Physics of reaction waves

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Reaction waves, in which an energy source sustains a wave front, occur in many areas of physics. The most important of them is a solitary wave or autowave, which is described on a coarse scale as a flamon, a surface separating zones. Mathematically, the waves are described by nonlinear transport equations, whose approximate solution gives propagation velocities of interfaces and stability criteria for the wave fronts. The instabilities of the autowave can produce complicated behavior such as periodic waves or spirals in two dimensions. Manifestations of the complex behavior include Gunn domains and cellular front structures. Important parameters that permit one to classify the wave and its stability are the Lewis number and the Zel'dovich number. A reaction wave can also have a more complicated inner structure, with several zones responsible for different physical properties. [S0034-6861(99)00204-4]

CONTENTS

I. INTRODUCTION

The ''reaction'' waves to be discussed in this review will include not only chemical reactions, but also electron and phonon excitation, ionization, recombination, and so on. A simple and practical approach to our topic is obtained through a macroscopic kinetic treatment.

Macroscopic kinetics considers matter as a continuous medium. For this reason the molecular mechanism of diffusion and other irreversible processes remain beyond the scope of this type of theory. These phenomena are normally described by means of specified kinetic coefficients, which obey symmetry principles (Onsager, 1931). Macrokinetics deals with a system that cannot come to equilibrium with a thermostat (or heat bath) due to external influences such as feeding or pumping. Such a system is termed active. Without pumping, the system approaches equilibrium with the bath; after the relaxation time τ its state is independent of the initial one. For times greater than τ, the behavior of an active system cannot depend on the initial conditions, since the effect of the initial state is suppressed by contact with the bath. Therefore the behavior will be the same for different initial conditions. Such special behavior is said to represent a pattern. In the space of macrostates of a system (also termed the phase space), such a pattern is represented by an attractor, i.e., the manifold to which all the phase trajectories converge.

Smooth variations of control parameters (e.g., pressure, thermostat temperature, pumping intensity, etc.) result in smooth variations of the characteristics (internal parameters) of the established pattern as long as this pattern remains stable. At certain critical values of the parameters, this pattern breaks up due to the appearance of instabilities. After such an event, the evolution of the system results in the establishment of a new pattern. The interrelation between new and old patterns depends on the nonlinear stage of the evolution of the instability, two cases of which will be discussed.

The characteristics of the new pattern will be close to those of the old one if fluctuation growth is suppressed in the nonlinear stage. Differences between patterns gradually grow as the parameters move away from their critical values. When nonlinearity promotes fluctuation growth (explosive instability), the characteristics of the new pattern, generally speaking, have nothing in common with the characteristics of the old one. In such a case, the stability regions in the space of control parameters are partially overlapping, so that the reverse transition is accompanied by hysteresis.

In the first case, the transition between the two pattern is called ''soft,'' while for the second case it is called ''hard.'' Though the old and new patterns are quantitatively close at the soft transition, in terms of symmetry there is always a qualitative difference between them. In particular, the soft initiation of self-oscillations (see, for example, Landau and Lifshitz, 1987, Chap. 26) becomes possible due to the different symmetries of the stationary and periodic patterns with respect to translations in time: for a stationary pattern, all times are equivalent, while for a periodic pattern only those times that are multiples of the period of the oscillations are equivalent. For hard transitions, changes in symmetry are not necessary. This is exemplified by ignition and extinction in an instantaneous-mixing reactor (Frank-Kamenetskii, 1939a, Zel'dovich, 1941a), which exhibit transitions between patterns of the same symmetry.

The above properties of hard and soft transitions are similar to thermodynamic phase transitions of the first and second order, respectively. Note that equilibrium may be considered as a special case of an established pattern, which corresponds to a vanishing intensity of the external influence on a system placed in a thermostat. Variation of the thermostat parameters (temperature, pressure) shifts the equilibrium position until a given phase becomes unstable at some critical conditions, at which a phase transition takes place. A second-order transition to the asymmetric phase may be sometimes interpreted as a Bose-Einstein condensation of corresponding quasiparticles (Cooper pairs, for instance, in the case of the superconducting transition). The wave vector of particles of the condensate is zero, since the condensate is a ground state. On the other hand, the transition to an asymmetric pattern is interpreted as a condensation of short-wavelength fluctuations into long-wavelength modes, the macroscopic filling of which is termed chaos ordering (Martin, 1965; Haken, 1978). In contrast to transitions of second order, the fluctuation spectrum in active systems is of course different from the thermodynamic equilibrium spectrum (Keldysh and Tikhodeev, 1986). The space of control parameters of active systems is partitioned into regions of established patterns. Such a partitioning is similar to that of thermodynamic phase diagrams; in particular, polycritical points are possible (Merzhanov and Rumanov, 1987).

Up to this point we have assumed that the influence preventing active systems from reaching equilibrium is external. Another scenario is possible when the feed source is included in the system. The expanded system interacts only with a thermostat, and eventually equilibrium is reached. However, now the equilibrium onset time is determined by the ''resource'' of the feed source (the capacity of the electric battery in a radio transmitter, the reservoir volume containing a reactive mixture, etc.). As a rule, this time is much greater than τ, the relaxation time of the system in the absence of the feed source. In view of this, established patterns different from equilibrium may appear during the limited interval before the source is consumed. From the mathematical point of view, such patterns represent intermediate asymptotics (Barenblatt and Zel'dovich, 1971).

Regular macrokinetics studies were probably first initiated in investigations of the transition from laminar to turbulent flow (Reynolds, 1883) and of strata in gaseous discharges (Langmuir and Compton, 1931). Important stages in the further development of macrokinetics were the exploration of explosive instabilities (Inge, Semenoff, and Walther, 1925; Semenoff, 1928), the development of the theory of excitation and quenching of self-oscillations (see Andronow, Vitt, and Khaikin, 1987), and that of solitary reaction waves (Kolmogorov, Petrovskii, and Piskunov, 1937; Fisher, 1937; Zel'dovich and Frank-Kamenetskii, 1938a). These results were partially generalized in the book of Frank-Kamenetskii (1969), the first edition of which appeared in 1947. Extensive studies in the field were initiated only after World War II. Among the topics studied were the complicated patterns of the Belousov-Zhabotinskii reaction (Zhabotinskii, 1974; Vasil'ev, Romanovskii, and Yakhno, 1979), pinches, domains, and other patterns in semiconductors (Volkov and Kogan, 1968) and superconductors (Gurevich and Mints, 1987), and the rearrangement of combustion waves in condensed systems (Merzhanov, 1983; Zel'dovich, Librovich, and Merzhanov, 1985).

Symmetry between molecules and crystals is due to the fact that atoms at low temperatures appear near the points of equilibrium. These points are distinguished and thereby ordered. Similarly, the specific position of a pattern in the space of macrostates implies some symmetry. Such a symmetry as well as the critical nature of transitions between patterns can excite the fancy of a researcher. Thus such poetic terms as ''self-organization of dissipative structures'' (Nicolis and Prigogine, 1977), ''synergetics'' (Haken, 1978), and ''catastrophe theory'' (Thom, 1975) were generated. Simple models that admit the realization of a large number of regular and chaotic patterns (Gaponov-Grekhov and Rabinovitch, 1979; Kerner and Osipov, 1989) were studied, as were the symmetry effects of pumping on the structure of an established pattern (Zaslavskii and Sagdeev, 1988).

Since, in phase space, an attractor corresponds to each established pattern and the transitions between patterns are described by the bifurcations of these attractors, bifurcation theory is sometimes presented as the theory of active systems and pattern formation. This viewpoint was developed, for instance, in the extensive survey of Cross and Hohenberg (1993). However, a purely mathematical approach appears to be insufficient. The convergence of phase paths to an attractor is in fact the consequence of the heat bath, which erases the influence of the initial state. Furthermore, one can introduce the phase space and attractors only if the concept of macrostates is valid, i.e., if the characteristic space and time scales are large in comparison with those of the atoms. But the established behavior of an active system is possible also in the absence of such a limitation, in which case the description requires another language than phase trajectories, bifurcations, and so on. Keldysh (1964a) developed the general procedure for determination of the established pattern, based on the diagram technique for the density matrix.

Let us consider a conservative system. Its behavior depends on the initial conditions. However, a sufficiently complicated system displays chaotic behavior due to the instability of trajectories (Krylov, 1950; Born, 1955), and the statistical properties that arise are independent of the initial conditions. More accurately, they are almost independent because the (initial) phase volume is conserved. Switching on dissipation (i.e., the interaction with the heat bath) destroys the remaining conservation, and the effect of the initial state disappears altogether. At a macrolevel, we see an equilibrium, so that chaotic motions are essentially thermal fluctuations. After pumping is switched on, the system becomes active. Its established patterns may be significantly influenced by the "conservative part." Thus the frequency of self-oscillations in a clock or radio transmitter due to resonance is close to the eigenfrequency of a conservative subsystem. The study of the latter may sometimes be of independent interest.

But there exist active systems that are organized differently. When the terms responsible for pumping and dissipation are removed from the equations describing such a system, then practically nothing will remain. These are the equations of chemical kinetics, in particular, the equations for the Belousov-Zhabotinskii reaction. Active systems with essentially no conservative part may be termed purely kinetic. These are the very systems for which the specific solitary waves were first found and studied and which will be discussed in this paper.

The most widely known example of such waves is the combustion front that separates the regions of the initial mixture and the reaction products. The propagation velocity and structure of the combustion wave are independent of initial ignition conditions, so we are dealing with an established pattern. Moreover, the distribution of temperature and concentration within the combustion wave depends only on $x+ut$, where u is the velocity of combustion propagation, t is time, and the x axis is oriented opposite to the direction of propagation. Hence the wave's phase remains undetermined. In other words, a given established pattern has one degree of freedom. The number of degrees of freedom is convenient for the classification of established patterns. The simplest is a uniform system described by variables that depend on time but not on the spatial coordinates. Self-oscillations require one degree of freedom. Their space of states is no less than two dimensional, and the attractor in this space is a closed line (limit cycle), i.e., a one-dimensional manifold.

In nonuniform systems the space of states has infinite dimensionality. Obviously, the established patterns inherent to the uniform system (stationary state, self-oscillation, quasiperiodic regime, etc.) can exist in the nonuniform case. However, new kinds of patterns appear to be possible, such as the combustion wave. We saw that it has one degree of freedom, surely not a self-oscillation). The minimal number of degrees of freedom for patterns is 0. For "added" patterns (which are absent in concentrated systems) the minimal number is 1.

Another example of such waves is the motion of the interface between metastable and equilibrium phases. For both cases (the combustion wave and the interface), a free-energy source is present in the initial metastable phase, equilibrium being established behind the wave. In the presence of an external feed source, solitary waves propagating in an active medium are similar to those in the examples above. When the system parameters admit the occurrence of only one homogeneous stationary pattern, this pattern is eventually recovered after the reaction flash, so we come to a traveling pulse, the leading edge of which is similar to the combustion wave. When the parameters admit two homogeneous patterns (bistability), the solitary wave converts an active medium from one such pattern to another (a switching wave). The switching wave is similar to a propagating interface.

The set of established inhomogeneous patterns in active media are sometimes termed "autowaves." These are the steady states (so-called "dissipative structures"), traveling pulses and periodic waves, spirals, vortices, etc. The traveling waves, solitary and periodic, have one degree of freedom. However, the periodic autowave represents a set of traveling pulses (see Vasil'ev *et al.*, 1979). We come to the point where, among autowaves, one can distinguish a class of solitary waves which exhibits the simplest patterns with one degree of freedom and cannot exist in the case of concentrated systems. We shall term these autowaves "flamons." (Of course, it is difficult to forecast the destiny of a new term.)

In various active media, flamons exhibit internal structures that may be represented as a sequence of layers, or zones. Each of these zones has its own function in the structure of a given flamon. At some critical values of the parameters, the zonal structure undergoes rearrangement, and at this moment the dependence of the flamon velocity on the control parameters is qualitatively changed. But the flamon motion in a homogeneous active medium does not always remain uniform and rectilinear. Instabilities may lead to the development of self-oscillations and more complicated patterns that are superimposed on the initial uniform motion. All these effects are discussed below.

We start from the simple models of the combustion wave and the traveling interface. Then, systems with external feeding are considered, in which these two models are replaced by the traveling pulse and the switching wave, respectively. The interrelations between them are discussed. We show briefly how a flat wave can transform to a spiral wave because of some kinematic mechanism. Analogous kinematic effects are responsible for the suppression of flamon diffusional instabilities, to which Sec. VI is devoted. In our survey, attention is paid mainly to these instabilities and related patterns as well as to the complicated multizonal structure of flamons (Sec. VII).

A subject like the present one determines the style of our writing. We avoid the formal approach, the so-called "basic models" (with the exception of Sec. VI.B.2), the "normal forms," etc. They would be of little use for our purpose, shifting the focus to things that are not essential from the physical viewpoint. Our approach originates from the standard macrokinetic concepts as they were briefly outlined above. These concepts will be discussed in detail in the following sections.

This paper was conceived as a tribute to the memory of Ya. B. Zel'dovich, 1914–1987, who played an important role in developing a theory we present as the theory of flamons. Combustion waves have a long research history and the relevant literature is vast. We have not attempted to review the subject of solitary reaction waves as a whole.

II. COMBUSTION WAVES

As mentioned above, two major groups can be distinguished among various flamons. The simplest representative of the first group is the combustion wave, while the traveling interface represents the second. First let us consider these simplest waves.

A. Structure and velocity

From a hydrodynamic point of view, the combustion wave is a propagating boundary between an initial mixture and reaction products. Due to the thermal expansion of products, this boundary turns out to be unstable (Darrieus, 1944; Landau, 1944a). We shall return to the problem of stabilizing the boundary in Sec. VI.A. Let us now consider the internal structure of the boundary defined by the following equations:

$$\frac{d}{dx}\left(\kappa\frac{dT}{dx}\right)-\rho uc\frac{dT}{dx}+Q\Phi(\eta,T)=0, \tag{1}$$

$$\frac{d}{dx}\left(\rho D\frac{d\eta}{dx}\right)-\rho u\frac{d\eta}{dx}+\Phi(\eta,T)=0, \tag{2}$$

and the boundary conditions

$$x\to-\infty,\quad T=T_0,\quad \eta=0, \tag{3}$$

$$x\to\infty,\quad \frac{dT}{dx}=\frac{d\eta}{dx}=0. \tag{4}$$

It is assumed that only one reaction takes place; η is the concentration of its product. Here, T is temperature, ρ is the density, u is the wave velocity, c is the specific heat, κ is thermal conductivity, D is the diffusivity, and Q and Φ are the heat and the rate of reaction, respectively. In a frame of reference that moves together with the wave, the problem is stationary. The wave velocity u is not specified but must be found together with the distributions $T(x)$ and $\eta(x)$. Due to the invariance of Eqs. (1)–(4) with respect to translations along the x axis, these functions have the form $T(x+x_0),\eta(x+x_0)$, where x_0 is an arbitrary constant ("phase" of the wave) that is not determined by conditions (3) and (4). Therefore the problem would seem to be overdetermined (four conditions for three remaining arbitrary constants) if the value of u were not considered to be unknown together with T and η (for more details, see Frank-Kamenetskii, 1969).

The problem defined by Eqs. (1)–(4) has an intriguing feature: it has no formal solution. The reaction rate is finite at any temperature, including the initial temperature T_0 [the activation dependence is standard, i.e., $\Phi\propto\exp(-\epsilon/T)$, where $\epsilon\sim10^3-10^5$ K], so that condition (3) cannot be satisfied. The physical reason for this incompatibility is as follows. The heat supplied by the reacting matter to the neighboring cold layers accelerates the reaction due to thermal activation, the heat released is transferred to the next layer, etc. (this is the mechanism of wave propagation). At $x=-\infty$ the reaction is complete before the heat will come there.

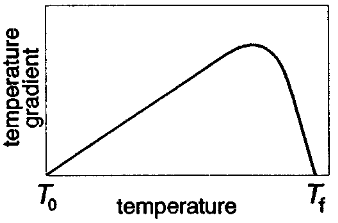

FIG. 1. Projection of the phase trajectory in the $(T,q=dT/dx)$ plane. The point $T=T_0,\eta=0,q=0,d\eta/dx=0$ corresponding to the initial state of a medium is a saddle point. From the first integral of Eqs. (1) and (2) with account for Eqs. (3) and (4), it follows that $c(T_f-T_0)=Q\eta_f$, where $T_f=T(x=\infty)$, and $\eta_f=\eta(x=\infty)$. If the reaction in the combustion wave is complete, then $\eta_f=1$, and $T_f=T_0+(Q/c)$. The final point $(T_f,1,0,0)$ of the phase trajectory is also a saddle point.

Zel'dovich and Frank-Kamenetskii (1938a) overcame this difficulty by setting $\Phi=0$ at low temperatures (see also Zel'dovich, 1948). Of course, in computer-aided calculations, such a "distortion" of a source is unnecessary. But it makes problem (1)–(4) mathematically well defined and moreover allows us to see the separation of the combustion wave into two zones: the heating zone and the zone of heat release within which a source acts. Separation into zones is clearly seen in Fig. 1. Within the heating zone, the relationship between q and T is linear (Michelson, 1889):

$$\kappa q=\rho cu(T-T_0). \tag{5}$$

In view of the exponential dependence of Φ on T, the temperature of the reaction zone varies within the range $\propto T_f^2/\epsilon$. Normally, $T_f^2/\epsilon\ll(T_f-T_0)$, as was taken into account in Fig. 1. According to Eq. (5), for a narrow reaction zone, the heat flux to the heating zone is roughly equal to $\rho cu(T_f-T_0)$. From dimensional considerations, the same quantity may be estimated as $\sim Q\Phi_f\delta$, where Φ_f is a mean value of Φ within the reaction zone and δ is the width of this zone. As can be seen in Eq. (5), the width of the heating zone is about $\sim(\kappa/\rho cu)$, and accordingly $\delta\sim(\kappa/\rho cu)(cT_f^2/\epsilon Q)$. We then let $\Phi_f\approx\Phi(T_f,\eta_f)$, where $\eta_f\approx\exp[-(\kappa/\rho cuD)(cT_f^2/\epsilon Q)]$. The latter result was obtained by extrapolation of the solution to Eq. (2) from the heating zone to the reaction zone (Zel'dovich *et al.*, 1985). Finally, we obtain

$$(\rho u)^2\sim\kappa T_f^2\Phi_f/\epsilon Q. \tag{6}$$

The estimate Eq. (6) for the combustion velocity holds when, as $\eta\to1$, the function $\Phi\propto(1-\eta)^\alpha$, where $\alpha\leqslant1$. The opposite case will be considered in Sec. VII.D.

The value obtained for the velocity is not necessarily unique, as was the case for Eq. (6) (for details see Sec. VII.C). However, the "spectrum" of u should be discrete. In this respect, flamons do not differ from other established patterns. A continuous spectrum would imply an infinitely close position of attractors in the space of states. This is impossible, since each of them is surrounded by a basin of attraction of finite dimension. In one of the first studies on reaction waves, Kolmogorov, Petrovskii, and Piskunov (1937) considered the diffusion equation with the source $\Phi(\eta)\propto\eta(1-\eta)$. Here the initial point $\eta=0$ is unstable, and a continuous spectrum of velocities bounded from below emerges. Each corresponding "fast" wave is due to a certain initial distribution of η that is slowly decreasing as $x\rightarrow-\infty$. Such waves are sometimes termed phase waves; they cannot be used for transmission of signals. The solution actually describes an "explosion" of uncoupled regions of the medium. Some delay in the reaction flash between various regions produces an illusion of wave propagation. These solutions disappear when the source is cut off, i.e., $\Phi(\eta<\eta_0)=0$. The remaining single solution corresponds to the boundary of the phase-wave spectrum. This solution is essentially a flamon (for details see Aldushin, Zel'dovich, and Khudyaev, 1979). At the same time there have been mathematical attempts to select a "real" solution, a wave propagating through an unstable medium (Aronson and Weinberger, 1975; Ben-Jacob *et al.*, 1985).

The condition $\Phi(T<T_*)=0$ is closely related to the fact that the combustion wave (as well as other established patterns in active systems with an inner feed source—see Sec. I) is described by intermediate asymptotics. When only a thermostat is assumed to be external with respect to a system, the limit $t\rightarrow\infty$, strictly speaking, corresponds to equilibrium. To investigate established patterns different from equilibrium, some distortion is needed in formulating the problem (e.g., considering a clock operation as an established pattern, we have to forget about exhausting the storage battery). Aldushin *et al.* (1978) have calculated $u(T_*)$ and demonstrated that almost the entire interval (T_0,T_f) is occupied by a plateau $u\approx\text{const}$. When T_* approaches T_f, the velocity diminishes, since cutting off shortens the reaction zone. As $T_*\rightarrow T_0$, the wave velocity grows to infinity due to the low stability of the initial state in this limiting case. Due to the presence of the plateau, the quantity u obtained by solving Eqs. (1)–(4) makes sense as a physical quantity. It is called the combustion velocity.

