Kinetic and gasdynamic processes in nonequilibrium molecular physics

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We review the propagation of optical and hydrodynamic perturbations in a gas having nonequilibrium internal degrees of freedom. We discuss the nonequilibrium processes that lead to variation of the refractive index and self-focusing via the effect of kinetic cooling and nonequilibrium vibrational excitation of molecules. We analyze the propagation of small and nonlinear perturbations, as well as shock waves, in nonequilibrium gases.

INTRODUCTION

Interest in nonequilibrium phenomena in the physics of gases arose at the end of the twenties of this century in connection with studies of anomalous dispersion and absorption of ultrasonic waves. The explanation of anomalous absorption (and dispersion) required departing from the usual views of dissipation of the energy of ultrasonic waves via processes of viscosity and heat conduction and bringing in the mechanism of retarded energy exchange between the translational and internal degrees of freedom of the molecules. Thus the physics of gases faced for the first time real processes that lead to breakdown of equilibrium among the internal degrees of freedom of the molecules. Translational nonequilibrium, i.e., breakdown of equilibrium among the translational degrees of freedom of the molecules, began to be studied considerably earlier, at the end of the past century and the beginning of this century, in connection with problems of calculating transport coefficients. The viscosity, heat conductivity, and diffusion coefficients, as was shown in the theory of inhomogeneous gases, differ from zero only in the case in which the velocity distribution functions differ from Maxwellian. However, this type of a nonequilibrium at that period was of more interest to engineers than to physicists, since the physicists in their experimental practice had not yet faced real processes that lead to an appreciable breakdown of the Maxwell distribution.

An entirely different fate overtook acoustic nonequilibrium. Already in the forties, after the prediction of broadening of shock waves owing to relaxation processes, it became clear that the acoustic breakthrough into nonequilibrium is not an exception. One will encounter fast processes with a nonequilibrium distribution of energy among the internal degrees of freedom each time whenever the characteristic time of an external agent is of the order of the relaxation time.

However, essentially the establishment of nonequilibrium molecular physics as an independent science began only in the sixties, and is due to the laser revolution in physics and chemistry. One of the fundamental results of the laser revolution, besides the invention and incorporation into practice of the unique laser technology, consists in attracting the attention of physicists to nonequilibrium media, and in particular, to nonequilibrium gases.

Nonequilibrium gases include not only the active medium of gas lasers. They include the upper atmosphere, the interstellar medium, including the interstellar clouds, discharge plasmas, etc. From the physical standpoint a nonequilibrium molecular gas amounts to an unusual state of matter, the peculiarity of whose properties is determined by the possibility of varying within certain limits the store of internal energy and its distribution among the degrees of freedom of the molecules.

The study of nonequilibrium gases essentially enables physicists to discover a new stratum of phenomena. For many centuries humanity used only the mechanical properties of gases, then in turn came in the thermal, electrical, and chemical properties. Precisely these fields for many years defined the face of molecular physics. Then the situation changed. The shape of modern molecular physics is determined by the study of nonequilibrium phenomena.

At present nonequilibrium molecular physics is taking its first steps. Among its advances we should mention the development of nonequilibrium kinetics of atomic and molecular processes in reacting gases and the active media of gas lasers, as well as the theories of propagation of optical and hydrodynamic perturbations in nonequilibrium gases. Whereas the former group of problems has been dealt with in considerable detail in the review and monograph literature, the hydrodynamic and optical aspects of the behavior of a nonequilibrium gas have essentially been presented only in the original studies.

The interest in the optical properties of a nonequilibrium gas involves the fact that here the most striking nonequilibrium effects have been revealed up to now. We can classify them into two groups: nonequilibrium emission and propagation of optical perturbations in nonequilibrium media. While nonequilibrium emission has been rather well studied, the interaction of laser radiation with nonequilibrium gases is only beginning to be studied.

The interest in the hydrodynamics of nonequilibrium systems is governed primarily by the fact that this is one of the new fields of modern hydrodynamics. In classical hydrodynamics, to speak simply, the role of physicists ended at the instant when the fundamental hydrodynamic equations had been established. Further development here took the path of overcoming mathematical difficulties. The situation was different in the hydrodynamics of nonequilibrium systems. It now is passing through the stage of formulating the fundamental equations and for revealing new physical effects. In many ways this is a field of activity of physics, and naturally the role of physicists is large here.

The plan of the review is as follows. Section 1 reviews

the fundamental properties of a vibrationally nonequilibrium gas. Section 2 is devoted to the optical properties of a nonequilibrium gas. Primarily here we discuss the nonequilibrium processes that lead to a change in the refractive index and self-focusing owing to the effect of kinetic cooling and nonequilibrium vibrational excitation of molecules. Section 3 discusses the hydrodynamic behavior of a nonequilibrium gas: the propagation of small perturbations, waves of finite amplitude, and shock waves.

1. A NON-EQUILIBRIUM GAS

1.1. The hierarchy of relaxation processes in molecular kinetics

Generally speaking, molecular collisions in a gas are accompanied by a change in the translational, rotational, vibrational, and electronic energy of the collision partners. Moreover, chemical reaction and ionization of the particles can occur. The probabilities (or effective cross sections) of these elementary processes, as a rule, differ strongly among themselves. The latter situation has the result that the excitation of certain groups of degrees of freedom in molecular gases requires differing numbers of collisions. Thus one can speak of the rates of individual relaxation processes or of the characteristic times (relaxation times) of individual processes. We understand a relaxation process to be one of establishment of an equilibrium or quasiequilibrium energy distribution in a group of individual degrees of freedom in the molecular gas.

At temperatures of the order of 10^3 K the characteristic times of the individual relaxation processes in a molecular gas form the following hierarchy:

$$\tau_{\rm TT} < \tau_{\rm RT} < < \tau_{\rm VV} < < \tau_{\rm VT} < < \tau_{\rm ch} < < \tau_{\rm J}, \tag{1.1}$$

Here $\tau_{\rm TT}$, $\tau_{\rm RT}$, $\tau_{\rm VT}$, and $\tau_{\rm J}$ are the characteristic times of establishment of equilibrium among the translational, rotational, vibrational, and electronic degrees of freedom, $\tau_{\rm VV}$ is the characteristic time of exchange of vibrations among molecules (VV exchange), and $\tau_{\rm ch}$ is the characteristic time of chemical transformations. One can understand the physical cause of the difference in relaxation times, which is a consequence of the difference of probabilities (or cross sections) of the different elementary events upon estimating the magnitude of the Massey parameter.

The greatest efficiency of energy exchange between the translational and internal degrees of freedom of the molecules is observed in collisions for which the Massey parameter is

$$\Delta Er_0/hv \sim 1$$
 (1.2)

Here ΔE is the difference in energy of the levels between which the transition occurs, v is the mean velocity of relative motion of the pairs of colliding particles, and r_0 is the radius of intermolecular interaction. When

$$\Delta Er_0/hv \gg 1 \tag{1.3}$$

energy exchange is difficult. One can see this even from the example of a collision of a harmonic oscillator with a structureless particle. The condition (1.3) implies that the perturbation of a molecule by an incident atom, which is the cause of the vibrational transition, is adiabatic in character. Yet as we know, in this case $\mathscr{C}/\widetilde{\omega}$ is an invariant (\mathscr{C} is the

vibrational energy, and $\tilde{\omega}$ is the frequency of the vibrations). That is, the vibrational energy is not changed by the collision. More exactly, the change in the vibrational energy is $\Delta E \sim e^{-F}$, where F is an adiabatic factor proportional to the Massey parameter.

The Massey parameter for a vibrational excitation as a rule is much greater than unity, and for rotational excitation is of the order of unity. Actually, for O₂-Ar collisions accompanied by vibrational excitation we have $w_e = E/h = 1580 \text{ cm}^{-1}$, $r_0 \sim 10^{-8} \text{ cm}$, and $v \sim 3 \times 10^4 \text{ cm/s}$. Thus we have $\Delta E r_0/hv \sim 14$.

In the rotational excitation of homonuclear molecules we have $\Delta E = E_{j+2} - E_j = Be(4j+6)$, where $j = j \sim (k_B T/Be)^{1/2}$. Since for O₂ we have Be = 1.45 cm⁻¹, then for T = 300 K we have $Be/j \sim 12$, while $\Delta Er_0/hv \sim 1.4$.

The hierarchy of (1.1) pertains to the typical case. For light molecules or molecules lying in upper rotational levels we have $\tau_{\rm RT} \gg \tau_{\rm TT}$. For heavy molecules $\tau_{\rm VT}$ is considerably smaller than for light molecules. Hence the case can occur in which $\tau_{\rm VT} \sim \tau_{\rm VV}$. With increasing temperature $\tau_{\rm ch}$ decreases more rapidly than $\tau_{\rm VT}$, and therefore, beginning at a certain temperature we have $\tau_{\rm ch} \sim \tau_{\rm VT}$. For example, for an O₂-Ar mixture this boundary is 8000 K.^{1,2}

The meaning of the hierarchy of relaxation times of (1.1) for analyzing nonequilibrium processes is that under certain conditions the process of relaxation of individual groups of degrees of freedom can be treated in isolation. In this case the certain conditions mean that, in analyzing concrete relaxation processes, one selects time scales on which all the faster processes have finished, while the slower ones have not started. As applied to problems of vibrational relaxation this means that, at times of the order of $\tau_{\rm VT}$, one can assume the processes of translational and rotational relaxation to have finished and take account only of their resultthe formation of a Maxwell-Boltzmann distribution with a single temperature for the translational and rotational degrees of freedom. On the other hand, for times of the order of $\tau_{\rm VT}$ one need not take account of dissociation processes, since they are not yet started.

1.2. Kinetic processes in a vibrationally nonequilibrium gas

Among all the relaxation processes, vibrational relaxation can be singled out in terms of its energy capacity and duration. The vibrational reservoir of an *N*-atom molecule includes 3*N*-6 degrees of freedom (for a linear molecule 3*N*-5). However, only 6 (or 5) degrees of freedom belong to the fraction for translational motion and rotation. The duration of vibrational relaxation is determined by the time $\tau_{\rm VT}$. For O₂ at room temperature $\tau_{\rm VT}$ amounts to ~ 10⁸ τ_0 , while at temperatures 5×10³ K it is of the order of 10² τ_0 , where τ_0 is the mean time of free flight.³

The noted features of vibrational relaxation explain the rather high level at which it has been studied and the widespread use of nonequilibrium vibrational effects in physics.

There are several levels of description of vibrational relaxation. The most widespread ones are description in terms of macroscopic variables (e.g., the mean vibrational energy) and the microscopic description by using the distribution function of the vibrational energy or the populations of the individual vibrational levels (level kinetics). The choice of the level of description depends on the specifics of the problem and the phenomenon being studied. For example, in relaxational hydrodynamics as a rule one can restrict the treatment to the macroscopic description. Conversely, in chemical kinetics or laser physics, one requires a level description.

In the macroscopic description the fundamental equation is the relaxation equation for the mean vibrational energy ε per unit mass, which for diatomic molecules has the form

$$d\varepsilon/dt = -(\varepsilon - \varepsilon_0)/\tau_{\rm VT}.$$
(1.4)

Here ε_0 is the equilibrium value of the mean vibrational energy per unit mass, and $\tau_{\rm VT}$ is the vibrational relaxation time. For a system of harmonic oscillators we have

$$\epsilon_0(T) = \hbar \widetilde{\omega} / m \left[\exp(\hbar \widetilde{\omega} / k_{\rm B} T) - 1 \right],$$

where *m* is the mass of the molecule, and $\hbar \widetilde{\omega}$ is the magnitude of the vibrational quantum.

Equation (1.4) has a rather broad region of applicability. It functions well up to a temperature of the order of the characteristic temperatures, i.e., where one can neglect anharmonic effects. The characteristic temperatures for most molecules are rather high. Thus, for H₂ we have $\hbar\tilde{\omega}/k_{\rm B}$ = 6300 K, for N₂ 3400 K, for CO 3100 K, for O₂ 2300 K, etc.

Equation (1.4) is valid for polyatomic molecules if in the latter the exchange of energy between the different vibrational modes occurs faster than the energy exchange between the translational degrees of freedom and the low-frequency vibrational mode. In this case we should understand ε_0 to be the mean energy of the low-frequency mode, while we substitute $\tau = \tau_{\rm VT} c_{\rm V}/c_1$ in place of $\tau_{\rm VT}$, where c_1 is the heat capacity of the low-frequency mode, and $c_{\rm V}$ is the total heat capacity of all the vibrational degrees of freedom.

Despite the relatively simple form of the relaxation equation (1.4), it allows one to predict or explain rather subtle effects. Let us explain what we have said using the example of a nonequilibrium thermal explosion.⁴

Upon intense pumping of energy into the vibrational degrees of freedom of a molecular gas (e.g., in a discharge or under the action of laser infrared radiation), a nonequilibrium two-temperature gas is formed. The vibrational temperature $T_{\rm v}$ of such a gas can appreciably exceed the temperature of the translational degrees of freedom. We can speak of a vibrational temperature if VV exchange is the fastest process. However, such a two-temperature state may prove to be unstable. With increasing pumping intensity $T_{\rm v}$ will increase, and hence also the energy transferred to the translational degrees of freedom. If it cannot be removed from the system by heat exchange with the surrounding medium, then the gas will begin to heat up. Increase of the gas (translational) temperature will lead to acceleration of the process of VT exchange ($\tau_{\rm VT}$ decreases with increasing temperature), which heats the gas even more, etc. The result of this process will be an avalanche-like discharge of the excess vibrational energy into the translational degrees of freedom (thermal explosion) and formation of a new high-temperature regime with $T \approx T_{\rm v}$. Thus thermal explosion (along with dissociation) is an upper bound of the store of vibrational energy that can be accumulated in the system.

