

Stability problems in a nonequilibrium gas

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Abstract. We consider the stability problem for a plane gas layer whose nonequilibrium state is maintained by pumping energy into the molecular vibrational degrees of freedom and by heat removal through the walls. Two approaches to the study of gas stability are discussed, which consider the evolution of small hydrodynamic perturbations and thermal explosion. We have studied in detail the Rayleigh – Benard problem of convection instability and the Semenov – Frank-Kamenetskii problem of thermal explosion, and generalised them to the case of a nonequilibrium gas. Some unsolved problems of the physical hydrodynamics of a nonequilibrium gas have been outlined as well.

1. Introduction

Studying fluid motion, hydrodynamics deals with a wide variety of structures. Essentially, any hydrodynamic state undergoes structural transformations as external conditions change. It will suffice to mention the transition of laminar flow into the turbulent one, initiation of the convection, thermal explosion, and so on. The number of examples can be easily increased. We notice that changes in the regimes show a threshold behaviour and take place at certain critical values of dimensionless parameters such as the numbers of Reynolds, Rayleigh, etc. From the standpoint of the phase transition theory, these parameters are the controlling ones, while the structural transformation is of character of the nonequilibrium phase transition of the second order.

The study of the stability problem brings up two groups of questions: (i) under which conditions and how the stability originates; (ii) what is the structure of a new stable state replacing the former state which lost its stability. In the

present paper we intend to consider only the first group of questions, calling our special attention to the stability problem of a nonequilibrium gas.

Nonequilibrium gas differs from the equilibrium one by the presence of additional ‘degrees of freedom’ providing the means of varying the nonequilibrium excess energy over individual degrees of freedom. This excess energy gives rise to a new channel of energy exchange primarily between translational and internal degrees of freedom, which can degrade or enhance the mechanism of instability occurrence. In this connection, the critical parameters, at which the stability loses, cease to be ‘universal’ in character and begin to depend on the rate of relaxation processes and on the energy excess falling within individual degrees of freedom, i.e. in essence, on the power of a source responsible for the nonequilibrium energy distribution in the system. Such problems have come to the attention of researchers only in recent years, when they started to deal with the large volumes of nonequilibrium gas, such as active media of gas lasers, discharge plasma, chemically reacting gases, etc.

Notice that a nonequilibrium gas also occurs under natural conditions. For example, it appears to be feasible in the upper atmosphere of the Earth and other planets, interstellar gas, etc.

One point is to be made. When studying stability in a classic equilibrium hydrodynamics, we essentially deal with a nonequilibrium gas too. Actually, formation of the gradients of thermodynamic variables in the system (which do have a sufficient effect on instability) disturbs immediately the Maxwell-Boltzmann distribution of particles. Gas becomes nonequilibrium. However, a departure from the equilibrium state is small (the velocity distribution function differs slightly from the equilibrium one). It is essential only in calculating the transport coefficients, and does not play a significant part in the stability problems. For simplicity, this weakly nonequilibrium gas will be called the equilibrium one, as is customary.

The question of gas stability first arose late in the nineteenth century in studies of two, at first sight, quite different phenomena, such as a turbulence and thermal explosion. At present it is clear that we deal with the loss of stability in both the cases. However, we would like to emphasize the principal

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difference between the classical hydrodynamic instability and the thermal explosion. In classic hydrodynamics, the analysis of stability was carried out for equilibrium media, while the chemically nonequilibrium gas was studied in the theory of thermal explosion [1, 2]. The chemical nonequilibrium state possesses formal evidences which are rather similar to those of a state with nonequilibrium internal degrees of freedom (for example, deactivation of vibrationally excited molecules can be considered as an exothermic reaction). In this connection, the theory of thermal explosion in a nonequilibrium gas is being developed under the strong influence of the modern theory of thermal explosion in chemically reacting media.

Quite a different situation takes place in the theory of hydrodynamic stability. On studying the hydrodynamic stability of a nonequilibrium gas, one should take into account a new channel for amplified perturbations, which conveys the excess energy from internal degrees of freedom to the hydrodynamic perturbations.

The review is arranged as follows. In Section 2, we discuss the hydrodynamic stability of both the equilibrium and nonequilibrium gas with respect to small perturbations, the nonequilibrium state being supported by external energy pumping and heat removal through the boundary. Section 3 deals with the classic theory of thermal explosion in chemically reacted media as well as in vibrationally excited gas.

It should be emphasized that the system stability is primarily analyzed by the example of simplified models allowing us to investigate the physical mechanisms of instability occurrence and to reveal the ranges of medium parameters and wave vectors of perturbations, which are firstly amplified in the system.

2. Hydrodynamic instability

In this section we take an approach to the stability problem associated with the analysis of small perturbations in the linear approximation. It is worthy of note that all the problems of stability loss formulated for an equilibrium gas (for instance, instabilities of various types of flows [3]) can also apply to a nonequilibrium gas, but in the latter case most of these problems are steel to be solved. In this connection, we consider only one equilibrium problem of hydrodynamic stability related to the convection stability of a plane gas layer, which can be easily extended to a nonequilibrium case.

2.1 Small perturbations in an equilibrium gas

Theoretical investigation of the transition of a laminar flow to the turbulent one, originated as early as at the end of the nineteenth century, has introduced into hydrodynamics a method for studying the stability loss, which is based on the analysis of time-dependent small hydrodynamic perturbations. The stability of steady states has been mathematically treated by linearization of the initial equations with respect to small perturbations. The resulting homogeneous set of linear differential equations with time-independent coefficients has the solution of the $\exp(-i\omega t)$ type. If among the found roots $\omega = \omega_0 + i\omega_1$ there are ones for which $\omega_1 > 0$, then the state is unstable. This approach yields correct results in most cases. But it should be remembered that our finding is valid only to first order of perturbation theory. An account of the next order approximations can change the pattern. Furthermore, in a moving infinite medium, perturbations can be carried

over even if they increase, while in a confined space we should take into account the flow reflection from the walls. In the linear approximation, the arbitrary perturbation can be presented as a sum of separated perturbations, each satisfying the proper set of equations. This is the so-called mode representation similar to that of small oscillations in mechanical systems with a large number of degrees of freedom as a superposition of normal oscillations. In the framework of mode representation, the stability problem is reduced to the study of time evolution for the individual mode perturbations. The system can be stable with respect to perturbations of a mode, and unstable with respect to that of another mode.

In the three-dimensional case, three perturbation modes can be revealed in an equilibrium gas: the thermal (entropy) mode, the acoustic mode, and the mode pertinent to generation and transfer of vorticity (rot \mathbf{v}) [4]. In the nonequilibrium hydrodynamics, the number of perturbation modes increases with the number of kinetic processes (additional kinetic equations) taken into account. We emphasize once again that the mode representation of perturbations is only possible in the linear approximation.

For example, the above approach was advantageously applied to the Rayleigh–Benard problem on convection stability of fluid. This problem is of interest in itself as it models a large class of self-organizing systems and can be easily extended to the case of a nonequilibrium gas.

The occurrence of convection instability fits the instability with respect to small thermal perturbations which transform into the convective one under gravity. Actually, gravity-related term in the equation of motion gives rise to the thermal mode traffic. The question of the convection stability will be discussed in detail in Section 2.3.

2.2 Acoustic and thermal perturbations in a nonequilibrium gas

With advances in physics of gas lasers and physics of discharges in the mid-1960s, the question of the amplification of acoustic perturbations has come under the scrutiny of science [5, 6]. The mechanism of this phenomenon is concerned with changes in the energy flux from internal degrees of freedom to the translational ones in an acoustic wave under temperature variation. It is just this flux that leads to the wave amplification. We emphasize, however, that for a long time the uniform case has been dealt with. The results of these studies have been detailed in the review [7]. But in the study of the system stability, analysis of the uniform case alone appears to be inadequate and the consideration of the feedback pertinent to finite dimensions of the system is required. This necessitates the explicit consideration of boundary conditions not only for the velocities and the translational temperature but for the internal energy as well.

