

Dynamical and statistical behavior of discrete combustion waves: A theoretical and numerical studyNaine Tarun Bharath,¹ Sergey A. Rashkovskiy,^{2,*} Surya P. Tewari,¹ and Manoj Kumar Gundawar^{1,†}¹*Advanced Centre of Research in High Energy Materials (ACRHEM), University of Hyderabad, Prof C R Rao Road, Gachibowli, Hyderabad, Andhra Pradesh 500046, India*²*Institute for Problems in Mechanics, Russian Academy of Sciences, Vernadskogo Ave., 101/1 Moscow 119526, Russia*

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We present a detailed theoretical and numerical study of combustion waves in a discrete one-dimensional disordered system. The distances between neighboring reaction cells were modeled with a gamma distribution. The results show that the random structure of the microheterogeneous system plays a crucial role in the dynamical and statistical behavior of the system. This is a consequence of the nonlinear interaction of the random structure of the system with the thermal wave. An analysis of the experimental data on the combustion of a gasless system ($\text{Ti} + x\text{Si}$) and a wide range of thermite systems was performed in view of the developed model. We have shown that the burning rate of the powder system sensitively depends on its internal structure. The present model allows for reproducing theoretically the experimental data for a wide range of pyrotechnic mixtures. We show that Arrhenius' macrokinetics at combustion of disperse systems can take place even in the absence of Arrhenius' microkinetics; it can have a purely thermal nature and be related to their heterogeneity and to the existence of threshold temperature. It is also observed that the combustion of disperse systems always occurs in the microheterogeneous mode according to the relay-race mechanism.

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I. INTRODUCTION

A combustion wave represents a self-organized process in which a chemical reaction, localized in a relatively narrow layer (the so-called the reaction front), propagates throughout the reaction media, converting initial reactants into combustion products. Depending on the nature of the reaction media, the process can be either homogeneous, such as in premixed gas flames or the combustion of double-based energetic materials, or heterogeneous, in the case of a medium consisting of several phases. The phenomenon of heterogeneous combustion is observed in a variety of processes including combustion synthesis of materials [1–9], burning of solid propellants [10–14], coals and biomass [15–17], forest fires [18–20], reaction propagation in fluidized beds [21–23], and in clouds of solid particles or spray combustion [24–27]. The simplest heterogeneous systems are the powder mixtures in which a so-called gasless combustion is realized. Gasless combustion waves commonly occur in heterogeneous mixtures of powder reactants such as $\text{Ta} + x\text{C}$, $\text{Ni} + x\text{Al}$, $\text{Ti} + x\text{Si}$, and so on [1–9]. A locally initiated exothermic reaction can propagate through the mixture in the form of a bright glowing combustion front, without notable gasification. The absence of a gaseous flame and solid state of the combustion products allow us to term the process as solid-flame combustion [28]. Self-sustained combustion can be realized within some concentration limits for a given binary mixture. Since the combustion products consist of valued refractory compounds, gasless combustion makes a basis of combustion synthesis technology [1–9,28], the so-called self-propagating high-temperature synthesis (SHS). Therefore, the behavior of the combustion wave at different *concentrations* is of interest not only from the academic point of view, but also for the

practical synthesis of materials and products with a tailored chemical composition. Despite extensive investigations, the mechanisms of reaction propagation in heterogeneous media are not completely understood. The powdered combustible systems are characterized by random (disordered) spatial distribution of different kinds of particles. The structure of heterogeneous condensed mixtures is one of the major factors affecting the combustion wave characteristics as well as the properties of the products. An important role of the sample structure in such processes became especially evident after experimental studies using *in situ* high-resolution microscopic video recording [5–9]. Such microscopic studies have shown that at small time scales the behavior of self-propagating high-temperature reaction waves can become complex [5–9]. High-speed microscopic video recording has revealed [5–9] a microheterogeneous mechanism of steady-state combustion in this system: The combustion front was found to consist of microscopic hot spots caused by flash burning of individual particles in the mixture.

In homogeneous systems, the combustion process, including its stability, is defined by only thermophysical and chemical-kinetic properties of the system. It is well known [29,30] that in homogeneous systems under certain conditions a stationary process of combustion can be replaced by a more complex, oscillating, mode of combustion, and under certain other conditions the combustion becomes impossible. This is connected with the nonlinearity of the system considered, in which instability occurs under certain conditions: The system undergoes a Hopf bifurcation, resulting in a combustion front that moves with a pulsating speed. In homogeneous systems, this instability has a thermal nature. Such a behavior is characterized for a wide class of nonlinear phenomena from physics to life sciences [31]. Under certain conditions, it is associated with the development of complex behaviors such as multiple states, abrupt transitions, periodic or chaotic oscillations, waves, and spatial patterns [32,33]. In the combustion of heterogeneous systems, a propagation of the thermal wave

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is complicated by the heterogeneous structure of the system. This results in micro-oscillations of the combustion wave even at stable stationary modes. As a result, the combustion of microheterogeneous systems is always a random process, in which the nonlinear interaction of the combustion wave with random structure of the system occurs. The extensive investigations in the field of heterogeneous combustion have been carried out in the last decade; however, most of the works were devoted to the experimental investigation of different aspects of the combustion of heterogeneous systems. Only very few reports were devoted to the theoretical analysis of the combustion of heterogeneous systems [34–39] and there were only a few attempts in the literature to take into account the system randomness and its effect on the combustion of heterogeneous systems. A random process of the propagation of the combustion wave in a heterogeneous system, stimulated by the interaction of the combustion wave with a random structure of the system, has, first of all, a fundamental interest since it is the simple example of such kind of processes. Of special interest is the investigation of the influence of variations of the system structure on combustion process. These problems remain uninvestigated till now.

The present work attempts to investigate these problems. In this work, we have studied the dynamical, structural, and statistical properties of the combustion of a one-dimensional disordered heterogeneous system. The use of gamma distribution for the distances between the adjacent cells allows us to study the wide variations in the structure of the system, ranging from clusters to completely disordered systems and further up to regular periodic systems. We consider the model of discrete combustion waves (percolate combustion) [35,38], which has very interesting behavior, similar to the behavior of the combustion of actual heterogeneous systems.