In the simplest case thermal explosion is described by a

system of two equations corresponding to the balance of vibrational and translational-rotational energies. The equation of balance of the vibrational energy

$$\frac{d\varepsilon}{dt} = -\frac{\varepsilon - \varepsilon_0}{\tau_{\rm VT}} - \frac{\varepsilon - \varepsilon_0}{\tau_d} - \frac{\varepsilon}{\tau_r} + \frac{q}{m}$$
(1.5)

is obtained if one adds to Eq. (1.4) terms describing the diffusion loss of vibrationally excited molecules upon interaction with the wall (the second term on the right-hand side, where $\tau_d \sim R_0^2/D$ is the characteristic time of diffusion, *D* is the diffusion coefficient, and R_0 is the radius of the tube), describing radiation deactivation (the third term), and the intensity of pumping.

The equation of balance of the thermal (translationalrotational) energy has the form

$$\frac{\mathrm{d}}{\mathrm{d}t} \left(\frac{5}{2} k_{\mathrm{B}} T m^{-1} \right) = \frac{\varepsilon - \varepsilon_{\mathrm{0}}}{\tau_{\mathrm{VT}}} - \frac{k_{\mathrm{B}}}{m} \frac{T - T_{\mathrm{w}}}{\tau_{\mathrm{d}}}, \qquad (1.6)$$

where T_w is the temperature of the wall. In the steady-state case with account taken of $\tau_{\rm VT} \gg \tau_{\rm d}$, $\tau_{\rm r}$ and $\varepsilon \gg \varepsilon_0$, equations (1.5) and (1.6) imply that

$$k_{\rm B}(T-T_{\rm w})\frac{\tau_{\rm VT}}{\tau_{\rm d}} = q\tau^*, \ \tau^* = \frac{\tau_{\rm r}\tau_{\rm d}}{\tau_{\rm r}+\tau_{\rm d}}.$$
 (1.7)

If we represent the temperature dependence of $\tau_{\rm VT}$ with the exponential

$$\tau_{\rm VT} = \tau_{\rm VT}^0 \exp(-\widetilde{b}\widetilde{\Theta}),$$

$$\widetilde{\theta} = (T - T_{\rm w})/T_{\rm w}, \ \tau_{\rm VT}^0 = \tau_{\rm VT}|_{T = T_{\rm w}},$$

then (1.7) acquires the form

$$\widetilde{\theta} = \varkappa \exp(\widetilde{b}\widetilde{\theta}), \tag{1.8}$$

where $x = q\tau^*\tau_d/(\tau_{VT}^0k_BT)$. Equation (1.8) has one stable solution for $x \sim 1/\tilde{b}e$, where e is the base of natural logarithms, and it has no solution when $x > 1/\tilde{b}e^{.5}$ The lack of a solution means that the initial physical assumptions are false. First of all, the assumption of the existence of a twotemperature regime in which the transport of heat occurs via a diffusion mechanism, is not valid. The new regime will be close to equilibrium with $T \approx T_V$, and it must be studied by using the kinetic equations. The change of regime corresponds precisely to thermal explosion.

The microscopic (level) description of relaxation processes is based on a system of gas-kinetic equations of balance type for the populations of the individual vibrational levels N_n ² For a single-component diatomic molecular gas this system has the form

$$\frac{dN_n}{dt} = \left(\sum_m P_{mn}N_m - \sum_m P_{nm}N_n\right) + \frac{Z}{N}\left(\sum_{m,s,l} Q_{mn}^{sl}N_m N_s - \sum_{m,s,l} Q_{nm}^{ls}N_n N_l\right), \ n, m, s, l = 0, 1, 2, \dots.$$
(1.9)

Here P_{mn} is the probability of a m-n vibrational transition in a single collision (the probability of VT exchange), Z is the number of collisions undergone by a molecular per unit time, and Q_{mn}^{sl} is the probability of a transition (VV exchange) in which two colliding molecules in the vibrational states mand s go after collision into the states n and l. When l = s we have

$$\frac{Z}{N}\sum_{m,s,l}Q_{mn}^{sl}N_mN_s = \frac{Z}{N}\sum_m \left(\sum_s Q_{mn}^{ss}N_s\right)N_m = Z\sum_m P_{mn}N_m,$$

if Q_{mn}^{ss} depends weakly on *s*, while $N = \sum_{s} N_{s}$. In (1.9) we have $m \neq n, s \neq l$.

The singling out of the terms describing VV exchange into a separate group is justified by the fact that, among all the possible processes of VV exchange, the most effective one is resonance (or near-resonance) exchange, in which $|(E_m - E_n) - (E_l - E_s)| \ll k_B T$. The characteristic time of resonance VV exchange is $\tau_{VV} \ll \tau_{VT}$. For example, for NO at room temperature⁶ we find

$$\begin{aligned} \tau_{\rm VV} &\sim \left(1/Z Q_{10}^{01} \right) \cdot 68 \tau_0 \ (\tau_0 = 1/Z), \\ \tau_{\rm VT} &\sim 1/Z P_{10} \sim 3.2 \cdot 10^3 \tau_0 \,. \end{aligned}$$

The gas-kinetic equations (1.9) are valid when two conditions are fulfilled. First, the inequality must be fulfilled that $\tau_{\rm VT}$, $\tau_{\rm VV} \gg \tau_{\rm RT}$; second, one can neglect triple collisions under the conditions being studied. The first condition enables us to consider P_{mn} and Q_{mn}^{sl} to be functions of a single translational-rotational temperature. In other words, when $\tau_{\rm VT}, \tau_{\rm VV} \gg \tau_{\rm RT}$, the process of vibrational relaxation occurs on the background of a Maxwell-Boltzmann distribution of energy among the translational and rotational degrees of freedom. The second condition, as in the classical Boltzmann equation, imposes an upper bound on the pressure. The ratio of the number of triple to double collisions is of the order of Nr_0^3 , where N is the number density of particles, while r_0 is the radius of intermolecular interaction $(r_0 \sim 2 \times 10^{-8} \text{ cm})$. If we denote by $P_{mn}^{(2)}$ and $P_{mn}^{(3)}$ the probabilities of VT exchange in double and triple collisions, respectively, then the condition for neglecting triple collisions can be written in the form

or

 $Nr_0^3 P_{mn}^{(3)} / P_{mn}^{(2)} << 1,$

$$p \cdot 10^{-4} P_{mn}^{(3)} / P_{mn}^{(2)} << 1,$$
 (1.10)

where p is the gas pressure in atmospheres. In (1.10) the probabilities of VV exchange can also appear instead of the probabilities of VT exchange.

The ratio $P_{mn}^{(3)}/P_{mn}^{(2)}$ is not known. If we assume rather arbitrarily that the ratio is of the order of 10 to 100, the role of triple collisions must be analyzed starting at pressures of 10 to 100 atmospheres.

As we have already pointed out, the system (1.9) has two characteristic time scales- τ_{VT} and τ_{VV} . Since as a rule $\tau_{VT} \gg \tau_{VV}$, we can speak of a quasi-steady-state distribution that is formed at times $t \ll \tau_{VT}$. In this case the first term on the right-hand side of (1.9) need not be considered at all, and we can find the steady-state distribution from the condition of vanishing of the second term. As was shown in Ref. 7, this is equivalent to the condition

$$Q_{mn}^{sl} N_m N_s = Q_{nm}^{ls} N_n N_l.$$
(1.11)

If we examine systems of harmonic oscillators and restrict the consideration to only single-quantum transitions (they occur with overwhelming probability²), then we can write (1.11) in the form

$$Q_{n+1,n}^{s,s+1}N_{n+1}N_s = Q_{n,n+1}^{s+1,s}N_nN_{s+1}.$$
(1.12)

Equation (1.12) with allowance for the detailed-balance relationship

$$2_{n+1,n}^{s,s+1} \exp[-(E_{n+1} + E_s)/k_{\rm B}T] = Q_{n,n+1}^{s+1,s} \exp[-(E_n + E_{s+1})/k_{\rm B}T]$$
(1.13)

implies that

$$N_i = N_0 \exp(-E_i / k_{\rm B} T).$$
(1.14)

Here the vibrational temperature T_v is determined by the store of vibrational energy existing at the given instant.

In an isolated system the distribution of (1.14) relaxes (with the characteristic time $\tau_{\rm VT}$) to a Boltzmann distribution with $T_{\rm V} = T$, where T is the gas (translational) temperature.

In a closed system in which, for example, a constant population of the first vibrational level is maintained, T_v will always differ from T.

The Boltzmannization of the existing store of vibrational energy via VV exchange leads to a number of interesting effects. Let us study one of them. In spectroscopic practice, to measure the vibrational temperature of the non-radiating components (homonuclear molecules), one often uses the following method. One adds to the non-radiating system a small admixture of radiating molecules (e.g., one adds NO or CO to N₂). One assumes that the vibrational temperatures of the radiating and nonradiating molecules are equal. Therefore by measuring the emission spectrum of the admixture one can find the vibrational temperature of the main component. Let us examine the accuracy of this "molecular thermometer" from the standpoint of the relaxation processes that occur.

In a binary mixture of diatomic molecules, owing to VV exchange in collisions of identical molecules in each of the components A and B, a Boltzmann distribution is established with its own vibrational temperature. If the vibrational quanta of the A and B molecules do not differ very strongly ($|\omega_A - \omega_B|/\omega_A \ll 1$), then exchange of vibrational quanta in collisions of differing molecules A and B (VV' exchange) occurs more slowly than VV exchange in each component, but faster than VT exchange. Thus at times $t \sim \tau_{VV}$, $\ll \tau_{VT}$ one can speak of a quasi-steady-state distribution of vibrational energy between the components. It is found from an equation analogous to (1.12):

$$Q_{n+1,n}^{s,s+1}(\mathbf{A},\mathbf{B})\mathcal{N}_{n+1}^{\mathbf{A}}\mathcal{N}_{s}^{\mathbf{B}} = Q_{n,n+1}^{s+1,s}(\mathbf{A},\mathbf{B})\mathcal{N}_{n}^{\mathbf{A}}\mathcal{N}_{s+1}^{\mathbf{B}}.$$
 (1.15)

Upon taking account of the principle of detailed balance

$$Q_{n+1,n}^{s,s+1}(A,B) \exp\left(-\frac{E_{n+1}^{A} + E_{s}^{B}}{k_{B}T}\right)$$

= $Q_{n,n+1}^{s+1,s}(A,B) \exp\left(-\frac{E_{n}^{A} + E_{s+1}^{B}}{k_{B}T}\right)$ (1.16)

and the presence of a Boltzmann distribution in each of the components $(N_n^A = N_0^A \exp(-E_n^A/k_B T_V^A) \text{ and } N_l^B = N_0^B \exp(-E_l^B/k_B T_V^B))$, then Eq. (1.15) implies that²

$$\frac{E_1^{\rm A} - E_1^{\rm B}}{k_{\rm B}T} = \frac{E_1^{\rm A}}{k_{\rm B}T_{\rm V}^{\rm A}} - \frac{E_1^{\rm B}}{k_{\rm B}T_{\rm V}^{\rm B}}.$$
(1.17)

The relationship (1.17) shows that VV' exchange, i.e., exchange of vibrational quanta between the components, mixes the initially existing store of vibrational energy, while establishing correspondence between the vibrational temperatures T_{V}^{A} and T_{V}^{B} .

We also see from (1.17) that the "molecular thermometer," e.g., B, always shows a different temperature from component A, i.e., $T_V^A \neq T_V^B$. Thus, for example, for a mixture of N₂ and CO $(E_1(N_2)/k_B = 3390 \text{ K}, E_1(CO)/k_B = 3120 \text{ K})$ upon rapid expansion to T = 1000K the difference $T_V(CO) - T_V(N_2) \sim 150 \text{ K}$ when $T_V(CO) \sim T_V(N_2) \sim 2000 \text{ K}.$

At high levels of vibrational excitation at which the mean vibrational energy of the molecule is larger than a vibrational quantum, one must take into account the anharmonicity of the molecular vibrations. Molecular anharmonicity weakly affects VT exchange. It can alter the rate of VT exchange but not the final state. The final steady state in the region where VT exchange predominates will always be described by a Boltzmann distribution with a vibrational temperature equal to the translational temperature. The situation is completely different in VV exchange. The steady state in a system of anharmonic molecules that is formed under the action of an actually predominating single-quantum VV exchange differs in principle from a Boltzmann distribution. Equation (1.12) implies, with account taken of (1.13), that the steady-state distribution has the form

$$N_n = N_0 \exp\left[-\gamma_{\rm Tr} n - (E_n/k_{\rm B}T)\right], \qquad (1.18)$$

Here $\gamma_{Tr} = (E_1(k_B T_1) - (E_1/k_B T))$ is determined by the total store of vibrational quanta at the given instant of time. Here T_1 is the "temperature" of the first vibrational level $(N_1 = N_0 \exp(-E_1/k_B T))$, while $E_n = nE_1 - \Delta En(n-1)$, where ΔE is the anharmonicity constant. The distribution (1.18) was first derived in the study of Treanor, Rich, and Rehm, and is often called the Treanor distribution.⁸ When $\Delta E = 0$ it goes over into a Boltzmann distribution with $E_1/k_B/T_V = \gamma_{Tr} + (E_1/k_B T)$.