There exists also another important reason related to the fact that the steady nonequilibrium medium is not uniform in principle, since heat removes from the system due to thermal conductivity, i.e. it depends on the gradient of translational temperature and that of vibrational energy (vibrational temperature). The greater is a departure from the equilibrium state, the larger is the nonuniformity. Many authors pointed out the necessity to take into account the system nonuniformity, but the works considering this effect appeared only recently [8]. So far we have dealt with acoustic perturbations. But in full measure above considerations are also appropriate for thermal modes. In several works (see, for example, [9]), thermal perturbations were studied in a uniform system.

The nonuniform case was considered in [10] by viewing the simplest models.

In solving the problem of nonequilibrium gas stability with respect to small perturbations, the simplest model from the standpoint of geometry is a plane layer with heat removal through the walls. In this case, the main parameters of the problem depend solely upon a single Cartesian coordinate (we denote it by z). As indicated above, the energy pumping into internal degrees of freedom is rendered possible in a rather complicated kinetic way, which increases significantly the number of equations, with unknown as a rule kinetic coefficients. To reveal the general relationships in both uniform and nonuniform cases, we will consider a vibrationally-nonequilibrium gas and use two models. In the first model, the power I of the energy pumping into the vibrational degrees of freedom is assumed to be constant. This model takes into account the energy pumping in the simplest way. In another approximation, the vibrational energy per unit mass ε is considered to be constant. In the case of discharge this approximation is justified by the fact that 'intensive vibrational excitation by electrons has a chance to maintain the steady value of T_v ' (T_v is the vibrational temperature) [11]. In practice, the comparison of typical times in a discharge [12] indicates that the energy is fastly transferred from electrons to the vibrational degrees of freedom and the temperature T_v for rather long hydrodynamic times will be equal to the electron temperature, which is proportional to E/ρ , where E is the electric field strength, ρ is the gas density. This quantity is not obviously constant with the presence of perturbations. In a more general case (without surveying a discharge), the condition $\varepsilon = \text{const}$ means that, by varying the relaxation term (for example, as $(\varepsilon - \varepsilon_{\text{eq}})/\tau$, where $\varepsilon_{\text{eq}}(T)$ is the equilibrium value of ε for a given translational temperature T , τ is the vibrational relaxation time), the term including ε' (as is customary, primed symbols denote the varied or 'perturbed' quantities) should be much less than the other terms:

$$\left| -\frac{\varepsilon - \varepsilon_{\text{eq}}}{\tau^2} \frac{d\tau}{dT} T' - \frac{c_v(T) T'}{\tau} \right| \gg \frac{c_v(T_v) T'_v}{\tau}, \quad (1)$$

where c_v is the heat capacity of vibrational degrees of freedom (in deriving (1), we assume τ to be dependent mainly on T). When the first term in the left side of (1) is vastly more than the second one, then inequality (1) is simplified for the discharge and takes the form

$$\frac{\varepsilon - \varepsilon_{\text{eq}}}{\tau} q \frac{T'}{T} \gg \frac{c_v(T_v) T'_v}{\tau} \left(\frac{E'}{E} - \frac{\rho'}{\rho} \right),$$

where $q = -d \ln \tau / d \ln T > 0$. If the discharge is stabilized with respect to current, the quantity in parenthesis in the right side of this relation is small due to a strong dependence of the ionization constant on electron temperature [13], and Eqn (1) is fulfilled.

Both the approximations considered certainly simplify the real situation, but they give an insight into the peculiarities of the phenomena studied. Notice that the physical content of these models is different. At $I = \text{const}$, the temperature T_v changes and thermal conductivity becomes of importance. At $\varepsilon = \text{const}$, the relaxation equation disappears and the quantity ε becomes a parameter of the problem. Therefore, on comparing the results obtained by the two models, we can estimate the effect of pumping source on various properties of the system.

In Ref. [8], the stability of a nonuniform vibrationally-nonequilibrium gas with respect to acoustic perturbations was studied for a plane layer with a fixed translational temperature $T = T_w$ at its boundaries $z = \pm L$ (L is the layer half-width). We consider here a set of equations of relaxation hydrodynamics involving equations of continuity, motion, and relaxation:

$$\frac{d\rho}{dt} + \rho \operatorname{div} \mathbf{v} = 0,$$

$$\rho \frac{d\mathbf{v}}{dt} + \operatorname{grad} p - \eta \Delta v - \frac{\eta}{3} \operatorname{grad} \operatorname{div} \mathbf{v} = 0, \quad (2)$$

$$\frac{\gamma}{\gamma - 1} \frac{dT}{dt} - \frac{T}{p} \operatorname{div} (\lambda_T \nabla T) - \frac{T}{p} \frac{dp}{dt} - \frac{m}{k_B} \frac{\varepsilon - \varepsilon_{\text{eq}}}{\tau}$$

$$= \frac{\eta}{2} \sum_{i,k} \left(\frac{\partial v_i}{\partial x_k} + \frac{\partial v_k}{\partial x_i} - \frac{2}{3} \delta_{ik} \operatorname{div} \mathbf{v} \right)^2,$$

$$\frac{d\varepsilon}{dt} - \frac{1}{\rho} \operatorname{div} (\lambda_v \nabla T_v) = I - \frac{\varepsilon - \varepsilon_{\text{eq}}}{\tau},$$

where \mathbf{v} , T , p are the gas velocity, temperature and pressure, respectively, m is the molecular mass, k_B is the Boltzmann constant, γ is the adiabatic index without regard for the vibrational degrees of freedom, η , λ_T , and λ_v are the coefficients of viscosity, translation-rotational and vibrational thermal conductivities, respectively. If we linearize Eqn (2) and introduce the notation

$$a'(x, y, z, t) = \tilde{a}(z) \exp(i\omega t - ik_x x - ik_y y), \quad (3)$$

where a' is a perturbation, then for the sound mode we obtain the equation in \tilde{v}_z :

$$\frac{d^2 \tilde{v}_z}{dz^2} + A(z) \frac{d\tilde{v}_z}{dz} + B(z) \tilde{v}_z = 0, \quad (4)$$

where $A(z)$ and $B(z)$ are determined by the steady distribution of unperturbed parameters. In the case of solid walls one gets

$$\tilde{v}_z(z = \pm L) = 0. \quad (5)$$

It should be pointed out that in determining the unperturbed parameters the boundary conditions must be also specified for T_v . These conditions depend on the rate constant of the heterogeneous reaction on the surface of the walls, and all the possible variants are restricted by two limiting cases determined by the ratio between the rates of the energy input and relaxation. If the relaxation on the surface is rather fast, then

$$T_v(z = \pm L) = T_w. \quad (6)$$

If the relaxation rate on the surface is small, then the vibrational energy flux through the boundary is equal to zero and

$$\frac{dT_v}{dz}(z = \pm L) = 0. \quad (7)$$

The calculations for the model $I = \text{const}$ show that the gain, i.e. the quantity ω_1 in the expression $\omega = \omega_0 + i\omega_1$, is determined by two factors, each being additive. The first

factor is the same as in the uniform case (the nonequilibrium effect and dissipative effects of viscosity and thermal conductivity). The only difference consists in integrating the corresponding expression for the uniform case over the whole layer width. The second factor is novel and related to the influence of the gradients of thermodynamic parameters. Figure 1 presents neutral curves ($\omega_1 = 0$) against the dimensionless pumping intensity Y and dimensionless inverse time of vibrational relaxation ξ ($Y = Iq\rho L^2/2\lambda_T T_w$, $\xi = k_B\rho L^2/m\lambda_T\tau_w$, all the values are determined at $z = \pm L$). These calculations were carried out under boundary conditions (7). Notice that the condition of fast heterogeneous relaxation (6) does not yield radically new result, but only slightly shifts the critical curves.