In case of detonation, the heating zone is replaced by the shock wave that heats and compresses a combustible mixture. The velocity of the detonation wave is not determined by Eq. (6). The wave pressure P, volume $V=1/\rho$, and velocity u are interrelated by (Michelson, 1889)

$$P-P_0=(\rho u)^2(V_0-V), \tag{7}$$

where (P_0,V_0) belongs to the initial state. Along with the energy balance, Eq. (7) determines a continuous set of final states and a continuous set of velocities u. Analyzing experimental data, Chapman (1899) found the "selection rule": the wave velocity is equal to the velocity of sound u_s in the detonation products. If it were the case that $u<u_s$, the pattern would be destroyed by a rarefaction wave which could reach it (see Jouget, 1917). But why are waves with $u>u_s$ impossible? Zel'dovich (1940), von Neumann (1942), and Döring (1943) showed that in such waves inaccessible states should appear between shock front and products. The transition to a final state via a new shock jump is also impossible: there are no rarefaction jumps.[1]

According to the selection rule of Chapman, u is a purely hydrodynamic quantity and therefore is independent of the reaction rate. With respect to the fresh matter, the detonation wave is always supersonic. As to the pattern with a heating zone, according to Eq. (6), the velocity of this wave (the so-called deflagration) is

$$u\approx\sqrt{(T_f/\epsilon)(\chi/\tau_r)}, \tag{8}$$

where τ_r is the characteristic time of reaction and χ is the thermal diffusivity of hot products. Representing the latter as $\chi\sim\tau u_s^2$, where τ is the impact time (since not every collision is accompanied by a reaction), we find that $u\ll u_s$. Meanwhile, anomalously high thermal conduction (e.g., electronic or radiative conduction in thermonuclear fusion) may provide a supersonic value of u in Eq. (8). Both the deflagration and detonation waves may propagate through the same combustible mixture. Transitions between these two patterns have been studied inadequately. Clearly, this study should not be confined to consideration of the zone that separates products and fresh matter, but must also consider the entire flow structure in the system. There is also the vast field of gaseous flames that deals with a tangle of chemistry and fluid dynamics (turbulent flames; see, for example, Clavin, 1985; Kuhl *et al.*, 1994), to which front propagation through a random medium (see, for example, Ronney *et al.*, 1995) can be related. Such problems are obviously beyond our capabilities. As for combustion waves in condensed matter, they show a multizonal structure, to which we shall turn in Sec. VII.

Besides conventional combustible mixtures, combustion-wave propagation have also been observed in the recombination of "frozen" free radicals in a cold matrix (Broida and Pellam, 1954). Such a wave can propagate due to damage to the matrix by thermal stresses that promote recombination (Barelko *et al.*, 1982, 1988). Also studied were the waves of thermal deactivation of electronic excitations (Makshantsev and Finkel'berg, 1974) and vibrational molecular excitations (Margolin and Shmelev, 1978) which are similar in structure to the pattern described above. The Belousov–Zhabotinsky reaction gave rise to intensive activity in the field (see, for example, Field and Burger, 1985; Ross

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[1] Actually, rarefaction shock waves are possible but only under very special conditions, which are not met here (see for details, Zel'dovich, 1946; Kutateladze *et al.*, 1980).

et al., 1988). This reaction is usually studied in a flow reactor, and the reaction wave takes the form of a traveling pulse; it will be discussed in Sec. IV.B.

B. Limits

Let us assume that the combustion wave propagates through a tube of finite diameter d. Let $d \gg \kappa/\rho c u$. According to Eq. (5), the right-hand side of this inequality is of the order of the width of the flamon under consideration, so that the influence of d on the flamon structure may be neglected. The influence of this diameter is reduced due to the effect of heat losses causing a decrease in u. However, this retardation is interesting not in itself, but in its qualitative sequel described below.

Let us consider the one-dimensional problem (1)–(4) after adding to the left-hand side of Eq. (1) the term

$$-\frac{N\kappa}{d^2}(T-T_0), \tag{9}$$

describing heat losses. Here, N is the Nusselt number, which depends on the sample cross section and the type of heat exchange. For the simplest case, to which we restrict ourselves here and in the following sections, $N \sim 1$. From condition (4), it follows that $T \to T_0$ as $x \to +\infty$; the zone of cooling is located behind the reaction zone. According to Zel'dovich (1941b), the value of u is found by matching the outer solutions (within the zones of heating and cooling) to the inner solution (within the reaction zone). The latter relates u to the temperature in the reaction zone T_m. Within the narrow reaction zone, the added term (9) may be neglected, and estimate (6) remains valid upon replacing T_f by T_m. Now it may be written in the form

$$U^2 = \rho k e^{-\epsilon/T_m} \kappa T_m^2/\epsilon Q, \tag{10}$$

where $U \equiv \rho u$ is a quantity that is conserved in the case of one-dimensional stationary flow, and k is a constant with the dimensions of frequency (s^{-1}).

On a coarse scale, the reaction zone is a surface at which the following condition is fulfilled:

$$\kappa(q_+ - q_-) = QU, \tag{11}$$

where q_+ and q_- are the temperature gradients at the interfaces between the reaction zone and the zones of heating and cooling, respectively,

$$\kappa q_\pm = (T_m - T_0)\left[\frac{Uc}{2} \pm \sqrt{\left(\frac{Uc}{2}\right)^2 + \frac{N\kappa^2}{d^2}}\right]. \tag{12}$$

Since the flamon width is smaller than d, the difference $T_f - T_m$ is also small, so that from Eqs. (10)–(12) we obtain

$$S = \exp(AS), \tag{13}$$

where $S = (U_0/U)^2$, $U_0 = U|_{d\to\infty}$, and $A = 2N\epsilon(T_f - T_0)T_f^{-2}(\kappa/U_0 c d)^2$. When heat losses are small, $A < 1/e$, and Eq. (13) has two solutions, the smaller one being unstable. With diminishing d there occurs a breakdown due to the confluence of a stable solution with an unstable one, so that the flame cannot propagate in a tube of sufficiently small diameter. The inability of flame to penetrate the small cells of a copper network was used by H. Davy at the beginning of the nineteenth century in explosion-safety lamps for miners.

The minimal value of U corresponding to breakdown is only $\sqrt{e}$ times smaller than the maximal value U_0. Hence to estimate the flamon velocity only, the cooling zone need not be taken into consideration; it is important only from the point of view of the breakdown effect. As will be shown, the breakdown effect is displayed in studies of several flamons. To clarify the nature of this effect and physical meaning of the minimal velocity, let us consider a chain reaction wave in a strongly diluted mixture, when heat release may be neglected. The wave is assumed to propagate due to diffusion of active particles (radicals) into a fresh mixture. In such a "cold" flame, Voronkov and Semenoff (1939) observed the breakdown effect due to loss of the radicals at the tube walls. The simplest problem that exhibits breakdown, which was numerically solved by Novozhilov and Posvyanskii (1973), is close to Eqs. (1)–(4) and Eq. (9):

$$f'' - uf' = f\phi^2, \tag{14}$$

$$\phi'' - u\phi' = -f\phi^2 + \beta\phi, \tag{15}$$

$$\xi \to -\infty:\quad f=1,\quad \phi=0;\qquad \xi\to\infty:\quad f'=\phi'=0. \tag{16}$$

Here, f and ϕ are the relative concentrations of the initial reactant and the active intermediate product, $\xi = x/\sqrt{D\tau}$, D is the diffusivity (the same for both substances), τ is the characteristic time of reaction, D/τ is the velocity scale, and the term $\beta\phi$ [similar to Eq. (9)] describes loss of active particles.[2]

At $\beta = 0$, the problem (14)–(16) has the following integral:

$$\phi' = (1/\sqrt{2})\phi(1-\phi), \qquad u = 1/\sqrt{2}, \tag{17}$$

$$f + \phi = 1. \tag{18}$$

Zel'dovich and Frank-Kamenetskii (1938b) also used Eq. (18) for $\beta > 0$. They assumed this equation to be invalid only at the back side of the flamon, where both ϕ and f were small. Accurate description of the back side was assumed not to be essential for determining the wave velocity.

From Eqs. (14), (15), and (18), the following equation may be obtained:

$$\phi'' - u\phi' = -\phi^2(1-\phi) + \beta\phi. \tag{19}$$

It has three homogeneous solutions (for $\beta < 1/4$):

$$\phi_1 = 0, \quad \phi_2 = 1/2 - \sqrt{1/4 - \beta}, \quad \phi_3 = 1/2 + \sqrt{1/4 - \beta}. \tag{20}$$

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[2] Besides the problem (14)–(16), a variety of traveling-wave models with diffusion of active (intermediate) product were reported after the work of Belousov and Zhabotinsky (1974)—see, for example, Ortoleva and Ross (1975), Showalter *et al.* (1979), Murray (1989).

There is also an inhomogeneous solution in the form of a boundary between the regions with stable values ϕ_1 and ϕ_3:

$$\phi' = \frac{1}{\sqrt{2}}\phi(\phi_3 - \phi). \tag{21}$$

This boundary moves with a velocity

$$u = \frac{1}{\sqrt{2}}(3\sqrt{1/4-\beta} - 1/2). \tag{22}$$

Formulas (21) and (22) describe a flamon that strongly differs in its properties from a solution to the original problem (14)–(16). According to Eq. (22), as β grows, the velocity u indeed becomes zero (at $\beta = 2/9$) and then changes sign. Such behavior is typical of the interphase boundary: under certain conditions, the phases are in equilibrium $(u=0)$. A change in conditions causes the displacement of an interface in one direction or the other, depending on which phase becomes metastable under the new conditions. The use of Eq. (18) for all ξ (including those behind the reaction wave) indicates replenishment with fresh reactant (e.g., through the porous walls of a tube). Under this condition, intense reaction behind the front will replenish the consumption of radicals and thus maintain the established pattern with $\phi = \phi_3$.

There is no such replenishment in Eqs. (14)–(16) or in corresponding experiments. The numerical integration mentioned above showed that there exists a critical value of β (corresponding to breakdown) and accordingly there is a minimal velocity u of a flamon under consideration. A similar breakdown when the propagation velocity is bound from below was found in studies of the simplest model of nerve pulses (Casten *et al.*, 1975; Kudryashov and Yakhno, 1978) and in many other cases (see Scott, 1970; Vasil'ev *et al.*, 1979). Such flamons will be termed q waves. Equations (21) and (22) describe a flamon belonging to another category, namely, s waves. We shall continue the discussion in Secs. III and IV.

C. Flamon and stationary regimes

The properties of structures given by Eqs. (21) and (22) will be considered in Sec. III. Now we shall consider yet another modification of heat exchange with the reaction wave, namely, longitudinal rather than transverse heat exchange [as in Eq. (9)]. Let us consider the flow of a reacting mixture through a tube, at the output of which a high temperature T_1 is maintained, so that any reaction at the initial temperature T_0 may be neglected (Aldushin, 1987). Due to translational invariance, a flamon in a coordinate frame that moves at velocity u looks like a stationary pattern. For this reason, its peculiarities may be better displayed in comparison with the stationary pattern of reaction in a flow.

For $T_1 < T_f = T_0 + (Q/c)$, two stationary solutions correspond to each value of flow rate v. Such a situation is encountered in the problem of thermal explosion (Frank-Kamenetskii, 1939b), when a high-temperature solution is unstable. The solutions meet at the critical ignition conditions $v = v(T_1)$; at lower flow rates the combustion wave forms and propagates toward the input. When $T_1 = T_f$, this critical velocity is equal to the normal velocity of the combustion wave $u(T_f)$ determined above.

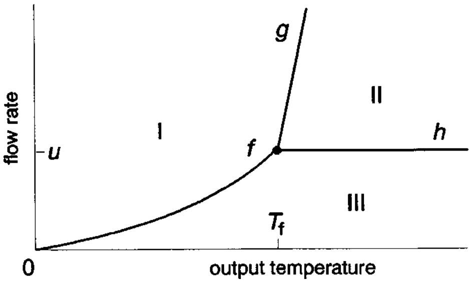


FIG. 2. Stationary patterns near the hot output: the space of parameters.

When $v > u$, the combustion wave cannot move in a direction opposite to the flow, even if $T_1 > T_f$, the reaction regime being stationary. The plane of control parameters (T_1, v) is shown in Fig. 2. Region I corresponds to a stationary pattern with incomplete conversion of reactants, region II to complete conversion. Stationary patterns are impossible in region III—in this case, the combustion wave runs toward the input (so that the $0fh$ line may be termed the ignition curve). The point $f \equiv (T_f, u)$ separates this curve in two portions; the segment $0f$ is the critical curve of confluence of the stable solution with the unstable one.

An increase in temperature T_1 (for $v > u$) results in an increase in the output $\eta(x=0)$, which reaches 1 at the line fg. In region II, the reaction zone is shifted from the output by a distance of

$$l = (\kappa/\rho c v)\ln[(T_1 - T_f)/(T_* - T_f)],$$

where T_* is the temperature within the reaction zone determined by $u(T_*) = v$.

Therefore a specific point in the plane of control parameters corresponds to the combustion wave in the system under consideration (a plug-flow reactor). On the one hand, this is the point at which the critical line $0f$ terminates (line of the confluence of the stable and unstable solutions for patterns of incomplete conversion); on the other hand, this is a corner point for the region of complete conversion. Being a control parameter for stationary patterns, the flow rate v may vary continuously. Thus the inner parameters of the pattern, $\eta(x=0)$ in region I and l in region II, are continuously changed. The combustion wave has no free parameter; its velocity is fixed.

Such a property is also inherent to other flamons. Changes in initial conditions may shift a "phase" $(x + ut)$, but have no influence on the wave velocity. Solutions with a continuous spectrum of velocities are obtained for problems with an unstable initial state, as discussed in Sec. II.A. We note that these phenomena were understood in the early work of Taffanel (1913, 1914).

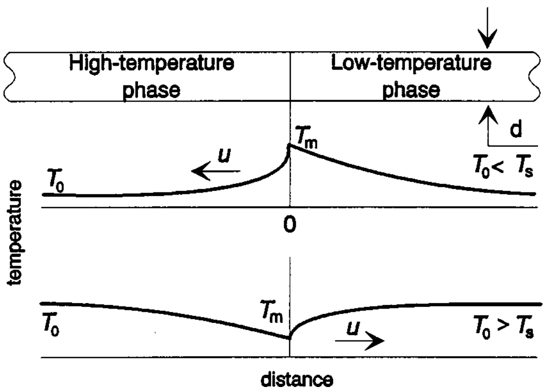


FIG. 3. Temperature profiles in the vicinity of the traveling interface. At $T_0 < T_s$, the low-temperature phase is growing, while at $T_0 > T_s$, the high-temperature phase grows.

Unfortunately, not much attention was paid to this work.

III. MOTION OF INTERPHASE BOUNDARIES

In passing through matter, the combustion wave changes its state, and in this respect it is similar to a traveling interphase boundary. To see the difference between them, let us consider a phase transition in a substance placed in a tube of diameter d. Let a phase that is stable at high temperatures be on the left, as shown in the upper part of Fig. 3, where T_s is the temperature of the phase transition (at a given pressure). Then Eqs. (11) and (12) hold, where T_m is now the temperature at the boundary and Q is the heat of the phase transition. As to the inner solution, the interface, generally speaking, has an atomic width, so that the problem turns out to be beyond the scope of macrokinetics. We shall confine ourselves to the case of low metastability when the thermostat temperature T_0 is close to T_s. The velocity U may be assumed to be proportional to the difference between the chemical potentials of the metastable and equilibrium phases, and this difference is proportional to the deviation of T_m from T_s, so that

$$U = K(T_s - T_m), \tag{23}$$

where K is a positive constant. From Eqs. (11), (12), and (23) we obtain

$$U = \frac{2\sqrt{N}(\kappa/dQ)(T_s - T_0)}{1 + 2\sqrt{N}(\kappa/dKQ)},$$

$$T_m = T_s - \frac{T_s - T_0}{1 + (dKQ/2\sqrt{N}\kappa)}. \tag{24}$$

For $d \gg 2\sqrt{N}(\kappa/KQ)$, the propagation velocity is determined by heat exchange and is independent of K. This regime of propagation may be termed the Stefan regime. For the opposite inequality we have $T_m \approx T_0$, and the velocity is determined by the solution to the inner problem.

The most significant feature of Eqs. (24) is the change in sign of U when $(T_s - T_0)$ changes sign. The former metastable phase becomes stable and grows. For this reason, the velocity can be made infinitesimally small, whereas the delay of the combustion wave leads to its extinction. We shall find many flamons that are similar in this respect to an interface. They are termed here s waves, while the flamons that do not survive retardation are termed q waves. Returning to Sec. II.B, we can state that Eq. (19) represents the s wave, whereas the front of a chain reaction represents the q wave.

Now let us return to the reaction zone. Its solution may be obtained (Malomed and Rumanov, 1985) when the state of the substance is close to a critical point. Then the characteristic spatial scale x_0 that, in particular, determines the boundary width turns out to be macroscopic:

$$x_0 \sim a\sqrt{T_c/(T_c - T)}, \tag{25}$$

where T_c is the critical temperature, while a is of the order of a molecular dimension and may be related (Zel'dovich and Todes, 1940) to the coefficient of surface tension α between the phases:

$$\alpha = \frac{8}{\sqrt{3}} a P_c \left(\frac{T_c}{(T_c - T)} \right)^{3/2}, \tag{26}$$

where P_c is the critical pressure. It will be assumed that $(T_c - T) \ll T_c$, so that the boundary structure may be described in terms of a hydrodynamic approximation.

Near the critical point, the van der Waals equation of state holds:

$$p = 4t + 6tr + (3/2)r^3 - a^2 \Delta r. \tag{27}$$

Here, $p = (P - P_c)/P_c, r = (\rho - \rho_c)/\rho_c, t = (T - T_c)/T_c$, ρ is the density, and the coefficients were selected according to the law of corresponding states. The term with the Laplacian in Eq. (27) is used to describe regular inhomogeneity, i.e., the interface, rather than to account for fluctuations. The fluctuation region in the (p,t) plane (Landau and Lifshitz, 1978; Patashinskii and Pokrovskii, 1979) will not be considered here, and so the fluctuations will be neglected.

Under the condition of equilibrium between the phases, $p = 4t$, and Eq. (27) has three homogeneous solutions:

$$r_0 = -2\sqrt{-t}, \quad r_1 = 0, \quad r_2 = 2\sqrt{-t}. \tag{28}$$

(Since we consider a two-phase system, the temperature is below criticality, i.e., $t < 0$.) If, for the sake of definiteness, we consider the critical point in a liquid-vapor system, then r_0 and r_2 correspond to the vapor and liquid, respectively; the solution r_1 is thermodynamically unstable: $(\partial p/\partial r)_t < 0$. The inhomogeneous solution

$$r = 2\sqrt{-t} \tanh\left(\frac{x}{a} \sqrt{-3t} \right) \tag{29}$$

describes the plane boundary between the vapor, $r(x \to -\infty) = r_0$, and the liquid, $r(x \to \infty) = r_2$. As can be seen from Eq. (29), the order of the boundary width is given by Eq. (25).

Now we shall discuss a traveling boundary. Let us consider, for example, condensation of a supercooled vapor. The possible densities of the initial state are confined to the interval

$$-2\sqrt{-t}<r_0<-2\sqrt{-t/3}, \tag{30}$$

at the upper limit of which (spinodal) thermodynamic stability is lost. According to the meaning of the "inner" problem, the temperature may be assumed to be constant $(T=T_m)$. Using a coordinate frame that moves together with the boundary, let us supplement Eq. (27) with the equation of continuity and the Navier-Stokes equation:

$$\rho u=\rho_0 u_0, \tag{31}$$

$$\rho u u'=-p'+\nu u'', \tag{32}$$

where $\nu=(4/3)\eta+\zeta\,\eta,\zeta$ are the first and second viscosities, a prime denotes differentiation with respect to x, and the subscript 0 corresponds to the state ahead of the boundary (in the inner scale, $x\to-\infty$) so that u_0 is the velocity of the boundary in the lab frame. Eliminating $u(x)$ and $p(x)$ from Eqs. (27), (31), and (32) as well using new variables and parameters,

$$\xi=\frac{x}{x_0},\quad \theta=\frac{r}{\sqrt{-t}},\quad v=\frac{u_0}{\sqrt{-tP_c/\rho_c}},$$

$$g=\frac{\nu/a}{\sqrt{P_c\rho_c}}, \tag{33}$$

one can obtain the equation for the "density" $\theta(\xi)$,

$$\frac{d^2\theta}{d\xi^2}-gv\frac{d\theta}{d\xi}=\frac{3}{2}(\theta^3-\theta_0^3)-(6+v^2)(\theta-\theta_0), \tag{34}$$

which, together with the conditions

$$\xi\to-\infty:\quad \theta=\theta_0;\quad \xi\to\infty:\quad d\theta/d\xi=0, \tag{35}$$

allows the velocity and structure of the traveling boundary (density wave) to be determined.

In contrast to Eq. (19), the right-hand side of Eq. (34) depends on v, which stems from the momentum balance Eq. (32). From Eqs. (34) and (35) it follows that

$$d\theta/d\xi=(\sqrt{3}/2)(\theta-\theta_0)(\theta_2-\theta), \tag{36}$$

$$v=-(3\sqrt{3}/2g)\,\theta_1, \tag{37}$$

where

$$\theta_{1,2}=-\frac{\theta_0}{2}\mp\sqrt{4-(3/4)\theta_0^2+(2/3)v^2}. \tag{38}$$

Therefore the density of the final state θ_2 depends on the velocity of the boundary motion. According to Eqs. (30) and (33), possible values of the initial density θ_0 lie in the interval $(-2,-2/\sqrt{3})$. As can be seen from Eq. (38), $\theta_2\geqslant 2$, which corresponds to the density of the equilibrium phase (liquid). For small $\epsilon=\theta_0+2$, we have $v\approx(3\sqrt{3}/g)\epsilon$, or, in dimensional form,

$$u_0\approx\frac{3\sqrt{3}aP_c}{\nu}\left(\frac{T_s-T_m}{T_c-T_s}\right). \tag{39}$$

Comparison with Eq. (23) gives the value of K. The approximation given by Eq. (39) is valid for $(T_s-T_m)\ll(T_c-T_s)$.

In explicit form, the v dependence on θ_0 and the "viscosity" g is given by

$$v=\frac{q\,\theta_0}{2\sqrt{3}\left(\frac{2}{9}g^2-1\right)}\pm\left[\frac{g^2\theta_0^2}{12\left(\frac{2}{9}g^2-1\right)^2}+\frac{3}{2}\left(\frac{4\theta_0^2}{\frac{2}{9}g^2-1}\right)\right]^{1/2}. \tag{40}$$

The problem (34) and (35) is not symmetric with respect to the boundary conditions. The initial state is chosen at $\xi\to-\infty$, so only the values $v>0$ should be considered in Eq. (40); the density behind the traveling boundary $\theta(\xi\to\infty)=\theta_2$ must be determined along with v. The $v(\theta_0)$ dependence turns out to be different for different g (i.e., for different substances).

