DEVIATIONS FROM THERMODYNAMIC EQUILIBRIUM DURING RECOMBINATION OF A DISPERSING PLASMA

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The relaxation of a dense low-temperature plasma during cooling of the electrons on heavy particles and during dispersion of a plasma cluster into a vacuum is examined. The population kinetics is analyzed in the limiting cases of free escape and radiation capture. The results are presented for a numerical solution of the self-consistent (with respect to temperature and concentration of free electrons) problem of the relaxation of an atomic hydrogen plasma.

1. Relaxation Times. The study of the nonstationary process of decay of a dense, nonequilibrium, low-temperature plasma requires taking into account the variation with time of a large number of parameters connected amoung each other by nonlinear relationships. In many cases the relaxation times of different plasma characteristics differ sharply. This can be used to simplify the problem by taking the faster processes as having become established and describing them in a quasi-stationary approximation when considering the relaxation of the relatively slowly varying characteristics.

The following is a possible classification of relaxation times. The fastest process, whose characteristic time is on the order of the time of several electron–electron collisions, is the "Maxwell" velocity distribution of the free electrons, i.e., the formation of the electron temperature T_e. In this time a Boltzmann distribution united with the continuum is established for the upper discrete levels of excitation of the atoms whose ionization potential is on the order of T_e or less. We determine these levels as belonging to the quasi-equilibrium spectrum.

The next somewhat slower process is the establishment of a stationary sink of electrons with respect to levels. In this case a quasi-stationary nonequilibrium population distribution of the lower excited levels is formed, determined by the instantaneous values of the temperature T_e and concentration N_e of free electrons. The process of equalization of the temperatures of the free electrons and heavy particles has a somewhat longer characteristic time.

The slowest process is the decrease in the density of free electrons through recombination and filling of the ground state of the atoms. It leads to the establishment of an equilibrium distribution of electrons over all the levels, if there are no steadily acting sources maintaining the nonequilibrium. The processes of association of atoms into molecules and the relaxation of excited molecules will not be discussed here.

If at the initial time the plasma is far from an equilibrium state then in the course of relaxation it passes through a series of stages corresponding to the processes enumerated above. The times of establishment of each stage of plasma decay depend strongly on the parameters of the plasma. In a dense low-temperature plasma at high enough N_e the electron collisions play the main role, so that atom–atom collisions can be ignored in this case. The contribution of photorecombination and photoionization can also be neglected in comparison with recombination during triple collisions and ionization by electron impact.

2. Statement of the Problem. We will confine ourselves to a study of a spatially homogeneous model of the relaxation of a low-temperature plasma consisting of electrons, singly charged ions, and neutral atoms. Suppose the concentration N of heavy particles varies with time by an exponential law

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$$N(t) = N_0 (t_0 / t)^{\mu} \tag{2.1}$$

Thus does the density vary in the inertial stage of dispersion of a plasma cluster. The parameter t_0 is connected with the initial dimension r_0 of the cluster and the dispersion velocity u by the equation $t_0 = r_0/u$. The exponent μ characterizes the dispersion geometry ($\mu = 1, 2, 3$); $\mu = 0$ corresponds to a stationary plasma cluster.

The equations of the population kinetics of excited levels of the atoms in a spatially homogeneous model can be written in the form [1]

$$\frac{dN_n}{dt} = \sum_{m=1}^{n_1} K_{nm} N_m + D_n - \frac{\mu}{t} N_n \equiv \Gamma_n - \frac{\mu}{t} N_n \tag{2.2}$$
$$(n = 1, 2, \ldots, n_1)$$

where N_n are the populations of discrete levels and n_1 is the number of discrete levels not joined with the continuous spectrum. The matrix $\{K_{nm}\}$ is called a relaxation matrix. The nondiagonal element K_{nm} characterizes the number of transitions per unit time from state m to state n. The diagonal element K_{nn} is equal in absolute value to the number of transitions per unit time from state n to all the other states. The quantity D_n is equal to the number of particles per unit volume entering state n per unit time from the continuum and the levels of the quasi-equilibrium spectrum joined with it.