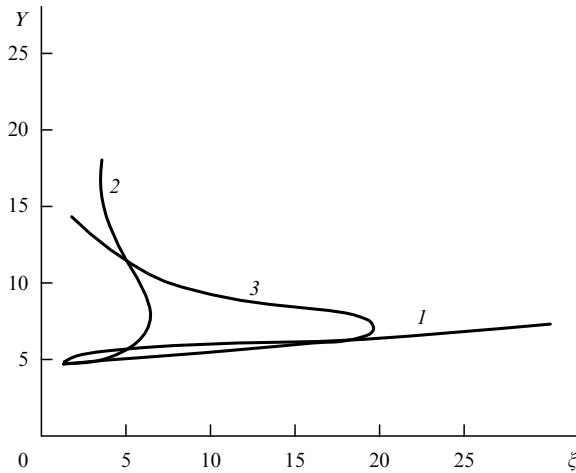


Figure 1. Plots of neutral curves ($\omega_1 = 0$): 1 — approximation of uniform gas; 2 — critical curve without considering gradient terms; 3 — critical curve accounting for the gradient terms.

The calculated results for the model $\varepsilon = \text{const}$ show that the instability region is absent, i.e. the way of energy pumping significantly affects the results. The main finding following from Fig. 1 is that the account of spatial inhomogeneity by far narrows the region of unstable modes in a nonequilibrium gas.

Thermal instability of the plane layer of a nonequilibrium gas was studied in Ref. [10]. It was found that in the case of $\omega = 0$ (corresponding to the thermal critical mode) thermal perturbations do not give rise to a hydrodynamic motion (equations for the perturbed velocity and pressure are separated from the equations for the energy and relaxation and have only zero solutions). The unstable modes were shown to be possible for the model $\varepsilon = \text{const}$ only under the boundary condition (7), while for the model $I = \text{const}$ the instability takes place only under boundary condition (6). A detailed discussion of the results of Ref. [10] will be carried out in the next section.

2.3 Convection instability

In the simplest case, the Rayleigh–Benard problem of convection instability looks as follows. The stability of a horizontal liquid layer confined between two parallel solid surfaces and affected by gravity forces is studied. Temperature T_1 of the lower surface is higher than that (T_2) of the upper surface. The problem of convection instability is based

on the solution to equations of continuity, motion, and energy and is usually considered within the approximation of incompressible liquid. The temperature-dependent changes in density are taken into account only in a term describing the pull of gravity (Boussinesq approximation). In this approximation, the equations for perturbations take the form [14]

$$\begin{aligned} \text{div } \mathbf{v}' &= 0, \\ \rho \frac{\partial \mathbf{v}'}{\partial t} &= -\text{grad } p' + \eta \Delta \mathbf{v}' - \beta T' e \rho g, \\ \mathbf{v}' \text{ grad } T + \frac{\partial T'}{\partial t} &= \chi \Delta T'. \end{aligned} \quad (8)$$

Here

$$\beta = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_p, \quad \chi = \frac{\lambda_T}{c_p \rho},$$

c_p is the specific heat capacity at constant pressure, g is the acceleration of free fall, e is a vector directed downwards along the z axis and perpendicular to the surfaces confining the system.

If all the unperturbed variables are considered as independent of time and x and y coordinates, then the solution to set (8) can be written in the form of (3). In this case \tilde{v}_z can be found from

$$(D^2 - k^2)^3 \tilde{v}_z = -Ra \frac{k^2 \tilde{v}_z}{(2L)^4}, \quad (9)$$

where $D = d/dz$, L is the layer half-width, $k^2 = k_x^2 + k_y^2$, $Ra = -\rho g \beta (2L)^3 \Delta T / (\eta \lambda)$ is the Rayleigh number, ΔT is the temperature difference at the boundaries. The boundary conditions at $z = \pm L$ can be expressed as

$$\tilde{v}_z = 0, \quad D\tilde{v}_z = 0, \quad (D^2 - k^2)^2 \tilde{v}_z = 0. \quad (10)$$

Similar equations can be also written for $\tilde{T}_z(z)$.

Thus, the problem is reduced to the eigenvalue problem for Ra . At fixed k^2 , the nonzero solution for \tilde{v}_z , satisfying boundary conditions (10), occurs only at several particular values of Ra . The minimum value $(Ra)_{\text{cr}} = 1708$ is reached at $k = 3.12(2L)^{-1}$.

Notice that the above deducing of the critical Rayleigh number is based on the Boussinesq approximation. The latter is not primarily determined by medium properties and more likely by the processes occurring in this medium. For instance, acoustic waves are described by this approximation in neither gases nor liquids, since we cannot neglect the substance compressibility, however low it may be. In other words, small coefficients, which are determined by the medium properties' do not assure small values of the corresponding terms described by the process under consideration. This fact can be clearly demonstrated by studying the applicability of the Boussinesq approximation in gases and liquids for a thermal mode near the critical threshold regime. In comparison with the well-known works [15, 16] where the applicability of the approximation was considered in a wide range of parameters, this fitting does not require additional assumptions about parameters (apart from the fact that this regime is close to the critical one) and yields simple criteria for the layer width. The Boussinesq approximation can be used if a general

set of equations for perturbations in a steady medium is reduced to set (8):

$$\begin{aligned} \frac{\partial \rho'}{\partial t} + \rho \operatorname{div} \mathbf{v}' + \mathbf{v}' \operatorname{grad} \rho &= 0, \\ \rho \frac{\partial v'_i}{\partial t} &= -\frac{\partial p'}{\partial x_i} + \sum_k \frac{\partial}{\partial x_k} \left[\eta \left(\frac{\partial v'_i}{\partial x_k} + \frac{\partial v'_k}{\partial x_i} - \frac{2}{3} \delta_{ik} \operatorname{div} \mathbf{v}' \right) \right] \\ &\quad + \rho' g \mathbf{e}_i, \quad (11) \\ c_p \rho \mathbf{v}' \operatorname{grad} T + c_p \rho \frac{\partial T'}{\partial t} + \rho T \left(\frac{\partial S}{\partial p} \right)_T \left(\frac{\partial p'}{\partial t} + \mathbf{v}' \operatorname{grad} p \right) \\ &= \operatorname{div} (\lambda'_T \nabla T + \lambda_T \nabla T'), \end{aligned}$$

where S is the specific entropy.

This reduction of the system is possible only for the thermal mode ($\omega = 0$), given the fulfillment of following inequalities:

$$\begin{aligned} \rho' \operatorname{div} \mathbf{v} \gg \mathbf{v}' \operatorname{grad} \rho; \quad \Delta \mathbf{v}' \gg \operatorname{grad} \operatorname{div} \mathbf{v}'; \\ \left| \left(\frac{\partial S}{\partial p} \right)_T \rho T \operatorname{grad} p \right| \ll |c_p \rho \operatorname{grad} T|. \quad (12) \end{aligned}$$

We also assume that $\Delta \rho_{\max} / \rho_{\min} \ll 1$, where $\Delta \rho_{\max}$ is the maximum density difference in the volume considered, ρ_{\min} is the minimum density. These inequalities can be represented as

$$\frac{(Ra)_{\text{cr}}}{A_2} \ll 1, \quad (k_T p) A_1 \ll 1, \quad (\beta T)^2 \frac{A_1 A_2}{A_3} \ll (Ra)_{\text{cr}}. \quad (13)$$

Here $k_T = (1/\rho)(\partial \rho / \partial p)_T$ is the coefficient of isothermal compressibility, $(Ra)_{\text{cr}} = 1708$; $A_1 = \rho g(2L)/p$; $A_2 = \rho g(2L)^3 / (\chi \eta)$; $A_3 = c_p \rho T / p$; $\chi = \lambda_T / (c_p \rho)$. Inequalities (13) restrict the range of applicability of the Boussinesq approximation, mainly in magnitude of $2L$. In liquids this range covers 10^{-4} – 0.2 m, and it is 10^{-3} – 0.2 m in gases. The lower limit is less affected by the parameters of the system than the upper one, which is largely determined by the last inequality in (13). The estimations for gases were made at a pressure of 1 atm. As pressure changes, the lower limit L varies as $p^{-2/3}$, while the upper one as $p^{-1/4}$.

Notice that the widely used criterion of the Boussinesq approximation (see, for example, [17])

$$\left(\frac{\partial \rho}{\partial T} \right)_p \theta \gg \left(\frac{\partial \rho}{\partial p} \right)_T \Delta \rho_{\max},$$

which is based on the assumption that the density varies with temperature rather than with pressure, leads in the case of liquids to incorrect small sizes of the system in which the convection instability can be described employing the Boussinesq approximation.

