1-E_2$. If this difference is large, the inelastic collisions affect $f(\varepsilon)$. In turn, there is an effect on the resultant frequency of excitation events, z_{12}, given by

$$z_{12}=\int_{\Delta E_1}^\infty z_{12}(\varepsilon)f(\varepsilon)\sqrt{\varepsilon}\,d\varepsilon.$$

We recall that for a Maxwell distribution, i.e., with $f(\varepsilon)=f^0(\varepsilon)$, z_{12} is given by Eq. (2.11). We will add a superscript "0" (z_{12}^0) to emphasize that this frequency is calculated from $f^0(\varepsilon)$. The second term in (3.15) corresponds to collisions of the second kind, which involve slow electrons. We thus have $z_{21}=z_{21}^0$.

We first consider the important limiting case in which collisions of the second kind can be ignored ($y_2\ll y_1$) and in which the excitation can be described in terms of an infinitely strong electron sink at the threshold energy[68,69] $\varepsilon=\Delta E_1=E_1-E_2$. By this we mean that those electrons which diffuse under the influence of elastic collisions out of the low-energy region toward the threshold energy ΔE_1 rapidly disappear there as the result of excitation events. There is an extremely pronounced depletion of the tail of $f(\varepsilon)$: The quantity $f(\Delta E_1)$ is approximately zero. Then by integrating Eq. (3.14) from $\varepsilon=\Delta E_1$ to infinity, we find an equation convenient for calculating z_{12} when there is a very strong deviation from equilibrium:

$$n_1z_{12}=-n_e\nu_{ee}\varepsilon^{3/2}T_e\frac{\partial f}{\partial\varepsilon}\Big|_{\varepsilon=\Delta E_1}.$$

We can easily find the form of the distribution $f(\varepsilon)$ for $\varepsilon\leqslant\Delta E_1$ directly by integrating (3.14) and using the boundary condition $f(\Delta E_1)=0$; the result is

$$f(\varepsilon)=f(0)\left[\exp\left(-\frac{\varepsilon}{T}\right)-\exp\left(-\frac{\Delta E_1}{T}\right)\right]=f^0(\varepsilon)-f^0(\Delta E_1).$$

Substituting $f(\varepsilon)$ into the preceding equation, we find an equation for z_{12}:

$$n_1z_{12}=-n_e\nu_{ee}\varepsilon^{3/2}T_e\frac{\partial f_0}{\partial\varepsilon}\Big|_{\varepsilon=\Delta E_1}. \tag{3.16}$$

The excitation rate is thus determined by the frequency of elastic collisions at the threshold and by the distribution function f_0, which was calculated without taking excitation into account. In this case f_0 is a Maxwell distribution. Equation (3.16) is quite general in nature. For example, it holds for a plasma in strong external fields which affect the distribution $f(\varepsilon)$. Then $f^0(\varepsilon)$ is a distribution of the Druyvesteyn type.

The atomic excitation cross section appears only in the applicability condition for (3.16), derived in Refs. 16 and 70:

$$\frac{z_{12}^0}{\nu_{ee}\varepsilon\partial\ln f^0/\partial\varepsilon}\Big|_{\varepsilon=\Delta E_1}\gg\frac{\Delta E_1}{T_e}\gg1. \tag{3.17}$$

The second of these inequalities states that only the tail of the distribution $f(\varepsilon)$ is perturbed. The first inequality is essentially a condition on the degree of ionization. To put it in a more specific form, we assume that f^0 is the Maxwell distribution. Then we find

$$c=\frac{2n_1}{n_e}\frac{T_e}{\Delta E_1}\frac{\Lambda_1}{\lambda}\gg1,$$

which is the limit opposite that in (2.19).

The infinite sink approximation thus corresponds to a larger value of the parameter c, introduced earlier. We can write an approximate equation for the excitation frequency, which holds over the entire range of c:

$$z_{12}\approx z_{12}^0(1+c)^{-1}. \tag{3.18}$$

This equation is a satisfactory approximation of the more complicated equations which have been derived in a series of papers (Refs. 71, 72, etc.). Wojaczek[71] has demonstrated that the results are relatively insensitive to the behavior of the excitation cross section near the threshold.

If collisions of the second kind cannot be ignored,

[5)] Much work has been carried out under the assumption that collisions of the second kind can be ignored.[67] This assumption greatly simplifies the problem, since the ionization rate becomes independent of the level distribution of the atoms.

we cannot use the infinite sink approximation, and a more complicated procedure must be used to solve the Boltzmann equation. We proceed immediately to the result, in which we can easily see both limiting cases:

$$z_{12}=z_{12}^0\left[(1-c)^{-1}\left(1-\frac{y_2}{y_1}\right)+\frac{y_2}{y_1}\right].$$

If $y_2 \to y_1$, then $z_{12} \to z_{12}^0$; in the opposite case, with $y_2 \ll y_1$, we have a transition to (3.18).

Using this result, we can find the interrelated solutions $f(\varepsilon)$ and n_k. For this purpose, we should write $n_1 z_{12} - n_2 z_{21}$ in the first equation of the system of balance equations in (2.6) as $n_1 z_{12}^0 (1+c)^{-1}(y_1 - y_2)$. Incidentally, it is easy to see that we can use solution (3.1)–(3.3), found previously, if we replace z_{12}^0 by $z_{12}^0(1+c)^{-1}$. The solid curve in Fig. 12 shows the nonequilibrium populations of excited atoms and the electron energy distribution calculated for the experimental conditions of Ref. 73. Under the conditions of Ref. 73, in the positive column of an argon discharge, the electron density is $n_e = 0.77 \cdot 10^{13}$ cm^{-3}, the electron temperature is $T_e = 1.3 \cdot 10^4$ °K, the gas pressure is 5 torr, and the current is 0.4 A. The dashed curve in Fig. 12 shows how the populations of the excited states would behave if the deviation from a Maxwell distribution were ignored in the calculation (for the same values of n_e, n, and T_e). The points in Fig. 12 are the measurements from Ref. 73.