Collisional transitions are characterized by a transition rate, i.e., the number of transitions per unit time normalized to the concentration of particles giving rise to the transition.

The nondiagonal elements of the relaxation matrix can be written in the form

$$K_{nm} = V_{nm} N_e + A_{nm} \qquad (n \neq m;\ n,\ m = 1, 2, \ldots, n_1)$$

where V_{nm} is the transition rate from state m to state n from the effect of electron impact, and A_{nm} is the rate of the spontaneous radiative transition $m \to n$; $A_{nm} = 0$ when $m < n$.

By definition the diagonal elements are

$$K_{nn} = -\left(\sum_{\substack{m=1 \\ m \neq n}}^{n_1} K_{mn} + V_{en} N_e \right) \qquad (n = 1, 2, \ldots, n_1)$$

where V_{en} is the rate of ionization by electron impact.

The free term has the form

$$D_n = V_{ne} N_e^2 N_+ \qquad (n = 1, 2, \ldots, n_1)$$

where N_+ is the ion concentration and V_{ne} is the rate of triple recombination.

To Eqs. (2.1) and (2.2) must be added an equation of balance of heavy particles

$$N = N_+ + \sum_{m=1}^{n_1} N_m \tag{2.3}$$

a condition of quasi-neutrality

$$N_e = N_+ \tag{2.4}$$

and, since recombination in a dense plasma leads to considerable heat release, an equation of heat balance.

From the point of view of the energy balance a low-temperature dense plasma can be considered as a collection of three relatively weakly interacting subsystems, formed by the translational degrees of freedom of the plasma electrons (A), the translational degrees of freedom of the heavy particles (B), and the energy levels of the bound electrons (C). Subsystem (C) also loses energy through radiation.

The exchange of energy between subsystems (A) and (B) is produced by the temperature difference $\Delta T = T_e - T$ (where T is the temperature of the heavy particles) and is accomplished by elastic collisions between electrons and heavy particles; equalization of the temperatures T_e and T is a relatively slow process with a relaxation time τ_T on the order of $(\nu_e m/M)^{-1}$, where M is the mass of the heavy particles,

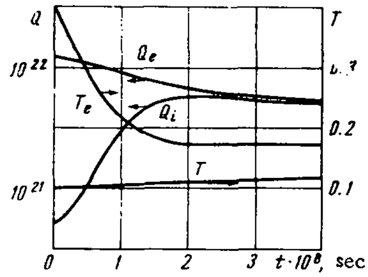

Fig. 1

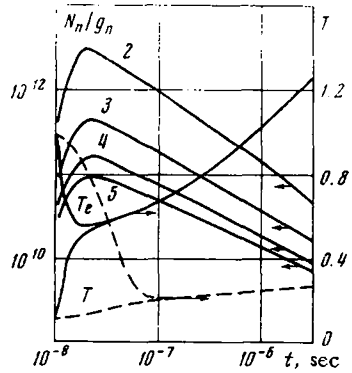

Fig. 2

m is the electron mass, and ν_e is the effective collision frequency of electrons with ions and neutral particles. Inelastic collisions, accompanied by a change in electron binding energy, lead to energy exchange between subsystems (A) and (C).

Only a small fraction ($\sim$ m/M) of the change in binding energy is transferred to the heavy particles during inelastic collisions of electrons with atoms or recombination collisions with ions. The contribution of inelastic collisions between heavy particles is also small. Therefore, it can be assumed that direct exchange between subsystems (B) and (C) is practically absent.

The amount of heat transmitted to the heavy-particle gas (per unit volume and unit time) by free electrons during elastic collisions equals [2]

$$Q_e = 3\,(m\,/\,M)\nu_e N_e (T_e - T)$$

The heat release in the electron gas through inelastic collisions is determined by the equation

$$Q_i = N_e \sum_{n=1}^{n_1} \left(N_n \sum_{\substack{m=1 \\ m \neq n}}^{n_1} E_{nm} V_{mn} + E_n (V_{ne} N_e^2 - V_{en} N_n) \right)$$

where E_n is the ionization energy of the n-th level and $E_{nm} = E_m - E_n$.