We emphasize once again that the Boussinesq approximation imposes limits primarily on the process at hand but not the medium properties. As was pointed out above, the convective mode makes the thermal one, where motion is brought about by gravity. The Boussinesq approximation should be fulfilled just for this mode, while the acoustic modes are merely lacking in this approximation.

The Rayleigh–Benard problem can be easily extended to the case of a nonequilibrium gas. The convection instability of a plane layer was considered in [18] for a vibrationally-nonequilibrium gas in the framework of the model with $\varepsilon = \text{const}$. This problem differs from the equilibrium case considered above: first, there exists a nonequilibrium energy supply, and, second, there also appears a nonmonotonic temperature distribution along the z axis.

A set of equations relating to relaxation hydrodynamics with experimental layer half-width L is reduced to the equation in \tilde{v}_z , viz.

$$(D^2 - a^2 - s_0)(D^2 - a^2)^2 \tilde{v}_z = -(Ra_0 + rz) a^2 \tilde{v}_z, \quad (14)$$

where $a = 2Lk$ (perturbations are considered in the form of (3)),

$$r = \left(\frac{dR}{dz} \right)_{z=0}; \quad Ra = -\frac{g\rho(2L)^3}{\chi\eta} \frac{d \ln T}{dz} \equiv -\tilde{R}a \frac{d \ln T}{dz};$$

$$s(z) = \frac{(2L)^2}{\chi} \left(\frac{\gamma - 1}{\gamma} \frac{m}{k_B} \right) \left(\frac{\varepsilon - \varepsilon_{\text{eq}}}{\tau^2} \frac{d\tau}{dT} + \frac{c_v}{\tau} \right);$$

$$\delta_1 = T_2 - T_1; \quad Ra_0 = -\tilde{R}a \frac{\delta_1}{T_0}.$$

In (14), the variable z is dimensionless and expressed in units of $2L$. The subscript ‘0’ stands for the values of parameters in the centre at $z = 0$.

Eqn (14) generalizes the corresponding Eqn (9) to the case of a nonequilibrium gas. New terms therewith arise, first of them is the nonequilibrium state factor s_0 allowing for the nonequilibrium excess vibrational energy ($\varepsilon - \varepsilon_{\text{eq}}$) and the temperature dependence of the relaxation time, whereas the second term $Ra_0 + rz$ is determined by a nonmonotonic distribution of parameters over the layer width.

As seen from Eqn (14), the surface of critical numbers $Ra_0(s_0, r)$ separating the unstable modes from the stable ones [$s_0 = (\delta_2 T q + (2L)^2 c_v / (\chi \tau))_0$; $r = (\tilde{R}a / T_0)(\delta_2 + \delta_1^2 / T_0)$; $\delta_2 = (\varepsilon - \varepsilon_{\text{eq}} / \chi \tau)(2L)^2$; δ_1 and δ_2 correspond to an approximation of the temperature profile by the quadratic relation $T = T_0 + \delta_1 z - \delta_2 z^2 / 2$] appears in a nonequilibrium gas instead of a single critical Rayleigh number equal to 1708 in the equilibrium case. Figure 2 displays the critical surface $(Ra_0)_{\text{cr}}$. The instability region lies above this surface. As seen from Fig. 2, at $s_0 < 0$ and $r > 0$, the Rayleigh number $(Ra_0)_{\text{cr}}$ decreases. Thus due to the nonequilibrium state effect, the critical Rayleigh number $Ra = 1708$ is unwrapped into the surface of critical numbers Ra , and the amplification of convective perturbations is conceivable even at $T_1 = T_2$.

3. Theory of thermal explosion

3.1 Classic theories of thermal explosion

The problem of thermal explosion first arose late in the nineteenth century. Thermal explosion constitutes a sharp increase in temperature and pressure in an enclosed volume under conditions when heat released by exothermic reactions has no time to dissipate by exchanging with environment. This phenomenon has yet been discussed by Van't Hoff, however a detailed quantitative theory was developed only to the mid twentieth century, mainly, in the works by Semenov and Frank-Kamenetskii [1, 2].

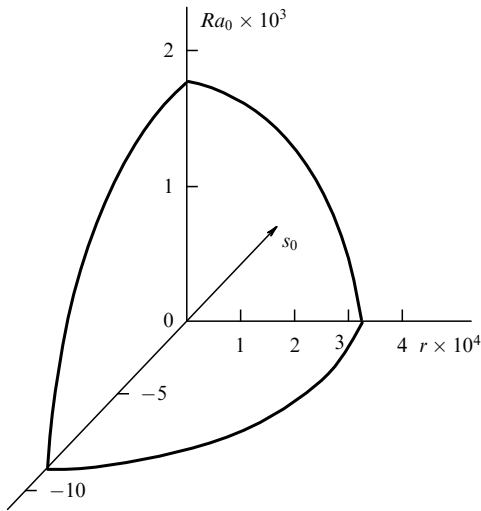


Figure 2. Surface of critical numbers $Ra_0(s_0, r)$.

Noteworthy are two peculiarities of the theory of thermal explosion. The simplest theory developed by Semenov deals with a homogeneous reacting mixture, wherein heat releases proportionally to the reaction rate with the Arrhenius temperature dependence, i.e. proportionally to $\exp[-E^*/(RT)]$, where E^* is the activation energy. The rate of heat removal is assumed to be proportional to the temperature difference $\alpha(T - T_w)$, where T_w is the environment temperature, and α is the coefficient of heat transfer (temperature equalization in the interior of the reacting system due to thermal conduction is assumed in the Semenov's theory to proceed far and away faster than the heat exchange with an environment, i.e. the Bio number is small: $Bi = \alpha L / \lambda_T \ll 1$). Figure 3 depicts schematically the intensity of heat release (curves 1–3) and intensity of heat dissipation into environment (curve 4) as functions of temperature. If heat in the system releases according to 3, while heat exchange follows that of 4, then heat dissipation through the wall has

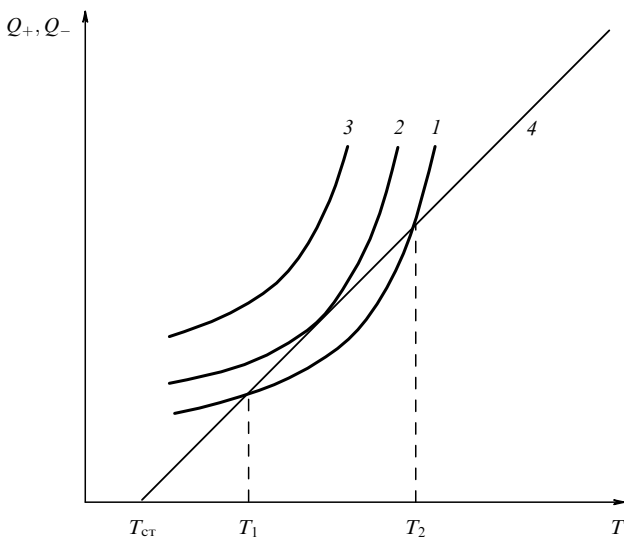


Figure 3. Temperature dependences of heat release Q_+ (curves 1–3) and heat removal Q (straight line 4) rates.

no time to compensate for heat release in the volume. In this case the steady reaction is impossible and thermal explosion occurs. If heat releases and removes in accordance with 1 and 4, then the existence of two steady regimes is possible. One of them corresponding to temperature T_1 is stable, while the other is unstable at T_2 . It can be easily seen by varying temperature and considering subsequent temperature changes as the system evolves. Notice that the availability of several steady regimes is not a specific feature of the Semenov's theory. A variety of steady regimes is typical for all the problems pertinent to the stability loss. Minimum values of the parameters, at which the thermal explosion is possible (explosion conditions), correspond to curves 3 and 4 and are determined by the condition that the rates of heat release and removal as well as their derivatives should be equal at the point T .