C. Nonequilibrium degree of ionization

An example of a plasma with a nonequilibrium degree of ionization is a steady-state discharge in an argon-cesium mixture, as studied in Ref. 18. Figure 13 shows the electron temperature T_e, the "ionization temperature" T_i, and the electron density n_e, all as functions of the cesium vapor pressure. Here T_e is understood as that temperature which relates the densities of atoms and electrons in the plasma through the ionizational equilibrium condition:

$$n_i K_1(T_i) = n_e^2,$$

where K_1 is the ionizational-equilibrium constant, given by the Saha equation; and $K_1(T_i) = 2\sum_i (g_1 h^3)^{-1}(2\pi m T_i)^{3/2}\exp(-E_1/T_i)$, where $\sum_i$ is a sum over the states of the residual ion, and g_1 is the statistical weight of the atomic ground state. In the experiments of Ref. 18, the plasma was underionized ($T_i < T_e$), because charged particles diffuse out of the plasma to the walls the emission of radiation caused the excited levels to deviate from an equilibrium population. An ionizational equilibrium was reached as n_e was increased, at $n_e \gtrsim 10^{14}$ cm^{-3}.

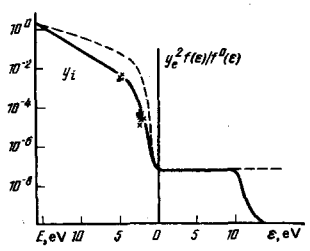

FIG. 12. Reduced populations of the excited states of the argon atoms and electron energy distributions. Plotted along the ordinate in the left part of the figure (as a function of the binding energy E) are the values of $y_i = n_i/n_i^0$. Shown at the right (as a function of the electron energy) are the values of $y_e^2 f(\varepsilon)/f^0(\varepsilon)$. The points are the measurements of Ref. 73.

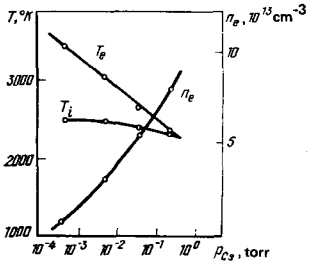

FIG. 13. Values of T_e, T_i, and n_e as functions of the cesium vapor pressure.[18] The argon pressure is 240 torr; $I = 0.5$ A.

The nonequilibrium electron density can be determined from the balance equation in (2.15) if we know how the ionization and recombination coefficients β and α and the flux j vary with the plasma properties.

This flux j may result from ionization caused by an external agent, e.g., a beam of fast electrons. Then the flux is negative, $j < 0$, and is given by $j = -n_1 F q$, where F is the flux density of beam electrons, and q is the cross section for ionization of the atom from its ground state. The flux j may also be caused by the loss of charged particles by diffusion; in this case it would be positive, equal to $j \approx n_e/\tau_D$, where τ_D is the diffusion time.

Let us take a closer look at the coefficients α and β, which must be found as functions of several characteristics of the plasma through the ionization-recombination kinetics and that of the populations jointly excited state. Expressions for α and β follow immediately from Eq. (3.1) for the flux j (the first equation):

$$\beta = (n_e n_1^0 R_{1e}\Pi_1)^{-1}, \quad \alpha = [n_e (n_e^0)^2 R_{1e}]^{-1}. \tag{3.19}$$

Let us first examine the extreme cases of high and low temperatures under conditions such that emission does not affect the kinetics, and the two coefficients are related by the ionizational-equilibrium constant, $\beta = K_1 \alpha$.

At high temperatures, the ionization energy of the first excited state is comparable to the electron kinetic energy, so it can be assumed that each excited atom which appears is ionized instantaneously (the "immediate-ionization" approximation). In this case, we have $R_{1e} = R_{12}$ in Eq. (3.19), and the ionization rate equals the excitation rate, $n_1 z_{12}$. Then

$$\beta = \beta_1 = \frac{\Gamma \Lambda_1}{1+c}\frac{(\mathrm{Ry})^{3/2}}{\sqrt{T_e}(E_1 - E_2)}\exp\left(-\frac{E_1 - E_2}{T_e}\right), \tag{3.20}$$

$$\Gamma = \frac{4\sqrt{2\pi}\,e^4}{\sqrt{m}\,\mathrm{Ry}^{3/2}} = 1.73 \cdot 10^7 \text{ cm}^3/\text{sec}.$$

At low temperatures, only the highest-lying excited states are ionized immediately. Then the diffusion approximation can be used to calculate α and β. For the recombination coefficient in this case we have the familiar expression $\alpha_2 \sim T_e^{-9/2}$, while for β we have

$$\beta = \beta_2 = \frac{2}{3\sqrt{\pi}}\Gamma\bar{\Lambda}\frac{\Sigma_i}{g_1}\left(\frac{\mathrm{Ry}}{T_e}\right)^3 e^{-E_1/T_e}, \quad \bar{\Lambda} = 0.2. \tag{3.21}$$

We can write an interpolation equation which is valid for any temperature and which leads to Eqs. (3.20) and (3.21) in the low- and high-temperature limits:

$$\beta^{-1} = \beta_1^{-1} + \beta_2^{-1}\chi\left(\frac{E_2}{T_e}\right). \tag{3.22}$$

This equation follows from (3.19) if, after the first term (R_{12}) is singled out in R_{1e}, we go over to a diffusion description of the bound electron motion in the ionization process over the rest of the energy range. Equation (3.22) gives values in satisfactory agreement with experiment and numerical calculations.[16]

If the emission of radiation strongly affects the kinetics, then α and β become complicated functions of n_e and other plasma properties. The equation analogous to (3.22) is[16]

$$\beta^{-1} = \beta_1^{-1} + \beta_2^{-1}\chi\left(\frac{E_2}{T_e}\right)\Pi_1, \quad \beta = K_1\alpha\Pi_1^{-1}. \tag{3.23}$$

Equation (2.15) can be solved in each particular case by using the appropriate approximations for α, β, and j. Let us consider some limiting cases.

If the flux j gives rise to particle escape by diffusion, while the kinetics is purely collisional, then Eq. (2.15) is a quadratic in n_e:

$$n_e^2 + K_1 n_e - K_1 n\left[1 - (\beta\tau_D n)^{-1}\right] = 0, \tag{3.24}$$

where $n = n_1 + n_e$ is the total density of heavy particles. Conditions under which (3.24) holds were met in the experiments of Ref. 8, discussed in Subsection 2a and Ref. 12.

