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Nonlinear vibrational excitation waves in a molecular plasma with negative ions

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The stability of chemically active multi-component plasma with negative ions produced in collisions between electrons and vibrationally excited molecules is investigated theoretically. The conditions are found for which sections with a negative differential conductivity exist on the volt-ampere characteristics (VAC). The characteristic time of development of the instability is derived from the dispersion equation for small perturbations. It is shown that during the nonlinear stage of the discharge a vibrational excitation wave is formed and transforms the system into a stable stationary state. The structure and velocity of the traveling wave front are found. The results explain the experimentally observed onset of instability of a molecular plasma in which nitrous oxide is introduced.

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There is a large class of collective phenomena which are some way or other associated with the presence of an internal structure of the plasma particles. As well known examples, we can mention ionization waves¹ and various thermonuclear instabilities (see, for example, Ref. 2).

The singularity of a low-temperature plasma is that the electron, along with motion in a continuous energy spectrum, can execute transitions in the space of discrete states. Here localization of the electron on a neutral particle frequently turns out to be energetically more favorable than its existence in the free state.³ A negative charge in such a plasma will be connected both with the electron and with the ion components, and the concentration of the latter can significantly exceed the electron concentration, especially in a plasma of molecular gases.⁴ The presence of negative ions leads to the appearance of specific collective processes in the plasma. Thus, for example, in discharges in O₂ and CO_2 , and also in CO_2 -N₂-He mixtures, instability of dissociative sticking, observed in the form of strata, ⁵⁻⁸ is most effectively excited. The reason for its appearance is the dependence of the rate of dissociative sticking k_a on the electron temperature T_e . However, if the dissociative sticking (DS) reaction $AB + e \frac{k_d (T_g)}{2}A + B^$ has the activation energy $E_{th} = D - U \leq kT_e$ (D is the energy of dissociation of the molecule AB, and U is the energy of affinity to the complex B), then $\partial \ln k_a / \partial \ln T_e$ $\ll 1$ and the excitation of DS the mode becomes impossible.^{5,7,9,10} In this work we shall show that another mechanism of instability of DS is possible in a plasma of molecular gases, and can be realized even at E_{th} $\leq kT_e$.

It is known that the relative contribution of the vibrationally excited molecules to the total rate of production of negative ions can be large, in spite of their relative small population. Such an effect is observed in the formation of O[°] from O₂ and CO₂; in N₂O it appears more strongly—the quantity k_a increases by four orders of magnitude when the vibrational temperature T_V charges from 30 to 1000 K.¹¹ The reason for such a strong $k_a(T_V)$ dependence is connected with the important role of flexural vibrations of the molecule (0/0) in the DS process. With increase in the degree of excitation of the flexural mode, the conditions for stabilization of the negative ion relative to electron emission are improved. Along with this, the capture of low-energy electrons becomes energetically possible, which also leads to an increase in the rate of DS, since the capture cross section is proportional to v_e^{-2} (Ref. 12) $(v_e$ is the velocity of the electron taking part in the DS reaction).

The existence of such a phenomenon leads to an instability, the necessary and sufficient conditions for which, and also its nonlinear stage, will be the subject of our analysis. As the model we consider a discharge in an N_2O -He mixture with a pressure of the order of several dozen torr.

KINETICS OF THE PROCESSES WITH PARTICIPATION OF CHARGED PARTICLES

Since the number of reactions that occur in such a binary system is very large, while their contribution to the balance of the number of charged particles is different, we limit ourselves to consideration only of the most important reactions (see the table). We neglect the effect of the dissociation products on the change in the composition of the initial gas mixture, which is valid for time intervals $\leq 10^{-1}$ sec.^{16,17} Taking into account the volume character of the ionization-recombination processes, and neglecting the radial distribution, we write down the stationary equations of the balance of the density of the charged particles in the following form:

$$n(n_{e}k_{i}+S)-n_{e}n_{+}k_{r}e-n_{m}n_{e}k_{a}+n_{m}n_{-}k_{d}=0,$$
(1)

$$n_m n_s k_a - n_m n_- k_d - n_- n_+ k_r^i = 0,$$
 (2)

$$n_{+}=n_{e}+n_{-}.$$
 (3)

Here n_e , n, and n_{-} are the concentrations of the electrons and neutral particles and total concentration of negative ions, $n = n_a + n_m$, n_a is the concentration of atoms of helium, n_m is the concentration of molecules of nitrous oxide, k_i is the effective rate of ionization, k_r^e and k_r^i are the coefficients of electron-ion and ion-ion recombination, k_d is the rate of destruction of the negative ion. The possibility of the existence of an external source of ionization is reflected in the equations by the quantity S.