Another peculiarity of the theory of thermal explosion lies in the analytical approach to the explosion conditions calculation using the steady temperature distribution [2]. We illustrate it considering a plane gas layer between two solid surfaces with fixed temperatures, which was studied by Frank-Kamenetskii. The stationary equation takes the form

$$\lambda_T \frac{d^2 T}{dz^2} = -Q(T) \tag{15}$$

with the boundary conditions

$$T = T_w \quad \text{at} \quad z = \pm L, \tag{16}$$

where $2L$ is the layer width. Frank-Kamenetskii chose the intensity of a bulk heat source as

$$Q = Q_0 \exp(\beta(T - T_w)), \tag{17}$$

that well approximates the Arrhenius dependence at small heat-up ($T - T_w \ll T_w$). The analysis of Eqn (15) together with (16) shows that the stationary solution satisfying boundary conditions (16) is possible only for a few values of parameters entering this solution. In particular according to [2], there is no solution to (15)–(17) provided

$$\beta Q_0 \frac{L^2}{\lambda_T} > 0.88 \tag{18}$$

at maximum temperature T_{max} attainable in the centre and satisfying the condition $\beta(T_{max} - T_w) = 1.2$.

The disappearance of the stationary solution is identified with the thermal explosion in the Frank-Kamenetskii theory. We point out at once the limitations of this approach. The disappearance of the stationary solution indicates that the initial equation fails to account for all the processes. In particular, if heat releasing in the bulk results from a chemical reaction, then the approximation of Q by the Arrhenius dependence or by expression (17) is valid only for the initial stage of the process. In the course of the reaction, inverse processes arise, which decrease the reaction rate (and heat release) up to zero in the limiting case of the equilibrium state (for more details, see the next section).

Here an important fact is noteworthy. Semenov's theory differs essentially from that of Frank-Kamenetskii's in one point. In the Semenov's theory, heat transfer is limited by the external heat removal ($Bi = \alpha L / \lambda_T \ll 1$), whereas in the Frank-Kamenetskii treatment, by thermal conduction ($Bi \gg 1$). Thus, Frank-Kamenetskii explicitly takes into account the temperature gradient. The influence of the temperature gradient on the gas stability can be estimated by (18). With $Q_0 / \lambda_T = \text{const}$, then Q_0 decreases as λ_T

diminishes, which corresponds to an increased average temperature gradient. We can also compare the critical supply energies at which the thermal explosion occurs in the two limiting cases: in the Semenov's theory $Q_{0S} = \alpha/(\beta L e)$, $Bi \ll 1$, while in the Frank-Kamenetskii's treatment $Q_{0F} = 0.88 \lambda_T/(\beta L^2)$, $Bi \gg 1$. Average temperatures are approximately equal in both the cases, although the ratio $Q_{0S}/Q_{0F} \gg 1$ exceeds greatly unity. Thus, the stability of a nonequilibrium gas decreases as the average temperature gradient rises.

3.2 Thermal explosion in a nonequilibrium gas

The theory of thermal explosion having been developed since the late 1920s took up a new impulse in the 1970s due to the progress in laser physics. The work [19] resulted from one of the first investigations where special attention was given to the thermal instability of a nonequilibrium gas in active media of gas lasers.

The modern theories of thermal explosion are developed in the following directions:

(1) The consideration is not limited by heat supply from chemical reactions. Laser or electron energy pumping may present as the heat sources. They produce a nonequilibrium reserve of vibrational energy, transferring subsequently into the translational degrees of freedom, namely, into heat.

(2) The problem of thermal explosion is formulated using a time-dependent energy equation which takes into account all the main processes (for example, direct and inverse reactions). Within this approach, the concept of thermal explosion disappears. Instead, a sharp temperature growth takes place on some time intervals, which can be considered as a thermal explosion. This approach was also used in studying the chemical reactions of explosive type. However, a new factor related to vibrational thermal conduction appears in a nonequilibrium gas, which changes the mechanism of thermal explosion. In the Semenov's theory, the thermal explosion results from the predominance of heat release over heat removal, while in a nonequilibrium gas the thermal explosion may be caused by the energy redistribution over the translational and vibrational degrees of freedom.

(3) The problem of the system stability is considered generally with respect to perturbations of all modes, the thermal explosion being treated as an instability originated in one (thermal) mode. Thus, the stability problem is reduced to finding the order of priority, i.e. to clarifying a question which mode is first perturbed in the system.

We shall only illustrate these directions by some examples, since the complete theory of thermal explosion has not been developed so far.

As pointed out above, the work by Eletskiĭ and Starostin [19] was one of the first appeared in this field. They considered molecular gas in a steady-state discharge with cooling walls. The initial set of equations describes the balance of the vibrational and translational energies in the gas with a uniform distribution of parameters:

$$Q^* \frac{h\omega}{m} = \frac{\varepsilon - \varepsilon_{\text{eq}}(T)}{\tau} + \frac{\varepsilon - \varepsilon_{\text{eq}}(T_w)}{\tau_d} + \frac{\varepsilon}{\tau_r}, \quad (19)$$

$$\frac{Xm}{h\omega} \frac{\varepsilon - \varepsilon_{\text{eq}}(T)}{\tau} + \alpha_1 Q^* = \frac{T - T_w}{\tau_d} \frac{k_B}{h\omega},$$

where $h\omega$ is the vibrational quantum, Q^* is the intensity of electron energy pumping ($Q^* = \text{const}$), α_1 is the portion of the electron energy spent for the direct heating of a gas ($\alpha_1 \ll 1$), X

is the fraction of molecules, τ_d and τ_r are the typical diffusion and radiative deactivation times, respectively. If $\tau/\tau_d \gg 1$ and $\varepsilon \gg \varepsilon_{\text{eq}}$, Eqns (19) are reduced to

$$k_B \frac{T - T_w}{h\omega} \frac{\tau}{\tau_d} = \frac{Q^* X}{1/\tau + 1/\tau_d + 1/\tau_r}. \quad (20)$$

If we suppose that $\tau \sim \exp(\sigma T^{-1/3})$ and use the Frank-Kamenetskii transformation [2]

$$\exp(-\sigma T^{-1/3}) = \exp(-\sigma T_w^{-1/3}) \exp(b\theta), \quad (21)$$

where $\theta = (T - T_w)/T_w$, $b = \sigma T_w^{-1/3}/3$, then (16) can be written as

$$\theta = \varkappa \exp(b\theta), \quad (22)$$

where $\varkappa = Xh\omega\tau_d^* Q^* \tau_d / (k_B T_w \tau_w)$, $\tau_d^* = \tau_r \tau_d / (\tau_r + \tau_d)$, $\tau_w = \tau(T_w)$. Eqn (22) was shown by Frank-Kamenetskii [2] to have no solutions at $\varkappa > 1/(be)$, which is interpreted as an occurrence of thermal explosion.

Thus, the work [19] reproduces the Semenov's calculation scheme for the thermal explosion, but considers a different source of heat release. The main result of Ref. [19] is the evidence that a great difference between vibrational and translational temperatures is impossible in the discharge. The strong temperature dependence of the vibrational relaxation time τ (analog of feedback) restricts the real energy capacity of the vibrational degrees of freedom at any pumping, bringing it closer to the equilibrium value in the limit of very significant energy pumping.

Practical applications following from the unstable regime found in [19] were discussed in [20], where the development of thermal instability is shown to be accompanied by a considerable temperature drop between the axis and the walls of the discharge tube, leading to a discharge compression. The theory of thermal instability of vibrationally excited molecular gas was further developed in [21], where the problem of thermal explosion in gas with an excess vibrational energy of molecules was considered in the framework of the Semenov's treatment, i.e. in a uniform system. In contrast to [19], the paper [21] took into account the change in the excess vibrational energy, which resulted in a more complicated temperature dependence of the heat release rate as compared to the Semenov's theory. If, following the latter, we assume the rate of heat release and removal to be equal, then it is possible to find several stationary states, including necessarily the unstable one. One of the stable states was predicted in [19] and corresponds to the finite deference between the vibrational and translational temperatures. Another stable state observed at high-energy pumping arises when the vibrational and translational temperatures compare well with each other.