In the other limit, diffusion is unimportant, and the emission of radiation is so important that condition (2.8) does not hold for the first two excited states. We can thus use the equation for Π_1 in (2.12). In this simple case, however, we can work directly from the balance equations for the populations of the lower atomic levels:

$$n_1 z_{12}\left(1 - \frac{n_2}{n_2^0}\right) - n_2 A_{21} = 0, \quad n_2 z_{23}\left(1 - \frac{n_3}{n_3^0}\right) - n_3 A_{32} = 0.$$

Noting that the third level is in relative equilibrium with the continuum under these conditions, $n_3/n_3^0 = (n_e/n_e^0)^2$, we find a quadratic equation for n_e:

$$n_e^2 + n_e\left(\frac{A_{21}}{z'_{21}} + \frac{A_{32}}{z'_{32}}\right) - \left(n_1 K_1 - \frac{A_{21}A_{32}}{z'_{21}z'_{32}}\right) = 0. \tag{3.25}$$

Here z'_{21} and z'_{32} are the values per electron (i.e., $z_{21} = n_e z'_{21}$). If condition (2.8) does not hold for the third level also, the equation for the nonequilibrium ionization becomes cubic. It has two positive roots, one of which is unstable, so that the uniformity of the system is disrupted and a contraction can occur in the plasma under these conditions.[74]

Let us consider an example of a plasma state which is strongly affected by the nonequilibrium factors taken into account by both Eqs. (3.24) and (3.25). Under these conditions, Eq. (2.15) becomes

$$n_e^2 + n_e\frac{K_1}{\Pi_1} - \frac{K_1}{\Pi_1}n\left(1 - \frac{1}{n\tau_D\beta}\right) = 0. \tag{3.26}$$

Sayer *et al.*[22] have studied a discharge in cesium vapor, finding the variation of n_e with T_e shown in Fig. 14 for $n_{Cs} = 10^{15}$ cm^{-3}. The electron density was determined from the recombination continuum intensity and by probe methods. Figure 14 shows three calculated

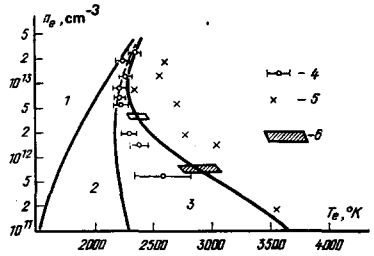

FIG. 14. Variation of the electron density with the temperature at the center of the discharge tube.[22] 1) Equilibrium values; 2) with emission of radiation; 3) with emission and ambipolar diffusion; 4) values of n_e determines from the measured recombination continuum; 5) values of n_e measured by the probe method; 6) scatter of the calculated curve corresponding to a twofold variation of the diffusion coefficient.

curves: (1) the Saha equation; (2) a curve incorporating the emission radiation (with $\theta = 10^{-3}$ for the resonant line): (3) the same, but with ambipolar diffusion also. We see that this last curve agrees best with the experimental data. It is not sufficient to merely take emission into account. The deviations from the Saha equation are extremely large.

Let us consider the conditions under which the immediate-ionization approximation, $\beta = \beta_1$, is valid, and volume recombination can be ignored, since recombination occurs at the walls:

$$n_1 n_e \beta_1 = \frac{n_e}{\tau_D}. \tag{3.27}$$

If $c \ll 1$, i.e., if a high degree of ionization is present, and there is a Maxwell distribution, then the balance equation in (3.27) does not tell us the magnitude[6)] of n_e. In such a case, n_e is determined by other factors. In the positive column of a glow discharge, for example, n_e is governed by the external circuit parameters. If $c \gg 1$, on the other hand, we find the following solution for Eq. (3.27), using Eq. (3.20):

$$n_e = \frac{1}{n_1\tau_D}\frac{T_e\sqrt{mT_e}}{2\sqrt{2}\pi e^4\lambda}e^{(E_1 - E_2)/T_e}. \tag{3.28}$$

Equation (3.28) does not contain the inelastic cross sections (in accordance with the discussion in the preceding section). Under the experimental conditions of Ref. 73, in the plasma of the positive column of an intermediate-pressure argon discharge, the density was $n \approx 10^{17}$ cm^{-3}, the electron temperature was $T_e \approx 1$ eV, and the tube radius was $R \approx 1$ cm. The expression found for n_e yields $n_e/n \approx 10^{-5}$, in accordance with the measurements.

4. NONEQUILIBRIUM DECAYING PLASMA

Excitation, ionization, and recombination do not always manage to change the state of a time-varying plasma fast enough to keep up with changing external conditions. In this situation the plasma decays without reaching equilibrium. A decaying plasma arises in many situations, e.g., when plasma is heated by an external field, when plasma emerges from a nozzle, and

[6)] Situations in which (2.15) has several positive roots are analogous, and the question arises of finding additional information in order to identify which solution is correct.

as a shock front passes. Despite the wide variety of problems involved here, which depend on the particular initial conditions, the solutions have certain common features. These arise because the various plasma components decay at different rates, reaching relative equilibria as time passes. The first and most important step is studying the relaxation is to identify the slowest process.

Let us introduce some characteristic times, which thus scale the various processes. Specifically, we use τ_k, the characteristic time for excited state k to relax to an approximately steady-state population; τ_T, the relaxation time of the temperature T_e; and τ_i, the ionizational relaxation time. To see the meaning of these times, we consider τ_k. For the atoms to an approximately steady-state distribution in excited states means that as the time-dependent process evolves it "adjusts itself" to other, comparatively slowly varying properties (n, n_e, T_e, etc.). Then it can be assumed that n_k does not depend explicitly on the time but only through the functions $n_1(t)$, $n_e(t)$, $T_e(t)$, etc.

Under a broad range of conditions the slowest step is ionization (or recombination), so that

$$\tau_k \ll \tau_T \ll \tau_i. \tag{4.1}$$

This is not always the case, and this circumstance is very important in describing plasma decay. Below we will discuss these times and their relationships and certain problems of a time-dependent nonequilibrium plasma.

A. Relaxation time of excited states

The analysis in the preceding subsection of the distribution of atomic excited states for ionization or recombination situations in a plasma was based on the assumption that the excited levels were approximately in steady state. The validity of this approximation is closely related to the inequality

$$\sum_{k>1} n_k \ll n_1, n_e, \tag{4.2}$$

which is satisfied over a broad range of conditions. This inequality stems from the low density of excited states in comparison with the ground state and the continuum. Under condition (4.2), the states n_1 and n_e are particle "reservoirs": The particles flow from one reservoir to another through the "narrow channel" represented by the excited states. The approximately steady state of excited levels is discussed in Refs. 36, 38, 75, and 76.