The heat-balance equations have the form

$$\frac{3}{2} N_e \frac{dT_e}{dt} = \frac{3}{2} T_e \sum_{n=1}^{n_1} \Gamma_n - N_e T_e \frac{\mu}{t} + Q_i - Q_e \tag{2.5}$$

$$\frac{3}{2} N \frac{dT}{dt} = Q_e - NT \frac{\mu}{t} \tag{2.6}$$

Thus, the relaxation of a dense low-temperature plasma in the spatially homogeneous model of inertial diffusion is described by the system of equations (2.1)-(2.6). Cauchy's problem is solved for this system with the following initial conditions at $t = t_0$:

$$N_n(t_0) = N_{n0}\ (n = 1, 2, \ldots, n_1),\ T_e(t_0) = T_{e0},\ T(t_0) = T_0$$

3. Method of Solution. Numerical solutions of Cauchy's problem are obtained with the help of an electronic computer for a number of initial conditions both for a stationary plasma ($\mu = 0$) and for the case of spherical dispersion ($\mu = 3$). The calculations are conducted for a partially ionized plasma of atomic hydrogen. The relaxation matrix is taken from [3]. Calculations with different values of n_1 showed that when $n_1 \geq 9$ the results differ little. The following values of the plasma parameters were chosen to an order of magnitude: $t_0 \gg 10^{-7}$ sec, $T_{e0} \sim T_0 \ll 1$ eV, $N_0 \sim 10^{17}$ cm^{-3}, $N_e \sim 10^{16}$ cm^{-3}.

The difference of orders of magnitude in the relaxation times of the plasma characteristics was used in the method of solution. The differential equations for the slowly varying parameters N_1, T_e, and T were solved by the Runge–Kutta method with automatic step selection. The populations of excited levels N_A, ($n = 2, 3, \ldots, n_1$) were determined in a stationary sink approximation, i.e., from a system of $n_1 - 1$ linear algebraic equations which is obtained from Eqs. (2.2) if one sets the time derivatives equal to zero in them when $n \geq 2$. This system was solved at each time step by Seidel's integration method.

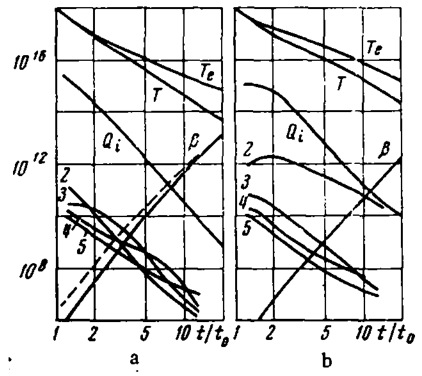

Fig. 3

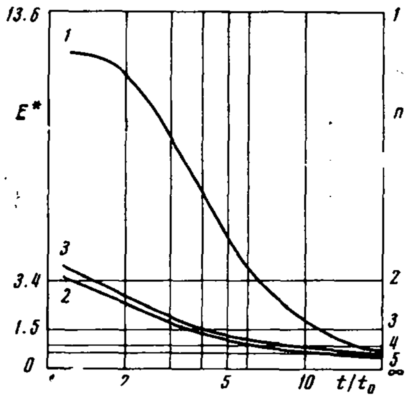

Fig. 4

The use of a quasi-stationary approximation in calculating the populations of excited levels is admissible if the characteristic times τ_n for the establishment of populations of levels with $n \geq 2$ are small compared with τ_Δ – the minimum of the characteristic times of variation of the plasma parameters N_1, N_e, T_e, T

$$\tau_n \ll \tau_\Delta \tag{3.1}$$

In the case of a stationary plasma

$$\tau_n = \tau_n{}^\circ \approx \lambda_n^{-1}, \qquad \tau_\Delta = \tau_r \approx N_e \,|\, dN_e / dt\,|^{-1}$$