Further progress in the theory of thermal instability is concerned with a concrete choice of the source of energy supply into the system. The stability of initially nonequilibrium gas was considered in [21] without any external energy source; in [19], the electron pumping served as a source of the vibrational energy. According to [22–27], the energy delivered into the system due to an optical pumping by resonance radiation. In [28], the system was heated via molecular photodissociation. A great number of physical effects associated with the instability occurrence in the

system have been studied in detail in [26, 29 – 31]. The work [31] dealt with the phenomenon of explosive absorption of CO₂-laser radiation in the atmosphere, lying in the fact of sharp increase in absorption and caused by strong self-heating in the laser beam channel. A self-oscillating regime accompanied by a periodic clarification or blackening of the medium was studied in [30] (see also [32, 33]). Possible practical applications of the effect of thermal absorption have been analyzed in [26].

All the above refers to the studies of instability in a uniform medium with the Bio number $Bi \ll 1$ (the Semenov's approach). Nonuniformity of parameters distribution and its effect on the thermal explosion occurrence were first taken into consideration in [21], where the problem is formulated as follows. A plane layer of vibrationally-nonequilibrium gas is considered with the boundary conditions at the walls ($z = \pm L$) $T = T_w$ and $\varepsilon = 0$. The equations of steady-state balance for the translational and vibrational energies take the form

$$\frac{\varepsilon - \varepsilon_{\text{eq}}(T)}{c\tau} + \frac{\lambda_T}{c\rho} \frac{d^2 T}{dz^2} = 0, \quad (23)$$

$$\frac{\varepsilon - \varepsilon_{\text{eq}}(T)}{\tau} + D \frac{d^2 \varepsilon}{dz^2} + I = 0,$$

where c is the heat capacity per unit mass pertaining to the translational and vibrational degrees of freedom, D is the diffusion coefficient of vibrationally excited particles, which is assumed equal to $\lambda_T/(c\rho)$. In the approximation

$$\frac{\varepsilon - \varepsilon_{\text{eq}}(T)}{I\tau} \sim \frac{L^2}{2D\tau} \ll 1, \quad \varepsilon \gg \varepsilon_{\text{eq}}, \quad (24)$$

in view of Eqn (17), set (23) is reduced to the equation [21]

$$\frac{d^2 \theta}{dz^2} = -\tilde{\delta}(1 - z^2) \exp \theta, \quad (25)$$

where

$$\theta = \frac{\sigma}{3T_w^{4/3}}(T - T_w), \quad z' = \frac{z}{2L}, \quad \tilde{\delta} = \frac{L^2 \sigma I}{6T_w^{4/3} D^2 c \tau_w}. \quad (26)$$

Eqn (26) is similar to that of Frank-Kamenetskii. It has a solution at $\tilde{\delta} \leq \tilde{\delta}^* = 1.02$. The absence of a solution at $\tilde{\delta} > \tilde{\delta}^*$ is treated as a thermal explosion occurrence. The explosion parameters are determined by the conditions $\tilde{\delta}^* = 1.02$ and $\theta_{\text{max}} = 1.15$.

Notice that Eqn (25) lies beyond the accuracy dictated by the approximation (24). A more rigorous derivation of (25) and discussion of its applicability were given in [10] and they will be considered below.

The thermal explosion in a plane layer of a nonequilibrium gas was studied in great depth in [10]. Statement of the problem is analogous to that considered in the previous section. Stationary equations of balance for the translational and vibrational energies are investigated with the boundary conditions (16) and (17) for two models of the energy pumping: $I = \text{const}$ and $\varepsilon = \text{const}$.

Figure 4 plots the dependence of dimensionless variable $\bar{\varepsilon} = m\varepsilon/(k_B T_w)$ on temperature T_{max} in the centre of the layer ($\varepsilon(z) = \text{const}$ is a parameter of the problem) for O₂ and N₂ at various pressures. Curve 3 with a point of inflection corresponds to the boundary of the thermal instability. It is seen

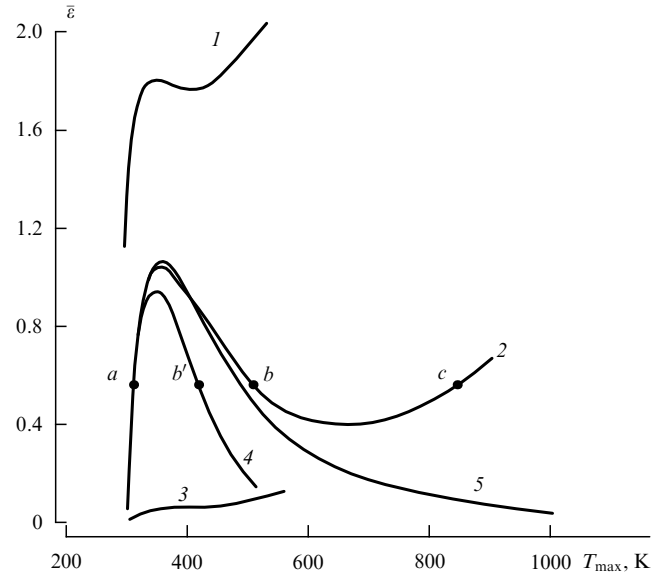


Figure 4. Plots of $\bar{\varepsilon}(T_{\text{max}})$ ($\bar{\varepsilon} = m\varepsilon/(k_B T_w)$): 1 — N₂ at $p_* = 3.5 \times 10^5$ Pa; 2 — O₂ at $p_* = 2000$ Pa; 3 — O₂ at $p_* = 7950$ Pa (the boundary of thermal instability); 4 — calculation of curve 2 by the Frank-Kamenetskii theory; 5 — calculation of curve 2 without considering inverse processes.

that the same value $\bar{\varepsilon}$ corresponds to three different steady states a , b , and c , two of which (a and c) being stable, and one (b) unstable. Actually, in the region where $d\varepsilon/dT_{\text{max}} < 0$, the increment $\delta\varepsilon > 0$ lowers the average temperature gradient. As a result, the thermal flux through the boundary falls and $\delta\varepsilon$ further increases. Parameters of the stable regimes a and b can be found by the Frank-Kamenetskii approach. In this case, we should suppose that

$$\varepsilon \gg \varepsilon_{\text{eq}}, \quad (27)$$

and the temperature dependence of τ needs to be approximated as

$$\tau = \tau_0 \exp [b(T - T_0)].$$

Then the energy equation from set (19) is reduced to the known Frank-Kamenetskii equation

$$\frac{d^2 \theta}{dz^2} = -\delta \exp \theta, \quad (28)$$

where

$$\delta = \frac{mp\varepsilon(2L)^2 b}{k_B T_w \tau_w \lambda_T}, \quad z' = \frac{z}{2L}, \quad \theta = b(T - T_w).$$

Eqn (28) has two roots at fixed ε , which correspond to stable (point a) and unstable (point b') states. The stable state c cannot be obtained with the Frank-Kamenetskii approach, since the term $\varepsilon_{\text{eq}}/\tau$ responsible for the curve rising from the minimum point in Fig. 4 was discarded. The maximum point (the stability boundary) is determined by the disappearance of solution (28) and corresponds to

$$\delta = 0.88; \quad T_{\text{max}} = T_w + \frac{1.2}{b}. \quad (29)$$

Minimum τ , at which the stability loses, can be estimated from (29), if we suppose $\varepsilon \sim \varepsilon_{\text{eq}}(T_{\text{max}})$ and use the expression for τ following from the Schwartz–Slawsky–Herzfeld

theory. The limiting curve, separating the stable region from the region where the thermal explosion is possible, can be found from the relation

$$\exp\left(-\frac{h\omega}{k_B T_w}\right) = 0.88 \frac{k_B T_w}{h\omega} \frac{\lambda_T T_w}{\rho L^2 b}. \quad (30)$$

The calculations show that the thermal instability is possible in a vibrationally-nonequilibrium gas at $\varepsilon = \text{const}$ only in the case of molecules with large vibrational quanta and long relaxation times. The instability region can be determined by the method of small hydrodynamic perturbations as well. If these perturbations are supposed to be in the form of (13), then the thermal mode ($\omega = 0, v' = 0, \varepsilon = \text{const}$) will be only described by two remaining equations: an equation for unperturbed temperature

$$\frac{d^2 T}{dz^2} = \Phi(T, \rho), \quad (31)$$

and that for perturbed temperature

$$\frac{d^2 T'}{dz^2} = \frac{\partial \Phi}{\partial T} T', \quad (32)$$

where $\Phi = (-mp/k_B T)(\varepsilon - \varepsilon_{\text{eq}}/\tau\lambda_T)$. In deriving (32), we neglect the weaker dependence of Φ on ρ .