For $g^2>9/2$ only one branch in Eq. (40), corresponding to the + sign, is positive. For $g^2<9/2$, both branches are positive; the branch corresponding to the − sign is ascending, while the other is descending. The solution corresponding to the descending branch is unstable. When $g<2$, the branches merge at $\theta_0<-2\sqrt{3}$. At low viscosity, the velocity of the boundary motion first grows sharply with supercooling but, at a critical value of θ_0, this pattern is broken up. Change in decomposition of the metastable substance is usually related to achieving the spinodal state, where the barrier to formation of a new phase becomes zero (see, for example, the review of Skripov and Skripov, 1979). For a sufficiently fluid substance $(g<2)$, other critical conditions of the decomposition kinetics are seen to take place. According to Eq. (40), the critical value of θ_0 is given by

$$\theta_*=-2\sqrt{\frac{1-(2g^2/9)}{1-(g^2/6)}},\quad (g<2). \tag{41}$$

The occurrence of breakup at $\theta_0=\theta_*$ may be explained as follows. Due to the difference in the chemical potentials $\Delta\mu$ for the metastable and equilibrium phases, the interface is moving. Upon acceleration of the boundary, the pressure difference and hence increase in $\Delta\mu$ lead to a further increase in the rate of condensation. Similarly, upon evaporation of the superheated liquid, the acceleration of the boundary results in additional expansion of the equilibrium phase (vapor) and in an increase of $\Delta\mu$.

The breakup of the boundary motion was observed (Zhukov and Barelko, 1992) upon evaporation of a superheated liquid. A wire was placed in the liquid, which had a temperature slightly below the boiling point. A voltage was applied to the wire, and if the electric current was sufficiently large, a superheated layer was formed. An evaporation wave could thus be excited and was observed to propagate within this layer along the wire. The speed of the boundary motion as a function of wire temperature obtained in this study is shown in Fig.

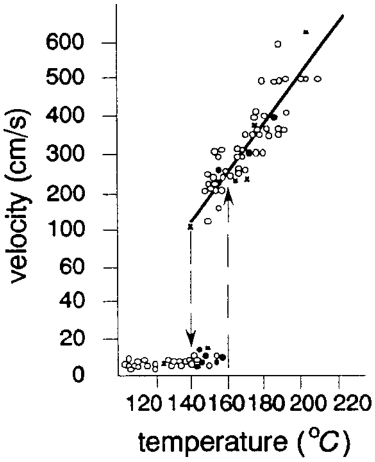


FIG. 4. The toluene evaporation wave velocity as a function of wire temperature (the wave propagates along the wire). The toluene temperature is 20 °C. From Zhukov and Barelko (1992).

4 in simplified form. The speed of the boundary motion is seen to grow together with superheating until breakup accompanied by hysteresis occurs. The solution of the fast boundary motion is absent in Eq. (40). This is probably due to the fact that we used the equation of state, Eq. (27), containing no higher orders of density.

Generally, the behavior of interfaces in different substances is universal only under conditions that are close to equilibrium when the velocity of the boundary motion is small. In the flamons under consideration here, the s waves that may come to a halt and change the direction of their motion, and the q waves that are quenched if they slow down due to variation of control parameters, represent two limiting cases. This may be illustrated by a model of the frontal crystallization in an amorphous film (Shklovskii, 1982, 1994).

Let the substrate temperature T_0 decrease. When T_0 is in the vicinity of T_s the boundary motion is close to that of the s wave: at $T_0=T_s$, the velocity U passes through zero. Then U grows, but at some $T_0=T_A$ breakdown occurs. Such a breakdown is similar to that of the combustion wave described in Sec. II.B. However, unlike flames, where breakdown means extinction, the interface does not disappear (which is clearly impossible), but sharply slows down. An increase in T_0 leads, at $T_0=T_B>T_A$, to a reverse jump from the slow branch of velocity to the fast one. In the vicinity of T_A, the structure and behavior of the crystallization front correspond to those of the q wave. It should be noted that the stable branch of low velocities is present formally in the system given by Eqs. (10)–(12); however, for the combustion wave, such a solution is physically meaningless: as $U \to 0$, reactions in the cold substance should be taken into account, and the wave solution disappears.

IV. SOLITARY WAVES IN SYSTEMS WITH AN EXTERNAL FEED SOURCE

The state of the medium ahead of and behind a flamon is homogeneous. In the absence of an external feed, equilibrium is established behind the wave, while the initial state is metastable. In the presence of an external source, equilibrium is impossible, and either a new homogeneous steady-state pattern is established or the initial one is recovered. Of course, in the latter case, the flamon cannot be an s wave. Let us first consider flamons that give rise to a new homogeneous stationary pattern.

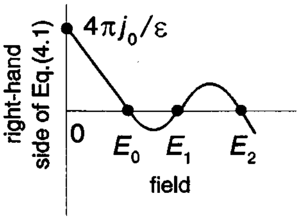


FIG. 5. Bistability: When the electron mobility $\mu(E)$ decreases, there exists the range of j_0 within which three stationary values of E correspond to each j_0.

A. Switching wave

The propagation of a flamon that gives rise to a new homogeneous steady-state pattern implies that one of the patterns is "more stable" than the other, although the old and new patterns may exist for the same values of control parameters (bistability). The condition for such a flamon (s wave) to have zero velocity is similar to the condition for equilibrium between thermodynamic phases. In Sec. III, in considering the propagation of an interface, we stated that the direction of this motion is determined by the sign of the difference between the chemical potentials. This quantity does not exist for the patterns in an active system. The only way to compare their stability is to investigate the s wave.

In what was, as far as we know, the first such study Copeland (1966) dealt with the distribution of the electric field E in a semiconductor with an N-shaped voltage-current characteristic, i.e., exhibiting negative resistivity dE/dj at some field strength. The equation for $E(x,t)$ has the form (Kadomtsev, 1988)

$$\frac{\partial E}{\partial t}-D\frac{\partial^2 E}{\partial x^2}-\mu E\frac{\partial E}{\partial x}=\frac{4\pi}{\epsilon}(j_0-en_0\mu E), \tag{42}$$

where D is the diffusivity of the conduction electrons, μ and n_0 are their mobility and mean density, respectively, ϵ is the dielectric constant, and j_0 is the current in an outer circuit. To obtain a negative resistivity, one has to use a substance for which $\mu(E)$ decreases over an interval of E. Equation (42) is interesting because it may be used to describe the Gunn effect (Gunn, 1963). We shall return to the Gunn domains, but for now let us consider other solutions.

Homogeneous patterns correspond to zeros of the right-hand side of this equation. When $\mu(E)$ behaves as described above, bistability occurs within a certain range of j_0, as shown in Fig. 5. In this case, both $E=E_0$ (the low-field pattern) and $E=E_2$ (the high-field pattern) are possible, while the point E_1 is unstable. Let us study an inhomogeneous pattern subject to the boundary conditions $E(x=-\infty)=E_0$, $E(x=+\infty)=E_2$, in which the regions of low and high fields are separated by an intermediate layer (s wave). By introducing the automodel variable $\xi=x+ut$ and the notation $dE/dx=q$, we obtain

$$D\frac{dq}{dE}=-\frac{1}{q}\frac{\partial W}{\partial E}-k, \tag{43}$$

$$q(E_0)=q(E_2)=0, \tag{44}$$

where

$$W(E)=\frac{4\pi}{\epsilon}\left(j_0E-en_0\int \mu E dE\right), \quad k=\mu E-u. \tag{45}$$

Mathematically, Eq. (43) is similar to the equation for the phase trajectories of a particle undergoing one-dimensional motion in the field with potential W, where E plays the role of the coordinate and k is the friction coefficient. Conditions (44) select the trajectory, for which the maxima of $W(E)$ are turning-points. The difference in potentials of these points should be equal to the work of the friction force:

$$W(E_2)-W(E_0)=\frac{4\pi}{\epsilon}\left[j_0(E_2-E_0)-en_0\int_{E_0}^{E_2}\mu E dE\right]$$
$$=\int_{E_0}^{E_2}(u-\mu E)q dE. \tag{46}$$

According to Eq. (46), the flamon velocity u increases with j_0. As long as the current is small, we have $u<0$, and the high-field "phase" transforms to the low-field one. At some $j_0=j_{00}$, the velocity passes through zero and becomes positive. We remark that when $u=0$, and the phases of the low and high fields may be considered as being in equilibrium, the current through the interface does not vanish. The interface under consideration has a positive charge.

So far, we have assumed that $q>0$, i.e., that the high-field phase is on the right of the interface (we assume $j_0,E>0$). Problem (43) and (44) also has a solution for which $q<0$ and the high-field phase is on the left of the interface. Such an interface has a negative charge. According to Eq. (46), $u(j_0)$ is decreasing for $q<0$ and increasing for $q>0$. In Sec. III, when we considered the propagation of a thermodynamic phase boundary, it was insignificant which phase was on the left and which on the right of the interface. Equation (34) is invariant with respect to the transformation $\xi\rightarrow-\xi, v\rightarrow-v$. In the case we consider now, such a symmetry is absent, because of the presence of the applied field.

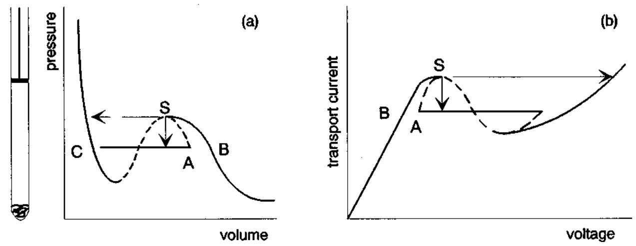


FIG. 6. The coexistence of phases. (a) van der Waals isotherm; dashed lines show the states that are unstable to small fluctuations. The horizontal portion corresponds to equilibrium between the phases; (b) The N-shaped characteristic of a semiconductor. The horizontal portion is due to the occurrence of a high-field domain in a sample.

The macroscopic kinetics of a phase transition is determined by experimental conditions. For instance, let us isothermically compress the vapor in the cylinder shown on the left of Fig. 6(a). If we apply some (programmed) force to a piston, the vapor volume will be determined by the pressure at a given moment. Another experimental approach is to specify the piston position at each moment (i.e., the substance volume). The difference between these approaches will be insignificant as long as the vapor remains homogeneous. When growing (with pressure) boiling temperature reaches the system temperature [point B in Fig. 6(a)], condensation begins to occur. At a given force, the interface between the vapor and the liquid in the tube travels until the vapor completely disappears. By specifying the piston position, we stop the interface, and the size of "liquid domain" is determined by a control parameter which is the substance volume. By neglecting the surface energy, the isotherm portion in Fig. 6(a) that corresponds to the equilibrium between both phases may be considered to be horizontal. However, if the liquid volume is sufficiently small, the two-phase state becomes thermodynamically unfavorable. At point A, the branch of the two-phase state merges with the branch of unstable states, and the latter extends until it joins the line of homogeneous states at point S. The unstable solutions forming the AS branch correspond to the critical drop surrounded by vapor according to Gibbs (1961). The BS portion is made up of the homogeneous metastable states (supercooled vapor). Stability with respect to small fluctuations is lost at point S, and spinodal decomposition takes place (see Skripov and Skripov, 1979). At a given pressure, vapor undergoes complete transition to liquid [horizontal arrow in Fig. 6(a)]; at a given volume, decomposition leads to an inhomogeneous (two-phase) state (vertical arrow).

The above detailed discussion of various modifications of vapor condensation is needed to reveal a similarity to the "phase transition" in a semiconductor separated into regions with high and low fields. The current voltage characteristic for such a semiconductor is shown in Fig. 6(b). There are three stable (with respect to small fluctuations) branches, two of which represent the homogeneous states (of low and high field), while the third (horizontal one) corresponds to the states with the Gunn domain. The homogeneous low field is metastable within the region BS, i.e., it is not destroyed by small fluctuations. However, if the electric current is fixed and the domain is formed, it will grow until it covers the entire sample. If the voltage is fixed, the domain width l will be determined by the "lever rule":

$$V=E_0(L-l)+E_2 l, \tag{47}$$

where V is the voltage and L is the sample length. Equation (47) holds as long as the width of the domain boundary (s wave) is small compared to l.

The pressure at the horizontal portion of the isotherm in Fig. 6(a) is such that the liquid/vapor interface is motionless. The current j_B, which corresponds to the horizontal portion of the characteristic in Fig. 6(b), is determined in a somewhat different way. The Gunn domain cannot remain motionless since, according to Eq. (46), the velocities of the left and right interfaces become zero at different currents. As mentioned above, the velocity of the left interface is an increasing function of j_0, while that of the right one is decreasing. For $j_0 = j_B$, these velocities should be equal, which determines the value of j_B. Indeed, at $j_0 < j_B$, the right interface moves faster than the left one, and the domain shrinks. In this case, the sample resistance diminishes, and current grows until the value of j_B is recovered. The frequency of self-oscillations is given by $\omega \approx u(j_B)/L$, where the domain velocity $u(j_B)$ is independent of voltage within the plateau in Fig. 6(b), i.e., always when two phases exist. Therefore the representation of the regions of low and high fields as "phases" that are separated by the s wave is very convenient for the description of the Gunn effect. For a more detailed discussion, see the review of Volkov and Kogan (1968).

As mentioned above, Eq. (19), which describes the simplest s wave in a system with an external influence was suggested as early as 1938. However, at that time, no physical system was found to be modeled by this equation. In 1969, Zel'dovich and Pikel'ner considered a gas cloud heated by cosmic rays. The balance between heating and radiative heat loss was furnished by two density values within a certain pressure range. The higher value corresponded to the cold neutral gas, the lower one to the hot plasma. An inhomogeneous pattern is also possible when these two "phases" are separated by an s wave (in this case, the ionization wave). If a phase transition accompanied by a change in conductivity is possible in a substance, then, upon heating by current, the s wave may coincide with a real interface. Such waves in semiconductors, normal metals, and superconductors were reviewed by Gurevich and Mints (1987).

In distributed chemical systems with thermal bistability, s waves were studied in detail. Frank-Kamenetskii (1939a) was the first who pointed to such bistability in studying a problem in which a reactive gas was blown over a catalytic surface. The concentration a and the surface temperature T satisfy the following equations:

$$da/dt = \beta(a_0 - a) - ak \exp(-\epsilon/T), \tag{48}$$

$$dT/dt = Qc^{-1}ak \exp(-\epsilon/T) - \alpha(T - T_0), \tag{49}$$

where Q is the reaction heat, c is the specific heat, α and β are the inverse times of heat and mass exchange, respectively, and the subscript "0" denotes values outside the boundary layer. From Eqs. (48) and (49), it follows that there exist two stationary patterns at some values of parameters. Similar bistability also occurs in a flow reactor (Zel'dovich, 1941a). The bistability region is schematically drawn in Fig. 7. The low-temperature pattern is broken up at the upper boundary of this region: the temperature rises sharply, and transition to the high-temperature pattern (ignition) is observed. If the parameters are changed in the opposite direction, the high-temperature pattern is retained down to the lower boundary, at which extinction occurs. Ignition and extinction are the critical phenomena that are similar to the spinodal decomposition mentioned above. They are caused by instability with respect to small fluctuations. Just as in the case of phase transitions, inhomogeneous patterns (analogs of coexisting phases) should be added to the picture above.

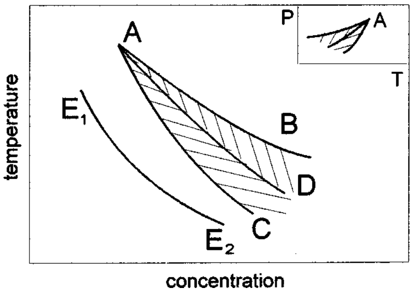


FIG. 7. Location of the stationary patterns of heterogeneous reaction in the (a_0, T_0) plane of parameters. The bistability region is shaded. A is a critical point. Within the bistability region, the line AD indicates "phase equilibrium." The insert shows the phase diagram for the liquid-vapor system. The significance of the line E_1E_2 will be explained in Sec. IV.B.

The ignition and extinction of catalytic reactions on platinum surfaces was studied by Buben (1947), who used a wire installed transversely to the flow of reactants (the first experiments with such a wire were performed by Davies, 1934). The wire was heated by an electrical current, the intensity of which served as a convenient control parameter. Inhomogeneous reaction patterns for which the low-temperature regime occurs at one end of the wire, while the high-temperature regime occurs at the other end, were later studied theoretically (Merzhanov *et al.*, 1975) and experimentally (Barelko *et al.*, 1976; see also, for later experimental results, Cordoner and Schmidt, 1989; Philippov and Luss, 1993). The temperature jump takes place within a narrow ("interface") region, which may move. If the current is small, the cold region grows; if the current is large, the hot one grows. The condition $u = 0$ determines the line of "phase equilibrium" in Fig. 7. The picture is quite similar to the structure of the "temperature-pressure" plane for a liquid-vapor system, provided that, along with the line of the phase equilibrium, the lines of stability loss with respect to small fluctuations in supercooling vapor and superheated liquid are plotted. Such a diagram is shown in the insert to Fig. 7. Just as a continuous transition between liquid and vapor may be reached by bypassing the critical point in the (T, P) plane, a high-temperature pattern may be reached without ignition and a low-temperature pattern without extinction if one varies the flow parameters T_0, a_0 along a route that bypasses point A in Fig. 7. The structure in the (T_0, a_0) plane of parameters with a critical point is determined by the fact that both patterns have the same symmetry: they are spatially homogeneous and stationary.

We consider the wire as a one-dimensional system and introduce the term $\chi T''$ into the right-hand side of Eq. (49), where χ is the thermal diffusivity of platinum and a prime denotes differentiation with respect to the coordinate x along the wire. The characteristic time of heat exchange between the gas flow and the wire is large compared to the time of mass exchange between the flow and the boundary layer near the wire, so that $\beta \gg \alpha$. This inequality allows the left-hand side of Eq. (48) to be neglected. Eliminating the concentration a and using the reference frame attached to the "interface," we obtain

$$uT' - \chi T'' = Q a_0 c^{-1} (\beta^{-1} + k^{-1} e^{\epsilon/T})^{-1} - \alpha(T - T_0), \tag{50}$$

where Q is the reaction heat per gas unit mass and c is the specific heat of platinum. The right-hand side of Eq. (50) has three zeros for values of T_0 and a_0 that lie in the shaded area in Fig. 7. Let us denote them by T_1, T_2, and T_3 in order of increasing size. Similarly to Eqs. (43)–(46), we may write

$$u = \left(\int_{T_1}^{T_3} q(T)\, dT \right)^{-1} \int_{T_1}^{T_3} F(T)\, dT, \tag{51}$$

where $q \equiv T'$ and $F(T)$ is the right-hand side of Eq. (50). According to Eq. (51), the condition of "phase equilibrium" has the form

$$\int_{T_1}^{T_3} F(T)\, dT = 0, \tag{52}$$

which reminds us of the condition of "equal areas" $\int_C^B V\, dP = 0$, which determines the position of the horizontal portion of the isotherm in Fig. 6(a).

The Joule heat of current through the wire is not accounted for in Eqs. (49) and (50). Since the temperature dependence of electrical resistance R is weaker than the activation of the reaction, the role of the Joule heat is reduced mainly to the renormalization of T_0. Utilizing this weak dependence, it is possible to design a regulator (Mashkinov *et al.*, 1975) that provides fixed R and therefore fixed mean temperature of the wire. In experiments with this regulator, jumps in the heat release were found to occur at certain critical values of R (Barelko and Volodin, 1973). They are related to the transitions between the homogeneous and inhomogeneous patterns of reaction, the latter represented by a hot domain, the width l of which, similar to Eq. (47), is given by

$$\rho_1 (L - l) + \rho_3 l = R, \tag{53}$$

where L is the wire length and ρ_1 and ρ_3 are the specific resistance values at T_1 and T_3, respectively (Grachev and Rumanov, 1981). The thermal domain does not move; the velocities of both the s waves corresponding to the left and right interfaces become zero under the same condition (52). Of course, an equality like Eq. (53), where the width of the s wave is not taken into account, is a rather rough approximation. An analysis that did not depend on the smallness of $\chi/\alpha l$ was carried out by Sigov and Chechetkin (1985). It should also be noted that the surface reactions do not necessarily obey the activation dependence in Eqs. (48) and (49), the adsorbed reactants form various phase modifications, adsorption and surface reconstruction are interrelated, etc. These phenomena, observed mainly by tunnel microscopy and spectroscopy, have been analyzed by Keldysh (1985). Reaction waves were observed for CO oxidation on a Pt (100) surface (Cox *et al.*, 1985). The boundary line between (1×1) and hex structures was seen to move by diffusion of adsorbed CO. Laser irradiation initiated the desorption of CO, followed by the chemical wave propagating from this irradiated spot at a velocity of about 2 mm/min at 480 K (Fink *et al.*, 1990; see also Ertl, 1991).