II. MODEL OF THE SYSTEM

A. Discrete combustion waves

The traditional description of solid-phase combustion is based on the heat equation with a source term representing an exothermic reaction [40]. In experimental situations, the reacting sample usually has a cylindrical geometry and in many circumstances the variation of the temperature field along the transversal direction is small and can be ignored. Upon neglecting transversal heat losses, the one-dimensional macroscopic equation can be used for the description of the evolution of the temperature of such a system. A one-dimensional system, consisting of reaction cells (particles), the point heat sources, distributed along an axis x , similar to our earlier reports on the combustion of a system with periodic and uniform random distribution, have been considered here [35,38]. However, in this study, we have introduced a gamma distribution among the distances between the adjacent cells. The medium filling the space between the reaction cells is characterized by thermal conductivity κ , density ρ , and heat capacity c . The cells are considered to be immobile and are characterized by an ignition temperature T_{ign} . When the temperature of an unburnt cell reaches the value T_{ign} , the ignition and instantaneous burning away of the cell occurs with the release of heat Q_i . The model under consideration

simplifies essentially the kinetics of an actual combustion process and reduces it to two parameters: ignition temperature T_{ign} and amount of heat release Q_i . If we consider this model as applied to the gasless combustion of heterogeneous systems [1–9,28], the sense of ignition temperature becomes apparent. The gasless combustion systems represents a mixture of powders, each of which is chemically inert by itself. However, as a result of interaction, they are capable of releasing a large amount of heat, which is enough for self-sustained combustion. The initial particles of the powder components constituting the systems of gasless combustion are in the solid state. In this state they are unable to enter into a chemical reaction with each other because the reaction can proceed only after the mixing of components. Thus, the melting of components is a necessary condition for the beginning of the chemical reaction in such systems. Experimental data [5–9] show that the chemical reaction between the components starts practically immediately after the appearance of the liquid phase in the system and the burn-out time for the active particles is always essentially less (at least on order) than the characteristic time of the heating of the particles from the initial temperature up to ignition temperature. This allows us to consider the process of the burn-out of the active elements (reaction cells) of the system as instantaneous and the instant of reaching of some threshold temperature T_{ign} , at which a liquid phase (e.g., molten materials or eutectic) appears in the system, can be considered as an instant of the ignition of the cells.

The problem under consideration is described by a one-dimensional equation of thermal conductivity with delta sources which has the solution (see [38])

$$\begin{aligned} T(t, x) &= T_{\text{in}} + \sum_{i(t)} \Delta T_i(t - t_i, x - x_i); \quad \Delta T_i(t, x) \\ &= (Q_i / c\rho) \frac{1}{2\sqrt{\pi\kappa t}} \exp\left(-\frac{x^2}{4\kappa t}\right), \end{aligned}$$

where T_{in} is the initial temperature of the system; t_i is the instant of ignition of the i th cell, located at x_i .

For a system of identical heat sources $Q_i = Q_0$. The analysis is conveniently carried out in nondimensional variables [38]

$$t = t(\kappa/l_0^2), \quad x = x/l_0, \quad \theta = \frac{T - T_{\text{in}}}{T_{\text{ad}} - T_{\text{in}}}, \quad \varepsilon = \frac{T_{\text{ign}} - T_{\text{in}}}{T_{\text{ad}} - T_{\text{in}}}, \quad (1)$$

where $T_{\text{ad}} = T_{\text{in}} + \frac{Q_0}{\rho c l_0}$ is the so-called adiabatic temperature or burning temperature of the system; $l_0 = \lim_{N \rightarrow \infty} ((x_N - x_0)/N)$ is the mean distance between neighboring heat sources in the system. In nondimensional variables the governing equation between the ignition temperature and time is given by [35,38]

$$2\sqrt{\pi}\varepsilon = \sum_{i=-\infty}^{k-1} \frac{1}{\sqrt{t_k - t_i}} \exp\left(-\frac{(x_k - x_i)^2}{4(t_k - t_i)}\right). \quad (2)$$

For a given ignition temperature, this relationship enables the finding of the ignition moment of the k th cell, t_k , if all t_i (for $i < k$) are known. In general Eq. (2) has a set of solutions, however, the ignition moment t_k corresponds only to the minimal solution of all such possibilities. Thus,

Eq. (2) allows the calculation of the sequence of the times of ignition of all heat sources in the system, and, by doing so, to determine the dynamics of combustion. We note that the system under consideration is single-parametric: All solutions for this system depend on the system structure and on the single parameter ε , the nondimensional ignition temperature of the sources. Using the solution of Eq. (2) for a specific system, it is possible to find the burning rate both of the system as a whole and in its different parts. For example, a mean burning rate for the section between the cells i and $k > i$ is equal to

$$\omega = (x_k - x_i)/(t_k - t_i). \quad (3)$$

In particular, for a periodic system, consisting of identical hot spots, the steady-state burning rate Eq. (3) will be the same for all i and k , and Eq. (2) becomes [35]

$$\varepsilon = \varepsilon_p(\omega), \quad (4)$$

where we introduced the function

$$\varepsilon_p(\omega) = \frac{\sqrt{\omega}}{2\sqrt{\pi}} \sum_{k=1}^{\infty} \frac{1}{\sqrt{k}} \exp(-\omega k/4). \quad (5)$$

The calculation of the nonsteady burning rate, which always takes place in disordered systems and even in periodic systems at the initial period of combustion immediately after the initiation of the system and also beyond the stability threshold [35], is necessary to solve the nonlinear algebraic equation (2). The exothermic reaction is commonly initiated by heating one end of the cylindrical sample. From a theoretical point of view, this is equivalent to setting the temperature at one of the boundaries, say $x = 0$, to a specific value $T_i > T_{\text{ign}}$, and the rest of the sample at the ambient temperature T_{in} at $t = 0$. To achieve a stable ignition of the sample in our calculations, we considered, as an initial condition, that the 1000 of first heat sources are inflamed compulsorily and consistently with time intervals $\tau = 200$; after that the system was left to itself, and the process developed in accordance with Eq. (2). For a given ε , t_k was varied in small steps until the summation in Eq. (2) reached the values of ε . Basically, once the reaction was initiated, one observed the formation of a heat front that, after a short delay, started to propagate with a constant speed up to the vicinity of the outer boundary $x = L$. However, under some particular circumstances, this “stationary regime” may become unstable. The system under consideration is a nonlinear one and it posses the complex and interesting behavior depending on its structure and ignition temperature ε [35,38].

B. Characterization of system structure

Combustion of the systems with two different structures has been considered in [35,38]: (i) with periodic spacing of the reaction cells and (ii) with random uniform distribution of the reaction cells along the axis x . At the same time, the analysis of experimental data [9] shows, that the structure of the actual system changes with a change in the concentrations of powder components; this results in changing in the burning rate of the system even if all other the parameters remain constant (e.g., at the constant burning temperature). For this reason it is interesting to investigate the model system with wide variations in structure which allows studying the effect of system structure on its combustion.