Figure 5 presents the neutral curves in dimensionless variables $\varepsilon/\varepsilon_{\text{eq}}$ and

$$\zeta = \frac{mp_* \varepsilon_{\text{eq}}(T_w) L^2}{\tau_w k_B \lambda_T T_w^2}$$

(where p_* is the pressure at a zero pumping), which enclose the instability region. The curves were obtained by numerical calculation of Eqs (31), (32) for O_2 at various pressures. The curves in Fig. 5 enclose the region corresponding to the unstable regime at the same ζ . This region corresponds to the descending branch connecting the maximum and minimum values of ε on curve 2 in Fig. 4.

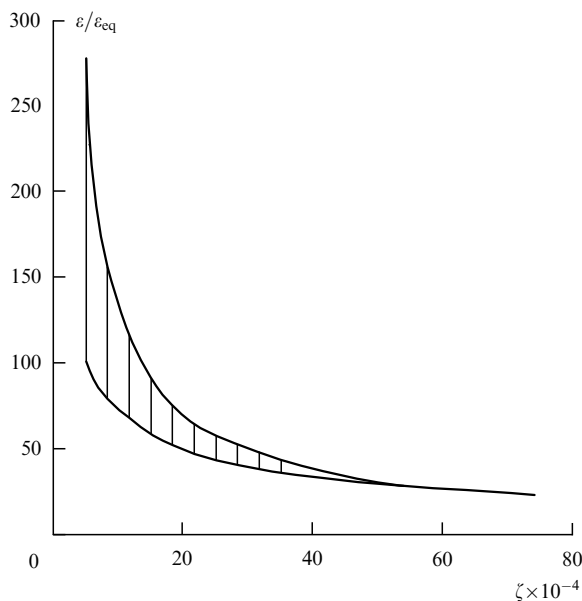


Figure 5. Area of unstable solutions (dashed portion) in the plane of dimensionless variables: vibrational energy $\varepsilon/\varepsilon_{\text{eq}}$ — inverse relaxation time ζ .

In the second particular case $I = \text{const}$, both the relaxation equations should be taken into account. If we choose the boundary conditions on the walls in the form of (6), then the bifurcation of temperature profiles $T(z)$ and $T_v(z)$ is possible at $I = \text{const}$, since

$$\left. \frac{dT}{dz} \right|_{z=\pm L} \quad \text{and} \quad \left. \frac{dT_v}{dz} \right|_{z=\pm L}$$

are not fixed, and only the total energy flux is fixed through

$$-\lambda_T \left. \frac{dT}{dz} \right|_{z=\pm L} \quad \text{and} \quad -\lambda_v \left. \frac{dT_v}{dz} \right|_{z=\pm L},$$

where λ_v is the coefficient of vibrational thermal conductivity.

The numerical calculation of the dependence of \bar{I} on T_{max} is presented in Fig. 6. The parameters of curves 1 and 2 are the same as those of curves 1 and 2 in Fig. 4.

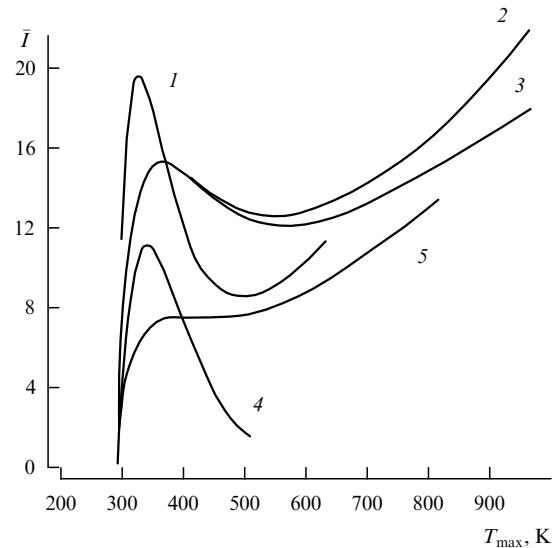


Figure 6. Plots of $\bar{I}(T_{\text{max}})$ ($\bar{I} = Imp_* L^2 / \lambda_v k_B T_w^2$): 1 — N_2 at $p_* = 10^5$ Pa; 2 — O_2 at $p_* = 1000$ Pa; 3 — calculation of curve 2 without considering inverse processes; 4 — calculation of curve 2 by the Frank-Kamenetskii theory; 5 — O_2 at $p_* = 3000$ Pa (the boundary of thermal instability).

The shape of curves in Fig. 4 matches that in Fig. 6, but the nature of the process is somewhat different. Actually, curve 3 in Fig. 6 corresponds to the case when the inverse processes can be neglected. This curve goes through two extrema, in both these points $\varepsilon \gg \varepsilon_{\text{eq}}$ ($T_v \gg T$) in contrast to the case $\varepsilon = \text{const}$. Therefore, the minima arising on curves 1 and 2 cannot be attributed to the effect of inverse processes, i.e. effect of ε_{eq} . Figure 7 presents the fluxes of the vibrational and translational energies through the wall. As seen, the following inequality takes place up to rather large pumping intensities:

$$q_v = \lambda_v \left. \frac{dT_v}{dz} \right|_{z=\pm L} \gg q_T = \lambda_T \left. \frac{dT}{dz} \right|_{z=\pm L}.$$

The maximum arising on the curve $I = \bar{I}(T_{\text{max}})$ (see Fig. 6) can be described analytically. Two balance equations for the vibrational and translational energies can be reduced to

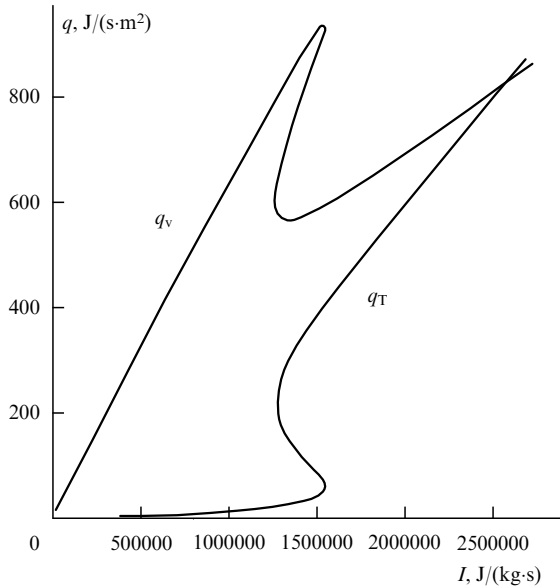


Figure 7. Dependence of thermal wall fluxes on the pumping intensity I for O_2 at $p_s = 900$ Pa, $T_w = 300$ K.

$$\frac{d^2 T}{dz^2} = \frac{\rho^2 c_v I}{2\lambda_T \lambda_v \tau_w} (L^2 - z^2), \quad (33)$$

if we assume that

$$\varepsilon \gg \varepsilon_{eq}, \quad T - T_w \ll T_w \quad \text{and} \quad \varepsilon = c_v T_v. \quad (34)$$

Eqn (33) coincides with Eqn (25) derived in [21], with D replaced by $\lambda_v/(c_v \rho)$, and τ presented in the form $\tau = \tau_0 \exp(b(T - T_w))$. The solutions to Eqn (25) exist only at $\delta \leq 1.02$. Figure 6 illustrates the accuracy of approximating (33) by the exact dependence $I = \bar{I}(T_{max})$.