TABLE I.

Type of reaction	Reaction rate constant (cm ³ -sec ⁻¹)*	Literature
$\begin{array}{c} e + N_2 O + 2e + N_2 O + \\ e + N_2 O + N_2 + O - \\ O - + N_2 O + N O + N O - \\ N O - + N_2 O + N O + N_2 O + e \\ N O - + N_2 O + N_2 O + N_2 O + e \\ N_2 O + N_2 O + N_3 O + N_2 O + \\ N O - + N_3 O + N O + N_2 O \\ e + N_2 O + N O + N \end{array}$	Given in the form of a graph $3 \cdot 10^{-8} \exp \left(-4600/T_{\nu}\right)$ $2,2 \cdot 10^{-10} \exp (3,8 \cdot 10^{-12} \exp (3,8 \cdot 10^{-12} \exp (-1100/T_{\nu}))$ $4 \cdot 10^{-10} \exp \left(-1100/T_{\nu}\right)$ $9 \cdot 10^{-6} T_{-\frac{1}{2}}$ $6.5 \cdot 10^{-8} T_{e}^{-\frac{1}{2}}$	[⁵] [¹⁴] [¹⁴] [¹⁵] [¹⁴] [¹⁴]

* T_e is expressed in eV, T_V , and T in deg. K. **The cited values correspond to T = 300 K.

***The dependence of the detachment rate constant on T_{V} is due to the participation of vibrationally excited molecules in the reaction: $A^{-}+N_{2}O(V=1) \rightarrow A+N_{2}O(V=0)+e$. Having in mind discharge conditions, where the evolution of the translational-rotational and vibrational degrees of freedom take place within a time that is much greater than the characteristic times of relaxation of the electron temperature and the concentration of the charged particles, we write down the equations for the gas, vibrational, and electron temperatures in the form of the following system:¹⁾

$$d_{i}(n\varepsilon(T)) + (n\varepsilon(T) + P) \nabla \mathbf{u} = \frac{n_{m}}{\tau_{v\tau}} (\varepsilon_{v}(T_{v}) - \varepsilon_{v}(T)) - \nabla g_{\tau}, \qquad (4)$$

$$d_{t}(n_{m}\varepsilon_{v}(T_{v})) + n_{m}\varepsilon_{v}(T_{v})\nabla \mathbf{u} = \mathbf{j}\mathbf{E} - \frac{n_{m}}{\tau_{vr}}(\varepsilon_{v}(T_{v}) - \varepsilon_{v}(T)) - \nabla g_{v}, \qquad (5)$$
$$\mathbf{j}\mathbf{E} = nn_{v}k_{v}kT_{e}, \qquad (6)$$

which, together with Eqs. (1)-(3) form the complete set of the initial equations. In Eqs. (4)-(6), $\varepsilon = (3n_a)$ $+5n_m)kT/2n$ is the mean translational-rotational energy per particle, $\varepsilon_v(T_v) = \overline{\varepsilon}(\exp(\overline{\varepsilon}/kT_v) - 1)^{-1}$ is the mean vibrational energy per molecule, $\overline{\varepsilon}$ is the value of the vibrational quantum, $\tau_{vT} = (n_a k_{10} (1 - \exp(-\overline{\varepsilon}/kT)))^{-1}, k_{10}$ is the relaxation rate of the N₂O molecules on the He atoms, P = nkT, u is the mean mass velocity, g_T $=-\Theta_T \nabla T$, $\mathbf{g}_{\mathbf{v}} = -\Theta_{\mathbf{v}} \nabla T_{\mathbf{v}}$; Θ_T and $\Theta_{\mathbf{v}}$ are the coefficients of thermal conductivity, k_v is the rate of vibrational excitation by direct electron impact, j is the current density, and E is the electric field intensity. Writing the balance equations in the form (4) implies that the energy release in the system takes place with the excitation of the vibrational degrees of freedom of the molecules, which then relax on the atoms of the buffer gas, which also dissipates the heat.