The relaxation time of state k is easily estimated from the balance equation, assuming that the population of the given state k experiences a slight perturbation. It turns out that this perturbation decays with typical times τ_k given approximately by

$$\tau_2^{-1} \approx A_{21}^* + (z_{21} + z_{23}),$$
$$\tau_k^{-1} \approx \sum_{i=k} A_{ki}^* + \frac{\sqrt{2\pi\Lambda} n_e e^4}{\mathrm{Ry}\sqrt{mT_e}} \left(\frac{\mathrm{Ry}}{E_k}\right)^2, \quad k>2. \tag{4.3}$$

Equations (4.3) give us an estimate of τ_k and allow us to follow the qualitative variations in these times. The times τ_k are usually in the range $10^{-8}-10^{-12}$ sec, i.e., short. The first excited states have the longest times. As n_e decreases, the times τ_k naturally increase linearly, but they become constant at low values of n_e. In this case the times depend only on radiative transitions. Radiative decay strengthens the coupling between levels and accelerates the relaxation.

Values of τ_k have been tabulated by several workers for hydrogen plasmas. Table II and Fig. 13 show results calculated for a plasma which is optically dense for the Lyman series but otherwise transparent.[76] The table lists the values of τ_2, i.e., the decay time for the second level. The electron density here is assumed to be 10^{16} cm^{-3}. Figure 15 shows τ_k as a function of n_e for a given temperature $T_e = 10^4$ °K and for the same assumptions.

For certain problems, the approximation of a nearly steady state may break down. This is the case, for example, when population inversion can take place for some pair of levels in the course of a rapid plasma decay. In this case it is necessary to solve the time-dependent system of balance equations; calculations of this type can be found in Ref. 77.

As an example of a situation in which excited levels are not approximately in steady state we can cite the terms of the electronic ground configuration of the oxygen and nitrogen atoms. With excitation energies on the order of 1 eV, these terms are important in the partition function at high T_e; their contribution is comparable to that of the ground state [this violates inequality (4.1)]. This situation arises behind strong shocks in nitrogen and air, where the temperature is of order 1 eV. The state of the ground configuration relaxes over a time comparable to the ionizational relaxation time, and it is important in the kinetics.[78]

B. Relaxation of the electron temperature and ionization

The ionization and recombination times are introduced with the help of the ionization and recombination coefficients:

$$\tau_i = \frac{1}{n_1\beta}, \quad \tau_r = \frac{1}{n_e^2\alpha}. \tag{4.4}$$

Correspondingly, the temperature relaxation time is the characteristic time for heating or cooling of the electrons. In the problem of heating by an external electric field, for example, we would have

$$\tau_T = \frac{T_e n_e}{\sigma \mathscr{E}^2}. \tag{4.5}$$

These quantities are characteristic times, and their ratio determines the course of the relaxation. Introducing these times does not mean, however, that (for example) n_e increases exponentially with a typical time τ_i. The nature of the growth (or decay) of n_e is largely determined by how β and α themselves vary with n_e. For this reason, the first step in the growth of ionization is frequently nonexponential. It is extremely im-

TABLE II.

T_e, °K	4000	6000	8000	12 000	16 000
τ_2, sec	$2.1\cdot10^{-9}$	$1.9\cdot10^{-9}$	$1.5\cdot10^{-9}$	$8.9\cdot10^{-10}$	$5.8\cdot10^{-10}$

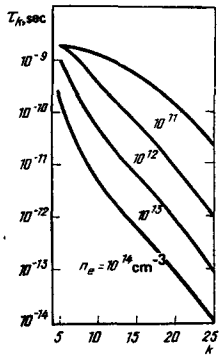

FIG. 15. Variation of the times τ_k with n_e for $T_e = 10^4$ °K.

portant to note that the relaxation of T_e and that of n_e are interrelated.

Sometimes it is convenient to depict the ionizational relaxation on the $\{n_e, T_e\}$ plane (Fig. 16). The time varies along the curves in this plane; n_e increases in time. For definiteness, let us examine the evolution of ionization. There are three possibilities: In case 1, the ionization rate is so high that an ionizational equilibrium is established at each instant [n_e and T_e are related by the Saha equation, $n_e^0(T_e)$]. In this case, inequality (4.1) does not hold, and the relaxation rate is determined by the electron heating rate. In cases 2 and 3, in contrast, there is no local ionizational equilibrium. Over the time τ_T there is an increase in T_e, but the electron density does not manage to change significantly. Case 3 differs from case 2 in that the electrons temporarily become relatively hot.

Let us examine the relaxation in a simple case. We assume that at $t = 0$ a field $\mathscr{E}$ stronger than the initial field $\mathscr{E}_0$ is imposed on a steady-state, weakly ionized plasma. As a result, the electron density and the electron temperature both increase:

$$\frac{dn_e}{dt} = n_1 n_e \beta - n_e^3 \alpha, \tag{4.6}$$

$$\frac{3}{2} n_e \frac{dT}{dt} = \sigma \mathscr{E}^2 - E_1 (n_1 n_e \beta - n_e^3 \alpha). \tag{4.7}$$

For simplicity we are incorporating in the electron energy balance only the inelastic loss, and we are also assuming $E_1 \gg T_e$. To study the relationship between n_e and T_e, we write the derivative

$$\frac{3}{2} \frac{d \ln T_e}{d \ln n_e} = \frac{\tau_i}{\tau_T} \frac{1}{1 - y_e^2} - \frac{E_1}{T_e}. \tag{4.8}$$

working from Eqs. (4.4)–(4.7). Let us first determine the conditions corresponding to cases 2 and 3 (Fig. 16).

At $t = 0$, the ratio τ_i/τ_T is very large, since it is inversely proportional to β and [according to (3.29)] proportional to $\exp[E_1/T_e(0)]$. Consequently, T_e while n_e charges slightly. Over a time of order τ_T, the temperature reaches values near the approximately steady-state value. If $y_e^2 \ll 1$, the approximately steady-state values of $T_e(t)$ are found from

$$\sigma \mathscr{E}^2 - E_1 n_e n_1 \beta = 0. \tag{4.9}$$

It follows directly from (4.4), (4.5), and (4.9) that we have $\tau_i/\tau_T \approx E_1/T_e$. This value is much smaller than the original value of $\tau_i/\tau_T(0)$ but still quite large: $E_1/T_e \gg 1$. The quantity $d \ln T_e/d \ln n_e$ is the difference between two large quantities, so in practice it may be either a small positive quantity or a small negative quantity. Accordingly, T_e varies slowly as ionization evolves, and the electrons may become relatively hot.

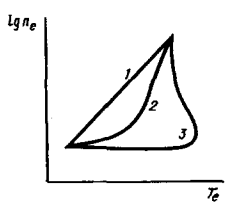

FIG. 16. Possible paths for the evolution of ionization.