The analysis of Eqn (33) shows that the instability is made possible with the condition

$$\lambda_v \frac{1.02 \tau_w k_B}{m p L^2 b c_v} > 1. \quad (35)$$

As in the case $\varepsilon = \text{const}$, Eqn (35) holds only for gases with long relaxation time. Thus, the thermal instability appears to be possible in vibrationally-nonequilibrium gases only at long relaxation times and large vibrational quanta in the molecular modes, which determine the rate of vibrational relaxation.

Using the results obtained in [8, 10], we can find which mode is first perturbed. The stability limits and the mechanism itself of instability occurrence are shown to depend strongly on the pumping source [8, 10]. Actually, the acoustic modes are always stable in the case $\varepsilon = \text{const}$ and the thermal instability is possible here. In the case $I = \text{const}$ and under the boundary conditions (17) there is no thermal instability, although the acoustic perturbations can amplify. It is thus seen that we do not know *a priori* perturbations of what mode are firstly amplified, hence the stability of all modes should be analyzed. The above examples clearly demonstrate the limitations of the theory of thermal explosion as applied to reveal gas stability, since the stability with respect to the thermal mode does not guarantee that to other perturbation modes.

The second direction in the theory of thermal explosion is related to the study of time evolution of this explosion. It has

been conducted in [28], where the time evolution was considered for molecular photodissociation, at which the average kinetic energy of dissociated atoms exceeded the thermal energy of surrounding particles. The set of time-dependent balance equations for the translational and vibrational energies was solved numerically, the pumping intensity being varied, while the distribution of parameters was considered uniform ($Bi \ll 1$). There appear several regimes depending on the pumping intensity. At small intensities I , the rate of heat release inside the system is comparable to the rate of heat removal and the system involved smoothly approaches the steady-state regime in the course of evolution. In this regime the gas temperature T rises as I increases (see curve 1 in Fig. 8). Further increase in I , especially after the threshold, results in a sharp increase in the rate of heat release and gas temperature, leading to higher photodissociation rate and, hence, cumulative growth of gas temperature. The thermal explosion occurs and the system changes to a new stable steady-state regime (see curve 2 in Fig. 8).

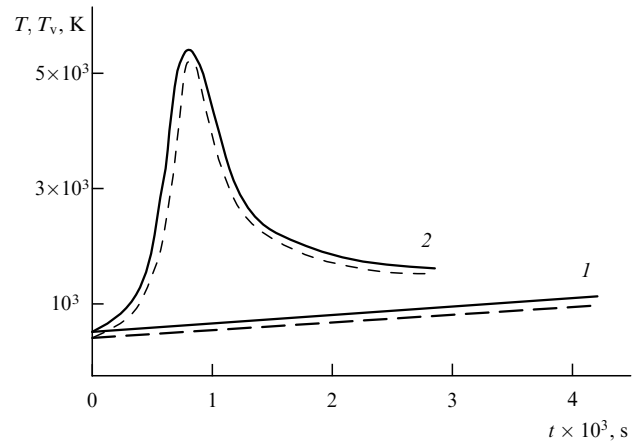


Figure 8. Time dependence of translational T (solid line) and vibrational T_v (dashed line) temperatures at $H = 20$ (1) and $H = 70$ (2) (H is the dimensionless pumping intensity).

Noteworthy is an important peculiarity of the time evolution of parameters in the course of thermal explosion. During the thermal explosion, temperature goes through the maximum, i.e. it becomes higher than the further steady-state value. The similar effect was observed at the thermal explosion in a chemically reacting system [34].

Figure 9 plots the time dependence of entropy production during the thermal explosion. As seen, the entropy production rises sharply at the moment of the explosion, and then it becomes equal to the steady-state value, which is higher than that before the explosion. We notice an important fact. Figure 10 depicts the entropy production σ in the steady state as a function of the dimensionless energy pumping H ($H = 2\pi\Sigma\tau_w I/(h\bar{\omega})$, Σ and $\bar{\omega}$ are the absorption cross section and frequency of laser emission, respectively). In addition to the increase in σ , the general conclusion results from Fig. 10, i.e. σ is less in a new structure than the entropy production which could be in the system in the absence of the structural transition (thermal explosion). This result agrees with the principle of minimum entropy production during the self-organization process, which has been introduced in [35].

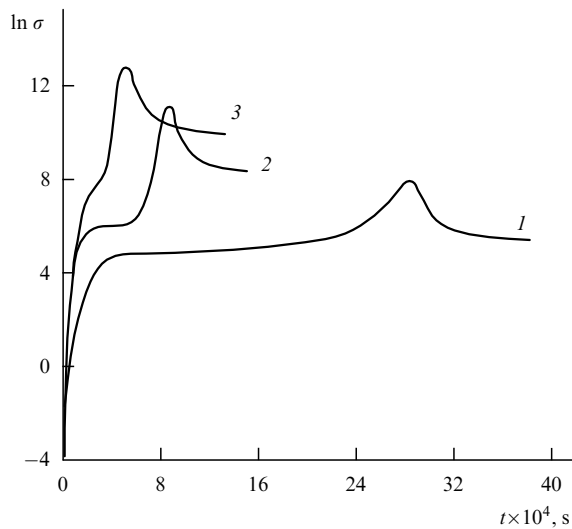


Figure 9. Time dependence of the entropy production at $H = 30$ (1), $H = 70$ (2), and $H = 250$ (3).

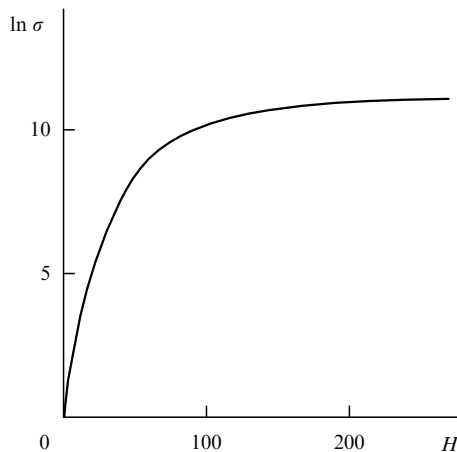


Figure 10. Dependence of the entropy production on the dimensionless pumping intensity H .

4. Conclusions

Nonequilibrium gas comprises a peculiar state of the substance with its specific physicochemical and hydrodynamic properties. The stability problems of a nonequilibrium gas considered in the present review, form only a small part of the great problem related to the development of the hydrodynamic theory of a nonequilibrium gas. The hydrodynamics of nonequilibrium gas is a new field of physicochemical hydrodynamics, where, in essence, only first steps have been made so far. Figuratively speaking, this field is covered with 'blank spaces' of unresolved problems. Even if we restrict ourselves to only the stability problem, it involves a lot of questions. We outline here only a few of them. In fact, the main mechanisms of stability loss in a nonequilibrium gas were revealed only for the Benard problem and the problem of thermal explosion. The Reynolds problem of the transi-

tion of laminar flow into the turbulent one, as well as the Lin stability problem of flow between two parallel surfaces, and Rayleigh–Taylor stability problem for a rotational flow between two rotating cylinders, etc. have not yet been extended to the case of a nonequilibrium gas. Moreover, the state in which a nonequilibrium gas goes after the first bifurcation point (for instance, at Reynolds and Rayleigh numbers higher than the critical ones) is still to be investigated. But the first bifurcation can be followed by the second, the third, etc. As in the case of the Benard effect, when the hexagonal structure of flow begins breaking down and transforms into the turbulent convection as the Rayleigh number rises.

There is a large number of questions beyond the scope of stability problems in nonequilibrium hydrodynamics. For instance, the propagation of hydrodynamic perturbations in a nonequilibrium gas. There, only simplest problems have been solved, which are related to perturbations of initially equilibrium but relaxing media (the nonequilibrium state effect results from hydrodynamic perturbations) and in the initially nonequilibrium gas. The unresolved problems in this field refer to the study of the propagation of strong shock waves, when they lose their stability. Special attention should be also given to the problems of a nonequilibrium gas flow near solid surfaces subject to peculiarities of catalysis, i.e. various heterogeneous reactions occurring at these surfaces.

The scope of unresolved problems extends continually, since new problems arise in the fields of permanent interest, namely, in gas dynamics of re-entry vehicles and physics of gas lasers.

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