As we have seen, a unique value of the heating current (or T_0) corresponds to phase equilibrium ($u = 0$) when the other parameters are fixed. On the other hand, in many experiments the s wave does not move within a finite (although not large) range of currents. Gurevich and Mints (1984) assumed that the stoppage of the s wave is determined by macroscopic inhomogeneities in the medium through which the wave propagates. Another mechanism of stoppage was suggested by Temkin (1989). He considered the influence of a small admixture on interface propagation when the power of the heat source is different in different phases. In the problem of current in a conductor, this difference arises due to a resistance change upon phase transition (Kalafati *et al.*, 1979; Merzhanov *et al.*, 1980), in other examples the reaction rate is different for different phases of adsorbed reactants, the heat removal from a wire is more efficient for nucleate boiling than for film boiling when the wire surface is surrounded by vapor (Zhukov *et al.*, 1979), etc. Restricting ourselves to low s-wave velocities, we shall approximate the right-hand side in Eq. (50) for all these problems by the piecewise-linear function:

$$\alpha(T_1 - T)\,\theta(T_s - T) + \alpha(T_3 - T)\,\theta(T - T_s), \tag{54}$$

where T_s is the interface temperature and θ is the Heaviside function, $\theta(T<0)=0$, $\theta(T>0)=1$. Then Eq. (52) takes the form

$$T_s = (T_1 + T_3)/2. \tag{55}$$

For a pure substance, T_s has a prescribed value (phase-transition temperature); in the presence of an impurity, it has to be determined along with the impurity concentrations on both sides of the interface. The concentration $b(x)$ is given by the solution to the diffusion equation,

$$Db'' - ub' = 0, \tag{56}$$

with boundary conditions

$$b(x \to -\infty) = b(x \to +\infty) = b_0, \tag{57}$$

$$b(x = -0) = b_1(T_s), \quad b(x = +0) = b_2(T_s). \tag{58}$$

In Eq. (58), subscripts 1 and 2 refer to the low- and high-temperature phases, respectively. As before, let us

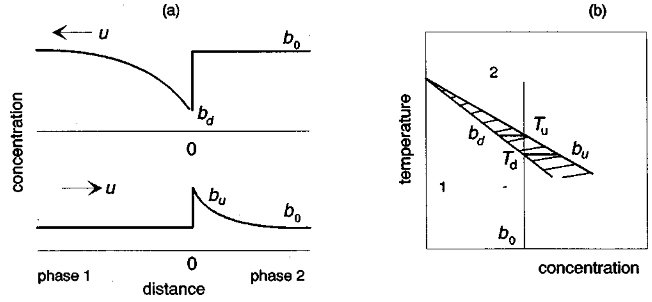


FIG. 8. Effect of impurity on the s wave. (a) Concentration profiles in the vicinity of the interface for $u>0$ (upper curve) and for $u<0$ (lower curve); (b) portion of the phase diagram for small concentration of impurity; the two-phase region is shaded. At $T_s=T_u$, the concentration in the low-temperature phase 1 is b_d, and in phase 2 it is b_0. When $T_s=T_d$, these concentrations are b_0 and b_u, respectively.

assume that the high-temperature phase occupies the region $x>0$ in the reference frame attached to the interface (see Fig. 8). From Eqs. (56) and (57), it follows that $b(+0)=b_0$ for $u>0$, and $b(-0)=b_0$ for $u<0$. For this reason, T_s turns out to depend on the direction of the s-wave propagation: $T_s=T_u$ for $u>0$, and $T_s=T_d$ for $u<0$ (T_u and T_d are found from the phase diagram schematically represented in Fig. 8). The range of current (or other control parameter), for which $u=0$, according to Eq. (55) is determined by the conditions

$$T_d<(T_1+T_3)/2<T_u. \tag{59}$$

B. Recovery zone

The occurrence of s waves is possible for control parameters in the bistability region (for the heterogeneous reaction this is the shaded area in Fig. 7). Is it possible to excite a flamon when the point (a_0,T_0) is below the shaded area and the unique homogeneous pattern is a low-temperature one? First, let us note that among the phase trajectories of a system similar to Eqs. (48) and (49) there are trajectories that emerge from points with $a=a_0$ and relatively low temperature to the region of high temperatures and low concentrations and then “return” to an attracting node (Abramov and Merzhanov, 1975). These trajectories correspond to the ignition of a mixture in a reactor, but the flow of the cold substance “blows out” the reaction, and a low-temperature pattern is established. Upon going from the concentrated system to the extended one, we consider the reactor oriented transverse to the flow.

In deriving Eq. (50), we have taken into account heat conduction along the x axis and neglected the left-hand side in Eq. (48) in view of the inequality $\beta\gg\alpha$. In the reference frame attached to the flamon, the left-hand side contains the term $u\,da/dx$, the magnitude of which depends on the flamon velocity u. Since now we are not going to restrict ourselves to slow s waves, this term should not be neglected, and both equations (for temperature and concentration) must be analyzed. If the (a_0,T_0) point is chosen from the shaded area in Fig. 7, the s waves can propagate along the x direction. In the region BAD, such a wave transforms the low-temperature pattern into the high-temperature one, while in the portion CAD, the transition is in the reverse direction.

Now let us consider a region below the line AC and imagine for a moment that there is no flow of reactants through the reactor. The cold mixture that fills the reactor may be ignited. Then a combustion wave will be formed, behind which the reaction products will be gradually cooled. If the flow rate is not zero but is sufficiently small, the flow will have no time to influence the wave structure, which consists of the heating, reaction, and cooling zones. The role of flow is reduced here to the slow replacement of the products by fresh substance, and the steady-state low-temperature pattern will be recovered. Assuming the recovery to be slow, we can omit the term $-\beta a$ in Eq. (48) in treating the first three zones of the flamon. Such a problem has already been analyzed in Sec. II.B. It has two solutions, and the solution for which u is greater is stable. When stable and unstable branches merge, breakdown occurs. The dependence $T_0(a_0)$ corresponding to the merger is schematically drawn as the line E_1E_2 in Fig. 7. It represents the lower limit for the occurrence of the q waves (obviously, the upper limit is given by the ignition line AB, above which a homogeneous low-temperature pattern is impossible). However, the line AB is not the upper limit for the existence of s waves. For some T_0, the solution corresponding to the s wave coalesces with the unstable solution, the flamon is transformed into a q wave, and its velocity increases discontinuously. The breakup of the s wave may be explained as follows. For $u>0$, the reaction consumes not only the substance that is supplied at this moment but also the fresh mixture ahead of the wave in the cold part of the vessel (Aldushin, 1977). The greater the wave velocity, the greater is the fraction of this “additional feed”; a positive feedback arises, which explains self-acceleration of the s wave leading to breakup.

The zonal structure of these flamons is shown in Fig. 9. For parameters belonging to the region between the lines E_1E_2 and AC in Fig. 7, propagation of only the q wave is possible. Behind such a wave, the initial low-temperature pattern is recovered. Sometimes such a wave is termed a traveling pulse (e.g., Vasil’ev *et al.*, 1987; Loskutov and Mikhailov, 1990). If parameters belong to the shaded area in Fig. 7, a return to the low-temperature pattern is impossible; after reaching a maximum, the temperature decreases to T_3. The main difference with the traveling pulse is in its rear edge. The reaction zones have the same structure, hence the velocities are the same: the $u(T_0)$ curve for the q waves is continuous in passing through AC in Fig. 7, after which their structure changes. The fact that the rear edge of the flamon exhibits no influence on its velocity allows a simple estimate for the velocity of a nerve pulse (Kompaneets and Gurovich, 1966). Although the Belousov-Zhabotinsky reaction is not thermally activated, the traveling pulse structure obtained by Wood

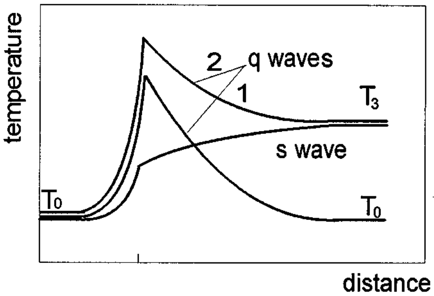


FIG. 9. Temperature profiles of a flamon in a flow reactor: (1) q wave (traveling pulse) which can propagate if (a_0,T_0) falls in the region between the lines E_1E_2 and AC in Fig. 7; (2) q wave for (a_0,T_0) above the line AC; (3) s wave, whose region of existence lies from the line AC up to the line of merger with the unstable branch. In the corner point of each $T(x)$ line, the flamon consumes fresh mixture located in its path.

and Ross (1985) is similar to that shown in Fig. 9. Recovery of the initial state behind the pulse permits its splitting by an inhibiting light flash (Muñuzuri *et al.*, 1997). After the flash, part of the excitation survives and ignites two pulses moving in opposite directions.

Below the line AC in Fig. 7, the velocities of the s and q waves differ in direction. This implies that the metastability of the high-temperature pattern in the region CAD in Fig. 7 is not absolute. Excitation of the s wave transforms this pattern to the low-temperature one. However, for the same (a_0,T_0) the low-temperature pattern may be transformed to the high-temperature one by exciting the q wave (for more details, see Merzhanov and Rumanov, 1987, page 303).

A good deal of attention has been paid in the literature to traveling pulses, i.e., flamons, behind which the initial homogeneous pattern is recovered (e.g., Scott, 1970; Polak and Mikhailov, 1983; Romanovskii, Stepanova, and Chernavskii, 1984; Meron, 1992), because traveling pulses are claimed to model propagation of a nerve excitation. As shown above, there are two ways to organize a traveling pulse in a system with an external feed source. Either the q wave is excited under conditions when only one homogeneous pattern is possible and its recovery behind the wave is unavoidable; or the same velocity of the s waves (that separate the excited domain from regions with a homogeneous pattern) is maintained (e.g., by electric current) under conditions of bistability. In the latter case, the active medium is clearly anisotropic.

V. SPIRAL FRONTS

The recovery of initial patterns behind the traveling pulse makes it possible to twist the plane front into a spiral. Let us consider again the "one-dimensional" reactor of Sec. IV.B and make it ring shaped. The pulse may run in this ring indefinitely since it always finds a fresh mixture, provided that the ring radius is large compared to the pulse width including the recovery zone.

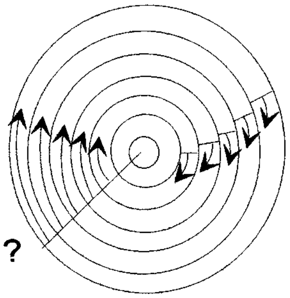


FIG. 10. How spirals arise. Rotation of the ray is impossible; pulses in the rings of larger radii lag and, instead of a rotating ray, a spiral is obtained.

Now let us imagine an active medium as a set of concentric rings (Fig. 10) and let pulses be excited simultaneously at different points along the same radius. In this case, we cannot obtain a rotating ray for which the linear velocity of each point is proportional to its radial coordinate. Instead, the velocity is constant, so that the pulses at larger radii lag behind, thus forming a spiral.

Therefore, under certain conditions, we may obtain a periodic pattern representing a reaction wave in the form of a rotating spiral (Wiener and Rosenblueth, 1946). Various spirals have been observed in cells with the Belousov reaction (Winfree, 1972; Zhabotinskii, 1974). Of course, the concentric rings of Fig. 10 are merely an illustration. To evaluate the rotation rate and shape of the spiral, let us consider its small portion in the polar coordinate system. The equation for a spiral may be written as

$$\phi+\omega t=\phi_0(r), \tag{60}$$

where ϕ is the polar angle and r is the radius. This equation is similar to the familiar equality $x+ut=x_0$ for a plane wave. In time dt, a given portion of the front travels the distance $\omega r dt$ along a circle of radius r, whereas the displacement in the direction normal to the front is udt, where u is the velocity of the plane flamon. Let α be the angle between the normal and tangent to the circle at the point under consideration (Fig. 11). It is clear that

$$u=\omega r\cos\alpha. \tag{61}$$

On the other hand, small displacements dr and $d\phi_0$ along the $\phi_0(r)$ line are related by

$$r\,d\phi_0=(-\tan\alpha)dr, \tag{62}$$

so that

$$\cos\alpha=1/\sqrt{1+r^2(d\phi_0/dr)^2}. \tag{63}$$

From Eqs. (61) and (63), we obtain

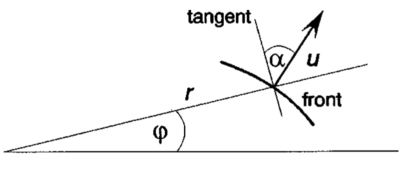


FIG. 11. Geometry of the spiral wave shape.

$$\phi_0(r)=\int\sqrt{\left(\frac{\omega}{u}\right)^2-\frac{1}{r^2}}\,dr+\text{const.}\tag{64}$$

For large radii, this is the Archimedes spiral with pitch

$$\Delta r\sim 2\pi u/\omega.\tag{65}$$

Equation (61) is meaningful only for $r>r_0=u/\omega$. It follows that a spiral rotating at frequency ω cannot penetrate inside a circle of radius r_0. For $r<r_0$, a homogeneous pattern occurs. The occurrence of a spiral structure with a motionless core is apparently related to the fact that the width of the traveling pulse (as well as other flamons) is finite. The arguments based on Figs. 10 and 11, in which the front is depicted as a line, do not hold for radii comparable to the pulse width Δx. Assuming $r_0\sim\Delta x$, we obtain an estimate for the frequency,

$$\omega\sim u/\Delta x,\tag{66}$$

since for $r=r_0$ the front velocity is tangent to the core, according to Eq. (61).

Away from the core, where the characteristic dimensions (specifically, the radius of curvature of the spiral) are large compared to Δx, the representation of the traveling front as an oriented line seems to be convincing. However, for a description of the core vicinity and, accordingly, a more accurate determination of its radius, as well as of the frequency ω, the inner structure of the traveling pulse (considered in Sec. IV.B) must be taken into account. In addition, one would like to improve the simple description by an oriented line, in order to extend its range of applicability (for details, see the review of Davydov *et al.*, 1991).

Taking into account the dependence of the front velocity on its curvature K is an example of such an improvement. Markstein (1951) postulated that this dependence has the form

$$u(K)=u_0-DK,\tag{67}$$

where u_0 is the velocity of a planar front and D is the effective transport coefficient. This expression was used in an attempt to explain the damping of the hydrodynamic instability of combustion waves (see also Sec. VI.A). The linearity of Eq. (67) makes it applicable only for small K with $DK\ll u_0$. The rotating spiral is terminated at the core boundary $r=r_0$. There will be the termination of the free end of a finite wave front if its transverse growth depends on K. Let us assume (Davydov and Mikhailov, 1987) that the velocity of growth $v(K)$ is given by

$$v(K)=\gamma(K_c-K),\quad \gamma>0.\tag{68}$$

To maintain a steady rotation of the spiral, its curvature $K(r_0)$ at the end must be equal to the critical value K_c. According to Eq. (68), which allows a change in the sign of v, the traveling front may be regarded as a certain one-dimensional phase with respect to the homogeneous pattern in a two-dimensional active medium. Indeed, Eq. (68) is similar to dependence (23) for the velocity of an interface.

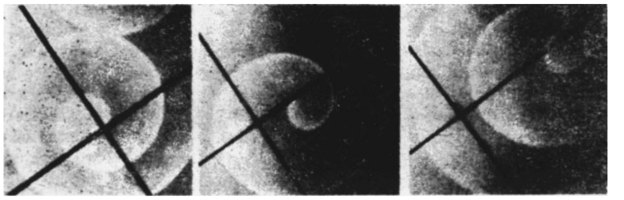


FIG. 12. Drift of the spiral wave of the Belousov-Zhabotinskii reaction. The reference lines, along one of which the spiral center displaces, are imposed on the photographs. The interval between shots is ten minutes. From Agladze *et al.* (1987).

A consistent realization of the idea of describing a front as an oriented line is provided by an equation that relates the arc length l to K. Such an equation was suggested by Zykov (1984) and then modified by Brazhnik *et al.* (1986) and by Davydov and Mikhailov (1987). In a modified form, it is

$$\frac{\partial K}{\partial t}+\frac{\partial K}{\partial l}\left(\int_0^l Ku\,d\zeta+v\right)=-K^2u-\frac{\partial^2u}{\partial l^2},\tag{69}$$

where u and v are defined by Eqs. (67) and (68), respectively. The arc length in Eq. (69) is measured from the free end. The quantities u_0, D, γ, and K_c in Eqs. (67)–(69) play the role of phenomenological parameters, which can be determined from experimental data. Since the spiral curvature increases as we approach the core, the applicability of Eq. (67) for all l in view of Eq. (68) is determined by the condition $DK_c\ll u_0$.

Using Eqs. (67)–(69), one can describe a number of phenomena exhibited by spiral waves. Upon periodic illumination of the tray in which the spiral wave of the Belousov–Zhabotinskii reaction was rotated, a drift of the spiral center was observed (Agladze *et al.*, 1987). Photographs from this work are presented in Fig. 12. The period of variation in lighting was the same as the period of spiral rotation found independently. In a theoretical and numerical investigation of the periodic action (Davydov *et al.*, 1988) based on Eqs. (67)–(69), it was assumed that the time dependence of K_c was sinusoidal. The solution corresponds to the motion of the spiral center along a circle, the radius of which is inversely proportional to $(\omega_1-\omega)$, where ω_1 is the frequency of action. When the frequencies are exactly equal, the center moves along a straight line. A complicated picture of "nonlinear resonance" was also observed (Rehberg *et al.*, 1988; Petrov *et al.*, 1997).

Upon steady rotation of the spiral, the trajectory of the free end, i.e., the core boundary, is a circle. However in experiments on the Belousov-Zhabotinskii reaction (Winfree and Janke, 1989; Skinner and Swinney, 1990), a deviation of the end point of the front from a circular trajectory was observed; in this case, the core center was shifted after each revolution. These displacements were due to the finite width of the pulse (Zykov, 1986; Zykov and Morozova, 1990). The initial state in the range of small radii had no time to recover during one revolution, and the front "tried to seek" regions containing fresh mixture (see also Kessler and Kupferman, 1997).

If an active medium is inhomogeneous (e.g., contains inert inclusions), an inhomogeneity may become a core for a rotating spiral. However, the condition $K_0=K_c$ at the core boundary is not fulfilled in this case. Curvature may grow to a higher value K_l, at which front propagation becomes impossible in view of Eq. (67) [more precisely, in view of a nonlinear generalization of this formula (Zykov, 1980), breakdown occurs, at which the velocity $u(K_l)$ is finite]. In numerical studies (Pertsov *et al.*, 1984) of the spiral rotation around an inert core, hysteresis of the rotation frequency as a function of the core radius was found to occur.

Equation (69) was generalized to the case of a curved surface (Brazhnik *et al.*, 1988); a kinematic description of three-dimensional structures was given (Brazhnik *et al.*, 1987); spiral behavior in an anisotropic medium was studied (Davydov and Zykov, 1989), and other problems were studied as well (a recent result is a freakish twist of spirals in a circle and sphere, Zykov *et al.*, 1997). Although the kinematic approach does not permit analysis of the inner structure of the flamon, as a matter of fact all of the studies mentioned in this section assumed the occurrence of a q wave with a recovery zone. As shown in Sec. IV.B, a traveling pulse can also be constructed using a pair of s waves, but one or another type of anisotropy in the medium is necessary. Moreover, the distortion of the plane front does not necessarily have a kinematic origin. In the next section, we shall consider the situation in which the inner flamon structure is essential not only at distances of the order of its width Δx or times $\approx \Delta x/u$. For details on two- and three-dimensional spirals, see, for example, Fife (1985), Meron and Pelce (1988), Keener and Tyson (1991), Winfree (1991), and Goryachev and Kapral (1996, the influence of chaos in the medium); the interaction of spirals has been studied theoretically (Pismen and Nepomnyashchy, 1992) and experimentally (Ruiz-Villarreal *et al.*, 1997).

VI. DIFFUSIVE INSTABILITY

The beginning of studies on diffusive instability is traditionally associated with the work of Turing (1952), who studied stratification of an active medium caused by differences in diffusivities. However, qualitative arguments that provided an understanding of the mechanism of this instability were already suggested by Zel'dovich as early as 1944. In his book (Zel'dovich, 1944) he analyzed the experiments of Kokochashvili (1942) on the combustion of the H_2+Br_2 mixture, lean in hydrogen. Flame propagation was impossible in such a mixture, but luminous spherelike reaction sites were observed. Zel'dovich suggested that this phenomenon occurred because of the fast diffusion of hydrogen to the reaction site, thereby supporting it. Flame propagation in such a mixture is suppressed because of low thermal diffusivity, which is determined by the abundant heavy component (Br). Of course, such a reaction pattern can be established for a limited time only, until Br at the site burns off completely.

In the simplest possible realization of diffusive instability, an active medium is characterized by two diffusion coefficients. Correspondingly, the "reaction rate"—the source in the diffusion equations—is a function of two concentrations. Such a function increases with one of them in a nonlinear fashion and decreases with the other. The first substance is called an "activator" and the second one an "inhibitor." When related to simple exothermic reactions, which are the main focus of attention here, heat is an activator while the reaction product is an inhibitor. Most publications consider the case of fast diffusion of an inhibitor. These include Nicolis and Prigogine, 1977; Tyson and Keener, 1988; Kerner and Osipov, 1991; and Pearson, 1993, among the theoretical studies and Castets *et al.*, 1990; Lengyel and Epstein, 1991; Ouyang and Swinney, 1991; and Lee *et al.*, 1993 among the experimental studies. In this case, the stratification mechanism described above forms all the structures mentioned above: the local spherelike reaction sites, excited domains, dissipative structures, etc. Instability due to the fast diffusion of an inhibitor, resulting in the formation of the corresponding structures in flamons, will be considered in Sec. VI.A. At the same time, there is a specific instability of the flamons when the fast diffusion of an activator occurs. It is easy to understand the relationship between the two kinds of diffusive instability in the example of combustion waves.

Let us discuss the stability of the solution to Eqs. (1)–(4), which describes a combustion wave. The ratio of the diffusivity D to the thermal diffusivity $(\kappa/\rho c)$ is called the Lewis number L_e. This ratio was introduced by Drozdov and Zel'dovich (1943). In accordance with the above consideration, fast diffusion of the inhibitor is characterized by the inequality $L_e>1$. The $L_e>1$ case is that of gaseous mixtures in which some heavy component is abundant. For combustion waves in a condensed medium, $L_e \ll 1$. The study of the instability can be simplified significantly if we take into account (Barenblatt *et al.*, 1962; Zel'dovich *et al.*, 1985) that the source in Eqs. (1) and (2) can be neglected everywhere except for a narrow reaction zone. Now we shall consider the reaction zone as a surface that separates the heating zone and that of the products. When outer solutions are matched across such a surface the inner solution serves as an additional boundary condition. This allows one to obtain the stationary solution in a simple analytical form that in turn leads to relatively simple linearized equations for fluctuations of T and η. If $\sqrt{\kappa\tau_r/\rho c}$ and $\sqrt{\kappa/\rho c\tau_r}$ are used as the scales of length and velocity, respectively [τ_r is the characteristic reaction time at the temperature $T_0+(Q/c)$], then the equations for fluctuations contain two parameters: L_e and the Zel'dovich number Z,

$$Z=(Q/c)(\partial \ln u/\partial T_0), \tag{70}$$

where u is the velocity of the stationary wave. For $u^2 \propto \exp(-\epsilon/T_f)$, we obtain $Z=\epsilon Q(2cT_f^2)^{-1}$.

In their study on the linearized problem, Barenblatt *et al.* (1962) found an instability boundary $L_e(Z)$ located in the region $L_e>1$. Later, independent studies by

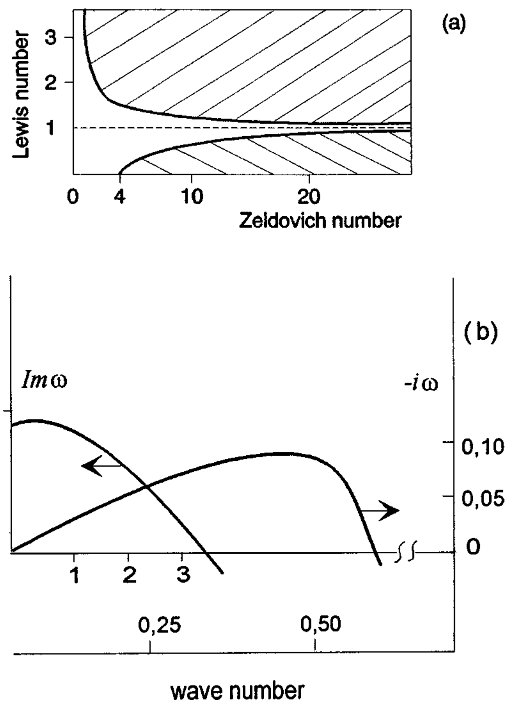


FIG. 13. Stability of the combustion wave: (a) the plane of parameters (Z,L_e); shaded regions are those of aperiodic (positive slope of shading lines) and oscillatory (negative slope of shading lines) instabilities; (b) the growth rate of these instabilities.

Makhviladze and Novozhilov (1971) and Maksimov and Shkadinsky (1971) revealed instability also at $L_e=0$. The latter was foreseen by Lewis and von Elbe (1934). A complete picture was presented in the works of Aldushin and Kasparian (1978, 1979), from which Fig. 13 is taken. There are two instability regions which expand as Z increases, with their boundaries asymptotically approaching the horizontal line $L_e=1$. If the modes of fluctuations are characterized by a complex frequency $\omega(k)$, then $\mathrm{Re}\,\omega=0$ near the instability boundary for $L_e>1$. The growth rate $\mathrm{Im}\,\omega(k)$ is shown in Fig. 13(b). Short-wavelength modes grow rapidly since, for $L_e>1$, protrusions on the front are better supplied with fresh mixture (Zel'dovich, 1944). The increasing dependence of $\mathrm{Im}\,\omega$ on k becomes decreasing only for $k>\sqrt{\rho c/\kappa\tau_r}$, since heat conduction smoothes small-scale fluctuations of temperature. The existence of a well-pronounced maximum in the growth rate $\mathrm{Im}\,\omega$ is typical of systems characterized by fast diffusion of an inhibitor. Although the properties of the new pattern are determined by the instability's nonlinear stage of evolution, the fastest growing mode that corresponds to the maximum determines the scale of the developing dissipative structure. We shall discuss this problem further in Sec. VI.A.

Let us now return to the instability boundary in the region $L_e<1$. When the imaginary part of the frequency $\omega(k)$ passes through zero, its real part remains finite, and the oscillatory modes grow. A pictorial explanation of the evolution of the instability was given by Zel'dovich (1979, 1981). When $L_e<1$, the heating zone is not depleted of fresh fuel. The enthalpy in this zone is greater than that in both the fresh cold substance and the heated products. The reaction wave can run through such a preheated medium at higher velocity. In this case the instability is one-dimensional. The growth rate $\mathrm{Im}\,\omega$ appears to be almost flat for small k [Fig. 13(b)]. It should be noted that Makhviladze and Novozhilov (1971) found a weak maximum in the growth rate. In any case, the dependence of $\mathrm{Im}\,\omega$ on k is weak until $k>\sqrt{\rho c/\kappa\tau_r}$, when it drops due to heat conduction.

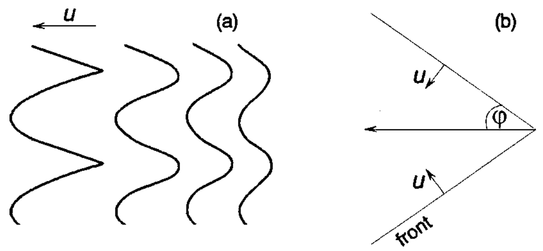


FIG. 14. Why cellular structure forms: (a) nonlinear evolution of the sinusoidal front; (b) vicinity of the corner point on a larger scale.

A. Cellular structure

As we have seen, the growth rate $\mathrm{Im}\,\omega(k)$ has a clearly visible maximum when $Le>1$. For a sample of finite diameter only a discrete set of k values is possible. Consequently there is a parameter region near the instability boundary where $\mathrm{Im}\,\omega>0$ for one such k while all the remaining modes decay. Petersen and Emmons (1961) pointed out a specific kinematic phenomenon that might provide for nonlinear stabilization of the growing mode (see also Zel'dovich, 1966).

We assume that the stationary wave that loses stability is planar. Then the coefficients in the linearized equations for the fluctuations do not depend on the coordinate y along the front. The dependence of the solution on y can be written as

$$\sin(k_m y+\alpha_m), \tag{71}$$

where k_m is the wave number of the growing mode, and the value of α_m is determined, together with k_m, by the boundary conditions. The evolution of a sinusoidal front is shown in Fig. 14. The sine function (71) is distorted due to an increase in the amplitude as well as to displacement of each small interval of the front in the normal direction. Cavities on the front narrow, thereby forming corner points. Such a corner point moves with a velocity of $u/\sin\phi$, where 2ϕ is the angle for which the given point is a vertex. The increased velocity is solely a phase effect—this becomes obvious when comparing to Eq. (61) and Fig. 11.

As the protrusions of the front move more rapidly, the angle ϕ narrows. As a result the difference in velocities of the protrusion and corner point is compensated, and the front moves uniformly but becomes wavy. The scale of the wavy structure is determined by k_m. Assuming that the wave amplitude A is small relative to k_m^{-1},

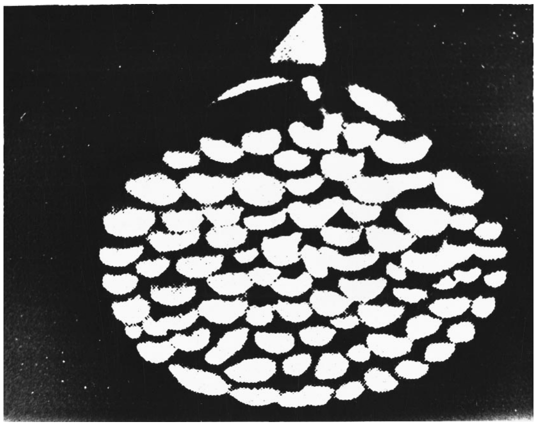


FIG. 15. Cellular flame. The photograph was taken at an angle from below, $p = 414$ torr. Mixture composition: nitrogen, oxygen, and butane; the butane concentration is 1.39 times greater than the stoichiometric value). From Markstein (1949).

we compare the protrusion velocity $\sim A\ \mathrm{Im}\,\omega$ to the correction of the corner-point velocity. Thus we obtain the approximation

$$A \sim \mathrm{Im}\,\omega (uk_m^2)^{-1}. \tag{72}$$

Such a wavy front moves faster than a planar one, the increase in velocity being $\sim u^{-1}(\mathrm{Im}\,\omega/k_m)^2$. Numerical calculations of combustion-wave propagation for $L_e > 1$ (Aldushin, Kasparyan, and Shkadinskii, 1979) are in reasonable agreement with these qualitative arguments. It was found that the maximal temperature is reached at the front protrusions, and curvature maxima are in the cavities (at the corner points). Transition from a planar to a wavy front results in an increase of velocity. The cellular structure was also analyzed by Joulin and Clavin (1979), Matkowsky *et al.* (1980), Sivashinsky (1983), Garbey *et al.* (1989), and other authors. The development of instabilities was studied by Bradley and Harper (1994) and by Bayliss and Matkowsky (1997).

The experiments of Markstein (1949) on cellular flames were known prior to the theoretical results described above. As already mentioned, the first data were obtained as early as 1942 by Kokochashvili. In his experiments Markstein used flammable mixtures of air with heavy hydrocarbons (such as butane, etc.) lean in oxygen relative to stoichiometric composition. As we saw earlier, the deficit of a light component corresponds, to some extent, to the condition $L_e > 1$. The photographs presented by Markstein were used in the well-known book by Lewis and von Elbe (1961). One of them is reproduced in Fig. 15. Brightness reaches its maximum at the center of each cell; the darker boundaries between the cells should be considered as lines composed of the corner points. Equation (67), which was accepted as an explanation of geometric spirals, implies that the convex portions of front move faster than the concave ones. But the effect of the corner points ensures stabilization, as described above. Nevertheless, calculations of nonplanar fronts using Eq. (67) have continued (e.g., Grindrod *et al.*, 1992; Mulholland and Gomatam, 1996).

Since stabilization by the corner points is a purely kinematic phenomenon, it may be expected to hold true not only for diffusive but also for hydrodynamic flame instability. The latter was independently predicted by Landau (1944a) and Darrieus (1944). From a hydrodynamic point of view, one should consider the combustion wave as an interface between cold fresh substance and heated products. Let us consider this interface to be plane and examine distortions due to fluctuations. The dependence $\omega(k)$ for fluctuation modes is found from the linearized hydrodynamic equations as

$$-i\omega(k) = -\frac{kuv}{u+v} \pm \left(\frac{k^2u^2v^2}{(u+v)^2} + k^2uv\frac{v-u}{u+v} \right)^{1/2}, \tag{73}$$

where v is the velocity of products in the reference frame that moves with the combustion wave. The combustion velocity u is related to v by $\rho_0 u = \rho v$, where ρ_0 and ρ are the densities of fresh substance and reaction products, respectively. Since products are heated, the inequality $v > u$ practically always holds. Therefore $\mathrm{Re}\,\omega = 0$, and one of the two values of $\mathrm{Im}\,\omega$ is positive. The plane front is always hydrodynamically unstable. The instability manifests itself by the rapid growth of shortwave modes (with k_m limited by viscosity), so that stabilization occurs as described above. However, the supercriticality in Eq. (73) is not small, and the modes with $k < k_m$ are also growing. According to Zel'dovich (1981), when the mode k_m has stabilized, the role of the long-wave modes increases, short distortions flatten out, and, as a result, only one mode having the smallest k survives in the tube. Therefore the planar front changes into the bulging one. Such a bulge was also found in a different way by Thual *et al.* (1985) for a special case representing an instability of the front expanding in an active medium from the point of excitation (see Gostintsev *et al.*, 1989; Filyand *et al.*, 1994; Kupervasser *et al.*, 1996). The developing front can accelerate. In a closed chamber, the pressure and temperature grow due to the developing front, and this growth sometimes leads to stability (Bychkov and Liberman, 1997).

Thus, for $L_e > 1$, we observe effects similar to those found in other cases of fast diffusion of the inhibitor, e.g., in Castets *et al.* (1990); Ouyang and Swinney (1991); Hagberg and Meron (1994); Schenk *et al.* (1997).

There is a similarity between the equation describing hydrodynamic fluctuation of a smooth flame surface (Sivashinsky, 1977a) and the one describing diffusive fluctuations (Sivashinsky, 1977b). An analogous equation was devised by Kuramoto and Tsuzuki (1976). The Kuramoto-Sivashinsky equation was a favorite of theoreticians, and is now numbered among the often used "model equations." When the perturbation methods or model equations are applied to the problem of instability of the combustion wave, its translation symmetry (see Sec. II.A) is important. The equations (1)–(4) (as well as those considered in Secs. II–IV) have an infinite family of solutions, displaced with respect to each other along the x axis. Due to this feature, the perturbation spectrum for such a solution contains the eigenvalue $\omega = 0$, whose eigenfunction is the derivative of the solution with respect to x (Barenblatt and Zel'dovich, 1957). This so-called "Goldstone mode" is important at weak supercriticality: $\omega(k_m)$ [Fig. 13(b)] is close to zero, and one can expect some coupling between the unstable and translation modes. It may decrease the stability of the wrinkled front (Tribelskii, 1997).

When the parameters L_e and Z are deep in the unstable region, the behavior of the cellular front becomes complicated. The transformation into nonstationary patterns has been studied by numerical simulation (Bayliss and Matkowsky, 1990, 1997; see also Aldushin *et al.*, 1994). The complication was observed experimentally (el-Hamdi *et al.*, 1993). However, in this and subsequent experiments (see, for instance, Gorman *et al.*, 1994) a porous plug burner was used, and rearrangement in cellular structure was reached by variation in flow rate. It is doubtful whether the cells are due to diffusive instability: they may be small torches (see Sec. VII.C and Fig. 26 therein). These regimes are beyond the scope of this article. For more on the porous plug burner see, for example, Buckmaster, 1982; McIntosh, 1985.

B. Fast diffusion of activator

As mentioned above, the oscillatory modes ($\mathrm{Re}\,\omega \neq 0$) with small k increase when $L_e<1$. Since Z is positive, the velocity u grows with T_0 according to Eq. (70), so that we can consider the heating zone as a medium for secondary combustion-wave propagation with a higher velocity and lower width than that of the primary wave. After the heated layer burns off, the process is depressed until a new heated layer forms due to heat conduction and flares up again. Therefore the velocity and other characteristics of the combustion wave are periodic in time.

This behavior does not take into account the breakdown effects that were discussed in Secs. II.B and IV.B. A stationary combustion wave cannot propagate if heat losses exceed a critical value. It seems obvious that the depression stage is particularly sensitive to heat losses. Apparently, in the case of propellants and explosives, when the reaction is accompanied by gasification, the instability causes extinction in most cases. Thermites and other mixtures yielding condensed reaction products are a different matter. Heat stored in these products plays a stabilizing role (Merzhanov, 1981). Stable patterns of nonstationary waves form for a certain range of parameters.

Below we shall consider the case in which combustion instability does not result in extinction, so that heat losses do not change the flamon behavior qualitatively. As mentioned above, a heating zone with excess enthalpy is favorable for propagation of the secondary combustion wave, which is faster and narrower than the primary one. When the secondary wave travels in the same direction as the initial (stationary) wave, as presented schematically in Fig. 16(a), in-phase oscillations occur. The stages in which the heated layer burns down rapidly and the temperature in the reaction zone exceeds the adiabatic value $T_0+(Q/c)$ alternate with stages in which the front stops and a new heated layer forms.

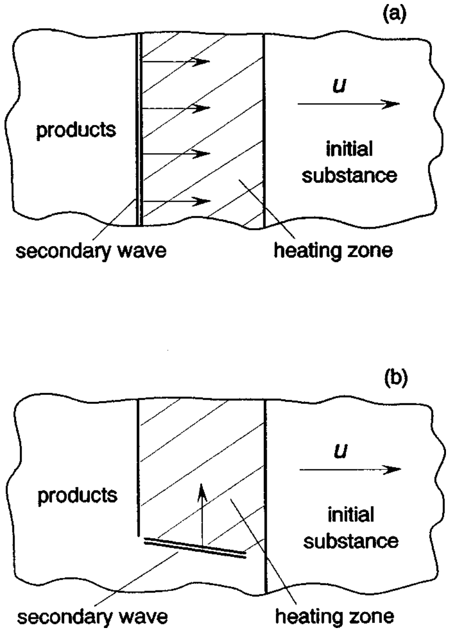


FIG. 16. The secondary waves propagating (a) longitudinally and (b) transversely with respect to the velocity of the main flamon.

The secondary wave can also propagate through the heated zone along the front (Ivleva *et al.*, 1978; Istratov, 1985). The combination of such a motion and slower initial wave propagation can be described in a different manner (Zel'dovich, 1981): the flash-depression interchange allows one to consider the combustion wave as a self-oscillatory system characterized by a certain frequency and amplitude. However, the phases at different sites on the oscillating front are not necessarily identical. Close phase values are maintained only at distances $\sim\sqrt{\tau_r \kappa/\rho c}$ at which heat exchange is possible during the reaction time τ_r. We have already met this quantity—the only parameter that has the dimensionality of length in the reaction-wave problem. More distant front sites cannot affect each other. The phase difference yields inhomogeneous oscillations. The reaction-wave width is relatively small compared to the sample diameter, so from the standpoint of the oscillations it can be compared to a thin plate or membrane. In a frame of reference that moves uniformly with velocity u the membrane is at rest. If the propagation is unstable, the membrane oscillates either homogeneously (in-phase oscillations) or inhomogeneously (like Lissajous figures). Let us consider both cases in turn.

1. In-phase oscillations

Following the discussion concerning Fig. 16(a), let us try to construct a simple mathematical model based on these considerations (Rumanov, 1994). At time t, the combustion wave can be characterized by the instantaneous values of temperature T and width l. Variations in l are due to the difference between the instantaneous velocity $u(T)$ and stationary velocity u_s,

$$\frac{dl}{dt}=u_s-u(T). \tag{74}$$

The temperature T satisfies a thermal balance equation which can be written as

$$\rho c\delta\frac{dT}{dt}=Q\rho u(T)-\kappa\frac{T-T_0}{l}-\kappa\frac{T-T_f}{a}, \tag{75}$$

where δ is the thickness of the layer with an average temperature T and the terms on the right-hand side correspond, respectively, to heat release by the surface chemical source, heat exchange between the fresh substance, of temperature T_0, and the products, of temperature $T_f=T_0+(Q/c)$. Taking into account the exponential dependence of the reaction rate on temperature, we represent u as

$$u(T)=u_s\exp[\epsilon(T_f^{-1}-T^{-1})]. \tag{76}$$

$$l_s=\kappa/\rho c u_s. \tag{77}$$

To solve the equations we consider δ to be constant, $\delta=b\kappa/\rho c u_s$ with $b<1$. The distance a at which the temperature relaxation occurs is also taken to be constant.

We first transform the equations using the new variables

$$\xi=l l_s^{-1}-1,\quad \theta=(T-T_f)(T_f-T_0)^{-1},$$

$$\tau=t\rho c u_s^2\kappa^{-1},$$

so that Eqs. (74) and (75) become

$$\dot{\xi}=1-e^{Z\theta}, \tag{78}$$

$$b\dot{\theta}=e^{Z\theta}-\frac{1+\theta}{1+\xi}-\frac{\theta}{\alpha}, \tag{79}$$

where $\alpha=a\rho c u_s/\kappa$ and the dot denotes the derivative with respect to τ. Linearization of the system of equations (78) and (79) about the stationary point ($\xi=0,\theta=0$) leads to the following expression for the frequency of the critical modes:

$$\omega\approx\pm\sqrt{\frac{Z_c}{b}-\frac{g^2}{4b^2}}+i\frac{g}{2b}, \tag{80}$$

where

$$g=Z-Z_c,\quad Z_c=1+\alpha^{-1}. \tag{81}$$

For $Z>Z_c$, two modes having different signs of $\mathrm{Re}\,\omega$ grow. Such a bifurcation was first investigated by Andronow (1929; see also Andronow and Leontovich-Andronowa, 1939), followed by Hopf (1942).

Instability with frequencies given by Eq. (80) causes a soft excitation of the front oscillations. The oscillation amplitudes for l and T are

$$A_l=\frac{\kappa r_0}{\rho c u_s}Z_c b,\quad A_T=(T_f-T_0)r_0, \tag{82}$$

where

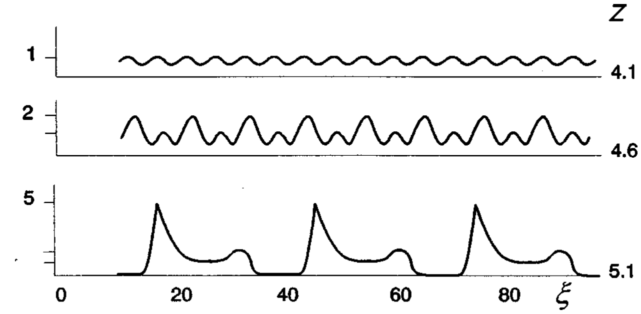


FIG. 17. The oscillations of the front velocity for different Z as calculated by Aldushin *et al.* (1973). The sequence of period doublings can be clearly seen.

$$r_0^2=4g(Z_c^3-2bZ_c^2+4bZ_c)^{-1}. \tag{83}$$

A substance in which the combustion wave can propagate is characterized by $Z\gg 1$. The critical value for propagation was obtained as $Z_c\approx 4$ by Maksimov and Shkadinskii (1971) as well as by Makhviladze and Novozhilov (1971). We now turn to the stabilizing effect of condensed products. Such an effect is provided by the last term in Eq. (75). Without heat exchange between the product and reaction zones, the stationary combustion wave would be unstable for all realistic values of Z. As in the distributed problem, the instability occurs for $Z>Z_c$, and $\mathrm{Re}\,\omega$ decreases with increasing g as we move further into the instability region (see below). Oscillations of the combustion-front velocity with hard initiation were found by Novozhilov (1970, 1973), who generalized the model of propellant combustion suggested by Zel'dovich (1942). As the supercriticality g and consequently the oscillation amplitude increases, the oscillations differ more and more from sinusoidal. For relatively large g, the model considered (with constant α and b) loses even qualitative similarity with the numerical solution to the extended one-dimensional model, which we shall now discuss.