where λ_n is the corresponding proper value of the relaxation matrix and τ_r is the characteristic recombination time of the electrons. In the case of a dispersing plasma

$$\tau_n^{-1} = (\tau_n{}^\circ)^{-1} + \mu t^{-1}, \qquad \tau_\Delta^{-1} = \tau_r^{-1} + \mu t^{-1}$$

and the condition (3.1) can be represented in the form

$$(\tau_r^{-1} + \mu t^{-1}) \,/\, ((\tau_n{}^\circ)^{-1} + \mu t^{-1}) \ll 1 \tag{3.2}$$

In the approximation of a stationary sink for $n \geq 2$ we obtain from (2.2) the estimate

$$N_n / N_e \sim \tau_r^{-1} / ((\tau_n{}^\circ)^{-1} + \mu t^{-1})$$

which permits us to rewrite (3.2) in the form

$$N_n / N_e \ll 1 / (1 + \mu \tau_n{}^\circ t^{-1}) \tag{3.3}$$

When $\mu = 0$, i.e., in a stationary plasma, this condition is converted into the criterion of applicability of the stationary-sink approximation

$$N_n / N_e \ll 1 \tag{3.4}$$

It is seen from (3.3) that the inequality (3.4) occurs when $t > \tau_n{}^\circ$. In the case of an optically thin plasma the value $\tau_n{}^\circ$ is limited from above by the value $A_{1n}^{-1} \sim 10^{-8}$ sec, i.e., the approximation of a stationary sink is valid in the entire range of parameters.

If the ratio τ_n / τ_r is considered as a small parameter with the derivative in Eqs. (2.2) for $n \geq 2$, the validity of using the stationary-sink approximation in calculating the population of excited levels can be justified from a mathematical point of view [4].

The solution of the entire system of differential equations by the Runge–Kutta method or some other traditional method without using the stationary-sink approximation would require a time step much smaller than τ_n (at $n = n_1$). Since we are considering a variation in plasma parameters over time intervals of $\Delta t \gg \tau_\Delta$, which exceed τ_n by three to four orders of magnitude for the plasma parameters given above, this would lead to extremely long calculation times and a loss of accuracy caused by the accumulation of rounding errors.

4. Discussion of Results. Some results of a numerical solution of the system of equations (2.1)–(2.6) for an optically thin stationary ($\mu = 0$) plasma are presented in Figs. 1 and 2. The plasma is cooled only through luminescence. The calculations are conducted with the following initial conditions: $T_{e0} = 0.4$ eV,

$T_0 = 0.1$ eV, $N_0 = 10^{17}$ cm^{-3}, $N_{10} = 0.99 \cdot 10^{17}$ cm^{-3} (Fig. 1) and $T_{e0} = 1$ eV, $T_0 = 0.1$ eV, $N_0 = 10^{16}$ cm^{-3}, $N_{10} = 0$ for the solid curves and $N_{10} = 0.9 \cdot 10^{16}$ cm^{-3} for the dashed curves (Fig. 2); $N_{n0} = 0$ for $n = 2, 3, \ldots, n_1$. The time is laid out along the abscissa in a linear scale in Fig. 1 and in a logarithmic scale in Fig. 2. A linear temperature scale in electron volts is placed on the right in both figures.

The initial temperature gap between T_e and T decreases over a time $\tau_T \sim M(m\nu_e)^{-1}$. At a low degree of ionization ($\alpha_0 = 0.01$) a certain temperature gap is preserved rather long since the cooling of the electron gas through elastic collisions Q_e is compensated for by recombination heating Q_i (in Fig. 1 Q is given in eV $\cdot$ cm^{-3} $\cdot$ sec^{-1} on the logarithmic scale to the left). At a high degree of ionization the temperatures T_e and T are practically equalized after a time on the order of τ_T and subsequently remain identical (in Fig. 2 the solid curve corresponds to $\alpha_0 = 1$ and the dashed curve to $\alpha_0 = 0.1$). Subsystem (C) continues to heat subsystems (A) and (B) so that the electron temperature, having reached a minimum, begins to increase slowly while the populations of excited levels N_n correspondingly decrease. The values of N_n/g_n in cm^{-3} are given in the logarithmic scale on the left in Fig. 2 and the numbering of the curves coincides with the principal quantum numbers n of the corresponding levels (g_n is the statistical weight of the level).