STATIONARY STATES

Given the values of the current density and the intensity of the external ionizer, we now find the stationary solutions of the set (1)-(6). As an example, we choose the mixture 0.2 $N_2O-0.8$ He at a pressure of 20 Torr, located in a tube of diameter d = 2 cm and wall temperature $T_0 = 200$ K. Here we use the following simplifying assumptions. We take the diffusion of the vibrationally excited molecules into account approximately by introducing the probability of diffusion decay according to Ref. 19. Moreover, as estimates show, at the typical values of the energy input $10-50 \text{ W/cm}^3$, the gradients of the gas temperature are small. Therefore, the term describing the thermal conductivity can be put approximately in the form $\Theta_T(T - T_0)/d^2$, where $\Theta_T = 5 \times 10^{-4}$ erg-cm⁻¹ = sec⁻¹ - deg^{-1,20} By the same token, we disregard the radial distribution of the temperature, and hence of the particles.

The relaxation of the vibrations of the N₂O molecule on He is well described by the Landau-Teller model, with a deactivation constant k_{10} equal to $4 \times 10^{-10} \exp(-80$ $T^{-1/3})$ cm³-sec⁻¹. As for the rate of vibrational excitation by direct electron impact, there are no reliable experimental and theoretical data on the $k_V(T_e)$ dependence for most molecules. It is known only that the function $k_V(T_e)$ has a maximum value of the order of 10^3 cm³sec⁻¹ in the region of 2 eV and depends weakly on the electron temperature at the higher energies.²¹

The results of numerical solution of the set of equa-



FIG. 1. Family of voltampere characteristics (continuous curves) and the dependence of the vibrational temperature T_v on the electron temperature T_e (dashed) for selfmaintained discharge at various values of a; k_d $= a \exp(-1100/T_v)$: 1) $a = 8 \times 10^{-10}$, 2) $a = 4 \times 10^{-10}$; 3) $a = 2 \times 10^{-10}$, 4) a = 1 $\times 10^{-10}$.

tions (1)-(6) in the stationary case enables us to construct the static volt-ampere characteristics (VAC) shown in Fig. 1 (self-maintained discharge) and Fig. 2 (non-self-maintained discharge).

For the self-maintained discharge, calculations have been carried out at various values of the pre-exponential factor a of the constant of destruction of the negative ions. This allows us to assess qualitatively the role of the ion-molecule reactions of fragmentation and destruction of the negative ions, which is not taken into account in our scheme because of the absence of data on the form of the VAC. As is seen from Fig. 1, at $a \le a^* = 6$ $\times 10^{-10}$, a section appears on the VAC with negative differential resistance, the absolute value of which increases with decrease in k_d .

At $S \neq 0$, the presence of a decreasing portion of the VAC is not as sensitive to the value of k_d and the production of a negative differential resistance takes place over a very wide range of stationary parameters.

Formation of a portion with

$$\sigma_{d} = \frac{\partial j}{\partial E} = \sigma_{0} \left(1 + \frac{E}{n_{e}} \frac{\partial n_{e}}{\partial E} \right) = \sigma_{0} \left(1 + 2 \frac{\partial \ln n_{e}}{\partial \ln T_{e}} \right) < 0$$

takes place because of the increase in the effective mass of the negative carriers with increase in the electric field (concentration nonlinearity), and in this sense it is similar to the recombination mechanism of formation of an N-shaped VAC in semiconductors with repelling centers (for example, in Ge alloyed with Au, Ref. 19).

A uniform state of the plasma over the portion with $\sigma_a < 0$ is unstable relative to inhomogeneous fluctuations



FIG. 2. Family of voltamplitude characteristics (continuous curves) and the dependence $T_V(T_g)$ for various values of the intensity of the external ionizer $(A = 4 \times 10^{-10})$; 1) S = 2.5 $\times 10^{-1}$, 2) $S = 2.5 \times 10^2$, 3) $S = 2.5 \times 10^{-3}$, 4) S = 2.5 $\times 10^{-4}$. of the field; the characteristic time of development of the instability can be found from linear analysis.