A similar situation arose in the experiments of Novichkov and Glebov.[79] They studied the relaxation which occurs when a square voltage pulse is imposed on a steady-state discharge in an argon-cesium mixture. Figure 17 shows the measured variation of dT_e/dt with $\mathscr{E}/\mathscr{E}_0$ when $\mathscr{E}$ is applied. The conditions for heat removal from the electrons were such that the approximately steady-state value of T_e corresponded to 3000 °K–6000 °K. Then we can estimate τ_T to be on the order of a microsecond. Similar values of τ_T have been found in several other studies, e.g., in Ref. 80 in the plasma behind a shock wave and in Ref. 82 during the imposition of a heating pulse on a decaying plasma.

Figures 18 and 19 show the time evolution $n_e(t)$ and the corresponding variation $n_e(T_e)$ from Ref. 79 for voltage pulses of various heights $\mathscr{E}/\mathscr{E}_0$. The curves are drawn through the experimental points. The ionizational-relaxation time is usually 10–100 μsec in plasmas in the laboratory. The electron temperature, temporarily goes much higher than the heavy-particle temperature. The straight line in Fig. 19 corresponds to case 1 in Fig. 16, which did not occur in the experiments of Ref. 79.

As the ionization evolves along path 1 in Fig. 16, there is an equilibrium $n_e^0(T_e)$ at each instant. Under these conditions, we obviously have $\tau_i \lesssim \tau_T$. Actually, since we have $d \ln T_e/d \ln n_e = 2T_e/E_1 \ll 1$ in this case, it follows from (4.8) that

$$\frac{\tau_i}{\tau_T} = \frac{E_1}{T_e} (1 - y_e^2).$$

Since $1 - y_e^2$ is small, this quantity is on the order of or less than unity. The temperature T_e is thus not approximately steady. On the contrary, the ionizational-relaxation time depends on the electron heating rate, rather than the ionization coefficient:

$$\frac{dn_e}{dt} = -\frac{\sigma \mathscr{E}^2}{E_1} \qquad n_e = n_e^0(T_e). \tag{4.10}$$

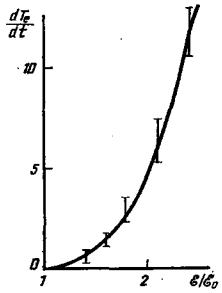

FIG. 17. Variation of the initial value ot dT_e/dt (in units of 10^8 deg/sec) with the overvoltage $\mathscr{E}/\mathscr{E}_0$.

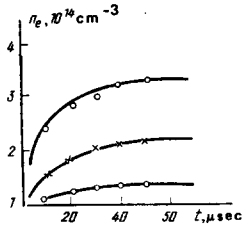

FIG. 18. The time evolution $n_e(t)$ for various heights of the voltage pulse. 1) $\mathscr{E}=2.0$ V/cm; 2) 2.5 V/cm; 3) 3.4 V/cm.

This is the slow heating case, which may occur in low fields $\mathscr{E}$. This type of ionization occurs behind shock waves in mercury vapor at velocities corresponding to Mach numbers[78] $M_1 \approx 10$. As the shock front passes, the translational temperature of the gas (T) increases rapidly, while the electrons remain cool. Through elastic collisions, the atoms and ions heat the electrons (so that the Joule heating, $\mathscr{E}^2$, in the equations above must be replaced by heating due to elastic collisions, S_{el}), and these electrons ionize the gas. Behind the shock front in mercury vapor, the conditions are $T \approx 1.5 \cdot 10^4$ °K and $T_e \approx 1.0 \cdot 10^3$ °K.

C. Spectral-line emission

The emission in the spectral lines of a relaxing plasma is interesting because the intensity of several of these lines goes through a maximum.

For very short times $t < \tau_k$, it would not be possible to carry out any sort of general analysis; it would be necessary to solve the system of balance equations for the particles with the specific initial values $n_k(0)$. At $t \geq \tau_k$, on the other hand, the results of Section 3 for the excited-level distribution of atoms can be used in the almost-steady state approximation. Here we will take into account the basic feature of the n_k distribution: For levels lying below the bottleneck, $E_k \geq (3/2)T_e$, there is a tendency toward an equilibrium with the ground state, $n_k \approx n_1(t) \exp[-(E_1 - E_k)/T_e(t)]$, according to Eq. (3.11). In the opposite limit, there is a relative equilibrium with the continuum:

$$n_k \sim n_e^2(t) e^{E_k/T_e(t)}. \qquad (4.11)$$

Frequently, of course, these distributions are greatly distorted by the emission of radiation, but these equations are adequate for a qualitative analysis.[81]

Let us first examine the behavior $n_k(t)$ during the onset of ionization. If this density takes path 2 or 3 in Fig. 16, the populations of the low-lying excited states

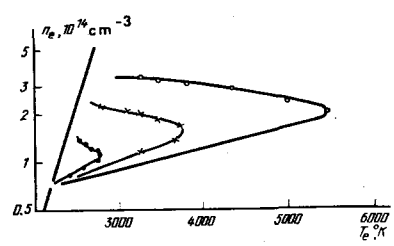

FIG. 19. Ionizational relationship $n_e(T_e)$ for the cases in Fig. 18.

increase rapidly over short times because of the rapid increase in T_e. These populations pass through a maximum if there is a temporary heating of electrons (case 3 in Fig. 16). As for the populations of the highly excited states, we note that they increase slowly and smoothly in accordance with (4.11). These basic qualitative results were obtained in the early work by Cool and Zukoski,[82] who observed an emission maximum in the $4P-4S$ line of potassium.

In a decaying plasma, the relaxation of T_e is initially similar, but in this case this temperature is falling instead of rising. After this initial relaxation, T_e remains approximately constant, while n_e falls off slowly. As a result, the situation with emission in the spectral lines is the opposite of that discussed above for the evolution of ionization. The populations of the highly excited states $n_k(t)$ go through a maximum and then decay because of a decrease in $n_e(t)$. For the low-lying levels, $n_k(t)$ falls off monotonically. One of the early studies in which an intensity maximum was observed in spectral lines was that by Aleskovskiĭ.[83a] Figure 20 shows the time dependence of the relative populations $n_k(t)$ in a cesium plasma.[83b] There are two groups of levels, $5D$ and $11F$, which behave in accordance with the discussion above, and there is also a group of levels ($8S$) in the bottleneck region with a more complicated behavior. The reader is referred to Ref. 53 for a more detailed review of this question.