The calculations for the case of spherical dispersion ($\mu = 3$), the results of which are presented in Figs. 3 and 4, are conducted with the following initial conditions at $t_0 = 2.4 \cdot 10^{-6}$ sec: $T_{e0} = T_0 = 0.88$ eV, $N_0 = 5.2 \cdot 10^{16}$ cm^{-3}, $N_{10} = 4.4 \cdot 10^{16}$ cm^{-3} ($\alpha_0 = 0.15$) for $M = 14 M_H$, where M_H is the mass of a hydrogen atom.

The variation with time of a number of values is shown in Fig. 3 in the case of an optically thin plasma (a) and with complete reabsorption of the Lyman series radiation (b). The values $T^2 \cdot 10^{18}$ eV^2, $Q_i \cdot 10^{-6}$ eV $\cdot$ cm^{-3} $\cdot$ sec^{-1}, $\beta \cdot 10^{32}$ cm^6 $\cdot$ sec^{-1}, and N_n/g_n cm^{-3}, n = 2, 3, 4, 5 refer to a single logarithmic scale along the ordinate. The time is laid off in relative units in a logarithmic scale along the abscissa.

A characteristic property of the kinetics of a dispersing plasma is the appearance of a temperature gap: T_e and T decrease but the value $(T_e - T)/T$ increases with time. This is caused by the rapid shutting off of the mechanism of cooling of electrons on heavy particles because of the drop in density. The reabsorption of radiation leads to an increase in heat release Q_i in the electron gas and a decrease in the triple recombination coefficient β. At first, when T_e is large and the recombination coefficient is small, Q_i in a transparent plasma can be larger than in an optically dense plasma, while the rate of temperature drop is practically the same in the two cases. Then the heat release becomes greater under conditions of reabsorption of radiation than in a transparent plasma, while the temperatures T_e and T decrease more slowly.

The time dependence of the triple recombination coefficient β shown by solid curves is obtained in the solution of the self-consistent system of equations (2.1)-(2.6), with allowance for the entire set of processes determining the populations of levels, and the electron concentration and temperature from the equation

$$\beta = \sum_{m=1}^{n} (V_{me} - V_{em} N_m / (N_e N_+)) \tag{4.1}$$

The behavior of the recombination coefficient calculated from the equation [5]

$$\beta = 8.75 \cdot 10^{-27} \; T_e^{-9/2} \tag{4.2}$$

(T_e is in electron volts), based on a model of diffusion of a bound electron in an atom along the energy axis, is shown by a broken line in Fig. 3a for comparison. At the initial values of the parameters ($T_e \sim 1$ eV, $N_e \sim 10^{16}$ cm^{-3}) the value of β given by Eq. (4.2) is about five times greater than the value obtained according to (4.1), and only at $T_e \leqslant 0.1$ eV and $N_e \sim 10^{13}$ cm^{-3} do the two equations give close values of the triple recombination coefficient. This confirms the restricted nature of the region of applicability of the "diffusion" model. (The region of applicability of Eq. (4.2) was discussed in [6].)

The reabsorption of radiation alters the nature of the population of levels especially strongly. If all the radiation freely escapes from the plasma an inversion occurs in the population of the lower excited levels n = 2, 3, 4, 5 in the process of dispersion. If the radiation of the Lyman series is blocked, the inversion does not occur and the population of level n = 2 is anomalously large and drops more slowly than t^{-3}. This is connected with the fact that the effect of the collisional mechanism which, solely in this case, provides for the clearing of this level is weakened in proportion to the dispersion.