The distribution of (1.18) differs substantially from a Boltzmann distribution. When $T_1 < T$, which corresponds to conditions in the relaxation zone behind the front of a shock wave, we have $\gamma_{Tr} > 0$, while the population in the higher vibrational levels is lower than the equilibrium value at the temperature T. Conversely, when $T_1 > T$, i.e., under conditions of rapid expansion of the gas or intense vibrational pumping, we have $\gamma_{Tr} < 0$, and the population of the upper vibrational levels is greater than the equilibrium value. Figure 1 (curve 1) shows the Treanor distribution for CO molecules for $T_1 = 2700$ and T = 325 K.

The rising branch of the Treanor distribution, which corresponds to an absolute inversion, is not realized in practice. This involves the fact that processes of VT exchange predominate on the upper levels, leading to a Boltzmann distribution with a vibrational temperature equal to the temperature of the translational degrees of freedom. In the intermediate region of vibrational quantum numbers where the probabilities of VT and VV exchange become comparable (e.g., for CO at room temperature we have $P_{n+1,n} \sim Q_{n+1,n}^{01}$ for $n \sim 20$ -30), the Treanor distribution goes smoothly over into the Boltzmann distribution through a plateau (see Fig. 1).



FIG. 1. Relative populations of vibrational levels of CO molecules at $T_1 = 2700$ K and various gas temperatures. Curve *l* corresponds to the Treanor distribution at T = 325 K.

The important role of Treanor distributions with a plateau and a descending branch (see Fig. 1) is determined by the fact that when $T_1 > T$ the mean store of vibrational energy per molecule for such distributions is larger or considerably larger than for a Boltzmann distribution with a vibrational temperature equal to T_1 . The latter circumstance is widely employed in laser physics, e.g., in CO lasers based on vibrational-rotational transitions.⁹ Other examples of optical manifestations of vibrational nonequilibrium are discussed in the next section.

2. OPTICAL MANIFESTATIONS OF NONEQUILIBRIUM 2.1. Polarizability of vibrationally excited molecules

The optical manifestations of nonequilibrium in gases encompass a very large set of phenomena. A nonequilibrium energy distribution among the internal degrees of freedom on molecules determines such well-known effects as the amplification and generation of laser radiation, changes in the absorption and emission spectra of nonequilibrium gases, and finally, changes in molecular characteristics (dipole moments, polarizabilities, hyperpolarizabilities, magnetic susceptibilities, nuclear quadrupole coupling constants, chemical shifts, etc.).

In this section we shall discuss the optical properties of a nonequilibrium gas involving a change in the polarizability of molecules upon nonequilibrium vibrational and rotational excitation.

Vibrational and rotational excitation of molecules, as, e.g., effected by optical or electronic pumping, leads to a change in the geometric structure of the molecules. Thus, upon vibrational excitation the mean distance between the atoms in the molecule increases (owing to mechanical anharmonicity), as does the amplitude of vibration of the molecules. The change in the mean (and mean-square) dimensions of the molecules affects the electrical characteristicsthe dipole moment, the polarizability, and the hyperpolarizability. Actually all the listed characteristics depend on the geometric dimensions of the molecules: the dipole moment contains the length to the first power, the polarizability has the dimensions of volume, etc.

The change in the electrical characteristics of the molecules leads to a change in the optical properties of the medium. Thus, in line with the Lorenz–Lorentz formula

$$\frac{n^2 - 1}{n^2 + 3} = \frac{4}{3}N\alpha,$$
(2.1)

where *n* is the refractive index, *N* is the number density of the molecules, and α is the mean polarizability. If we denote by α_s the polarizability of molecules in the *s*th vibrational-rotational state, then $\alpha = \sum_s y_s \alpha_s$, where y_s is the population of the *s*th level normalized to unity.

We see from (2.1) that a nonequilibrium vibrationalrotational excitation alters the refractive index by altering the mean polarizability of the molecules. In turn this leads to the appearance of new effects. Let us take up two of them, which must be taken into account in the interferometry of a nonequilibrium gas and in describing the propagation in it of resonance infrared radiation. In the adiabatic approximation we can represent the mean polarizability α of the molecules in the form of the sum of electronic, vibrational, and rotational components. The electronic component of the polarizability is determined by the electronic transitions from the given vibrational-rotational state. The vibrational and rotational components respectively depend on the vibrational-rotational and rotational transitions.

In the visible region of the spectrum the vibrational and rotational components of the polarizability are small in comparison with the electronic component. According to the estimates given in Ref. 10, the vibrational polarizability for CO_2 in the visible region (6328 Å) amounts to 3.9×10^{-3} Å³, while the total polarizability is $\alpha(\tilde{\omega}, 300 \text{ K}) = 2,636$ Å³. The total static polarizability is $\alpha(300 \text{ K}) = 2.93$ Å³, while the contribution of the vibrational polarizability is 0.33Å³. As we proceed into the infrared region, the contribution of the vibrational polarizability increases and becomes appreciable in a region close to single-photon vibrational resonance. Below, if not especially stipulated, we shall understand the mean polarizability to be the electronic component of the polarizability.

Direct calculation of the electronic polarizability by the Kramers-Heisenberg formula is difficult, since usually we do not know the dependence of the strengths of the electronic transitions on the vibrational and rotational quantum numbers. Therefore it is more convenient to expand the polarizability in a series in terms of the normal coordinates. If we restrict the treatment to terms of second order of smallness in the normal coordinates Q, then we can write for diatomic molecules

$$\begin{aligned} \alpha_{s} \langle s \, | \, \alpha \, | \, s \rangle &= \alpha^{(0)} \\ &+ \frac{\hbar}{m\widetilde{\omega}} \left[-\frac{3b_{3}}{\hbar\widetilde{\omega}} \frac{\hbar}{m\widetilde{\omega}} \left(\frac{\partial \alpha}{\partial \widetilde{Q}} \right)_{0} + \frac{1}{2} \left(\frac{\partial^{2} \alpha}{\partial \widetilde{Q}^{2}} \right)_{0} \right] \left(s + \frac{1}{2} \right) \\ &+ \frac{1}{\hbar\widetilde{\omega}} \frac{\hbar}{m\widetilde{\omega}} \left(\frac{\partial \mu}{\partial \widetilde{Q}} \right)_{0}^{2} \cdot \end{aligned}$$
(2.2)

Here $\alpha^{(0)}$ is the polarizability of the excited molecule, the first term in the square brackets stems from the mechanical anharmonicity (b_3 is the coefficient of \tilde{Q}^3 in the expansion of the potential of the intramolecular interaction in the normal coordinates), the second term is the electrooptical anharmonicity, and the last term in (2.2) involves the correction to the energy in second-order perturbation theory. The values of the derivatives of the dipole moment with respect to the normal coordinates are calculated by quantum-mechanical methods or are determined from spectroscopic data.¹⁰

The generalization of (2.2) to the case of polyatomic

molecules is rather obvious. We must sum (2.2) over all the normal coordinates, take into account the degeneracy of the normal vibrations, having replaced s + (1/2) with $s + (r_j/2)$, where r_j is the degeneracy, and include terms arising from the anharmonic interaction of the normal vibrations. A concrete expression for α_s for CO₂ in a given vibrational-rotational state is given in Ref 10. Expressions for the dipole moment, the polarizability, and the hyperpolarizability of polyatomic molecules in the ground state were derived in Ref. 11, and in a vibrationally excited state in Refs. 12–16. (Misprints are found in the formulas for the dipole moment, the polarizability in Refs. 12–16.)

The contribution of vibrational-rotational transitions to the polarizabilities of molecules of CO were studied theoretically in Ref. 17. A detailed review of the studied (bibliography of about 130 names) on the influence of vibrational and rotational excitation of molecules on the static and dynamic polarizability and hyperpolarizability is found in Ref. 18.

We see from (2.2) that the vibrational contribution α_v to the electronic polarizability ($\alpha_v = \alpha_s - \alpha^{(0)}$) is proportional to the vibrational quantum number s or, after averaging over the distribution on vibrational energy, to the mean number of vibrational quanta \bar{s} per molecule. The value of s varies depending on the distribution function. Thus, for the CO molecule at T = 75 K and the temperature of the first vibrational level $T_1 = 2050$ K, averaging over the Boltzmann distribution ($N_s = N_0 \exp(E_s/k_B T)$) yields $\bar{s} = 0.3$, while averaging over the Treanor distribution ($N_s = N_0 \exp[-\gamma_{\rm Tr} s - (E_s/k_B T)]$, $\gamma_{\rm Tr} = [(T_1^{-1} - T^{-1}) E_1/k_B]$) yields $\bar{s} \approx 0.8$.²

Apparently the maximum value of s amounts to several times unity, which corresponds to the appearance of vibrationally excited CO molecules in chemical reactions.

The absolute contribution of the vibrational increment to the electronic polarizability is small. According to the estimates¹⁰ for CO₂ the total vibrational and centrifugal (rotational) contribution to the electronic polarizability varies $(\text{in units of } a_0^3 = 0.14818 \text{ Å}^3) \text{ from } 0.163 \text{ at } 300 \text{ K to } 0.648 \text{ at}$ 3000 K, which corresponds to a relative change in the refraction of 2.7% over the interval 300-3000 K at $\lambda = 6328$ Å. The estimates that we have presented correspond to an equilibrium state of the carbon dioxide gas. In nonequilibrium excitation of CO₂ the fraction of α_v in the electronic polarizability can increase severalfold. The significance of this result is not restricted to the fact that the vibrational contribution to the polarizability can be measured. An important role of the vibrational increment consists in the fact that it governs an entire set of new effects. In particular, this pertains to the change in the refractive index upon vibrational excitation of a molecular gas.

2.2. Interferometry of a nonequilibrium gas

The interferometric study of gas flows (or gases at rest) is one of the most widespread methods of determining the density and gas temperature. The interferometric method of determining density is based on the Gladstone-Dale relationship, which connects the refractive index n with the density ρ

$$(n-1)/\rho = K, \tag{2.3}$$

where K is the Gladstone-Dale constant, which depends on the composition of the gas and the wavelength of the light. Equation (2.3) follows from (2.1).

In an interferometric experiment one measures the phase difference of two beams (shift of interference bands), from which one easily calculates the change in the refractive index n, which is associated with the change in the density $\Delta \rho$ by the relationship $\Delta n = K \Delta \rho$. Generally the constant K will depend also on the temperature. The temperature dependence of K was first studied in Ref. 19, and can be represented in the form

$$K = K_0(1 + \varkappa T),$$
 (2.4)

where $\kappa \sim 10^{-5} \text{ deg}^{-1}$. The correction κT , in line with the abovesaid, takes account of the variation of the polarizability with the temperature. Thus we have

$$\Delta n = (\partial n / \partial \rho) \Delta \rho + (\partial n / \partial T) \Delta T.$$
(2.5)

In equilibrium heating the contribution of the second term is small (see Ref. 10). It can be estimated if one uses (2.3) and (2.4) and the equation of state of an ideal gas. In this case we have²⁰

$$\frac{\Delta n_T}{\Delta n_\rho} \approx \frac{(\partial n/\partial T)\Delta T}{(\partial n/\partial \rho)\Delta \rho}.$$
(2.6)

When $T \sim 10^2 - 10^3$ K we find $\Delta n_T / \Delta n_\rho \sim 10^{-2} - 10^{-3}$.

In nonequilibrium vibrational heating the contribution of the second term becomes appreciable. Neglecting it in calculating the density from interferometric data can lead to errors. Thus, according to the estimates of Ref. 12 for CO at T = 300 K and $T_V = 5000$ K, the ratio of the density ρ^* calculated from (2.3) with account taken of the nonequilibrium vibrational contribution to the Gladstone-Dale constant to the density ρ determined from the ordinary Gladstone-Dale relationship equals $\rho^*/\rho \sim 0.85$.

If we proceed from the density to the gas temperature, then replacement of ρ by ρ^* will lead to a change in *T*. This effect must be taken into account, e.g., in determining the depth of kinetic cooling and recalculating experimental data on the characteristic relaxation times.²¹

Taking account of Δn_T in nonequilibrium vibrational excitation does not amount only to determining the correction to the measured magnitude of the density ρ . There is a large group of experiments in which vibrational excitation precedes heating of the gas. Thus, for example, in pulsed laser infrared excitation of a molecular gas, initially the vibrational degrees of freedom are heated, and only then in the course of the time of VT exchange (or time of nonresonance VV' exchange) the temperature of the translational degrees of freedom varies. Thus, in the pulsed excitation of the vibrational degrees of freedom the change in the refractive index in the first instants of time will track the redistribution of energy within and among the vibrational degrees of freedom and only later reflect the heating of the gas. Direct interferometric observation of the contribution of vibrational excitation to the change in the refractive index was performed in Ref. 20 for the gases SF_6 and C_2H_4 .

We note that vibrational excitation also alters other mo-

lecular characteristics, e.g., the hyperpolarizability,¹⁸ the magnetic susceptibility,²² the NMR spectral parameters,²³ etc. Moreover, the change in polarizability upon vibrational excitation must affect the intensities of Rayleigh and Raman light scattering. However, all these problems have practically not been developed as applied to a nonequilibrium gas.

2.3. Self-focusing of laser radiation induced by nonequilibrium vibrational excitation of molecules

The change in the refractive index upon nonequilibrium vibrational excitation can serve as the cause of another effect-self-focusing of laser radiation. Attention was called to this first in Ref. 24.