5. EFFECT OF HEAVY-PARTICLE COLLISIONS ON THE DEGREE OF IONIZATION AND THE LEVEL POPULATIONS

We have been discussing the kinetics when the most important elementary processes are electron-atom collisions and radiative processes. Over a wide range

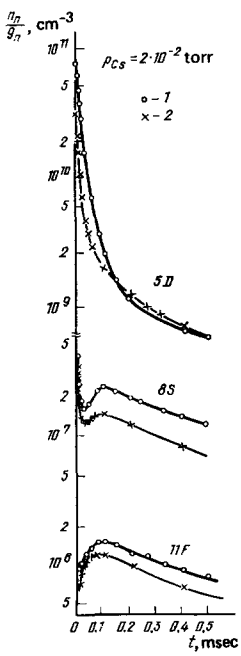

FIG. 20. Time evolution of the populations of the cesium levels.[83b] $p = 2 \cdot 10^{-2}$ torr. 1) Measurements; 2) calculations from Ref. 83b.

of conditions, however, the inelastic collisions of heavy particles having a translational temperature different from the electron temperature may be important. These collisions cause transitions between excited states as well as ionization. A reaction such as dissociative recombination or associative ionization involving heavy particles leads to the formation or loss of particles in excited states. When these collisions are dominant, the atomic states are described by a Boltzmann distribution with a heavy-particle temperature T. In real situations, heavy-particle collisions compete with electron collisions, which tend to establish a Boltzmann distribution with temperature T_e, and they also compete with radiative processes which lead to the loss of excited particles.

A. Some criteria

It is important to determine when heavy-particle collisions become important. For highly excited states, we can estimate the efficiency of collisions with heavy particles by comparing the diffusion coefficients in energy space. The diffusion coefficient for a bound electron and for diffusion due to collisions with heavy particles has been calculated by Pitaevskiĭ[44]:

$$B^a(E)=\frac{128\sqrt{2m}T\,\sigma_{ea}\,n}{3\pi M}E^{3/2}, \tag{5.1}$$

where M is the atomic mass, and σ_{ea} is the cross section for the scattering of a slow electron by an atom. Equation (5.1) holds for

$$e^2 n\sigma_{ea}\sqrt{\frac{m}{M}}\ll T\ll\frac{e^2}{a}\sqrt{\frac{m}{M}},$$

where a is a quantity on the order of atomic dimensions.

The diffusion coefficient corresponding to collisions with electrons is of the same form as (3.7) when $E \ll e^2/a$. Comparing (5.1) with (3.7), we find that atom-atom collisions are predominant if

$$\frac{32}{3\pi^{3/2}}\frac{m}{M}\frac{T\sqrt{E}}{T_e^{3/2}\Lambda}\frac{\sigma_{ea}}{(e^2/T_e)^2}\frac{n}{n_e}\gg 1. \tag{5.2}$$

The values of $B(E)$ for those collisions of an atom with molecules in which the rotational quantum number of the molecules charger were calculated in Refs. 84–86.

For transitions between low-lying excited states we can compare the transition frequencies for transitions caused by electrons, heavy particles, and emission. Let us compare the frequency at which some level k is depopulated by atoms and electrons in a transition to the closest lower level $k-1$. Depopulation by atoms becomes important if

$$nv_a\sigma^a_{k,k-1}\gg n_e v_e\sigma_{k,k-1}, \tag{5.3}$$

where v_a and v_e are the relative velocities of the atoms and electrons, and $\sigma^a_{k,k-1}$ and $\sigma_{k,k-1}$ are the corresponding cross sections for the depopulation of the levels. Cohen[87] recently calculated the cross sections for those collisions of helium atoms with helium which cause transitions between excited states. According to those results, the cross section for the transition 3^3S-2^3P at $T=5000\,^\circ$K is $6\cdot10^{-16}$ cm^2. The cross section for depopulation by electrons, σ_{32}, can be estimated from the effective probabilities for single-quantum transitions, (2.10). For example, the cross section for a transition between states with principal quantum numbers $k=3$ and $k=2$, averaged over states with various values of l, can be written

$$\sigma_{32}=4\sqrt{\pi}f^2\frac{T_e E_2\Lambda_2}{(E_2-E_3)(E_1-E_3)}, \tag{5.4}$$

where $f=e^2/T_e$ is the Coulomb scattering amplitude, and E_1, E_2, and E_3 are the energies of the ground state and the two excited states. With $T_e=1$ eV we have $\sigma_{32}\approx10^{-14}$ cm^2. Substituting these values for the cross section into (5.3), we find that for the particular case considered here atom-atom collisions become important at $n_e/n\approx6\cdot10^{-4}$. If the decay is radiative, the inequality in (5.3) should be written

$$n_a v_a\sigma_{k,k-1}\gg\sum_{n<k}A^a_{kn}.$$

There are data in literature on the cross sections for atom-atom collisions for specific elements and specific transitions (see, for example, Refs. 88–93).

B. Effect of ion charge exchange

The ions may react with other heavy particles. If the temperature of the heavy particles is different from the electron temperature, these reactions will cause nonequilibrium effects. They affect the nonequilibrium degree of ionization, the distribution with respect to atomic levels, and so forth. As an example we consider a mixture of two atomic gases of species A and B. The following ion reactions can occur:

$$\mathrm{A}+e\underset{\alpha_{\mathrm{A}}}{\overset{\beta_{\mathrm{A}}}{\rightleftarrows}}\mathrm{A}^+ +2e,$$

$$\mathrm{B}+e\underset{\alpha_{\mathrm{B}}}{\overset{\beta_{\mathrm{B}}}{\rightleftarrows}}\mathrm{B}^+ +2e,$$

$$\mathrm{A}^+ +\mathrm{B}\underset{\gamma_2}{\overset{\gamma_1}{\rightleftarrows}}\mathrm{A}+\mathrm{B}^+ +\delta E,$$

where $\delta E=E_{1A}-E_{1B}$ is the difference in ionization energies, α_A and β_A are the recombination and ionization coefficients of the atom of species A, and γ_1 and γ_2 are the charge exchange rates for A^+ ions with the atoms of species B and vice versa.