ANALYSIS OF THE INSTABILITY

We investigate the instability of the stationary states of the system (1)-(6) relative to small perturbations of the form $\exp(i\omega t - i\mathbf{x} \cdot \mathbf{r})$, where ω is the complex frequency in a system of coordinates moving with the gas, and \mathbf{x} is the wave vector. We recognize that the characteristic time of the problem is greater than the time of propagation of the sound perturbation, while the direction of maximal growth of the perturbation in the case of N-shaped VAC is identical with the direction of the stationary current flow.¹⁹ This enables us, by using the condition P = const, to write down the onedimensional dispersion equation in the form

$$\omega^2 - i\omega b - c = 0.$$

Here

$$\begin{split} b &= \tau_{0r}^{-1} + \tau_{0r}^{-1} + \tau_{rr}^{-1} + \tau_{r}^{-1} (2 + \hat{\tau}_{vr}) + \tau_{v}^{-1} (n_{e} | T_{v}), \\ & c &= \tau_{vr}^{-1} (\tau_{0r}^{-1} + \tau_{r}^{-1} (1 - (n_{e} | n))) \\ & + (\tau_{0r}^{-1} + \tau_{r}^{-1} (2 + \hat{\tau}_{vr})) (\tau_{0v}^{-1} + \tau_{v}^{-1} (n_{e} | T_{v})), \\ (n_{e} | T_{v}) &= R^{-1} (1 + \hat{k}_{v}) (k_{r}^{+} (n_{+} + n_{-}) + k_{r}^{*} n_{e}) (k_{d} \hat{k}_{d} (n_{-} / n_{e}) - k_{a} \hat{k}_{a}) n_{m}, \\ & (n_{e} | n) &= R^{-1} (1 + \hat{k}_{v}) (k_{s} k_{r}^{*} (n_{e} / n_{-}) - k_{s} k_{r}^{*} (n_{-} / n_{e}) n_{m} n_{+}, \\ R &= 2nk \hat{k}_{i} (k_{r}^{i} n_{-} + k_{o} n_{m} (n_{e} / n_{-}) + (1 + \hat{k}_{v}) ((k_{r}^{*} k_{d} (n_{-} / n_{e}) + k_{r}^{*} k_{a} (n_{e} / n_{-})) n_{m} n_{+} + S (n / n_{e}) (k_{a} m_{m} (n_{e} / n_{-}) + k_{r}^{*} n_{-})), \end{split}$$

(7)

 τ_{T} and τ_{V} are the characteristic times of heating of the gas and of the vibrational degrees of freedom,¹⁸

$$\tau_{\Theta V} = \frac{n_m (\partial \varepsilon_V / \partial T_V)}{\Theta_V \kappa^2} \qquad \tau_{\Theta T} = \frac{(5n_a + 7n_m)k}{2\Theta_T \kappa^2}$$

are the characteristic times of the thermal conductivity, and $\hat{f}(x) \equiv \partial \ln f/\partial \ln x$.

If the rate of dissociative sticking does not depend on the vibrational temperature, then the dispersion equation (7) has stable solutions, excepting only the case in which $-\tau_T^{-1}(2+\hat{\tau}_{VT}) > \tau_{ev}^{-1} + \tau_{eT}^{-1} + \tau_{VT}^{-1}$, which corresponds to the excitation of a thermal mode.^{18, 22, 23}

At $\hat{k}_{\sigma}(T_{V}) \neq 0$, the necessary condition for the development of the DS instability is the satisfaction of the inequality $(n_{\sigma} | T_{V}) < 0$ or, which amounts to the same thing,

$$n_{s}k_{a}\hat{k}_{a} > n_{-}k_{d}k_{d}.$$
(8)