It was noted in Sec. 2.1 that the contribution of the vibrational polarizability to the total polarizability of molecules is small. However, the pattern changes if resonance interaction of the radiation with the material occurs. In agreement with the Kramers-Heisenberg formula, the vibrational polarizability $\tilde{\alpha}_{\rm V}$ can be written in the form

$$\langle s | \widetilde{\alpha}_{\mathbf{V}}^{\sigma,\tau}(\widetilde{\omega}) | s \rangle = \frac{2}{\hbar} \sum_{s',s} \frac{\widetilde{\omega}_{s's} \langle s | p_{\sigma} | s' \rangle \langle s' | p_{\tau} | s \rangle}{\widetilde{\omega}_{s's}^2 - \widetilde{\omega}^2},$$
(2.7)

where the $p_{\delta,\tau}$ are the components of the dipole moment, and $\widetilde{\omega}_{s,s} = (E_{s,r} - E_{s})/\hbar$ is the frequency of the vibrational transition. We see from (2.6) that, in the region close to singlephoton resonance $(\tilde{\omega} \rightarrow \tilde{\omega}_{s,s})$, the magnitude of $\tilde{\alpha}_{v}$ becomes appreciable and can compete with the electronic-vibrational contribution α_v by enhancing or weakening the action of α_v (the signs of $\tilde{\alpha}_v$ and α_v can differ). The authors of Ref. 20 explain the increased change in the refractive index of SF_6 upon vibrational excitation with increasing wavelength in the interferometer by the influence of the vibrational polarizability. The relative changes in $\Delta n/(n-1)$ observed in Ref. 20 at the wavelength $\lambda = 0.63 \ \mu m$ amounted to from $(6.0 \pm 0.5) \times 10^{-3}$ to $(2.3 \pm 0.3) \times 10^{-2}$ upon changing the vibrational temperature T_v from 800 to 1800 K. At $\lambda = 3.39 \ \mu m$ the deviation $\Delta n/(n-1)$ varied from $(1.2 \pm 0.3) \times 10^{-2}$ to $(4.4 \pm 0.7) \times 10^{-2}$ upon changing $T_{\rm v}$ from 900 to 1900 K (Fig. 2).

An increase in the polarizability of the molecules, and hence in the refractive index, owing to excitation of vibra-



FIG. 2. Change in the refractive index of SF₆ upon vibrational excitation.

tional degrees of freedom in the interaction with resonance infrared radiation can lead to focusing. Actually, in the propagation of high-power laser radiation a medium is formed in the channel of a laser beam with a nonequilibrium vibrational excitation of the molecules, i.e., with an elevated refractive index, which is the cause of self-focusing.

For a qualitative estimate of the effect of self-focusing we can use the known expression for the self-focusing length

$$R_{\rm f} = a_0 (n/2\Delta n)^{1/2}$$

Here *n* is the refractive index of the medium before arrival of the laser radiation. Δn is the change in refractive index induced by the laser radiation, and a_0 is the initial radius of the light beam. If we use the results of Ref. 20, i.e., assume that for SF₆ $n/(n-1) = 2.3 \times 10^{-2}$ at $T_v = 1800$ K, while $n-1 = 2 \times 10^{-6}$ at p = 2 Torr, then when $r_0 = 1$ mm, we have $R_f \sim 3 \times 10^3$ mm.

Reference 25 presented experimental dependences of the radius of the light beam on the distance in a cuvette containing the gas SF₆ for different values of the intensity of laser radiation at an SF₆ pressure of 6.4 Torr, which could be explained by the excess vibrational excitation of the SF₆. The self-focusing length varied in the range $(0.6-1) \times 10^3$ mm upon varying the intensity of the laser radiation from 0.1 to 1 J/cm².

In quantitative estimates of self-focusing one must take account of two other possible effects besides the change in polarizability-the fall in temperature due to kinetic cooling and electrostriction.

The effect of kinetic cooling involves the situation that, under certain conditions in the first instants after absorption of infrared radiation by polyatomic molecules, the gas will be cooled rather than heated.²⁶ One can understand the physical cause of this effect using the example of air. Upon passage of the high-power radiation of a CO₂ laser through the atmosphere, the CO₂ molecules absorbing the radiation go from the 10⁰0 to the 00⁰1 level. The reverse conversion of the vibrational energy of CO₂ and of the N₂ molecules in resonance interaction with CO₂ into thermal energy (into energy of the translational degrees of freedom) occurs more slowly than the process of populating the 10⁰0 level, which has been depleted by the resonance absorption of energy. Therefore, in the first instants of time after the action of the radiation, one will observe cooling of the gas, rather than heating. Cooling of the gas under conditions of constant pressure will be accompanied by an increase in density. In turn this leads to increased refractive index, i.e., focusing. Detailed calculations of self-focusing owing to the effect of kinetic cooling were performed in Refs. 27 and 28. In particular, it was shown in Ref. 28 that the light beam of a CO_2 laser of power 500 kW/cm² and radius 0.5 cm propagating in dry air with a 5% addition of CO₂ undergoes self-focusing owing to kinetic cooling in which the intensity on the axis at a distance of ~ 8 m increases almost seven fold. The influence of the effect of electrostriction on the change in refractive index is usually small. It is of the same order of magnitude as the change in the refractive index due to the Kerr effect.²⁰ However, we note that the problem of the Kerr effect in a nonequilibrium gas has not been solved, although the Kerr constant (just like the Gladstone-Dale constant) must depend on the vibrational temperature, or more exactly, on the mean store of internal energy. The influence of electrostriction on the variation of density has been analyzed in greater detail in Ref. 29.

Detailed calculations of the change in refractive index due to the factors listed above and of the dynamics of selffocusing have been performed in Refs. 29–33.

Figure 3, taken from Ref. 29, shows the dynamics of focusing of the radiation of a pulsed HF laser in an $H_2O-N_2-O_2$ medium close to the composition of the moist atmosphere at altitudes of 10-40 km. Here I/I_0 is the intensity of the radiation normalized to the initial intensity ($I_0 = 100$ MW/cm²). $\bar{r}_0 = r/a_0$ is the radial distance in the beam with respect to the initial radius of the light beam ($a_0 = 10$ cm), $\bar{Z} = Z/L_D$ is the distance along the track with respect to the diffraction length ($L_D = 976.2$ m). We see from Fig. 3 that, owing to formation of a focusing lens in the channel of the beam, the radiation intensity on the axis of the beam increases (the maximum value of I is reached in the cross section $\bar{Z} = 1$), although it should decline owing to diffractional divergence and absorption (dot-dash line). With increasing time the maximum of I is shifted toward larger



FIG. 3. Focusing of the radiation of a pulsed HF laser in an $H_2O-N_2-O_2$ medium. Solid line- I/I_0 , dot-dash line- I/I_0 at t = 0, i.e., without taking account of formation of a focusing lens, dashed line- $\delta n/n$. The values of I/I_0 and $\delta n/n$ pertain to the instant of time $t = 4.5\tau_p$, where the relaxation time τ_p of the absorbed vibrational energy is much shorter than the pulse duration.

values of Z, while in the cross section Z < 1 the decrease in density caused by heating of the medium begins to have an effect (in Fig. 3, which corresponds to the time $t = 4.5\tau_p$, cooling of the medium occurs). For large t a further shift of the maximum in the I(Z) distribution occurs, and a region is formed on the axis of the beam with $\delta n < 0$.

The possibility of controlling the dynamics of self-action enables one to attain a decreased loss of energy to scattering in a given cross section of the track of propagation and to obtain the maximum power density.

As we have already stated, the optical manifestations of nonequilibrium are not restricted to a change in the molecular characteristics. Vibrational-rotational nonequilibrium is distinctly manifested in many phenomena, e.g., in the infrared radiation of the upper atmosphere of the Earth and other planets. The upper atmospheres of the planets are rarefied gases subjected to the constant action of the corpuscular and electromagnetic radiation of the Sun. Under this influence a nonequilibrium molecular medium is formed in the upper atmospheres, which governs the nonequilibrium character of the infrared radiation in vibrational-rotational transition. The interest in nonequilibrium infrared radiation is primarily determined by the fact that it plays an extremely important role in the thermal regime of the upper atmospheres and can yield interesting information on the processes in these media. In particular, it was shown in Ref. 34 that at altitudes above 115 km for Venus and 70 km for Mars an inverted population exists in the 001 and 100 levels of CO_2 molecules. Thus one can classify Venus and Mars as the first natural laser objects in the infrared range that have become known to us (the atmospheres of Venus and Mars predominantly consist of CO_2 molecules).

3. HYDRODYNAMIC PROPERTIES OF A NONEQUILIBRIUM GAS

The hydrodynamic behavior of a nonequilibrium gas is characterized by two features that distinguish it from an equilibrium gas. First, in a change in the parameters of the medium caused by hydrodynamic movement, the flux of energy between the internal and translational degrees of freedom of the molecules is altered. In turn, this affects the hydrodynamic and thermodynamic parameters of the medium. Second, a perturbation of the fields of the hydrodynamic and thermodynamic quantities in a nonequilibrium medium directly affects the intensity of heat loss and energy pumping due to an external energy source (discharge, laser radiation, chemical reaction, etc.), which determine the nonequilibrium store of energy in the internal degrees of freedom and the heating of the gas. The joint action of these two factors leads to the appearance of new effects that will be discussed in the last part of the review using the example of propagation of small and finite perturbations, as well as shock waves, in a nonequilibrium gas.

3.1. Propagation of small perturbations in a nonequilibrium gas

As is known, when small hydrodynamic perturbations appear in a homogeneous flow of a gas of structureless particles, two types of waves arise-acoustic, which propagate with a velocity determined by the sum of the velocities of the flow and of sound, and entropy waves, which move with the velocity of the flow.³⁵ In the entropy waves the variations of the pressure and the velocity are zero, and only the density and the temperature vary. From the mathematical standpoint the appearance of acoustic and entropy waves involves the features of the solution of the linearized hydrodynamic equations, which lead to a finite set of eigenvalues and eigenfunctions, with which one can describe any small perturbation arising in the gas. In the simplest case of one-dimensional motion, the linearized system of hydrodynamic equations (equations of continuity, motion, and energy) will consist of three first-order equations with respect to the three independent variables (e.g., p', ρ' , and v', corresponding to perturbations in the pressure, density, and velocity). The solution of this system of equations defines three eigenfunctions (and the eigenvalues corresponding to them), two of which will describe acoustic waves propagating in opposite directions, and one an entropy wave.

In the propagation of perturbations in a molecular gas initially at equilibrium the picture is complicated primarily by the breakdown of equilibrium between the internal and translational degrees of freedom. The nonequilibrium energy distribution alters the adiabatic compressibility, which determines the velocity of sound, which leads to anomalous dispersion of sound waves. This effect is well known experimentally. The first theory of this phenomenon was proposed by Herzfeld and Rice,³⁶ and was subsequently developed successfully by Knezer (see Ref. 37). A general thermodynamic theory of relaxation processes in a sound wave was first created by Mandel'shtam and Leontovich.³⁸

If the hydrodynamic perturbations are propagating in a nonequilibrium gas new effects arise. In particular, sound waves can be amplified. The physical mechanism that leads to amplification consists in the following. The exchange of energy among the internal and translational degrees of freedom in different periods of the sound wave occurs in different ways. The discharge of energy into the translational degrees of freedom in the half-period of the sound wave corresponding to temperature increase can exceed the reverse process in the half-period where the temperature is below the equilibrium value (the fundamental factor affecting the rate of energy exchange is the temperature, and as the latter increases the discharge of energy is enhanced).

To understand the fundamental features of propagation of sound waves, let us study the very simple case of propagation of a sound wave in a gas whose steady but nonequilibrium state is being maintained by pumping energy into the vibrational degrees of freedom by a power I and a heat withdrawal from the translational degrees of freedom of power Q (I and Q are referred to unit mass).^{39,40} The equations of continuity, motion, and energy will have the following form:

$$\frac{\partial \rho}{\partial t} + \operatorname{div}(\rho \mathbf{v}) = 0, \tag{3.1}$$

$$\rho \frac{\mathrm{d}\mathbf{v}}{\mathrm{d}t} = -\nabla p,\tag{3.2}$$

$$\frac{\mathrm{d}H}{\mathrm{d}t} - \frac{1}{\rho} \frac{\mathrm{d}\rho}{\mathrm{d}t} = I - Q, \qquad (3.3)$$

Here $H = \gamma p/[(\gamma - 1)\rho] + \varepsilon$, where γ is the adiabatic index without taking account of the vibrational degrees of freedom, ρ , p, and v are the density, pressure, and velocity of the gas, and ε is the vibrational energy per unit mass. We shall write the relaxation equation for ε in the following form:

$$\frac{\mathrm{d}\varepsilon}{\mathrm{d}t} = \frac{\varepsilon_0(T) - \varepsilon}{\tau} + I, \qquad (3.4)$$

Here $\varepsilon_0(T)$ is the equilibrium value of the vibrational energy for the given temperature T, and $\tau(\rho, T)$ is the vibrational relaxation time. Together with the equation of state, the system (3.1)-(3.4) forms a closed system of equations. Small perturbations are described by the linearized equations that arise upon substituting into (3.1)-(3.4) solutions in the form

$$A + A' \exp(ikx - i\omega t), \tag{3.5}$$

Here $A \equiv \rho$, p, T, v, or ε -the parameters of the unperturbed medium, while A' is the perturbation, which is assumed to be small. Substitution of (3.5) into (3.1) and (3.4) enables one to find the dispersion relation associating the frequency ω with the wave vector k. The concrete relationships are determined by the boundary conditions. For a running sound wave of frequency ω , the complex value of the wave vector Re $k(\omega) = i \operatorname{Im} k(\omega)$ determines the phase velocity and the coefficient of absorption (or amplification) of the sound wave. The variation of $k(\omega)$ throughout the range of frequencies has been analyzed in Ref. 39. The frequency dependence of Im $k(\omega)$ is determined by the concrete form of the characteristics of the heat removal and the pumping, especially in the region $\omega \tau \leq 1$. Its distinctive feature is the existence under certain conditions of a critical frequency $\omega_{\rm cr}$. Figure 4 shows the dispersion curve for one of the variants of the calculation. In the general case the critical frequency ω_{cr} is determined by the form of the thermal fluxes that bring about heat removal and pumping. However, it will always decrease with increasing pumping intensity and relaxation time, and increase with increasing efficiency of heat removal. That is, it will be determined by the store of vibrational (internal) energy and the rate of the transition into the vibrational degrees of freedom.