A one-dimensional system in which the distances L between neighboring reaction cells are random ones adhering to the gamma distribution which is an extension for Eq. (12) in [38]

$$p(L) = \frac{a^a}{\Gamma(a)} L^{a-1} \exp(-aL), \quad (6)$$

where a is a shaping parameter has been considered in this study. The case $a = 1$ corresponds to the random uniform distribution of the cells in the system considered in [38]. The mean distance between cells is always equal to unity in nondimensional variables. The presence of an additional parameter a in the distribution Eq. (6) allows varying the system structure in the wide ranges and investigating the effect of the structure on the propagation of the combustion wave. Probability density for gamma distribution, calculated by using the expression Eq. (6) and obtained numerically by the Monte Carlo method, are shown in Fig. 1. One of the most important characteristics of random structure is a pair distribution function $g(r)$, which is defined for the one-dimensional system as follows

$$g(r) = \frac{N(r, dr)}{2\langle n \rangle dr}, \quad (7)$$

where $N(r, dr)$ is the number of reaction cells on the segment $[r, r + dr]$, located on the distance r from a given cell, averaged throughout the cells of the system; $\langle n \rangle$ is the mean density of the reaction cells on the axis x , in nondimensional variables $\langle n \rangle = 1$. The pair distribution function (7) is shown in Fig. 2, calculated for different values of shaping parameter a .

From Figs. 1 and 2 it can be seen that the formation of long-range order in the system occurs with an increase in parameter a in the range $a > 1$ and at $a = \infty$ the system becomes a periodic one. On the contrary, the probability of very closely spaced reaction cells increases for $a < 1$. We can say that the clusterization of the reaction cells occurs in the system for $a < 1$: The cells are collected in dense groups (clusters). The distance between cells in the cluster can be very small ($r \ll 1$), resulting in the practically simultaneous ignition of all cells in the cluster. This means that the cluster can participate in combustion as a unified reaction cell with a bigger heat release, which is equal to the sum of heat released by all elementary reaction cells incorporated into the cluster. It is necessary to note that the number of elementary reaction cells in the cluster will be random and the total heat release is quantized: $Q_0 n$, where Q_0 is the heat release of single elementary reaction cell, $n = 1, 2, \dots$, is the random integer, equal to the number of elementary reaction cells incorporated in the cluster. Thus, the system with a gamma distribution of distances between neighboring reaction cells (6) allows modeling the systems with wide-range variations in its structure: From clusters ($a < 1$) to completely disordered ($a = 1$) and further up to regular periodic systems ($a = \infty$).

III. BURNING FRONT PROPAGATION

A. Results of simulation

Propagation diagrams of a discrete burning front, obtained by the solution of Eq. (2) for different values of shaping parameter a and different ignition temperatures ε , are shown

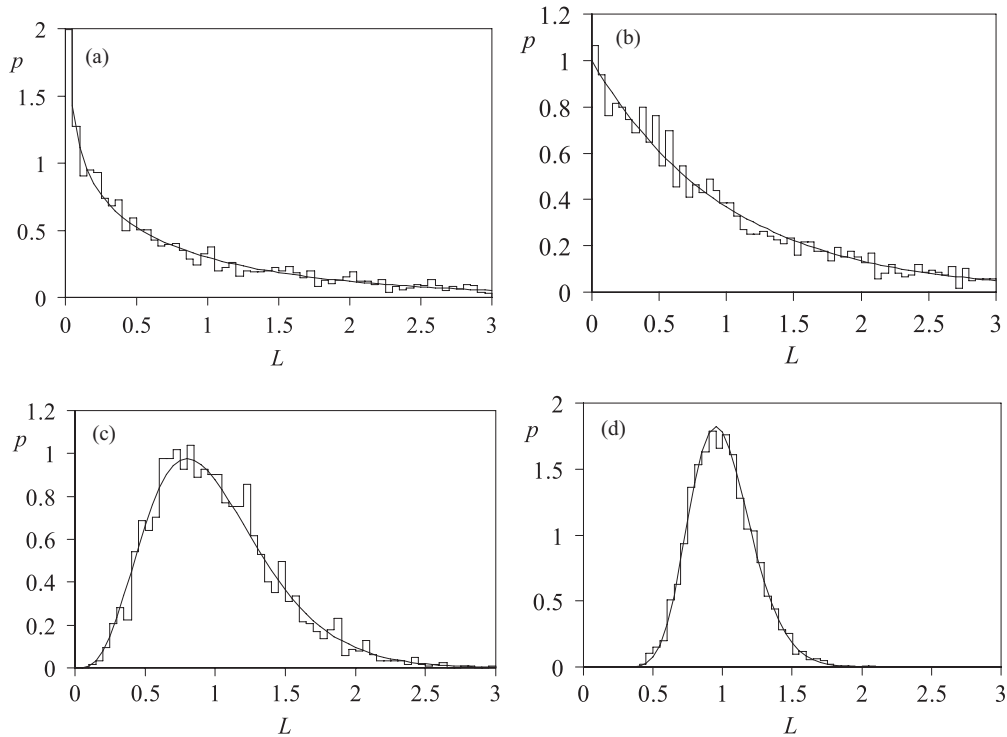


FIG. 1. Distribution of the distances between neighboring hot spots. The polygonal lines are the histogram of specific realization, smooth lines are theoretical probability density Eq. (6). (a) $a = 0.7$; (b) $a = 1$; (c) $a = 5$; (d) $a = 20$.

in Fig. 3. All lines in Fig. 3 for single parameter a , but for different values ε , correspond to the same realization of the random structure of the system. A comparison of the data in Fig. 3 with the experimental data [5–9] on the combustion of powder gasless mixtures shows their similarity. Combustion occurs in the form of consequent jumps: Relatively long periods of front stopping (induction periods) are followed by the fast burning-out of some part of the sample with a practically constant burning rate, and followed by a new induction period again. The duration of induction periods and periods of “continuous” combustion are random and it is connected with the random structure of the system [5–9]. In experiments [9], the change of mixture parameters and in concentrations of powder components (e.g., a changing in stoichiometric coefficient x in mixture $\text{Ti} + x\text{Si}$) results in either the regularization or stochastization of the combustion process. The former resulting from the fluctuations of the duration of the induction periods decrease and the process becomes more stable, and the latter when combustion becomes more a random one with long and random induction periods. A similar behavior of the burning front is observed in the model under consideration. It follows from Fig. 3 that a stability of the combustion process decreases with a decrease in parameter a : the lesser the parameter a the more pronounced a discrete and random nature of the process. For the same values of parameter a , the process is more regular at smaller ε ; the more ε the more random is the process, the stronger effect of the fluctuation of the random structure of the system on the burning front propagation. Calculations show that for $\varepsilon > 0.45$ it is impossible to have a stable combustion process for any initial conditions: The system is extinguished after burning-out

of some number of reaction cells. Theoretically, this appears as follows: Due to the system’s random structure there are always neighboring pairs of reaction cells with an extremely long distance between them. The induction period for these pairs is also extremely long. The ignition delay time increases with an increase in nondimensional ignition temperature ε for all pairs of reaction cells but more rapidly for pairs with long distances. This is clearly seen in Fig. 3 [especially in Figs. 3(a) and 3(b)]. At $\varepsilon \sim 0.45$ the induction period for one of the pairs of hot spots having a long distance becomes so much bigger that the temperature field in the system has enough time to level off due to thermal conductivity. As a result, the temperature of the next unburned hot spot does not reach the ignition temperature and its ignition does not occur. This immediately results in the stopping of the combustion of the system as a whole.

