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Kinetics of electrons in gases and condensed systems

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<u>Abstract.</u> Kinetics of electrons moving in a gas or a plasma under the action of external fields is considered. Elementary processes of elastic and inelastic electron – atom collisions responsible for electron kinetics in weakly ionized atomic gases are analyzed. Various regimes of evolution of electrons in a gas or a plasma in external fields are considered, and the character of atom excitations under these conditions is studied. Methods of describing the electron kinetics in gases and plasma are applied to modeling the electron drift in condensed systems. It is shown that the electric properties of metals and the behavior of an excess electron in dielectrics have common features with electron drift in gases and plasmas. The drift of an excess electron in condensed inert gases is reviewed.

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1. Introduction

The behavior of a gas with an admixture of electrons is of importance for various problems of the physics of weakly ionized gases and gas discharges [1-16]. A peculiarity of this two-component system is that if it is placed in an external electric field, the energy is transmitted from the field to the electron subsystem, and then electrons transfer the energy to a gas as a result of electron – atom collisions. Therefore, in spite of thermodynamic equilibrium for a gas, the thermodynamic equilibrium for the electron subsystem can be violated even under relatively weak fields. Nevertheless, due to a small ratio of electron mass to atomic mass, the electron distribution function can be found under various conditions by solving the Boltzmann kinetic equation.

Note that, in contrast to the traditional hydrodynamic description of a two-component gaseous system where interaction between subsystems is taken into account by a collision time of particles of these subsystems, the kinetic analysis of this problem allows one to use real cross sections of electron-atom or electron-molecule collisions. Hence, the kinetic analysis results in a strict theory instead of a model description on the basis of hydrodynamic methods. In particular, the Ramsauer effect consisting in a sharp minimum in the cross sections of electron scattering by some

Though the problem of studying the electron evolution in a gas has a long history, its new aspects demand revisions, and this is a goal of this review. Next, one can use the results of this problem's solution for analyzing condensed atomic systems with electrons. For example, we consider the drift of an excess electron in condensed rare gases. In a wide range of parameters, an electron's behavior in this system is similar to that in gases, and the electron mobility in condensed rare gases may exceed that of metals. The reason of this is a weak electron interaction with the environment, so that some parameters of electron drift in condensed systems are similar to those in gases, and therefore gaseous models may be useful for condensed systems.

In considering the evolution of electrons in gaseous and model systems, we restrict ourselves to simple conditions where these systems are spatially homogeneous. Hence, certain phenomena of gas discharges due to specific space distributions of particles are outside this review. Next, in analyzing different regimes of the behavior of the electron subsystem, we will try to be guided by rarefied and condensed inert gases that allows us to consider peculiarities of the evolution of these systems in detail. Thus, the aim of this review is to consider theoretically the kinetics of electrons in gases in external electric fields from the standpoint of contemporary problems with the attraction of experimental data to construct a general picture of these processes. This theory is useful for the analysis of electron drift in condensed systems.

2. Kinetics of electrons in a gas in an external electric field

2.1 Kinetic equation for electrons in gas

We consider first the equilibrium state between individual electrons and atomic gas, when an external electric field acts on the electrons. Then, the Boltzmann kinetic equation for the velocity distribution function $f(\mathbf{v})$ of electrons has the form

$$\frac{e\mathbf{F}}{m_{\rm e}}\frac{\partial f}{\partial \mathbf{v}} = I_{\rm ea}(f)\,. \tag{2.1}$$

Here, **F** is the electron field strength, m_e is the electron mass, I_{ea} is the electron – atom collision integral which accounts for electron – atom collisions and is given by (see, for example, Refs [16–22])

$$I_{ea}(f) = \left[f(\mathbf{v}') \,\varphi(\mathbf{v}'_{a}) - f(\mathbf{v}) \,\varphi(\mathbf{v}_{a}) \right] \,\mathrm{d}\sigma \,\mathrm{d}\mathbf{v}_{a} \,. \tag{2.2}$$

Here, \mathbf{v}, \mathbf{v}' are the electron velocities before and after collision, $\mathbf{v}_a, \mathbf{v}'_a$ are the atomic velocities before and after collision, and $d\sigma$ is the differential cross section of the electron-atom scattering.

Because the number density $N_{\rm e}$ of electrons is small in comparison to the number density $N_{\rm a}$ of atoms, the presence of electrons in a gas does not affect the Maxwell distribution function $\varphi(v_{\rm a})$ of the atoms, which takes the form

$$\varphi(v_{\rm a}) = N_{\rm a} \left(\frac{M}{2\pi T}\right)^{3/2} \exp\left(-\frac{M v_{\rm a}^2}{2T}\right),\tag{2.3}$$

where *M* is the atomic mass, and *T* is the gas temperature. The specifics of electron - atom collisions in a gas follows from the small ratio of electron mass $m_{\rm e}$ to atomic mass M. Even collisions with large scattering angles lead to a small change of the electron energy. This gives the basis for expansion of the electron distribution function in terms of spherical harmonics, and this problem was solved successfully in Refs [23-28], and the results were summed up in Ref. [29]. As a result, the expansion of the electron distribution function over spherical harmonics allows us to solve strictly the problem of electron drift in a gas in an external electric field, and this problem will be given below. Note that, along with the electron drift in gases, this problem was developed simultaneously for the electron mobility and conductivity of semiconductors, when the electron drift velocity is comparable or exceeds the speed of sound [30-33].

Thus, because of a small energy exchange in electron – atom collisions, the velocity distribution of electrons moving in a gas in an external electric field is nearly symmetrical with respect to directions of electron motion and can be represented in the form

$$f(\mathbf{v}) = f_0(v) + v_x f_1(v), \qquad (2.4)$$

where the x-axis is aligned with the electric field **F**. Since the electron – atom collision integral has a linear dependence on the distribution function $f(\mathbf{v})$, from formula (2.2) on the basis of the principle of detailed balance it follows that

$$I_{\rm ea}(f) = I_{\rm ea}(f_0) + I_{\rm ea}(v_x f_1).$$
(2.5)

Let us consider the second term of this formula. According to formula (2.2) we have

$$I_{\text{ea}}(v_x f_1) = \int (\mathbf{v}' - \mathbf{v})_x v \, \mathrm{d}\sigma \, f_1(v) \, \varphi(v_a) \, \mathrm{d}\mathbf{v}_a \,,$$

where \mathbf{v} , \mathbf{v}' are the electron velocities before and after collision, and \mathbf{v}_a is the atomic velocity. Because of a small atomic velocity, the character of scattering does not depend on \mathbf{v}_a , and the integration over atomic velocities gives $\int \varphi(v_a) d\mathbf{v}_a = N_a$, where N_a is the atomic number density. Next, we represent the electron velocity after collision as

$$\mathbf{v}' = \mathbf{v}\cos\vartheta + v\mathbf{k}\sin\vartheta\,,$$

where ϑ is the scattering angle, and **k** is the unit vector located in the plane that is perpendicular to the initial electron velocity **v**. Since this vector has an arbitrary direction in a given plane, we obtain $\int \mathbf{k} \, d\sigma = 0$ to give $\int (\mathbf{v}' - \mathbf{v})_x \, d\sigma =$ $-v_x \sigma^*(v)$, where $\sigma^*(v) = \int (1 - \cos \vartheta) \, d\sigma$ is the diffusion cross section of electron-atom scattering. Finally, we arrive at

$$I_{\rm ea}(v_x f_1) = -v v_x f_1(v), \qquad (2.6)$$

where $v = N_a v \sigma^*(v)$ is the rate of electron – atom collisions.

The kinetic equation (2.1) taking into account Eqns (2.4) and (2.6) takes the form

$$\frac{eF}{m_{\rm e}}\left(\frac{v_x}{v}\frac{\mathrm{d}f_0}{\mathrm{d}v} + f_1 + v_x^2\frac{\mathrm{d}f_1}{\mathrm{d}v}\right) = -vv_xf_1 + I_{\rm ea}(f_0)\,.\tag{2.7}$$

To extract the spherical harmonics from the last equation, we integrate it over $d\cos\theta$, where θ is the angle between the

vectors **v** and **F**, and, multiplying this equation by $\cos \theta$, integrate it over the angles. We then obtain instead of equation (2.7) the following set of the equations

$$a \frac{\mathrm{d}f_0}{\mathrm{d}v} = -vvf_1, \quad \frac{a}{3v^2} \frac{\mathrm{d}}{\mathrm{d}v}(v^3f_1) = I_{\mathrm{ea}}(f_0), \quad (2.8)$$

where $a = eF/m_e$. This set of equations establishes the connection between the spherically symmetric and nonspherically symmetric parts of the distribution function. From this it follows for the electron drift velocity in a gas, i.e. for the average electron velocity,

$$w_{\rm e} = \int v_x^2 f_1 \,\mathrm{d}\mathbf{v} = \frac{eF}{3m_{\rm e}} \left\langle \frac{1}{v^2} \frac{\mathrm{d}}{\mathrm{d}v} \left(\frac{v^3}{v} \right) \right\rangle, \tag{2.9}$$

where an average is carried out with the spherically symmetric distribution function of the electrons. In particular, if v = const, the electron drift velocity w_e and the mean energy $\bar{\epsilon}$ are given by

$$w_{\rm e} = \frac{eF}{m_{\rm e}v}, \quad \bar{\varepsilon} = \frac{3}{2} T + \frac{M}{2} w_{\rm e}^2.$$
 (2.10)

2.2 Spherically symmetric part of the electron – atom collision integral

For determining the collision integral $I_{ea}(f_0)$ from the spherically symmetric distribution function f_0 , we account for the fact that the electron energy change after one collision with an atom is small compared to the energy itself. Note that the kinetic equation for the relaxation of the electron distribution function to equilibrium as a result of electron– atom collisions has the following form

$$\frac{\partial f_0}{\partial t} = I_{\text{ea}}(f) \,. \tag{2.11}$$

The continuous character of variation of the energy of a test electron in collisions with atoms leads to Fokker–Planck's form of this kinetic equation, so that the collision integral in the electron energy space is equal to

$$I_{\text{ea}}(f) = -\frac{1}{\rho(\varepsilon)} \frac{\partial j(f)}{\partial \varepsilon}$$

and then equation (2.11) takes the form of a continuity equation in the electron energy space. Here, the density of states ρ in the electron energy space is $\rho(\varepsilon) \sim \varepsilon^{1/2}$, and the electron flux j(f) in the energy space can be represented in the linear form

$$j = A\rho f - B \, \frac{\partial(\rho f)}{\partial \varepsilon} \,,$$

and the coefficients of this expansion are determined by electron-atom collision processes. Accounting for the nature of the Fokker-Planck equation [34-36], these quantities are defined by the expressions

$$\begin{split} A(\varepsilon,t) &= \lim_{\tau \to 0} \frac{1}{\tau} \int (\varepsilon - \varepsilon') W(\varepsilon,t;\varepsilon',t+\tau) \,\rho(\varepsilon') \,\mathrm{d}\varepsilon' \,, \\ B(\varepsilon,t) &= \lim_{\tau \to 0} \frac{1}{2\tau} \int (\varepsilon - \varepsilon')^2 W(\varepsilon,t;\varepsilon',t+\tau) \,\rho(\varepsilon') \,\mathrm{d}\varepsilon' \,, \end{split}$$

where $W(\varepsilon, t; \varepsilon', t + \tau)$ is the probability of a given variation of the electron energy during a time τ . It follows thence that the collision integral of electrons as a result of collisions with atoms equals

$$I_{\rm ea}(f_0) = \frac{1}{\rho(\varepsilon)} \frac{\partial}{\partial \varepsilon} \left[-A\rho f_0 + \frac{\partial}{\partial \varepsilon} (B\rho f_0) \right].$$
(2.12)

It is essential here that under thermodynamic equilibrium, i.e. if the distribution function coincides with the Maxwell distribution function at the gaseous temperature of electrons, the collision integral becomes zero. This gives the connection between the quantities A and B in the form A = -B/T [37, 38]. Finally, from this we obtain for the collision integral of the spherically symmetric part of the electron distribution function:

$$I_{\text{ea}}(f_0) = \frac{1}{\rho(\varepsilon)} \frac{\partial}{\partial \varepsilon} \left[\rho(\varepsilon) B(\varepsilon) \left(\frac{\partial f_0}{\partial \varepsilon} + \frac{f_0}{T} \right) \right], \qquad (2.13)$$

where T is the gaseous temperature.

By definition, the quantity $B(\varepsilon)$ is expressed in the following way

$$B(\varepsilon) = \frac{1}{2} \left\langle \int (\varepsilon - \varepsilon')^2 N_{\rm a} v \, \mathrm{d}\sigma \, (\varepsilon \to \varepsilon') \right\rangle. \tag{2.14}$$

Here, the angle brackets mean averaging over atomic energies, and $d\sigma$ is the electron – atom collision cross section which corresponds to a given change in electron energy. Let us use the law of conservation of the relative electron – atom velocity as a result of their elastic collision, i.e. $|\mathbf{v} - \mathbf{v}_a| = |\mathbf{v}' - \mathbf{v}_a|$, where \mathbf{v} , \mathbf{v}' are the electron velocities before and after collision, and \mathbf{v}_a is the atomic velocity which does not change during the collision with an electron, because the atomic momentum is large in comparison with the electron momentum. From this it follows that $v^2 - (v')^2 = 2\mathbf{v}_a(\mathbf{v} - \mathbf{v}')$, and formula (2.14) takes the form

$$B(\varepsilon) = \frac{m_{\rm e}^2}{2} \left\langle \frac{v_{\rm a}^2}{3} \right\rangle \int (\mathbf{v} - \mathbf{v}')^2 N_{\rm a} v \,\mathrm{d}\sigma = T \, \frac{m_{\rm e}^2 v^2}{M} \, N_{\rm a} v \sigma^*(v) \,,$$
(2.15)

where $\langle v_a^2/3 \rangle = T/M$, *T* is the gaseous temperature, m_e , *M* are the electron and atomic masses, $|\mathbf{v} - \mathbf{v}'| = 2v \sin(\vartheta/2)$, ϑ is the scattering angle, and $\sigma^*(v) = \int (1 - \cos \vartheta) \, d\sigma$ is the diffusion cross section of electron-atom scattering. Thus, using $\rho(\varepsilon) \sim \sqrt{\varepsilon}$, we have for the collision integral of the spherically symmetric part of the electron distribution function:

$$I_{\rm ea}(f_0) = \frac{m_{\rm e}}{M} \frac{\partial}{v^2 \partial v} \left[v^3 v_{\rm ea} \left(\frac{1}{m_{\rm e} v} \frac{\partial f_0}{\partial v} + \frac{f_0}{T} \right) \right], \qquad (2.16)$$

where $v_{ea} = N_a v \sigma^*(v)$ is the rate of electron – atom collisions. This part of the collision integral describes the electron energy change in electron – atom collisions.

2.3 Equilibrium conditions for electrons moving in a gas in an external electric field, and the electron distribution function

In considering the equilibrium of the electron and atomic subsystems when electrons are moving in a gas in an external electric field, we have to account in a general case for electron-atom collisions and collisions between electrons. Then the electron distribution function f satisfies the

$$\frac{e\mathbf{F}}{m_{\rm e}}\frac{\partial f}{\partial \mathbf{v}} = I_{\rm ee}(f) + I_{\rm ea}(f). \qquad (2.17)$$

Here, **F** is the electric field strength, m_e is the electron mass, I_{ea} is the electron – atom collision integral defined in accordance with formulas (2.6), (2.16), and I_{ee} is the collision integral due to electron – electron interaction. The character of the equilibrium of this system depends on the ratio between I_{ee} and I_{ea} .

Above we considered the limiting case $I_{ee} \ll I_{ea}$. Let us estimate the collision integrals as follows

$$I_{\rm ea} \sim \frac{m_{\rm e}}{M} v \sigma_{\rm ea} N_{\rm a} f, \quad I_{\rm ee} \sim v \sigma_{\rm ee} N_{\rm e} f,$$

where v is a typical electron velocity, m_e , M are the masses of electrons and atoms, N_e , N_a are the number densities of electrons and atoms, and σ_{ea} , σ_{ee} are the typical cross sections for collisions of electrons with atoms and with electrons, respectively. Hence it follows that the above-mentioned limit corresponds to the criterion

$$N_{\rm e} \ll \frac{m_{\rm e}}{M} \frac{\sigma_{\rm ea}}{\sigma_{\rm ee}} N_{\rm a} \,.$$
 (2.18)

Because $m_e \ll M$ and $\sigma_{ea} \ll \sigma_{ec}$, this criterion can be valid for an ionized gas with a weak degree of ionization. For example, for an argon plasma criterion (2.18) takes the form $c_e \ll 2 \times 10^{-7}$ at temperature $T_e = 1000$ K, where $c_e = N_e/N_a$ is the electron concentration, and at $T_e = 10^4$ K this criterion goes to $c_e \ll 5 \times 10^{-6}$.

In the opposite limiting case with respect to Eqn (2.18) we have

$$I_{\rm ee}(f) = 0.$$
 (2.19)

The solution of this equation leads to the Maxwell distribution function similar to Eqn (2.3), which has the form

$$\varphi(v) = N_{\rm e} \left(\frac{m_{\rm e}}{2\pi T_{\rm e}}\right)^{3/2} \exp\left(-\frac{m_{\rm e}v^2}{2T_{\rm e}}\right),\tag{2.20}$$

where the electron temperature T_e can differ from the gaseous temperature T in formula (2.3) and is determined by both interaction of electrons with an electric field and their collisions with atoms. The electron temperature is governed by the character of the energy transfer from an external electric field to a gas. Then the energy transfers first from an external field to the electrons, and later from the electrons to atoms as a result of their collisions. One can draw this conclusion from the kinetic equation (2.17) directly.

Let us multiply it by the electron energy $m_e v^2/2$ and integrate with respect to electron velocities. As a result, we have

$$\int \frac{m_{\rm e} v^2}{2} I_{\rm ee} \, \mathrm{d}\mathbf{v} = 0$$

because of the physical sense of the collision integral and the conservation of the total energy in the electron subsystem. Hence, we arrive at the following integral relation

$$eFw_{\rm e} = \int \frac{m_{\rm e}v^2}{2} I_{\rm ea} \,\mathrm{d}\mathbf{v}\,,\tag{2.21}$$

where w_e is the electron drift velocity. This relation constitutes the energy balance equation for electrons, so that the lefthand side of this relationship is the power which an individual electron obtains from the electric field, and the right-hand side defines the power transmitted from an electron to atoms as a result of their collisions. From equation (2.17) it follows that the ions give a small contribution to the power transmission between an external electric field and a gas in comparison with electrons, because the electron drift velocity exceeds remarkably the ion drift velocity. Thus, the character of the power transmission in a weakly ionized gas from an external electric field to electrons, and from electrons to atoms, does not depend on criterion (2.18). If this criterion is violated, one can consider electrons as an isolated subsystem. If this criterion holds true, we have another character of equilibrium for the electron-atom system.

Thus, the distribution function of electrons when they are located in a gas in an external electric field depends on the validity of criterion (2.18). If this criterion is violated, the Maxwell electron distribution function (2.20) follows from equations (2.17) and (2.19). Using this circumstance in the first equation of the set (2.8), we find

$$f_1 = \frac{eF}{vT_e} f_0 \,, \tag{2.22}$$

and the electron drift velocity equals

$$w_{\rm e} = \frac{eF}{3T_{\rm e}} \left\langle \frac{v^2}{v} \right\rangle. \tag{2.23}$$

The electron temperature T_e is a parameter which can be found from the balance equation (2.21) for the power transmitted from an electric field to electrons and from electrons to atoms of a gas. This equation, using formula (2.16) for the electron-atom collision integral of the spherically symmetric part of the electron distribution function, takes the form

$$eFw_{\rm e} = \int \frac{m_{\rm e}v^2}{2} I_{\rm ea}(f_0) \,\mathrm{d}\mathbf{v} = \frac{m_{\rm e}^2}{M} \left(1 - \frac{T}{T_{\rm e}}\right) \langle v^2 v \rangle \,. \tag{2.24}$$

On the basis of formula (2.23) for the electron drift velocity in a gas, we obtain from above relation that

$$T_{\rm e} - T = \frac{Ma^2}{3} \frac{\langle v^2 / v \rangle}{\langle v^2 v \rangle} , \qquad (2.25)$$

where $a = eF/m_e$. In particular, in the case v = const, it follows

$$w_{\rm e} = \frac{eF}{m_{\rm e}v}, \qquad T_{\rm e} - T = \frac{Mw_{\rm e}^2}{3}.$$
 (2.26a)

If $\sigma^{*}(v) = \text{const}$, formulas (2.9), (2.24) yield $[\lambda = (N_{a}\sigma^{*})^{-1}]$

$$w_{\rm e} = \frac{2eF}{3m_{\rm e}} \left\langle \frac{1}{v} \right\rangle = \frac{2\sqrt{2} \, eF\lambda}{3\sqrt{\pi T_{\rm e}m_{\rm e}}} = 0.532 \, \frac{eF\lambda}{\sqrt{m_{\rm e}T_{\rm e}}} \,, \qquad (2.26b)$$
$$T_{\rm e} - T = \frac{3\pi M w_{\rm e}^2}{32} \,.$$

On the basis of formula (2.24), we obtain the balance equation for establishing the average electron energy $\overline{\epsilon}$:

$$\frac{\mathrm{d}\bar{\varepsilon}}{\mathrm{d}t} = eFw_{\mathrm{e}} - \frac{m_{\mathrm{e}}^2}{M} \left(1 - \frac{T}{T_{\mathrm{e}}}\right) \langle v^2 v \rangle \,.$$

Let us write down this equation in the form

$$\frac{\mathrm{d}T_{\mathrm{e}}}{\mathrm{d}t} = -v_{\varepsilon}(T_{\mathrm{e}}-T_{0})\,,$$

where T_0 is the equilibrium electron temperature, T_e is the current electron temperature, and v_e is the relaxation rate of the electron temperature. We can take this rate in the limiting cases:

$$v_{\varepsilon} = 2 \frac{m_{\rm c}}{M} v$$
, $v = {\rm const}$, (2.27a)

and

$$v_{\varepsilon} = \frac{16}{3\sqrt{\pi}} \frac{m_{\rm e}}{M} \frac{1}{\lambda} \sqrt{\frac{2T_{\rm e}}{m_{\rm e}}}, \quad \sigma^*(v) = {\rm const.}$$
(2.27b)

A typical time of change in electron momentum, $\tau \sim 1/\nu$, is $M/m_{\rm e}$ times less than a typical time of variation of electron energy, $\tau_{\varepsilon} \sim M/(m_{\rm e}\nu)$.