At high frequencies ($\omega \tau \gg 1$) the condition for amplification has the form

$$\operatorname{Im} k = \frac{m(\gamma - 1)^2}{2k_{\mathrm{B}}(\gamma p/\rho)^{1/2}\tau\gamma} \times \left[\left(\frac{2}{\gamma - 1} - \frac{\partial \ln \tau}{\partial \ln T} \right) \frac{\varepsilon - \varepsilon_0}{T} - \frac{\partial Q}{\partial T}\tau - c_{\mathrm{V}} \right] > 0,$$
(3.6)

where *m* is the mass of the molecule, $k_{\rm B}$ is the Boltzmann constant, and $c_{\rm V} = \partial \varepsilon_0 / \partial T$ is the heat capacity of the vibrational degrees of freedom. The amplification effect increases with increasing dependence of the relaxation time on the temperature ($\partial \ln \tau / \partial \ln T < 0$) and with increasing vibrational nonequilibrium ($m(\varepsilon - \varepsilon_0) / k_{\rm B} T$). The last term in



FIG. 4. Frequency dependence of the absorption curve.

(3.6) corresponds to the ordinary dissipation of sound in a gas having internal degrees of freedom. With increasing relaxation time the amplification coefficient declines; however, with decreasing magnitude of τ a larger magnitude of pumping *I* is required to maintain the same degree of non-equilibrium, since $\varepsilon - \varepsilon_0 = I\tau$. For CO at p = 100 Torr, T = 500 K, and for the vibrational temperature $T_V = 700$ K, we obtain Im $k = 10 \text{ m}^{-1}$. Let us point out for comparison that the amplification coefficient for infrared radiation in a CO laser is of the order of 0.1 m⁻¹.

We note that the presented scheme of discussions is generally valid also in analyzing nonequilibrium for the other degrees of freedom, and also for a more complex dependence of the pumping intensity on the parameters of the system.

A brief history of the theoretical studies of the amplification of sound waves is the following. The possibility of amplifying sound waves was first studied using the example of a gas discharge under conditions in which the temperature of the electrons exceeds the temperature of the heavy particles.41,42 Reference 43 discussed the possibility of manifestation of this amplification mechanism for a nonequilibrium population of the other degrees of freedom. Reference 44 studied the mechanism of amplification of sound waves in a system of two-level and multilevel particles having a nonequilibrium population, and performed numerical calculations for an H₂-CO mixture. Reference 45 analyzed different mechanisms of amplification of sound waves in a discharge with account taken of the internal degrees of freedom of the gas molecules, and found the conditions of amplification. Srinivasan and Vincenti⁴⁶ studied a nonequilibrium gas whose state was being maintained by a chemical reaction, radiation, or energy transfer from electronically excited impurities. As a result they obtained the conditions of amplification of high-frequency perturbations. References 47-57 were devoted to various aspects of the theory of propagation of sound in nonequilibrium media. In particular, Ref. 54 took account of the possibility of a nonequilibrium state, not only of the vibrational, but also of the rotational degrees of freedom. Reference 56 found the conditions of sound amplification for a gas having a nonequilibrium store of energy in excited electronic states of molecules. As we have already noted above, the behavior of a nonequilibrium gas over a broad range of variation of the parameters must not be analyzed without taking account of the influence of pumping and heat removal. This situation was pointed out in Refs. 39 and 40. A brief review of the results obtained in these studies is given at the beginning of this section.

Up to now we have been discussing the study of the dispersion relationships for a running sound wave. However, we should note that the entire complex of traditional problems of acoustics arises in problems of propagation of sound in a nonequilibrium gas, e.g., the study of standing waves, reflection of sound, etc. These problems have been studied very little up to today, although recently several studies have been published, $^{58-60}$ where results have been used to solve them that were obtained in the analysis of the propagation of radiation in an active medium. We should note that this analogy has been noted already rather long ago, while even in Ref. 44 the possibility of amplification of a sound wave was discussed from the standpoint of the acoustic analog of a laser (we note also the recently published paper, Ref. 61, where it was proposed to use a supersaturated vapor as the nonequilibrium medium for such a system). However, the transfer of the results of optics to acoustics demands a certain caution. And while for the steady-state vibrations of a bounded medium⁵⁸ such a transfer is apparently possible, in problems of reflection of sound one must approach this analogy with caution. For example, in the reflection of sound from the boundary of equilibrium and nonequilibrium gases, oscillations of the boundary arise, which can strongly affect the result of calculations (at least this influence is substantial in analogous problems for an equilibrium medium³⁵).

The analysis that we have performed of sound propagation did not take account of the influence of the viscosity terms. We see from (3.6) at high frequencies the "relaxation" amplification (or absorption) does not depend on the frequency, whereas with increasing frequency the influence of the viscosity terms increases (upon taking account of the viscous forces, the imaginary part of the wave vector is proportional to the square of the frequency³⁵). The limiting frequency above which one must take account of viscous effects is determined by the relationship $\omega \sim (\tau \tau_0)^{-1/2}$, where τ_0 is the time of free flight.^{62,63} The influence of the viscous terms will have the strongest effect in a nonlinear regime, which will be discussed in the following sections.

In the low-frequency region ($\omega \tau \ll 1$) the imaginary part of the wave vector will be, just as for the viscous effects, proportional to the square of the frequency. This enables us to draw an analogy between these processes, since the action of the relaxation absorption is analogous to the action of viscous forces. This analogy has a deeper grounding. When $\omega \tau \ll 1$ one can eliminate the relaxation equation by considering the relaxation process in the zero-order approximation in $\omega \tau$ to have finished, while its incompleteness (in the first order in $\omega \tau$) is manifested in the equation of motion in the form of an additional term corresponding to the second viscosity. We note that this approach imposes no restrictions on the magnitude of the perturbation. The small parameter is the quantity $\omega \tau$ (in this case we should treat ω^{-1} as a certain characteristic time that appears in the problem). This procedure for an equilibrium gas has been discussed in detail in Ref. 1, while the nonequilibrium case has been presented in Ref. 64 and will be discussed in detail in the next section.

At the same time, it will be incorrect to speak of a second viscosity at frequencies $\omega \tau \gtrsim 1$, since at these characteristic times we cannot reduce the equations of relaxation hydrodynamics (3.1)-(3.4) to the equations of equilibrium hydrodynamics with an additional dissipation. An analogous situation arises generally also with the shear viscosity. One can derive the Navier-Stokes equation from the gaskinetic Boltzmann equation only under the condition $\omega \tau_0 \ll 1$. If the condition $\omega \tau_0 > 1$ is satisfied in the propagation of sound, then this phenomenon must be treated on the basis of the Boltzmann equation.

In closing the review of the theoretical studies, we note an important circumstance. The study of sound waves at frequencies $\omega \tau \gtrsim 1$ in a nonequilibrium gas without taking account of the gradients of the unperturbed parameters and the boundary conditions is qualitative in nature. Actually, in real steady-state systems either the bounded volume of the nonequilibrium gas (in flow-through systems the characteristic dimension in $L^* \leq v^* \tau$, where v^* is the velocity of flow, whereby the gradients of the unperturbed parameters are significant at this distance), or in the case of a gas at rest, considerable temperature gradients arise from the heat removal. Therefore in real systems the influence of inhomogeneity of the nonequilibrium gas is imposed on the effects discussed above, and this must be taken into account in concrete calculations.

The experimental data on the study of amplification of sound waves are very meager. The study of acoustic instabilities in discharges began at the beginning of the sixties. In Ref. 65, upon modulating a dc glow discharge over a broad range of modulation frequencies, oscillations were found in the discharge at certain frequencies corresponding to the acoustic modes of the discharge tube. In Ref. 66 a modulation was observed in the electron density and in the emission in the process of decay of a discharge, which was explained by the appearance of pressure waves generated by the discharge, while in Ref. 67 acoustic vibrations were detected that arose in the discharge under certain conditions. The interaction of a sound wave with a discharge leading to modulation of the emission and of the electron density was studied in Refs. 68-72. The characteristics of sound waves created in a discharge were studied in Refs. 73-76. The amplification coefficient of a sound wave in a discharge tube in inert gases was measured in Ref. 75. In the recently published Ref. 76 the amplification coefficient was measured not only in the inert gases (He, Ne, Ar), but also in molecular gases (N_2 , air, and an N_2 -Ar mixture). We note the fundamental experimental results of these studies. The sound amplification coefficients measured in Refs. 75 and 76 are of about the same order of magnitude. However, as was noted in Ref. 76, they exceed by about tenfold the theoretical value, while in Ref. 75, as was shown in Ref. 76, good agreement of the theory with experiment was erroneously obtained. Reference 76 discussed a number of the factors that might depress the theoretical estimate and, in particular, studied the limitations of the hydrodynamic approach under the conditions being discussed. Since quantitative estimates are lacking in Ref. 76, we can consider the problem of the discrepancy of the theoretical and experimental data on amplification of sound waves in a discharge to be open.

We note also a number of experiments to study the propagation of sound waves in a reacting gas with the exothermic reaction $H_2 + Cl_2 \rightarrow 2HCl^{.77-79}$ These experiments observed a difference between the absorption of sound in the gas without reaction and in the process of reaction. The decreased absorption in the reacting gas could be explained by the appearance of amplification caused by the heating of the gas by the exothermic reaction. The mechanism of amplification is determined by the dependence of the reaction rate on the temperature. The agreement of theory and experiment in the region of low reaction rates was rather good. At high reaction rates the calculated coefficient exceeded the experimental value by twofold. We must note that in interpreting the results of Refs. 77-79, and also in the numerical simulation,^{48,79} the strong vibrational excitation of the HCl molecules being formed was not taken into account. The characteristic times of the vibrational relaxation processes in these experiments coincide in order of magnitude with the period of the sound vibrations. The experiments in Refs. 77-79 were performed in the buffer gases $Ar^{77,78}$ and SF_{67}^{79} which were used to decrease the reaction rate. However, we should take account of the fact that a new process arises on

adding SF_6 -exchange of vibrational energy between SF_6 and the vibrationally excited HCl molecules formed in the reaction. This process has not been studied at present. Taking account of vibrational nonequilibrium and the broader frequency spectrum in the experiments enable one to study more fully the influence of a chemical reaction and vibrational nonequilibrium on the propagation of sound.

3.2. Nonlinear low-frequency perturbations and the second viscosity coefficient

Amplification of hydrodynamic perturbations should lead to the appearance of nonlinear effects, which in turn will hinder further growth of the perturbations. The process of propagation of the perturbations is described by the standard system of equations of continuity, motion, energy, and relaxation. However, it is rather complicated to find an analytic solution of this system in a general form. Therefore a number of methods have been developed in the literature for describing nonlinear perturbations. These methods can be successfully used also for a nonequilibrium gas. The further plan of presentation is the following. First we shall discuss the scheme of description of finite hydrodynamic perturbations in which the relaxation processes are taken into account by using the second viscosity coefficient. Then we shall analyze the effects of quadratic nonlinearity for highfrequency perturbations.