When combustion instability due to fast activator diffusion was discovered, there were simultaneous computations of the transition to in-phase oscillations (Shkadinskii *et al.*, 1971). In subsequent work, Aldushin *et al.* (1973) investigated the evolution of the periodic pattern with increasing Z (see Fig. 17). One can clearly see that not only does the frequency decrease with Z, but also that period doublings occur (see also Bayliss *et al.*, 1989). Analyzing the results of numerical computations, Barenblatt (1971) suggested that such period doublings lead to chaotic front motion. The chaotic motion of fire is of course well known, but is caused by the hydrodynamical turbulence of heat convection. In the case we discuss now, there is no mechanical motion—this mathematical model includes reaction and heat conduction only. Transition to chaos by period doublings was modeled numerically by Bayliss and Matkowsky, 1990; see also Margolis, 1991. During the twenty years that separate the prediction of chaotic behavior in these systems and simulation of this behavior, the remarkable scaling and universality properties of period doublings were discovered (Feigenbaum, 1978, 1979).

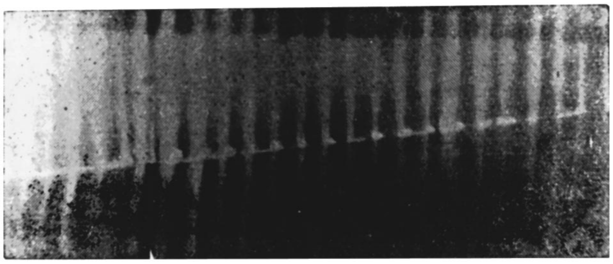
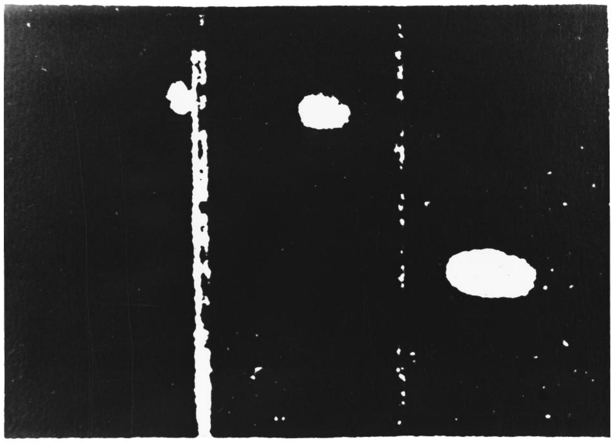


FIG. 18. Experimental evidence for the periodic pattern. The combustion wave traveled in a propellant. From Maksimov (1963).

In experimental studies on combustion of thermites (Belyaev and Komkova, 1950), stopping and starting of front motion was observed. Later, Maksimov (1963) published a photographic record (Fig. 18) clearly showing the periodic front propagation in propellants. A systematic investigation of reaction waves yielding condensed products was then performed, associated with development of a method for self-propagating high-temperature synthesis (Merzhanov and Borovinskaya, 1972). It was found that in-phase oscillations of the front could be observed in a large number of systems diluted by an inert component—usually reaction products (Merzhanov *et al.*, 1973). Dilution with an inert component decreases the combustion temperature T_f and, according to Eq. (70), increases Z. Thus the conclusion that the reaction wave undergoes transition from uniform to periodic motion has been confirmed experimentally. It was also found that the oscillation frequency decreases with increasing dilution by an inert component. Further, the experiments of Shkiro and Nersisyan (1978) can be interpreted as an indication of period doublings.

2. Spinning patterns

As discussed above, in-phase oscillations resulting from the secondary wave propagation [see Fig. 16(a)] came under experimental attention only after theoretical works were published, except for one or two early experimental papers already mentioned. Unlike the case with in-phase oscillations, periodic inhomogeneous patterns, of which the secondary wave shown in Fig. 16(b) is an element, were not predicted theoretically. Motion of a reaction spot along the spiral winding on the surface of a cylindrical sample was the first such pattern observed (Merzhanov *et al.*, 1973). It was called spinning combustion, by analogy to spinning detonation (Campbell and Woodhead, 1926; see also Scelkin and Troshin, 1963). It should be noted that these phenomena are really similar: the arguments illustrated by Fig. 16 can be easily applied to the case of a detonation wave. A secondary detonation wave can propagate through compressed matter heated by shock waves, both in the direction of the main front propagation [see Fig. 16(a)] and in the tangential direction [Fig. 16(b)]. Detonation waves in any medium including a gaseous one are subject to oscillatory instability for the very same reason as deflagration waves in condensed matter.



(a)

(b)

FIG. 19. Spinning waves: (a) movie shots of spinning combustion. From Dvoryankin and Strunina (1991); (b) metallographic specimen of the sample burnt in a spinning pattern. From Maksimov *et al.* (1979).

The motion of a reaction spot has been filmed; some pictures are shown in Fig. 19(a). It can be seen at the polished section of the burnt sample [Fig. 19(b)] that the helix pitch is small compared to the diameter of the sample (Maksimov *et al.*, 1979). Thus the velocity of the luminous spot along the surface should be considerably higher than that of the main front moving along the sample axis, as has indeed been observed. Spin patterns involving two or more reaction sites that move in the same direction are possible (Merzhanov *et al.*, 1973). Transitions from one to two and then to three reaction spots can occur if the diameter of the sample is increased (Maksimov *et al.*, 1981). When the sample in the form of a thin disk was ignited at the center, the reaction site was seen to move along an unwinding spiral, appearing or disappearing for some time on the disk surface (Merzhanov *et al.*, 1982). Figure 20 shows the photograph of the burnt disk, with the reaction spot traces. The spinning combustion of gaseous mixtures with a light inert component (helium), corresponding to the $L_e<1$ situation, was presented by Pearlman and Ronney (1994).

These and other experimental results concerning spinning patterns initiated a number of theoretical studies that we shall discuss now. One cannot observe the processes occurring inside the sample: the only thing we can see is a reaction spot moving along its surface. A spinning pattern was originally found in experiments with

FIG. 20. Photograph of the burnt disk. The front traveled from the center to the periphery. Traces of the reaction spot appear on the surface. From Merzhanov *et al.* (1982).

metallic samples burning in nitrogen, with the reaction occurring in a relatively narrow surface layer (Merzhanov *et al.*, 1973). As a first attempt to investigate this phenomenon, Ivleva *et al.* (1978) carried out a numerical simulation with a two-dimensional model in which the front was a line rather than a surface. They considered propagation of a nonstationary wave in a strip of width d. When d was small enough, only in-phase oscillations occurred. But for $d > (\kappa/\rho c u_s)$, the front developed a wave—protrusions alternating with caverns. Protrusions were characterized by a higher temperature and associated with the reaction sites. If the strip were to be rolled as a cylinder such that periodic boundary conditions $[T(y=0)=T(y=d), T'(y=0)=T'(y=d)]$ were applied at its edges, a given phase, e.g., a protrusion, would move in the laboratory frame of reference in a helical fashion. The length λ of the propagating wave is selected by the obvious condition

$$d = n\lambda/2, \tag{84}$$

where n is an integer. If the supercriticality g is small, the value of λ is bounded from below,

$$\lambda \geqslant (\kappa/\rho c u_s) \tag{85}$$

[see Fig. 13(b)]. Therefore the number of reaction sites can increase if the diameter of the sample is increased. This qualitatively agrees with experimental observations. Recently, even ordering of reaction spots into a lattice was reported (Schenk *et al.*, 1997).

A phenomenological (model) equation for the front $\xi(y)$ in a two-dimensional problem was suggested by Aldushin *et al.* (1980):

$$\ddot{\xi} + |\omega|^2 \xi = 2\,\mathrm{Im}\,\omega \left[\dot{\xi} - \frac{4}{3}(A|\omega|)^{-2}\dot{\xi}^3 + l^2 \frac{\partial^2 \dot{\xi}}{\partial y^2} \right]. \tag{86}$$

Here, ω and A are, respectively, the complex frequency and amplitude of in-phase oscillations at given supercriticality g; $l \sim (\kappa/\rho c u_s)$ is the distance over which heat interaction between the front regions is appreciable; a dot above a letter denotes the derivative with respect to time. Each front region is considered as a nonlinear oscillator similar to Van der Pol's model (1920). Heat conduction along the front assures that the oscillations are in phase over distances $< l$. Simulation of a cylindrical sample is achieved by periodic boundary conditions $\xi(y) = \xi(y+d)$ for the strip. As in the numerical experiment in the strip, for small d there are solutions only in the form of in-phase oscillations. As d increases, waves propagating along the front with one, two, or more protrusions appear. However, such spinlike solutions are not stable—they become stable only when their amplitude, which increases with d, reaches $(1/\sqrt{3})A$.

In the asymptotic limit $g \to 0$, when the periodic patterns are almost sinusoidal, it is possible to calculate the patterns using perturbation methods. A general scheme of such calculations for an extended system was described by Landau (1944b; see also Landau and Lifshitz, 1987). Certainly, perturbation theory is applicable only if the transition from a stationary wave to a periodic pattern is soft, i.e., the amplitude of the pattern is small. This approach was applied (Volpert *et al.*, 1982a, 1982b) to a three-dimensional problem. The complete structure was obtained not just for the perimeter but for the entire front. It was assumed that, for small g, only one mode increases. There were also numerical studies on the three-dimensional problem performed by Scerbak (1983; see also Weber *et al.*, 1997).

Novozhilov (1992a) returned to the two-dimensional model of front propagation along a strip, this time without the requirement of small supercriticality. The heating zone in this study was viewed as a specific kind of flow reactor. This seems rather obvious if we consider the frame of reference attached to the front. Such a one-dimensional reactor was described in Sec. IV.B. Now the role of the parameter β is played by the quantity ul^{-1}, where u is the velocity of the main front and l is the width of the heating zone. As we saw, a traveling pulse can propagate through the reactor. The leading zone of the pulse is a combustion wave, and behind it low temperature is recovered. If we again roll the strip into a cylinder using the periodic boundary conditions $T(y+d) = T(y), \eta(y+d) = \eta(y)$, a periodic pattern with frequency

$$\omega = 2\pi u_1/d \tag{87}$$

forms, where u_1 is the velocity of the traveling pulse. In the laboratory frame of reference there is a hot spot (reaction site) moving along a helix with pitch $2\pi u/\omega$. On the other hand, the same pitch is given by l. Indeed, while the secondary wave completes one turn, thereby burning down the heated layer, the recovery of this layer has to take place [see also Fig. 16(b)]. As we saw, $l \sim \kappa/\rho c u$, so that

$$2\pi \frac{u^2}{\omega} = m \frac{\kappa}{\rho c}, \tag{88}$$

where m is a numerical factor ~ 1. It is interesting that the left-hand side of Eq. (88) contains purely kinematic quantities such as velocity and frequency, while the right-hand side is a material constant (heat diffusivity). For more details, see Novozhiliv (1992b, 1993).

If we regard the heating zone as a flow reactor we have to consider more than the surface of the sample available for visible examination. In other words, the flow reactor we are dealing with is not a circle, but a thin disk. Consequently, in the frame of reference that moves with velocity u, the spinning pattern represents a rotating spiral described by Wiener and Rosenblueth (1946). We discussed its properties in detail in Sec. V. The rotating spirals are clearly seen in the photographs presented by Pearlman and Ronney (1994). They used the gaseous mixture $C_4H_{10}+O_2+He$ to model the $L_e<1$ region, making use of the high heat diffusivity of He and the low diffusivity of C_4H_{10}. The results for gases compared to those for solid samples do not imply that the spinning patterns are due to peculiarities of the solid-state reaction, only that suitable values of L_e and Z are necessary.

The motion of the luminous spot along the surface of the sample (when spinning combustion or spinning detonation take place) is a pure phase wave, formed by spiral front regions subsequently reaching the surface. The measured velocity of the spot u_1 is related to the physical quantity u_0—the spiral front velocity in the normal direction—by Eq. (61) (u_0 is the same for all front regions and equals the traveling pulse velocity in a one-dimensional reactor). In the new notation, $\omega r = u_1$. According to Eq. (66), the rotation frequency ω is $\sim u_0/\Delta x$, while the pulse width $\Delta x \sim u_0/\beta \sim u_0\chi/u^2$, and we again arrive at Eq. (88). The visual dimensions of the hot spot are χ/u along the cylinder axis and $u_1\chi/u^2$ in the perpendicular direction, respectively.

The structure of the spinning combustion wave seems to be clear enough. This is not true with regard to the relation between the spin patterns and in-phase oscillations,[3] which we discuss next.

C. Interaction between periodic patterns

First, we shall consider the possibility of change in patterns due to an increase in Z with fixed sample diameter. As we noted above, Barenblatt (1971) has pointed out the doublings of the period in numerically calculated in-phase oscillations (Shkadinskii *et al.*, 1971). He suggested that, as Z increases, a transition to chaotic propagation of the plane reaction wave occurs. Such a transition occurs as a result of a number of sequential period doublings. Later inhomogeneous periodic patterns, including spinning ones, have been found experimentally (see Sec. VI.B.2). Naturally, the question arises of what transitions occur between patterns in situations that are not artificially constrained to be one dimensional.

FIG. 21. Photograph of a sample burnt in the multiple-point regime. From Strunina *et al.* (1983).

In experiments, an increase in Z is most often achieved by dilution of a fresh mixture, so that temperature T_f decreases. The combustion of a Ti–B mixture diluted with Cu was investigated by Maksimov *et al.* (1981), as was that of Fe–Zr thermite diluted with reaction products, by Strunina *et al.* (1983). These experiments gave the following result: as the concentration of an inert component increases, the in-phase oscillations turn into irregular motion of one or more reaction sites. These reaction spots appear and disappear on the sample surface. They move along the front, either following each other or moving in opposite directions. This type of front motion was named multiple-point combustion (Strunina *et al.*, 1983). A photograph of the sample burnt in the multiple-point combustion regime is shown in Fig. 21. Further dilution of the fresh mixture with an inert component results in the ordering of multiple-point combustion into a spinning pattern.

One can imagine that the loss of stability by in-phase oscillations at some critical value of Z_1 creates a spinning pattern. As long as the difference $Z-Z_1$ is small, the two periodic patterns, having generally speaking incommensurable frequencies, are seemingly superposed. As a result of such superposition, we see a quasiperiodic pattern that can be distinguished from the chaotic one only by special analysis. But as the amplitude of the new (spinning) periodic pattern increases, the linear picture of such superposition is no longer suitable. Frequency locking takes place (see Landau and Lifshitz, 1987, Chap. 30) and the quasiperiodic pattern becomes purely periodic, becoming a spinning pattern.

There is another possible mechanism. First, the in-phase oscillations evolve to a chaotic pattern. This can happen by period doubling or in some other way, but the chaotic pattern thus generated appears to be essentially inhomogeneous. Then the regular spinning pattern arises from chaos. The appearance of regular patterns from chaos is not unusual. One well-known example is the transformation of the Lorenz attractor (Lorenz, 1963) into a limit cycle with an increase of the bifurcation parameter. As we saw with the two possible scenarios for the transition from in-phase oscillations of the combustion front to spinning combustion, there are different interpretations of the experimentally observed site pattern (multiple-point combustion). In one case, it is thought to be quasiperiodic, while in the other it is chaotic. An experiment by Strunin *et al.* (1994) seems to favor the latter interpretation.

In this experiment, the burning of a thermite in the multiple-point regime was videotaped. Using the video

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[3] Besides the rotating spirals, Pearlman and Ronney (1994) observed radial pulsations (see also Maksimov, *et al.*, 1981). It is not excluded that in-phase oscillations are in some sense the traces of radial pulsations at the surface of a burning sample.

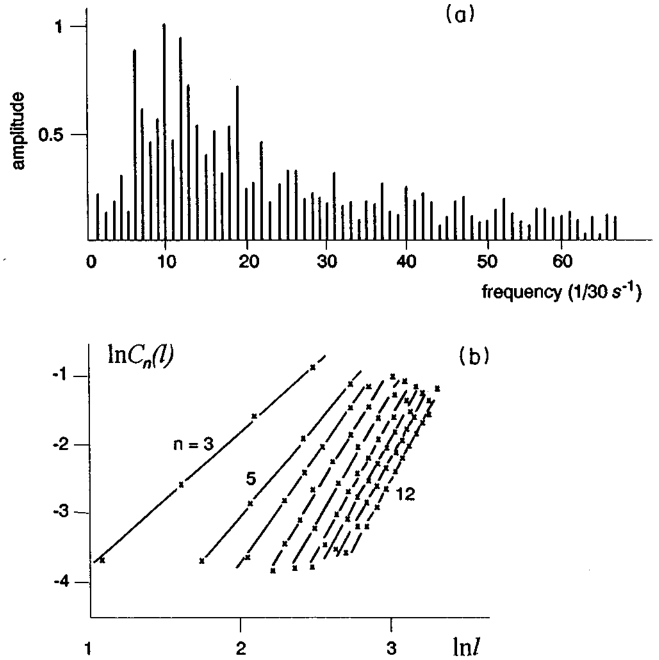

FIG. 22. Chaotic reaction wave: (a) Spectrum of the function $x_0(t)$; (b) plots of the correlation integrals $c_n(l)$ at different n in logarithmic coordinates. From Strunin *et al.* (1994).

film and photographic record, Strunin *et al.* obtained the dependence of $x_0 = x + ut$ on time; here, x is the position of the front at time t on the chosen generatrix of the burning cylindrical sample and u is the average velocity of the front. If the front motion were uniform, $x_0(t)$ would be constant. The discrete spectrum of $x_0(t)$ with two main maxima at main frequencies (for in-phase oscillations and spinning) and their overtones would correspond to a quasiperiodic motion of the front. The spectrum in Fig. 22(a) is of a different kind. It is continuous, which is typical of a chaotic pattern. More precisely, the spectrum consists of peaks that are comparable in height, separated by a distance $\sim t_0^{-1}$, where t_0 is the total burning time of the sample. The upper bound for the frequency is $u^2\chi^{-1}$, where χ is the heat diffusivity. The high-frequency tail is due to measurement errors, etc.

In order to get an idea of the attractor structure that corresponds to a chaotic pattern in the space of states, the correlation properties of the function $x_0(t)$ were studied by the method suggested by Grassberger and Procaccia (1983). In this approach, the sequence $x_k = x_0(k\tau), k = 0,1,\ldots,$ is considered, with the time scale $\tau \sim \chi u^{-2}$. The correlation integral is defined as

$$c_n(l) = 2(N-n)^{-1}(N-n-1)^{-1}\sum_{i,j=n}^{N-n}\theta(l-\Delta_{ij}^n), \qquad (89)$$

where N is the number of points x_k, θ is the Heaviside function, and

$$\Delta_{ij}^n = \left[\sum_{p=1}^{n}(x_{i-n+p}-x_{j-n+p})^2\right]^{1/2}.$$

Graphs $c_n(l)$ for sequential values of n are plotted in the double-logarithmic scale in Fig. 22(b). The value of n, above which the slope of these curves in the limit $l \to 0$ becomes independent of n, is the embedding dimensionality d_e. It is the minimal dimensionality of a smooth manifold in the space of states in which the attractor can be embedded. In the same limit, the value $lc_n^{-1}(l)(dc_n/dl)$ is the correlation dimensionality d_c. It is seen that $d_e = 7, d_c \approx 4.4$. These numbers should be considered together with the dimensionality Γ of the space of states. To estimate Γ, we consider the flamon as a disk (see the end of Sec. VI.B.2). The diameter of the disk is the same as the diameter of the sample d, and its thickness is $\sim \sqrt{\chi\tau}$. Since the inner scale is also $\sqrt{\chi\tau}$, we find

$$\Gamma \sim (ud/\chi)^2.$$

If $\chi = 10^{-2}\,\mathrm{cm^2\,s^{-1}}$, $d = 1$ cm, and $u = 0.1$ cm/s, we have $\Gamma \sim 10^2$. We remark also that the chaotic patterns obtained in the numerical experiment (Bayliss and Matkowsky, 1990; see also Margolis, 1991) are one dimensional and cannot be related to the observed site-combustion pattern. As can be seen in Fig. 13(a), both instability domains are separated only by a narrow strip near L_e exactly equal to 1 for sufficiently large Z. The patterns at weak supercriticality are quite different for $L_e > 1$ (stationary wrinkled) and $L_e < 1$ (oscillating). But the difference gradually diminishes as the supercriticality grows. For instance, the rotating cells of gaseous flame ($L_e > 1$) are somewhat similar to the multihead spin in a burning specimen ($L_e \approx 0$). The chaotic patterns arising from the diffusive instability of flamons can be expected to be, at an "impression" level, independent of L_e. The experimental results of Pearlman and Ronney (1994) and Pearlman (1997), who studied a wide range of gaseous mixtures modeling a variety of L_e values, are in qualitative agreement with these considerations.

VII. MULTIZONALITY

Let us return to the uniformly propagating flamons discussed in Secs. II–IV. We began their study with the simplest combustion waves consisting of two zones, namely, the heating zone and the reaction zone. Then a third, cooling, zone, which arises due to heat losses, was considered (Sec. II.B). The vicinity of a moving interface has a similar three-zone structure (Fig. 5), while the Gunn domain has a more complex structure involving two "interfaces" (see Sec. IV.A). When control parameters are varied, they can take on certain critical values at which a given zonal structure becomes unstable. A new pattern then forms which in a number of cases represents a flamon having a different zonal structure. Both the wave speed and its dependence on the control parameters change qualitatively as a result of this transition. The only way to understand the origin of this change is to study the zonal structure of the flamon. The kinematic approach of Sec. V, where the reaction wave was considered as a moving surface, turns out to be insufficient.