In the limiting case when the criterion (2.18) holds true, the solution to the set of equations (2.8), found using formula (2.16) for the collision integral, gives

$$f_0(v) = A \exp\left(-\int_0^v \frac{m_e v' \, dv'}{T + M u^2 / 3}\right), \quad f_1(v) = \frac{m_e u f_0}{T + M u^2 / 3},$$
(2.28)

where

.....

$$u = \frac{eF}{m_{\rm e}v} = \frac{eF}{m_{\rm e}N_{\rm a}v\sigma^*(v)}, \qquad (2.29)$$

and the distribution function is normalized on the number density of electrons:

$$\int_{0}^{\infty} 4\pi v^2 f_0 \,\mathrm{d}v = N_{\rm e} \,. \tag{2.30}$$

From this we get the expression for the electron drift velocity in a gas:

$$w_{\rm e} = \frac{1}{3} \int_0^\infty v^2 f_1 4\pi v^2 \, \mathrm{d}v = \frac{4\pi}{3} \int_0^\infty \frac{m_{\rm e} u f_0}{T + M u^2 / 3} \, v^4 \, \mathrm{d}v \, .$$

In particular, in the case v = const, the electron drift velocity w_e and the mean energy \overline{e} have the form

$$w_{\rm e} = \frac{eF}{m_{\rm e}v}, \qquad \bar{\varepsilon} = \frac{3T}{2} + \frac{Mw_{\rm e}^2}{2}, \qquad (2.31)$$

which coincides with expressions (2.26a) based on the opposite criterion for the electron density. If $\sigma^*(v) = \text{const}$, distribution functions (2.28) yield in the limit $\bar{\varepsilon} \ge T$ [here $\lambda = 1/(N_a \sigma^*)$]:

$$w_{\rm e} = 0.857 \left(\frac{m_{\rm e}}{M}\right)^{1/4} \sqrt{\frac{eF\lambda}{m_{\rm e}}}, \qquad (2.32)$$
$$\bar{\varepsilon} = 0.427 eF\lambda \sqrt{\frac{M}{m_{\rm e}}} = 0.530 M w_{\rm e}^2,$$

which corresponds to another dependence of the electron drift velocity on the field strength as compared to Eqn (2.26b).

2.4 Kinetics of electrons during electron – electron collisions

We now consider the case of high electron density for the motion of electrons in a gas in an external electric field. Then the equilibrium for the electron subsystem results from collisions between electrons. The collision integral characterizing the establishment of this equilibrium has the form

$$I_{ee}(f) = -\int [f(\mathbf{v}_1) f(\mathbf{v}_2) - f(\mathbf{v}_1') f(\mathbf{v}_2')] |\mathbf{v}_1 - \mathbf{v}_2| \, d\sigma_{ee} \, d\mathbf{v}_2 ,$$
(2.33)

where $d\sigma_{ee}$ is the differential cross section for scattering of two electrons which have velocities \mathbf{v}_1 , \mathbf{v}_2 before collision, and \mathbf{v}'_1 , \mathbf{v}'_2 after collision. The peculiarity of the collision integral $I_{ee}(f)$ lies in the fact that this quantity is determined by a small change in the electron velocity during the collisions. If the velocity of a test electron varies by small portions, the collision integral can be expressed as a divergence of a flux in the velocity space. This form of the electron–electron collision integral is called the Landau collision integral which becomes [18, 19, 39]

$$I_{\rm ee}(f) = -\frac{\partial j_{\beta}}{\partial v_{1\beta}}, \qquad (2.34)$$

where the flux in the space of electron velocities is determined by [39]

$$j_{\beta} = \int d\mathbf{v}_{2} \left(f_{1} \frac{\partial f_{2}}{\partial v_{2\beta}} - \frac{\partial f_{1}}{\partial v_{1\beta}} f_{2} \right) D_{\alpha\beta} ,$$

$$D_{\alpha\beta} = \frac{1}{2} \int \Delta_{\alpha} \Delta_{\beta} W d\Delta \mathbf{v} .$$
(2.35)

Here, α, β are the components of vectors and tensors $(\alpha, \beta \equiv x, y, z)$, the summation is taken over twice repeating indices, the velocity variation is $\Delta \equiv \Delta \mathbf{v} = \mathbf{v}_1 - \mathbf{v}'_1 = \mathbf{v}'_2 - \mathbf{v}_2$, and $W(\mathbf{v}_1, \mathbf{v}_2 \rightarrow \mathbf{v}'_1, \mathbf{v}'_2)$ is the transition rate per unit volume resulting from the collision between two electrons.

This symmetric form of the electron – electron collision integral, namely, the Landau collision integral, is a modification of the Fokker–Planck equation in the velocity space. Let us evaluate the tensor $D_{\alpha\beta}$. The force acting on a test electron from another one due to their Coulomb interaction is $\mathbf{F} = e^2 \mathbf{r}/r^3$, where *r* is the distance between electrons, and *e* is the electron charge. This gives for the momentum change of a test electron after collision:

$$\Delta \mathbf{p} = \mathbf{n} \int_{-\infty}^{\infty} \frac{e^2 \rho}{r^3} \, \mathrm{d}t = \frac{2e^2}{\rho g} \, \mathbf{n} \,. \tag{2.36}$$

Here, **n** is the unit vector along the impact parameter of collision $\mathbf{\rho}$, and we consider a free motion of electrons: $r^2 = \rho^2 + g^2 t^2$, where $g = |\mathbf{v}_1 - \mathbf{v}_2| = |\mathbf{v}_1' - \mathbf{v}_2'|$ is the relative velocity of colliding electrons, and *t* is time. From this we get for the variation of the velocity of a test electron after collision $(\mathbf{\Delta} = \mathbf{\Delta}\mathbf{v})$:

$$\Delta_{\alpha} = \frac{2e^2 \rho_{\alpha}}{\rho^2 g m_{\rm e}} \,. \tag{2.37}$$

$$D_{\alpha\beta} = \frac{1}{2} \int \Delta_{\alpha} \Delta_{\beta} W d\Delta \mathbf{v} = \frac{1}{2} \int \Delta_{\alpha} \Delta_{\beta} g d\sigma$$
$$= \frac{2e^4}{m_e^2 g} \int \frac{\rho_{\alpha} \rho_{\beta}}{\rho^4} d\sigma = \frac{4\pi e^4}{m_e^2 g} n_{\alpha} n_{\beta} \ln \Lambda .$$
(2.38)

Here, n_{α} , n_{β} are components of the unit vector **n** directed along $\mathbf{\rho}$, and the Coulomb logarithm ln Λ is defined as

$$\ln \Lambda = \int_{\rho_{<}}^{\rho_{>}} \frac{\mathrm{d}\rho}{\rho} \,. \tag{2.39}$$

This integral diverges at both limits of integration. Its divergence at small impact parameters results from ignoring of trajectory distortion owing to the Coulomb repulsion of electrons, so that this limit of integration follows from the estimate $e^2/\rho_{<} \sim \varepsilon$, where ε is a typical electron energy. The divergence at large impact parameters is the peculiarity of the Coulomb interaction potential. But in a plasma, the Coulomb field is shielded at distances $\rho_{>} \sim r_{\rm D}$, where $r_{\rm D}$ is the Debye–Hückel radius of this plasma. We evaluate the quantities $\rho_{<}$, $\rho_{>}$ with the accuracy up to a constant factor, and because $\rho_{>} \gg \rho_{<}$, this leads to a small error. Thus, the Coulomb logarithm is large for an ideal plasma and is given by

$$\ln \Lambda = \ln \frac{r_{\rm D}\varepsilon}{e^2} \,. \tag{2.40}$$

From this result we have for the diffusion cross section for electron – electron collisions in a plasma:

$$\sigma^* = \int_0^\infty 2\pi\rho \,\mathrm{d}\rho \,(1 - \cos\vartheta) = \int_0^\infty 2\pi\rho \,\mathrm{d}\rho \,\frac{\vartheta^2}{2}$$
$$= \pi \left(\frac{2e^2}{m_{\rm e}g^2}\right)^2 \ln\Lambda = \frac{\pi e^4}{\varepsilon^2} \ln\Lambda \,, \tag{2.41}$$

where the scattering angle is equal to $\vartheta = 2e^2/(\rho m_e g^2) = e^2/(\rho \varepsilon)$, and ε is the energy of an incident electron in the laboratory frame of reference, where another electron is motionless.

For evaluation of the tensor $D_{\alpha\beta}$, let us first choose the direction of the collision velocity **g** along the *x*-axis, and *xy* as a plane of motion. Then only Δ_y is nonzero, so that only the tensor component D_{yy} is nonzero. For this component of the tensor we obtain

$$D_{yy} = \frac{2e^4}{m_e^2 g} \int \frac{1}{\rho^2} 2\pi \rho \, \mathrm{d}\rho = \frac{4\pi e^4}{m_e^2 g} \ln \Lambda \,,$$

where we evaluated the integral over impact parameters as above. Taking into account that the direction of the relative velocity of interelectron collisions is a random quantity, one can rewrite the expression for the tensor $D_{\alpha\beta}$ in an arbitrary frame of reference. Because this tensor is symmetric with respect to its indices, it can be constructed on the basis of symmetrical tensors $\delta_{\alpha\beta}$ and $g_{\alpha}g_{\beta}$. Evidently, it has the form [39]

$$D_{\alpha\beta} = \frac{4\pi e^4}{m_e^2 g^3} g_{\alpha} g_{\beta} \ln \Lambda \,. \tag{2.42}$$

Thus, the Landau collision integral taking account of collisions between electrons has the form

$$I_{ee}(f) = -\frac{\partial j_{\beta}}{\partial v_{1\beta}}, \quad j_{\beta} = \int d\mathbf{v}_2 \left(f_1 \frac{\partial f_2}{\partial v_{2\alpha}} - \frac{\partial f_1}{\partial v_{1\alpha}} f_2 \right) D_{\alpha\beta},$$
$$D_{\alpha\beta} = \frac{4\pi e^4}{m_e^2 g^3} g_{\alpha} g_{\beta} \ln \Lambda.$$
(2.43)

This nonlinear form of the collision integral represents a generalization of the right-hand side of the Fokker–Planck equation in the velocity space.

The Landau collision integral is nonlinear with respect to the electron distribution function. The above expression can be simplified by considering only fast electrons whose velocity v is large in comparison with a typical electron velocity in a plasma. In this limiting case, the tensor $D_{\alpha\beta}$ does not depend on the velocity of slow electrons and can be written in the form

$$D_{\alpha\beta} = \frac{4\pi e^4}{m_e^2 v^3} \, v_\alpha v_\beta \ln \Lambda \,,$$

where v is the velocity of a fast electron. In this case, according to formula (2.13) the collision integral for fast electrons takes the form

$$I_{\rm ee}(f_0) = \frac{1}{m_{\rm e}v^2} \frac{\partial}{\partial v} \left[v B_{\rm ee}(\varepsilon) \left(\frac{1}{m_{\rm e}v} \frac{\partial f_0}{\partial v} + \frac{f_0}{T} \right) \right], \qquad (2.44)$$

where the energy of a test fast electron is $\varepsilon = m_e v^2/2$, and by definition we have

$$\begin{split} B(\varepsilon) &= \frac{1}{2} \left\langle \int (\varepsilon - \varepsilon')^2 N_{\rm e} v \, \mathrm{d}\sigma(\varepsilon \to \varepsilon') \right\rangle \\ &= \frac{N_{\rm e}}{2} \int (\varepsilon - \varepsilon')^2 W \, \mathrm{d}\Delta \mathbf{v} \\ &= \frac{N_{\rm e}}{2} \int m_{\rm e} v_{\alpha} (v_{\alpha} - v_{\alpha}') \, m_{\rm e} v_{\beta} (v_{\beta} - v_{\beta}') W \, \mathrm{d}\Delta \mathbf{v} \\ &= N_{\rm e} m_{\rm e}^2 v_{\alpha} v_{\beta} \, \frac{1}{2} \int (v_{\alpha} - v_{\alpha}') (v_{\beta} - v_{\beta}') W \, \mathrm{d}\Delta \mathbf{v} = N_{\rm e} m_{\rm e}^2 v_{\alpha} v_{\beta} D_{\alpha\beta} \,, \end{split}$$

where the summation is taken over identical indices. Here, N_e is the electron number density, ε , ε' are the energies of a fast electron before and after collision, and the angle brackets mean averaging over velocities of slow electrons. We account for a small variation in the velocity of a fast electron as a result of the collision event, so that $\varepsilon - \varepsilon' = m_e v_\alpha (v_\alpha - v'_\alpha)$. From this we get, using formula (2.43) for the tensor $D_{\alpha\beta}$ and taking into account that for a fast electron $g_\alpha = v_\alpha$ [40]:

$$B_{\rm ee}(\varepsilon) = 4\pi e^4 v N_{\rm e} \ln \Lambda \,. \tag{2.45}$$

Thus, the collision integral for fast electrons has a simple form and is linear with respect to their distribution function.

It should be emphasized that in considering electron behavior in a weakly ionized gas we accounted for electron collisions with electrons and atoms assuming on the validity of the criterion (2.18). Even if this criterion was violated, we supposed that the average electron momentum is established as a result of collisions with atoms. But along with electron– atom collisions, the electron–ion collisions may be essential at a high degree of gas ionization. Indeed, the cross section for electron-ion collisions (2.41) exceeds the electron-atom scattering cross section σ_{ea} because of a long-range character of the Coulomb interaction in electron-ion collisions. The rate of electron-ion collisions has the form [41]

$$v_{\rm ei} = \frac{2\sqrt{2\pi}}{3} \frac{N_{\rm i} e^4}{T_{\rm e}^{3/2} m_{\rm e}^{1/2}} \left(\ln \frac{T_{\rm e}^3}{2\pi N_{\rm i} e^6} - 2C \right), \qquad (2.46)$$

where e, m_e are the electron charge and mass, N_i is the ion number density, T_e is the electron temperature, and C = 0.577 is the Euler constant. This expression is based on the Maxwell distribution function of electrons with an electron temperature T_e , and because the ionized gas is ideal $(N_e e^6 \ll T_e^3)$ and quasi-neutral $(N_e = N_i)$, the value of the function in parentheses is much greater than unity. By comparing the electron-ion collision rate v_{ei} with the electron-atom collision rate $v = N_a v \sigma^*(v)$, one can ascertain the role of electron-ion collisions in the evolution of plasma electrons.

3. Electron – atom collisions

3.1 Elastic electron – atom scattering

In considering the evolution of electrons in a gas in an external electric field, we took into account the fact that a typical electron energy is usually far less than the excitation energy of the atoms colliding with the electrons. If it is violated, the electrons can excite the atoms and lose energy. At low electron energies, only elastic electron-atom scattering takes place, and below we will consider the peculiarities of this scattering [42-46]. If the atomic spin is nonzero, there are two possible states of the system involving a colliding electron and atom, and such a system is developed in each channel independently (we ignore the relativistic effects). For simplicity, we consider electron scattering on a structureless atom (being guided by rare gas atoms) when there is a single electronic state for the electron-atom system.

Within the context of phase scattering theory, the parameters of electron-atom collisions can be expressed through the scattering phases δ_l characterizing the partial scattering of an electron with an orbital momentum *l* with respect to a target atom. In particular, the differential cross section $d\sigma$ for electron-atom scattering is given by [43, 44, 47, 48]

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\cos\vartheta} = 2\pi \left| f(\vartheta) \right|^2, \quad f(\vartheta) = \sum_{l=0}^{\infty} f_l P_l(\cos\vartheta),$$

$$f_l = \frac{1}{2\mathrm{i}q} (2l+1) \left[\exp\left(2\mathrm{i}\delta_l\right) - 1 \right], \quad (3.1)$$

where ϑ is the scattering angle, i.e. the angle between the initial and final directions of electron motion, $f(\vartheta)$ is the scattering amplitude, $P_l(\cos \vartheta)$ is the Legendre polynomial, and f_l is the spherical component of the scattering amplitude. From this we have for the total σ_t and diffusion σ^* cross sections of electron-atom scattering, expressing them through the scattering phases δ_l :

$$\sigma_{t} = \int \mathrm{d}\sigma = \frac{4\pi}{q^{2}} \sum_{l=0}^{\infty} (2l+1) \sin^{2} \delta_{l}, \qquad (3.2)$$

$$\sigma^* = \int (1 - \cos \vartheta) \, \mathrm{d}\sigma = \frac{4\pi}{q^2} \sum_{l=0}^{\infty} (2l+1) \sin^2(\delta_l - \delta_{l+1}) \,. \tag{3.3}$$

When the electron velocity v (or the wave vector $q = m_e v/\hbar$, where \hbar is the Planck constant) tends to zero, the scattering phases δ_l also approach zero, and in the case of a short-range electron – atom interaction $\delta_l \sim q^{2l+1}$. Hence, at low electron energies a finite number of phases contributes to the scattering cross section. In particular, restricting ourselves to the principal term of an expansion, we have $\delta_0 = -Lq$, where L is the scattering length, and the cross section for scattering of a slow electron by an atom is equal to

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\cos\vartheta} = 2\pi L^2, \qquad \sigma = 4\pi L^2, \tag{3.4}$$

where $\sigma = \int d\sigma$ is the total cross section for scattering of an electron with zero energy.

From this formula it follows that the electron scattering is isotropic at zero energy, i.e. the cross section is determined by the scattering of an s-electron. Next, the electron-atom scattering length may be expressed through the wave function Ψ of the scattered electron as

$$\left. \frac{\mathrm{d}\ln\Psi}{\mathrm{d}r} \right|_{r=0} = -\frac{1}{L} \,, \tag{3.5}$$

where r is the distance of the scattering electron from the atomic center. Note that the scattering length is determined by electron-atom interaction inside the atom, where a oneelectron approximation is not correct, i.e. the wave function of an incident electron is entangled with the wave functions of atomic electrons, and the resultant exchange interaction of an electron with atom takes a complex form. Hence, we consider the scattering length as a parameter which results from a combination of a short-range electron-atom interaction, including an energy exchange between incident and atomic electrons, and a long-range interaction. This allows us to expand the scattering phases over a small parameter at low collision energies [49, 50]. We account for a short-range interaction only for the zero-th scattering phase, and a longrange interaction for all the scattering phases within the framework of the perturbation theory that is valid at low collision energies.

Let us apply the Fermi formula for the short-range electron – atom interaction potential [51-53]:

$$U_{\rm sh} = 2\pi L \, \frac{\hbar^2}{m_{\rm e}} \, \delta(\mathbf{r}) \,, \tag{3.6}$$

where \mathbf{r} is the electron coordinate. Along with a short-range electron – atom interaction, a long-range interaction can give a contribution to scattering parameters. In contrast to a short-range interaction, at low collision energies the contribution from a long-range interaction to the scattering amplitude is determined by an electron location region far from the atom, where the coordinates of incident and atomic electrons may be separated. Constructing on these features the perturbation theory, we obtain for the scattering amplitude the following expression by separating short-range and a long-range interactions [48]:

$$f(\vartheta) = -L + \frac{1}{2\pi} \int \left[1 - \exp\left(-i\mathbf{K}\mathbf{r}\right) \right] U_l(r) \,\mathrm{d}\mathbf{r} \,, \tag{3.7}$$

where $U_l(r)$ is the spherical component of the potential of an electron-atom long-range interaction, and $K = |\mathbf{q} - \mathbf{q}'| = 2q \sin(\vartheta/2)$ is the variation of the electron wave vector as a

result of scattering. From this we have for the particular case of a polarization interaction potential $U(r) = -\alpha e^2/(2r^4)$, which is realized at large electron-atom distances r (α is the atomic polarizability):

$$f(\vartheta) = -L - \frac{\pi\alpha}{4a_0} K = -L - \frac{\pi\alpha q}{2a_0} \sin\frac{\vartheta}{2}, \qquad (3.8)$$

where $a_0 = \hbar^2/(m_e e^2)$ is the Bohr radius. As a matter of fact, it is an expansion of the scattering amplitude at low collision energies. This gives the following expressions for the total and diffusion cross sections of electron-atom scattering at low electron energies in this approximation [41]:

$$\sigma_{t} = 4\pi \left(L^{2} + \frac{2}{3} \pi \frac{\alpha q L}{a_{0}} + \frac{\pi^{2}}{8} \frac{\alpha^{2} q^{2}}{a_{0}^{2}} \right)$$
$$= 4\pi L^{2} \left(1 - \frac{4}{3} x + \frac{1}{2} x^{2} \right), \qquad x = -\frac{\pi \alpha q}{2La_{0}}, \qquad (3.9)$$

$$\sigma^* = 4\pi \left(L^2 + \frac{4}{5} \pi \frac{\alpha q L}{a_0} + \frac{\pi^2}{6} \frac{\alpha^2 q^2}{a_0^2} \right)$$
$$= 4\pi L^2 \left(1 - \frac{8}{5} x + \frac{2}{3} x^2 \right).$$
(3.10)

The important conclusion resulting from these formulas consists in a sharp minimum in the cross sections of electron atom scattering at small collision energies if the scattering length L is negative. This is just the Ramsauer effect [54, 55], and the reason for a sharp minimum in the cross sections is that the zero-order phase δ_0 becomes zero when the contribution of the other phases to the cross section is relatively small because of a low electron energy. The Ramsauer effect is observed in elastic scattering of electrons by argon, krypton and xenon atoms. As follows from formula (3.9), the total cross section in this approximation passes the minimum $4\pi L^2/9$ at the electron wave number $q_{\rm min} = -8La_0/(3\pi\alpha)$ (x = 4/3). The minimum of the diffusion cross section in this approximation is equal to $4\pi L^2/25$ and corresponds to the electron wave vector $q_{\min} = -12La_0/(5\pi\alpha)$ (x = 6/5)according to formula (3.10) [41]. Thus, within the framework of this approximation, the scattering cross section drops by an order of magnitude at low electron energies that is of importance for processes proceeding in gases or plasmas involving electrons.

Table 1 lists some parameters of electron scattering by rare gas atoms. Along with measurements of the cross sections for electron-atom scattering at zero electron temperature, the scattering length L is determined from a shift of spectral lines of highly excited atoms located in a gas. The data collected in Table 1 for the electron-atom scattering length were taken from Refs [56-60], and the

Figure 1. The diffusion cross section of electron scattering by a xenon atom as a function of the electron energy. Experimental data: solid curve — [61], open circles — [62], dotted curve — [63], black triangles — [64], black squares — [65]; the black rhombi give the cross section at zero energy at the minimum in accordance with formula (3.10) and the data from Table 1. available accuracy for the scattering lengths is several percent. The minimal total cross sections of electron – atom elastic scattering, as well as the energy of such a minimum, are evaluated by formula (3.10) and contain an additional error. In order to demonstrate the error in these data, we give in Fig. 1 the energy dependence for the diffusion cross section of electron scattering by a xenon atom in accordance

section of electron scattering by a xenon atom in accordance with the results from Refs [61–65]. Comparison of data in Fig. 1 with those calculated by formula (3.10) shows that this formula is valid at low energies below the cross section minimum, while at higher energies the difference between calculated results and experimental data can be significant. Moreover, the cross section minimum is observed at higher energies than formula (3.10) gives, and the cross section minimum is several times as low as the value calculated with formula (3.10).