As was already noted in Sec. 3.1, formally the second viscosity coefficient can be calculated from the imaginary part of the wave vector. However, the physical meaning of the second viscosity coefficient is revealed most distinctly if we transform from the equation of relaxation hydrodynamics to the equations of ordinary equilibrium hydrodynamics. In this case terms arise in the equations of motion that correspond to the appearance of a second (bulk) viscosity. Here the small parameter that enables one to transform from the system of equations of relaxation hydrodynamics to the equations of equilibrium hydrodynamics will not be the dimensionless magnitude of the deviation of the hydrodynamic quantities from the equilibrium values, but the product of the characteristic frequency and the relaxation time $\mu = \omega \tau$. In this case we can assume that in the zero-order approximation ($\mu = 0$) the relaxation process is completed, while the remaining local nonequilibrium in the next order of approximation at each instant of time is determined by the fields of the hydrodynamic quantities at that very instant of time. In this case the variables ε and p can be represented in the form¹ (s is the total entropy per unit mass):

$$\varepsilon = \varepsilon^{(0)}(r, \rho, s, v) + \mu \varepsilon^{(1)}(r, \rho, s, v) + ...,$$

$$p(\rho, s, \varepsilon) = p^{(0)}(\rho, s) + \mu \left(\frac{\partial p}{\partial \varepsilon}\right)_{\rho, s, \varepsilon^{(0)}} \varepsilon^{(1)} +$$
(3.7)

Here the values with zero indices correspond to the equilibrium parameters. Thus, for example, $p^{(0)}(\rho,s)$ corresponds to the pressure that would exist in the system having the given density ρ and entropy s if the system were in equilibrium with respect to the internal degrees of freedom (in this case vibrational). This approach is analogous to the Enskog-Chapman method and was studied in Ref. 1 for a gas initially in equilibrium. The values of the parameters with zero indices can vary depending on the choice of the independent variables. Thus, for example, we have $\varepsilon^{(0)}(\rho,s) \neq \varepsilon^{(0)}(\rho,T)$, but here also the value of the relaxation time τ is changed. This feature was noted in Ref. 80 for the case of a gas initially in equilibrium (see the note there in the section on anomalous sound absorption). After determining $\varepsilon^{(1)}$ and eliminating it from the linearized system of equations, we obtain the equation of motion in the form being sought

$$\rho \frac{\mathrm{d}\mathbf{v}}{\mathrm{d}t} = -\operatorname{grad} p^{(0)} + \operatorname{grad}(\xi \operatorname{div} \mathbf{v})$$
(3.8)

with the second viscosity coefficient

$$\xi = -\frac{\partial p}{\partial \varepsilon} \tau \frac{\partial \varepsilon^{(0)}}{\partial \rho} \rho, \text{ or } \xi = \tau \rho (c^2 - c_0^2).$$
(3.9)

Here c_0 and c are the equilibrium and frozen velocities of sound. Thus the transformation to describing nonequilibrium in terms of second viscosity means a contraction of the means of description-instead of the four variables ρ , s, v, and ε that satisfy the system of equations of relaxation hydrodynamics, three remain- ρ , s, and v, which are determined by solving the equations of ordinary hydrodynamics. This simplification is attained at the cost of coarsening the time scale. Processes that occur at times of the order of the relaxation time are not studied, while only their result is important, leading to the expansion in (3.7).

The amplification of sound in nonequilibrium media (negative absorption coefficient) can be interpreted as the existence of a negative second viscosity coefficient in the vibrationally nonequilibrium gas.^{52.54} The method of obtaining this coefficient from analyzing the propagation of a sound wave was discussed in the first subsection of this section. A rigorous derivation of the expression for the second viscosity coefficient in a medium initially in equilibrium, not restricted to the acoustic approximation, and based on the general idea of contracting the method of description presented above, is given in Ref. 64. A nonequilibrium system with pumping and heat removal is characterized, besides the relaxation time, also by the effective time of pumping and heat removal, the smaller of which we shall denote by au_{source} . If $1/\tau_{\text{source}} \ll \omega \ll 1/\tau$, then the intensity of the sources can be considered constant, and the scheme of calculation presented above is retained. The change in the entropy s is determined by the equation

$$\frac{\mathrm{d}s}{\mathrm{d}t} = \left(\frac{1}{T_{\mathbf{V}}} - \frac{1}{T}\right)\frac{\varepsilon_0 - \varepsilon}{\tau} + \frac{I}{T_{\mathbf{V}}} - \frac{Q}{T},\tag{3.10}$$

where T_v is the vibrational temperature. In a nonequilibrium gas the quantity *s* will already be of the second order of smallness. Therefore *s* in this case will not be distinguished in any way among the other variables. Depending on the choice of independent variables, the values of the equilibrium internal energy will differ. This, as has already been pointed out, is characteristic also of a gas initially at equilibrium. Here the values of $p^{(0)}$ and *s* will be changed. One can derive the following expression⁶⁴ for the second viscosity coefficient in the variables of the total energy per unit mass *E* and ρ :

$$\xi = \frac{(\gamma - 1)k_{\rm B}\rho\tau}{m} \\ \times \left\{ p^{(0)} \left[\frac{mc_{\rm V}(\gamma - 1)}{k_{\rm B}} + \frac{\varepsilon - \varepsilon_0}{\tau} \frac{\partial\tau}{\partial E} \right] \rho^{-2} - \frac{\varepsilon - \varepsilon_0}{\tau} \frac{\partial\tau}{\partial\rho} \right\} \\ \times \left[\frac{mc_{\rm V}(\gamma - 1)}{k_{\rm B}} + 1 - \frac{\partial\tau}{\partial E} \frac{\varepsilon - \varepsilon_0}{\tau} \right]^{-2}.$$
(3.11)

Here γ is the adiabatic index without taking account of the vibrational degrees of freedom. If $\tau \sim \tau_{\rm source}$, in the time τ in the zero-order approximation not only is the relaxation process completed, but also the process of synchronization of the sources with the instantaneous fields. This leads to a change in the expression for the pressure, which acquires the form

$$p = p^{(0)}(\rho) + \mu \frac{\partial p}{\partial \varepsilon} \varepsilon^{(1)} + \mu \frac{\partial p}{\partial E} E^{(1)}.$$
 (3.12)

Here, in addition to $\varepsilon = \varepsilon^{(0)} + \mu \varepsilon^{(1)} + ...$, one takes account of the expansion $E = E^{(0)} + \mu E^{(1)} + ...$. The corresponding second viscosity coefficient has a rather unwieldy form (see Ref. 64).

We note two substantial differences in the properties of the second viscosity of gases initially in equilibrium and in nonequilibrium. First, in introducing the second viscosity coefficient for a nonequilibrium medium a further contraction of the method of description occurs. Besides the process of relaxation of the energy, also one does not treat the process of synchronization of the sources with the hydrodynamic fields. In the former case ($\omega \tau_{\text{source}} \ll 1$) this process is considered to be frozen, and in the latter case ($\omega \tau_{\text{source}} \ll 1$) it is regarded to be very fast and only its result is considered. Second, the second viscosity coefficient, just like the absorption coefficient, loses its original meaning as a characteristic of the medium in the case $\omega \tau_{\text{source}} \ll 1$ when $\tau \rightarrow \tau_{\text{source}}$, since it begins to depend on the concrete form of the sources of heat removal and pumping.

The second viscosity coefficient can acquire a negative value (see (3.11)). This situation does not contradict the second law of thermodynamics, in line with which the material constants of the medium (coefficients of shear viscosity, diffusion, and heat conductivity) are always greater than or equal to zero. The appearance of a negative second viscosity is consistent with thermodynamic concepts if the production of entropy is not negative. In the case under discussion we have

$$\sigma = \left(\frac{1}{T_{\rm V}} - \frac{1}{T}\right) \frac{\varepsilon - \varepsilon_0}{\tau}$$
(3.13)

and we have $\sigma \ge 0$ independently of the sign of ξ . In (3.13) we can separate out the term associated with ξ :

$$\sigma = \sigma_0 + \tilde{A}\xi \operatorname{div} \bar{v}. \tag{3.14}$$

In contrast to ordinary thermodynamics, where $\sigma = \xi (\operatorname{div} \overline{v})^2$, a negative value of ξ does not change the sign of σ , since the additional term in the entropy production proves to be small in comparison with the production of entropy σ_0 under unperturbed steady-state conditions.

We note that the description of the hydrodynamic behavior of the system by using the equations of motion with a negative second viscosity coefficient is bounded in time. With increasing amplitude of the perturbation and development of nonlinearity, higher harmonics arise, and the condition $\omega \tau \ll 1$, under which the second viscosity has a meaning, ceases to be fulfilled. Apparently this situation must be taken into account in treating the quadratic nonlinearity for perturbations with $\omega \tau \ll 1$ in a medium having a negative second viscosity, ^{52,81} since the growth of the higher harmonics can occur far faster than the appearance of the nonlinear effects obtained from analyzing the Burgers equation with a negative second viscosity. An example of the acceleration of the formation of harmonics owing to nonequilibrium will be discussed in the next subsection for perturbations with the characteristic frequency $\omega \gg 1/\tau$.

3.3. Nonlinear hydrodynamic waves in a nonequilibrium gas

Nonlinear equations of motion (Euler's equations) were first integrated without the assumption of smallness of the nonlinearity by Riemann (see Ref. 35). Riemann started with the equations of hydrodynamics in the one-dimensional case supplemented with the equation of state $p = p(\rho)$. The Riemann method consists in the idea that the nonlinear system of equations is reduced to a linear one by substitution of variables. This can be done in the one-dimensional case. Analysis of the solution showed that the regions of compression move in the course of propagation at velocities greater than the rarefaction regions. This leads to deformation of the profile of the wave as it propagates. The front of the wave becomes steeper until the condensation wave converts into a shock wave. The further treatment ceases to be valid, since it takes no account of either the viscosity or the heat conductivity, the roles of which increase with increasing gradients.

In the Riemann solution, as we have already said, the nonlinearity is not considered to be small. However, from the physical standpoint the formulation of the problem by Riemann is restricted to the region of applicability of the equation of state $p = p(\rho)$. The adiabatic equation of state describes isentropic processes, while the real change in entropy of acoustic waves is of the third order of smallness (in the Mach number $Ma_s = v/c_s$). Thus the Riemann solution correctly describes the behavior of an intense sound wave in the second approximation.

One can take simultaneous account of the nonlinear and dissipative effects by using the Burgers equation.⁷⁹ It is not exact, since it cannot be derived from the equations of hydrodynamics of a viscous liquid without additional simplifications. At the same time, it describes rather well nonlinear waves in media with dissipation, since it takes account of all the fundamental terms of the second order of smallness.

If we denote by primes the deviations of the hydrodynamic quantities from the steady-state values, then the Burgers equation for p' has the form

$$\frac{\partial p'}{\partial x} - bp' \frac{\partial p'}{\partial \theta} - \delta \frac{\partial^2 p'}{\partial \theta^2} = 0, \qquad (3.15)$$

where $\theta = t - (x/c_s)$, the dissipative coefficient is $\delta = [(4\eta/3) + (\gamma - 1)^3 \gamma^{-1}] \times (2c_s^3)^{-1}$, and the nonlinear parameter is $b = (\gamma + 1)/2c_s^3$. The equation for v also has exactly the same form, since for simple waves $\rho = \rho(v)$, p = p(v).

The Burgers equation for a small nonlinearity goes over into the known linear equation for dissipative media, while in the absence of dissipation it goes over into the Riemann equation for simple waves.⁸²

The qualitative picture of the evolution of a sound wave of finite amplitude described by the Burgers equation looks as follows. In the first stage in the process of propagation of the wave, a distortion of the form of the profile occurs and culminates in formation of a sawtooth signal. In the second stage the form of the front is stabilized. In the competitive conflict of the nonlinear and dissipative effects, "equilibrium" arises. However, the oscillating value of the signal amplitude declines, since the action of the dissipative effects is not compensated in any way. In the third stage the amplitude of the wave no longer depends on is value at the input. The wave again becomes harmonic and decays according to the laws of linear acoustics. A solution of the Burgers equation describing the evolution of an initially harmonic perturbation was obtained by Khokhlov (see Ref. 82).

A new factor appears in the propagation of nonlinear hydrodynamic waves in nonequilibrium gases having an excess of vibrational energy-energy exchange between the vibrational degrees of freedom and the hydrodynamic motion. The additional energy "feeding" the wave process can lead to two new effects. First, the process of inversion of the wave is accelerated. The amplification of the wave in the vibrationally nonequilibrium gas enhances the role of the nonlinear factor, and the nonlinear effects are manifested earlier. Second, energy pumping begins to compete with the dissipative processes. This can have the result that, after reversal of the wave, a steady-state regime is formed, in which the dissipative losses will be fully compensated by the influx of energy from the internal degrees of freedom.

A quantitative description of the evolution of nonlinear hydrodynamic perturbations in a vibrationally nonequilibrium gas was given in Refs. 62 and 63. The starting point is the generalized Burgers equation (for $\omega \tau \ge 1$)

$$\frac{\partial p'}{\partial x} - bp' \frac{\partial p'}{\partial \theta} - \delta \frac{\partial^2 p'}{\partial \theta^2} - \beta p' = 0, \qquad (3.16)$$

This differs from (3.15) in the term $\beta p'$, which takes account of the amplification of the wave by energy exchange between the internal degrees of freedom and the hydrodynamic modes. In (3.16) we have

$$\beta = -\frac{(\gamma - 1)\rho}{2(\gamma p/\rho)^{1/2}\tau} \left[\frac{T(\gamma - 1)c_{\rm V}}{\gamma p} + I \frac{\partial \tau}{\partial p} - \frac{\partial Q}{\partial p}\tau \right].$$
 (3.17)

Just as in (3.6), c_v denotes the heat capacity of the vibrational degrees of freedom ($c_v = \partial \varepsilon_0 / \partial T$), $\tau = \tau(p,s,\varepsilon)$, $Q = Q(p,s,\varepsilon)$.

The generalized Burgers equation (3.16) is obtained from the equations of continuity and motion, supplemented with the relaxation and entropy equations (3.4) and (3.10) in the approximation $\omega \tau \gg 1$, apart from terms of the second order of smallness inclusively in the small hydrodynamic perturbations. In the frequency range $\omega \tau \gg 1$, where the generalized Burgers equation (3.16) is valid, the dissipative (viscosity), nonlinear, and relaxation effects are manifested in different ways. As was already noted in Sec. 3.1, the ratio of the viscosity term $\delta(\partial^2 p'/\partial \partial^2)$ to the relaxation term is of the order of $\omega^2 \tau \tau_0$. Thus, at frequencies

$$\frac{1}{\tau} << \omega << \frac{1}{(\tau \tau_0)^{1/2}}$$
(3.18)

the relaxation effects predominate over the viscosity effects. Therefore in (3.16) we can neglect the third term, which describes the Stokes (viscous) absorption. The quasilinear equation obtained here is relatively simple to analyze. If a perturbation is propagating in the medium whose profile for x = 0 has the form

$$p'(0,\theta) = f(\theta), \tag{3.19}$$

then we have⁶²

$$p' = \exp(\beta x) f(z), \quad \theta - z = b f(z) \left[1 - \exp(\beta x)\right] / \beta. \quad (3.20)$$

The solution (3.20) describes the amplification (or damping) of the wave and the distortion of its profile. We can most easily convince ourselves of the latter if we treat the case $\beta x \leq 1$. In this approximation we have

$$p'(x, t) = f(\theta - x(c_s^{-1} - bp')).$$

Then, with respect to the stationary medium, a fixed value of p' will propagate with the velocity $c_s^{\bullet} = (c_s^{-1} - bp')^{-1}$, which is greater for greater p'. The distance at which reversal of the wave occurs and a break is formed, as determined by the condition dp'/dx = 0, is

$$l_{\rm p} = \ln \left[1 + \beta (bf')^{-1}\right] \beta^{-1}. \tag{3.21}$$

Equation (3.21) implies that a break is formed only when $\beta/bf' > -1$. For positive β , corresponding to an excess of vibrational energy in the nonequilibrium gas, this condition is always satisfied. When $\beta < 0$, a break is formed only whenever the profile has a sufficiently great steepness $f' < -\beta/b$.

The distortion of the profile of the wave in the process of propagation alters the harmonic composition of the perturbation. If $f(z) = p'_0 \sin(z)$, then the solution (3.20) acquires the form

$$p' = p'_{0} \exp(\beta x) \sum_{n=1}^{\infty} \frac{2J_{n}(n\Delta) \sin(n\omega\theta)}{n\Delta},$$

$$\Delta = \frac{(\gamma + 1)\omega p'_{0}}{2\gamma c_{s} p} \frac{\exp(\beta x) - 1}{\beta}.$$
 (3.22)

We see from (3.22) that, in addition to a uniform increase in the amplitudes of all the harmonics proportional to $\exp(\beta x)$, an accelerated pumping of energy occurs from the first harmonic into the higher harmonics, since $[\exp(\beta x) - 1]/b > x$, and a break is formed more rapidly. With increasing amplitude of the higher harmonics, the Stokes absorption begins to play a substantial role. Therefore in the region of wave reversal one must take account of the omitted viscosity term. Equation (3.16) can be solved in general form by using the Hopf-Cole substitution $p' = 2\delta(\partial \ln \varphi / \partial \theta)/b$. As a result we obtain

$$\frac{\partial \varphi}{\partial x} - \beta \varphi \ln \varphi = \delta \frac{\partial^2 \varphi}{\partial \theta^2}.$$
 (3.23)

In the steady-state case we have $\phi(\theta, x)$, and Eq. (3.23) can be easily integrated:

$$\frac{\partial y}{\partial \theta} = \pm \left\{ \frac{\beta}{\delta} [C - C \exp(-2y) - y] \right\}^{1/2}, \qquad (3.24)$$

where $y = \ln \varphi$, while the value of C is determined by the initial and boundary conditions.

The pressure profile in a steady-state regime is determined by (3.24). At small y, which corresponds to small θ (Fig. 5), we have

$$p' = \frac{2\delta}{b} \frac{\partial y}{\partial \theta} = -\beta(1 - 2C)\theta b^{-1}.$$
 (3.25)

In the neighborhood of $y_0 = \ln(2C)/2$, corresponding to the extremum of $\partial y/\partial \theta$, we find

$$p' = 2\left[C - \frac{1}{2} - \frac{\ln(2C)}{2}\right] (\delta\beta)^{1/2} \cos\left[(\beta\delta^{-1})^{1/2}(\theta - \theta^*)\right] b^{-1},$$
(3.26)

where $y(\theta^*) = y_0$. Finally, when $y \sim y_2$, where $\theta \sim \tilde{T}/2$ (\tilde{T} is the period of the perturbation), we have

$$p' = [1 - 2C \exp(-2y_2)] \frac{\beta}{b} \left(\frac{T}{2} - \theta\right).$$
 (3.27)

The solutions (3.25)-(3.27) show that an initially sinusoidal signal propagating in a vibrationally excited gas acquires in the course of time a steady-state sawtooth form, and subsequently evolves without change of form. We emphasize that the arguments that we have presented do not take account of the change in the temperature regime of the medium and describe the formation of discontinuities moving with a Mach number of the order of unity.

Finally, at very high frequencies, at which $\omega^2 \tau \tau^0 \ge 1$, the relaxation processes prove to be frozen, and can be neglected as compared with the Stokes absorption. In this case the process of propagation is described with good accuracy by the Burgers equation (3.15).

The conversion of a weak discontinuity into a shock wave has been studied both for a gas initially at equilibrium^{83,84} and for a nonequilibrium gas,^{85–87} including account taken of continuous pumping.⁸⁷ The approach of these studies is based on applying the conditions of compatibility for a weak discontinuity. The advantage of this method consists in the fact that in enables one to describe the behavior of the leading front of the perturbation also for a non-steady state of the gas ahead of the wave. However, one can find the time for formation of a shock wave only in the case in which the discontinuity is formed at the leading front of the perturbation. If the gas ahead of the front is homogeneous and in a



FIG. 5. Pressure profile at the initial instant of time (1) and in a steady-state regime (2).

steady state, then the results obtained by the method presented in this subsection completely coincide with Refs. 85 and 86, but the treatment performed in the steady-state case has a number of advantages, since it enables one to obtain more information.

An equation of the type of (3.16) is known in the theory of plasmas⁸⁸ and of chemically reacting suspensions in gases.⁸⁹ In Ref. 62 Eq. (3.16) was derived for a vibrationally nonequilibrium gas and analyzed in detail. A steady-state solution of (3.24) was found also upon studying the Burgers equation in a medium having parameters varying according to a certain law, and was analyzed in Ref. 90, which was published simultaneously with Ref. 62.

An equation similar to (3.16) was derived in Ref. 91 for a medium having a source of the release, while in Ref. 92 the results of Ref. 62 were generalized to the case of cylindrical and spherical waves. We note Ref. 93, which studied analytically the propagation of nonlinear perturbations in a vibrationally nonequilibrium gas under the condition $\omega \tau \gg 1$ and other simplifying assumptions for the case in which the parameters of the medium ahead of the wave depend on the time, as well as Ref. 94, which studied the propagation of a sound wave in a vibrationally nonequilibrium gas in a nonlinear regime in the case in which the relaxation time strongly depends on the temperature.

To calculate the formation of a shock wave in a flow of gas mixture with variable parameters, one must consider a more complicated system of kinetic equations instead of (3.4). Such calculations were performed in Ref. 95 for a $CO_2:N_2:H_2O$ mixture being used in hydrodynamic CO_2 lasers, where the propagation was studied of sound and entropy waves, as well as the influence of various parameters of the system on shock-wave formation.

There are no direct experiments on the propagation of nonlinear hydrodynamic perturbations in a nonequilibrium gas at present. We note the experimental studies, Refs. 96– 98, where the interaction was studied of sound waves with a discharge. The linear effects that arise in this interaction were studied in Refs. 68–72 (see Sec. 3.1). With increasing wave amplitude new processes arise-variation of the discharge current, and appearance of combination frequencies, 96,98 which indicate the nonlinear character of the interaction of the sound wave with the discharge. No theoretical analysis of these effects has been performed.

3.4. Features of the propagation of shock waves in nonequilibrium gases

The propagation of a shock wave is accompanied by heating of the gas. In diatomic and polyatomic gases the heating process is two-step in type. At first, behind the front of the shock wave, in the viscous density jump, one observes an increased temperature of the translational degrees of freedom. The thickness of the viscous condensation jump for sufficiently strong shock waves is of the order of the mean free path. Then, in the extended relaxation zone an excitation of the internal degrees of freedom occurs (the rotational degrees of freedom have certain specific features: the rotational relaxation time for most molecules does not strongly differ from the time of free flight; therefore usually the translational and rotational degrees of freedom are considered jointly in studying kinetic processes in a shock wave).

In the excitation of the internal degrees of freedom the

translational temperature falls, while the temperature of the internal degrees of freedom rises (Fig. 6). It is convenient to analyze the distribution of the parameters behind the front of the shock wave on the pV diagram ($V = 1/\rho$). The thermodynamic parameters on both sides of the shock discontinuity are connected by the laws of conservation of mass flow, momentum, and energy. For a one-dimensional flow in a system of coordinates associated with the front of the shock wave, we can write the conservation laws in the form

$$\rho v = \rho_1 v_1, \ p + \rho v^2 = p_1 + \rho_1 v_1^2,$$

$$H + (v^2/2) = H_1 + (v_1^2/2).$$
(3.28)

Here the subscript 1 denotes the parameters of the gas in the region ahead of the shock wave. The equations of (3.28) correspond to the case in which the partial derivatives with respect to time in the equations of continuity, motion, and energy can be neglected. This is possible if the length L_{\star} of the region being studied following the wave is substantially shorter than the characteristic length at which the parameters of the gas vary owing to non-steady-state processes. Here the parameters ρ , v, p, H, ρ_1 , v_1 , p_1 , and H_1 can depend on the time, but the relationships of (3.28) remain valid. In the case being studied, L_{\star} corresponds to the relaxation zone.

We can establish a connection between the values of p, V, and p_1 , V_1 from Eq. (3.28):

$$H_1 - H + \frac{1}{2}(V_1 + V)(p - p_1) = 0, \qquad (3.29)$$

Here we have $H_1 = H(p_1, V_1)$, H = H(p, V). By analogy with the Poisson adiabatic, Eq. (3.29) is called the Hugoniot shock adiabatic. For an ideal gas we have $H = \gamma p V / (\gamma - 1)$, and (3.29) acquires the form

$$\frac{p}{p_1} = \frac{(\gamma+1)V_1 - (\gamma-1)V}{(\gamma+1)V - (\gamma-1)V_1}.$$
(3.30)

If we fix the initial state of the gas p_1 , V_1 , then the shock adiabatic (3.30) defines the set of possible final states of the gas (Fig. 7). The concrete choice of p and V depends on the velocity v_1 of the shock wave. Graphically this velocity is determined by the slope of the straight line AB drawn from



FIG. 6. Temperature distribution in a shock wave. Region *I*-unperturbed gas, region *II*-relaxation zone, wave moving from right to left.



FIG. 7. Hugoniot adiabatic. Curves I and II differ in the value of $\gamma(\gamma_1 > \gamma_2)$.

the initial to the final state (the ratio $(p - p_1)/(V_1 - V)$ equals the slope of the line). Thus, by fixing the initial conditions p_1 and V_1 and the velocity of the shock wave (the slope of the line AB), one can find the final state p_2 , V_2 . The position of the Hugoniot adiabatic in the pV plane depends on the magnitude of γ . The value of γ will differ at the beginning and at the end of the relaxation zone. At the beginning of the relaxation zone all the degrees of freedom except the translational and rotational ones can be considered to be frozen, since the relaxation time $\tau \gg \tau_0$. Therefore at the beginning of the relaxation zone we have, for example, $\gamma = 7/5$ for diatomic molecules. At the end of the relaxation zone a state is reached of complete thermodynamic equilibrium, and, for example, for diatomic molecules at high enough temperatures we have $\gamma_2 = 9/7$ (dissociation and ionization are not taken into account). Thus, in general, two Hugoniot adiabatics can start at the point p_1 , V_1 . One of them (I) corresponds to excitation of the rapidly relaxing degrees of freedom (translational and rotational) and describes the state of the gas at the beginning of the relaxation zone. The second one (II) determines the parameters of the gas at the end of the relaxation zone, i.e., in the region where complete statistical equilibrium is reached. The adiabatic I steeper than II, since at the same density the pressure under conditions of freezing of the vibrational degrees of freedom will lie higher than in a state of complete equilibrium, inasmuch as the energy of compression is distributed over a smaller number of degrees of freedom.

Thus the relaxation processes in the shock wave occur as follows in agreement with the shock adiabatic. Initially the system transforms jumpwise from the state A to the state B (this process is localized at the front of the shock wave). Then the system slowly evolves from the state B to the state C along the segment BC.

Now let us discuss how shock waves propagate in a nonequilibrium gas (for the sake of definiteness, in a gas of vibrationally excited molecules). Let a shock wave pass through the nonequilibrium gas, whose velocity is such that the translational temperature directly behind the front of the shock wave will be smaller than the vibrational temperature ahead of the front. As before, in the relaxation zone processes of vibrational-translational energy exchange will occur, but they now lead to a different result. Under the conditions being discussed the process runs in the opposite direction: the vibrational degrees of freedom are cooled, while the translational ones are heated (Fig. 8). At first glance this seems to be a curious, but an inessential difference. Actually, the inverted course of the temperature leads to a fundamental difference.

In problems corresponding to Fig. 7, the distribution of the parameter behind the shock wave are fully determined by the velocity of the shock wave or the Mach number Ma. For example, for an ideal gas the temperatures ahead of the front (T_1) and behind the front (T_2) are associated by the relationship³⁵

$$\frac{T_2}{T_1} = \frac{[2\gamma Ma^2 - (\gamma - 1)][(\gamma - 1)Ma^2 + 2]}{(\gamma + 1)^2 Ma^2},$$
(3.31)

where, as usual, the Mach number Ma equals the ratio of the velocity of the shock wave v_1 to the local velocity of sound in the unperturbed gas.

In a nonequilibrium gas the situation fundamentally changes. Now the temperature T_2 will depend not only and not so much on the number Ma as on the initial conditions. Thus a shock wave entering into a nonequilibrium gas will (under certain conditions) change in velocity until full agreement of all parameters sets in. As will be shown below, this is possible only for velocities that exceed or equal a certain minimum value determined by the initial distribution of temperatures and type of gas.

Actually the conservation equations in the form (3.28) remain valid also in the case of a gas initially not in equilibrium. The sole difference consists in the fact that, in the specific enthalpy in the region ahead of the shock wave (for a gas of diatomic molecules)

$$H_{1} = (5k_{\rm B}T_{1}/2m) + \varepsilon_{1} + (p_{1}/\rho_{1})$$
(3.32)

the mean vibrational energy per unit mass ε_1 will no longer equal the equilibrium value determined by the temperature T_1 . In the simplest case the nonequilibrium store of vibrational energy ahead of the front of the shock waves can be characterized by the temperature T_{v_1} . The connection between ε_1 and T_{v_1} is determined by the relationship



FIG. 8. Temperature distribution in a shock wave propagating in a nonequilibrium gas. Region *I*-unperturbed nonequilibrium gas, region *II*relaxation zone, wave moving from right to left.

$$\varepsilon_1 = \frac{\hbar \widetilde{\omega}}{m} \left(\exp \frac{\hbar \widetilde{\omega}}{k_{\rm B} T_{\rm VI}} - 1 \right)^{-1}, \qquad (3.33)$$

where *m* is the mass of the molecule, and $\hbar \tilde{\omega}$ is the magnitude of a vibrational quantum. When $T_{Vl} = T_l$ the problem reduces to the previous one, i.e., to the problem of propagation of shock waves in a gas initially in equilibrium.

Solving the system (3.28) with account taken of (3.32) leads to the relationship^{99,100}

$$\frac{p_2}{p_1} = \frac{7Ma^2 - 1}{6} + \frac{7(Ma^2 - 1)}{12} \left\{ \left[1 - \frac{9,6Ma^2m(\epsilon_1 - \epsilon_2)}{7(Ma^2 - 1)^2k_BT_1} \right]^{1/2} - 1 \right\}.$$
(3.34)

Here p_2 and ε_2 correspond to the end of the relaxation zone, while the Mach number is calculated for the velocity of sound with frozen vibrations.

We see from Eq. (3.34) that steady-state shock waves exist when

$$\left(\frac{\mathrm{Ma}^2-1}{\mathrm{Ma}}\right)^2 \ge \frac{9.6m(\varepsilon_1-\varepsilon_2)}{7k_{\mathrm{B}}T_1}.$$
(3.35)

Under ordinary conditions, i.e., in the propagation of a shock wave in an equilibrium gas, we have $\varepsilon_2 > \varepsilon_1$. Therefore the inequality (3.3) is fulfilled for any value of Ma. Conversely, for shock waves in a vibrationally excited gas under conditions where $\varepsilon_2 < \varepsilon_1$ there is a minimum Mach number whose value is determined by the initial conditions and the properties of the gas. For example, for HF under the initial conditions $T_1 = 300$ K, $T_{V1} = 2000$ K, and $p_1 = 5$ Torr, the minimum number Ma = 1.8. At the same initial translational temperature pressure at $T_{V1} = 3000$ K, the minimum number Ma is now equal to 2.6. The appearance of a minimum Mach number can be interpreted on the basis of detonation concepts.

Let us study the process of variation of the parameters of the gas in a shock wave propagating in a gas initially in nonequilibrium in the pV diagram (Fig. 9). In the diagram



FIG. 9. Hugoniot adiabatic for a shock wave in a nonequilibrium gas.

curve I corresponds to the Hugoniot adiabatic for the gas with frozen vibrational degrees of freedom. The point p_1 , V_1 corresponds to the initial conditions. The adiabatic I describes the state of the gas directly behind the front of the shock wave at the beginning of the relaxation zone. One can construct a shock adiabatic for the equilibrium state of the gas at the end of the relaxation zone. As before, it is described by Eq. (3.29), with the difference that H_1 is determined by Eq. (3.32) with the nonequilibrium value of ε_1 , and H_2 with the equilibrium value of ε_2 . The latter situation is fundamental, since H_2 does not go over into H_1 when $p_2 = p_1$, $V_2^* = V_1$. Therefore the equilibrium adiabatic (curve II) will lie higher than the frozen adiabatic. Then the intersections of the adiabatics corresponds to the values of p_2^* and V_2 at which the equilibrium value of ε_2 equals ε_1 . The transition from the state p_1 , V_1 to the state p_2 , V_2 occurs in the same way as in the equilibrium case. Initially in the shock front the gas transforms jumpwise from the state 1 to the state 2' on the frozen adiabatic. Then in the relaxation zone the gas is additionally heated and its pressure increases. A different situation arises if the final state 3 lies below the point of intersection of the adiabatics. As in the previous case, the gas transforms jumpwise to the state 3 ' on the frozen adiabatic. Then in the relaxation zone the gas reaches the state 3, whereby the variation of the parameters on the path 3-3' will be opposite to that which is observed in the transition 2-2'. Namely, in the relaxation zone on the path 3-3'the translational temperature will increase, while the pressure and the density fall. The minimum value of the Mach number at which steady-state propagation of shock waves is possible is determined by the slope of the tangent to the equilibrium adiabatic drawn from the point I.

Also another form of solution is possible, which arises in the case of intersection of the straight lines proceeding from the point I with the adiabatic II when $V > V_1$. These regimes correspond to combustion waves^{35,101} propagating with a low velocity and having a broad relaxation zone. In a number of cases for a chemically reacting gas such waves are observed experimentally.¹⁰¹

The propagation of shock waves in nonequilibrium gases is a new field of physical gasdynamics, which at present is developing intensively. Let us list briefly the fundamental studies pertaining to this field.

The similarity between the behavior of nonequilibrium, chemically reacting gases, and of vibrationally excited gases has been noted in Ref. 102, which treated the possibility of appearance of detonation and combustion waves in a vibrationally excited medium. Calculation of the steady-state regimes of propagation of shock waves in a gas with vibrational and dissociative nonequilibrium was made in Refs. 99, 100, and 103 (we note also Ref. 104, which treated combustion waves). The structure of the relaxation zone of a detonation wave was studied in Ref. 105, and numerical calculations of the structure of the relaxation zone of a steady-state wave for a strongly nonequilibrium gas were conducted in Ref. 106. The stability of detonation waves was discussed in Ref. 107 on the basis of the criterion of Shchëlkin.¹⁰¹ However, one should note that the Mach numbers corresponding to a detonation regime for a gas in vibrational nonequilibrium, in contrast to the Mach numbers of a classical detonation, are not very large, while the dependence of the time of vibrational relaxation on the temperature is weaker than the

Arrhenius relation (see Sec. 3.1). This situation does not allow one to study a two-front model for describing a detonation in a vibrationally excited gas. Moreover, the Shchëlkin criterion, which determines the stability of a detonation wave, is approximate in character and one needs a rigorous solution of the problem of stability, namely a treatment of the stability of the wave with respect to small perturbations for the concrete kinetic scheme of the processes in the relaxation zone. For a chemically reacting gas in the case of a simple irreversible reaction with a rate constant determined by the Arrhenius relationship, such a problem has been treated (see, e.g., Ref. 108). For a vibrationally nonequilibrium gas no solution of this problem exists at present.

A numerical calculation of the formation of a shock wave and a non-steady-state regime of its propagation in a vibrationally nonequilibrium gas was performed in Ref. 109–112. The problem of non-steady-state propagation is simulated in an experiment in which the shock wave enters a restricted region occupied by a nonequilibrium gas. The fundamental question here consists in how rapidly this wave is accelerated (decelerated) and approaches a steady state of propagation, and also what is the structure of the region behind the front of the wave.

The degree of nonequilibrium for the same degree of pumping will be greater, the greater is the relaxation time τ , but here the time of attaining a steady-state regime will increase with increasing τ , and realistic dimensions of the experimental apparatus can prove insufficient for formation of steady-state regimes. A decrease in the relaxation time behind the wave front is possible only as a result of an increase in the degree of nonequilibrium produced by an increase in the intensity of pumping. In such a case, the wave velocity is higher and the time of attaining a steady state regime is lower. However, one can obtain high degrees of nonequilibrium only in a pulsed regime (or in the flow-through case-over a limited length) owing to the finite rate of heat removal. But, in this case the increase in the velocity of the wave is still restricted, since in the process of propagation of the shock wave the degree of nonequilibrium of the unperturbed gas decreases.

Numerical calculations confirm these qualitative conclusions. For example, for nitrogen with fixed translational and vibrational temperatures of 300 and 200 K, respectively, the time to reach a steady-state regime amounted to 7 s,¹⁰⁰ which corresponds to a distance of several kilometers. At the same time, for a greater degree of nonequilibrium (for a temperature of the first level of 400 K), owing to a decrease in the relaxation time because of anharmonic effects, the required time now amounts to $20 \mu s$. However, maintenance of such a nonequilibrium for times greater than the relaxation time seems problematical.

To decrease the relaxation time, Ref. 113 proposed using a mixture of nitrogen and water vapor. Of course, this diminishes the actually attainable degree of nonequilibrium under steady-state conditions. Reference 113 also studied the propagation of a shock wave through a non-steady-state relaxing gas. As we should expect, the amplification of weak shock waves upon pulsed vibrational pumping is substantially smaller than for the steady-state case. In other words, the wave is not able to approach in velocity the steady-state Jouguet regime corresponding to the initial nonequilibrium. The factors that we have discussed restrict the variation of velocity of the wave owing to nonequilibrium effects, although these effects are large enough that one can establish them experimentally.

In recent years many studies have been published on experimental investigation of shock waves in nonequilibrium gases. We note first of all the general features of these studies. As a rule, one studies the propagation of a shock wave in a discharge plasma of different types, and one must take account not only of the relaxation of the energy of the internal degrees of freedom, but also of the change of state, both owing to relaxation effects and to the reaction of the plasma to the change of state of the medium. Another factor that influences the velocity of a shock wave is an inhomogeneous distribution of the temperature that always exists between the discharge and the equilibrium gas. This distribution leads to acceleration of the wave upon entering the discharge zone, and one requires sufficiently precise experiments to distinguish the "nonthermal" effects.

In Refs. 113-116 a great increase was observed experimentally in the velocity of shock waves in the plasma of a glow discharge and a considerable decrease in their amplitude. The observations were performed with pressure transducers and probes. In Ref. 117 in studying the propagation of a pulsed gasdynamic perturbation in a decaying plasma of an electron-free UHF discharge in air, a substantial decrease was observed in the amplitude of the pulse and also an increase in its width. The authors attributed this to the possible influence of relaxation phenomena. The results of other experiments¹¹⁸⁻¹²² did not confirm the strong change in amplitude and velocity of the wave on entering the discharge region. In Refs. 118 and 122 good agreement was obtained for a glow-discharge plasma in air with calculation of the acceleration of the wave owing to the temperature gradient. In Refs. 119 and 121 in studying the propagation of shock waves in a HF discharge in CO₂, a 10 to 20% increase was found in the velocity of the wave as compared with the predicted values obtained by taking account of the acceleration of the wave due to the temperature gradient. References 119-121 are of interest in that an interferometric method was used to measure the waves, which enabled obtaining more complete information than with pressure transducers. Reference 121 also measured the intensity of the CO₂ radiation at the wavelength of 2.7 μ m, which proved higher than the calculated value. The authors explained this effect by the excitation of the vibrational degrees of freedom behind the front of the wave. We note also Refs. 123 and 124, where the interaction of a shock wave with the decaying plasma of a laser spark in air was studied. In Ref. 123 in recording a wave by a shadow method, disappearance of the wave in the plasma region was found, with subsequent restoration of the front on exit from the plasma. It was found in Ref. 124 in recording by an interferometric method that on entering a plasma the front of the wave was transformed into vortex structures. These effects, which were associated with the manifestation of the inhomogeneity of the problem, at present have practically not been studied.

The study of the laws of propagation of shock waves and other hydrodynamic perturbations in nonequilibrium gases essentially constitute a new field in hydrodynamics. From the physical standpoint we can distinguish here two sets of problems whose study can lead to new effects. First is the problem of stability of motion of a nonequilibrium gas. The presence or nonequilibrium can damp or amplify small perturbations that arise in gasdynamic flows. Second is the problem of controlling the intensity of shock waves. By changing the properties of the medium through which the shock wave is propagating, one can attenuate or amplify the wave.

All these problems now are increasingly attracting the attention of physicists.

CONCLUSION

As we have already pointed out, the field of interests of nonequilibrium molecular physics is not restricted to studying the optical and hydrodynamic properties of nonequilibrium gases. The existence of an excess store of internal energy alters practically all the properties of the medium, and this affects a very large number of the micro- and macroprocesses in the most varied fields of physics, including acoustics, physical gasdynamics, optics, and physicochemical kinetics. In this regard nonequilibrium molecular physics faces the problem of analyzing anew all the processes in nonequilibrium media that depend on the store of internal energy and the rate of energy exchange between the translational and internal degrees of freedom of the molecules, and discovering the new effects that arise here. The investigation of this set of problems is just beginning. Of course, now it is difficult to estimate in full scope the results that can be obtained in nonequilibrium molecular physics. However, the prospects that open up here are very alluring, since already the first advances have led to a laser revolution.

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