From the mathematical point of view, the problem of a multizonal flamon appears, as a rule, to be hard and awkward. A straightforward numerical simulation not supported by preliminary analysis will hardly lead to success. It is possible sometimes to construct an approximate solution at a qualitative level by a method specific to a given problem. It was found (in each case analyzed) that a complex wave could be divided into several zones according to their "functional properties." The system of equations that describes the flamon can be simplified in a specific way when being considered inside each zone. The similarity between this approach and the boundary-layer idea (Prandtl, 1904; see also Landau and Lifshitz, 1987) that was later developed into the method of matched asymptotic expansions (van Dyke, 1964) can be easily seen. The difference between the two approaches stems from the fact that separation into the outer and inner regions in the "match" method is based on the presence of essentially different scales in the problem, while the presence of different scales is not necessary to identify a zonal structure. As mentioned above, identification of a zonal structure is based on the functional properties of the zones.

A. The controlling zone

Equation (8) for the combustion-wave velocity contains the heat diffusivity in the reaction zone and the reaction time, but there are no parameters for other zones. If the wave contains several zones of heat release rather than one, it is like that the dynamics is controlled by one of these zones. This appears to be the case not only for combustion waves but also for a variety of other q waves.

Reaction waves propagate due to the transport of heat, radicals, or other active particles into the fresh mixture. In case of a multizonal flamon, the sources in its "front" are the objects of such transport from the "rear" sources. Let us, for definiteness, talk now only about heat transfer. The flamon velocity is determined by one controlling zone because, due to heating of the front reaction zones, the processes there adjust themselves to the pace of the controlling zone. The controlling zone cannot be heated by rear zones since in this case it would not be controlling. This argument does not mean that the controlling zone is necessarily a rear one and necessarily has the highest temperature. The point is that if the distance between "front" and "rear" heat sources is large enough, the influence of the latter appears to be negligible. The quantity

$$l=\chi u^{-1}\sim\sqrt{\chi\tau_r} \tag{90}$$

can serve as a scale of distance of influence, where the parameters χ and τ_r are now those of the controlling zone. Hence the distance between the controlling zone and the front edge of the flamon is not more than $\sim l$.

The intensity of the transport processes in the part of the flamon behind the controlling zone is relatively small. The gradients of the temperature, concentrations, and other quantities are correspondingly small. However, the variations of these quantities may be large if the flamon is sufficiently wide. In this case, boundary conditions at $x\rightarrow\infty$ similar to Eq. (4) are not important for calculating the wave velocity. On the other hand, upon identifying the controlling zone, it is possible sometimes to obtain relations of the form

$$f(T,a_1,a_2,\ldots)=0 \tag{91}$$

for temperature, concentrations, etc. at the rear edge of this zone. It is possible to use such relations as boundary conditions for determining the flamon velocity. Combustion waves as well as other q waves whose controlling zone is located at the rear, so that boundary conditions of the form Eq. (4) are important, will be called for brevity "reaction waves of the first kind." Conversely, waves in which the leading zone is followed by a wide region, so that Eq. (91) can be more effectively used as a boundary condition than Eq. (4), will be called "reaction waves of the second kind" (Merzhanov, 1969, 1977). We dealt with the simplest models of the first kind in Secs. II and IV. Now we turn to the waves of the second kind.

B. Combustion waves of the second kind

As typical examples of combustion waves of the second kind, we shall look at a wave in which a phase transition occurs (Aldushin and Merzhanov, 1977) and one in which dissociation of the product accompanies synthesis (Aldushin, 1984).

1. Wave with a phase transition

Here, we consider the situation in which the fresh substance is condensed and the medium remains condensed after both the phase transition and chemical transformation. In this case we can neglect diffusion and set $D=0$ in Eq. (2). Eliminating the reaction rate in Eq. (1) through Eq. (2), we obtain the integral

$$\kappa T'-\rho ucT+Q\rho u\eta=\text{const}=-\rho ucT_0. \tag{92}$$

The value of the constant was found using conditions (3). Equations (92) and (2) yield the "phase" equation (Novozhilov, 1961)

$$\frac{dT}{d\eta}=\frac{(\rho u)^2}{\kappa}[c(T-T_0)-Q\eta](\rho\Phi)^{-1}, \tag{93}$$

which is convenient for analysis of the simplest reaction waves in a condensed medium. Let Φ be $f(\eta)k\exp(-\epsilon/T)$.

Hitherto, the medium was considered a "two-component" one, i.e., consisting of the fresh mixture and product characterized by concentration η. To study purely the effect of the phase transition, we now introduce an inert component of concentration a and assume that this very component undergoes the phase transition. The transition temperature T_s lies in the interval (T_0,T_f), where T_f is the combustion temperature,

$$T_f=T_0+[Q(1-a)-Q_sa]c^{-1}, \tag{94}$$

and Q_s is the transition heat. As previously the specific heat is, for simplicity, assumed to be constant in Eq.

(94). The phase transition of the first order can be described as a δ-function singularity of the specific heat. Then, in the left-hand side of Eq. (92) and, respectively, in the numerator in the right-hand side of Eq. (93), the term

$$-Q_s \rho u a \theta(T-T_s) \tag{95}$$

should be added. Also the factor $1-a$ should be added to the term $Q\rho u \eta$. The Q_s is positive since transition to a high-temperature phase is always accompanied by consumption of heat.

Let the difference $T_f - T_s$ be large enough so that the interface is located in the heating zone, $\eta(T_s)\approx 0$. According to Eqs. (92) and (95), there is a jump in the heat flux across the front of the phase transition. Let us now decrease T_0, so that T_f also decreases and approaches T_s. The $\eta(T_s)$ value starts to grow and the reaction zone is separated into two parts by the interface. We call them the L and H zones. The heat release in the L zone is insufficient for wave propagation with velocity u. Propagation with this velocity is supported by the additional heat flux coming through the interface. This additional heat flux decreases as T_s and T_f get closer. If $\eta_s = \eta(T_s) = \eta_c$,

$$\eta_c = c(T_s - T_0) Q^{-1}(1-a)^{-1}, \tag{96}$$

the heat flux through the interface to the L zone becomes zero. Further decrease in T_0 results in the reconstruction of the flamon. The reaction L zone takes over the leading role. The wave velocity

$$u \approx \left[(\kappa/\rho) \int^{T_s} k e^{-\epsilon/T} dT \right]^{1/2} \times \left(\int_{T_0}^{T_s} [c(T_s - T_0) - Q(1-a)\eta] d\eta \right)^{-1/2} \tag{97}$$

is independent of T_f (a wave of the second kind). The phase transition occurs due to volumetric nucleation rather than nucleation at a moving interface. The phase transition zone (M zone) forms, within which the temperature is constant.

The condition under which a wave with a frontal phase transition transforms into a wave having a temperature plateau, or M zone, has the form

$$\epsilon T_s^{-2}(T_f - T_s) \approx \int_{\eta_c}^{1} (1-\eta) f^{-1} d\eta \times \left[\int_0^{\eta_c} (\eta_c - \eta) f^{-1} d\eta \right]^{-1} < 1. \tag{98}$$

Here, we have restricted ourselves to first-order terms with respect to the small parameter $T_s^2 \epsilon^{-1}$. Since $T_f - T_s$ is small,

$$\eta_c \approx 1 - Q_s a Q^{-1}(1-a)^{-1}. \tag{99}$$

The dependence of the temperature coefficient of the velocity Z, given by Eq. (70), on the initial temperature T_0 is shown in Fig. 23. As long as $T_0 < T_s - Q(1-a)c^{-1}$, the phase transition does not occur, and Z decreases in a typical way $\propto T_0^{-1}$ due to an increase in the combustion temperature T_f. However, further increase in T_0 leaves the temperature T_f constant at $T_f = T_s$, since a part of the reaction heat is spent for the phase transition. The coefficient Z drops to zero abruptly. If $T_0 = T_s - [Q(1-a) - Q_s a]c^{-1}$, the reaction heat is sufficient for the phase transition, and T_f again increases with T_0. This growth leads to the formation of the H zone. However, the M zone does not disappear, the L zone remains controlling, and Z is still zero. As we can see, the interval in T_0, for which this structure of the flamon occurs, is not large. It is determined by Eq. (98). Finally, at $T_0 = T_{0c}$ the leading role shifts to the H zone, and Z is again $\propto T_0^{-1}$. Thus a wave of the second kind with $Z=0$ occurs in the interval of values of T_0 slightly greater than $(Q_s a/c)$.

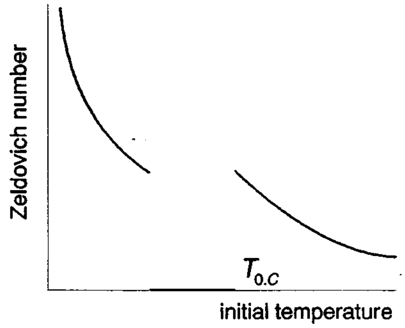

FIG. 23. Changes in the propagation regime for the reaction wave due to a phase transition. The width of the graph portion with $Z=0$ is approximately $Q_s a c^{-1}$.

2. Dissociation of products

Heating of substance in the wave of synthesis can cause thermal dissociation of products, so that transformation of the initial reactants will be incomplete. To better understand this effect, let us consider the dissociation temperature T_d at which the equilibrium between synthesis and dissociation, independent of the depth of conversion η, is instantaneously achieved. If $T_d < T_0 + (Q/c)$, then the depth of conversion in such wave is bounded by

$$\eta_0 = c(T_d - T_0) Q^{-1} \tag{100}$$

(Merzhanov, 1977). If heat losses are taken into account, then it turns out that the maximum value of η is greater than this quantity, and appropriate heat losses can result in complete conversion (Aldushin, 1984). Let us examine the structure of such a wave of the second kind.

The combustion wave studied in Sec. II.B consists of three zones. The heat is transferred from the reaction zone both ahead of it (i.e., to the heating zone) and behind it, i.e., to the cooling zone. In the wave we discuss now, there are certainly heating and cooling zones, and the heat fluxes at the boundaries of these zones are still given by Eq. (12) with the reaction-zone temperature T_m replaced by T_d. But a temperature plateau with $T = T_d$ is located right behind the reaction zone rather than the cooling zone. At each point of this plateau, the heat of synthesis exactly compensates for the heat losses.

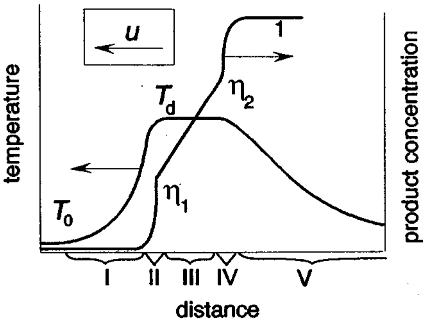

FIG. 24. The structure of a flamon generated by synthesis and dissociation of products, consisting of the heating zone (I), the front reaction zone (II), the zone of displacing equilibrium (III), the rear reaction zone (IV), and the cooling zone (V). From Aldushin (1984).

The zonal structure is shown in Fig. 24. The jump in heat flux at the boundary between the temperature plateau and the cooling zone indicates the presence of the second reaction zone. Complete conversion within the plateau cannot occur: the heat flux from the plateau to the cooling zone, additional to the heat losses, causes a decrease in temperature near the boundary of the cooling zone. Therefore the dissociation stops and the synthesis continues until either $\eta=1$ or it is frozen due to fast cooling,

$$\eta_1=\frac{\eta_0}{1-A},\quad \eta_2=1-\frac{A}{1-A}\eta_0, \tag{101}$$

where

$$A=N(\kappa/\rho c u_0 d)^2. \tag{102}$$

Here u_0 is the flamon velocity in the absence of heat losses, when $\eta_1=\eta_0$. As $A\rightarrow 0$, the width of the plateau increases without bound. At the same time, the structure shown in Fig. 24 assumes $\eta_2\geqslant\eta_1$. Therefore, for

$$A>A_c=\frac{1-\eta_0}{1+\eta_0}, \tag{103}$$

the plateau disappears, the rear reaction zone reaches the front one, and they merge. Now the structure of the combustion wave is that considered in Sec. II.B. As we saw, the decrease T_f^2/ϵ in the maximum temperature caused by heat losses leads to breakdown. If $(T_f-T_d)>T_f^2/\epsilon$, the structure without a plateau is unstable, and Eq. (103) determines the critical conditions for existence of a given flamon, in particular, the critical value of diameter d.

C. Two narrow reaction zones

In Sec. VII.B, we considered combustion waves propagating due to the occurrence of one exothermic reaction, while the processes of heat consumption, such as a phase transition or dissociation, led to splitting of the reaction zone. Khaikin *et al.* (1968) have considered a wave in which sequential transformations occur: first, intermediate products are formed from the fresh mixture, and then the intermediate products participate in the second reaction, yielding final products.

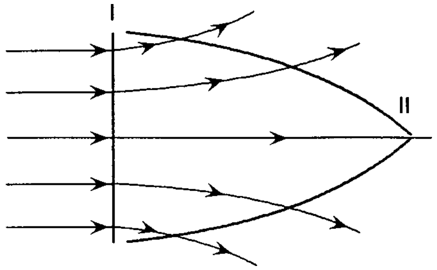

FIG. 25. Two-dimensional flamon structure; the first reaction zone is flat, while the second one forms a torch. The streamlines in the flamon frame are marked with arrows.

There are now two reaction zones; the zone of the second reaction controls the motion of the first one by the heat flux. As the distance l between the zones increases, the temperature T_1 decreases, causing the first reaction zone to slow down, so that the original value of l is recovered. Therefore this flamon structure is stable. However, controlled propagation disappears when the temperatures are such that the heat flux into the first zone vanishes. This zone becomes leading and escapes from the second one. A third kind of behavior is that the two zones fuse.

The regimes of control, escape, and fusion were studied first numerically (Khaikin *et al.*, 1968) and then by asymptotic analysis (Merzhanov, Rumanov, and Khaikin, 1972), the results of which are briefly described above. The phenomenon of escape was studied even earlier (Zaidel and Zel'dovich, 1962; Merzhanov and Filonenko, 1963) in the case of a wave near the plug-flow reactor input.

The wave that escapes has a long "tail" at which self-ignition of the second reaction occurs and, in common with all other flamons discussed in this section, has a one-dimensional structure (which corresponds to combustion of a reactive mixture in a tube). For a different geometry, another structure is possible, as in Fig. 25 (Khaikin, 1969). In this case, the second reaction zone does not necessarily lag behind, due to its larger area. So far, both heats of reaction Q_1 and Q_2 have been assumed to be positive. The controllling zone can clearly be only a zone with positive heat release. When $Q_1<0$, only the regimes of control and fusion can occur. If $Q_2<0$, then there is a region of parameters within which regimes of both fusion and escape are possible. In the escape regime, which is faster than the regime of fusion, the first reaction heats the substance up to temperature $T_0+(Q_1/c)$, after which the substance cools to temperature T_2 (Borovikov *et al.*, 1983; Nekrasov and Timokhin, 1984).

D. Zone of propagation

If the reaction is stronglly inhibited by the product the wide reaction zone forms in the combustion wave (Aldushin *et al.*, 1972). The structure is similar to that of

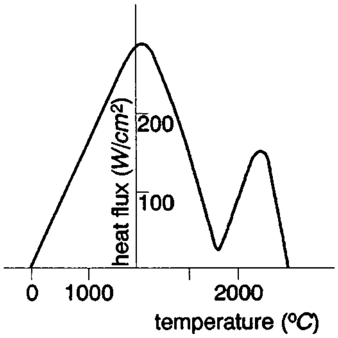

FIG. 26. Temperature dependence of the heat flux for a wave of niobium boride synthesis (Zenin *et al.*, 1980).

escape regime: the zone of propagation (controlling) is placed ahead, then the "tail" follows (burn-off zone). Let us return to the problem of interaction between two flamons. An example of such interaction is the regime of control discussed in Sec. VII.C: the second flamon "pushes" the first one by its heat flux. When transition to the escape regime occurs, the region of the second reaction loses the features of a flamon and hence cannot be considered to have a normal velocity. In case of interaction between two wide reaction zones, the situation is different. The distance between them can exceed the length over which heat from the second reaction zone can influence the first one. The second reaction occurs in the burn-off zone of the first one, fed by its products. Because the second propagation zone may shift along the burn-off zone of the first reaction, an additional parameter l appears, the distance between the propagation zones, which allows the velocities of the zones to be equal—thus a two-wave structure forms.

Such a structure was revealed in studies on the synthesis of niobium boride (Zenin *et al.*, 1981). The heat-flux distribution in this wave is shown in Fig. 26. There is no heating of the first wave by the second one (escape regime). On the other hand, there is a second heating zone (linear growth of the heat flux). According to Zenin *et al.*, first niobium diboride is formed, which, when all boron is consumed, recovers to monoboride (the second reaction). For more details on the zonal structure of combustion waves see Merzhanov and Khaikin (1988).

E. Density jump in the flamon structure

So far we have not considered phenomena related to density change, except for a brief mention of detonation waves in Sec. II.A, the inner structure of the interface in Sec. III, and some remarks concerning the hydrodynamic stability of slow combustion in Sec. VI.A. The phase transition studied in Sec. VII.B.1 was considered only from the point of view of the effect of latent heat on the reaction zone. The most pronounced effects of density change can be expected in the transition of condensed matter to gas. Such a transition occurs in the structure of combustion waves in propellants and explosives since the reaction products are gaseous. Analyzing his experimental data, Belyaev (1940) suggested that the condensed matter first evaporates and then reacts; the heat released in reaction is transferred to the burning surface of sample, thus giving rise to evaporation. Zel'dovich (1942) treated this idea quantitatively and gave a description of the nonstationary processes by using the difference in heat relaxation times between the gas adjacent to the burning surface and that in the heated surface layer of the sample. In subsequent experiments, it was found that a significant part of the heat is liberated in the surface layer of the condensed matter (Pokhil, 1953). This means that a large amount of gas is produced in the surface layer. But the question arises, what is the influence of this gas on the wave structure?

If the condensed layer adjacent to the burning surface is solid and porous, then the gas can leave the solid by percolation through the pores (Khaikin and Merzhanov, 1967). Because of the high temperatures, the surface layer is most likely to be liquid rather than solid. Assuming equilibrium gas release (Maksimov and Merzhanov, 1966), we shall obtain a structure in which almost all the heat is liberated in the region with low density (froth, or a mixture of droplets and gas). This conclusion does not essentially change when dissolution of the gas product in liquid reactants is taken into account (Margolin and Pokhil, 1963), since, in the systems under consideration, the solubility $\eta_0 \ll 1$, provided the pressure is not too high. However, gas release can be considered as equilibrium only if its characteristic time is small compared to the reaction time. If the gas release time is greater than the reaction time (Rumanov and Khaikin, 1982), then the gas produced by the reaction has no time to release, and a supersaturated solution is formed, $\eta > \eta_0$. The $\eta(x)$ profile is nonmonotonic: η grows from 0 to η_s due to the reaction and then falls sharply to η_0 in a distance $\sim D/u$, where D is the diffusivity of gas in liquid and u is the combustion velocity. Such a "diffusion zone" is much narrower than the reaction zone. A structure with a diffusion zone is possible if the products spend less time in the reaction zone than the time of decomposition of a supersaturated solution formed in this zone (for estimation of the decomposition time see, Skripov and Skripov, 1979; Rumanov and Merzhanov, 1996).

The $\eta(x)$ distribution looks like a temperature profile of a substance evaporating under laser heating. The heat is released in a layer of finite width ($\sim \mu^{-1}$, where μ is the absorption coefficient), and there is a heat sink at the surface due to evaporation. The maximum temperature is located at a finite distance from the surface (Anisimov *et al.*, 1980). The flat evaporation surface appears to be unstable. A similar instability is probably inherent to burning surfaces in question. The origin of the instability can be explained in the following way. If a cavity is formed on the burning surface, then the width of the diffusion zone decreases, hence the velocity of propagation of the surface increases, making the cavity deeper. A similar argument explains the growth of a bulge at the surface. As explained in Sec. VI.B, there should be a secondary effect of developing large-scale inhomogeneities. Due to corrugating, the area of the

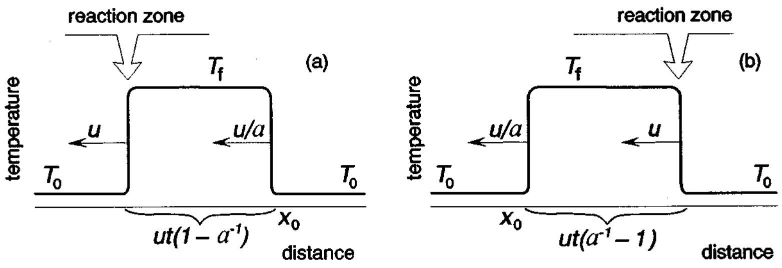

FIG. 27. Heat structure of filtration combustion waves: (a) the reaction zone is followed by a temperature plateau within which all released heat is accumulated; (b) inverse structure: the gas flow carries all the heat into the expanding layer ahead of the reaction zone. From Aldushin and Seplyarskii (1979).

burning surface increases. This accelerates gas removal from the reaction zone and reduces the role of the volumetric gas release that causes the drop in density.

F. Filtration waves

When a flamon propagates through a porous medium, interaction between phases produces a very peculiar zonal structure. One of the first studies in the field was a solution to the adsorption wave problem by Zel'dovich in the late 1930s. The circumstances of that time were such that these results could not be published; they were cited much later by Rachinsky (1964). If the filtration flux v is constant, then the boundary between the "pure" and saturated sorbent regions moves uniformly. Its velocity u is determined by the equality

$$un_0=(v-u)n, \tag{104}$$

where n_0 is the number of particles saturating a unit volume of the porous material and n is the initial concentration in the flow. As the mixture percolates, separation occurs, since the adsorption waves of its components have different velocities (this phenomenon is the basis of chromatography, discovered by Tsvet in 1903). A chemical interaction between a gas flow and a solid porous material leads to a more complex zonal structure and, consequently, to new phenomena, which have been extensively treated, as have experimental (Merzhanov, Borovinskaya and Volodin, 1972) and theoretical (Aldushin *et al.*, 1974) aspects of this interaction. We shall be limited here to considering only one example of gas filtration and one example of liquid filtration.