The charge-exchange reaction is characterized by the gas temperature. If the charge-exchange rates are much higher than the rate of impact-radiative recombination,

$$\gamma_1 n_{1\mathrm{B}},\ \gamma_2 n_{1\mathrm{A}}\gg\beta_{\mathrm{B}}n_{\mathrm{B}},\ \alpha_{\mathrm{B}}n_e^2,\ \beta_{\mathrm{A}}n_{1\mathrm{A}},\ \alpha_{\mathrm{A}}^2 n_e^2, \tag{5.5}$$

then the ratio of reduced ion densities is[94,95]

$$\frac{y_{\mathrm{B}}^+}{y_{\mathrm{A}}^+}=\frac{\Gamma(T)}{\Gamma(T_e)}, \tag{5.6}$$

where $\Gamma(T)$ is the equilibrium constant for the reaction $A^+ + B \rightleftarrows A + B^+$. Since $T\neq T_e$, the ion density ratio does not correspond to the equilibrium value at T_e, and it shifts toward the element with the lower ionization potential if $T<T_e$. The result is a change in the net ionization rate, which is determined by

$$n_e n_{1\mathrm{A}}\beta_{\mathrm{A}}+n_e n_{1\mathrm{B}}\beta_{\mathrm{B}}-n_e^2 n_{\mathrm{A}}^+\alpha_{\mathrm{A}}-n_{\mathrm{A}}^+ n_{\mathrm{B}}^+\alpha_{\mathrm{B}}.$$

In the steady state, there is thus also a change in the

nonequilibrium value of n_e itself. The quantities $y_e y_A^+$ and $y_e y_B^+$ affect the level distribution of atoms. A change in the ratio of A^+ and B^+ ions has a direct effect on the excited states population.[94,95]

The charge-exchange cross section falls off rapidly with increasing difference between the ionization potentials of the atoms of species A and B. Whether (5.5) is satisfied thus becomes problematical, if the emission of radiation is important, however, charge exchange strongly affects the ratio of ion densities, even for elements with approximately equal ionization potentials. Specifically, if we assume that charge exchange does not occur we find the following result from the conditions for an ionizational equilibrium incorporating (2.16):

$$\frac{y_B^+}{y_A^+} = \frac{y_{1B}\,\Pi_{1A}}{y_{1A}\,\Pi_{1B}}. \tag{5.7}$$

Comparing this expression with (5.6), we see that if the ionization potentials for atoms A and B are approximately equal, so that $\Gamma(T)/\Gamma(T_e) \approx 1$, then the values of y_B^+/y_A^+ given by (5.7) and (5.6) may be very different when Π_{1A} and Π_{1B} are very different. This case arises, for example, if one of the gases is a small admixture in the other. The conditions for radiation turn out to be different.

An effect of charge exchange on the population of excited states was observed in the experiments of Ref. 96, where study was made of rf discharges in the mixture $Ar + H_2$. The charge-exchange reaction $Ar + H^+ \rightleftarrows Ar^+ + H$ led to the formation of substantial numbers of Ar^+ ions, which did not correspond to the equilibrium at T_e. Taking this circumstance into account, we see that the observed distributions of the argon and hydrogen populations agree with the calculations.

C. Ion conversion, associative ionization, and dissociative recombination

Another group of reactions involves the conversion of atomic into molecular ions, dissociative recombination, and associative ionization. As a rule, these reactions involve excited atoms:

$$A^+ + 2A \underset{k_2}{\overset{k_1}{\rightleftarrows}} A_2^+ + A + \delta E_2, \tag{5.8}$$

$$A_2^+ + e \underset{\beta_k^a}{\overset{\alpha_k^d}{\rightleftarrows}} A + A(k) + \delta E_3. \tag{5.9}$$

The flux of atoms formed in reaction (5.9) is

$$j_k^M = \alpha_k^d n_2^+ n_e - \beta_k^a n_k n_1.$$

From the steady-state solution of the system of equations associated with reactions (5.8), (5.9) we find

$$n_2^+ = \frac{k_1 n^+ n_1^2 + \sum_k \beta_k^a n_k n_1}{k_2 n_1 + \sum_k \alpha_k^d n_e}.$$

Let us examine the conditions under which molecular ions are consumed primarily through dissociative recombination,

$$\sum_k \alpha_k^d n_e \gg k_2 n_1, \tag{5.10}$$

and are formed through conversion. According to Refs. 95 and 97, condition (5.10) holds for those gases where the dissociation potential of the molecular ion is higher than the ionization potential of the atom (nitrogen, oxygen, and so forth) with $n_1 < 3 \cdot 10^{-19}$ cm^{-3} at essentially all temperatures. This condition may also hold for the opposite relation between the ionization and dissociation potentials of the A_2^+ ion if the equilibrium for reaction (5.9) is shifted toward the formation of molecular ions. For example, near atmospheric pressure this is the case at $T < 2 \cdot 10^3$ °K for hydrogen and at $T < 10^3$ °K for argon. In the equation for the flux j_k^M the first term is retained under these conditions; this term is independent of the densities of excited atoms.

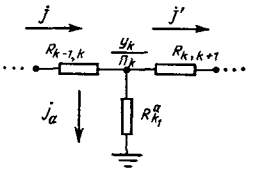

FIG. 21. Equivalent circuit for the case of associative ionization from state k.

In Eq. (3.1) for the flux there are "sources" which furnish atoms in state k through dissociative recombination. The term $n_e^+ n_e \alpha_k^d$ causes only a slight complication of the solution of (3.2), (3.11).

There is another possible limiting case:

$$k_2 n_1 \gg \sum_k \alpha_k^d n_e. \tag{5.11}$$

In this case, molecular ions are formed through associative ionization and consumed by conversion to atomic ions. In this case the flux $j_k^M = -\beta_k^a n_k n_1$ is very sensitive to the distribution of excited atoms. The problem becomes difficult to solve in its general form, but situations frequently arise in which the ionization occurs preferentially from some level k (or from group of levels near k). To solve this problem we can use the analogy with current flow in an electric circuit, discussed in Section 3.

We denote by j the flux for the state with $E > E_k$ and by j' the flux for the state with $E < E_k$. The equivalent circuit is shown in Fig. 21. We can evidently write Kirchhoff's law for the junction: $j = j' + j_a$, where j_a is the associative-ionization flux $j_a = n_k w_k^a = y_k / R_k^a$, and w_k^a is the probability for the associative ionization of level k ($w_k^a = n_1 \sigma_k^a v_a$, where σ_k^a is the corresponding cross section).