The reabsorption of Lyman-series radiation under conditions of dispersion leads to a continuous increase in the effective relaxation time τ_2 of the first excited level, and τ_2 becomes greater than the

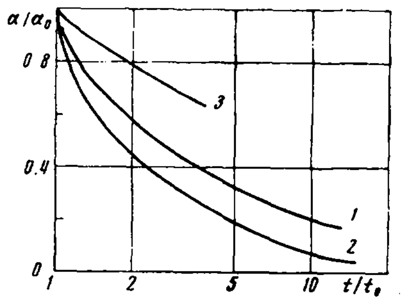

Fig. 5

characteristic time of dispersion at some moment $t = t_1$. This is especially clearly seen from Fig. 4, where the energy E^* transferred to the electron gas in one act of recombination is laid out in eV in a linear scale along the ordinate; the horizontal lines correspond to the hydrogen-atom energy levels and the principal quantum numbers n are given on the right. In an optically thick plasma when $t < t_1$ almost all the energy liberated in one act of recombination is transferred to subsystem (A), i.e., goes to heating electrons (curve 1), in contrast to an optically thin plasma where a large part of the energy is radiated off (curve 2). When $t > t_1$ the heat release drops sharply to values characteristic for an optically thin plasma: although resonance radiation remains blocked the mechanism of collisions ceases to be effective and the energy is "frozen" in the first excited level.

For a transparent plasma a calculation of the fraction of energy transferred to the electrons (curve 2), based on a solution of the system (2.1)-(2.6), gives a value close to that obtained in [7] using the model of electron diffusion along the energy axis (curve 3). The freezing of the nonequilibrium population of the level during rapid expansion of the plasma, accompanied by a decrease in the heat release per act of recombination, should also be expected in those cases where the atom has a metastable state with a large excitation energy (for example, in the case of inert gases).

The dependence of the degree of ionization α on time during the spherical dispersion of a hydrogen plasma into a vacuum is shown in Fig. 5. The initial conditions are given at the moment of breakdown of ionization equilibrium $t_0 = 10^{-5}$ sec, estimated according to [6]. Curve 1 corresponds to the case of $T_{e0} = T_0 = 1$ eV, $N_0 = 1.7 \cdot 10^{16}$ cm^{-3}, $\alpha_0 = 0.58$ and curve 2 to the case of $T_{e0} = T_0 = 1$ eV, $N_0 = 4 \cdot 10^{16}$ cm^{-3}, $\alpha_0 = 0.34$. Curves calculated in the diffusion model with the same initial conditions are presented in [7]. (In determining the moment of breakdown of ionization equilibrium in [7] β was calculated from Eq. (4.2), which leads to $t_0 = 2 \cdot 10^{-6}$ sec.)

The degree of ionization decreases somewhat faster in curve 1 (Fig. 5) and slower in curve 2 than in the corresponding curves in [7], which there represent two qualitatively different cases: "freezing" of the unrecombined electrons and ions; recombination proceeds to the end and the degree of ionization is already reduced to zero at $t \approx 10t_0$ (the authors of [7] explain this result by the approximate nature of the equations which they used). Curve 3 corresponds to the same initial conditions as curve 2 but on the assumption of reabsorption of radiation. Conditions are possible where in a plasma transparent for radiation recombination proceeds practically to the end during diffusion, but freezing occurs in the case of radiation capture.

It should be noted that for the resonance level $n = 2$ in the presence of reabsorption of radiation the criterion of applicability of the quasistationary approximation (3.2) is satisfied only in the section $t/t_0 \lesssim 3$, so that for longer times the results for an optically thick plasma may not be fully correct.

During rapid expansion of a dense low-temperature plasma besides ionization and temperature nonequilibrium a nonequilibrium population of excited states can also arise. Experimental observations of these deviations from thermodynamic equilibrium in an expanding plasma of hydrogen in a mixture with other gases, and in particular the population inversion, are described in [8, 9]. The possibility of obtaining an inverted population of levels in an expanding plasma was indicated in [10, 11]. Analogous results were obtained in [12] for the relaxation of partially ionized xenon upon expansion in a nozzle.

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