1. Superheating and inversion

Let us consider the flamon formed in the case of so-called "coflow" filtration, when the gas flows to the reaction zone through a layer of products (Aldushin and Seplyarskii, 1979; see also Aldushin, 1993). We assume the gas velocity v to be prescribed. As we shall see, the temperature distribution in the porous medium depends on the concentration of a reactive component of the gas. Similarly to Eq. (92), one can write down the first integral of the heat conduction equation in the form

$$\chi T'+Qc^{-1}u\eta=[u-\rho\rho_s^{-1}mv(1-m)^{-1}](T-T_0), \tag{105}$$

where χ is the effective heat diffusivity, m is the porosity, i.e., the volume fraction of pores, and ρ is the gas density, and ρ_s is the density of the cast solid (without pores). Here it is assumed for simplicity that specific heats of all the substances are equal, and that the reaction does not change the porosity and density of the solid matrix. The flamon velocity is determined by the obvious relation

$$\rho_s(1-m)u=\rho mva, \tag{106}$$

where the dimensionless coefficient a is determined by reaction stoichiometry and the concentration of reactant in the gas.

Let us first assume that $a>1$. (Since the concentration cannot exceed unity, this inequality means that the stoichiometric ratio of the masses of the reactants, gaseous to solid, is sufficiently large.) The temperature distribution is shown in Fig. 27(a). To the right of the reaction zone, $\eta=1$, so that the temperature

$$T_f=T_0+(Q/c)(1-a^{-1})^{-1} \tag{107}$$

is higher than that of heat-insulated burned substance (superheating). The point is that the incoming gas flux (having initially the temperature T_0) cools the reaction products and transfers heat into the region of the "temperature plateau" [Eq. (107)]. The width of the plateau is evidently $1/(1-a^{-1})$ of the entire burned layer.

If $a<1$, then Eq. (107) does not make sense. In this range of concentrations, the structure of the filtration wave is essentially different. The convective heat transfer is so large that the high-temperature plateau appears ahead of the reaction zone [Fig. 27(b)]. Behind the reaction zone (where $\eta=1$), the temperature is equal to T_0. An inversion of the structure of the combustion wave takes place. The constant in Eq. (105) was taken in accordance with the condition $\eta=0, T=T_0$. In the case of the inverse structure, the condition $\eta=1, T=T_0$ should be used to determine the constant. Then the term $-Qu/c$ arises in the left-hand side of Eq. (105), and the temperature ahead of the reaction zone is

$$T_f=T_0+(Q/c)(a^{-1}-1)^{-1}. \tag{108}$$

In the inverse combustion wave, the temperature decreases rather than increases. Ahead of the wave, there is no chemical conversion in the hot substance, since only an inert component of the gas is delivered there. The active component is completely consumed in the reaction zone. As follows from Eq. (108), filtration through the products allows us to effectively heat the fresh solid even in the case of low heat release in the reaction (e.g., in poor oil strata, etc.) by choosing a (the gas composition). Similarly to the case $a>1$, the width of the hot region here increases with time.

Let t be the time elapsed since the beginning of combustion, so that the width of the burnt layer is ut. Then the width of the plateau in Fig. 27(a) is $ut(1-a^{-1})$, and hence its rear boundary moves at a velocity of u/a. In an inverse wave, the velocity of the front boundary of the plateau with width $ut(a^{-1}-1)$ is also u/a, but now this quantity exceeds the combustion velocity, since inversion corresponds to $a<1$. The boundaries of the plateau are shown as temperature jumps, as they are on the scale of the plateau itself. The inner structure of the boundary containing the reaction zone can vary depending on the parameters of the reaction and composition of the gas. Such phenomena as incomplete conversion or product tempering are possible (Aldushin and Merzhanov, 1987). As to the rear boundary in Fig. 27(a) and the front boundary in Fig. 27(b), their structure is determined by heat conduction. Due to heat conduction, the width of each of these boundaries increases with time and reaches, at time t, a value of the order $(\chi t)^{1/2}$. Since the width of the plateau $\propto t$, the boundaries can be considered to be narrow at practically any time ($t \gg \chi u^{-2}$): this is shown in Fig. 27. The width of the boundary at which the reaction occurs does not depend on time for any a and has a value of $\sim \chi u^{-1}$. The time spent by the substance in such a wave, $\sim(\chi t)^{1/2}u^{-1}$ or χu^{-2}, is large compared to the time of heat exchange between the phases $\rho_s d^2(\rho\chi)^{-1}$, where d is the diameter of grains in the porous medium. The situation is very different in the case of an interphase heat exchange during melting of a porous solid, which is our next topic.

2. Melting of porous material

Let us consider melting occurring due to the heat liberated in the melt. The source of heat may be a reaction that occurs only in the liquid or, say, electric current if the solid phase is an insulator and the liquid is a metal. Melting of a dielectric by high-frequency currents excited in a conducting melt was suggested by Aleksandrov *et al.* (1973). When heating of the solid phase is due to heat conduction, the wave of melting is similar to a combustion wave. The heating zone is located in the solid, and the zone of heat release is in the liquid. But if the initial solid is a porous medium, there is a more effective mechanism for heating of solid grains, namely, by the melt's spreading into the pores (Rumanov, 1982a; Merzhanov and Rumanov, 1987). The spreading is due to the fact that liquid always wets its own solid phase. Using the quantities characterizing spreading, one can form the combination

$$\alpha d/\eta = \chi_{eff}, \tag{109}$$

where α is the surface tension for the liquid, d is the grain or pore size (since these quantities are usually of the same order), and η is the viscosity. The quantity χ_{eff} has the dimensionality of heat diffusivity. For liquid metals, the case we consider now, its value is 10^4-10^5 times greater than that of heat diffusivity.

For definiteness, let us assume that the heat is liberated due to induction currents excited by a high-frequency field in a conducting liquid. The presence of solid grains does not interfere with these currents. Indeed, any two points of the liquid in any plane can be connected by a continuous contour (in fact, in many different ways). Thus the melt spreading through the pores is, at the same time, transporting the heat source. This wave cannot be separated into zones of heat release and heating, as has been done so far for all other flamons, analogs of slow combustion waves. The thermal structure of this wave is two dimensional: in addition to the direction of propagation (direction normal to the macroscopic boundary "charge-melt"), there is a coordinate of microscopic heat exchange along which the heat flux from the liquid is directed to each solid grain.

This flux is due to the usual heat conduction. But the area of the contact surface between the phases increases drastically due to spreading. It is x_1/d times greater than the area of contact in the case of a melt and cast (pore-free) solid, where x_1 is the penetration depth of the melt into the porous material. Correspondingly, the melting rate of the porous material has to be greater than that of the cast material. As was shown in the cited work (Rumanov, 1982a; Merzhanov and Rumanov, 1987), solidification of the liquid occurs at the front edge of the two-phase region rather than melting of the solid. The heat flux into a grain is high at the front edge, and the heat flux to the surface of solid grains from the liquid is insufficient to compensate for the heat spent on heating of these grains, so that the melt begins to freeze on the surface of grains. In the course of heating, the intensity of heat exchange between the phases decreases, and, at some distance from the front edge, the release of Joule heat completely compensates for the heat sink to the solid phase. The direction of phase transition changes—melting begins.

The fraction of liquid in the two-phase melting wave is not a monotonic function of distance x from the spreading front. It has a minimum at a certain $x=x_d$. Since the high-frequency energy is absorbed by the melt only, partial crystallization leads to weakening of the heat source. As a result, stable propagation of the melting wave due to filtration of the melt is possible only if the thermal power F exceeds a certain critical value F_t. At the minimum point $x=x_d$, one can write

$$m_d(m_0-m_d)=\frac{m_0F_t}{4F},$$

$$F_t=\frac{4\kappa_s}{m_0d^2}(T_s-T_0)^2\left(T_s-T_0+\frac{Q}{c}\right)^{-1}, \tag{110}$$

where κ_s is the thermal conductivity of solid, T_s and Q are the temperature and latent heat of melting, and $m_d = (x_d)$. For $F > F_t$, two values of m_d are possible, the smaller one corresponding to an unstable solution. In the regime of stable spreading, there is a certain amount of the "confined" substance that moves together with the wave. The confined substance periodically changes its state: it crystallizes at the front edge of the two-phase region; then, as the front moves, it melts, flows to the front edge, crystallizes, etc. For typical values of the parameters, F_t is very large ($F_t \sim 10^4$ W cm^{-3}), and the wave velocity ($u \sim 10$ cm/s) is much greater than usual for a frontal phase transition. For $F < F_t$, the regime of capillary spreading is unstable, and the melt that penetrates into the pores crystallizes, thus forming a region of continuous solid that separates the porous charge from the melt. This region slowly melts due to heat conduction. When the melt contacts the porous charge again, fast spreading that results in formation of a new frozen region occurs, etc.

The melting front propagation is thus periodic. Its average velocity is determined by the slow stage of melting of the frozen layers,

$$u_c \sim \sqrt{\chi/\tau}, \tag{111}$$

and the period of velocity oscillations is

$$t_c \sim (d/\chi)\sqrt{\chi_{eff}\tau}, \tag{112}$$

where χ is the heat diffusivity of the liquid. As soon as F reaches F_t, the velocity increases discontinuously, while the melt overheating drops. Until now, experimental heating powers have been in the $F < F_t$ regime. The experimental results of Aleksandrov *et al.* (1991) corroborate the oscillatory fashion of front motion. For $F = 10^2$ W cm^{-3} and the above values of other parameters, we obtain $u_c \sim 10^{-2}$ cm s^{-1} and $t_c \sim 10^2$ s.

Let us return to the uniform motion of the wave and consider the "sandwich model": solid plates separated by gaps, i.e., pores. The two-dimensional picture of the flow is shown in Fig. 28(a). The streamlines are drawn not only for the liquid but also for the solid—in the form of straight lines, since, in the frame of reference used, the solid moves as a rigid body at velocity u. Some of these streamlines are closed, so that there is substance that moves periodically: it flows to the front edge of the two-phase region, then freezes, melts, again flows to the front edge, etc. In other words, there is a "confined" portion of the substance that moves together with the wave. The temperature distribution in the liquid has a saddle form [Fig. 28(b)], which is caused by the Joule source and escape of heat to the solid.

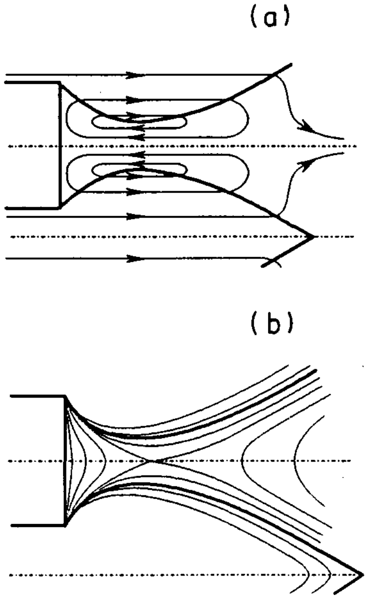

FIG. 28. Structure of the two-phase region for a "sandwich model": (a) streamlines; (b) isotherms. The bold curves correspond to interfaces. The dash-dotted lines are traces of the planes of symmetry. The distance between them equals a half period of the "sandwich" structure $d/2$.

G. Gunn domain in a capillary

A detailed comparison between a moving Gunn domain and phase equilibrium in a system with a given volume was made in Sec. IV.A. Now we turn to fluid-dynamic systems with a negative resistivity. This occurs in liquid flow through a tube when the viscosity of the liquid increases with temperature in some temperature range, as for example with liquid sulfur or liquid helium. Let us set the viscosity $\eta(T)$ to be

$$\eta(T < T_c) = \eta_1, \quad \eta(T > T_c) = \eta_2, \quad \eta_1 < \eta_2. \tag{113}$$

Averaged over the cross section of the tube, the equations for the temperature $T(x)$ of the liquid and its velocity v have the form

$$\rho c \frac{\partial T}{\partial t} = \kappa \frac{\partial^2 T}{\partial x^2} - \rho v c \frac{\partial T}{\partial x} + 12\eta \frac{v^2}{d^2} - \frac{2\alpha}{d}(T - T_0), \tag{114}$$

$$\frac{dP}{dx} = -12\eta \frac{v}{d^2}. \tag{115}$$

Here, ρ is the density, c the specific heat, κ the thermal conductivity, and P the pressure of the liquid. The numerical coefficients correspond to the case of a flat channel of width d and coefficient α of heat transfer to the environment with $T_0 < T_c$. The velocity v is assumed to be small, and the heat processes are assumed to be slow compared to the fluid-dynamic ones. It was also assumed that $\alpha d \ll \kappa$.

The conductance (i.e., the dependence of the velocity v on the decrease in pressure ΔP between the ends of the tube) consists of two rectilinear Poiseuille segments. One of them, given for $0 < \Delta P < P_1$, has the slope $\propto \eta_1^{-1}$, while the other, for $\Delta P > P_2$, has a lower slope $\propto \eta_2^{-1}$, where

$$P_{1,2} = \eta_{1,2} L d^{-3/2} 2\sqrt{6\alpha(T_c - T_0)} \tag{116}$$

and L is the length of the tube. In the case of a continuous function $\eta(T)$—a smoothed curve of Eqs. (113)—an N-shaped characteristic with a descending part within the segment $P_1 < \Delta P < P_2$ is obtained. The descending part is unstable: when ΔP falls in this region, a thermal domain is formed in the tube, i.e., a region heated by dissipation, with $T > T_c$ (Rumanov, 1982b). The domain can be regarded as a viscous cork carried by the flow. The domain boundaries are the s waves that separate the phases with temperatures T_1 and T_2,

$$T_{1,2} = T_0 + 6\eta_{1,2} v^2 (\alpha d)^{-1}. \tag{117}$$

The velocity v is determined by the condition of phase equilibrium

$$T_c - T_1 = T_2 - T_c, \tag{118}$$

which is quite similar to Eqs. (52 and (55). Since, according to Eqs. (117) and (118), v does not depend on pressure, a plateau appears on the characteristic, and it takes the form shown in Fig. 6(b). When the viscous domain leaves the tube through the end, the resistance drops, and the process repeats. The oscillation frequency may be estimated as $\omega \approx v L^{-1}$.

Similarly to Eq. (47), the width of the domain is determined by the lever rule:

$$\Delta P = 12 v d^{-2} [\eta_1 (L - l) + \eta_2 l], \tag{119}$$

while the width of the s waves at the boundaries is $\sim \sqrt{\kappa d/\alpha}$. The structure does not move with respect to the liquid and is carried by the flow.

Different behavior is exhibited by flow of liquid helium in a capillary (Rumanov, 1978, 1982b). When the capillary is placed in a thermostat at temperature T_0 below T_c, the superfluid transition temperature He II, then it will flow like the normal fluid (He I) if the pressure difference satisfies $\Delta P > P_2$. In this case, the temperature T_2 in the capillary will be higher than T_c due to the frictional heating. When $\Delta P < P_2$, the flow of normal He I is unstable, and part of the liquid transforms into He II. The thermal domain in this case is the domain of He I, the width of which is determined by ΔP. In order to find this width and the velocity of the flow, we have to consider the motion of the boundary He I-He II relative to the liquid. Unlike the case of an ordinary, nonsuperfluid liquid, such a motion always occurs. In the He-II phase, far from the boundary, the normal component is considered to be motionless, the pressure to be constant, and the temperature to be equal to T_0. In the region adjacent to the boundary, the temperature rises from T_0 to T_c, and the heat is effectively transferred by the flow of the normal component. Let us call this region the convective zone. Since the velocity is small, the temperature and pressure are related in the convective zone by the equation (London, 1939)

$$dP/dT = \rho s, \tag{120}$$

where s is the specific entropy. Equation (120) together with the entropy transport equation and Eq. (115), allows one to find the profiles of P, T, and velocity of normal motion w. These profiles found for convective zones in He II cannot be immediately matched with the solution for He I at $T = T_c$. This is seen from the fact that the velocity of the normal motion, which is responsible for heat transport, is always directed opposite to the temperature gradient. At the other side of the boundary in He I, the liquid velocity has the opposite direction if the region of He I is located downstream. Thus between the convective zone and the boundary there is a narrow (in temperature range and therefore in space) boundary zone, in which the flow rearranges. It is not necessary to study this zone if we want to determine the velocity of the boundary He I-He II. The reason is that, since the zone is narrow, momentum and heat transfer to the walls of the capillary can be neglected, so that the jumps in the temperature, velocity, and pressure will be determined by conservation laws applied to the quantities at both sides of the zone. The temperature jump on the boundary He I-He II was found by Peshkov (1956). In his experiments, a region of He I arose around a heater in a cm-sized chamber. In this region, strong convective turbulence was observed, and vortices penetrated into He II through the interface. Now we consider a narrow capillary in which vortices cannot form.

Under these conditions the boundary always moves relative to the liquid, with the upstream phase growing (Rumanov, 1978). This result can be understood in the following way. Let us consider a frame of reference connected with the liquid. In the frame moving with the liquid, the capillary walls move in the direction opposite to the flow. If the region of He I is located downstream of the boundary, then the normal component in He II, pulled by the walls, intensely removes heat from the boundary and He I transforms into He II. If the region of He I is located upstream, then the removal of heat from the boundary is impeded, and the inverse phase transition occurs. The difference in the behavior of the left and right boundaries reminds us of the properties of the high-field domain discussed in Sec. IV.A. At the same time, the motion of the normal phase in a superconductor (Volkov and Kogan, 1974) shows complete symmetry between the left and right boundaries of the thermal domain, which do not move.

If the width of the He I region exceeds the heat scale $\sqrt{\alpha^{-1}\kappa d}$, the motion of the left and right boundaries can be considered as independent. Using the asymptotic estimate given by the scheme described above, one can obtain the qualitative dependence of the phase-transition rate at these boundaries on the helium flow velocity v. This is shown in Fig. 29. Solutions exist only for $v > v_m$, where v_m is the minimal flow velocity that admits the existence of the He I region, $T_2(v_m) = T_c$. The velocities of the boundaries are equal at $v = v_D$, where

$$v_D^2 \approx [1 + c(T_0) c_1^{-1}] (\alpha d / 6\eta)(T_c - T_0). \tag{121}$$

Here, c and c_1 are the specific heats of He II and He I, respectively. It is easy to see that this very velocity will be established in a capillary with a domain for a given ΔP. Indeed, if $v < v_D$, then the right boundary moves faster than the left one, the region of He I shortens, the drag decreases, which increases the flow velocity, etc. Since v_D does not depend on ΔP, there should be a

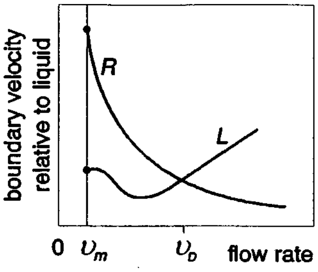

FIG. 29. Phase-transition rate at the left (L) and right (R) boundaries of the He I domain as a function of helium flux through the capillary.

plateau on the characteristic for $0<\Delta P<P_2$. In order for the plateau and oscillations in the flow velocity to be observed, the quantity v_D must be less than the "ordinary" critical velocity of superfluidity destruction occurring due to formation of vortex rings. If $T_0=2$ K, $d=10^{-5}$ cm, and $\alpha=10^{-5}$ W cm^{-1} K^{-1}, the velocity v_D is about 7 cm s^{-1}. As we saw, the flamon has a five-zone structure: there are two convective zones, two boundary zones, and the heat release zone, i.e., the He I region.

VIII. CONCLUSION

In active media a variety of patterns can form and propagate as reaction waves. Systems that exhibit such behavior range from the cells of thermal convection to the rotating spirals in the dish of a reacting chemical mixture. The flamon is the simplest reaction wave, describable on a coarse scale as a surface dividing two uniform semispaces. On a finer scale, the dynamics is governed by individual zonal characteristics, but there are common features. The zone in which an activator is generated and the zone in which the activator is transported forward to excite the transition are always present. Frequently the transport is due to diffusion, though other ways such as shock waves or resonant photons are also possible. Flamons can be divided into types, those which are abe to stand called *s* waves, and those which must propagate through the medium at some minimal velocity, the *q* waves.

The simple flamon is subject to many kinds of instability, depending on the parameters. We have not discussed in detail hydrodynamic instabilities, which give a wrinkled front instead of the plane one. The scale of corresponding cellular structure is determined by the viscosity of the medium. Diffusive instability, which we have discussed in various contexts, can lead to similar cells with a scale determined by the diffusivity. However, the instability associated with diffusion of activators generally causes time-dependent patterns such as pulsating fronts, reaction spots, and spirals moving regularly or in a chaotic manner. These complicated forms can be explained as the nonlinear stabilization of the unstable growing modes predicted by linear theory.

Active research continues on reaction waves and, in particular, flamons. The question of diffusive instability, nonstationarity, and chaotization have attracted much attention. Space limitations have forced us to consider only certain selected problems. Among those left out, there are two large areas: (i) crystallization fronts with dendritic form originating from the diffusive instability; and (ii) waves of ionization. The latter involve propagating discharges such as optical discharges and plasma domains moving along a laser beam (Bunkin *et al.*, 1969; Raizer, 1974, 1980). These can be studied experimentally as a stationary transition in a flowing gas. Then specific relations between the wave and stationary regimes arise, as we discussed in a different context in Sec. II.C. Besides the *q* and *s* waves discussed here there are flamons whose velocity can approach zero but not negative values such as the front of fog clearance by laser (Sukhorukov *et al.*, 1971). An even more peculiar phenomenon is the wave of self-induced transparency (McCall and Halm, 1969; see also Lugovoi and Prokhorov, 1973).

Ideas concerning oscillations and waves infuse physics in its entirety. Flamons have become a common concept in chemical physics, fluid dynamics, solid-state physics, optics, and even astrophysics (see, for example, Zel'dovich and Pikelner, 1969). While the universal characteristic of various oscillations is their spectra, and interactions of modes produce endless variety, the universal characteristic of a flamon is its zonal structure. However, the term "zone" seems to be more intuitive than mathematical. Not much is known about stability and transformation of flamons having a complex zonal structure. This direction of research may offer future promise.

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