Let us write Ohm's law for these regions:

$$j = \frac{y_1 \Pi_1^{-1} - y_k \Pi_k^{-1}}{R_{1k}}, \quad j' = \frac{y_k \Pi_k^{-1} - y_e y^+}{R_{ke}}, \quad j^a = \frac{y_k}{R_k^a}. \tag{5.12}$$

It follows from the solution of system (5.12) that the effect of associative ionization depends on the ratio of the conductance of the associative-ionization channel, $(R_k^a)^{-1}$, and the conductance of the $(1-k)$ and $(k-e)$ channels (R_{1k}^{-1} and R_{ke}^{-1}, respectively). An interesting case is that in which associative ionization is very important, and we have[7] $(R_k^a)^{-1} \gg R_{ke}^{-1} + R_{1k}^{-1}$. Using (3.10),

[7] In the opposite limit, associative ionization affects the way the the levels are populated only slightly, and problems involving the population of levels and their associative ionization can be solved separately.

we see that $R_{ke}^{-1}+R_{1k}^{-1}\sim[\chi_k(1-\chi_k)]^{-1}$. The function $[\chi_k(1-\chi_k)]^{-1}$ is weak if the argument satisfies $1<(E_k/T_e)<4$. As the criterion we take the value of this function at its minimum, $[\chi_k(1-\chi_k)]^{-1}=4$. Then the preceding criterion can be rewritten

$$\frac{n_k^0}{n_e^0(n^+)^0}w_k^a \gg 4n_e\alpha. \tag{5.13}$$

As an example, we consider associative ionization in cesium. According to Ref. 98, the cross section for the associative ionization of the $6D$ level in collisions with ground-state atoms is $4\cdot10^{-16}$ cm^2. Assuming $T_e=0.2$ eV and $T=1$ eV, we find that inequality (5.13) holds if $n/n_e=3.5\cdot10^6$, i.e., at very low degrees of ionization. Such conditions may prevail behind a shock front in the initial part of the ionizational-relaxation zone, where $T>T_e$ and where the degree of ionization is very low. The importance of associative-ionization processes behind shock fronts was pointed out in Ref. 78.

Interestingly, under condition (5.13) the rate of associative ionization is independent of w_k^a and is determined by

$$j^a=\frac{y_1\Pi_1^{-1}}{R_{1k}}+\frac{y_e y^+}{R_{ke}}\approx n_1 n_e\beta\frac{1}{1-\chi_k}+n_e^2 n^+\alpha\frac{1}{\chi_k}. \tag{5.14}$$

The total ionization rate is

$$j\approx\frac{y_1}{\Pi_1 R_{1k}}\approx n_1 n_e\beta(1-\chi_k)^{-1}. \tag{5.15}$$

This result means that an electron which reaches level k is instantaneously ionized by an associative process. The factor $(1-\chi_k)^{-1}$ describes the increase in the ionization rate due to "contraction" of the ionization channel. For the example discussed above, we would have $(1-\chi_k)^{-1}=1.8$. We note that by substituting the flux equation in (5.15) into (3.1) we would find an equation for the nonequilibrium electron density in the case of pronounced associative ionization.

D. Penning ionization

A very fast process in a mixture of gases of species A and B is the ionization of atoms of species B in collisions with excited atoms of species A if the excitation energy $(E_1-E_2)_A$ exceeds the ionization energy E_{1B}. This reaction,

$$A^*+B\to A+B^++e, \tag{5.16}$$

does not have a threshold. It turns out to be most important if the state A^* is metastable (the Penning effect), and it has a large effective cross section,[99] $10^{-16}-10^{-15}$ cm^2. Then even a comparatively small admixture of the atoms of species B strongly affects the rate at which electrons appear in the mixture, as is well known in the theory of gas discharges.

Penning processes can occur in a pure gas. Reactions of this type are the thresholdless ionization reactions $(E_1\geq 2E_2)$

$$A^*+A^*\begin{cases}\longrightarrow A+A^++e\\ \longrightarrow A_2^++e.\end{cases} \tag{5.17}$$

The ionization cross sections in the collision of two metastable mercury or helium atoms are of order 10^{-14} cm^2. At low electron densities, the process in (5.17) can become the primary ionization channel.[100] This is the case, for example, in the positive column of a low-pressure glow discharge in helium,[101] $T=77$ °K. The 2^3S helium metastable states take part in reaction (5.17). These states are produced by electrons; electrons are also produced in reaction (5.17), and they diffuse to the wall. A very nonequilibrium plasma results with $n\approx10^{17}$ cm^{-3}, $n_e\approx10^{10}$ cm^{-3}, and $n^*\approx10^{12}$ cm^{-3}.

At such small values of n_e we have $\Pi_1\gg1$. Then if the impact-radiative ionization rate is low we would have $n_1 n_e\beta\ll n^{*2}\beta_\Pi$, provided that the metastable level population is sufficiently high. This is also the case at a low value of n_e, for which electrons do not manage to "mix" the radiative and metastable states. This mixing would lead to a common value of y_k for the metastable and nearest resonant levels. Penning ionization thus "shunts" the region of highly excited states. The populations of these states are in a relative coronal equilibrium, $y_{k-1}/\Pi_{k-1}=y_k/\Pi_k$. They do not have any significant effect on the state of the plasma.

In this situation, collisions between heavy particles have an interesting effect on the electron energy distribution[102,103] $f(\varepsilon)$. The electrons which appear as the result of Penning ionization have high energies, $\varepsilon\approx18$ eV, so the tail of the distribution $f(\varepsilon)$ does not fall off as rapidly. This circumstance is important for the resultant ionization rate.

6. CONCLUSION

The extensive experimental and theoretical work on the subject has made it possible to construct a quite general description of qualitatively different nonequilibrium states of a low-temperature atomic plasma. The description takes into account the actual energy structure of the atoms, the various elementary processes, the relationships between the energy distributions of the different plasma components, and the effects of various factors which cause deviations from equilibrium. It is extremely important to note that there are several criteria which define the regions of complete or partial equilibrium.

It has now become necessary to analyze more complicated situations, many of which are motivated by practical applications (in gas lasers, plasma chemistry, etc.).

First, there is the selective effect of external agents on the various components or even on certain transitions (for example, the effects of electron beams and radiation). We do not have an adequate understanding of the nonequilibrium states of an atomic-molecular plasma. To analyze this problem we would have to take into account a broader range of elementary processes, including collisions between heavy particles (atoms, molecules, and ions). The mutual effects of the populations of the excited states of the atomic and molecular components of a nonequilibrium plasma are extremely important. There is definite interest in excited state formation as the result of chemical reactions. It is

worthwhile to study how a plasma deviates from equilibrium when subjected to strong, time-varying electric fields and to study the deviation from equilibrium of plasmas in magnetic fields.

The two-temperature approximation has been used in most of the work on the instabilities of low-temperature plasmas. It would be worthwhile to study the instabilities over a broader range of conditions, with a greater departurer from equilibrium.

We believe that the approach outlined above to the study of nonequilibrium states will also prove useful for solving these more complicated problems.

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