The inequality (8) determines that region of the stationary parameters in which the destruction of negative ions with formation of electrons cannot compensate the local increase in the resistance of the medium because of processes of binding of the electrons by the DS. Under our conditions $\tau_{\Theta V}^{-1} < \tau_{\Theta T}^{-1}$, τ_{VT}^{-1} , which allows us to write down the following expression for the increment:

$$(=-\tau_{v\tau}^{-1}-\tau_{v}^{-1}(n_{e}|T_{v})).$$
(9)

The mechanism of this instability is based on the fact that the local perturbation of the vibrational temperature leads to density and temperature fluctuations of the electrons in phase, making possible the further increase in T_{ν} . The development of the perturbations has an aperiodic character, the characteristic time of growth amounts to a quantity of the order of 10^{-3} sec. The second solution of Eq. (7) is an increasing one if the local energy release in the gas, as a consequence of the vibrational relaxation, is not compensated by the thermal conduction

$$\tau_{r}^{-1}(2+\tau_{vr})-\tau_{v}^{-1}(n_{e}|T_{v}) > \tau_{\Theta r}^{-1}+\tau_{\Theta v}^{-1}+\tau_{vr}^{-1}.$$
(10)

In our case, it is damped out in a time τ_{er} .

The effect of the source of the ionization on the DS instability reduces to the following. A decrease in the characteristic time of vibrational excitation takes place with increase in S, since $\tau_V^{-1} \sim n_e^{-S}$; here $(n_e | T_V)$ does not depend on S. Thus the value of the increment increases while the region of the parameters at which the plasma loses stability widens, which is illustrated in Figs. 1 and 2.

PROPAGATION AND STRUCTURE OF FINITE PERTURBATIONS

The exponential growth of small perturbations as a result of the considered DS instability is limited during the nonlinear stage by the decrease in the rate of vibrational relaxation of the molecules by electron impact, by the increase in the specific contribution of the reactions accompanying the destruction of the negative ions, and by the stabilization as a result of thermal conductivity. For an analysis of the state that develops in the nonlinear stage, we use the fact that, as results of numerical calculations show. the gas temperature changed within only 5% when the plasma parameters were varied in a wide range. This makes it possible to use the approximation of "infinite thermal conductivity," and to assume the gas temperature to be constant. In this case the nonlinear equation which describes the evolution of the perturbations if edge effects are neglected will be the equation for the vibrational temperature:

$$\frac{\partial T_{\mathbf{v}}}{\partial t} - D \frac{\partial^2 T_{\mathbf{v}}}{\partial z^2} = f(T_{\mathbf{v}}), \quad -\infty < z < \infty,$$

$$T_{\mathbf{v}}(z, 0) = T_{\mathbf{v}0}(z),$$
(11)
(12)

where D is the coefficient of vibrational thermal diffusivity, and $f(T_v)$ is the nonlinear source that determines the rate of local energy release due to the set of inelastic processes and chemical reactions. At the chosen type of discharge (self-maintained, non-selfmaintained), the function $f(T_v)$ allows the existence, depending on the chosen stationary flow, of a different number of zeros. We therefore consider two cases:

A. Non-self-maintained discharge. In this case, at $S > S^*$ (under our conditions $S^* \approx 10^{-3} \sec^{-1}$) the source function $f(T_V)$ vanishes at two points $T_V^{(1)}$ and $T_V^{(2)}$, with $T_V^{(2)} > T_V^{(1)}$. Here the nonlinear equation for the function $y = (T_V - T_V^{(1)})/(T_V^{(2)} - T_V^{(1)})$ takes the following form:

$$y_i - Dy_{ii} = f(y), \quad y(z, 0) = y_0(z),$$

f(0)=f(1)=0, f'(0)=\alpha>0, f'(y)<\alpha, 0< y \le 1. (13)

We note that an equation of similar type was first used by Kolmogorov, Petrovskii and Piskunov²⁴ in connection with the biological problem of the propagation velocity of the genes that has an advantage in the



struggle for existence. The process of thermal propagation of flame in a homogeneous system is also described with its help. $^{25, 26}$

The character of the asymptotic behavior of the solution of Eq. (13) as $t \to \infty$ is determined by the form of the initial perturbation of $y_0(z)$. Actually, if the characteristic dimension \overline{z} of the initial perturbation satisfies the inequality

$$D/\overline{z}^{2} > \max_{0 \le y \le 1} (f(y)/y), \tag{14}$$

then, as $t \to \infty$, we have $y(z, t) \to 0$. In the opposite case, the local-perturbation evolution described by Eq. (13) leads to the formation of two diverging wave fronts of the Riemann type:

$$\lim_{t \to \infty} y(z, t) = y(z - ct + z_1) + y(-z - ct + z_2) - 1,$$
(15)

where c is the propagation velocity of the front, max y=1, min y=0, and z_1 and z_2 are constants. The quantity c represents the spectrum of possible velocities of wave front propagation and is limited below: $c \ge c^* = 2(D\alpha)^{1/2}$; however, only the lower point of the spectrum corresponds to the asymptotically stable solution.

Approximating the source function by a quadratic polynomial, we represent (13) in dimensionless variables. Here the structure of the front can be found from the equation

$$y_{xx} = -2y_{x} + y(y-1),$$
(16)

$$y|_{x+-\infty} = 1, \quad y_{x+\infty} = 0,$$

$$x = (z-c^{*}t) D^{-t_{0}} \alpha^{-t_{0}}.$$

Figure 3 gives the numerical solution of Eq. (16). The effective width of the front, defined as the distance between the abscissas of the points where the tangent at the inflection point (y''=0) intersects with the lines y=0 and y=1, is equal to $8D^{1/2}\alpha^{-1/2}$. Under the conditions that we have considered, the steadystate wave is a super-position of two traveling waves, propagating with velocity $\approx 10^3$ cm/sec and representing drops of the vibrational temperature with effective front width $10^{-1} - 10^{-2}$ cm.

B. Self-maintained discharge. In this case, the behavior of the system in the region of discharge currents at which the falling portion on the VAC is realized is described formally by Eq. (11), with the source function vanishing at the three points $T_V^{(1)}$, $T_V^{(2)}$, $T_V^{(3)}$ ($T_v^{(1)} < T_v^{(2)} < T_v^{(3)}$):

$$y_i - Dy_{ii} = f(y), \quad 0 \le y \le 1,$$

f(0) = f(\beta) = f(1) = 0, f'(0) = -\alpha'\beta, f'(1) < 0, (17)

where $y = (T_V - T_V^{(1)})/(T_V^{(3)} - T_V^{(1)}), \beta = (T_V^{(2)} - T_V^{(1)})/(T_V^{(3)} - T_V^{(1)}), \alpha'$ is a positive constant. Equation (17) has three stationary solutions: $y = 0, y = \beta, y = 1$, where y = 0 and y = 1 correspond to the stable states of the system, and the solution $y = \beta$ is unstable (bistable case). It should be noted that similar equations appear in the modeling of wave processes in nerve axons²⁷ and in lines with shunting nonlinear resistance.²⁸

The possibility of a transition of the system from the state 0(1) to the state 1(0) is determined by the sign of the integral

$$\Phi = \int f(y) \, dy, \tag{18}$$

which is in turn determined by the value of the fixed discharge current.

If $\Phi > 0$, then the transition 0 + 1 is possible under the condition that the level of the initial perturbation relative to the state 0 exceeds β , while its characteristic size \overline{z} satisfies the inequality

$$D/\tilde{z}^2 < \max_{\substack{\beta \leq y \leq i}} (f(y)/y)$$

The reverse transition $1 \rightarrow 0$ is impossible for the following reason. Any local reduction in the vibrational temperature relative to state 1 leads to an energy release in this region, since the quantity

$$\int_{0<\delta<1}^{1} f(y) \, dy \text{ if } \Phi > 0 \tag{19}$$

is positive. Together with the process of thermal conduction, this leads to the "collapse" of the original perturbation.

At $\Phi < 0$, the state 0 is stable relative to any perturbation. The state 1 is unstable relative to fluctuations, for which the inequalities are satisfied.

$$y_0(z) < \beta$$
, $D/\bar{z}^2 < \max_{x \in y \in z} (|f(y)|/y)$.

The asymptotic solution of Eq. (17), which describes the transition between the stationary states of the system, is a pair of diverging wave fronts of the form (15).²⁹ Their structure and velocity of propagation can be found by approximating $f(T_V)$ by a cubic polynomial and writing Eq. (17) in Riemannian variables:

$$y_{xx} + cy_{x} = y(y-\beta)(y-1),$$
 (20)

where $x = (z - ct)(\alpha'D)^{1/2}(T_V^{(3)} - T_V^{(1)})$. The solution of (20) at $c = 2^{1/2}(\frac{1}{2} - \beta)$ has the following form:²⁾

$$y = (1 + \exp(\pm x/2^{t_h}))^{-1}$$
 (21)

The effective width of the wave front is equal to $2^{5/2}D^{1/2}\alpha^{-1/2}(T_V^{(3)} - T_V^{(1)})^{-1}$ and is identical in order of magnitude, just as the propagation velocity, with the values given for the non-self-maintained discharge. The stability of the solution (21) relative to small perturbations can easily be proved by using the criteria put forth in Refs. 26 and 30.

We note a significant difference between the dynamics of nonstationary phenomena of non-self-maintained and self-maintained discharges. At $S \neq 0$, in the range of discharge currents corresponding to a decreasing portion on the VAC, the development instability in the nonlinear stage leads to the appearance of a large-amplitude wave, which brings about a transition to a state with a large value of the vibrational temperature, which is then maintained in the plasma (system with a single triggering). In contrast, the state 0 at $\Phi > 0$ (1 at $\Phi < 0$), can be considered to be metastable, since the transition $0 \rightarrow 1$ (1 $\rightarrow 0$) is produced only by large-scale fluctuations of large amplitude. Exceptions are the portions of the VAC near points corresponding to f'(y) = 0, where the transitions take place under the action of thermal fluctuations. The hard mode of instability onset leads to hysteresis phenomena in the variation of the discharge current density in the plasma of a self-maintained discharge.

We note also that analysis of the discharge conditions at which a significant change in the gas temperature occurs, testifies to the possibility of appearance of solutions of the soliton type.

DISCUSSION

The investigation of the mechanism of formation of nonlinear waves of large amplitude, based on the dependence of the rate of dissociative sticking of the electron to the molecule on the vibrational temperature, has been carried out by us in the example of the binary mixture N₂O-He. The discharge in $0.1N_2O-0.2N_2-0.7$ He has been considered by us in similar fashion. This case is of applied interest (see, for example, Ref. 31). The results are in qualitative agreement with what has been done above, independent of whether the vibrational degrees of freement of the N₂O are excited by direct electron impact or by the first vibrational level of the N₂.

Moreover, the mechanism of formation of waves of finite amplitude that we have considered can also be observed in a plasma of molecular gases, where the generation of negative ions is brought about by any reaction (for example, sticking in triple collisions), the rate of which depends on the vibrational temperature, and the process of destruction of the negative ions is determined by ion-ion recombinations.

We note the following circumstances. The initial assumption was that the group of vibrational levels responsible for the effectiveness of the DS reaction is characterized by a vibrational temperature T_V which exceeds the gas temperature T. However, the absence of reliable data on the probabilities of the processes of V - V and V - T reactions does not exclude a case in which $T_V \approx T$. Here instability of the DS can develop under conditions in which the heat exchange with the walls does not assure constancy of the gas temperature with increase in the energy input.

In conclusion, we turn our attention to the experiment of Bletzinger *et al.*,³² who investigated the effect of the molecular contributions to the properties of the discharge plasma in CO_2-N_2 -He mixtures. In particular, they established that even an insignificant amount of $N_2O(\leq 1\%)$ caused instability in a definite interval of pressure, impurity concentration and discharge current. Their attempt to explain the observed stratification as being due to the dependence of the rate of generation of negative ions on the value of T_e proved a failure, since $k_a(T_e) \approx \text{const for } N_2O$. At the same time, the theory given above enables us easily to interpret the results of the experiment of Ref. 32.

- ¹⁾The conditions of applicability of Eqs. (4)-(6) are discussed in detail in Ref. 18.
- ²⁾Equation (20) was first investigated by Huxley and bears his name (see Refs. 27 and 30 in this connection).
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