Because of the difference between the cross sections evaluated on the basis of formulas (3.9), (3.10) and experimental data, we consider this situation in detail. Basing on the phase scattering theory [Eqns (3.2), (3.3)], we find that under conditions of the Ramsauer effect, the zero-th scattering phase δ_0 becomes zero at low electron energies, where other scattering phases are small. In formulas (3.9) and (3.10) we took the long-range electron-atom interaction potential to be of the polarization one. Within the framework of this approach, the zero-th scattering phase is zero at an energy of 0.55 eV, and the total and diffusion scattering cross sections have minima at 0.44 eV and 0.35 eV energies, respectively, for scattering of an electron by the xenon atom. One can see from comparison of the phase theoretical results with the experimental data in Fig. 1 that a long-range interaction potential between an electron and a rare gas atom is less than the polarization potential.

Table 1. Parameters of electron scattering by rare gas atoms.

Parameter	He	Ne	Ar	Kr	Xe	
α, a_0^3	1.4	2.8	11	17	27	
L/a_0	1.2 [56]	0.3 [57]	-1.5[58-60]	-3.1 [56]	-5.7 [56]	
$\sigma_{\rm t}(\varepsilon=0),{\rm \AA}^2$	5.1	0.3	7.9	34	110	
ε_{\min}, eV	_	—	0.18	0.32	0.44	
$\sigma_{ m t\ min},{ m \AA}^2$	_	—	0.88	3.8	13	
$D_{\rm e}N_{\rm a},10^{21}~{\rm cm}^{-1}~{\rm s}^{-1}$	7.5	75	30	1.6	0.43	
$K_{\rm e}N_{\rm a}$, 10 ²³ (cm s V) ⁻¹	3.0	30	12	0.62	0.17	



Basing on the nature of a long-range interaction between an electron and an atom, we take it to be started from a certain distance between them, so that the effective electron – atom interaction potential can be written in the form of the sum of the short-range and long-range potentials:

$$U(\mathbf{r}) = 2\pi L \, \frac{\hbar^2}{m_{\rm e}} \, \delta(\mathbf{r}) - \frac{\alpha e^2}{2(r^2 + r_0^2)^2}$$

where r is the electron – atom spacing. Then, using this long-range interaction potential and formula (3.7) for the scattering amplitude, instead of Eqn (3.8) we obtain [66]

$$f(\vartheta) = -L - \frac{\pi\alpha}{4a_0r_0} \left[1 - \exp\left(-2r_0q\sin\frac{\vartheta}{2}\right) \right].$$
(3.11)

From this we have, in particular, for the reduced diffusion scattering cross section

$$\frac{\sigma^*}{4\pi L^2} = \frac{1}{4(r_0 q)^4} \int_0^{2r_0 q} z^3 dz \left\{ 1 - y \left[1 - \exp\left(-z\right) \right] \right\}^2,$$

$$y = -\frac{\pi \alpha}{4a_0 r_0 L}, \qquad z = 2r_0 q \sin\frac{\vartheta}{2}.$$
(3.12)

Introducing the electron wave vector q_{\min} corresponding to the cross section minimum and a new variable $t = 2r_0q$, we find the relation between the parameters x and t from the minimum condition $d\sigma^*/dt = 0$:

$$y = 2 \frac{(t^4/4) \left[1 - \exp(-t)\right] - \int_0^t z^3 \left[1 - \exp(-z)\right] dz}{(t^4/4) \left[1 - \exp(-t)\right]^2 - \int_0^t z^3 \left[1 - \exp(-z)\right]^2 dz}.$$
(3.13)

In particular, in the limit $r_0 \rightarrow 0$ we have $t \rightarrow 0$, which gives x = yt = 6/5 and $\sigma^*/(4\pi L^2) = 1/25$ in accordance with the result for the polarization interaction potential. The results for finite values of r_0 are given in Table 2 where the parameters of the cross section minimum are appropriate for electron scattering from a xenon atom. As follows from this table, an increase in r_0 leads to a decrease in the cross section minimum and an increase in the electron energy $\varepsilon_{\min} = \hbar^2 q_{\min}^2/(2m_e)$ at which this minimum is observed.

Table 2. The parameters of the Ramsauer minimum for electron scattering from a xenon atom.

r_0/a_0	ε_{\min}, eV	$\sigma_{\min}/4\pi L^2$	x _{min}
0	0.35	0.04	1.20
0.1	0.36	0.039	1.22
0.3	0.39	0.038	1.26
0.7	0.44	0.035	1.34
1.0	0.50	0.032	1.42
1.5	0.61	0.028	1.58
2.0	0.79	0.023	1.79
2.5	1.11	0.017	2.12
3.0	1.83	0.011	2.73

3.2 Mobility and diffusion of electrons in gas

Let us introduce the mobility K_e of electrons in a gas in an external electric field of strength **F** from the relation

$$\mathbf{w}_{\mathrm{e}} = K_{\mathrm{e}}\mathbf{F}\,,\tag{3.14}$$

where \mathbf{w}_{e} is the electron drift velocity. Then using formula (2.9), we obtain the following expression for the mobility of

electrons in a gas:

$$K_{\rm e} = \frac{e}{3m_{\rm e}} \left\langle \frac{1}{v^2} \frac{\rm d}{{\rm d}v} \left(\frac{v^3}{v} \right) \right\rangle. \tag{3.15}$$

At low electric field strengths, the electron mobility does not depend on the strength itself because the electric field perturbs weakly the Maxwell distribution function of electrons. At larger strengths, the dependence of the mobility on the electric field is determined by the velocity dependence of the cross section of electron – atom elastic scattering. In particular, if the rate of electron – atom elastic collision v does not depend on the electron velocity, formula (3.14) gives

$$K_{\rm e} = \frac{e}{m_{\rm e}v} \,. \tag{3.16}$$

If the diffusion cross section for electron – atom scattering σ_{ea}^* does not depend on the collision velocity, formula (3.14) yields for electron mobility in a gas in the limit of low strengths:

$$K_{\rm e} = \frac{2e\lambda}{3m_{\rm e}} \left\langle \frac{1}{v} \right\rangle = \frac{2}{3} \sqrt{\frac{2}{\pi}} \frac{e\lambda}{\sqrt{m_{\rm e}T}} = 0.53 \frac{e\lambda}{\sqrt{m_{\rm e}T}} \,, \qquad (3.17)$$

where $\lambda = 1/(N_a \sigma_{ea}^*)$ is the mean free path of electrons in a gas $(N_a$ is the number density of gas atoms, T is the gas temperature).

In the general case of a complex dependence v(v), as happens with rare gases, the electron mobility may be a nonmonotonic function of the electric field strength, and it is shown in Fig. 2 for gaseous xenon [67]. As may be seen, the mobility has a maximum at a certain electric field strength. In addition, the electron drift velocity can be independent of the electric field strength in a certain range of strengths, i.e. it shows a 'saturation' in this interval of strengths. This is demonstrated in Fig. 3a by the example of the electron drift velocity in xenon, and the same dependence was observed in other measurements [65, 68-73] of electron drift in gaseous xenon. In addition, Fig. 3b illustrates the saturation effect for electron drift in a mercury vapor according to measurements [74, 75]. In the case of electron drift in gaseous krypton, the saturation effect is weaker [68, 76, 77]. We will analyze this effect below in Section 7 for electron drift in condensed rare gases, where the saturation effect is strong. Note that in the case of monotonic dependence of the scattering cross section on the collision velocity, the mobility varies monotonically



Figure 2. The electron mobility as a function of the reduced electric field strength if an electron moves in an external electric field in xenon at the temperature T = 236 K and the number density of atoms $N_a = 3 \times 10^{20}$ cm⁻³ [67].



Figure 3. The saturation effect for the dependence of the electron drift velocity in a gas or vapor on the strength of an external electric field. (a) electron drift in xenon: open circles — [68], squares — [67], solid curve and triangles — [65]; (b) electron drift in a mercury vapor [74, 75].

with an increase in electric field strength. A nonmonotonic strength dependence of the electron mobility, as in the case of xenon in Fig. 2 [67], follows from the Ramsauer shape of the electron – atom collision cross section.

Let us establish the connection between the electron mobility K_e in a gas at low electric field strengths and the diffusion coefficient D_e of electrons in this gas. At low electric field strengths, the thermodynamic equilibrium is established for the electron subsystem, so that the space distribution for the number density of electrons is given by the Boltzmann formula

$$N_{\rm e} = N_0 \exp\left(-\frac{eFx}{T}\right),\tag{3.18}$$

where *F* is the electric field strength, *T* is the temperature, and the coordinate *x* is directed along the field. Because of a gradient in the electron number density, a diffusion flow arises, which tends to equalize the electron number density in the space. Under equilibrium, the diffusion flux is compensated for by a flux resulted from the action of an electric field, and the total electron flux \mathbf{j}_e is zero:

$$\mathbf{j}_{\rm e} = -D_{\rm e} \nabla N_{\rm e} + K_{\rm e} F N_{\rm e} = 0.$$
(3.19)

Using formula (3.18) for the electron density, we obtain the Einstein relation which connects the electron mobility K_e and the diffusion coefficient D_e of electrons in a gas [78–80]:

$$K_{\rm e} = \frac{eD_{\rm e}}{T} \,. \tag{3.20}$$

The Einstein formula is valid both at low field strengths, when an individual electron moves in a gas in an external electric field [the criterion (2.18)], and at any field strengths if the electron density is large and the electrons have the Maxwell distribution function over velocities. The electron temperature is then included in formula (3.20).

Table 1 contains the reduced diffusion coefficients of electrons in rare gases at room temperature, taken from Ref. [81] for He, Ne, and Ar, and from Ref. [61] for Kr and Xe. The experimental error of these data is approximately 10%, and within this accuracy these data agree with other measurements. The electron reduced mobilities at room temperature (see Table 1) were obtained from these data for the electron diffusion coefficient on the basis of the Einstein relation (3.20).

Expansion (2.4) for the velocity distribution function of electrons located in a gas is valid for any electric field occurring in the gas and acting on the electrons. Below we use this expansion for evaluating the diffusion coefficient of electrons in a gas when an electron flow results from a gradient in the electron concentration, and this electron flow tends to equalize the electron concentration at different points in space. We define the electron diffusion coefficient in a weakly ionized gas starting from the relation $\mathbf{j}_e = -D_e \nabla N_e$. The Boltzmann kinetic equation for electrons then has the form

$$v_x \nabla f = I_{\text{ea}}(f) \,, \tag{3.21}$$

where the electron distribution function in accordance with the expansion (2.4) is $f = f_0(v) + v_x f_1(v)$, and the *x*-axis is directed along the gradient of the electron density. Taking into account $f \sim N_e$, we find $\nabla f = f \nabla N_e / N_e$. Then we obtain by analogy with the first equation of the set (2.8) that

$$\frac{v_x f_0 \nabla N_{\rm e}}{N_{\rm e}} = -v v_x f_1$$

or, simply, $f_1 = -f_0 \nabla N_e / (\nu N_e)$. Let us evaluate the electron flux

$$\mathbf{j}_{\mathbf{e}} = \int \mathbf{v} f \, \mathrm{d} \mathbf{v} = \int v_x^2 f_1 \, \mathrm{d} \mathbf{v} = -\frac{\nabla N_{\mathbf{e}}}{N_{\mathbf{e}}} \int \frac{v_x^2}{v} f_0 \, \mathrm{d} \mathbf{v} = -\nabla N_{\mathbf{e}} \left\langle \frac{v_x^2}{v} \right\rangle,$$

where the angle brackets mean averaging over the electron distribution function. According to the definition of the electron diffusion coefficient D_e , the diffusive electron flux is

$$\mathbf{j}_{\rm e} = -D_{\rm e} \nabla N_{\rm e}$$
.

Comparing this formula with the above one, we obtain the following expression for the diffusion coefficient of electrons in a gas:

$$D_{\rm e} = \left\langle \frac{v^2}{3v} \right\rangle. \tag{3.22}$$

In the case of strong electric fields, formula (3.22) relates to transversal diffusion of electrons because only in this case can one separate the corrections to the spherically symmetric electron distribution function due to the action of the electric field and the gradient of the electron density. If the rate of electron-atom collisions v(v) does not depend on the electron velocity, the transversal and longitudinal diffusion



Figure 4. The reduced transversal (D_{\perp}) and longitudinal (D_{\parallel}) diffusion coefficients of electrons in xenon in an external electric field: solid curve — [65], open circles — [71].

coefficients of electrons in a gas coincide, just as in the case of low field strengths or high electron densities. Formula (3.22) for the electron diffusion coefficient is valid at any field strengths, but if the electron-atom collision rate v(v)depends on the electron velocity, the transversal and longitudinal diffusion coefficients of electrons in a gas are different at moderate fields. This is demonstrated in Fig. 4 where these quantities are given for the diffusion of electrons in xenon at various field strengths. Note that the maximum difference between the transversal and longitudinal diffusion coefficients of electrons in a gas occurs in the range with the strongest dependence v(v). The anisotropy in electron diffusion in gases in a strong electric field was first discovered and explained in Refs [82–84]. It was then the subject of special study (for example, see Refs [76, 85, 86]).

Note that transport coefficients of ions of a small mass in atomic gases, when the transport coefficients are determined by elastic ion-atom scattering, do not depend on the nature of the scattering, because for both the classical and quantum character of scattering the ion transport coefficients are expressed through the diffusion cross section $\sigma^*(v)$ of ion scattering. One can then use the results for classical motion of ions in atomic gases for analyzing the electron transport coefficients in gases in strong fields. In the case where the scattering rate v(v) is independent of the collision velocity, we have $D_{\perp} = D_{\parallel}$. In the other limiting case, when the cross section $\sigma^*(v)$ of ion-atom collisions does not depend on the collision velocity v, we have the following expressions for the ion drift velocity w and the diffusion coefficients in the limit of high fields ($M \ll m_a$, $eF\lambda \gg T$; M, m_a are the ion and atomic masses, respectively) [87-89]:

$$w = 0.897 \frac{\sqrt{eF\lambda}}{(m_{\rm a}M)^{1/4}}, \qquad D_{\perp} = 0.292 \left(\frac{m_{\rm a}}{M}\right)^{1/4} \sqrt{\frac{eF}{M}} \lambda^{3/2},$$

 $D_{\parallel} = 0.144 \left(\frac{m_{\rm a}}{M}\right)^{1/4} \sqrt{\frac{eF}{M}} \lambda^{3/2}.$

It is convenient to introduce the characteristic electron energy ε_{ch} at a given electric field strength on the basis of the Einstein relation, so that

$$\varepsilon_{\rm ch} = \frac{eD_{\rm e}}{K_{\rm e}} \,. \tag{3.23}$$

This energy characterizes the mean energy $\bar{\epsilon}$ of the electron

 $\overline{\varepsilon} = 3\varepsilon_{\rm ch}/2.$ By way of illustration of electron motion in a magnetic field, we determine below the transversal diffusion coefficient of electrons in a strong magnetic field, when the directions of the electric and magnetic fields coincide. This case corresponds to the criterion $\omega_H \gg v$, where $\omega_H = eH/(m_ec)$ is the cyclotron frequency for electrons. The projection of the electron trajectory onto the plane which is perpendicular to the field consists of circles whose centers and radii vary after each collision. By definition, the diffusion coefficient is $D_{\perp} = \langle x^2 \rangle / t$, where $\langle x^2 \rangle$ is the square of the electron displacement for a time t in the direction x which is perpendicular to the field. We have $x - x_0 = r_H \cos \omega_H t$, where x_0 is the x-coordinate of the center of the corresponding electron rotation, and $r_H = v_\rho / \omega_H$ is the Larmor radius, so that v_{ρ} is the electron velocity in the direction perpendicular to the field. By averaging over collision times it follows that $\langle x^2 \rangle = n \langle (x - x_0)^2 \rangle = n v_{\rho}^2 / (2\omega_H^2)$, where *n* is the number of collisions. Since t = n/v, where v is the rate of electron – atom collisions, we obtain [18]

distribution [17, 90, 91], and if the electron-atom collision

rate v(v) does not depend on the electron velocity v, we have

$$D_{\perp} = \left\langle \frac{v_{\rho}^2 v}{2\omega_H^2} \right\rangle = \left\langle \frac{v^2 v}{3\omega_H^2} \right\rangle, \qquad \omega_H \gg v, \qquad (3.24)$$

where the angle brackets mean averaging over the electron velocities. Combining this formula with Eqn (3.22), we obtain the following expression for the transversal diffusion coefficient of electrons which are located in a gas and are moving perpendicular to electric and magnetic fields [16]:

$$D_{\perp} = \frac{1}{3} \left\langle \frac{v^2 v}{\omega_H^2 + v^2} \right\rangle. \tag{3.25}$$

3.3 Excitation and quenching of an atom by electron impact

A typical electron energy in a gas is usually small compared to an excitation energy of atoms, and therefore the excitation of atoms in a weakly ionized gas occurs on the tail of the energy distribution function of electrons. Hence, we need for the threshold cross section of atom excitation by electron impact in order to analyze the character of atom excitation in an ionized gas. In the opposite limiting case, when the electron energy exceeds significantly the atomic excitation energy, the excitation cross section is determined in the Born approximation [43, 44, 47, 48]. The maximum cross sections corresponds to excitation of resonantly excited states, when the excitation cross section is given by the Bethe formula [43, 44, 47, 92]

$$\sigma_{0*} = \frac{4\pi}{\Delta \varepsilon a_0} |(D_x)_{0*}|^2 \Phi\left(\frac{\varepsilon}{\Delta \varepsilon}\right) = \frac{2\pi e^4}{\Delta \varepsilon^2} f_{0*} \Phi\left(\frac{\varepsilon}{\Delta \varepsilon}\right),$$

$$\Phi(x) \to \frac{\ln C\sqrt{x}}{x}, \quad x \to \infty.$$
 (3.26)

Here, subscripts 0 and * refer to the initial and final states of the atom excitation process, ε is the electron energy, $\Delta \varepsilon$ is the excitation energy, e is the electron charge, a_0 is the Bohr radius, $(D_x)_{0*}$ is the matrix element of the dipole moment projection for the atomic states of transition, f_{0*} is the oscillator strength for this transition, and C is a constant. Thus, in the case of excitation of resonantly excited atomic states, the excitation cross section is expressed through the parameters of radiative transitions for the atom. This connection follows from the analogy between the operators for the interaction of a fast charged particle with an atom and of an electromagnetic wave with an atom [44, 92-95].

One can extend the dependence (3.26) on the basis of experimental data to electron energies ε which are comparable with the atomic excitation energy $\Delta \varepsilon$ [96]. Then accounting for the threshold dependence of the atomic excitation cross section [47], we will find the following expression for the cross section near the threshold for excitation of resonantly excited states [96–98]:

$$\sigma_{0*}(\varepsilon) = \frac{2\pi e^4 f_{0*}}{\Delta \varepsilon^{5/2}} a \sqrt{\varepsilon - \Delta \varepsilon} , \qquad (3.27a)$$

and the numerical coefficient estimated from experimental data is [96, 97]

$$a = 0.130 \pm 0.007$$
. (3.27b)

Formulas (3.26), (3.27) can be used for determining the rate constant of atom excitation by electron impact in gas discharges [98, 99].

We now turn to determining the cross section and the rate constant of the quenching of a resonantly excited atom by a slow electron. Atom quenching is an inverse process with respect to atom excitation by electron impact, and we will find below the connection between the parameters of these processes which proceed according to the scheme

$$\mathbf{e} + \mathbf{A}_0 \longleftrightarrow \mathbf{e} + \mathbf{A}_* \,, \tag{3.28}$$

where A_0 , A_* denote an atom in the ground and resonantly excited states. The connection between the parameters of direct and inverse processes is established on the basis of the principle of detailed balance for processes (3.28). Let us place one electron and one atom in a volume Ω , and the atom can be found only in states 0 and *, so that transitions between these states result from collisions with the electron. Because this system is found under equilibrium, there is a certain relation between the rate constant w_{0*} of transition $0 \rightarrow *$ and the rate constant w_{*0} of transition $* \rightarrow 0$. Introducing the interaction operator V which is responsible for these transitions, we have the following expressions for the transition rates within the framework of the perturbation theory:

$$w_{0*} = \frac{2\pi}{\hbar} |V_{0*}|^2 \frac{\mathrm{d}g_*}{\mathrm{d}\varepsilon}, \qquad w_{*0} = \frac{2\pi}{\hbar} |V_{*0}|^2 \frac{\mathrm{d}g_0}{\mathrm{d}\varepsilon}. \tag{3.29}$$

Here, $dg_0/d\epsilon$, $dg_*/d\epsilon$ are the statistical weights per unit energy for the corresponding channels of the process. We apply the definition of the cross sections for these processes:

$$\sigma_{0*} = \frac{w_{0*}}{Nv_0} = \Omega \, \frac{w_{0*}}{v_0} \,, \qquad \sigma_{*0} = \frac{w_{*0}}{Nv_*} = \Omega \, \frac{w_{*0}}{v_*} \,, \tag{3.30}$$

where $N = 1/\Omega$ is the number density of the particles, and v_0 , v_* are the electron velocities for the corresponding channels (for simplicity, we consider an atom to be motionless). The time reversal operation gives the relationship for the matrix elements of the interaction operator: $V_{0*} = V_{*0}^*$. This leads to the following relation between the cross sections of direct and

inverse processes in electron – atom collisions [37, 19]:

$$\sigma_{0*} v_0 \frac{\mathrm{d}g_0}{\mathrm{d}\varepsilon} = \sigma_{*0} v_* \frac{\mathrm{d}g_*}{\mathrm{d}\varepsilon} \,. \tag{3.31}$$

Statistical weights for the corresponding channels of the processes (3.28) are equal to

$$\mathrm{d}g_0 = \Omega \, rac{\mathrm{d} \mathbf{p}_0}{\left(2\pi\hbar
ight)^3} \, g_0 \,, \qquad \mathrm{d}g_* = \Omega \, rac{\mathrm{d} \mathbf{p}_*}{\left(2\pi\hbar
ight)^3} \, g_* \,,$$

where g_0 , g_* are the statistical weights for given atom states. Then, finally, formula (3.31) takes the form [37, 19]

$$\sigma_{\rm ex} = \sigma_{\rm q} \, \frac{v_*^2 g_*}{v_0^2 g_0} \,, \tag{3.32}$$

where $\sigma_{ex} = \sigma_{0*}$ is the excitation cross section, and $\sigma_q = \sigma_{*0}$ is the quenching cross section. Taking near the excitation threshold

$$\sigma_{\rm ex} = A\sqrt{\varepsilon} - \Delta\varepsilon , \qquad \varepsilon - \Delta\varepsilon \ll \Delta\varepsilon , \qquad (3.33a)$$

where A is a constant, we arrive at the expression for the cross section of atomic quenching resulting from collisions with a slow electron of an energy $\varepsilon = E - \Delta \varepsilon \ll \Delta \varepsilon$:

$$\sigma_{\rm q} = A \, \frac{g_0 \Delta \varepsilon}{g_* \sqrt{E - \Delta \varepsilon}} \,. \tag{3.33b}$$

From this it follows that the rate constant of atom quenching by a slow electron (m_e is the electron mass) is described as

$$k_{\rm q} = v_f \sigma_{\rm q} = A \, \frac{g_0 \Delta \varepsilon \sqrt{2}}{g_* \sqrt{m_{\rm e}}} \,, \tag{3.34a}$$

and the rate constant k_{ex} of atom excitation by electron impact is given by

$$k_{\rm ex} = k_{\rm q} \, \frac{g_*}{g_0} \sqrt{\frac{\varepsilon - \Delta \varepsilon}{\Delta \varepsilon}} \,. \tag{3.34b}$$

It is of importance that the rate constant k_q of atom quenching depends neither on the electron energy nor on the energy distribution function for slow electrons. Hence, it depends only on the parameters of the transition atomic states, so that the rate constant of quenching is a convenient parameter that characterizes also the excitation of atoms by

Table 3. Parameter k_0 in formula (3.35) that was derived from the experimental data indicated. This parameter is expressed in 10^{-5} cm³ s⁻¹, if $\Delta \varepsilon$ is quoted in eV, and τ_{*0} in ns.

Atom	k_0 for T_e equal to								
Ref.	$6\times 10^3 \; K$	$8\times 10^3 \; K$	$10 \times 10^3 \text{ K}$	$12 \times 10^3 \text{ K}$					
$K(4^2P)$ [100]		4.1	4.2	3.9					
$Rb(5^2P)$ [100]	5.5	5.7	4.4	3.8					
Cs(6 ² P) [100]	3.4	3.1	2.8	3.4					
$K(4^2P)$ [92]	5.2	4.8	5.0	5.4					
$Rb(5^2P)$ [92]	4.6	4.8	5.0	5.0					
Cs(6 ² P) [92]	4.3	4.4	4.5	4.8					
$K(4^2P)$ [101]	3.4	3.7	4.1	4.2					
$Rb(5^{2}P)$ [101]	3.7	3.7	4.0	4.0					
$Cs(6^2P)$ [101]	3.9	4.3	4.6	4.9					

Table 4. Parameters of resonantly excited states of some atoms and the rate constants of quenching these states in collisions with a slow electron.

Atom (transition)	$\Delta \varepsilon$, eV	λ , nm	f	τ_{*0} , ns	$k_{\rm q},10^{-8}~{ m cm^3~s^{-1}}$
$H(2^1P \to 1^1S)$	10.20	121.6	0.416	1.60	0.79
$He(2^1P \rightarrow 1^1S)$	21.22	58.43	0.276	0.555	0.18
$He(2^1P \rightarrow 2^1S)$	0.602	2058	0.376	500	51
$He(2^3P \rightarrow 2^3S)$	1.144	1083	0.539	98	27
$Li(2^2P\to 2^2S)$	1.848	670.8	0.74	27	19
$Na(3^2P \rightarrow 3^2S)$	2.104	589	0.955	16.3	20
$K(4^2P_{1/2}\to 4^2S_{1/2})$	1.610	766.9	0.35	26	31
$K(4^2P_{3/2}\to 4^2S_{1/2})$	1.616	766.5	0.70	25	32
$Rb(5^2P_{1/2}\to 5^2S_{1/2})$	1.560	794.8	0.32	28	32
$Rb(5^2P_{3/2}\to 5^2S_{1/2})$	1.589	780.0	0.67	26	33
$Cs(6^2P_{1/2} \to 6^2S_{1/2})$	1.386	894.4	0.39	30	46
$Cs(6^2P_{3/2}\to 6^2S_{1/2})$	1.455	852.1	0.81	27	43

 Table 5. The rate constants of quenching metastable states of rare gas atoms in collisions with slow electrons on evidence from Ref. [102].

Atom (transition)	$\Delta \varepsilon$, eV	$k_{\rm q},10^{-10}~{ m cm^3~s^{-1}}$
$He(2^3S \rightarrow 1^1S)$	19.82	31
$Ne(2^3P_2 \rightarrow 2^1S)$	16.62	2.0
$Ar(3^3P_2 \rightarrow 3^2S)$	11.55	4.0
$Kr(4^3P_2 \rightarrow 4^2S_0)$	9.915	3.4
$Xe(5^3P_2 \rightarrow 5^2S_0)$	8.315	19

electron impact near the threshold. In particular, in the case of quenching a resonantly excited atomic state, when this process is effective, the rate constant of quenching is determined approximately within the framework of the perturbation theory, according to formula (3.27a), as

$$k_{\rm q} = {\rm const} \, \frac{g_0 \, f_{0*}}{g_* (\Delta \varepsilon)^{3/2}} = \frac{k_0}{(\Delta \varepsilon)^{7/2} \tau_{*0}} \,. \tag{3.35}$$

Here, f_{0*} is the oscillator strength for this transition, τ_{*0} is the radiative lifetime of the resonantly excited state, λ is the wavelength of the emitting photon, const and k_0 are numerical coefficients, the atom excitation energy $\Delta \varepsilon$ is expressed in eV, and the radiative lifetime is given in ns. The numerical coefficient $k_0 = (4.4 \pm 0.7) \times 10^{-5} \text{ cm}^3 \text{ s}^{-1}$ if we resort to the experimental data for the excitation cross sections of alkali metal atoms. As it follows from the data of Table 3, the accuracy of formula (3.36) for the rate constants of quenching of resonantly excited states is about 20%, and Table 4 contains the rate constants of quenching for several resonantly excited atoms by electron impact. The rate constants of quenching of atom metastable states by electron impact is lower than those for resonantly excited states because of a more weak coupling between these states during interaction with an electron. This is demonstrated by comparison of the data in Table 4 with those in Table 5 where the rate constants for quenching metastable rare gas atoms are compiled.

4. Electron transport processes in gas and plasma

4.1 Regimes of electron drift in gas in an external electric field

When electrons move in a gas in an external electric field, they acquire energy from the field and transfer it to gas atoms in collisions with them. As a result, electrons transfer energy from the field to the gas. Depending on the ratio between the rates of electron–electron and electron–atom collisions, we have different regimes of electron equilibrium in a gas in an external electric field. Let us consider the case of a high electron concentration, when it satisfies the criterion which is opposite with respect to criterion (2.18):

$$N_{\rm e} \gg \frac{m_{\rm e}}{M} \frac{\sigma_{\rm ea}}{\sigma_{\rm ee}} N_{\rm a} \,. \tag{4.1}$$

In this case, the electron distribution function is given by the Maxwell formula (2.20), and the electron temperature is determined by relation (2.25):

$$T_{\rm e} - T = \frac{Ma^2}{3} \frac{\langle v^2 / v \rangle}{\langle v^2 v \rangle} , \qquad (4.2)$$

where *M* is the atomic mass, and $a = eF/m_e$. In particular, in the case v = const, this gives

$$w_{\rm e} = \frac{eF}{m_{\rm e}v}, \qquad T_{\rm e} - T = \frac{Mw_{\rm e}^2}{3}.$$
 (4.3)

Since the rate v(v) of electron-atom collisions is proportional to the number density of atoms N_a , we present formula (4.2) in the form

$$T_{\rm e} - T = \left(\frac{F}{N_{\rm a}}\right)^2 g(T_{\rm e}), \qquad (4.4)$$

where

$$g(T_{\rm e}) = \frac{Me^2}{3m_{\rm e}^2} \frac{\langle v^2/k_{\rm ea} \rangle}{\langle v^2k_{\rm ea} \rangle}$$
(4.5)

depends neither on the electric field strength F nor on the number density of atoms N_a . Here, k_{ea} is the rate constant of electron – atom collisions with $k_{ea} = v/N_a = v\sigma_{ea}^*(v)$ and σ_{ea}^* being the diffusion cross section of electron – atom scattering. Figure 5 gives the function $g(T_e)$ responsible for electron drift in xenon [103]. Formula (4.4) connects the electron temperature in a given regime of electron drift with the reduced electric field strength F/N_a . This connection is illustrated in Fig. 6 for electron drift in xenon within a range of electron temperatures that are not too small [103] since, due to the Ramsauer effect, equation (4.4) possesses three solutions at small reduced field strengths F/N_a if they are below 0.03×10^{17} V cm² [103, 104] for xenon, which can be



Figure 5. Function $g(T_e)$ in formula (4.5) for electrons moving in xenon in an electric field [103].



Figure 6. The connection between the reduced electric field strength and electron temperature for electrons moving in xenon in an electric field [103].

considered as a critical field strength. Below this field strength and correspondingly at low gaseous temperatures, instabilities can be developed in the plasma. Because of low electron temperatures (below 3000 K), this fact is not of importance under real conditions.

The drift velocity of electrons in a gas in an external electric field is determined by formula (2.9) for both regimes of electron drift, and when the rate constant of electron – atom collisions k_{ea} depends sharply on the collision velocity, the drift velocity $w_e(F)$ as a function of the electric field strength has a kink in the range of electric field strengths corresponding to electron energies at the minimum of the electron – atom collision cross section. Then if the criterion (2.18) holds true, $w_e(F)$ near kink varies stronger than in the case of the opposite criterion (4.1), because the energy distribution function (2.28) for electrons in the first case drops more sharply than in the case of the Maxwell distribution function (2.20) in the second regime. This fact is confirmed by the curves in Fig. 7 where the electron drift



Figure 7. The drift velocity w_e of electrons moving in xenon in an external electric field: *I* — the limit of a low electron concentration in accordance with Fig. 3; *2* — the limit of a high electron concentration [103].

velocity in xenon is given as a function of the reduced electric field strength for two regimes of electron drift in the range of field strengths corresponding to the Ramsauer minimum for the electron – atom cross section [103].

Note that if the electron – atom collision rate v(v) does not depend on the collision velocity, we have the same expressions for the drift velocity as a function of the electric field strength, which are given by formulas (2.10) and (4.3). In this case, the characteristic electron energy ε_{ch} defined by formula (3.17) is equal according to formula (4.2) to

 $\varepsilon_{\rm ch} = T_{\rm e} - T$.

4.2 Conductivity of ionized gas and plasma

A simple method of the selective action of an external electric field on different degrees of freedom of a gaseous substance based on the interaction between electrons and an electric field. Field energy is then transmitted first from the field to electrons and then to atoms in a gas through their collisions with electrons. In this case there is a strong action of the electric field on electrons, and a weak action on atoms. As a result, the atoms have the Maxwell distribution function over energies, while the energy distribution function of electrons can differ remarkably from the Maxwell distribution.

Electrons of a weakly ionized gas determine its electric properties, and the plasma conductivity Σ is defined as the proportionality factor between the electric current density **i** and the electric field strength **F** in Ohm's law

$$\mathbf{i} = \Sigma \mathbf{F} \,. \tag{4.6}$$

The electric current represents a sum of two components — the electron current and the ion current:

$$\mathbf{i} = -eN_{\mathrm{e}}\mathbf{w}_{\mathrm{e}} + eN_{\mathrm{i}}\mathbf{w}_{\mathrm{i}}, \qquad (4.7)$$

where N_e , N_i are the electron and ion number densities, and \mathbf{w}_e , \mathbf{w}_i are the electron and ion drift velocities, respectively, which are expressed through the electron and ion mobilities K_e , K_i by formula (3.14). For the conductivity of a quasi-neutral ionized gas this gives

$$\Sigma = e(K_{\rm e} + K_{\rm i})N_{\rm e}\,.\tag{4.8}$$

From formula (3.17) one can estimate the mobility of a charged particle in a gas by the relation

$$K \sim \frac{e}{N_a \sigma \sqrt{\mu T}} \,, \tag{4.9}$$

where N_a is the number density of atoms, σ is a typical cross section of collisions between charged particles and atoms, and the temperature *T* characterizes an energy scale of such collisions. From this follows that $K_e \ge K_i$, i.e. electrons give the main contribution to plasma conductivity. Then from formulas (4.8) and (4.9) we have the following estimate for the conductivity of an ionized gas:

$$\Sigma \sim \frac{N_{\rm e}e^2}{N_{\rm a}\sigma_{\rm ea}^*\sqrt{m_{\rm e}T_{\rm e}}}\,,\tag{4.10}$$

where σ_{ea} is a typical cross section of electron-atom scattering. So, restricting ourselves with the electron part of plasma conductivity, we have

$$\Sigma = \frac{N_{\rm e}e^2}{3m_{\rm e}} \left\langle \frac{1}{v^2} \frac{\rm d}{{\rm d}v} \left(\frac{v^3}{v} \right) \right\rangle, \tag{4.11}$$

where $v = N_a v \sigma_{ea}^*$ is the electron-atom collision rate. In particular, introducing a collision time $\tau = 1/v$ and assuming it to be independent of the collision velocity v, we obtain the plasma conductivity in the traditional form

$$\Sigma = \frac{N_{\rm e}e^2\tau}{m_{\rm e}}\,.\tag{4.12}$$

Let us consider a strongly ionized plasma, where electron-ion collisions prevail over electron-atom collisions. Notice that electron-electron collisions do not change the total electron momentum and thus do not influence plasma conductivity. Because the electron-ion collision cross section exceeds the electron-atom cross section for elastic scattering, the term 'strongly ionized plasma' in which electron-ion collisions dominate, can refer to a plasma with a small degree of ionization. For a strongly ionized plasma, formula (4.8) together with formula (3.15) for electron mobility give

$$\Sigma = \frac{N_{\rm e}e^2}{3m_{\rm e}} \left\langle \frac{1}{v^2} \frac{\rm d}{\rm d}v \left(\frac{v^3}{v_{\rm ei}} \right) \right\rangle, \tag{4.13}$$

where $v_{ei} = N_i v \sigma^*$ is the electron–ion collision rate, and an averaging is made over electron velocities. Because of the plasma quasi-neutrality ($N_e = N_i$), its conductivity does not depend on the electron density. The diffusion cross section of electron–ion collisions is given by formula (2.41) which has the form $\sigma^* = \pi e^4 \ln \Lambda/\epsilon^2$, where ϵ is the electron energy, and the Coulomb logarithm equals $\ln \Lambda = \ln[e^2/(r_D T)]$, with r_D being the Debye–Hückel radius. Using the Maxwell distribution function of electrons, we have formula (2.46) for electron–ion collision rate. Substituting formula (2.46) into (4.13) and accounting for $v_{ei} \sim v^{-3}$, we obtain finally the Spitzer formula for plasma conductivity [105]

$$\Sigma = \frac{2^{5/2} T_{\rm e}^{3/2}}{\pi^{3/2} m_{\rm e}^{1/2} e^2 \ln \Lambda} \,. \tag{4.14}$$

4.3 Electrons in gas in an alternating electric field

As follows from the above consideration, there are two typical times for electron-atom collisions, when electrons are moving in an atomic gas in an external electric field. The first time $\tau = 1/\nu$ (ν is a typical rate of electron-atom collisions) characterizes an electron momentum variation, and the second time $\sim M/(m_e\nu) \sim \tau M/m_e$ is a typical time of variation of the electron energy as a result of collisions with atoms. We now consider electron motion in a gas in a harmonic electric field of strength $\mathbf{F} \cos \omega t$ under the condition of $\omega \tau \ge m_e/M$, so that the electron energy does not vary appreciably during the period of field variation. This condition simplifies considerably the problem [2, 106, 107]. The above condition for the field frequency corresponds to the following form of the distribution function instead of Eqn (2.4) [106]:

$$f(\mathbf{v},t) = f_0(v) + v_x f_1 \exp(i\omega t) + v_x f_{-1} \exp(-i\omega t),$$

where the *x*-axis is directed along the field. Substituting this expansion into the kinetic equation and separating the corresponding harmonics by the standard method, we obtain the following set of equations instead of Eqn (2.8):

. .

$$\frac{a}{2}\frac{df_0}{dv} + (v + i\omega)vf_1 = 0, \qquad \frac{a}{2}\frac{df_0}{dv} + (v - i\omega)vf_{-1} = 0,$$
$$\frac{a}{6v^2}\left[v^3(f_1 + f_{-1})\right] = I_{ea}(f_0).$$

From this, instead of formula (2.9), we have for the electron drift velocity

$$v_{e}(t) = \int v_{x}^{2} [f_{1} \exp(i\omega t) + f_{-1} \exp(-i\omega t)] d\mathbf{v}$$
$$= \frac{eF}{3m_{e}} \left\langle \frac{1}{v^{2}} \frac{d}{dv} \left(v^{3} \frac{v \cos \omega t + \omega \sin \omega t}{\omega^{2} + v^{2}} \right) \right\rangle.$$

This expression corresponds to the expansion in terms of a small parameter $m_e/(M\omega\tau)$ that allows us to ignore other terms of expansion over the spherical harmonics and time harmonics. Note that the parameter ω/v may take the arbitrary values in comparison with unity, and this ratio determines the phase shift for an electron motion with respect to an external field. The above expressions are valid for both criteria (2.18) and (4.1). We now write down these formulas when the criterion (4.1) holds true that allows us to introduce the electron temperature T_e . Then the electron drift velocity is given by

$$w_{\rm e}(t) = \frac{eF}{3T_{\rm e}} \left\langle v^2 \left(\frac{v \cos \omega t + \omega \sin \omega t}{\omega^2 + v^2} \right) \right\rangle, \qquad (4.15a)$$

and the difference in the electron and gaseous temperatures is equal to [19]

$$T_{\rm e} - T = \frac{Ma^2}{6\langle v^2 v \rangle} \left\langle v^2 \frac{v}{\omega^2 + v^2} \right\rangle.$$
(4.15b)

In the limit $\omega \ll v$, formula (4.15a) coincides at t = 0 with that following from Eqns (3.9), (3.15), (3.17), and formula (4.15b) is transformed into formula (4.2) if instead of the electric field strength *F* we employ in formula (4.15b) its effective value $F/\sqrt{2}$.

4.4 Thermal conductivity and thermal diffusion of electrons in gas

Because of a small mass of electrons, their transport can give a contribution to the thermal conductivity of a weakly ionized gas. Below we will evaluate the thermal conductivity coefficient of electrons. In this case, the electron number density satisfies the criterion (4.1), and an equilibrium is established in the electron subsystem, i.e., the velocity distribution function of electrons is a Maxwell distribution $\varphi(v)$ and is characterized by the electron temperature. Under the action of the temperature gradient this distribution function is disturbed and can be represented in the following form that is similar to the expansion (2.4):

$$f(\mathbf{v}) = \varphi(v) + (\mathbf{v}\nabla \ln T_{e})f_{1}(v). \qquad (4.16)$$

The kinetic equation $\mathbf{v}\nabla f = I(f)$ then takes the form

$$\varphi(v)\left(\frac{m_{\rm e}v^2}{2T_{\rm e}} - \frac{5}{2}\right)\mathbf{v}\nabla T_{\rm e} = I_{\rm ea}(f)$$

Here we took into account that the x-dependence of the electron distribution function appears owing to the electron temperature gradient and the electron pressure $p_e = N_e T_e$ is constant throughout a space. From this equation and formula (2.16) yielding $I_{ea}(v_x f_1) = -vv_x f_1$, we obtain the following expression for the asymmetric part of the distribution function:

$$f_1(v) = -\frac{\varphi(v)}{v} \left(\frac{m_e v^2}{2T_e} - \frac{5}{2} \right).$$

The electron heat flux is equal to

$$\mathbf{q}_{\mathrm{e}} = \int \frac{m_{\mathrm{e}} v^2}{2} v_x f(\mathbf{v}) \,\mathrm{d}\mathbf{v} = \int \frac{m_{\mathrm{e}} v^2}{2} v_x^2 \,\nabla \ln T_{\mathrm{e}} f_1(v) \,\mathrm{d}\mathbf{v} \,.$$

Introducing the thermal conductivity coefficient of electrons by the formula

$$\mathbf{q}_{\mathrm{e}} = -\kappa_{\mathrm{e}} \nabla T_{\mathrm{e}} \,, \tag{4.17}$$

we obtain

$$\kappa_{\rm e} = N_{\rm e} \left\langle \frac{v^2}{3v} \frac{m_{\rm e} v^2}{2} \left(\frac{m_{\rm e} v^2}{2} - \frac{5}{2} \right) \right\rangle, \tag{4.18}$$

where the angle brackets mean averaging over the Maxwell electron distribution function.

Assuming $v \sim v^n$, namely, $v(v) = v_0 z^{n/2}$, where $z = m_e v^2/(2T_e)$, from formula (4.18) we have

$$\kappa_{\rm e} = \frac{4}{3\sqrt{\pi}} \frac{T_{\rm e} N_{\rm e}}{v_0 m_{\rm e}} \left(1 - \frac{n}{2}\right) \Gamma\left(\frac{7 - n}{2}\right). \tag{4.19}$$

In particular, if v = const, this formula gives

$$\kappa_{\rm e} = \frac{5T_{\rm e}N_{\rm e}}{2\nu_0 m_{\rm e}} \,. \tag{4.20}$$

If n = 1, i.e. $v = v/\lambda$ (λ is the mean free path), we have from this formula one finds

$$\kappa_{\rm e} = \frac{2}{3\sqrt{\pi}} N_{\rm e}\lambda \sqrt{\frac{2T_{\rm e}}{m_{\rm e}}} \,. \tag{4.21}$$

In order to determine the electron contribution to the total thermal conductivity coefficient, it is necessary to connect the gradients of the electron (T_e) and atomic (T) temperatures. Let us consider the case where the difference in the electron and gaseous temperatures is determined by an external electric field, and the connection between the electron and gaseous temperatures is given by formula (2.25). If $v \sim v^n$, this formula yields

$$\nabla T_{\rm e} = \frac{\nabla T}{1 + n - nT/T_{\rm e}} \,. \tag{4.22}$$

Below we consider the case $T_e \ge T$. Then we have for the total thermal conductivity coefficient that

$$\kappa = \kappa_{a} + \kappa_{e} \, \frac{\nabla T_{e}}{\nabla T} = \kappa_{a} + \frac{\kappa_{e}}{1+n} \,, \tag{4.23}$$

where κ_a is the thermal conductivity coefficient of the atomic gas. If we use formula (4.20) as an estimate of the electron and gaseous thermal conductivity coefficients and substitute the atomic parameters in this formula for the electron parameters, we conclude that the electron thermal conductivity can give a contribution to the total quantity at low electron number densities $N_e < N_a$ due to a small electron mass and a high electron temperature. We assume the criterion (4.1) to be satisfied, so that an equilibrium is established in the electron subsystem, and this allows us to introduce the electron temperature separately.

The peculiarity of the electron thermal conductivity lies in the fact that cross-fluxes can be essential in these conditions. In the case of electron thermal conduction in a weakly ionized gas placed in an external electric field, when temperature gradients exist, we have the following expressions for fluxes

$$\mathbf{j} = N_{\mathrm{e}}K\mathbf{F} - D_T N \nabla \ln T_{\mathrm{e}}, \quad \mathbf{q} = -\kappa_{\mathrm{e}} \nabla T_{\mathrm{e}} + \alpha e \mathbf{F}.$$
 (4.24)

We consider the simplest cross-flux, namely, the electron flux under the action of a gradient of the electron temperature. This flux is equal to

$$\mathbf{j} = -D_T N \nabla \ln T_e \,, \tag{4.25}$$

where D_T is the thermodiffusion coefficient, and the last formula is its definition. We will find this quantity under conditions when the electron density is high enough, so that criterion (4.1) holds true, and we can introduce the electron temperature T_e . Then using expansion (4.16) for the electron distribution function and the relation (2.6) for the collision integral of the asymmetric part of the distribution function, we obtain the following equation for $f_1(v)$

$$v_x \frac{\partial \varphi}{\partial x} = -v v_x f_1 \,, \tag{4.26}$$

where *v* is the rate of electron – atom elastic collisions.

Let us calculate the electron flux that is created by the asymmetric part of the distribution function. Taking into

account that the flux is directed along the x-axis, we have

$$j_x = \int v_x f \, \mathrm{d}\mathbf{v} = \int v_x^2 f_1 \, \mathrm{d}\mathbf{v} = -\frac{1}{3} \int \frac{v^2}{v} \frac{\partial f_0}{\partial x} \, \mathrm{d}\mathbf{v}$$
$$= -\frac{\mathrm{d}}{\mathrm{d}x} \left[N_\mathrm{e} \left\langle \frac{v^2}{3v} \right\rangle \right],$$

where the angle brackets mean taking an average over the electron velocities. Since the *x*-dependence occurs due to a gradient in the electron temperature, we obtain from this formula that

$$j_x = -\nabla T_e \frac{\mathrm{d}}{\mathrm{d}T_e} \left(N_e \left\langle \frac{v^2}{3v} \right\rangle \right).$$

Comparing this expression with formula (4.25) we find the following relation for the thermodiffusion coefficient

$$D_T = T_e \frac{\mathrm{d}}{\mathrm{d}T_e} \left[\frac{N_e}{N} \left\langle \frac{v^2}{3v} \right\rangle \right] = T_e \frac{\mathrm{d}}{\mathrm{d}T_e} \left(\frac{N_e}{N} D \right), \qquad (4.27)$$

with the diffusion coefficient D of electrons in a gas being given by formula (3.22).

If the electron pressure $p_e = N_e T_e$ is unvaried, the above formula can be rewritten in the form

$$D_T = T_{\rm e}^2 \frac{N_{\rm e}}{N} \frac{{\rm d}(D_{\rm e}/T_{\rm e})}{{\rm d}T_{\rm e}} \,. \tag{4.28}$$

In particular, if v = const, this formula gives $D_T = 0$. In the case of power velocity dependence of the electron-atom collision rate $v \sim v^n$, we obtain

$$D_T = -n \frac{N_e}{N} D. ag{4.29}$$

This means that the direction of the electron flux with respect to the temperature gradient depends on the sign of n.

We now consider the case of electron transport when the displacement of electrons as a whole cannot violate the plasma quasi-neutrality that corresponds to plasma regions far from electrodes and walls. Then the mobility *K* in formula (4.24) is the electron mobility, and one can neglect ion mobility, including ambipolar diffusion. The expression for the electron thermodiffusion coefficient is given by formula (4.28), and formula (4.19) defines the thermal conductivity coefficient. Below we will determine the coefficient α in formula (4.24) by the standard method using expansion (2.4) of the electron distribution function over the spherical harmonics. Then, the first equation of the set (2.8) yields $f_1 = eFf_0/(vT_c)$, and the coefficient α is equal to

$$\alpha = \frac{m_{\rm e}N_{\rm e}}{6T_{\rm e}} \left\langle \frac{v^4}{v} \right\rangle = \frac{4T_{\rm e}N_{\rm e}}{3\sqrt{\pi}\,m_{\rm e}v_0}\,\Gamma\left(\frac{7}{2} - \frac{n}{2}\right),\tag{4.30}$$

where we set $v = v_0 (v / \sqrt{2T_e/m_e})^n$. This gives for n = 0:

$$\alpha = \frac{5T_{\rm e}N_{\rm e}}{2m_{\rm e}\nu}\,,\tag{4.31}$$

and for n = 1, when $v = v/\lambda$, this formula yields

$$\alpha = \sqrt{\frac{2T_{\rm e}}{m_{\rm e}}} \frac{\lambda}{3\sqrt{\pi}} = \frac{2\lambda N_{\rm e}}{3v_T} \,, \tag{4.32}$$

where $v_T = \sqrt{8T_e/\pi m_e}$ is the mean electron velocity.

Formulas (4.31) and (4.32), together with the corresponding expressions for the plasma kinetic coefficients, allow us to determine the electron heat flux under different conditions in the plasma. In particular, let us determine the effective thermal conductivity coefficient in the direction perpendicular to an external electric field **F**. If the plasma is placed into a metallic enclosure, the transverse electric field is absent (F = 0), and formulas (4.31) and (4.32) are added to formula (4.17). If the walls are dielectric, we have $\mathbf{j} = 0$, which corresponds to the regime of ambipolar diffusion, when electrons travel together with ions. In the electron scale of values, this gives $\mathbf{j}_e = 0$, i.e., an electric field of strength $\mathbf{F} = D_T \nabla \ln T_e/(N_e K)$ is established. We represent the heat flux in the form

$$\mathbf{q} = -C\kappa_{\rm e}\nabla T_{\rm e}\,,\tag{4.33}$$

where the coefficient $C = 1 - \alpha ND_T e/(\kappa_e T_e N_e K)$. Using formula (4.28) for the electron thermodiffusion coefficient and the Einstein relation $D = KT_e/e$, we obtain it in the form $C = 1 + \alpha n/\kappa_e$.

On the basis of formulas (4.28), (4.29), and (4.32) we have

$$C = \frac{n+2}{2-n} \,. \tag{4.34}$$

As may be seen, the effective thermal conductivity coefficient for electrons depends on n in the two considered cases of metallic and dielectric walls. For n = 0, this quantity takes identical values in both cases; for n = 1, its value is 3 times more in the second case than in the first one.

We analyze heat transport in a plasma under simple conditions. In gas discharges with moderate and high currents, heat processes can determine the properties of the discharge positive column [103, 108, 109]. Moreover, heat processes can be the principal cause of plasma instabilities. In particular, heat transport leads to contraction of the discharge current, resulting in an instability that compels a plasma to be concentrated only in the central part of the positive column [108, 110-113]. Next, along with the simplest transport processes, other fluxes may occur in a real gasdischarge plasma because of additional gradients, for example, due to a gradient or nonstationarity of the electric field strength. Each of these gradients causes a new flux, and the absence of equilibrium between the electron and atomic subsystems complicates the general character of transport processes in a plasma. It is convenient then to rely on the hydrodynamic description of electrons, which starts from the expansion of the electron distribution function in terms of the spherical harmonics. This expansion has the form (2.4) in the simple case and can account for other gradients or nonstationarities. The kinetic equation for the symmetric spherical harmonic f_0 of the distribution function is reduced to a hydrodynamic equation, and transport coefficients in this equation are evaluated independently. This approach allows one to model real conditions and to analyze specific effects in a real plasma [114-117]. Note that in contrast to traditional hydrodynamics, thermodynamic equilibrium between the electron and gaseous subsystems is absent in this case, and the above approach requires small gradients or slow processes which violate the equilibrium distribution of current. In addition, in contrast to the traditional hydrodynamic description, this approach accounts for real dependences of the collision rates on the electron velocity, which can be of importance.

4.5 The Hall effect

Let us consider the behavior of electrons in a gas when constant electric and magnetic fields are directed perpendicular to each other. Because an electron has a circular motion in a magnetic field in a plane perpendicular to the magnetic field, the action of electric and magnetic fields gives rise to an electron motion in the direction perpendicular to these fields. The Hall effect is connected with the creation of electron currents in the direction which is perpendicular to the electric and magnetic fields. In this case, the electron distribution function satisfies the kinetic equation

$$\left(e\mathbf{F} + e[\mathbf{vH}]\right)\frac{\partial f}{\partial \mathbf{v}} = I_{\mathrm{ea}}(f), \qquad (4.35)$$

where **F** is the electric field strength, **H** is the magnetic field strength, and we took the electric and magnetic field directions along the x- and z-axes, respectively. One can solve this equation by the same method as we used for electrons in a gas in a constant electric field. Then, instead of formulas (2.4), for the electron distribution function we have

$$f(\mathbf{v}) = f_0(v) + v_x f_1(v) + v_y f_2(v), \qquad (4.36)$$

and extracting spherical harmonics, we obtain now instead of the first equation of the set (2.8):

$$vf_1 = \frac{av}{v^2 + \omega_H^2} \frac{df_0}{dv}, \quad vf_2 = \frac{a\omega_H}{v^2 + \omega_H^2} \frac{df_0}{dv},$$
 (4.37)

where $a = eF/m_e$, and $v = N_a v \sigma_{ea}^*$ is the rate of electron collisions with atoms. These equations lead to the following expressions for the components of the electron drift velocity:

$$w_{x} = \frac{eF}{3m_{e}} \left\langle \frac{1}{v^{2}} \frac{d}{dv} \left(\frac{vv^{3}}{v^{2} + \omega_{H}^{2}} \right) \right\rangle,$$

$$w_{y} = \frac{eF}{3m_{e}} \left\langle \frac{1}{v^{2}} \frac{d}{dv} \left(\frac{\omega_{H}v^{3}}{v^{2} + \omega_{H}^{2}} \right) \right\rangle.$$
(4.38)

In the limit $\omega_H \ll v$, the first formula is transformed into Eqn (2.9).

In the absence of a magnetic field, the plasma conductivity is scalar. The presence of a magnetic field causes transformation of the conductivity of a weakly ionized gas into a tensor, and Ohm's law takes the form

$$j_{\alpha} = \Sigma_{\alpha\beta} F_{\beta} ,$$

where j_{α} is a component of the current density, and the summation is taken over twice repeating indices. In the case where the collision rate v does not depend on the electron velocity, the components of the conductivity tensor are given by

$$\Sigma_{xx} = \Sigma_{yy} = \Sigma_0 \frac{1}{1 + \omega_H^2 \tau^2},$$

$$\Sigma_{yx} = -\Sigma_{xy} = \Sigma_0 \frac{\omega_H \tau}{1 + \omega_H^2 \tau^2},$$
(4.39)

where $\tau = 1/v$.

In the limiting case $\omega_H \tau \ge 1$, the electric current is directed perpendicular to both the electric and magnetic fields. In this case, the plasma conductivity and electric current do not depend on the collision rate because the change in the direction of electron motion is determined by the electron rotation in a magnetic field. We have in this case

$$j_y = ecN_e \frac{F_x}{H} = \frac{F_x}{R_H H}, \qquad (4.40)$$

where $R_{\rm H} = 1/(ecN_{\rm e})$ is the Hall constant.

Let us determine the average electron energy in the case where the criterion (4.1) holds true. The balance equation for the electron energy has the form

$$eFw_x = \int \frac{m_{\rm e}v^2}{2} I_{\rm ea}(f_0) \,\mathrm{d}\mathbf{v} \,.$$

Using formula (4.38) for the electron drift velocity and formula (2.16) for the electron – atom collision integral, we obtain

$$T_{\rm e} - T = \frac{Ma^2}{3} \left\langle \frac{v^2 v}{v^2 + \omega_H^2} \right\rangle \frac{1}{\langle v^2 v \rangle} \,. \tag{4.41}$$

In particular, if v = const, this formula gives

$$T_{\rm e} - T = \frac{Ma^2}{3(v^2 + \omega_H^2)} \,. \tag{4.42}$$

In the limit $\omega_H \ge v$, formula (4.41) yields

$$T_{\rm e} - T = \frac{Ma^2}{3\omega_H^2} = \frac{Mc^2 F^2}{3H^2} \,. \tag{4.43}$$

Let us analyze the case where a weakly ionized gas is moving in a transverse magnetic field of strength H with an average velocity u. Then in the system of axes where the plasma is motionless, the electric field of strength F' = Hu/cis induced, where c is the velocity of light. This field creates an electric current which is used for obtaining the electric energy in magnetohydrodynamic (MHD) generators. The energy released through the action of this electric current results from the transformation of the flow energy of a gas into electric and heat energy. Correspondingly, this process leads to a deceleration of the gas flow and to a decrease in its average velocity. Along with this, the induction of an electric field causes an increase in electron temperature which is given by formula (4.42). As can be seen, the maximum increase in the electron temperature is achieved in the limit $\omega_H \gg v$. In this limit, formula (4.43) yields

$$T_{\rm e} - T = \frac{Ma^2}{3\omega_H^2} = M \frac{u^2}{3} .$$
 (4.44)

4.6 Acceleration of fast electrons in plasma

Let us take a look at the effect of runaway electrons in an ionized gas or plasma [18, 118, 119], which shows itself if electron –electron collisions are more intensive than electron collisions with neutral particles, i.e., the criterion (4.1) holds true. In particular, this may be realized in the course of deceleration of fast electrons in metals until electron – ion collisions stop them. Because the cross section of electron – electron or electron – ion collisions results from the Coulomb interaction potential between these charged particles, it decreases sharply with an increase in electron energy, and electrons resided at the tail of the energy distribution function are scattered more weakly than the main part of electrons.

Hence, an instability occurs when fast electrons moving along the electric field do not decelerate in collisions with electrons and ions. Therefore, a part of the electrons is accelerated and leaves the plasma with a high velocity. Below we will analyze the effect of runaway electrons in the simplest way, accounting for the fact that an acceleration of electrons in an external electric field will not be compensated for by electron deceleration in collisions with other electrons and ions, starting from certain electron velocities. For this analysis one can apply the Landau collision integral (2.44), (2.45) which takes into account deceleration of fast electrons in collisions with charged particles in a plasma.

Let us consider the evolution of a fast electron whose velocity significantly exceeds the typical energy of plasma electrons. We have the following balance equation for the momentum $m_e v_x$ of the test electron when it moves along the electrical field of strength *F*:

$$m_{\rm e} \, \frac{{\rm d} v_x}{{\rm d} t} = eF - \frac{1}{v_x} \frac{{\rm d} \varepsilon}{{\rm d} t} \,,$$

where $d\epsilon/dt$ is the variation of the electron energy per unit time in collisions with plasma electrons. We take into account the fact that an individual collision leads to electron scattering through small angles, and an individual act of collision is accompanied by a small variation of energy. This derivative is defined as

$$\frac{\mathrm{d}\varepsilon}{\mathrm{d}t} = \int N_{\mathrm{e}} v \, 2\pi\rho \, \mathrm{d}\rho \, \frac{\Delta p^2}{2m_{\mathrm{e}}} \, .$$

Here, v is the velocity of the test electron, $v \approx v_x$, N_e is the electron number density, ρ is the impact parameter of collision, and Δp is the momentum which is transferred from the test electron to a plasma electron during their collision. According to formula (2.37) we have

$$\Delta p = \frac{2e^2}{\rho v} ,$$

and we obtain

$$\frac{\mathrm{d}\varepsilon}{\mathrm{d}t} = N_{\mathrm{e}} \, \frac{4\pi e^4}{m_{\mathrm{e}}v} \ln\Lambda\,,$$

where the Coulomb logarithm is given by formula (2.40). Finally, we obtain the balance equation for the momentum of a fast test electron moving along an electric field in a plasma:

$$m_{\rm e} \, \frac{{\rm d}v_x}{{\rm d}t} = eF - N_{\rm e} \, \frac{4\pi e^4}{m_{\rm e} v^2} \ln \Lambda \,. \tag{4.45}$$

As follows from the balance equation (4.45), fast electrons accelerate in an electric field, starting from the energy

$$\varepsilon \geqslant \varepsilon_{\rm cr} = N_{\rm e} \, \frac{2\pi e^4}{eF} \ln \Lambda \,.$$

$$\tag{4.46}$$

In particular, if the electric field strength F is measured in V cm⁻¹, the number density of electrons N_e in 10¹³ cm⁻³, and the electron energy ε is measured in eV, the criterion (4.46) takes the following form, if we set ln $\Lambda = 10$:

$$\varepsilon_{\rm cr} = 13 \, \frac{N_{\rm e}}{F} \,. \tag{4.47}$$

5. Excitation of atoms in gas and plasma in collisions with electrons

5.1 Excitation of atoms in gas in an electric field by electron impact

Electrons moving in a gas in an external electric field can excite atoms of the gas, and the atomic excitation rate depends on the character of equilibrium between electrons and excited atoms in the gas. Below we will evaluate the rate of atomic excitation if a typical electron energy is small compared to the excitation energy, and the electrons which excite atoms are found at the tail of the energy distribution function of electrons located in a gas in an external electric field. Then, the asymmetric component of the velocity distribution function is of importance, in spite of its relative smallness, because the electron extracts energy from the electric field through its active participation. Let us consider first the excitation of gas atoms in collisions with individual electrons located in a gas in an electric field, when the criterion (2.18) is satisfied. We assume that collisions with atoms create a strong friction for electrons in an energy space, and the electron energy attains the excitation threshold after many elastic electron - atom collisions. The excitation rate of atoms by the electrons is then determined by motion toward the excitation threshold in a velocity or electron energy space.

For a description of this process, we use the expansion (2.4) for a nonstationary electron distribution function, and using the standard procedure, as in deducing the set of equations (2.8), we obtain

$$\frac{\partial f_0}{\partial t} + \frac{a}{3v^2} \frac{\partial (vf_1)}{\partial v} = I_{ea}(f_0), \qquad \frac{\partial f_1}{\partial t} + a \frac{\partial f_0}{\partial v} = -vvf_1. \quad (5.1)$$

Assuming the excitation energy flux to be relatively small, we ignore everywhere the nonstationarity, except for the first term which corresponds to a small flux in the energy space. As a result, one finds

$$\frac{\partial f_0}{\partial t} = I_{\text{ea}}(f_0) + \frac{a}{3v^2} \frac{\mathrm{d}}{\mathrm{d}v} \left(\frac{v^2}{v} \frac{\mathrm{d}f_0}{\mathrm{d}v}\right).$$
(5.2)

The nonstationarity of the distribution function is only due to atomic excitation. Hence, the excitation rate is given by

$$\frac{\mathrm{d}N_*}{\mathrm{d}t} = -\frac{\mathrm{d}N_\mathrm{e}}{\mathrm{d}t} = -\int 4\pi v^2 \,\mathrm{d}v \,\frac{\partial f_0}{\partial t}$$

where N_* is the number density of excited atoms. Using the collision integral (2.16) for the spherically symmetric electron distribution function f_0 , we obtain in the upshot

$$\frac{\mathrm{d}N_*}{\mathrm{d}t} = 4\pi \,\frac{m_\mathrm{e}}{M} \,v^3 v \left[\left(T + \frac{Ma^2}{3v^2}\right) \frac{\mathrm{d}f_0}{\mathrm{d}\varepsilon} + f_0 \right]_{\varepsilon = \Delta\varepsilon},\tag{5.3}$$

where $\varepsilon = m_e v^2/2$ is the electron energy, and $\Delta \varepsilon$ is the energy of atomic excitation.

We use the boundary condition $f_0(\Delta \varepsilon) = 0$ for the distribution function which satisfies the following equation under stationary conditions over the region below and far from the excitation threshold:

$$\left(T + \frac{Ma^2}{3v^2}\right)\frac{\mathrm{d}f_0}{\mathrm{d}\varepsilon} + f_0 = 0\,.$$

This signifies a fast absorption of electrons above the excitation threshold and gives the following expression for the distribution function

$$f_{0}(\varepsilon) = C \left[\varphi_{0}(\varepsilon) - \varphi_{0}(\Delta \varepsilon) \right]$$

= $C \left[\exp \left(-\int_{0}^{\varepsilon} \frac{d\varepsilon'}{T + Ma^{2}/3v^{2}} \right) - \exp \left(-\int_{0}^{\Delta \varepsilon} \frac{d\varepsilon'}{T + Ma^{2}/3v^{2}} \right) \right].$ (5.4a)

Here. $\varphi_0(\varepsilon)$ is the distribution function if we ignore the absorption of fast electrons due to the excitation process, so that far from the excitation threshold $f_0(\varepsilon) = \varphi_0(\varepsilon)$. The constant *C* follows from the normalization condition

$$C = N_{\rm e} \left[4\pi \int_0^{v_0} v^2 \, \mathrm{d}v \exp\left(-\int_0^{\varepsilon} \frac{\mathrm{d}\varepsilon'}{T + Ma^2/3v^2} \right) \right]^{-1}, \quad (5.4b)$$

where N_e is the number density of electrons, and the electron threshold velocity is $v_0 = \sqrt{2\Delta\varepsilon/m_e}$. Thus, we have for the rate of atomic excitation by individual electrons moving in a gas in an external electric field:

$$\frac{\mathrm{d}N_*}{\mathrm{d}t} = 4\pi v_0^3 \frac{m_{\mathrm{e}}}{M} v(v_0) \varphi_0(v_0)$$

$$= N_{\mathrm{e}} \frac{m_{\mathrm{e}}}{M} v(v_0) \exp\left(-\int_0^{\Delta \varepsilon} \frac{\mathrm{d}\varepsilon'}{T + Ma^2/3v^2}\right)$$

$$\times \left[\int_0^{v_0} \left(\frac{v}{v_0}\right)^2 \frac{\mathrm{d}v}{v_0} \exp\left(-\int_0^{\varepsilon} \frac{\mathrm{d}\varepsilon'}{T + Ma^2/3v^2}\right)\right]^{-1}, \quad (5.5)$$

where $\varphi_0(v_0) = \varphi_0(\Delta \varepsilon)$ is the electron distribution function at the excitation threshold if we neglect the atomic excitation process. In the special case $v(v_0) = \text{const}$, this formula takes the form

$$\frac{\mathrm{d}N_*}{\mathrm{d}t} = \frac{4}{\sqrt{\pi}} \left(\frac{\Delta\varepsilon}{T + Ma^2/3v^2}\right)^{3/2} N_\mathrm{e} \, \frac{m_\mathrm{e}}{M} \, v(v_0) \\ \times \exp\left(-\frac{\Delta\varepsilon}{T + Ma^2/3v^2}\right). \tag{5.6}$$

It is of interest now to find which portion ξ of the power taken by electrons from an external electric field is consumed on atomic excitation. We assume that the power absorbed by electrons from the electric field is transformed mostly into the thermal energy of the gas as a result of elastic collisions between electrons and atoms, and such a power per electron is eFw, where w is the electron drift velocity. In the case v = const, we have from formula (5.6), neglecting the atomic thermal energy ($T \ll Mw^2$):

$$\xi = \Delta \varepsilon \, \frac{\mathrm{d}N_*}{\mathrm{d}t} \frac{1}{eFwN_\mathrm{e}} = \frac{4}{3\sqrt{\pi}} \left(\frac{\Delta \varepsilon}{\overline{\varepsilon}}\right)^{3/2} \exp\left(-\frac{\Delta \varepsilon}{\overline{\varepsilon}}\right), \quad (5.7)$$

where $\bar{\epsilon} = Ma^2/(3v^2) = Mw^2/3$ is the average electron energy. Figure 8 shows the dependence of the efficiency ξ of atomic excitation on the electron energy $\bar{\epsilon}$ under these conditions.

The above formulas are based on the assumption that the atomic excitation rate is determined mostly by diffusion of electrons in an energy space from small energies up to the atom excitation energy. We now consider another limiting



Figure 8. The portion of electron energy which is consumed for atomic excitation from the energy obtained by an electron moving in a gas from an external electric field. It is assumed that the frequency of elastic electron – atom scattering is independent of the electron energy, and a test electron acquires excitation energy after many collisions with atoms.

case where excitation at the tail of the energy distribution function proceeds weakly and the efficiency of atomic excitation near the threshold is determined by individual electrons which move in a gas in an external electric field.

Let us first find the electron distribution function above the excitation threshold in the energy range $\varepsilon \ge \Delta \varepsilon$, including inelastic electron – atom collisions in the kinetic equation for electrons. We assume that quenching of the excited atom does not proceed by electron impact because of the small density of electrons. Then the second equation of the set (2.8) takes the form

$$\frac{a}{3v^2}\frac{d}{dv}(v^3f_1) = I_{ea}(f_0) - v_{ex}f_0, \qquad (5.8)$$

where $v_{ex} = N_a k_{ex}$, N_a is the number density of atoms, and k_{ex} is the rate constant of atomic excitation by electron impact. The collision integral I_{ea} takes into account elastic electron – atom collisions. Using the connection (2.8) between f_0 and f_1 , we obtain the following equation for f_0 :

$$\frac{a}{3v^2} \frac{d}{dv} \left(\frac{v^2}{v} \frac{df_0}{dv} \right) + I_{ea}(f_0) - v_{ex} f_0 = 0.$$
 (5.9)

Based on expression (2.16) for the electron-atom collision integral and neglecting the atomic kinetic energy ($\sim T$) as compared to the electron energy, we arrive at

$$\frac{a}{3v^2}\frac{d}{dv}\left(\frac{v^2}{v}\frac{df_0}{dv}\right) + \frac{m_e}{M}\frac{1}{v^2}\frac{d}{dv}(v^3vf_0) - v_{ex}f_0 = 0.$$
(5.10)

We assume the average electron energy $\bar{\epsilon}$ to be small compared to the atomic excitation energy $\Delta \epsilon$. Then, as follows from formula (2.25), the average electron energy is $\bar{\epsilon} \sim Ma^2/v^2$. In addition, we assumed that atomic excitation does not influence the electron distribution function below the excitation threshold, so that

$$v \gg v_{\rm ex} \gg v \frac{m_{\rm e}}{M} \frac{\Delta \varepsilon}{\overline{\varepsilon}}$$
 (5.11)

This allows us to neglect the second term in the kinetic equation (5.10). Let us solve the resultant kinetic equation for the tail of the electron distribution function on the basis of

the quasi-classical method, thus accepting $f_0 = A \exp(S)$, where S(v) is a smooth function, i.e., $(S')^2 \ge S''$. This gives $S' = \sqrt{3v_{ex}v}/a$, $a = eF/m_e$, and the distribution function for $\varepsilon \ge \overline{\varepsilon}$ has the form

$$f_0(v) = f_0(v_0) \exp\left(-S\right) = f_0(v_0) \exp\left(-\int_{v_0}^v \frac{\mathrm{d}v}{a} \sqrt{3v_{\mathrm{ex}}v}\right),$$
(5.12)

where $v_0 = \sqrt{2\Delta\varepsilon/m_e}$, and $f_0(v_0)$ is determined by elastic electron-atom collisions. Near the threshold of atomic excitation this formula reduces to

$$S = \frac{2v_0}{5a} \sqrt{3 \frac{g_*}{g_0}} v_q v_0 \left(\frac{\varepsilon - \Delta \varepsilon}{\Delta \varepsilon}\right)^{5/4}, \qquad (5.13)$$

where the rate of elastic electron – atom collisions at the excitation threshold is $v_0 = v(v_0)$, $v_q = N_a k_q$, with k_q being the rate constant of quenching of the excited atom by electron impact, g_0 , g_* are the statistical weights of the ground and excited atomic states, $a = eF/m_e$, and we used formula (3.34b) for the rate constant of atom excitation by electron impact, which connects this rate constant with the rate of quenching of an excited atom by a slow electron. Using formula (5.12) for the electron distribution function, we assume the logarithm derivative of the distribution function to be determined by the excitation process proceeding not far from the threshold.

Formula (5.12) gives the rate of atom excitation by electron impacts if this process proceeds mostly near the excitation threshold:

$$\frac{\mathrm{d}N_*}{\mathrm{d}t} = \int 4\pi v^2 \,\mathrm{d}v \,f_0(v_0) \exp\left(-S\right) v_{\mathrm{ex}}(v)$$
$$= 4.30 a v_0^2 \left(\frac{a}{v_0 v_0}\right)^{1/5} \left(\frac{v_q g_*}{v_0 g_0}\right)^{2/5} f_0(v_0) \tag{5.14}$$

and the distribution function is normalized by the condition (2.30).

Comparing formulas (5.6) and (5.14) for the rate of atomic excitation by individual electrons moving in a gas in an external electric field, one has to make a choice between these two limiting cases. Indeed, in the case

$$\left(\frac{a}{v_0 v_0}\right)^{6/5} \left(\frac{v_q g_*}{v_0 g_0}\right)^{2/5} \gg 1, \qquad (5.15)$$

the excitation process is restricted by electron diffusion in an energy space to the excitation threshold, and the rate of this process is determined by formulas (5.5) and (5.6). In the other limiting case, the excitation rate is determined by formula (5.14). Note that formula (5.14) is valid at low electric field strengths, whereas formula (5.6) holds true at high field strengths.

5.2 Excitation of atoms in plasma

When electrons are located in a plasma, the energy distribution function of electrons drops strongly at the tail due to the excitation of atoms and can be restored owing to collisions between electrons. Analyzing the character of atomic excitation in a plasma, we assumed for simplicity that excited atomic states were destroyed as a result of radiation, so that quenching by electron impact was absent, and the excitation energy did not return to the electrons. We assume the criterion (4.1) to be valid, so that we have the Maxwell distribution function of electrons. In the first limiting case, we assume the Maxwell distribution function to be restored at energies $\varepsilon \ge \Delta \varepsilon$ ($\Delta \varepsilon$ is the atom excitation energy) which are responsible for the excitation of atoms. Then the atomic excitation rate is equal to

$$\frac{\mathrm{d}N_*}{\mathrm{d}t} = N_\mathrm{a} \int 4\pi v^2 \,\mathrm{d}v \,\varphi(v) k_\mathrm{ex}(v) \,, \tag{5.16}$$

where N_* is the number density of excited atoms, N_a is the number density of atoms in the ground state, $\varphi(v)$ is the Maxwell distribution function of electrons, and k_{ex} is the rate constant of atom excitation by electron impact, which is given by formula (3.34b). Averaging k_{ex} over the Maxwell distribution function of electrons, we arrive at

$$\frac{\mathrm{d}N_*}{\mathrm{d}t} = N_\mathrm{a}N_\mathrm{e}\overline{k}_\mathrm{ex} = N_\mathrm{a}N_\mathrm{e}k_\mathrm{q}\,\frac{g_*}{g_0}\exp\left(-\frac{\Delta\varepsilon}{T_\mathrm{e}}\right),\tag{5.17}$$

where the average rate constant of atom excitation in the limit $\Delta \varepsilon \gg T_e$ (T_e is the electron temperature) is defined as

$$\overline{k}_{\rm ex} = \frac{1}{N_{\rm e}} \int 4\pi v^2 \,\mathrm{d}v \,\varphi(v) k_{\rm ex}(v) = \frac{g_*}{g_0} \,k_{\rm q} \exp\left(-\frac{\Delta\varepsilon}{T_{\rm e}}\right). \quad (5.18)$$

Let us turn to the other limiting case of excitation of atoms by electrons in a plasma, when the criterion (4.1) is valid, but the Maxwell distribution function of electrons is not restored due to electron–electron collisions above the excitation threshold because of absorption of fast electrons as a result of the excitation process. Then the excitation rate of atoms is determined by the rate of formation of fast electrons with energies $\varepsilon > \Delta \varepsilon$ as a result of elastic collisions with electrons. Then on the basis of the kinetic equation (2.17), using expression (2.44) for the electron–electron collision integral, we can deduce the excitation rate per unit volume:

$$\begin{aligned} \frac{\mathrm{d}N_*}{\mathrm{d}t} &= -\int_{v_0}^{\infty} 4\pi v^2 \,\mathrm{d}v \,\, \frac{\partial f}{\partial t} = -\int_{v_0}^{\infty} 4\pi v^2 \,\mathrm{d}v \,\, I_{\mathrm{ee}}(f_0) \\ &= -\frac{4\pi v_0}{m_\mathrm{e}} \,\, B_{\mathrm{ee}}(v_0) \left(\frac{f_0}{T_\mathrm{e}} + \frac{\mathrm{d}f_0}{\mathrm{d}\varepsilon}\right), \end{aligned}$$

where the distribution function f_0 is taken at the excitation energy $\varepsilon = \Delta \varepsilon$. The electron distribution function in this case is the solution of the equation $I_{ee}(f_0) = 0$ under the boundary condition $f_0(v_0) = 0$ which accounts for an effective absorption of electrons above the excitation threshold. We then obtain the following expression for the distribution function

$$f_0(v) = N_e \left(\frac{m_e}{2\pi T_e}\right)^{3/2} \left[\exp\left(-\frac{\varepsilon}{T_e}\right) - \exp\left(-\frac{\Delta\varepsilon}{T_e}\right) \right], \quad \varepsilon \leq \Delta\varepsilon.$$
(5.19)

From this it follows that the electron distribution function is of the Maxwell type far from the excitation threshold, while near the threshold this function tends to zero because of the absorption of fast electrons due to the excitation of atoms. Using such a distribution function and expression (2.45) for $B_{ee}(v)$, we obtain in this case for the rate of excitation:

$$\frac{\mathrm{d}N_*}{\mathrm{d}t} = 4\sqrt{2\pi} \,\frac{N_\mathrm{e}^2 e^4 \Delta\varepsilon \ln\Lambda}{m_\mathrm{e}^{1/2} T_\mathrm{e}^{5/2}} \exp\left(-\frac{\Delta\varepsilon}{T_\mathrm{e}}\right). \tag{5.20}$$

Table 6. The parameters of the criterion (5.21) for metastable rare gas atoms.

Metastable atom	$\Delta \epsilon, eV$	$k_{\rm ee}, 10^{-4} {\rm cm}^3 {\rm s}^{-1}$	$\left(\frac{N_{\rm e}}{N_{\rm a}}\right)_{\rm b},10^{-6}$
$He(2^3S)$	19.82	5.8	5.4
$Ne(2^{3}P_{2})$	16.62	2.9	0.69
$Ar(3^{3}P_{2})$	11.55	2.0	2.0
$Kr(4^{3}P_{2})$	9.915	1.7	2.0
$Xe(5^2P_2)$	8.315	1.4	13

Formula (5.20) is valid at high densities of electrons, when an equilibrium for the electrons is quickly established. The corresponding criterion takes the form

$$\frac{N_{\rm e}}{N_{\rm a}} \gg \frac{k_{\rm q}}{k_{\rm ee}} , \qquad (5.21)$$

where the effective rate constant of elastic collisions of electrons k_{ee} due to the Coulomb interaction of electrons follows from comparison of formulas (5.17), (5.20) and is given by

$$k_{\rm ee} = 4\sqrt{2\pi} \, \frac{g_0}{g_*} \frac{e^4 \Delta \varepsilon \ln \Lambda}{m_{\rm e}^{1/2} T_{\rm e}^{5/2}} \,. \tag{5.22}$$

Formula (5.20) is valid under the opposite condition with respect to criterion (5.21). As can be seen, criterion (5.21) is much stronger than criterion (4.1) because $m_e \ll M$. Thus, both the regimes considered for atomic excitation in a plasma are possible. At relatively small densities of electrons, their distribution function is given by formula (5.19), while the Maxwell distribution function of electrons is valid at high degrees of ionization. Correspondingly, the rate of atomic excitation in a plasma varies from that defined by formula (5.17) to that of formula (5.20) as the electron density increases.

As a demonstration of these results, Table 6 lists rate constants (5.22) for rare gas atoms under typical conditions $T_e = 1 \text{ eV}$, $\ln \Lambda = 10$, with the boundary ionization degree being given by the relation

$$\left(\frac{N_{\rm e}}{N_{\rm a}}\right)_{\rm b} = \frac{k_{\rm q}}{k_{\rm ee}} \tag{5.23}$$

for these parameters. The quenching rate constant for metastable rare gas atoms was taken from Table 5. Note that in the case of high electron densities, when the electron distribution function is of the Maxwell type in the basic range of electron energies, this quantity may be represented in the form $f = f(v_0) \exp(-S)$, with S being characterized by the following expression:

$$S = \frac{\varepsilon - \Delta \varepsilon}{T_{\rm e}} = 3v_0^2 \, \frac{\varepsilon - \Delta \varepsilon}{Ma^2} \,. \tag{5.24}$$

Here, for simplicity, we assumed v(v) = const. Because of criterion (5.21), formula (5.24) shows a more smooth decrease of the distribution function with an increase in electron energy if compared to formula (5.19) which holds true in the limit when collisions between electrons are not significant.

5.3 Equilibrium between excited atoms in gases and plasmas

Above we have supposed that the quenching of excited atoms in plasma is governed by processes other than electron impact. We now consider the other case, when quenching of excited atoms is determined by electron-atom collisions. Then, based on criterion (5.21), we reveal that fast electrons are produced and destroyed as a result of inelastic collisions between electrons and atoms. Because of the equilibrium between the atomic states considered, this gives

$$v_{\rm ex} f_0(v) v^2 \, \mathrm{d}v = v_{\rm q} f_0(v') v'^2 \, \mathrm{d}v' \,.$$

Here, $v^2 = 2\Delta \epsilon/m_e + v'^2$, and v, v' are the velocities of fast and slow electrons, $v_{ex} = N_a k_{ex}$, $v_q = N_* k_q$ are the rates of excitation and quenching of atomic states by electron impact, so that N_a , N_* are the number densities of atoms in the ground and excited states, respectively, and k_{ex} , k_q are the rate constants of the corresponding processes which are connected by the principle of detailed balance (3.34b). From this follows

$$\frac{N_{\rm a}}{g_0} f_0(v) = \frac{N_*}{g_*} f_0\left(\sqrt{v^2 - v_0^2}\right), \quad v > \sqrt{\frac{2\Delta\varepsilon}{m}}.$$
 (5.25)

This relation establishes the connection between the distribution functions of slow and fast electrons. The relation can be written down in the form

$$f_0(v) = \frac{f_0(v_0) f_0(\sqrt{v^2 - v_0^2})}{f_0(0)} .$$
(5.26)

In particular, for the Maxwell distribution function of slow electrons $[f_0 \sim \exp(-\varepsilon/T_e)]$ this formula gives

$$f_0(v) = f_0(v_0) \exp\left(\frac{\varepsilon - \Delta\varepsilon}{T_e}\right), \qquad (5.27)$$

where T_e is the electron temperature, and $\varepsilon = m_e v^2/2$ is the electron energy. Thus, inelastic collisions of electrons with excited atoms restore the Maxwell electron distribution function above the threshold of atom excitation.

The above cases of atomic excitation by electrons in a plasma show that this process depends on the character of establishment of the electron distribution function near the excitation threshold. The result depends both on the rate of restoration of the electron distribution function in electron – electron or electron – atom collisions and on the character of the quenching of excited atoms. Competition between these processes yields different means of establishing the electron distribution function rates depend on the collision processes which establish the electron distribution function here atoms and plasma. Thus, the excitation rates depend on the collision processes which establish the electron distribution function between the excitation threshold, and on the equilibrium between excited atoms.

6. Electrons in metals

6.1 Metallic plasma and degenerate electron gas

Let us analyze the electric properties of condensed systems, which are created by the electrons located in them. Comparing the behavior of electrons in condensed systems with that in gases in external fields, we restrict ourselves by condensed systems where electrons may be separated as a subsystem. First and foremost, this relates to metals whose electric properties are determined by electrons interacting with each other and with the environment. Therefore, we first consider a metallic plasma from this standpoint.

The simplest model of electrons in metals assumes the electrons to be free and is often called the Drude model [121, 122]. Within the framework of this approach, we first ignore the interaction of electrons with the lattice that leads to kinetic equation (2.19) for the electron distribution function. But because of the high density of electrons in metals, at room and low temperatures the solution of equation (2.19) is not the Maxwell distribution function (2.20) because the Pauli exclusion principle is of importance. Hence, we will take this principle into consideration. Assuming the electron subsystem in this case to be a degenerate electron gas, we have the Fermi–Dirac formula for the probability $n(\varepsilon)$ of electron location in a state with a given energy ε [120]:

$$n(\varepsilon) = \frac{1}{1 + \exp\left[(\varepsilon - \mu)/T\right)},$$
(6.1)

where T is the temperature, and μ is the chemical potential for this distribution. In the limiting case of zero temperature, this distribution function becomes stepwise, and the chemical potential of this distribution tends to the Fermi energy of electrons in the limit of a zero temperature. Below we will be guided by this limit which is realized for metals at room temperature. Electrons of this metallic plasma are then transformed into a degenerate electron gas. Though this approach is crude for real metals [124], it allows us to describe their behavior in the simplest way, and this description has an analogy with that for free electrons in gases in external fields.

Formulas for a degenerate Fermi gas are contained in many textbooks [120, 123–125], and we below give the simplest ones which will be used for determining the parameters of some metallic plasmas from the standpoint of the above consideration of the electron subsystem. At zero temperature, electrons have momenta p located within the range $0 \le p \le p_F$, where p_F is the Fermi momentum that can be found from the relation

$$n = \int n(\varepsilon) \frac{2 \,\mathrm{d}\mathbf{p} \,\mathrm{d}\mathbf{r}}{\left(2\pi\hbar\right)^3} = 2 \int_{p \,\leqslant\, p_{\mathrm{F}}} \frac{\mathrm{d}\mathbf{p} \,\mathrm{d}\mathbf{r}}{\left(2\pi\hbar\right)^3} \,, \tag{6.2}$$

where *n* is the total number of electrons, the factor 2 accounts for the two directions of the electron spin, and d**p**, d**r** are the elements of the electron momentum and a plasma volume, respectively. Introducing the electron number density $N_e = n/\int d\mathbf{r}$, we obtain the maximum electron momentum p_F , or the Fermi momentum, the maximum electron energy ε_F , or the Fermi energy, for this electron distribution, and the electron velocity v_F on the surface of the Fermi sphere:

$$p_{\rm F} = (3\pi^2\hbar^3N_{\rm e})^{1/3}, \quad \varepsilon_{\rm F} = \frac{p_{\rm F}^2}{2m_{\rm e}} = \frac{(3\pi^2N_{\rm e})^{2/3}\hbar^2}{2m_{\rm e}}, \quad v_{\rm F} = \frac{p_{\rm F}}{m_{\rm e}}$$
(6.3)

The distribution of electrons for a degenerate electron gas is given by the Fermi–Dirac formula with zero temperature, and the chemical potential $\mu = \varepsilon_{\rm F}$.

A degenerate electron gas is characterized by a small parameter

$$\eta = \frac{T}{\varepsilon_{\rm F}} \,. \tag{6.4}$$

Table 7. Parameters of univalent metals at room temperature.

Metal	Li	Na	Κ	Cu	Rb	Ag	Cs	Au
Lattice type	bcc	bcc	bcc	fcc	bcc	fcc	bcc	fcc
<i>a</i> , Å	3.51	4.29	5.34	3.61	5.71	4.09	6.09	4.08
$\rho, {\rm g}{\rm cm}^{-3}$	0.534	0.97	0.89	8.96	1.53	10.5	1.93	19.3
$N_{\rm e}, 10^{22} {\rm cm}^{-3}$	4.6	2.5	1.4	8.5	11	5.9	8.7	5.9
$\epsilon_{\rm F},{\rm eV}$	4.7	3.2	2.1	7.1	1.8	5.5	1.6	5.5
$v_{\rm F},10^8~{\rm cm}~{\rm s}^{-1}$	1.3	1.0	0.86	1.6	0.79	1.4	0.74	1.4
$\eta, 10^{-3}$	5.5	8.2	13	3.7	15	4.6	17	4.6
ξ	1.8	2.2	2.7	1.4	2.9	1.6	3.1	1.6

Note: These metals consist of atoms with one valence s-electron. Here, the lattice structure is bcc (body-centered cubic) or fcc (face-centered cubic), *a* is the lattice constant, ρ is the metal density which determines the number density of electrons $N_{\rm e}$. Other parameters are given by formulas (6.3) and (6.4).

From this it follows that $r_D^2 N_e^{1/3} \ll a_0$, where r_D is the Debye– Hückel radius for this electron gas, and $a_0 = \hbar^2/(m_e e^2)$ is the Bohr radius. The values of the parameter η for univalent metals at room temperature are given in Table 7. As can be seen, the degenerate electron gas of metals refers to a quantum system.

Let us find the total energy E_0 per unit volume of a degenerate electron gas at zero temperature:

$$E_0 = \int_0^{\varepsilon_{\rm F}} \varepsilon \, \frac{2 \mathrm{d} \mathbf{p}}{(2\pi\hbar)^3} = \frac{2\sqrt{2}}{5\pi^2} \, \frac{m_{\rm e}^{3/2} \varepsilon_{\rm F}^{5/2}}{\hbar^3} \,. \tag{6.5}$$

At low temperatures, the energy of the system per unit volume is equal to

$$E = \int_0^\infty \varepsilon \, \frac{2 \mathrm{d} \mathbf{p}}{(2\pi\hbar)^3} \, \frac{1}{\exp\left[(\varepsilon - \mu)/T\right] + 1} \, ,$$

where $\varepsilon = p^2/(2m_e)$, and the chemical potential for this distribution is $\mu = \varepsilon_F$ in the zero-order approximation. Expanding this formula in a power series of a small parameter (6.4), we obtain [120]

$$E = E_0 \left(1 + \frac{5\pi^2}{4} \frac{T^2}{\varepsilon_{\rm F}^2} \right).$$
(6.6)

Thus, the addition to the electron energy at moderate temperatures is determined by a small parameter (6.4) of the theory. From this follows the expression for the heat capacity per unit volume of a degenerate electron gas at low temperatures:

$$C = \frac{dE}{dT} = \frac{5\pi^2}{2} \frac{T}{\epsilon_{\rm F}^2} E_0 = \frac{m_{\rm e}^{3/2} T \sqrt{2\epsilon_{\rm F}}}{\hbar^3} .$$
(6.7)

Notice that the heat capacity of metals is determined by the phonons and electrons. At low temperatures, formula (6.7) determines the contribution to the heat capacity of metals due to electrons, and the contribution to this quantity due to phonons is proportional to T^3 . Therefore, at low temperatures the heat capacity of metals is determined by electrons.

We consider a metallic plasma as a degenerate electron gas, taking its positive charge to be distributed uniformly over a space. The Fermi energy is the parameter of a degenerate electron gas, and just this parameter must be used for the analysis of this quantum plasma. Let us introduce the ideality parameter of the quantum plasma as the ratio of the Coulomb interaction energy of electrons to the Fermi energy:

$$\xi = \frac{e^2}{r_{\rm W}\varepsilon_{\rm F}} = \frac{2^{5/3}}{3\pi a_0 N_{\rm e}^{1/3}} = \frac{0.337}{a_0 N_{\rm e}^{1/3}}, \quad r_{\rm W} = \left(\frac{3}{4\pi N_{\rm e}}\right)^{1/3}, \quad (6.8)$$

where r_W is the Wigner-Seitz radius for the electron gas, and a_0 is the Bohr radius. The ideal degenerate electron gas has a large number density compared to the typical atomic value, i.e., $N_e a_0^3 \ge 1$. This means that the properties of a degenerate electron gas are closer to the properties of a quantum plasma, the larger the electron density. On the contrary, the role of the Coulomb interaction between charged particles of the plasma decreases with an increase in electron density.

Let us apply the model of a degenerate electron gas to electrons of metals. Table 7 lists parameters of real metallic plasmas at room temperature. Metals under consideration contain atoms with one valence electron, and we assume that just these electrons of metal atoms form a degenerate electron gas. Parameters of this gas are determined by formula (6.3). As follows from the data of Table 7 [16, 40], the parameter η is small for real univalent metals, and hence the metallic plasma is a quantum system. But the Coulomb interaction involving electrons and ions of metals is comparable to the exchange interaction potential of electrons that is determined by the Pauli exclusion principle. Thus, a metallic plasma of these elements at room temperature is a quantum system where the potential of the Coulomb interaction of charged particles and the exchange interaction potential of electrons have the same order of magnitude.

6.2 Thermal and electric properties of metals

The above results concerning the behavior of electrons in an ionized gas can be used partially for electrons of metals if we change the interaction of electrons with surrounding atomic particles by an effective mean field. In such a mean field model, the behavior of metal electrons is similar to that of plasma electrons. But in contrast to a plasma, because of a high density of electrons in metals, the electrons degenerate at room or low temperatures. Therefore, we start from the model of a degenerate electron gas for metal electrons. Within the framework of this model, in a space of electron momenta or wave vectors, electrons occupy a domain inside the Fermi sphere. The electron distribution function over energies results from formula (6.1) and has the following form at low temperatures:

$$f(\varepsilon) = \text{const} \frac{N_{\text{e}}}{1 + \exp\left[(\varepsilon - \varepsilon_{\text{F}})/T\right]},$$
(6.9)

where N_e is the number density of valence electrons, and the chemical potential of this distribution at zero temperature coincides with the Fermi energy ε_F in accordance with formula (6.3). This distribution function is normalized by the condition

$$\int f(\varepsilon) \,\mathrm{d}\mathbf{v} = N_{\mathrm{e}} \,, \tag{6.10}$$

and the small parameter $T/\varepsilon_{\rm F}$ (6.4) relates to this distribution.

Within the framework of the Drude model where valence electrons of a metal are modelled by free electrons, the electron transport coefficients are determined by formulas of Section 4. In particular, one can use formula (4.13) for the conductivity of the metallic plasma, which takes the following form under assumption that the collision rate v is independent of the electron velocity [124, 125]:

$$\Sigma = \frac{N_{\rm e}e^2\tau}{m_{\rm e}}\,,\tag{6.11}$$

where $\tau = 1/v$ is the collision time. Next, one can repeat the deduction of formulas (4.18) and (4.19) for electron thermal conductivity having regard to the distribution function (6.9) instead of the Maxwell distribution function. For the thermal conductivity coefficient of a metallic plasma, when the electron-atom collision rate v does not depend on the electron velocity, this yields

$$\kappa = \frac{\pi^2}{3} \frac{N_e \tau T}{m_e} \,. \tag{6.12}$$

In particular, the Wiedemann–Franz law follows from this consideration:

$$\frac{\kappa e^2}{\Sigma T} = \frac{\pi^2}{3} . \tag{6.13}$$

We now consider a more real model for electrons in a metal, when the electron energy distribution function is given by formula (6.9). One could expect that transition from the Maxwell distribution function of electrons to the Fermi–Dirac one, namely, the transition from the model of free electrons to the model of a degenerate electron gas, could lead to a significant change in connection between the plasma conductivity and the electron density. But it is not so. We now consider the conductivity of a degenerate electron gas, assuming it to be found in a weak electric field. We represent the electron distribution function f in a form similar to formula (2.4):

$$f=f_0+f_1\,,$$

where f_0 is the distribution function (6.9) in the absence of an electric field, and the perturbation f_1 of the distribution function is proportional to the electric field strength: $f_1 \sim F$. We write down the kinetic equation (2.1) as an expansion in a power series of a small parameter F:

$$\frac{e\mathbf{F}}{m_{\rm e}}\frac{\partial f_0}{\partial \mathbf{v}} = I_{\rm col}(f_1), \qquad (6.14)$$

where $I_{col}(f_0) = 0$ because of the equilibrium in the absence of the electric field. Using formula (2.6) for the collision integral of the asymmetric part of the distribution function, we obtain from equation (6.14) the following result:

$$f_1 = -\frac{e\mathbf{F}\tau}{m_{\rm e}}\frac{\partial f_0}{\partial \mathbf{v}}\,,\tag{6.15}$$

where $\tau = 1/v$ is the collision time, and the drift velocity of an individual electron is given by

$$\mathbf{w} = \frac{1}{N_{\rm e}} \int \mathbf{v} f_1 \, \mathrm{d} \mathbf{v} \, .$$

Metal	Li	Na	K	Cu	Rb	Ag	Cs	Au
a, À	3.51	4.29	5.34	3.61	5.71	4.09	6.09	4.08
ho, g cm ⁻³	0.534	0.971	0.862	8.96	1.53	10.5	1.87	19.3
$\Sigma, 10^{16} { m s}^{-1}$	9.7	19	12	54	7.0	57	4.4	40
κ , W (cm C) ⁻¹	0.85	1.41	1.02	4.01	0.58	4.29	0.36	3.17
$\kappa e^2/(\Sigma T)$	3.6	3.1	3.4	3.1	3.4	3.1	3.4	3.3
$cR_{\rm H}, 10^{-4} {\rm cm}^3 {\rm C}^{-1}$	-1.7	-2.5	-4.2	-0.55		-0.84	-7.8	-0.72
$N_{\rm e}, 10^{22} {\rm cm}^{-3}$	3.7(4.6)	2.5(2.5)	1.5(1.4)	11(8.5)	(1.1)	7.4(5.9)	0.80(0.87)	8.7(5.9)
$K_{\rm e},{\rm cm}^2({\rm V}~{\rm s})^{-1}$	18	52	58	34	44	53	38	32
$N_{\rm e}/N_0$	0.79	0.98	1.1	1.3		1.3	0.92	1.5
$\tau, 10^{-14} \text{ s}$	1.0	3.0	3.3	1.9	(2.6)	3.0	2.2	1.8
λ/a	38	73	54	82	36	100	26	62
$\Theta_{\rm D}, {\rm K}$	370	158	90	310	52	220	54	185
m_*/m_e	1.40	0.98	0.94	1.01	0.87	0.99	0.83	0.99

Table 8. Parameters of single valence metals at room temperature, so that the atoms of these metals have one valence s-electron, and ρ is the metal density.

From this follows that the conductivity Σ of the degenerate gas $\Sigma = i/F$, where the current density equals

 $\mathbf{i} = e\mathbf{w}N_{e}$.

This leads to formula (6.11) for the conductivity Σ of a degenerate electron gas, if we assume the collision time τ to be independent of the electron velocity v, take the integral by parts, and use the normalization condition (6.10):

$$\Sigma = \frac{N_{\rm e}e^2\tau}{m_{\rm e}}\,.\tag{6.16}$$

Formulas (6.11) and (6.16) for the conductivity of a degenerate electron gas are identical to formula (4.12) for the conductivity of a gas of free electrons, though only a small portion of the electrons of a degenerate electron gas can be scattered, since the final states of a scattered electron can be occupied by internal electrons of this distribution, whereas the final states of scattering are free for a gas of free electrons. But the fact indicated for the degenerate electron gas is compensated for by a large derivative of the distribution function in formula (6.15) that leads to the identical formulas for conductivity in these two cases.

Shortly, we will note two types of electron scattering in metals: by defects of a crystal lattice, and by phonons. If an electron moves inside a regular crystal lattice at zero temperature, it is not scattered. When atoms are displaced from their equilibrium positions due to vibrations, the regular lattice field is disturbed, and the electrons undergo scattering by phonons, with the intensity of this scattering increasing with temperature, whereas scattering by defects does not depend on the temperature. The latter mechanism usually gives a small contribution to the plasma conductivity at room temperature.

We now apply the results of this analysis to the simplest metals whose atoms have one valence s-electron. Table 8 gives the parameters of electrons for these metals whose valence atomic electrons form a degenerate electron gas [126, 127]. The electron number density N_0 was taken from Table 7 and is obtained from the metal density. Another method for

finding the electron number density which determines the metal conductivity, is guided by using the Hall coefficient $R_{\rm H}$ (4.40) whose values are collected in Table 8. In this table, the electron number density $N_{\rm e}$ was obtained from the measured values of the Hall coefficient, and the values of N_0 from Table 7 are given in parentheses. If the ratio $N_{\rm e}/N_0$ exceeds unity, this means that internal p- and d-electrons of atoms give a contribution to the metal conductivity. According to the data of Table 8 we have the following value for the parameter in formula (6.13), averaged over these metals at room temperature: $\kappa e^2/(\Sigma T) = 3.3 \pm 0.2$, while according to the Wiedemann – Franz law (6.13) for a degenerate electron gas, this ratio should be 3.3. In addition, Table 8 contains the average mobility of electrons, which follows from formula (4.11):

$$K_{\rm e} = \frac{\Sigma}{eN_{\rm e}} = C \, \frac{\Sigma}{N_{\rm e}} \,, \tag{6.17}$$

and if the mobility is expressed in cm² (V s)⁻¹, the conductivity is measured in 10¹⁶ s⁻¹, and the electron number density is expressed as 10²² cm⁻³, then the proportionality coefficient is C = 6.94. In addition to Table 8, Fig. 9, constructed on the basis of data from handbooks [126, 127] contains electric and thermal parameters of metals at room temperature. Note that the ratio following from formula (6.12) in this case is $\kappa e^2/(\Sigma T) = 3.3 \pm 0.2$ according to the statistical treatment of the data in Fig. 9.

Next, we use formula (6.11) for determining typical time τ between neighboring acts of electron scattering in the metals, and corresponding values of this quantity for metals of the first group elements of the Periodic System are given in Table 8. The mean free path of electrons in metals is defined as $\lambda = v_F \tau$, where v_F is the electron velocity on the surface of the Fermi sphere, and its values are listed in Table 7. Since the parameter λ/a is large, with *a* being the lattice constant (see Table 8), one can consider the lattice to be transparent for electrons. Notice that the Debye temperatures Θ_D of the metals under consideration (see Table 8, and Fig. 9) are compared with room temperature, which allows us to consider lattice atoms as being classical in processes of electron scattering by these atoms.

Metals at room temperature																				
D · 1	Group														Ratio o	of the electr	on mean			
Period	Ι			II	I	II	IV			V	1	VI	VII		VIII		free pa	th to		
	52 • L i	0.534	97 • Be	1.85												/	the W1	gner – Seitz	radius	
2	Lithium	0.85	Berylliu	m 2.0										Symbo	1 82	19	.3—Densit	y, g cm ⁻³		
3	120 11 Na Sodium	0.97 19 1.4	120 12 Mg Magnes	1.74 21 ium 1.6	2.70 34 2.4	170 13 Al Aluminum							Atomic	e number Elemen	t Tungst	ien 1	17 Condu .7 Therm condu	uctivity, 10 ¹ ual ctivity, W c	$^{6} s^{-1} cm^{-1} K^{-1}$	
	100 19 K Potassium	0.89 12 1.0	180 20 Ca Calcium	1.54 27 2.0	9 21 Sc Scandium	2.99 1.6 0.16	17 22 Ti Titanium	4.51 2.1 0.22	21 23 V Vanadiun	6.0 4.6 n 0.31	44 24 Cr Chromiun	7.15 7.0 m 0.94	3 25 Mn Manganese	7.3 0.6 0.078	22 26 Fe Iron	7.87 9.4 0.80	60 27 C0 Cobalt	8.86 14 1.0	60 28 Ni Nickel	8.90 14 0.91
4	8.96 54 4.0	240 29 Cu Copper	7.14 15 1.2	72 30 Zn Zinc	5.91 5.2 0.41	27 31 Ga Gallium														
	170 37 Rb Rubidium	1.53 7.0 0.58	50 38 Sr Strontiu	2.64 6.9 m 0.35	9 39 Y Yttrium	4.47 1.5 0.17	$20 \\ 40 \mathbf{Zr} \\ \text{Zirconium}$	6.52 2.1 0.23	36 41 Nb Niobium	8.57 7.2 0.54	82 42 Mo Molybder	10.2 17 num 1.4	28 43 Tc Technecium	11 6 0.51	56 44 Ru Ruthenium	12.1 12 1.2	97 45 Rh Rhodium	12.4 20 1.5 H	40 46 Pd Palladium	12.0 8.5 0.72
5	10.5 57 4.3	280 47 Ag Silver	8.69 17 0.97	280 48 Cd Cadmium	7.31 11 0.82	63 49 In Indium	7.26 8.2 0.67	47 50 Sn Tin	6.68 23 0.24	140 51 Sb Antimony										
6	41 55 Cs Cesium	1.93 4.4 0.36	120 56 Ba Barium	3.62 3.3 0.18	10 57 La Lanthanu	6.15 1.5 um 0.13	15 72 Hf Hafnium	13.3 2.7 0.23	35 73 Ta Tantalum	16.4 6.9 0.58	82 74 W Tungsten	19.3 17 1.7	20 75 Re Rhenium	20.8 4.3 0.48	44 76 Os Osmium	22.6 9.5 0.88	79 77 Ir Iridium	22.5 17 1.5 H	40 78 Pt Platinum	21.5 8.5 0.72
0	19.3 40 3.2	200 79 Au Gold	13.5 0.94 0.083	5 80 Hg Mercury	11.8 5.0 0.46	29 ₈₁ Tl Thallium	11.3 4.4 0.35	26 82 Pb Lead	9.79 0.78 0.079	5 83 Bi Bismuth	9.20 2 0.2	13 ₈₄ Po Polonium								

Figure 9. Thermal and electric parameters of solids of pure elements with a metallic conductivity at room temperature [126, 127].

6.3 Character of electron transport in metals

Considering the behavior of electrons in metals within the context of the problem of electron drift in gases in external fields, we compare the description of electron transport in gases and metals. In this respect we find an analogy between the qualitative descriptions of electron drift in gases and metals, though the energy distribution function of free electrons in gases differs, in principle, from the Fermi-Dirac distribution function in the model of a degenerate electron gas relevant to metal electrons. Moreover, the model of a degenerate electron gas, whose electrons are located inside the Fermi sphere in a space of electron wave vectors at zero temperature, is crude for electrons in metals (see, for example, Refs [124, 128]), because it does not take into account the interaction of electrons with the lattice. In particular, if the Fermi surface at zero temperature intersects the boundary of the Brillouin zone, the Fermi surface becomes open, and electrons can pass freely to neighboring Brillouin zones. This leads to a specific character of the electron conductivity at low temperatures and cannot be taken into account by the simple models under consideration. But because our aim is to ascertain the possibility of employing the theory of electron transport in gases for a qualitative description of electron drift in condensed systems, we leave aside the special effects of electron behavior in metals.

Starting from a metallic crystal at zero temperature, we take into account the interaction between an electron and crystalline lattice on average by introducing the effective electron mass m_* instead of the free electron mass m_e , thus we reduce the problem of electron drift in the periodical lattice field to the motion of a free quasi-electron. There are two types of scattering when electron moves inside a metal. In the first one, the electron scattering proceeds from defects of the lattice and this mechanism is similar to elastic scattering of electrons by atoms if they move in a gas. The second type of electron scattering is due to atomic vibrations and proceeds owing to crystal inhomogeneities which result from the displacement of atoms from equilibrium positions. This character of electron scattering is similar to that of free electrons in a plasma, when electrons are scattered by charged particles of the plasma due to the Coulomb interaction, and scattering through small angles gives the main contribution to the mobility of an individual electron. Thus, we see an analogy between the electron drift in metals and that in a gas and plasma.

We will point out one more peculiarity of electron drift in metals. In the first approximation we ignore electron scattering, so that the electron subsystem can be considered as an isolated system in this approximation. Of course, the properties of the electron subsystem are governed by its interaction with the lattice that results in a specific form of the Fermi surface for electrons of a given metal. But this interaction can be taken into account on average, for all the electron subsystem as a degenerate electron gas located in a certain mean field. Electron collisions with the lattice distort this picture, but we consider the electrons in a metal to be large in comparison to the lattice constant or to the Wigner–Seitz radius r_W for electrons, which is defined as

$$r_{\rm W} = \left(\frac{3}{4\pi N_{\rm e}}\right)^{1/3} \tag{6.18}$$

and characterizes the size of the area occupied by one electron. Figure 9 contains the ratio λ/r_W , where the mean free path of electrons in metals is taken from formula (6.16) and is connected with a typical collision time τ for an individual electron through the formula

$$au = rac{\lambda}{v_{
m F}}$$

Here, v_F is the Fermi velocity for electrons, which is given by formula (6.3), and the electron subsystem is considered as a degenerate electron gas. Next, for simplicity we assumed in Fig. 9 that one valence electron relates to one metallic atom.

Note that the large ratio $\lambda/r_{\rm W}$ can be considered as the definition of metals where electrons may be separated as an individual subsystem. In this definition of a metal, we do not concretize specific properties of the total system, and hence one can consider from this standpoint both crystals and liquids, as well as amorphous metals. Within the context of this consideration, the lattice periodicity is not of basic importance for metals, and thus it does not influence significantly their conductivity. Indeed, though the conductivity of metals usually has a jump at the melting point, the metal conductivities for the solid and liquid phases do not differ in principle. Thus, summing up the above analysis, we conclude that the electron drift in metals is analogous to that in a gas and plasma. By definition, metals have a high conductivity, so that the mean free path of electrons is much larger than the typical size per atom in a metal. Correspondingly, the above theory of electron transport in a gas or plasma can be used successfully for a semiquantitative description of electron transport processes in metals.

7. Excess electrons in solids and liquids

7.1 Drift of excess electrons in condensed systems

It is customary to divide condensed systems of bound atoms into metals and dielectrics depending on the character of the electron levels and bands in these systems. If we are compressing a gas of atoms, transforming it into a condensed system, electron energy levels of individual atoms are transformed into energetic bands, and the upper occupied band is filled completely for dielectrics. Since the following free band is separated from this filled band by a gap, a certain energy is required for exciting an electron to another state. On the contrary, the upper electron band of metals is filled partially, and valence electrons can change their states by small changes of energy. In particular, if a metal is found in an external electric field, those states of individual electrons are preferable that are connected with their motion along the field. This effect determines the conductivity of a metallic plasma and is absent in dielectrics.

We now consider the case when an excess electron is inserted into a condensed system. This electron occupies an empty energetic band, so that the behavior of such individual electrons is identical, in principle, for metals and dielectrics. But in contrast to a gas system, where electron scattering proceeds independently of the position of other atoms, in a dense or condensed system of atoms a test electron interacts simultaneously with electrons of many atoms. Then, the system of interacting atoms can be considered as a whole electron system in which a test electron moves.

One can analyze the behavior of an individual electron in a condensed matter by introducing an effective potential energy



Figure 10. The character of motion of an excess slow electron in a condensed system of atoms depending on the position of the ground-state electron energy level: (a) dielectric type of mobility; (b) metallic type of mobility.

for motion of a test electron in a condensed system of atoms. Then two types of electron motion in a condensed system are possible in accordance with Fig. 10. In the first case (Fig. 10a), the electron is locked in a space between two neighboring atoms, and its transfer to a neighboring position requires it to overcome a barrier and lasts relatively long. This is a dielectric type of electron drift. In the second case of a metallic type of electron drift, the electron moves almost freely inside the condensed system (Fig. 10b). Note that these types of electron drift do not depend on the type of condensed system. In particular, we will show below that the drift of an excess electron in condensed rare gases has a metallic nature in a certain range of parameters.

Thus, in considering the drift of an excess electron in dielectrics [129–134], we observe two limiting cases in electron behavior. In the first case (Fig. 10a), the electron is displaced in jumps, and its mobility is relatively small, while in the second case the electron moves almost freely, thus imply its meaning that free path is relatively large. Of course, in this case of metallic mobility of a test electron in a dielectric, we account for the interaction between the electron and the environment, but it is taken into account on the average, through an effective field. Then, we introduce the energy V_0 of the ground state of an electron in this system as the solution of the Schrödinger equation for the electron wave function ψ_{α} :

$$-\frac{\hbar^2}{2m_{\rm e}}\Delta\psi_{\rm e} + V\psi_{\rm e} = V_0\psi_{\rm e}\,,\tag{7.1}$$

where the effective potential energy V corresponds to interaction of a test electron with other electrons and electrons of surrounding atoms. This interaction potential depends on the positions of nuclei. Assuming that the nuclei form a crystal lattice, we obtain the periodicity of the effective interaction potential. The eigenvalues of equation (7.1) may be represented then in the form [124, 125]

$$\varepsilon_{\mathbf{k}} = V_0 + \frac{\hbar^2 k^2}{2m_*} \,, \tag{7.2}$$

where m_* is the effective electron mass, and k is the electron wave vector. Parameters of electron-lattice interaction were included in the quantities V_0, m_* . These quantities characterize the drift of electrons in condensed systems if we treat this problem on the basis of the model of free electrons, and the interaction of an excess electron with the environment is



Figure 11. The ground state energy of an excess electron moving in a gas in an external electric field with respect to a vacuum as a function of the atomic number density: (a) argon [138]; (b) xenon [135].

taken into account in these quantities. In such a consideration there is no difference between crystals and liquids because their interaction with the electron is introduced in the above quantities. But, being restricted by the case of metallic conductivity of an excess electron, we are based on the criterion that the electron mean free path is large compared to the distance between neighboring atoms.

Table 9. Drift parameters of an excess electron in liquid rare gases.

Parameter	Ar	Kr	Xe
<i>V</i> ₀ , eV [135–138]	-0.3	-0.5	-0.8
$N_0, 10^{22} \mathrm{cm}^{-3}$	1.1	1.2	1.1
$T_{\rm max}, {\rm K}$	155	170	223
$N_{\rm max}, 10^{22} {\rm cm}^{-3}$	1.2	1.4	1.2
$a_{\rm max}$, A	4.9	4.7	4.9
$K_{\rm max}, {\rm cm}^2({\rm V}{\rm s})^{-1}$ [139]	1800	4600	6000
$T_{\rm tr}, { m K}$	85	117	163
$N_{\rm tr},10^{22}{\rm cm}^{-3}$	2.1	1.8	1.4
$a_{\rm tr}$, A	4.1	4.3	4.7
$K_{\rm tr}, {\rm cm}^2({\rm V}{\rm s})^{-1}[139-147]$	500 ± 70	1400 ± 300	2000 ± 700
$m_*/m_{\rm e}$ [148, 149]	0.55	0.4	0.3
<i>τ</i> ₁ , ns [150]	0.9	4.4	6.5
$\tau_{\rm s}$, ns [150]	0.5	2.2	4.4

7.2 Experimental study of the mobility

of an excess electron in condensed inert gases

We will be guided below by condensed rare gases Ar, Kr, and Xe, where both the dielectric and metallic types of mobility can be realized under different conditions. Figure 11 displays the ground-state electron energy V_0 in condensed argon [138] and xenon [135] as a function of the number density of atoms.



Figure 12. The dependence of the reduced mobility *KN* of an excess electron on the number density of xenon atoms at the temperature T = 236 K. Triangles refer to the zero-field mobility, circles relate to the maximum mobility at this number density of atoms, and squares correspond to the electric field strength F = 30 V cm⁻¹ [67].



Figure 13. The dependence on the reduced electric field strength for the reduced mobility of an excess electron in liquid argon at some temperatures and number densities of atoms [143] (the temperature *T* is expressed in kelvins, the number density *N* of atoms in 10^{22} cm⁻³): I - T = 288 K, N = 0.68; 2 - T = 278 K, N = 0.86; 3 - T = 216 K, N = 1.23; 4 - T = 163 K, N = 1.41.



Figure 14. The zero-field mobility of an excess electron in liquid argon and xenon against the number density of atoms at a constant pressure in argon [143] (a) and in xenon [135] (b).

Note that the quantity V_0 does not characterize the electron behavior inside the condensed system because it is measured with respect to a vacuum, i.e. V_0 is the difference between electron energies outside and inside this bulk system. In reality, electrons can form a layer on the boundary of a bulk condensed rare gas, and such a charged layer equalizes the potential on both sides of the interface. It should be emphasized that the ground-state energy V_0 of an excess electron in condensed argon, krypton, and xenon passes a minimum at the densities of atoms which are close to those related to the maximum of the electron mobility (see Fig. 11, and Table 9). Table 9 also contains the number densities N_0 of atoms for liquid rare gases, corresponding to the minimum of the ground-state electron energy V_0 . The atomic number density N_{max} , the temperature T_{max} , and the distance a_{max} between nearest neighbors relate to the maximum of the zerofield mobility of an excess electron in liquid rare gases. Next, $T_{\rm tr}$ and $N_{\rm tr}$ are the temperature and number density of atoms at the triple point, and $K_{\rm tr}$ is the electron mobility at the triple point. In addition, τ_1 and τ_s are the relaxation times for an excess electron in liquid and solid rare gases near the triple point. These times characterize thermalization of electrons excited by a pulsed electric signal, and the accuracy of these values is estimated as 10-20%.



Figure 15. The zero-field mobility of an excess electron in liquid argon versus the temperature at a pressure of 55 atm (a), and different pressures near the mobility maximum (b) [143].

Measurements of the reduced mobility of an excess electron in condensed rare gases show a strong variation of this quantity depending on the rare gas parameters and electric field strength. For example, Fig. 12 gives the reduced mobility of an excess electron in xenon [67], and this quantity varies within the limits of three orders of magnitude under variation of the number density of xenon atoms from the gaseous to condensed-phase values. In Fig. 13 is shown the dependence on the reduced electric field strength for the reduced mobility of an excess electron in liquid argon under different conditions [143]. It can be seen that the form of this dependence and the values of the reduced mobility are different at low electric field strengths, whereas in strong fields the mobility of an excess electron is not sensitive to the parameters of condensed argon. Figure 14 shows the dependence of the zero-field mobility on the number density of atoms in liquid argon [143] and xenon [135]. The temperature dependence for the zero-field electron mobility in condensed argon is given in Fig. 15 [143]. The above information shows that the mobility of an excess electron in condensed rare gases strongly depends on the number density of atoms, temperature, and pressure, especially in relation to low electric fields. Note also the correlation between the densities corresponding to the minimum of the ground-state electron energy V_0 and the maximum of the zero-field mobility of an excess electron as it follows from the data of Table 9 and Figs 11, 14.

At high field strengths, the electron motion in liquid rare gases resembles that in gases. As follows from Fig. 13, the reduced mobility of an excess electron as a function of the reduced electric field strength does not depend strongly on the number density of atoms and temperature. This can be explained by a small cross section of electron scattering by an individual center that makes this process similar to electron scattering in gases.

One more peculiarity of the excess-electron mobility in condensed rare gases relates to the 'saturation' of the electron drift velocity at some fields. Above (see Fig. 3) we considered



Figure 16. The dependence of the drift velocity of an excess electron on the electric field strength in liquid krypton [139, 142] (the temperature *T* is measured in kelvins, the number density *N* of atoms in 10^{22} cm⁻³): \bigcirc T = 170 K, N = 1.41; $\Box - T = 145$ K, N = 1.59; $\blacktriangle - T = 192$ K, N = 1.20; $\bigtriangledown - T = 117$ K, N = 1.76; $\blacktriangledown - T = 206$ K, N = 0.95, and $\blacksquare - T = 200$ K, N = 1.08.

this effect for gases and explained it by a strong variation of the cross section of electron-atom collisions in a narrow range of collision energies. This effect is more strong for condensed rare gases than for gases. In particular, for liquid xenon near the triple point, the excess-electron drift velocity increases only 2-3 times [from $(1-1.5) \times 10^5$ cm s⁻¹ up to $(3-4) \times 10^5$ cm s⁻¹] [142, 145, 147, 150, 151] if the electric field strength increases by three orders of magnitude $(10^2-10^5$ V cm⁻¹). In this range of fields, the characteristic electron energy increases by approximately two orders of magnitude (0.1-10 eV) [147, 152–154]. In addition, this effect depends on the parameters of the liquid (Fig. 16) [139, 142]. The saturation effect is also observed for solid rare gases (see, for example, Refs [133, 151, 155]), although the range of fields is narrower than in the case of a liquid.

Thus, though condensed rare gases are dielectrics, the drift of excess electrons in them is similar to that in metals. It is of interest to compare the mobility of excess electrons in liquid rare gases and metals if the parameters of condensed rare gases correspond to the maximum excesselectron mobility. Comparing the electron mobilities for alkali and coin metals, which are given in Table 8, with the data in Table 9, one can see that the maximum zero-field electron mobilities in liquid rare gases exceed the electron mobilities in metals by at least several times. This means that the mean free path of electrons in condensed rare gases under optimal conditions exceeds by several times the mean free path of electrons in alkali and coin metals at room temperature. Thus, the condensed rare gases can have metallic properties with regard to the drift of excess electrons.

7.3 Character of the mobility of an excess electron in condensed rare gases

The theory of the mobility of an excess electron in condensed rare gases [66, 154, 156-158] relates to a range of parameters where the electron mobility is relatively large and interaction between an excess electron and surrounding atoms is weak. Under such conditions, an excess electron has a metallic mobility, and the condensed rare gas is fairly transparent for its motion. In other words, the mean free path of an excess electron is large compared to the distance between neighboring atoms. The weakness of this interaction allows one to describe electron scattering in terms of formfactors, but because the electron scattering is determined by the exchange interaction with surrounding atoms, the formfactors for electron and neutron scattering in condensed rare gases are different, except maybe of high electron energies. This restricts the possibilities of the theoretical analysis of this problem.

Providing the theoretical description of the mobility of an excess electron in condensed rare gases within the framework of the perturbation theory by use of the formfactor, an electron motion in condensed matter is compared with electron scattering by individual atoms. Then, an increase in the electron mobility over some range of parameters ensures from the Ramsauer effect for electron scattering by many atoms. But the use of the theory of electron scattering by an individual atom for description of electron motion in a condensed system of atoms is not correct for the following reasons. First, the Ramsauer effect results from the correlation between a short-range exchange electron – atom interaction and the long-range polarization interaction between them (see Section 3). But the polarization interaction occurs at large electron-atom separations, and because of a simultaneous interaction of an electron with many atoms in a condensed matter, it has another nature in the case of condensed systems. This peculiarity can be taken into account as a collective effect which, in particular, creates the permittivity of the condensed system of atoms, but the total electron interaction is not a sum of electron interactions with individual atoms. Hence, an increase in the excess-electron mobility in condensed rare gases over some range of parameters does not have a direct analogy with the Ramsauer effect.

Second, restricting ourselves to a short-range electron – atom interaction, we have that electron scattering by an

individual atom proceeds at electron – atom separations of the order of the scattering length which is compared with the distance between nearest atoms for condensed atomic systems. Hence, electron scattering in condensed rare gases cannot be resolved into components of electron scattering by individual atoms, and the concept of electron scattering by an individual atom cannot be used for a strict theory of excesselectron mobility in condensed systems. Therefore, though it is convenient to explain observed high mobilities of excess electrons in condensed rare gases on the basis of the Ramsauer effect [140, 167-169], these phenomena are different in their nature. Correspondingly, the theoretical description of the mobility of an excess electron in liquid or solid rare gases on the basis of an electron interaction with an individual atom is not correct.

Keeping to the general scheme of this paper, we use a gaseous model for the drift of an excess electron in a condensed system of atoms, and this model holds true in the case of high electron mobilities. Within the framework of this model, we consider the electron motion in a gas of scattering centers, so that each scattering center is located on a corresponding nucleus, and the cross section of electron scattering by an individual center is small compared with the cross section of an individual atom. Then the electron mean free path is large compared to the distance between neighboring atoms, and we will use this model below. It is assumed that a test electron is scattered by individual centers independently, and each scattering center is modelled with a hard sphere. Parameters of this gaseous model for certain densities and temperatures of condensed rare gases, as well as for particular electric field strengths, can be found from experimental data, whereas the theory does not describe them strictly and reliably on the basis of the parameters of electron-atom scattering.

As a matter of fact, the gaseous model proceeds from the analogy between electron drift in gases and condensed systems, and we use this analogy throughout this paper. Assuming the electron mean free path to be independent of the electron velocity, we use formula (2.32) for the electron drift velocity, replacing the electron mass in this formula by the effective electron mass from Table 9. From this formula we find the effective cross section σ for the process of electron scattering by an individual center. Table 9 contains the distance a_{max} between nearest neighbors at the number density of atoms $N_{\text{max}} = \sqrt{2}/a_{\text{max}}^3$ at which the electron mobility passes its maximum, and the mean free path $\lambda_{\rm max} = 1/(N_{\rm max}\sigma_{\rm max})$ under these conditions. In the same way we find the mean free path of an excess electron in liquid rare gases near the triple point on the basis of data of Table 9. The resultant values are collected in Table 10, and as follows from this table, $\lambda_{\text{max}} \gg a_{\text{max}}$ and $\lambda_{\text{tr}} \gg a_{\text{tr}}$, namely, this dense atomic matter becomes transparent enough for electrons. Correspondingly, we have under these conditions $\sigma_{\max} \ll \pi a_{\max}^2$, and $\sigma_{tr} \ll \pi a_{tr}^2$. Moreover, the zero-field mobility of an excess electron in condensed rare gases under such conditions can exceed that in metals (compare the mobilities from Tables 8 and 9). Note that the transparence of condensed rare gases for excess electrons takes place only within a certain range of parameters. Table 10 also contains times τ_{ε} of thermalization of electrons in liquid rare gases near the triple point, which were evaluated on the basis of formula (2.27b) using the electron mean free paths from Table 10. Comparing them with experimental values τ_1 presented in Table 9, one can see that calculated values are several times

Gas	Ar	Kr	Xe
$\pi a_{\max}^2, a_0^2$	21	19	21
$\pi a_{\mathrm{tr}}^2, a_0^2$	14	16	19
$\lambda_{\rm max}, 10^{-6}~{\rm cm}$	9,6	21	24
$\lambda_{\rm max}/a_{\rm max}$	200	450	480
$\sigma_{\rm max}/\pi a_{\rm max}^2$	0.004	0.002	0.002
$\lambda_{\mathrm{tr}}, 10^{-6}~\mathrm{cm}$	2.6	6.3	7.8
$\lambda_{ m tr}/a_{ m tr}$	65	150	170
$\sigma_{\rm tr}/\pi a_{\rm tr}^2$	0.012	0.005	0.005
τ_{ε} , ns	5.0	22	36

 Table 10. Drift parameters of the gaseous model for an excess electron in liquid rare gases.

greater. Evidently, this is due to a difference in the energy exchange during elastic electron collisions with free and bound atoms.

Let us turn to the role of correlation if an electron interacts with several atoms at short-distances between interacting particles. We first consider an electron interaction with a diatomic molecule, when an electron can form a bound state with each atom, and the region of interaction with each atomic particle is relatively small. Characterizing an electron short-range interaction with each atom by negative scattering lengths L_1 and L_2 , we find that the electron scattering length on this diatomic molecule becomes zero at the distance Rbetween the atoms which is given by [159]

$$R = \sqrt{L_1 L_2} . \tag{7.3}$$

The general nature of this interaction is conserved, when atoms have a certain size [160]. Thus, the correlation in electron scattering by individual atoms is also of importance for electron-molecule scattering [161-163]. Parameters of a short-range electron interaction with individual atoms, as well as the structure of the total atomic system produced, determine the electron behavior in a chain molecule formed by individual atoms [163-166]. Thus, the correlation between the positions of individual atoms and the parameters of a short-range interaction potential of an electron with an individual atom governs the character of electron interaction with this atomic system. This correlation is of importance for the mobility of an excess electron in condensed rare gases, but the parameters of the resultant interaction cannot be expressed strictly through the interaction parameters of an electron and an individual atom.

Analyzing from this position the behavior of an excess electron inside liquid or solid systems of bound and weakly interacting atoms and restricting ourselves with a short-range interaction of an electron with each atom, we will represent the total interaction potential for an electron as the sum of the Fermi potentials [51-53] [see also formula (3.6)]:

$$U(\mathbf{r}) = \sum_{j} \frac{2\pi\hbar^2}{m_{\rm e}} L\delta(\mathbf{r} - \mathbf{R}_j), \qquad (7.4)$$

where L is the electron scattering length by an individual atom, **r** is the electron coordinate, and \mathbf{R}_j is the coordinate of the *j*th atom. From this it follows that the average interaction potential $V_0 = \overline{U(\mathbf{r})}$ of an electron with atoms varies monotonically with an increase in atomic density, while according to the data of Fig. 11, $V_0(N)$ has a minimum in a range of atomic number densities N, where the electron mobility has a maximum. This means the existence of an additional correlation in electron-atom interaction, which is of importance for the behavior of this electron inside the atomic system and depends on the number density of atoms. Next, according to the above assumption, the correlation effects leading to a high mobility of an excess electron are determined by the electron-atom scattering length L. One can then expect that a strong correlation takes place at number densities of atoms $N \sim 1/L^3$. But, in spite of the difference in the scattering lengths for Ar, Kr, and Xe, the maximum electron mobility for these condensed systems is observed at close concentrations of atoms. This testifies that the above simple scheme of correlation, when the electron mobility in a condensed rare gas is expressed through the parameters of electron-atom scattering, is not valid.

Let us turn to the character of electron influence on a condensed rare gas if an excess electron is moving inside it. In the case of a strong interaction with surrounding atoms, an electron can form a bubble by repulsion of atoms from the region around it [131, 133]. This takes place in helium and neon. If the bubble is conserved during electron motion, an electron has a high effective mass which is comparable to the atomic mass. In the case of other rare gases (Ar, Kr, and Xe), an electron creates a fluctuation in the region where it is located due to interaction with surrounding atoms [132]. Because of a high thermal electron velocity compared to the speed of sound in a condensed rare gas, this fluctuation exists in a region whose size is comparable to the mean free path λ of the electron. Let us estimate an additional pressure p which is created by an electron inside a rare gas due to electron scattering from atoms. Because of the random character of electron motion, this pressure is estimated as

$$p \sim \frac{f}{4\pi\lambda^2} \,, \tag{7.5}$$

where we assumed an electron to be locked in a region of size λ . The force *f* produced by an individual electron with a momentum $P = m_e v$ (*v* is the electron velocity) equals

$$f = \frac{\mathrm{d}P}{\mathrm{d}t} \sim \frac{m_{\mathrm{e}}v}{\lambda/v} \sim \frac{\varepsilon}{\lambda^3} , \qquad (7.6)$$

where ε is the electron energy. Hence, an additional pressure owing to electron motion inside a condensed rare gas is given by

$$p \sim \frac{\varepsilon}{4\pi\lambda^3} \,. \tag{7.7}$$

This effect is weak for a normal gas because of the high mean free path of the electron, but it can be remarkable for condensed rare gases. For example, let us take xenon under conditions of saturation of the electron drift velocity in it. We take $\varepsilon \sim 1$ eV, $\lambda \sim 10^{-7}$ cm, so that on the basis of formula (7.7) it is inferred that an additional pressure $p \sim 1$ atm, i.e., this effect may be noteworthy under real conditions. Note that this effect exists until the electron drift velocity is less than the speed of sound in this rare gas. The fluctuation considered facilitates an electron motion, namely, it increases the electron mobility. If this fluctuation disappears, the electron drift velocity decreases. Therefore, this effect of formation of the density fluctuation in a condensed rare gas due to electron scattering by atoms inside the rare gas can be an additional reason for the saturation effect concerning the electron drift velocity. This effect is added to a sharp velocity dependence of the scattering cross section of an electron by an individual center, as it takes place in gases.

The character of electron behavior in condensed systems, which is being considered, is realized for the metallic electron mobility, if interaction between an excess electron and atomic system is weak. Then the gaseous model is suitable for the description of electron behavior. Assuming the electron to be scattered by each atom with a small effective cross section σ , one can apply the gaseous model to electron mobility in condensed rare gases.

7.4 Emission of condensed rare gases under the action of drifting electrons

An atomic excitation inside condensed rare gases represents the simplest form of excitons in solids and liquids [170]. The basis of excitons in condensed rare gases is formed by excited atomic states, when a valence electron from the outer p-shell is transferred to the lowest free s-shell. But because of a strong interaction with the environment, an excited atom forms inside a condensed rare gas an excited diatomic molecule, and the emission spectrum of such molecules in condensed rare gases is a broadened spectrum of radiation of isolated molecules, as is demonstrated by Fig. 17. Excimer molecules emit radiation in the vacuum ultraviolet spectral range, and in condensed rare gases the radiation wavelengths are shifted to the red side in comparison with isolated excimer molecules due to the interaction with surrounding atoms.

Note that there exist two types of electron excitation depending on the total spin of an excited electron and a core. Because their total spin is zero for the ground state, the radiative lifetime of an exciton with total spin one exceeds



Figure 17. Emission spectra of condensed argon $(N = 1.1 \times 10^{22} \text{ cm}^{-3})$, krypton $(N = 1.2 \times 10^{22} \text{ cm}^{-3})$, and xenon $(N = 1.3 \times 10^{22} \text{ cm}^{-3})$: (a) for fast $({}^{1}\Sigma_{u}^{+} \rightarrow {}^{1}\Sigma_{g}^{+})$, and (b) slow $({}^{3}\Sigma_{u}^{+} \rightarrow {}^{1}\Sigma_{g}^{+})$ transitions. The absorption spectrum centers are at photon energies 11.480, 9.611 and 8.046 eV for argon, krypton and xenon, respectively [171].

Table 11. The radiative	e lifetimes fo	or excited	rare gas	atoms	(ns)	1.
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	Ar	Kr	Xe		
Gas	$\begin{array}{c} 3200 \pm 400 \\ (4.3 \pm 0.1) \dagger \end{array}$	$\begin{array}{c} 280 \pm 30 \\ (4.1 \pm 0.9) \end{array}$	$\begin{array}{c} 110 \pm 20 \\ (5.2 \pm 0.6) \end{array}$		
Liquid	$\begin{array}{c} 1300 \pm 200 \\ (5.2 \pm 0.9) \end{array}$	$90 \pm 10 \ (1.8 \pm 0.3)$	24 ± 5 (2.6 \pm 1.2)		
Solid	$\begin{array}{c} 1200 \pm 100 \\ (3.0 \pm 0.9) \end{array}$	$\begin{array}{c} 81\pm8\\ (1.3\pm0.1) \end{array}$	21 ± 4 (1.8 \pm 0.8)		
[†] The lifetimes are given for the molecular transitions $({}^{3}\Sigma_{u}^{+} \rightarrow {}^{1}\Sigma_{g}^{+})$ and $({}^{1}\Sigma_{u}^{+} \rightarrow {}^{1}\Sigma_{g}^{+})$ (in parentheses); they were obtained on the basis of data from Ref [171]					

significantly the radiative lifetime of an exciton with zero total spin, and in this way the emitted radiation is resolved into a slow and fast one, as is shown in Fig. 17, though the radiation spectra are close in these cases. In addition, Table 11 contains the radiative lifetimes for upper electronic states of molecular transitions in gases, liquids, and solids [171]. The radiative lifetimes for slow transitions are given in this table, and the lifetimes of fast transitions are contained in parentheses. One can see a tendency towards an increase in the transition rate with an increasing atomic density in the course of transfer from the gaseous state to the liquid and solid states, especially for slow radiative transitions.

The process of formation of excitons in condensed rare gases as a result of electron impact is similar to that in gases, and, as follows from Fig. 8, the efficiency of this process can be remarkable if the ratio of the average electron energy to the excitation energy is not very small. For example, according to Ref. [172] the efficiency of generation of the ultraviolet photons as a result of irradiation of a reflective photocathode is 10%, 17% and 31% for liquid argon, krypton and xenon, respectively. Condensed rare gases with excess electrons located in an external electric field may be a source of laser radiation [173, 174]. As a demonstration of this, emission of a broad line with a central wavelength of 175 nm was observed in liquid xenon [175] where electrons drift from a cold field-emission cathode into a strong electric field.

Note one more excitation process which can proceed in this case and is specified by the scheme [176]

$$\mathbf{e} + \mathbf{Rg} \to (\mathbf{Rg}^{-})^{**}, \tag{7.8}$$

where Rg is a rare gas atom. The autoionization state formed decays promptly (~ $10^{-14} - 10^{-13}$ s) with the production of a fast electron or as a result of emission of a UV photon during a time ~ $10^{-9} - 10^{-8}$ s, so that the probability of photon emission during decay of the autoionization state is relatively small. But this process may be repeated, and the process of photon emission through the channel (7.8) can be valuable. Note that the excitation energy of the autoionization states $(Rg^-)^{**}$ is lower than the excitation energy of Rg^{*}, as is the case for the excitation energy of the autoionization state ($Rg_2^-)^{**}$ in comparison with Rg_2^* . This difference can be estimated from the excitation energy of the autoionization state H($2s^2$) [176]. If the channel (7.8) is realized, the radiation spectrum is shifted to longer wavelengths [177].

8. Conclusion

The theory intended for describing the behavior of electrons in a gas and plasma in external fields uses a small parameter which is the ratio between the electron and atomic masses. The theory is based on solution of the Boltzmann kinetic equation for electrons whose velocity distribution function is almost isotropic. This approach allows us to analyze a variety of equilibrium regimes or evolution of the electron subsystem under various conditions using real dependences on the collision energy for the cross sections and rate constants of elementary processes in gases and plasmas involving electrons. This gives the possibility to analyze various aspects of the problem under real conditions. The simplicity and clearness of the theoretical methods and results for electron drift in gases and plasmas makes them useful for the analysis of electron drift in condensed systems, if the mean free path of electrons is relatively large as compared with the atomic scale. 425. The modeling of electron drift processes in condensed systems on the basis of gaseous concepts is convenient and holds much $\frac{100}{27}$ 27. promise.

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