The theory of inflammability limits was developed by Zel’dovich [42] and Spalding [43] for the steady propagation of flat premixed gas flames. According to this theory, an inflammability limit is a direct result of heat losses. Roughly speaking, the propagation of the combustion wave becomes impossible when the rate of heat losses into an ambient environment grows faster than the rate of heat release from an exothermic combustion reaction. The dilution of the initial mixture with an inert compound as well as the deviation from the optimal (Stoichiometric) ratio decreases the heat release, therefore, an inflammability limit can be reached in this way. This approach does not look so evident in the case when heat losses from the sample surface are negligible compared to heat release inside the sample (e.g., in the case of large samples). The classical theory suggests that, in the latter case, the inflammability limit is determined by radiative heat losses [44].

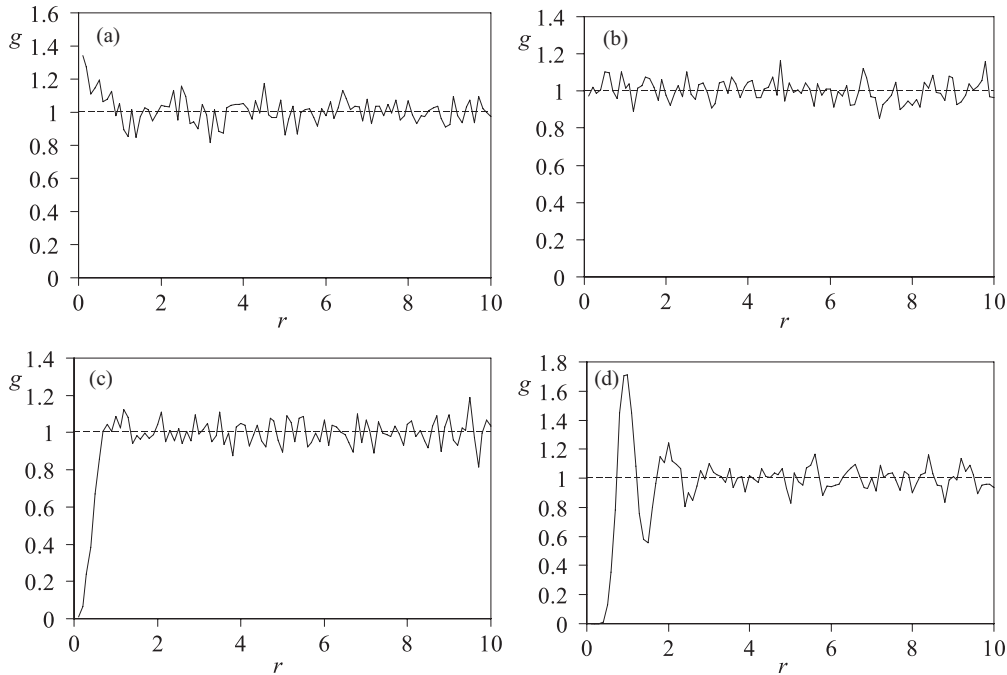


FIG. 2. Pair distribution function for cells in the system for different values of the shaping parameter. (a) $a = 0.7$; (b) $a = 1$; (c) $a = 5$; (d) $a = 20$.

This cannot be directly applied to gasless mixtures because they are opaque and, therefore, radiation cannot escape from the inner regions of the sample. The model under consideration shows that the inflammability limit can be reached due to a changing of the kinetic parameters of the system (e.g., the ignition temperature) even at the absence of heat losses. The analysis of Fig. 3 shows that a decrease in the nondimensional ignition temperature of hot spots ε and an increase in shaping parameter a results in the regularization of the combustion process. On the contrary, an increase in nondimensional ignition temperature ε and a decrease in shaping parameter a results in the stochastization of the combustion process with strong induction periods corresponding to the horizontal segments in Fig. 3. Because the combustion of the system under consideration represents the sequence of ignition of discrete hot spots, the burning rate is actually determined by the sum of ignition delay periods between neighboring hot spots. Therefore it is of interest to analyze a correlation of the ignition delay time between neighboring hot spots and the distances between them. From the definition of the nondimensional steady-state burning rate for a periodic system we can write

$$\tau = \omega_p^{-1} L^2, \tag{8}$$

where τ is the time interval between the ignition of neighboring sources; L is the nondimensional distance between neighboring sources; $\omega_p(\varepsilon)$ is the nondimensional burning rate for a periodic system with unit distances between neighboring sources [35,38]. Figure 4 shows the correlations between τ and L , obtained in calculations of the combustion of disordered system with gamma distribution (6) for different values of shaping parameters a and nondimensional ignition temperature ε .

A treatment of the results of calculations (Fig. 4) shows that the upper and lower boundaries of the interval of tolerance can

be described by the expression

$$\tau = b^\pm(\varepsilon, a) L^m, \tag{9}$$

where $m(\varepsilon, a)$ and $b^\pm(\varepsilon, a)$ are the parameters which depend on ε and a ; parameters $b^\pm(\varepsilon, a)$ characterize the upper and lower boundaries of the interval of tolerance. As mentioned above, for $a \rightarrow \infty$ the system under consideration turns into a periodic system for which, in accordance with Eq. (8), $m = 2$. The correlation analysis of the results of the numerical calculations of Eq. (2) for the system under consideration in a wide-range of parameters $a \in [0.7 \dots 20]$ and $\varepsilon \leq 0.45$ results in the following expression for the power $m(\varepsilon, a)$:

$$m = 2 + 0.2 \exp(3.18\varepsilon^{0.66} + (0.1 + 0.029 \ln \varepsilon)a - (0.0012 + 0.003\varepsilon)a^2) \tag{10}$$

having the correct limit $m \rightarrow 2$ as $a \rightarrow \infty$ and for $\varepsilon \rightarrow 0$. Let us note that in the limiting range $a \in [0.7 \dots 20]$ one can use the more simple expression

$$m = 2.2 - 0.01a + 2.23a^{0.27}\varepsilon \tag{11}$$

which has the same degree of accuracy but has not the correct limit $m \rightarrow 2$ at $a \rightarrow \infty$ and $\varepsilon \rightarrow 0$. The calculations show (Fig. 4) that a line

$$\tau = \varphi \omega_p^{-1} L^m \tag{12}$$

can be used for the fitting of the correlation under consideration, where φ is the fitting parameter of the order of unit.

B. Theoretical considerations

In this section a theoretical dependence of burn rates normalized to burn rates of a periodic is obtained and compared with numerical results. As it is shown in the Appendix a

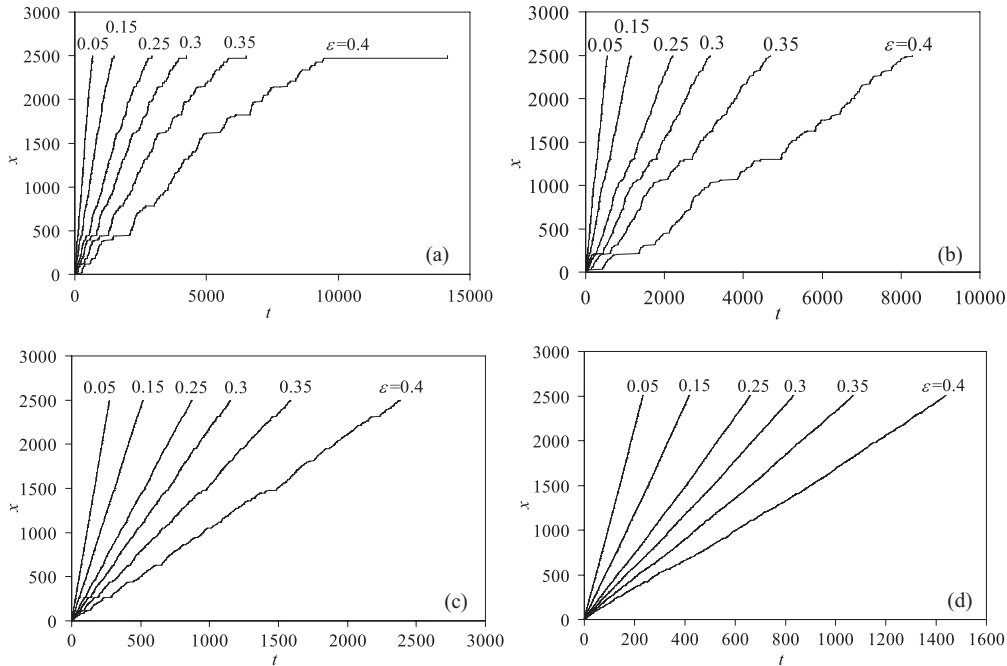


FIG. 3. Numerical propagation diagrams of discrete burning front for different ignition temperatures ε . The ignition temperatures are indicated over each line. (a) $a = 0.7$; (b) $a = 1$; (c) $a = 5$; (d) $a = 20$.

mean burning rate of a disordered system is described by the expression

$$\omega_r/\omega_p = \frac{1}{\varphi} a^m \frac{\Gamma(a)}{\Gamma(a+m)}. \quad (13)$$

In the limit $a \rightarrow \infty$ the system becomes periodic; this means that $\omega_r \rightarrow \omega_p(\varepsilon)$, moreover in accordance with Eqs. (8) and (9) $m \rightarrow 2$ in this limit. Taking into account this result we obtain $\lim_{a \rightarrow \infty} \frac{a^m \Gamma(a)}{\Gamma(a+m)} = 1$; thus one concludes that $\varphi \rightarrow 1$ in this limit. Figure 5 shows both the burning rates, obtained by direct numerical solution of Eq. (2) and the theoretical dependencies, calculated by using Eqs. (13) and (10) with $\varphi = 1$. It can be observed that theoretical dependence Eqs. (13) and (10) with $\varphi = 1$ correctly describes the results of direct numerical simulations in the whole range of parameters a and ε . For this reason, the dependence Eq. (12) with the condition $\varphi = 1$ will be used in further analysis of the combustion process in the system under consideration. Equation (13) generalizes

the results [38] on the case of the arbitrary value of shaping parameter a . In particular,

$$\lim_{\varepsilon \rightarrow 0} \{\omega_r(\varepsilon, a)/\omega_p(\varepsilon)\} = \frac{a}{a+1}. \quad (14)$$

Thus, the burning rate of a disordered system is always less than a burning rate of the periodic system with the same adiabatic burning temperature and the same ignition temperature T_{ign} .

The mathematical models with periodic structures are used very often for the simulation of the real heterogeneous systems [8,34,35]; In doing so, the periodic models have the same average characteristics as those for the real systems. It is usually assumed that the mean burning rate obtained in simulations of such a periodic model should be equal to a mean burning rate of a real disordered system. The results above show that this is not the case: A real system (e.g., aerosol, SHS-system, composite solid propellant, etc.), which

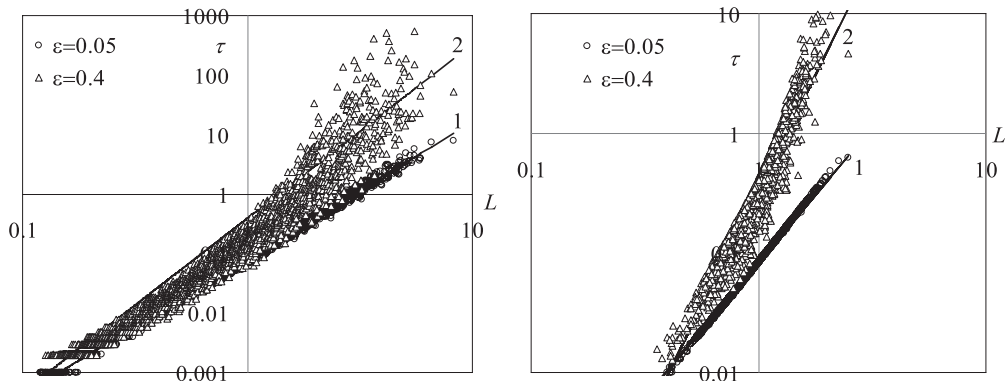


FIG. 4. Correlation of time between ignition of neighbor heat sources and distance between them for $a = 1$ (left) and $a = 15$ (right). Dots are results of numerical solution of Eq. (2), solid lines are correlation Eqs. (10) and (12) for $\varphi = 1$: line 1, $\varepsilon = 0.05$; line 2, $\varepsilon = 0.4$.

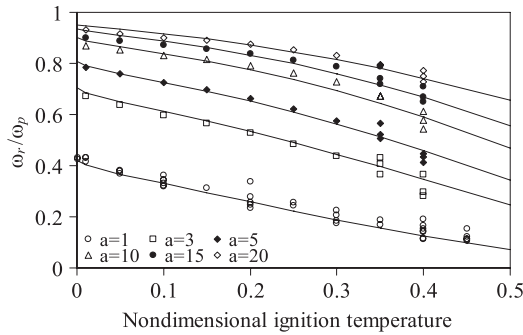


FIG. 5. Dependence of burning rate on ignition temperature ε for different values of shaping parameter a . Markers are the results of direct numerical solution of Eq. (2); lines are the theoretical expression Eqs. (13) and (10) with $\varphi = 1$.

has a disordered structure, cannot be substituted by a periodic system in simulations because their burning rate can differ by many times.

C. Self-similarity in burning front propagation

An analysis of the dependencies of the ignition time of hot spots on their coordinates $t(x)$ for the same random realization of the system structure but for different ε (Fig. 3) shows that they share a number of traits with each other. It is seen from Fig. 3 that the same features of function $t(x)$ present in dependencies $t(x)$ for all ε : At the same points x on all curves there are the similar heterogeneity; they differ by only a scale, which increases with ε . Thus, dependencies $t(x)$, corresponding to different ε , reproduce the same features of combustion wave propagation, reflecting the peculiarities in the internal structure of the system. The scale of these peculiarities on the curves $t(x)$ is different for different ε : The less the ε the less manifestation of the system structure in the process of the propagation of the combustion wave and, on the contrary, the more the ε the stronger the manifestation of the peculiarities of the system structure in combustion. This is a result of the nonlinearity of the system, which amplifies the fluctuations of the combustion process induced by the random structure of the system. For an analysis of these features, the dependencies $t(x)$ were processed in coordinates

$$\eta(x_i) = \frac{1}{A} (t(x_i) - (x_i + x_0)/\omega_r),$$

where ω_r is the burning rate of the system at a given (ε, a) ; parameters $A(\varepsilon)$ and $x_0(\varepsilon)$ were selected to give the best match of dependencies $\eta(x)$ at all ε for a given structure of the system. The results of such calculations for $a = 1$ are shown in Fig. 6. Similar dependencies $\eta(x)$ take place also for other values of parameter a . It can be seen that in the whole range of ε an almost identical dependence $\eta(x)$ is obtained, the differences exist only in fine details. The deviation from unified dependence in the initial period is connected, apparently, with the transient process, however, one can see even in this period all the dependencies $\eta(x)$ have the same features and repeat each other. Thus, one can say that the propagation of a combustion front over a given system of hot spots is described

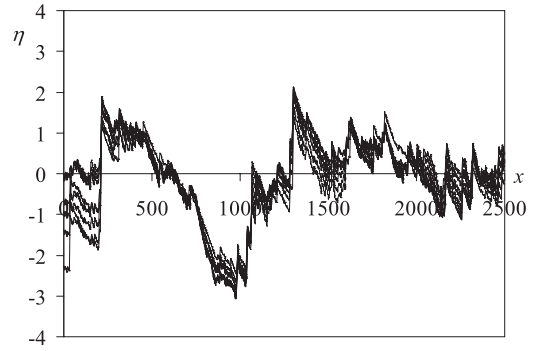


FIG. 6. Dependencies $\eta(x)$ for $a = 1$ and $\varepsilon = 0.05, \dots, 0.4$ with step 0.05.

by the unified dependence for all ε

$$t(x_i) = (x_i + x_0)/\omega_r + A\eta(x_i), \tag{15}$$

reproducing all the main features in the behavior of the combustion front; in doing so the function $\eta(x)$ does not depend on ε and it is determined only by the system structure, i.e., by the distribution of reaction cells in the system. This means that function $\eta(x)$ is different for different random realizations of the system structure. This allows one to say that the propagation of the combustion front in a one-dimensional system with a random distribution of hot spots is self-similar and function $\eta(x)$ is some structure function which characterizes mainly the structure of the system and weakly depends on its kinetic characteristics, in particular on ε . This means that function $\eta(x)$ will be the same both at relatively large values of ε and at $\varepsilon \ll 1$.

IV. STATISTICAL PROPERTIES OF COMBUSTION

A. Standard deviation of burning time

This section illustrates the relation between the relative standard deviation of the burning rate with the relative standard deviation of the burning time of a sample. Experimental data on combustion of powder mixtures [5–9] show that the process of the propagation of a discrete combustion wave in actual systems is random and it is accompanied with the essential fluctuations of both instantaneous and local parameters of the combustion wave and burning rate of the system as a whole. The results of modeling confirm these facts (Figs. 3 and 4). Fluctuations observed in the calculations are connected with both the random structure of the system and nonlinearity of the system as a whole: the nonlinearity of the system in combination with its random structure at certain conditions can amplify a nonuniformity of the combustion process up to its total termination. These results in the dependence of the parameters of a combustion wave (primarily the burning rate of the system) on a specific realization of the random structure of the system and have the essential fluctuation from experiment to experiment.

As it is shown in the Appendix a relative standard deviation of the system’s burning time is described by the expression

$$\frac{\sigma_t}{\langle t_N \rangle} = \frac{1}{\sqrt{N}} \sqrt{\frac{\Gamma(a)\Gamma(a + 2m)}{\Gamma^2(a + m)} - 1}, \tag{16}$$

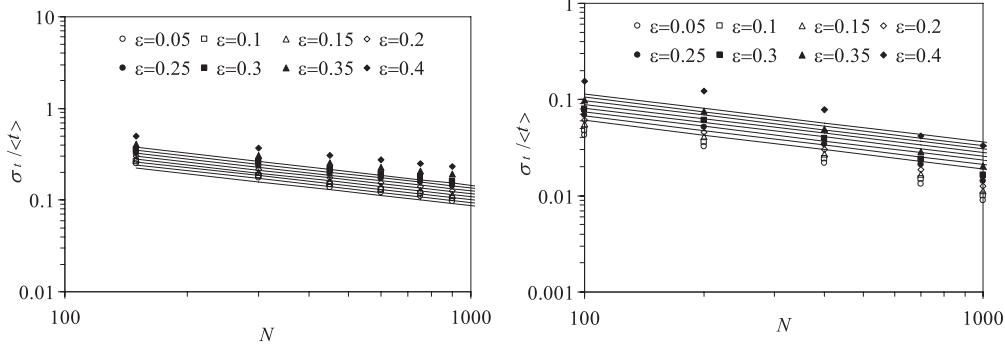


FIG. 7. Dependence of relative standard deviation of burning time on number of particles for different ignition temperatures ε . $a = 1$ (left), $a = 15$ (right). Markers are direct calculations; lines are theoretical dependence (16).

where the parameter m is determined by the correlation Eq. (10). Figure 7 shows the calculated dependencies of the relative standard deviation on the number of hot spots in the system for different values of ignition temperature ε for $a = 1$ and $a = 15$. The markers in Fig. 7 indicate the results of direct calculations using the dependences $x(t)$ obtained by a solution of the Eq. (2). In the later case, the time of burn-out of different segments with N hot spots for the same sample were analyzed. These segments were considered as separate samples (different realizations of the random structure), consisting of N hot spots. Such an analysis was carried out for different random realizations of the system for the same value of parameter a , in so doing the parameter a was varied in the range $[0.7, \dots, 20]$. As a consequence of this analysis, the mean value and standard deviation of the burning time were determined. The relative standard deviation of the burning rate approximately equals to the relative standard deviation of the burning time for the same sample. The dependence of fluctuations of the burning time on the number of hot spots in the system Eq. (16) is the standard one for Markov random processes [45].

B. Kinetic equation

Using the correlation Eq. (12) with $\varphi = 1$ and gamma distribution Eq. (6) for distances between adjacent cells, it is easy to find the distribution function of the ignition delay between adjacent cells

$$P_\tau(\tau) = \frac{\omega_p}{m} \frac{a^a}{\Gamma(a)} (\omega_p \tau)^{(a-m)/m} \exp(-a(\omega_p \tau)^{1/m}). \quad (17)$$

A comparison of the distributions of the ignition delay obtained by the numerical solution of Eq. (2) and calculated according to Eqs. (17) and (10) is shown in Figs. 8 and 9. It can be seen that the dependence Eq. (17), obtained from correlation Eqs. (12) and (10), satisfactorily describes the distribution of the ignition delay for a wide range of parameters a and ε . The best agreement is reached for small values of parameters a and ε . The curves in Figs. 8 and 9 are similar to the experimental dependencies obtained in [6,9] for the ignition delay of the individual particles in actual heterogeneous mixtures. The above results tell us that the propagation of a discrete combustion wave in the systems under consideration with sufficient accuracy can be considered as a Markov random process.

The analysis shows that the controlling factor in the propagation of the combustion front in the systems under consideration is not the dispersion of the coordinates of hot spots, but the dispersion of the ignition delay between adjacent reaction cells: If we replace the random system by a periodic one ($x = k$), retaining the actual ignition delays between the cells, the dependence $x(t)$ will be a little different from the exact one. This means that the dependence $t(k)$ (where the number of a cell k is considered as its coordinate) is more convenient to analyze than the dependence $x(t)$. Let us introduce a probability density $p(k, t)$ that a hot spot k ignites at instant t . Considering the process as a Markovian one, for probability density $p(k, t)$ one can write the Chapman-Kolmogorov equation [46]

$$p(k, t) = \int_0^\infty p(k-1, t-\tau) P_\tau(\tau) d\tau, \quad (18)$$

where $P_\tau(\tau)$ is the probability density that the ignition delay for hot spot k equal to τ ; it is determined by the expression Eq. (17). Note that equation (18) in general cannot be reduced to the diffusion equation (Fokker-Planck-like equation) since the solutions of the later give finite probability for “negative jumps”: there will be a finite probability that the combustion front will come into the point x_2 earlier than into the point $x_1 < x_2$, that is unacceptable. Therefore, Eq. (18) has no simple differential forms and should be solved in a general way.

Equation (18) can be easily solved by using the characteristic function. Let us introduce the characteristic function of the distribution of the burning-out time of the k th hot spot $p(k, t)$

$$\Phi(k, \lambda) = \langle \exp(-\lambda t) \rangle = \int_0^\infty p(k, t) \exp(-\lambda t) dt.$$

Using Eq. (18), we can write

$$\Phi(k, \lambda) = \left\langle \exp\left(-\lambda \sum_{i=1}^k \tau_i\right) \right\rangle$$

For a Markov process, the random variables τ_i at different i are independent and identically distributed ones; because of this

$$\Phi(k, \lambda) = \prod_{i=1}^k \langle \exp(-\lambda \tau_i) \rangle$$

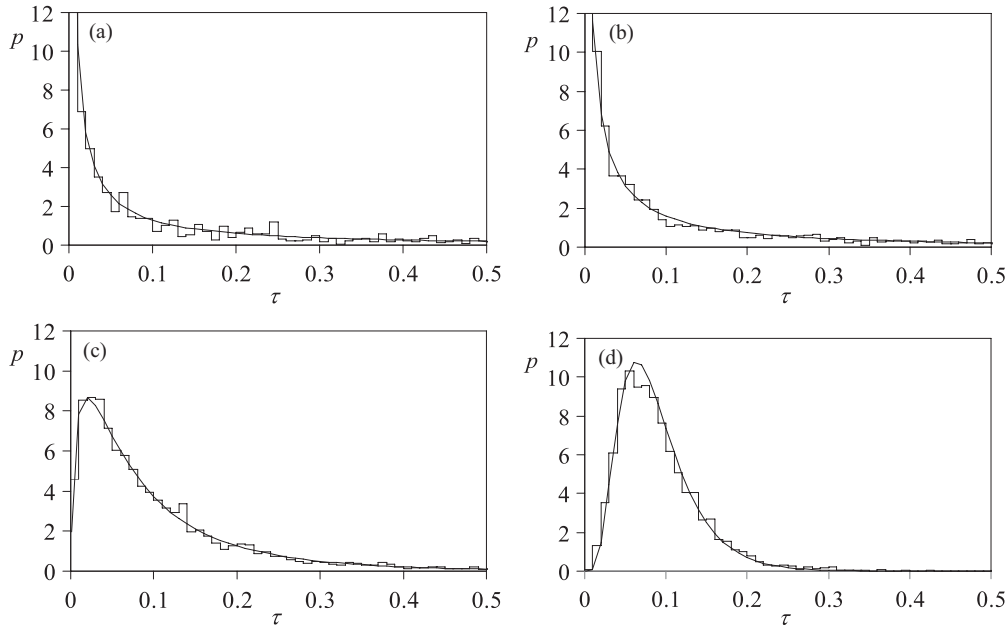


FIG. 8. Distribution of ignition delay between adjacent cells for $\varepsilon = 0.05$. Polygonal lines are the specific realizations obtained by numerical solution of the equation (2), smooth lines are the theoretical probability density Eqs. (17) and (10). (a) $a = 0.7$; (b) $a = 1$; (c) $a = 5$; (d) $a = 20$.

or

$$\Phi(k, \lambda) = \varphi^k(\lambda), \tag{19}$$

where

$$\varphi(\lambda) = \langle \exp(-\lambda\tau) \rangle = \int_0^\infty P_\tau(\tau) \exp(-\lambda\tau) d\tau \tag{20}$$

is the characteristic function for the distribution of the ignition delay between adjacent hot spots.

Taking into account the correlation expression Eq. (12) the expression Eq. (20) one can rewrite in the form

$$\varphi(\lambda) = \int_0^\infty p(L) \exp(-\lambda\omega_p^{-1}L^m) dL,$$

where function $p(L)$ is determined by the expression Eq. (6). Taking into account the distribution Eq. (17) one obtains

$$\varphi(\lambda) = \frac{1}{\Gamma(a)} \int_0^\infty \xi^{a-1} \exp\left(-\xi - \frac{\lambda}{\omega_p a^m} \xi^m\right) d\xi, \tag{21}$$

where $\xi = aL$.

The expressions in Eqs. (19) and (21) formally define the solution of the kinetic equation (18), which can be obtained by inverse Laplace transform of the function Eq. (19). For $a \gg 1$ (the system is close to a periodic one, weakly disordered system) the random process $t(x)$ can be approximately considered as a diffusive one with “drift” ω_r^{-1} and “diffusion coefficient” D . According to the definition [46]

$$D = \frac{1}{2} \frac{\sigma_r^2}{N}.$$

Taking into account Eq. (20) one obtains

$$D = \frac{1}{2} \sigma_z^2, \tag{22}$$

where σ_z^2 is determined by the expression in Eq. (31).

Thus in the limiting case $a \gg 1$, the kinetic equation (18) turns into a Fokker-Plank equation

$$\frac{\partial p}{\partial x} + \omega_r^{-1} \frac{\partial p}{\partial t} = D \frac{\partial^2 p}{\partial t^2}, \tag{23}$$

where $p(x, t)$ is the probability density that the combustion front will reach a given point x at random instant t . Equation (27) is solved at the initial condition

$$p(x, t) = \delta(t),$$

where $\delta(t)$ is the Dirac’s delta function, and it has the well-known solution [46]

$$p(x, t) = \frac{1}{\sqrt{4\pi D x}} \exp\left(-\frac{(t - \omega_r^{-1} x)^2}{4 D x}\right) \tag{24}$$

with a simple physical meaning.

V. COMPARISON WITH EXPERIMENTAL DATA

A. Ti-Si system

Here we demonstrate a possibility of the application of the developed theory for the description of actual heterogeneous mixtures. A solid phase reaction involving a mixture of silicon and titanium powders, known as the “Ti-Si system,” has been investigated experimentally in [9]. This can be considered as gasless combustion as the amount of gas released during the reaction turns out to be relatively small. This makes the Ti-Si system a very popular object of investigation of self-propagating high temperature synthesis [8,9]. The reactive process is commonly represented in the form $\text{Ti} + x\text{Si}$, where the stoichiometric coefficient x can be considered as the bifurcation parameter. The dependence of the measured average burning rate r on the stoichiometric coefficient is shown in Fig. 10, together with the calculated adiabatic burning temperature T_B . The markers in Fig. 10 correspond to the

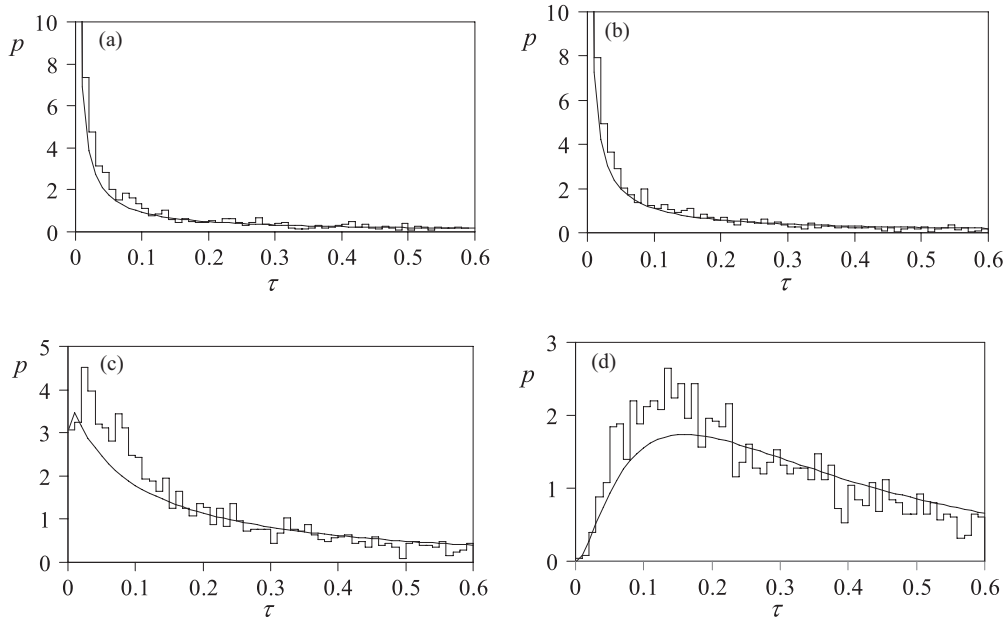


FIG. 9. Distribution of ignition delay between adjacent cells for $\varepsilon = 0.4$. Polygonal lines are the specific realizations obtained by numerical solution of Eq. (2), smooth lines are the theoretical probability density Eqs. (17) and (10). (a) $a = 0.7$; (b) $a = 1$; (c) $a = 5$; (d) $a = 20$.

data [9]. It was established that the combustion of $\text{Ti} + x\text{Si}$ systems occurs only in the range $x = [0.3, 1.5]$. The existence of combustion limits is well known in the literature. The maximum velocity (about 38 mm/s) coincides with the highest value of T_B for $x = 0.6$. The value $x = 0.6$ corresponds to the synthesis $5\text{Ti} + 3\text{Si} \rightarrow \text{Si}_3\text{Ti}_5$. The formation of this alloy releases the largest amount of heat which contributes to an increase of the corresponding burning temperature. The changing of the burning rate correlates with the changing of the burning temperature in the range $x = [0.3, 1]$: The more burning temperature the more burning rate. These results are in agreement with the theory [40,44], which predicted a

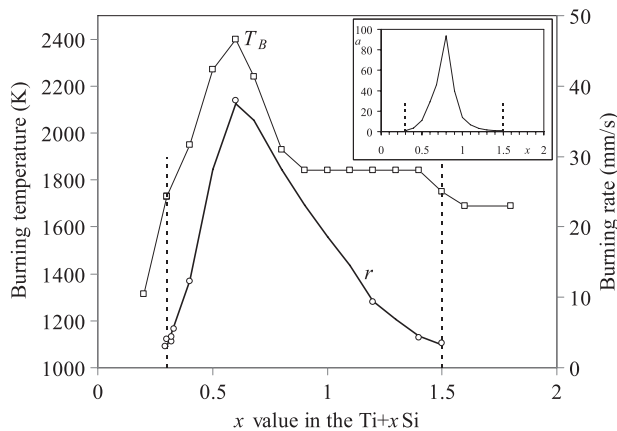


FIG. 10. Burning temperature T_B (squares: scale in K, on the left) and burning rate r (bullets: scale in mm/s, on the right) as a function of the stoichiometry x of the initial sample. Markers are data of [9], solid line $r(x)$ is the theoretical dependence (25) and (26) for gamma distribution. