Phenomena in gases and plasmas with negative ions

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This review is devoted to the phenomena induced by negative ion processes in weakly ionized gases and plasmas. It briefly describes the electron attachment and detachment processes. The consideration focuses on the salient features of charged particle transport in electronegative gases. New types of instability and wave modes in plasmas with negative ions are discussed. Relevance of the negative-ion processes to modern technologies is indicated with emphasis on the ecological aspects and environmental applications.

1. INTRODUCTION

Electrons, positive ions and neutral particles constitute the bulk of ordinary ionized gases or plasmas. Ionization of an electronegative gas can also produce new charged species—negative ions possessing individual properties. They are much heavier than electrons and unlike positive ions they can easily detach electrons under the impact of irradiation, in collisions with other particles, etc. This is due to the relatively weak coupling of the outer electron with the neutral core in the ion, which results in the low electron affinity (~ 1 eV) for atoms and molecules. There are many cases where negative ions play an important role.

Ambient air is an electronegative gas. Electronegative gases are of great importance in many areas of technology. Therefore, the past few decades have seen numerous experimental and theoretical studies of negative ion properties. This subject has been amply reviewed with the focus on general[1,2] or particular[3–12] problems. The properties of the isolated ion and negative-ion processes have received major emphasis, whereas the effect of negative ions on the macroscopic properties of gaseous media has drawn little attention. New applications have stimulated an increasing interest in the properties of electronegative gases, and there has been considerable advance in this field of research by the time of this writing.

The main objective of this review is to discuss the phenomena induced by negative ions in a weakly ionized gas and in plasmas. Some relationships between the rate coefficients for the negative-ion processes and macroscopic parameters of the gaseous medium will be briefly reviewed in Section 2. Section 3 discusses the transport processes of charged particles in gases and plasmas with negative ions. Sections 4 and 5 deal with instability and waves in such media. Finally, Sec. 6 gives examples of recent applications of ionized gases with negative ions.

2. NEGATIVE-ION PROCESSES

The reaction kinetics of negative ions has been amply reported (see, e.g., Refs. 1–12). The purpose of this section is to give examples of relationships between the rate coefficients (or cross sections) for negative-ion processes and the macroscopic plasma parameters (gas temperature, pressure, mean electron energy, etc.). Many of these relationships constitute the foundation of a formalism describing phenomena observed in gaseous media with negative ions.

Collisional negative-ion processes are known to include electron attachment, detachment and processes changing the negative-ion identity. These include the charge transfer mechanism

$$A^- + B \to A + B^-,$$

the clustering reaction

$$A^- + B + C \to AB^- + C,$$

and the ion-molecule reaction

$$AB^- + C \to A^- + BC$$

They have little or no effect on the subject under discussion and are beyond the scope of this review (for a comprehensive review of these reactions see, e.g., Refs. 3, 4, 13, and 14). Electron attachment and detachment processes are more important, for they affect significantly properties of the gaseous medium such as electrical conductivity or permittivity.

Negative ions are formed by several attachment reactions, the most important being the dissociative attachment

$$e + AB \to A^- + B, \tag{1}$$

the three-body attachment

$$e + A + B \to A^- + B \tag{2}$$

and the photoattachment

$$e + A \to A^- + \hbar\omega.$$

At medium gas pressures, electron photoattachment can be neglected.

The two-body attachment process is characterized by the cross section σ_a and the rate coefficient k_a which is determined from the balance equation for negative ion density [A]. For process (1) this equation has the form

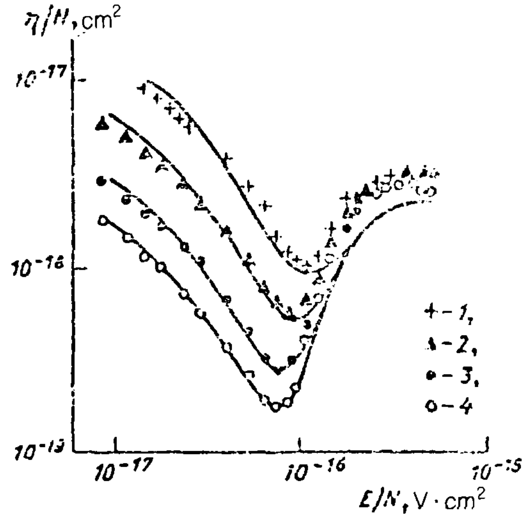

FIG. 1. Electron attachment coefficient as a function of E/N for O_2: circles (experiment[15]), curves (theory[16]). (*1*) $N(\mathrm{cm}^{-3})=7.24\cdot 10^{18}$, (*2*) $2.9\cdot 10^{18}$, (*3*) $1.2\cdot 10^{18}$, and (*4*) $6.92\cdot 10^{17}$.

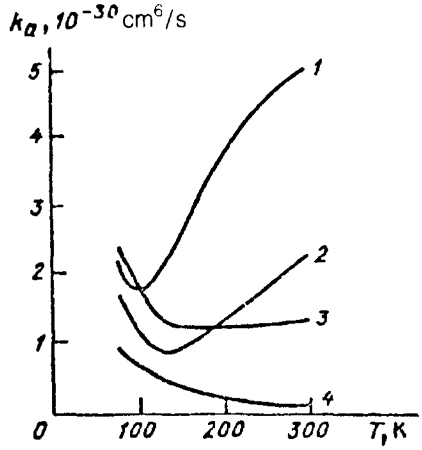

FIG. 2. Rate coefficient of three-body attachment to the molecules $^{18}O_2$ (curve *1*) and $^{16}O_2$ (curves *2–4*) as a function of gas temperature.[17] The third body is O_2 (1,2), CO (*3*), and N_2 (*4*).

$$\frac{d[A^-]}{dt}=k_a n_e[AB],$$

where n_e and [AB] are the densities of electrons and AB molecules, respectively. The quantities k_a and σ_a are related by

$$k_a=\langle\sigma_a v\rangle, \tag{3}$$

where the angular brackets indicate averaging over the electron velocities v. For three-body process (2), the cross section and the rate coefficient are introduced in a similar way.

The rate of electron attachment to a neutral particle depends rather strongly on the electron energy and on the particle internal energy. For the three-body process, the rate coefficient varies also with the translational and internal energy of the third species and sometimes with the gas pressure. When both dissociative and nondissociative electron-attachment processes proceed concomitantly, the dependence of the electron-loss rate on gas or plasma parameters becomes more complicated. We shall illustrate these statements by specific examples.

The O_2 molecule is the simplest molecule to which the electron can be attached by process (1) and process (2). Figure 1 shows the attachment coefficient η observed in oxygen[15] as a function of the reduced electric-field strength E/N (N is the neutral-gas density) which determines the mean electron energy in gases in an electric field. In most cases the attachment coefficient η and the attachment rate coefficient k_a are related by the expression

$$\frac{\eta}{N}=\frac{k_a}{w}, \tag{4}$$

where w is the electron drift velocity. Figure 1 also presents the results of the attachment coefficient calculation.[16] At high E/N values, the attachment results mostly from the dissociative reaction and the electron capture rate increases strongly with the mean electron energy because of the energy barrier of the process. A falling dependence is evident at low E/N, where the three-body attachment process prevails and the apparent two-body rate coefficient is proportional to N, that is, to the gas pressure. Hence, the competition of different attachment processes can result in the complicated dependence of the electron loss rate on the gaseous-medium parameters.

A non-monotonic temperature dependence of the rate coefficient for a separate attachment process can also be caused by a change of process mechanism. Figure 2 shows the rate coefficient data[17] for the three-body attachment of thermal electrons to O_2 molecules

$$e+O_2+M\rightarrow O_2^-+M \tag{5}$$

as a function of gas temperature T. This process is governed by two mechanisms.[12] According to the first, proposed by Bloch and Bradbury, the attachment proceeds in two stages via a transient unstable vibrationally-excited ion $(O_2^-)^*$. The second is connected with the electron attachment to the van der Waals molecule O_2M. The energy barrier ($\sim 10^{-1}$ eV) for the Bloch–Bradbury mechanism results in an increase of the attachment rate coefficient with T. In this case there is a high (~ 2) isotope effect, which can be neglected for the attachment to the van der Waals molecule. The rate coefficient for the latter type of attachment decreases when T increases because of the decomposition of the weakly bound O_2M molecule. For the rate of the three-body electron attachment to the O_2 molecule, the minimum shown in Figure 2 is due to a change of the process mechanism with increasing T. In this temperature range, for $M=N_2$ and CO, the Bloch–Bradbury mechanism is not significant any longer and the curve exhibits no minimum.

The possibility of many mechanisms for the electron attachment to a polyatomic molecule complicates the process. Figure 3 presents the cross sections of the electron attachment to SF_6 molecules[18] producing parent and fragment negative ions. An increase of the electron energy

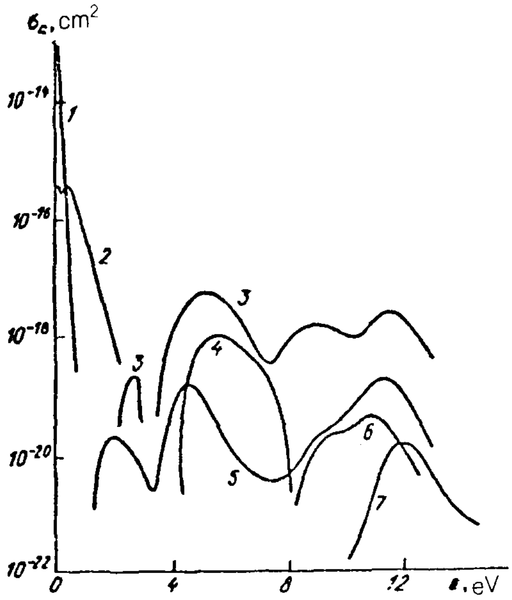

FIG. 3. Cross sections for negative ions produced by electron impact on SF_6 (Ref. 18). The ion produced is SF_6^- (*1*), SF_5^- (*2*), F^- (*3*), SF_4^- (*4*), F_2^- (*5*), SF_3^- (*6*), and SF_2^- (*7*).

changes both the process rate coefficient and the negative ion identity. Excitation of the molecule is known to enhance the electron attachment process (Refs. 2, 3, 7, 19, 20). For the process

$$e + N_2O \rightarrow O^- + N_2$$

the cross section measured as a function of temperature[21] is plotted in Figure 4. This dependence is caused by the excitation of the bending vibrational mode of an N_2O molecule. The process proceeds in two stages via the transient ion $(N_2O^-)^*$. Excitation of N_2O molecules decreases the threshold of the process and increases the probability of the

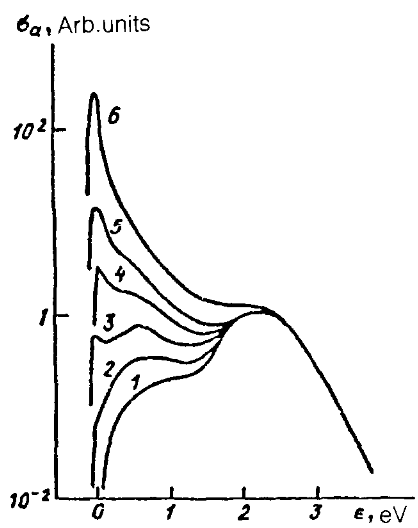

FIG. 4. Dissociative electron attachment cross section for N_2O at various T (Ref. 21). T = (*1*) 295 K, (*2*) 400 K, (*3*) 550 K, (*4*) 705 K, (*5*) 875 K, and (*6*) 1040 K.

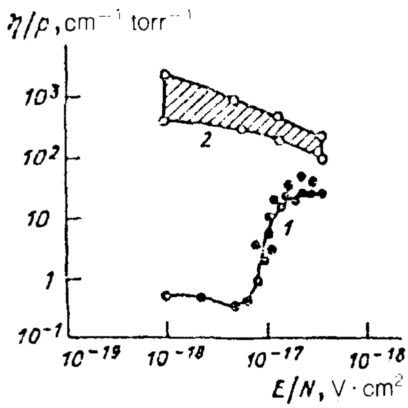

FIG. 5. Coefficient of electron attachment to excited HCl molecules produced by laser photodissociation of C_2H_3Cl in a buffer gas of He at various light intensities, S (Ref. 23). S[mJ/cm^2] = (*1*) 0 and (*2*) 0.9.

transition $N_2O \rightarrow (N_2O^-)^*$ because of the increase in the overlap integrals (Franck–Condon factors) of the vibrational wavefunctions for the respective states. A similar effect may be caused by an electronic excitation of molecules. For example, the maximum cross section for the reaction

$$e + O_2(a^1\Delta_g) \rightarrow O^- + O$$

exceeds[22] that involving a ground state O_2 molecule by a factor of 3–3.5 and its energy threshold is lowered by 1 eV as a result of excitation.

Enhancement of a laser-induced attachment[7,19,20] is of interest for many applied areas. This effect is explained by the photoexcitation of molecular vibrational and electronic states or by a photodissociation producing excited fragments. Figure 5 shows[23] the electron attachment in a mixture He:C_2H_3Cl which is photoenhanced by the formation of vibrationally excited molecules HCl(v).

Collisional electron detachment proceeds also via several mechanisms. Detachment of the outermost electron from a negative ion can be enabled by the chemical energy (an associative detachment, inverse to process (1)), or by the transfer of internal or translational energy of the colliding particles. Sometimes the necessary amount of energy is supplied by several sources. Figure 6 shows the rate coefficient calculated for the process

$$O_2^- + O_2 \rightarrow e + 2O_2$$

as a function of the gas temperature T and the parameter E/N determining the mean ion energy.[24] At high E/N, the translational energy of the O_2^- ion is large enough to detach the electron and depress the temperature dependence of the process rate. In the other limiting case, the ion's translational energy is equal approximately to the vibrational energy, which strongly increases the electron detachment rate with T. Consequently, the electron detachment rate depends on many parameters including the average internal energy of colliding particles and their translational temperatures.

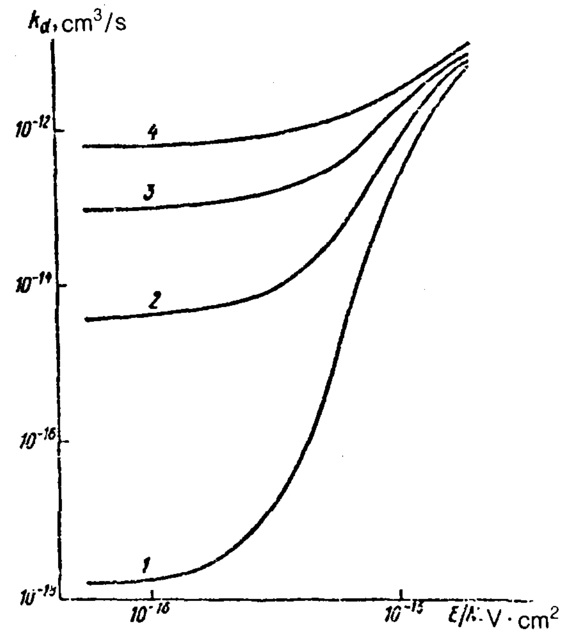

FIG. 6. Electron detachment rate coefficient for O_2^- in O_2 as a function of the gas temperature, T (Ref. 24). $T=(1)$ 300 K, (2) 500 K, (3) 700 K, and (4) 900 K.

It should be noted that the electron detachment can compete with other reactions. Figure 7 shows recent measurements[25] of cross sections for processes with F^- ions in SF_6, namely, the charge transfer

$$F^- + SF_6 \rightarrow F + SF_6^-$$

and the electron detachment

$$F^- + SF_6 \rightarrow e + F + SF_6.$$

At low energy the charge transfer prevails to form SF_6^- ions with a higher outer-electron binding energy than that in F^- ions. The electron detachment efficiency increases with energy.

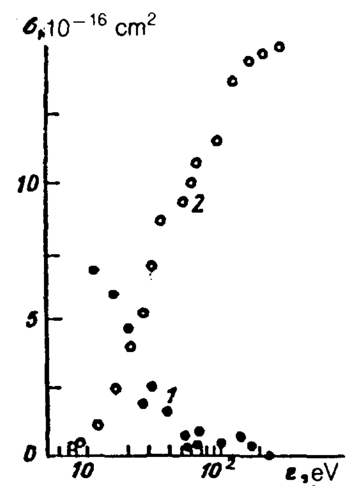

FIG. 7. Cross sections as a function of the kinetic energy (in the centre of mass frame) for (1) charge-transfer and (2) collisional detachment reactions of F^- in SF_6 target gas (Ref. 25).

Thus, a question of whether the electrical conductivity of a gaseous medium is determined by light electrons or by heavy ions depends on many factors. This results in many and varied physical phenomena observed in gases and plasmas with negative ions.

3. CHARGED PARTICLE TRANSPORT

Negative ion formation affects primarily the transport phenomena in gaseous media. An additional effective way of electron loss due to electron attachment changes the electron energy distribution and electron transport properties. Many interesting phenomena that may occur with electrons in a gas or a plasma with negative ions include attachment cooling, an absolutely negative conductivity of the gaseous medium, and the metastable negative-ion formation effect on electron drift and diffusion. Heavy negative species in plasma also cause a redistribution of the self-consistent, electric fields thus altering the plasma dynamic properties.

3.1. Attachment cooling for electrons

When ionization and electron attachment occur in a weakly ionized gas in an electric field, the electron balance equation may be written in the form (see, e.g., Refs. 26, 27)

$$\frac{\partial n}{\partial t} + \operatorname{div}(n\mathbf{w}) - \operatorname{div}\frac{\nabla(ND_T n)}{N} - \operatorname{div}[\varkappa_1 \mathbf{e}(\mathbf{e}\nabla n)] - \ldots$$
$$= (\nu_i - \nu_a)n. \tag{6}$$

Here D_T and $D_L = D_T + \varkappa_1$ are the transverse and longitudinal electron diffusion coefficients, respectively, and $\nu_i = k_i N$ and $\nu_a = k_a N$ are the ionization and attachment frequencies (k_i and k_a are the rate coefficients). The dots in the left-hand side of the equation represent the terms proportional to the gradient or the time derivative of E/N and other plasma parameters.

The electron transport and rate coefficients are determined by the electron velocity distribution function $f(\mathbf{v})$ which is derived from the Boltzmann equation

$$\frac{\partial f}{\partial t} + \mathbf{v}\frac{\partial f}{\partial \mathbf{r}} - \frac{e\mathbf{E}}{m}\frac{\partial f}{\partial \mathbf{v}} = S(f). \tag{7}$$

Here e and m are the electron charge and mass, respectively, and S is the collision integral. These equations are used to calculate electron transport parameters and to derive electron-atom (molecule) collision cross sections by comparison of experimental and theoretical transport data including the electron drift velocity, transverse and longitudinal diffusion coefficients, and ionization and attachment rate coefficients.[26] These calculations are normally carried out in the weak anisotropy approximation with only the two leading terms being retained in the expansion of the distribution function in spherical harmonics.

Until recently most studies of the energy distribution function of electrons in a weakly ionized gas in an electric field have been made by regarding the processes of ionization or attachment simply as additional inelastic processes. This is true provided that the frequency of the electron

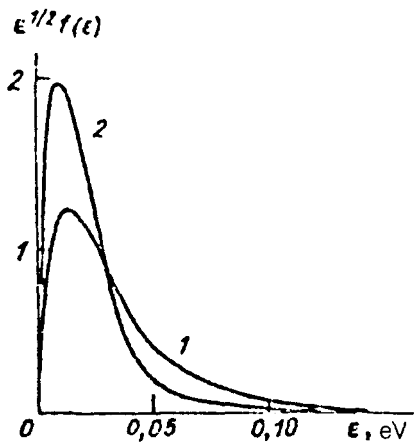

FIG. 8. Electron energy distribution function in O_2 at a pressure of 2.5 kPa. (*1*) Thermal Maxwellian distribution and (*2*) the function calculated by Scullerud[29] with allowance for attachment cooling.

energy relaxation ν_u far exceeds that of the electron generation/loss processes.[34] Without these idealizations the electron transport theory becomes more complicated. The peculiarity of the processes under consideration is more pronounced for a nonlinear pressure dependence of the rates. We consider this phenomenon using the example of three-body electron attachment to molecular oxygen (process (5)).[28]

At thermal energies process (5) with $M=O_2$ proceeds via two stages (Bloch–Bradbury mechanism).[12] In the first step, electrons with energy $\varepsilon_i \approx 0.08$–$0.09$ eV of the first autoionization state of the O_2^- ion are captured by an O_2 molecule to form vibrationally excited $(O_2^-)^*$ ions. These unstable ions may be autoionized or stabilized in collisions with other species,

$$e+O_2 \rightleftarrows (O_2)^*,$$

$$(O_2^-)^* + M \rightarrow O_2^- + M.$$

In the absence of attachment, detailed balancing ensures that the distribution function is Maxwellian. Indeed, the electron loss induced by vibrational excitation from some energy interval is restored by electrons which have gained energy in superelastic collisions. Attachment removes electrons from the medium. Therefore, there occurs a preferential loss of electrons with the energy of the autoionization state of the negative ion, ε_i, and so the loss is only partially restored by electron flows along the energy axis from other parts of the distribution. Figure 8 shows the electron energy distribution function calculated by Scullerud[29] in O_2 for a pressure of 2.5 kPa in comparison with the thermal Maxwellian distribution. The effect considered results in a lowering of the mean energy (i.e., "attachment cooling") and of the attachment rate coefficient. This takes place for $\nu_a \sim \nu_u$; $\nu_a \gg \nu_{ei}$, the electron-ion recombination frequency; and the electron temperature $T_e < \varepsilon_i$. (For $T_e > \varepsilon_i$, a reverse effect, "attachment heating," can be observed.) These conditions are fulfilled, for

TABLE I.

Pressure, kPa	Attachment rate coefficient, 10^{-30} cm^6/s
1	2.09
2.25	0.93
3.0	0.45

example, in gas mixtures with O_2 at an oxygen partial pressure $\gtrsim 1$ kPa, $n/N \ll 10^{-6}$ (N is the oxygen density) and $T < 10^3$ K.

It is important to note that the attachment cooling effect can be observed in oxygen as a result of the pressure dependence of ν_a. This is because ν_a is proportional to N^2 for a three-body process, whereas ν_u is proportional to N. Thus the attachment-cooling effect decreasing the attachment rate becomes more pronounced as N increases. The pressure dependence was clearly observed in measurements of the attachment rate coefficient for thermal electrons[30] (Table I). The data obtained were satisfactorily accounted for by Scullerud[29] who considered attachment cooling. This effect was also investigated for non-thermal electrons in a gas in an electric field[18,31] and for electron-beam-generated plasmas.[32] In particular, the observed pressure dependence of the non-thermal electron attachment rate[15] was given a theoretical explanation in Refs. 16 and 31. However, the pressure dependence detected in these experiments is an exception rather than the rule. In the case of dissociative attachment (process (1)), both ν_a and ν_u are proportional to N. Thus, even if attachment cooling (or heating) still occurs, the magnitude of the effect is no longer pressure dependent and therefore cannot be observed experimentally through a pressure dependence of the attachment rate coefficient. This may be important, and may lead, unless properly accounted for, to significant errors in calculating electron transport parameters or relating a measured attachment rate coefficient to cross sections. Unlike most other inelastic processes, electron attachment to a molecule removes an electron from the gas. This results in a dependence of the electron transport parameters, provided by swarm experiments[26] on the type of experiment. Electrons drifting in an electric field in front of the swarm have a higher mean energy than those at the rear. The dissociative attachment rate typically increases with the electron mean energy (see Figure 1). Consequently, more electrons are captured by molecules at the front face of an isolated swarm than at the rear, therefore the velocity of the centroid, the drift velocity by definition, is lower than the average velocity. The steady state Townsend experiment is normally used to determine the attachment (or ionization) coefficient.[26] Under the conditions of this experiment there is a uniform diffuse flux of electrons along the current caused by a uniform density gradient. This increases the mean energy (and ν_a) from the value it would have for an isolated swarm.

An electron transport theory taking into account production and/or loss of electrons was proposed by Thomas[33] and developed by Tagashira *et al.*[34] This approach is based on a numerical solution to the Boltzmann equation (7) obtained for a time- and space-varying distribution function. For example, for a steady-state Townsend experiment, equation (7) describing a symmetrical distribution function $f_0(\varepsilon)$ (in the usual two-term approximation[26]) is written in the form

$$\frac{1}{3\sigma_m}\left(\frac{\eta}{N}\right)^2 \varepsilon f_0+\frac{eE}{3N}\frac{\eta}{N}\left[\frac{\varepsilon}{\sigma_m}\frac{\partial f_0}{\partial\varepsilon}+\frac{\partial}{\partial\varepsilon}\left(\frac{\varepsilon}{\sigma_m}f_0\right)\right] +\frac{1}{3}\left(\frac{eE}{N}\right)^2\frac{\partial}{\partial\varepsilon}\left(\frac{\varepsilon}{\sigma_m}\frac{\partial f_{00}}{\partial\varepsilon}\right)+S_0(f)=0, \quad (8)$$

where σ_m is the collision cross section for momentum transfer, and S_0 is the electron-neutral collision integral. Equation (8) was derived using the relations

$$\frac{\partial(nf_0)}{\partial z}=-\eta n f_0,$$

$$\frac{\partial(nf_0)}{\partial t}=0.$$

Here the Oz axis is directed opposite to the external electric field. The last two terms in equation (8) represent the electron heating in an electric field and the energy loss in collisions with neutral particles. The first and second terms represent the change in the electron heating rate because of the electron density gradient induced by the attachment process. Under these conditions equation (4) breaks down so that

$$\eta/N=-\frac{w}{2ND_T}+\left[\left(\frac{w}{2ND_T}\right)^2+\frac{k_a}{ND_T}\right]^{1/2}. \quad (9)$$

In the limit of the weak attachment ($\nu_a \ll \nu_u$) equation (9) is reduced to (4) and the terms proportional to η/N may be neglected.

Attachment adds complexity to the distribution function and electron transport parameters calculations because equation (8) must be solved self-consistently with equation (9). It should be noted that in the problem at hand the main parameter is E/N as before. Calculations of electron transport parameters allowing for the effect of attachment were carried out in many electronegative gases, e.g., O_2 (Ref. 16), air,[31] SF_6 and SF_6:N_2 mixtures,[35,36] and F_2:He (Ref. 37).

3.2. Absolutely negative conductivity

Conductivity of gases and plasmas is generally determined by electrons. (An exception is negative-ion-rich plasmas with $n_i/n_e \gg \mu_e/\mu_i \gg 1$, where n_i and n_e are the negative-ion and electron densities, and μ_i and μ_e are the mobilities.) Electron attachment to a molecule may induce the interesting phenomenon of absolutely negative conductivity (ANC).

Several studies of this phenomenon in weakly ionized gases have been reported. ANC was predicted to occur in the electron thermalization of the heavier rare gases displaying a strong positive power dependence of collision frequency on the electron energy.[38] A similar result was obtained in a numerical simulation of electron relaxation with an initial delta-function distribution.[39] The effect under consideration was first observed by Warman and co-workers[40] in Xe. According to the studies cited above, ANC persists for a short relaxation time of the electron energy distribution. By calculations,[41–43] a steady ANC effect may be observed in electron-beam-generated plasmas with a strong attachment of low-energy electrons.

Neglecting the ion current, the conductivity of weakly ionized plasmas is given by

$$\sigma=en_e\mu_e,$$

where the electron mobility is equal to[26]

$$\mu_e=-\frac{1}{3N}\left(\frac{2e}{m}\right)^{1/2}\int_0^\infty \frac{\varepsilon}{\sigma_m}\frac{\partial f_0}{\partial\varepsilon}d\varepsilon =\frac{1}{3N}\left(\frac{2e}{m}\right)^{1/2}\int_0^\infty\left(\frac{\partial}{\partial\varepsilon}\frac{\varepsilon}{\sigma_m}\right)f_0 d\varepsilon. \quad (10)$$

Here, the distribution function $f_0(\varepsilon)$ is normalized,

$$\int_0^\infty f_0(\varepsilon)\varepsilon^{1/2}d\varepsilon=1.$$

For $\mu_e<0$, by equation (10) it is necessary (but not sufficient) that conditions

$$\frac{\partial f_0}{\partial\varepsilon}>0,$$

and

$$\frac{\partial}{\partial\varepsilon}\frac{\varepsilon}{\sigma_m}<0,$$

be satisfied for some electron energy range. The second inequality holds in heavier rare gases displaying Ramsauer minima in the momentum-transfer cross section. The first can be met owing to the peculiarities of the distribution-function relaxation[38] or by the initial conditions.[39] The positive energy derivative of f_0 can also result from a depletion of low-energy electrons attached to molecules.[41–43]

Figure 9 shows an electron energy distribution function obtained in electron-beam-generated plasmas of Ar:CCl_4 (1000:1 mixture), as a function of the electron beam current density j_b (Ref. 41). This function was obtained in the low-field limit by solving the Boltzmann equation. Here, the depletion of low-energy electrons is due to dissociative attachment to CCl_4 molecules. Figure 10 shows the electron conductivity in this mixture at a gas pressure of $p=300$ kPa and temperature $T=300$ K presented as a function of the reduced electric field strength E/N. ANC occurs at low E/N and disappears with an increase in the electric field because of the electron energy distribution function smoothing. Similar results have been obtained for mixtures Ar:F_2 (Ref. 42), Xe:F_2 (Ref. 43), and Ar:NF_3 (Ref. 44). Observation of ANC in a steady-state electronegative gas is still an open question. This seems to be a very attractive problem, for the system considered must generate an electronegative wave.

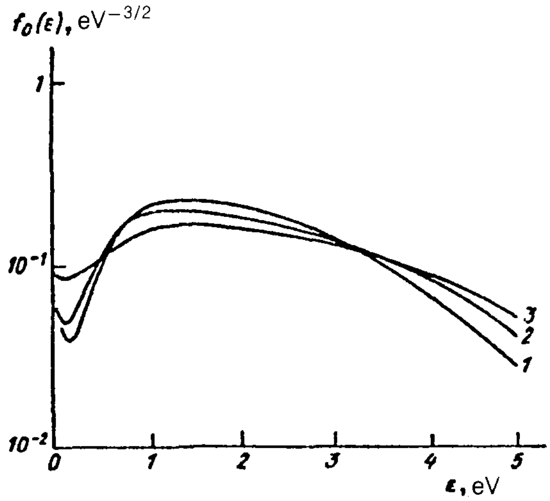

FIG. 9. Electron energy distribution function in electron-beam generated Ar:CCl_4=1000:1 plasma for different electron-beam currents, j_b (Ref. 41). j_b [A/cm^2]=(1) 1, (2) 3, and (3) 10.

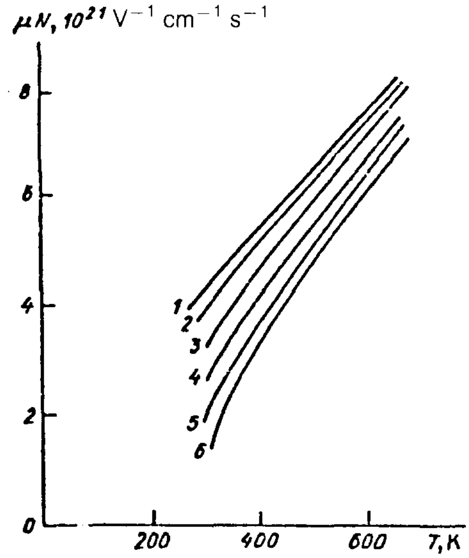

FIG. 11. Thermal-electron mobility in NH_3 at various neutral-particle densities, N. N [cm^{-3}]=(1) 0, (2) $4.86\cdot10^{19}$, (3) $9.72\cdot10^{19}$, (4) $1.46\cdot10^{20}$, (5) $1.94\cdot10^{20}$, and (6) $2.43\cdot10^{20}$.

3.3. Electron transport in a gas with unstable negative ions

In the preceding sections we assumed that negative ions were in a steady state. Negative ions can also occur in many unsteady states. Lifetimes of such states may differ by more than 13 orders of magnitude, from 10^{-15} to $>10^{-2}$ s (Ref. 7). A most significant mode of electron capture by molecules is via negative-ion metastable (resonance) states. Excitation of rotational, vibrational and electronic levels of molecules by electron impact proceeds often via a transient negative ion. Unstable negative ions can affect not only collisional cross sections but also electron transport parameters.

Earlier papers dealing with drift of electrons through gases claim that electron trapping could efficiently slow down the drift of electrons in an electric field,[45–48] particularly at high densities. A trapped electron captured by a gas molecule, converts it into an unstable negative ion. If an electron is trapped and released many times on its drift through the gas, it will be increasingly delayed by higher densities. Then, we have

$$\frac{p_e}{1-p_e}=\frac{n_e}{n_i},$$

where p_e is the probability of an electron to be free, and n_e and n_i are the equilibrium densities of electrons and unstable negative ions, respectively. The mobility of negative ions may be neglected because of their large mass. The ratio of the apparent electron mobility to the free-electron mobility is then[49]

$$\frac{\mu}{\mu_0}=p_e=\frac{1}{1+NF}, \tag{11}$$

where

$$F=\frac{g_i}{g_e g_m}\frac{\sqrt{2}\pi^2\hbar^3}{m^{3/2}}f(\varepsilon_i),$$

g_e, g_i and g_m are the statistical weights of the electron, negative ion, and molecule, respectively, and $f(\varepsilon_i)$ is the electron energy distribution function for an unstable-negative-ion energy ε_i. The ratio μ/μ_0 has a minimum at a mean electron energy $\bar{\varepsilon}\sim\varepsilon_i$, with $(\mu_0-\mu)/\mu_0\sim\lambda^3N$ with λ being the electron de Broglie thermal wavelength. Other reasons for the number-density dependence of electron mobility (multiple—scattering processes, etc.) yield[45–48] $(\mu_0-\mu)/\mu_0\sim\lambda\sigma_m N$. Considering that $\lambda^2\gg\sigma_m$, the effect of unstable negative ions on electron mobility can be observed at lower gas pressures.

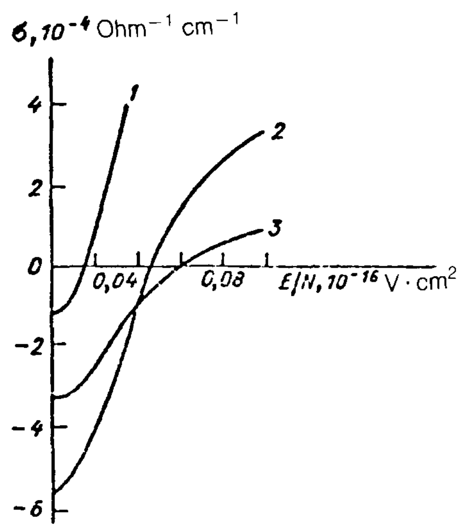

FIG. 10. Electrical conductivity in Ar:CCl_4=1000:1 plasma.[41] j_b ×[A/cm^2]=(1) 1, (2) 3, and (3) 10.

Electron mobility values measured[50] in NH_3 are given in Figure 11. A decrease in mobility observed with an increase in gas pressure is supposed to be due to electron trapping by polar NH_3, molecules to form unstable negative ions. Similar dependences have been obtained in many other molecular gases both experimentally[45–48] and theoretically.[51]

Unlike electron drift, diffusion of electrons in high-pressure gases has been poorly reported. Diffusion of electrons in a gas in a moderate electric field is anisotropic.[26] At first glance the effect of unstable negative ions on diffusion seems to result in a relation which is similar to equation (11):

$$\hat{D}=p_e\hat{D}_0,$$

where $\hat{D}$ is the apparent diffusion tensor, and $\hat{D}_0$ is the diffusion tensor for free electrons. However, this problem is not *that* simple.[52] In this case the electron diffusion flux is

$$\mathbf{\Gamma}_D=-p_e\hat{D}_0\nabla n_e-D^*(\mathrm{e}\nabla n)\mathrm{e}, \qquad (12)$$

where

$$\mathrm{e}=\frac{\mathbf{E}}{E},$$

$$D^*=\frac{\nu_a\nu_d}{(\nu_a+\nu_d)^3}(w_e-w_d)^2, \qquad (13)$$

ν_a is the electron attachment frequency, ν_d is the frequency of electron detachment from an unstable negative ion, and w_e and w_i are the drift velocities of electrons and ions, respectively. If many unsteady states of the negative ion are significant, equation (13) must be summed over all the states. Therefore, the formation of unstable negative ions not only decreases electron diffusion, by analogy with electron drift, but also leads to the renormalization of the longitudinal diffusion coefficient.

The anisotropic behavior of electron diffusion in gases in an electric field is primarily associated with the non-equilibrium electron-energy distribution.[26,27] This anisotropy disappears when the distribution is Maxwellian or the frequency of electron momentum relaxation, ν_m, is constant, while the anisotropy due to the formation of unstable negative ions remains. The quantity D^* is always positive, whereas the renormalization coefficient of the longitudinal diffusion induced by the non-equilibrium distribution can reverse its sign.

The mechanism of the additional diffusion along the electric field may be explained in the following way. Assume that an electron swarm is drifting in a gas in an electric field and the electrons are trapped and released many times while drifting through a gas. Then, the free electrons lead the swarm, whereas the electrons captured by molecules move in the rear. Both processes cause the electron swarm to spread along the electric field. For the ordinary diffusion coefficient, we have $D\sim v^2/\nu_m$ (v is the thermal electron velocity), whereas for D^*, the velocity v is replaced by the difference w_e-w_i, and ν_m by the frequency of electron attachment and detachment processes (see (13)).

This mechanism is analogous to electron diffusion in semiconductors which is associated with the transition of electrons from one energy valley to another.[53] A formula similar to (13) has been derived using the fluctuation theory in a nonequilibrium electron gas.[53] In the description of the unsteady negative ions effect on electron diffusion, it was assumed that the time of the electron drift is

$$t\gg\nu_a^{-1},\quad \nu_d^{-1}$$

and the distance from the centre of the electron swarm is

$$x\ll w_e t\frac{\nu_a}{\nu_a+\nu_d},\quad w_e\, t\frac{\nu_d}{\nu_a+\nu_d}.$$

Usually the diffusion coefficient is inversely proportional to the gas density, N. The density dependence of D^* is more complicated. It is obtained from equation (13) and the equations

$$\nu_a=k_aN,\quad \nu_d=\tau_i^{-1}+k_dN,$$

where k_a and k_d are the attachment and detachment rate coefficients, respectively, and τ_i is the lifetime of unstable negative ions. At low gas pressures ($k_aN\tau_i\ll1$, $k_dN\tau_i\ll1$), equation (13) reduces to

$$D^*=k_aN\tau_i^2(w_e-w_i)^2.$$

In the high-pressure limit ($k_aN\tau_i\gg1, k_dN\tau_i\gg1$),

$$D^*=\frac{k_ak_d}{(k_a+k_d)^3N}(w_e-w_i)^2.$$

Therefore, D^* initially increases with gas pressure (at a constant mean electron energy), then peaks, and at high N has the same density dependence as the ordinary diffusion coefficient.

Unstable negative ions have been estimated to affect the longitudinal electron diffusion in gas discharge plasmas in air with small admixtures.[52] Now D^* can be obtained by measuring the electron diffusion coefficient along the electric field for different gas pressures.

3.4. Drift shocks and steep density profiles in current-carrying plasmas

In a high-pressure gas with smooth density profiles, diffusion of charged particles in weakly ionized plasmas may be neglected. To a first approximation, the diffusion terms in transport equations are omitted. We shall discuss first the longitudinal structure of a gas discharge. The assumption of plasma quasineutrality and the electric-current conservation law result in simple algebraic relations between the densities of charged particles and the electric field. In the simplest case of a binary plasma these relations reduce the ion transport equation to[54]

$$\frac{\partial n}{\partial t}+V(n)\frac{\partial n}{\partial x}=Z-R, \qquad (14)$$

where n is the plasma density, Z and R are the rates of ion production and loss, respectively, and $V(n)$ is the apparent velocity known as the ambipolar drift velocity and is determined by the dependence of μ_e/μ_i on the electric field. The ambipolar drift velocity depends on plasma density and so causes perturbations of a density profile to move and to be distorted. Specifically, if $V(n)$ is an increasing function, then an increasing profile steepens (by analogy with a nonlinear wave in gas dynamics) and forms a shock wave similar to that in gas dynamics. If $V(n)$ is a decreasing function, then a shock wave may arise at the rear falling slope of the nonlinear wave. These shock waves can be moving and stationary. Nonuniformly distributed sources or boundary conditions may induce a nonuniform distribution of plasma density whose profile is governed by the ambipolar drift velocity and by the terms on the right-hand side of equation (14). Stability of the shock to longitudinal disturbances is determined by the so-called evolutional condition.[54]

It should be noted that the shock solution of equation (14) can be obtained in the drift approximation by neglecting the diffusion transport and the breakdown of the plasma quasineutrality assumption. It would be natural to refer to these solutions as drift shocks. An actual shock width is conditioned by diffusion processes and the violation of plasma quasineutrality.

An injection of negative ions into an electronegative gas can substantially affect the condition of an incipient shock, that of structure and stability. The reaction kinetics of charged particles becomes more complicated with rate constants varying over many orders of magnitude. Therefore, collision processes should be classified by their rate.

In gas discharge plasmas, electron attachment and detachment belong to fast processes, whereas ionization and recombination to slow reactions. In the fast process scale, the density of positive ions may be supposed constant. For slow processes, the ratio of the densities of electrons and negative ions may be deemed time invariant. This steady-state approximation reduces the initial problem of evolution of several ionic fluxes to the problem of a single flux of positive ions alone (when one species of positive ions is involved), i.e., to equation (14). In this case the apparent drift velocity may be a rather complicated function of n.

In general, introduction of negative ions increases the probability of an incipient shock in plasmas. In plasmas with negative ions, the shock may be described by equation (14), provided that not only the diffusion length or screening length is zero but also the length of establishing the relation between electron and negative ion densities is supposed to be zero. Finiteness of these lengths results in a relaxation area which is similar to that of the gas dynamic compression shock. The structure of these areas in plasmas with negative ions has been detailed in Ref. 54.

This steady-state shock can occur provided the ambipolar plasma flux $\Gamma(n)=\int V(n)\mathrm{d}n$ is a non-monotonic function (Figure 12). It is only in such circumstances that the flux may be continuous in passing through the shock. If $\Gamma(n)$ (or $\Gamma(E)$) has a shape shown in Figure 12, then a steady-state spatially periodic solution of the drift equations may be obtained,[55] which corresponds to the closed curve in Figure 12. It should be noted that to obtain this solution the right-hand side of equation (14) must be a sign-variable function of n. (In Ref. 55, equation (14) has been derived for an electric field, but this is immaterial.)

Stationary layers have been observed[55] in non-self-sustained gas discharges in Ar:H_2 (D_2) mixtures (Figure 13). The non-monotonic behavior of the ion flux is associ-

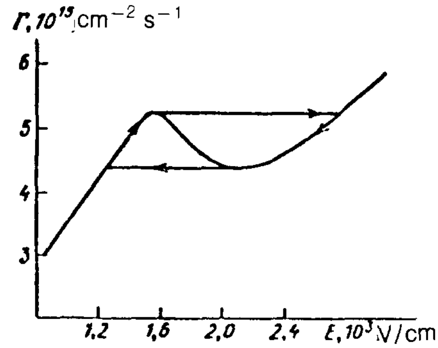

FIG. 12. Calculated ambipolar plasma flux as a function of electric field strength in externally-sustained discharge for H_2:Ar=1:9 (Ref. 55). Total gas pressure is 2.5 atm; electron-beam current density is 150 A/cm^2; discharge current density is 0.9 A/cm^2.

ated with the complicated kinetics of dissociative electron attachment to vibrationally excited molecules and detachment due to collisions with excited molecules.

Schottky's classical theory of the positive column in gas discharge fails when applied to a discharge in electronegative gases. Derivation of basic equations of radial transport of positive ions, negative ions and electrons in electronegative gases presents no problems. However, these are mathematically complicated equations dependent on many parameters. Extensions of the classical theories of positive discharge to include the negative-ion effect is a subject of wide interest. Many studies devoted to this subject are based on the concept of apparent ambipolar diffusion coefficient, by analogy with Schottky's theory. Several comprehensive experiments[56,57] and detailed self-consistent theory[5–8] have shown a congestion of negative ions at the center of the discharge for large ratios of the electron temperature to the negative-ion temperature. This phenomenon is observed in high-pressure plasmas with negative ions emerging and disappearing in a volume without transport to the walls. Then the electron density is small at the

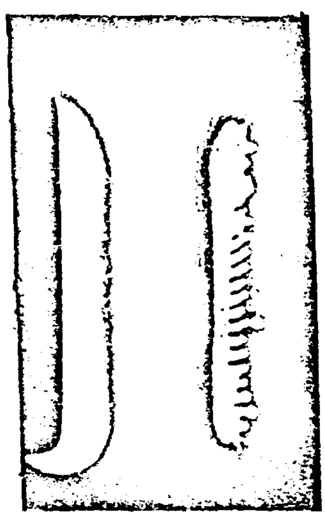

FIG. 13. Photograph of gas discharge for H_2:Ar=1:9. p=1 atm; j_b=14 μA/cm^2; j_d=0.2 A/cm^2; discharge voltage=4 kV; electrode separation is 3 cm. (The set-up is similar to that described in Ref. 55)

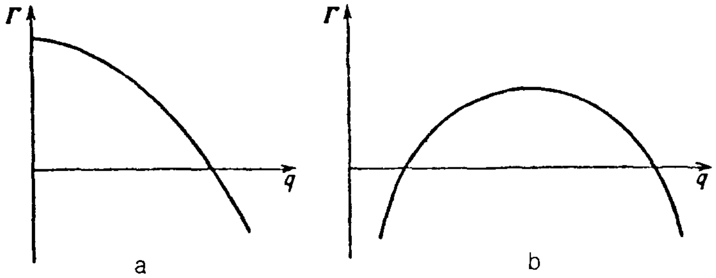

FIG. 14. Various curve profiles representing the instability increment as a function of the wave number.

center of the gas discharge, and a weak radial electric field is controlled by the ion temperature. At the walls, plasmas contain electrons and positive ions with small negative ion densities and a negative ion flux toward the center. This phenomenon has also been predicted in several calculations.[59–61]

4. INSTABILITIES AND WAVES IN COLLISION PLASMAS

Plasma stability is undoubtedly an aspect of intense interest. There are many situations in which negative ions play an important role. Heavy negative species affect the known domain[62] and thermal[63] instabilities of an externally sustained direct-current gas discharge, and also of the ionization-field instability[64] of a microwave discharge. In plasmas, negative ions excite new wave modes and instabilities. The negative-ion effect depends on the gas density. At high gas pressures (>1 torr) the collisional negative-ion processes are important, whereas at low pressures these processes can be neglected.

4.1. Attachment instability

High-pressure-gas plasmas are typified by a positive column of a glow discharge with electrons created by the collisional electron-atom (or molecule) ionization and destroyed by the electron-ion recombination or attachment to molecules. In terms of the characteristic times of these processes, the gas density is constant, and plasma disturbances are generally attenuated.[65]

An exception are the plasmas with an intense electron source which depends only slightly on the reduced electric field, E/N. Electrons can be created by an external ionizer in a non-self-sustained gas discharge or by detachment from negative ions colliding with atoms (radicals) and excited particles (processes inverse to the reactions (1) and (2)). This case brings about a new type of plasma instability whenever the attachment rate strongly increases with the electric field. Physically, this provides a mechanism for runaway of a local increase in the electron density n_e propagating along the electric field. To conserve current density, any slight increase in the electron density has to decrease the electric field. A decrease in the electric field causes a decrease in the electron attachment rate, whereas the birth rate of electrons remains almost constant. The electron density increases further producing an instability and the closed chain of process

$$n_e\uparrow \;\to E\downarrow \;\to k_a\downarrow \;\to n_e\uparrow .$$

This attachment instability causes solitary layers (domains) with a high electric field and a low electron density (or vice versa) to propagate between the electrodes in the high-pressure discharge. This phenomenon manifests itself primarily as oscillations of the electrical current or a voltage difference across the discharge gap.

According to the terminology of nonlinear physics[66,67] transverse plasma layers are referred to as autosolitons, whereas in gas-discharge physics these layers are known as striations (or domains). There are some reasons to use both terms. A type of plasma layer may be defined using the linear theory of stability of a steady homogeneous state as follows. The dependence of the instability increment, Γ, on the wave number, q, can have a profile shown in Figures 14a and 14b. At (a), perturbations with larger wavelengths increase preferentially, whereas at (b) waves with some nonzero q, which determines the period of the nonlinear system, exhibit the maximum increment. Historically, the latter structures, termed striations,[68] were investigated first. In Figure 14a, a more complicated evolution of autosolitons results in a soliton which was termed a domain,[69] by analogy with solitons in semiconductor plasmas.[70]

In recent years many experimental and theoretical studies of attachment instability in self-sustained and electron-beam-controlled gas discharges have been reported.[62,65,71–78] Gaseous mixtures containing O_2, CO_2, H_2O, and HCl revealed oscillations of plasma potential; evolution and movement of domains were investigated with an electronic image transformer in the photograph and linear sweeping exposure modes; oscillations of light emitted by the discharge were observed with a photomultiplier. Domains appeared near the electrodes and also throughout the volume. They were observed as a bright plane layer of variable thickness filling the entire cross section of the discharge in the absence of a gas flow. A typical current oscillogram and the optical scanning image in the O_2:Ar discharge are given in Figure 15 (Ref. 77).

In a microwave discharge, attachment instability leads also to self-oscillations of plasma glow and of the amplitude of the microwave electric field sustaining the freely localized discharge in an open resonator.[78,79]

Most of theoretical instability studies have been based on a linear approach which gives an instability threshold that agrees well with experimental data and approximates qualitatively the domain dynamics. The nonlinear approach is labor-consuming and seldom used in real gases where it fails to fit experimental data on domain dynamics.

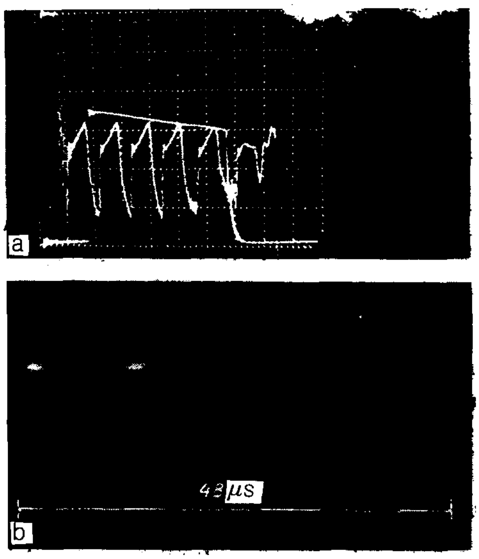

FIG. 15. Attachment instability of externally-sustained-discharge plasmas in O_2:Ar=2:98 mixture. $p=1$ atm, $j_b=430\ \mu A/cm^2$, 2 kV discharge voltage, 2.5 cm electrode separation, and $j_d=0.022\ A/cm^2$ (Ref. 77). (a) Current oscillogram, 10 μs/div; (b) oscillogram of optical sweep.

This is associated with the complex kinetics of charged particles in real gases and the lack of data on rate coefficients. Nevertheless, the qualitative properties of attachment instability dynamics are well known and may be described using the linear formalism.

Most studies of the instability linear stage have been based on the mean-electron-energy balance equation. It has been demonstrated that this equation is not included in the consistent system of hydrodynamic equations describing gas discharge plasmas with non-equilibrium electron energy distributions.[27,73,74] A consistent theory of attachment instability is based on a set of equations including balance equations of negative-ion density (n_n) and positive-ion density (n_p), an equation of current density (j) conservation, and electrodynamics equations[77,80,81]

$$\begin{aligned}
&\frac{dn_n}{dt}=\tilde{k}_a N n_e-\nu_d n_n-\beta_{ii}n_p n_n,\\
&\frac{dn_p}{dt}=\nu_i n_e-\beta_{ei}n_p n_e-\beta_{ii}n_p n_n,\\
&\operatorname{div}(n_e\tilde{w}_e+n_p w_p+n_n w_n)=0,\\
&\operatorname{div}\,\mathbf{E}=4\pi e(n_p-n_e-n_n),\\
&\operatorname{curl}\,\mathbf{E}=0,
\end{aligned}\tag{15}$$

where ν_i and ν_d are the frequencies of ionization and detachment, β_{ii} and β_{ei} are the ion-ion and electron-ion coefficients, w_p and w_n are the drift velocities of negative and positive ions, respectively, and $\tilde{k}_a$ and $\tilde{w}_e$ are the attachment rate coefficient and the electron drift velocity in plasmas with n_e and E gradients induced by the instability evolution.

This instability description is more illustrative if the following conditions are realized: the electron attachment and detachment rate is much higher than that of ionization and charged particle recombination, the ion drift may be neglected, and ν_d is constant. A constant frequency of detachment follows from the slow formation of active particles which are able to decompose negative ions in the gas discharge.[62] In the linear approximation the increment and velocity of long-wave disturbancies can be written as[77,80,81]

$$\begin{aligned}
&\Gamma=\nu_a\frac{\hat{k}_a}{\hat{w}}-\nu_a-\nu_d,\\
&v=\nu_a\left[\frac{\hat{k}_a-\hat{w}}{\hat{w}^2}\,w\tau_M+\frac{\hat{k}_a}{w\hat{w}}\left(D_L-\frac{D_E}{\hat{w}}\right)+k_L-\frac{k_E}{\hat{w}}\right],
\end{aligned}\tag{16}$$

where

$$\hat{\varphi}=\frac{\partial\ln\varphi}{\partial\ln(E/N)},\quad \tau_M=\frac{1}{4\pi\sigma}$$

is the relaxation time of the plasma charge, σ is the electrical conductivity, $\nu_a=k_a N$ is the attachment frequency, w is the velocity of electron drift in homogeneous plasmas, D_L is the electron longitudinal diffusion coefficient, and D_E is the coefficient describing electron transport due to an E/N gradient along the electric field. The coefficients k_L and k_E represent changes in the attachment rate coefficient caused by the spatial evolution of the electron-energy distribution in plasmas with the n_e and E/N gradients, respectively,

$$\begin{aligned}
&k_L=\frac{1}{k_a}\left(\frac{2}{m}\right)^{1/2}\int_0^\infty\sigma_a(\varepsilon)\varepsilon f_L(\varepsilon)d\varepsilon,\\
&k_E=\frac{1}{k_a}\left(\frac{2}{m}\right)^{1/2}\int_0^\infty\sigma_a(\varepsilon)\varepsilon f_E(\varepsilon)d\varepsilon,
\end{aligned}$$

where ε is the electron energy, σ_a is the attachment cross section, f_L and f_E are the coefficients in the expansion of the symmetrical part of the electron-energy distribution function in terms of gradients of plasma parameters:

$$f_0(\varepsilon,x)=f_{00}(\varepsilon)+f_L(\varepsilon)\frac{\partial\ln n_e}{\partial x}+f_E(\varepsilon)\frac{\partial\ln(E/N)}{\partial x}+\dots,$$

$f_{00}(\varepsilon)$ is the distribution function in spatially uniform plasmas. Here the anisotropy of the distribution function and plasma spatial gradients are supposed to be small (two-term approximation[26] with $\lambda_u\ll L$, where λ_u is the electron mean free path for the energy transfer, and L is the characteristic length of a nonuniform plasma). Expressions for the functions $f_L(\varepsilon)$ and $f_E(\varepsilon)$ have been given elsewhere.[80,82]

The dissociative attachment process has normally an energy threshold at least a few electron-volts higher than typical values of the mean electron energy in a discharge, i.e., $\hat{k}_a\gg 1$. Since $\hat{w}\sim 1$, when $\Gamma\sim\nu_a\hat{k}_a$ and an instability occurs at E/N values limited above and below. The lower bound corresponds to a decrease in $\nu_a\hat{k}_a$ in comparison with ν_d, whereas the upper bound is connected with ionization growth having a stabilizing effect.

The first term in equation (16) represents the transport of plasma disturbances due to the relaxation of the plasma charge and is of the order of $\hat{k}_a w \tau_M \nu_a$. The second and third terms, being of the order of $\hat{k}_a \nu_a \lambda_u$, describe the transport of perturbations connected with the nonlocal behavior of the function $f_0(\varepsilon)$ and the electron kinetic coefficients. The importance of any particular term is determined by the parameter

$$\nu_u \tau_M = \frac{E^2}{4\pi\, n_e \varepsilon_k}$$

(ε_k is the characteristic electron energy) which is equal to the ratio of electric field pressure to electron pressure. For $\nu_u\tau_M \gg 1$, the domain propagates from cathode to anode whereas for $\nu_u\tau_M \ll 1$, the domain may propagate also in the opposite direction. For example, when $\nu_u\tau_M \ll 1$, slow domains with velocities far less than $\hat{k}_a\nu_a\lambda_u$ were observed in an externally-sustained gas discharge in an O_2:He mixture.[83]

It should be noted that in gas discharge plasmas, the attachment instability is in many ways similar to the recombination instability in semiconductor plasmas[70,84] studied by linear and nonlinear theories. Specifically, a soliton type of solution has been obtained.

4.2. Coupled attachment and vibrational relaxation modes

As noted in Sec. 2, the rate of electron attachment to a molecule can sharply increase not only with E/N but also with the molecule vibrational excitation. This vibrational excitation can excite the coupled attachment and vibrational-relaxation modes of plasma instabilities.[85,86]

The mechanism of this instability may be explained in the following way. A slight increase in gas temperature T, results in a decrease in vibrational temperature T_V, due to the V-T relaxation, and consequently in a decrease in the attachment rate constant k_a. By analogy with the attachment instability, this causes the electron density n_e to increase. Owing to the Joule heating, the T perturbations increase further to close the cycle

$$T\uparrow\ \to T_V\downarrow\ \to k_a\downarrow\ \to n_e\uparrow\ \to T\uparrow .$$

The instability considered above can be described by using the balance of gas translation energy equation and the number of vibrational quanta (per molecule) ε_V (Ref. 62):

$$\frac{N}{\gamma-1}\frac{\partial T}{\partial t} - T\frac{\partial N}{\partial t} = \frac{N\varepsilon_V \hbar\omega}{\tau_{VT}} + \mathrm{div}(\varkappa \nabla T), \qquad (17)$$

$$\frac{\partial \varepsilon_V}{\partial t} = \frac{\eta_V\, jE}{N\hbar\omega} - \frac{\varepsilon_V}{\tau_{VT}}, \qquad (18)$$

where γ is the usual specific heat ratio, $\hbar\omega$ is the vibrational energy quantum, τ_{VT} is the V-T relaxation time, $\varkappa$ is the thermal conductivity, and η_V is the fractional power transferred by electrons to molecules in vibrational excitation.

Assuming that $\mathrm{div}\, \varkappa\nabla T = \varkappa (T-T_0)/l^2$ (T_0 is the wall temperature and l is the characteristic length of heat removal), the increment Γ for evolution of transverse disturbances is obtained from the linear analysis of equations (17) and (18). The quantity Γ can be expressed in the form

$$\Gamma\tau_{VT} = -\frac{b}{2} \pm \left(\frac{b^2}{4} - c\right)^{1/2}, \qquad (19)$$

where

$$b = \frac{\gamma-1}{\gamma}\frac{\varepsilon_V\hbar\omega}{T}\left(\hat{\tau}_{VT} + 1 + \frac{T}{T-T_0}\right) - \frac{\gamma}{\gamma-1}\eta_V \nu_{Tp}\tau_{VT}\frac{T}{\varepsilon_V\hbar\omega}\frac{\partial \ln n_e}{\partial \ln \varepsilon_V} - \mathring{\tau}_{VT},$$

$$c = (\mathring{\tau}_{VT} - 1)\left[\frac{\gamma}{\gamma-1}\eta_V\nu_{Tp}\tau_{VT} \times \left(\frac{\partial \ln n_e}{\partial \ln T} + \hat{w} + 1\right) + \hat{\tau}_{VT}\frac{\varepsilon_V\hbar\omega}{T}\right] - \left(\hat{\tau}_{VT} + 1 + \frac{T}{T-T_0}\right) \times \left[\frac{\gamma}{\gamma-1} - \eta_V\nu_{Tp}\tau_{VT}\frac{\partial \ln n_e}{\partial \ln \varepsilon_V} + \frac{\varepsilon_V\hbar\omega}{T}\mathring{\tau}_{VT}\right],$$

$$\hat{\tau}_{VT} = \frac{\partial \ln \tau_{VT}}{\partial \ln T}, \quad \mathring{\tau}_{VT} = \frac{\partial \ln \tau_{VT}}{\partial \ln \varepsilon_V},$$

$$\hat{w} = \frac{\partial \ln w}{\partial \ln (E/N)}, \quad \nu_{Tp} = \frac{\gamma-1}{\gamma}\frac{jE}{p}.$$

Equation (19) is derived by using the approximation of constant gas pressure, i.e., the time of sound wave propagation through a system must be smaller than that of a disturbance growth.

According to equation (19) an instability occurs when $c<0$ which can be true due to a strong inverse T-dependence of τ_{VT} and an inverse ε_V-dependence of n_e. Then,

$$\Gamma \sim \left(\frac{|\hat{\tau}_{VT}|\, \mathring{k}_a \nu_{Tp}}{\tau_{VT}}\right)^{1/2},$$

where

$$\mathring{k}_a = \frac{\partial \ln k_a}{\partial \ln T_v} \sim \frac{\partial \ln k_a}{\partial \ln \varepsilon_V}.$$

Disturbances with a maximum increment can propagate in different directions, as the case may be.

The question of an experimental identification of this type of instability remains open. This is partially due to competition of many modes which impedes interpretation of experiment.

4.3. Acoustic wave generation and amplification

Amplification of acoustic waves (acoustic instability) in gas-discharge plasmas has been observed many times as a growth of spontaneous acoustic oscillations.[68,87] At present several measurements of the gain of artificially generated acoustic waves in the positive column of a glow discharge have been reported.[88,90] The explanation of this effect (see, e.g., Ref. 91) goes essentially back to Rayleigh's studies.[92] The universal mechanism of sound amplification in gas-discharge plasmas is of a thermal nature. This is associated with bulk heating which depends on particle density.

The system of hydrodynamic equations describing a weakly ionized gas with Joule heating has the form[62]

$$\frac{\partial N}{\partial t}+\operatorname{div}(N\mathbf{V})=0,$$

$$\frac{\partial \mathbf{V}}{\partial t}+(\mathbf{V}\nabla)\mathbf{V}=-\frac{1}{NM}\nabla p, \tag{20}$$

$$\frac{\partial}{\partial t}\left(\frac{p}{\gamma-1}+N\frac{MV^2}{2}\right)+\operatorname{div}\left[\mathbf{V}\left(\frac{\gamma}{\gamma-1}p+N\frac{MV^2}{2}\right)\right]$$
$$=Q+\operatorname{div}(\varkappa\nabla T),$$

where V is the flow velocity, $p=NT$ is the gas pressure, M is the molecule mass. (With the exception of heat transfer to the wall, dissipative processes can be neglected at high gas pressures.) Then, the temporal gain of acoustic waves can be written in the form (neglecting the stabilizing effect of heat removal)

$$\Gamma=\frac{\nu_{\mathrm{Tp}}}{2}\operatorname{Re}\frac{\partial\ln(jE)}{\partial\ln N}, \tag{21}$$

where

$$\nu_{\mathrm{Tp}}=\frac{\gamma-1}{\gamma}\frac{jE}{p}$$

is the gas heating rate at constant pressure. Sound amplification along the electric field results from an increase in the bulk heating with increasing N in view of

$$j=\text{const},\quad \frac{\partial\ln E}{\partial\ln N}\gtrsim 1$$

whereas the conditions

$$E=\text{const},\quad \frac{\partial\ln j}{\partial\ln N}<0.$$

lead to a wave attenuation in the perpendicular direction.

This situation reverses in electronegative gases with a strong positive E/N-dependence of the electron attachment rate. Here, an increase in N at a constant electric field causes E/N and $k_a(E/N)$ to decrease. As for the mechanism of attachment instability, this leads to an increase in n_e and, consequently, in bulk heating Q. These relations can be written in the form

$$N\uparrow\ \to E/N\downarrow\ \to k_a\downarrow\ \to n_e\uparrow\ \to Q\uparrow\ .$$

Electron attachment to molecules can therefore cause acoustic-wave amplification in the direction normal to the electric field.[93]

This phenomenon has been observed for weak compression shocks (with Mach number in the range Ma $=1.001$–1.1) in an electron-beam-controlled gas discharge in CO_2 (Ref. 94). The amplification of the transverse shock was obtained in the range of E/N values which correspond to the rate of dissociative attachment process

$$e+CO_2\to O^-+CO$$

strongly increasing with E/N. A computer simulation[94] of this phenomenon by the equations of one-dimensional hydrodynamics has substantiated the experimental data.

A new mechanism of sound amplification in an externally-sustained gas discharge[95] relies on friction between electrons and neutral particles and is described by

$$\frac{\partial N}{\partial t}+\operatorname{div}(N\mathbf{V})=0,$$

$$N\ \mathrm{Ma}\frac{d\mathbf{V}}{dt}=-\nabla(p+p_e)+e\mathbf{E}(n_e-n_p),$$

$$\frac{\partial n_p}{\partial t}+\operatorname{div}[n_p(v_p+\mathbf{V})]=q_0N-\beta n_e n_p, \tag{22}$$

$$\operatorname{div}\mathbf{j}=0,$$

$$\operatorname{curl}\mathbf{E}=0,$$

$$\operatorname{div}\ \mathbf{E}=4\pi e(n_p-n_e),$$

where p_e is the electron pressure, q_0N is the specific rate of ionization. Having neglected the term $\operatorname{div}(n_pV)$ in the third equation of the system (22), the authors of Ref. 95 have drawn a wrong conclusion concerning the sound amplification possible in the transverse direction. An analysis of the system (22) with account for this term indicated that sound attenuates in this direction.[160]

This situation can also reverse in plasmas with negative ions provided that the electron attachment rate increases sharply with E/N. Substitution of k_an_eN for βn_en_p into the third equation of (22) results in a positive increment with the maximum value $\Gamma/\Omega\sim\hat{k}_ap_e/p$ ($k_a=\partial\ln k_a/\partial\ln(E/N)$) at frequencies $\Omega\sim\nu_a$.

This amplification of acoustic waves in the transverse direction is explained in the following way. An increase in N causes (at constant E) a decrease in E/N and in the attachment rate, and consequently in an increase in n_e. This leads to an increase in p_e which induces a variation of the velocity V due to the friction between electrons and neutral particles. This results in an increase in N due to the continuity of the medium. At frequencies $\Omega\sim\nu_a$ the variations in N and n_e are shifted in phase by about unity causing sound amplification. An experimental observation of this phenomenon is still an open question.

Acoustic instability which may grow at a high rate owing to the resonance interaction with the attachment instability has been predicted for an externally-sustained gas discharge.[96] Although the disturbances of hydrodynamic parameters increase steeply (with the increment of the attachment instability), they remain small in magnitude because of a significant difference between the velocities of acoustic and attachment instability disturbances. To achieve a resonance interaction between these instabilities the velocities must be equal to each other.[83]

4.4. Coupled detachment and thermal modes

A universal mechanism of instability which constricts gas discharge into a low-impedance arc-like channel is thermal in nature. In an electronegative gas, processes of electron detachment from negative ions colliding with active particles (see Sec. 2) can favor the thermal instability of the discharge plasmas;[62,75] the active particles produced in gas discharges include vibrationally and electronically excited molecules, atoms, and radicals.

Let us consider this effect, using an externally-sustained gas discharge and neglecting electron-ion recombination as an inferior process in comparison with electron attachment. Then, for low densities of active particles n_d, described by equation

$$\frac{\partial n_d}{\partial t}=k_g N n_e-\frac{n_d}{\tau_d}-\nu_d n_n, \tag{23}$$

(k_g is the collisional rate coefficient for the formation of active particles with apparent lifetime τ_d) the electron density is $q_0 N/\nu_a$. The time of relaxation for the active-particle density is generally much higher than that for the charged-particle density. Therefore, the densities of negative ions and electrons are

$$\begin{aligned} n_n&=\left(\frac{q}{\beta}\right)^{1/2}, \\ n_e&=\frac{q}{\nu_a}+\left(\frac{q}{\beta}\right)^{1/2}\frac{\nu_d}{\nu_a}. \end{aligned} \tag{24}$$

It should be mentioned that for $k_g N>\nu_a$ (this is generally true) the steady-state density of negative ions decreases steeply near the critical value of the specific rate of external ionization

$$q_{cr}=\beta(k_g N/\nu_a-1)^2 k_g^{-2}\tau_d^{-2}.$$

The rate constant k_g and frequency ν_a depend strongly on the parameter E/N which varies with gas expansion due to bulk heating. These dependences can be approximated by

$$k_g=k_{g0}\exp(A\theta),\quad \nu_a=\nu_{a0}\exp(B\theta), \tag{25}$$

where $\theta=\Delta T/T$ and A and B are constants determined by gas composition and E/N. In this notation, gas heating is described by the equation

$$\dot{\theta}=\nu_{Tp} n_e/n_{e0}. \tag{26}$$

The formation energy of active particles ordinarily exceeds the attachment threshold, therefore the relation $A>B\gg 1$ holds. Neglecting the loss processes of active particles in equations (23)–(26) results in θ that approaches infinity in the finite time

$$\tau_0=\frac{1}{\nu_{Tp}B}\int_1^{\infty}\frac{dx}{x^{A/B}+\lambda+1}, \tag{27}$$

with

$$\lambda=A\left(\frac{\beta}{q}\right)^{1/2}\frac{\nu_{a0}\nu_{Tp}}{k_d k_{g0} N}.$$

Usually $\lambda\ll 1$, and this reduces equation (27) to

$$\tau_0\approx\frac{\lambda\ln(1/\lambda)}{\nu_{Tp}A}\ll\nu_{Tp}^{-1}. \tag{28}$$

This equation agrees well with the calculation of τ_0 taking into account an electron-ion recombination and loss of negative ions.[97]

Under the circumstances the relaxation of plasma composition proceeds in two stages. In the first step, energy and active particles are slowly accumulated. This is followed by an explosion-like jump in the rate of electron detachment. As a consequence, the gas discharge contracts showing a rise of the electron density to a value of the order of $(q/\beta_{ei})^{1/2}\nu_a/q$ (Ref. 62). While this result has been obtained for a direct-current discharge, similar phenomena may be observed in a freely localized microwave discharge.[98] Dependences of k_g and of ν_a on ε_V (or vibrational temperature T_V) similar to relations (25) can also bring about this effect.

Experimental observation of this phenomenon presents difficulties because of the effect of other processes including stepwise ionization, superelastic collisions, vibrational relaxation, etc.

5. INSTABILITIES AND WAVES IN COLLISIONLESS PLASMAS

Collisions between particles, as a rule, cause attenuation of waves propagated in plasma. At low gas pressures, collisions play a negligible role and many modes of plasma oscillations are excited. Media of this sort occur in laboratory and natural environments including the lower ionosphere (D-layer) in which negative ions are important.

5.1. Linear waves

Negative ions affect only the lower frequency waves related to ion species in plasmas. Injection of negative ions modifies the dispersion law and induces new modes. We demonstrate this phenomenon for ion-acoustic waves.

In plasmas consisting of electrons and positive ions, ion-acoustic waves propagate only when $T_e\gg T_i$, where T_e and T_i are the temperatures of electrons and ions, respectively. With $T_e=T_i$ the velocity of ion-acoustic waves is close to the thermal ion velocity, and these waves experience strong Landau damping.

In plasmas with negative ions, the situation reverses and in the long-wavelength limit, the dispersion law derived by making use of the three-fluid pattern for isothermal plasma is[99]

$$(P-1)Z^4+\left(\frac{m_p}{m_n}+2-P\right)Z^2-2\frac{m_p}{m_n}=0, \tag{29}$$

where $P=n_n/n_p$, Z is the ratio of the wave phase velocity and the thermal velocity of positive ions, $u_p=(kT/m_p)^{1/2}$. Equation (29) yields two modes of propagation, a fast mode and a slow one. The slow mode is essentially the usual ion-acoustic mode, modified by the fact that some electrons are replaced by negative ions. In this case positive ions, negative ions, and electrons oscillate in phase. The

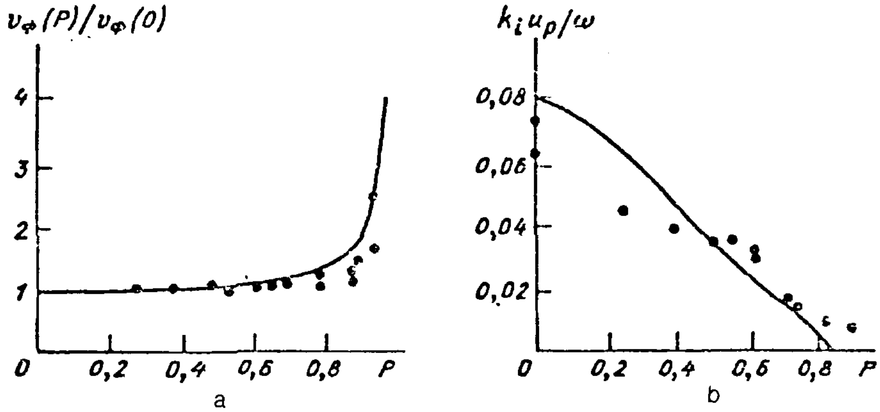

FIG. 16. Ion-acoustic fast mode in plasmas with reduced negative-ion density, P (Ref. 102). (a) Phase velocity; (b) damping at a frequency of 100 kHz. Dots are experimental data; solid lines are theoretical analyses.

new fast mode, on the other hand, has a markedly different behavior. The negative ion component oscillates by 180° out of phase with the positive ion component, whereas the electrons oscillate in phase with the positive ions. The phase velocity of the fast mode increases with P to become infinite at $P=1$. This growth corresponds to the transition from the relatively dispersion-free ion-acoustic mode in the absence of negative ions to a strongly dispersive ion-Langmuir mode in the absence of electrons.[99,100]

At high negative-ion densities the fast mode, slightly damped, can be easily detected. It was observed both in a gas-discharge plasma formed by Ar^+ and SF_6^- ions[101] and in a Q-machine plasma constituted by K^+ ions, SF_6^- ions, and electrons.[102] Experimental phase velocities[102] of the fast ion-acoustic mode at frequencies of 20–100 kHz are given in Fig. 16a. The phase velocity normalized to that at $P=0$ is shown as a function of negative ion concentration P. Wave damping data,[102] namely, the quantity $k_i u_p/\omega$, are shown in Fig. 16(b). Here k_i represents the imaginary part of the complex wave number, u_p is the thermal velocity of positive ions, and ω is the angular frequency. Curves given in the figures are predictions of kinetic theory.[99] While fluid theory gives similar results for the phase velocity, it fails when applied to wave damping. Experimental findings are seen to agree well with the theory. It should be noted that ion-acoustic oscillations in the night ionosphere can produce oscillations in the earth's magnetic field and in the nocturnal continuous emissions.[103]

In certain situations ion-acoustic waves in plasmas with negative ions may become unstable with respect to a transverse perturbation and bring about a self-focusing effect.[104] This effect can be explained qualitatively by the ponderomotive force which tends to expel the plasma from the wave potential. For $T_e \gg T_i$ electrons hardly respond to this force because of their high pressure. Positive ions alone can not move out of the wave potential independently. Hence, the charge neutrality condition is violated and the resulting electric field brings the ions back to the previous position. In plasmas with negative ions, these ions can leave the wave potential without violating the charge neutrality. As a result, the ion plasma frequency is lower and the permittivity is higher inside the potential than outside. The plasma itself acts as a convex lens, and focuses ion-acoustic waves. When ion temperature increases, ions hardly respond to the ponderomotive force and the region of self-focusing narrows.

In plasmas situated in external steady magnetic fields, electrostatic ion-cyclotron waves can be excited. The effect of negative ions on these waves was studied in Refs. 106 and 107. A dispersion law for these waves was derived[106] from the fluid pattern

$$\left[\omega^2-\left(\omega_p^2+k_x^2\frac{u_p^2}{1-P}\right)\right]\times\left[\omega^2-\left(\omega_n^2+k_x^2\frac{Pu_n^2}{1-P}\right)\right]=k^4\frac{Pu_p^2u_n^2}{(1-P)^2}, \tag{30}$$

where ω_p and ω_n are the cyclotron frequencies for positive and negative ions, respectively, $u_p^2=kT_e/m_p$, and $u_n^2=kT_e/m_n$. The magnetic field is directed along the positive z-axis; the wave propagates in the xz-plane with $k_z^2 \ll k_x^2$. Analysis of equation (30) shows that the electrostatic ion-cyclotron wave branches into low-frequency and high-frequency modes. For the former mode, the densities of charged particles vary in phase, whereas for the latter mode the density of negative ions is 180° out of phase. This is precisely the same behavior as has been discussed above for the fast ion-acoustic mode in plasmas with negative ions.

Experimental findings[107] in a Q-machine plasma consisting of K^+ ions, SF_6^- ions, and electrons have borne out this theory. Figure 17 shows the frequencies of the SF_6^- and K^+ modes measured as a function of P for a fixed magnetic field of 3500 G. The solid lines represent the fluid theory calculations based on equation (30).

In recent years there have been several theoretical studies of the effect of negative ions on other familiar instabilities of plasmas. For example, a tenuous electron-ion beam passing through a negative/positive ion plasma has been investigated in Ref. 100. If the beam is very tenuous, an electron beam instability is excited; when the beam density increases, a Buneman instability develops. The influence of negative ions on the Kelvin–Helmholtz instability has been examined in Ref. 108. Propagation of electromagnetic waves in negative ion plasmas has been studied in Refs. 109–112. There have been several investigations of the stimulated Brillouin (Refs. 113, 114) and Raman (Ref.

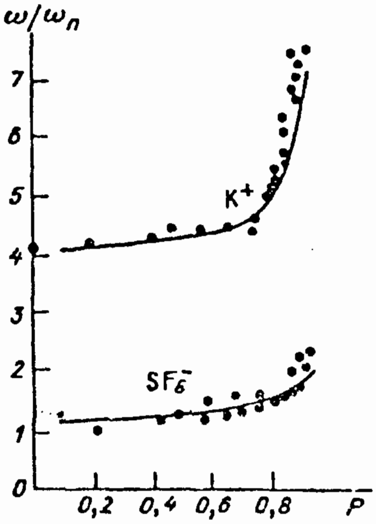

FIG. 17. Frequencies of the SF_6^- and K^+ modes measured as a function of percentage of negative ions (H=3500 G) (Ref. 107). Solid lines represent calculations.

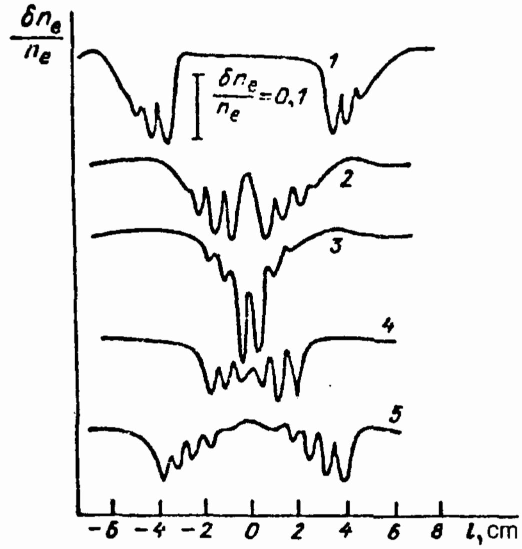

FIG. 18. Collision of rarefactive solitons propagating in plasmas with negative ions of P=0.48 (Ref. 122). t [μs]=(*1*) 20, (*2*) 25, (*3*) 27, (*4*) 30, and (*5*) 34.

115) scattering of electromagnetic waves in plasmas with negative ions. Both the magnitude of these negative-ion effects and the sign of these effects depend on relevant plasma parameters. Experimental verification of these instabilities in plasmas with negative ions is yet to be done.

5.2. Ion-acoustic soliton

Almost all studies of nonlinear waves in collisionless plasmas containing negative ions have dealt with ion-acoustic solitons. An exception is a theoretical investigation[116] of the propagation of nonlinear electromagnetic waves (ion cyclotron whistler) in a plasma situated in a magnetic field.

Ion-acoustic solitons in plasmas composed of electrons and positive ions have been extensively studied theoretically and experimentally (see, e.g., Refs. 117, 118). These waves are described by the Korteweg–de Vries equation in the form

$$\frac{\partial \varphi}{\partial \tau}+\varphi\frac{\partial \varphi}{\partial \xi}+\frac{1}{2}\frac{\partial^3 \varphi}{\partial \xi^3}=0, \tag{31}$$

where φ denotes, for example, the normalized wave potential. These solitons are compressions of plasma density, i.e., they have a positive electric potential. A broad compressive perturbation of a large amplitude breaks into a number of solitons as it propagates, whereas a rarefactive perturbation generates a subsonic wave train. No rarefactive or negative solitons can exist in plasmas without negative ions.

When negative ions are introduced into a plasma, the response of the plasma to disturbances is drastically modified owing to the large mass of negative ions. In such a plasma, ion-acoustic waves of long wavelength and weak nonlinearity are described by the following Korteweg–de Vries equation[119,120]

$$\frac{\partial \varphi}{\partial \tau}+\frac{1}{2}\left[\frac{3}{(1-P)S^4}-\frac{3P}{(1-P)\mu^2S^4}-1\right]\varphi\frac{\partial \varphi}{\partial \xi}+\frac{1}{2}\frac{\partial^3 \varphi}{\partial \xi^3}=0. \tag{32}$$

The time τ is normalized by the plasma frequency of positive ions. The distance ξ is normalized by the Debye length in the wave frame moving with the sound velocity

$$S=\left[\frac{1+(P/\mu)}{1-P}\right]^{1/2};$$

$\mu=m_n/m_p$. When the plasma has no negative ions, P=0, and equation (32) reduces to equation (31). It is interesting to note that the nonlinear coefficient of equation (32) may be negative at a sufficiently high density of negative ions and an ion-acoustic soliton of rarefactive nature may be possible instead of the compressional soliton.[119,120]

Rarefactive ion-acoustic (negative) solitons have been observed experimentally in plasmas, composed of Ar^+, SF_5^+, F^-, SF_5^- ions, and electrons.[121,122] The measured velocity, amplitude, and width of the rarefactive solitons agree with theoretical predictions based on equation (32). Head-on and overtaking collisions of these solitons have also been observed. Figure 18 shows that solitons are not affected by these collisions.

When the coefficient of the nonlinear term in equation (32) becomes zero, a higher-order term of the nonlinearity should be considered, which results in a modified Korteweg-de Vries equation for three-component plasmas[123]

$$\frac{\partial \varphi}{\partial \tau}+RS\varphi^2\frac{\partial \varphi}{\partial \xi}+\frac{S}{2}\frac{\partial^3 \varphi}{\partial \xi^3}=0, \tag{33}$$

where

$$R=\frac{1}{4}\left[\frac{15}{S^6(1-P)}+\frac{15P}{\mu^3S^6(1-P)}-1\right],$$

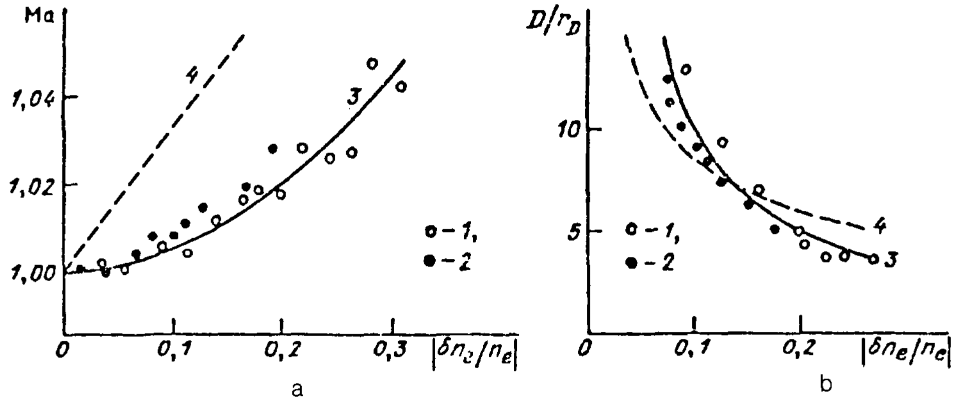

FIG. 19. (a) Velocities and (b) widths of compressive (open circles) and rarefactive (closed circles) solitons measured as a function of the amplitude (Refs. 124, 125). The solid line refers to equation (33); the dashed line refers to equation (32).

$$P=\frac{n_{\mathrm{n}}}{n_{\mathrm{p}}},\quad S=\left[\frac{1+(P/\mu)}{1-P}\right]^{1/2}$$

is the ion-acoustic velocity normalized to $(kT_e/m_p)^{1/2}$. The charge is assumed neutral and the ion temperature is neglected. Equation (33) has both a multisoliton solution and a single-soliton solution which can be written in the form

$$\varphi=\varphi_0\,\mathrm{sech}[(\tfrac{1}{3}R)^{1/2}\varphi_0(\xi-\tfrac{1}{6}RS\varphi_0^2\tau)]. \qquad (34)$$

While equation (32) admits either compressive or rarefactive solitons, equation (33) is independent of the sign of φ, that is, it allows both compressive and rarefactive solitons to propagate. These predictions have been supported by experiments,[124,125] both compressive and rarefactive solitons were observed at a critical density of negative ions. What is more, head-on collisions did not change the form of the modified solitons.

According to equation (34) the Mach number Ma and the width D of modified solitons are

$$\mathrm{Ma}=1+\tfrac{1}{6}R\varphi_0^2, \qquad (35)$$

$$\frac{D}{r_D}\left|\varphi_0\right|=(3/R)^{1/2}, \qquad (36)$$

(r_D is the Debye radius). The characteristics of modified solitons are different from those of the usual solitons. The difference Ma-1 (equation (35)) is proportional to the square of the amplitude φ_0, whereas for usual solitons it is proportional to the amplitude. The widths of modified solitons (equation (36)) and usual solitons are inversely proportional to the amplitude and to the square root of the amplitude, respectively. Velocities and widths of modified solitons have been measured in Refs. 124, 125 to make a quantitative comparison with the theory. Experimental evidence and theoretical values derived using equations (35) and (36) are presented in Figure 19. The experimental data are consistent with the predictions of the simple theory based on equations (33) and (32). Recently some special features of this phenomenon in plasmas with negative ions have been reported. Large-amplitude ion-acoustic solitons were considered in Ref. 126; the condition $R>0$ was proved and the description was generalized to plasmas constituted by electrons and ion species, each having its own mass, charge and temperature in Ref. 127. Transition from usual solitons to modified solitons was investigated in detail.[128] The effect of ion beams on solitons in plasmas with negative ions was considered in Ref. 129, whereas cylindrical and spherical ion-acoustic solitons were studied in Refs. 130, 131. Finally, the propagation of solitons in a relativistic plasma containing negative ions was analyzed in Ref. 132.

6. NEGATIVE IONS IN MODERN TECHNOLOGIES; ENVIRONMENTAL IMPLICATIONS

Negative ion processes play an important role in many areas of modern technology[1,133] including a variety of gas discharges. Electron attachment to molecules in electronegative gases decreases plasma conductivity and electrical current, and may excite instabilities as described above.

Relevance of negative ions to gas-discharge physics can be demonstrated with the electrical breakdown of gases. If an electrical field is applied to a gas it endows initiating electrons with energy and can produce avalanche ionization. For a uniform field, the breakdown criterion can be written as[65,134]

$$\nu_i(E)=\nu_d(E)$$

where ν_i is the ionization frequency, and ν_d is the frequency of electron loss. In electronegative gases, electrons attach to molecules and increase the breakdown threshold.

In specific cases, negative ions appear to be a source of electrons which initiate breakdown. For example, electron-ion pairs are created in atmospheric air as a result of background (α, β, γ and cosmic) radiation. Nevertheless, free electrons are removed because of a strong three-body attachment to O_2 molecules (process (5)). In order to initiate an electrical discharge in air, one has to free electrons from their bound states. This can be done by collisional electron detachment from negative ions which are accelerated in an electric field (the process inverse to (5)). This process has generally little or no effect on the breakdown threshold, yet it can sharply increase the breakdown time-lag.[134]

Gases with active particles are a special case because these particles can decompose negative ions and release electrons. This process decreases the apparent attachment rate constant and lowers the breakdown threshold. For instance, the formation of O_3 molecules in the prebreakdown stage can lead to pronounced reduction of the breakdown field in atmospheric air[162] due to the process

$$O^- + O_3 \rightarrow 2O_2 + e.$$

A drastic decrease of the breakdown threshold in air in a nonuniform field can also be caused by the production of O atoms[163] and excited $O_2(a^1\Delta_g)$ molecules[164] with further associative detachment of electrons from O^-.

Knowledge concerning negative ion processes is of great importance to many areas of modern technology. The available data on low-energy electron-molecule interactions may be used as a basis to optimize conventional gaseous dielectrics and to design new ones. An effective way to retard gas breakdown consists in electron attachment to gas molecules forming negative ions. In general, electron attachment to polyatomic molecules is quite effective at low energies. For this reason, mixtures of polyatomic gases are normally used as dielectrics in order to obtain an optimal combination of electron attaching and electron decelerating properties. Many technologies, including pulsed power gas switches, rely on the rapid change of properties of the gaseous matter from insulator to conductor, and vice versa. Optical enhancement of electron attachment (see Sec. 2) can be the basis for making the transition in fast switching or modulation of the conductivity characteristics of gaseous media from the microsecond to the nanosecond range.[133,135]

The main channel of producing beams of negative H^- (D^-) ions which are important for controlled thermonuclear fusion, is supposed to be dissociative electron attachment to vibrationally excited hydrogen molecules.[136] Many techniques for fine analysis of compounds in gases use basic electron and negative-ion reactions converting gas molecules into ions in order to improve their detection.[137] Finally, one of the main channels for the production of population inversion in excimer lasers is three-body recombination of negative ions with positive ions.[138]

The negative ion processes can be of importance in many areas of ecology and environment. Considerable attention has been drawn to these areas in the last few years. While some ideas in this field are still questionable, they will be considered below because of their importance.

There are significant distinctions between negative ions and other particles. First, charged-particle reaction rates are quite different from that of uncharged particles. Second, the binding energy of an outer electron in a negative ion is much smaller than the ionization potential or chemical binding energy of a molecule, and the ion can therefore be easily decomposed by an external force.

Irradiation by an electron beam or treatment by a gas discharge has been tested as a means for removing SO_2 and NO_x pollutants from the stack gases of power plants (see, e.g., Ref. 139). This pollutant removal technique involves several stages. Fast electrons produce highly reactive species (ions, radicals, excited fragments) which take part in the oxidation of SO_2 and NO_x to form nitric and sulphuric acids. By injection of ammonia, these acids are neutralized

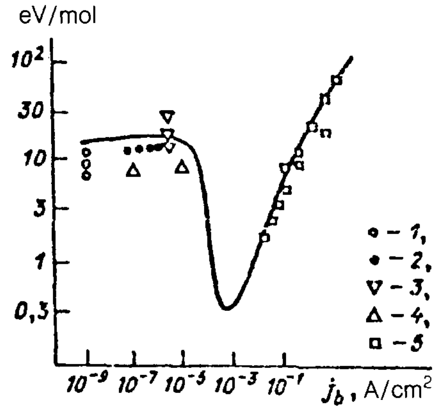

FIG. 20. Energy input for SO_2 oxidation as a function of the electron beam current. Experimental data: (*1*) (Ref. 143), (*2*) (Ref. 144), (*3*) (Ref. 145), (*4*) (Ref. 146), and (*5*) (Refs. 141, 142). Solid line is for a model calculation (Ref. 141).

and form an aerosol consisting of ammonium salts. The products of this process are of commercial value.

It has been shown that the high efficiency of SO_2 oxidation can be obtained through a catalytic cycle of negative particles.[140–142] One possible scheme can be written as

$$e + O_2 + M \rightarrow O_2^- + M.$$

$$O_2^- + SO_2 \rightarrow SO_2^- + O_2,$$

$$SO_2^- + O_2^* + M \rightarrow SO_4^- + M,$$

$$SO_4^- + O_2^* \rightarrow SO_3 + O_3^-,$$

$$O_3^- + SO_2 \rightarrow SO_3^- + O_2,$$

$$SO_3^- + H_2O \rightarrow e + H_2SO_4.$$

In air polluted with SO_2, electrons attach to O_2 molecules and form negative ions. Collisions with molecules, including vibrationally excited O_2 molecules, convert O_2^- ions to other negative ions, and associative detachment ultimately gives rise to free electrons and acid molecules. Then the electrons become involved in another cycle, and so on.

The advantage of negative ions over radicals is a threshold-free reaction of chain continuation. Positive ions would not suit this purpose because of the difficulty to close the catalytic cycle. This results from the high ionization potential of these species.

Experimental energies expended for SO_2 oxidation in a stack gas[141–146] are shown as a function of electron beam current in Fig. 20 along with a theoretical curve[141] which takes into account the negative-particle catalytic cycle. There is reasonable agreement between theory and experiment. The resonance form of this dependence can be explained as follows. At a high electron-beam current the catalytic chain is effectively terminated by the ion-ion neutralization, while at a low current, excited molecules are quenched by neutral particles. The data in Fig. 20 show that the negative-ion processes can sharply increase the efficiency of pollutant removal from stack gases.

Other air pollutants, among them freons (chlorofluorocarbons CCl_4 (Ref. 147), CCl_3F, and CCl_2F_2 (Ref. 148) can also be removed by plasma treatment. Unlike SO_2 and NO_x, freons are inert gases and their molecules react weakly (with one exception) with active species. Thermal electrons attach effectively to freon molecules ($e+CCl_4 \rightarrow Cl^- + CCl_3$, etc.) and decompose them. Then, the electron detachment in humid air can be due to fast reactions such as

$$Cl^- + H \rightarrow e + HCl,$$

which close the catalytic cycle. A theoretical analysis[147] and experimental data[148] confirm the possibility of cleaning the environment from freons by electron beams or microwave discharges. Nevertheless, the important problem of ultimate products of these treatments has been poorly studied.

At present there are many investigations of the negative ion effect on the earth's ozone layer. It is well known that some species including ClO_x, NO_x, and HO_x can catalytically destroy ozone.[149] The existence of a negative-ion catalytic cycle of the ozone decomposition has also been pointed out.[150] In the simplest form, this cycle can be written as

$$O_2^- + O_3 \rightarrow O_2 + O_3^-,$$

$$O_3^- + O_3 \rightarrow O_2^- + 2O_2.$$

This negative ion cycle is supposed to be important only at a high degree of air ionization because of the small rate coefficients.[151,152] However, this cycle may have a more complicated form[151]

$$X^- + O_3 \rightarrow XO^- + O_2,$$

$$XO^- + O_3 \rightarrow X^- + 2O_2$$

or

$$XO^- + O \rightarrow X^- + O_2,$$

and owing to the high efficiency of these reactions it could become more important for ozone decomposition.

Negative-ion processes can play also a positive role in the chemistry of atmospheric ozone. The main reason for the ozone layer destruction has been found to be the Cl catalytic cycle induced by an increased atomic chlorine density in the upper atmosphere.[149,153] It has been proposed to stop the stratospheric ozone destruction by converting neutral chlorine atoms into negative ions.[154–157] They are less reactive because the outer shell of Cl^- is filled. Negative ions could then be removed by electrostatic or electromagnetic fields. A computer simulation of atmospheric chemical kinetics involving more than 1000 reactions has shown that the beneficial effect on the negative ion conversion of active chlorine could compensate for the effect of increased chlorine density.[156,157]

Originally it had been proposed to remove chlorine atoms by making use of the electromagnetic wave effect on the lower-ionosphere plasma.[154] The plasma electrons are to be heated by an electromagnetic wave radiated by a ground-based power transmitter. The density of electrons increases with electron temperature owing to a decrease in the coefficient of electron-ion recombination. This causes the conversion of chlorine atoms into chlorine negative ions to increase. However, an analysis of this scenario[158] has shown that the electron-temperature dependence of attachment essentially decreases the effect in the earth's ionosphere.

Nevertheless, the development of this proposal is in progress. Recently injection of electric charges into the atmosphere has been suggested to produce from an airplane, rocket, or balloon[155] using a long wire or antenna biased at a sufficiently high negative voltage to release electrons by field emission. Another method of injecting low-energy electrons into the atmosphere is to use photoelectric emission of electrons from a metal surface under the action of a solar radiation.[155]

The idea of ozone conservation by the electron attachment to chlorine atoms is being tested in laboratory conditions. However, this idea is a challenge because of many difficulties that may be encountered in attaining the final goal.

Another method of cleaning the environment from freons[148] proposes to dissociate freon molecules in the troposphere so that the final products will fall out on earth with precipitation. This would prevent freon transport from the troposphere to the stratosphere. One of the main mechanisms of freon decomposition is supposed to be the dissociative attachment of electrons created by a freely localized microwave discharge. It is important that active particles (radicals and excited molecules) produced in the gas discharge cause electron detachment from negative oxygen ions and decrease the apparent electron attachment to O_2. Preliminary experimental results are rather encouraging.

Finally, there is a very important issue of the effect of negative atmospheric ions on human health,[159] but this problem is beyond the scope of this work.

7. CONCLUSIONS

Introduction of negative ions into plasmas affects the charged-particle composition and some important properties of the medium. Negative ions alter the transport of charged particles in plasmas and influence the stability of gas discharge. They modify the dispersion law of waves and branch some waves into fast and slow modes. The advances in this area are connected with the progress in many areas of modern physics, such as collisions of charged particles with atoms and molecules, transport processes in partially ionized plasmas, physics of gas discharge, and nonlinear physics. The success achieved has been stimulated by recent applications of negative-ion processes. Some of these applications (gaseous dielectrics, negative ion sources, etc.) have been the subject of international scientific conferences.

This review has been concerned with plasmas consisting of electrons and ions. However, many phenomena described above can be observed in other media, including ion-ion plasmas, positrons in a gas, and semiconductor plasmas. These subjects are beyond the scope of this review.

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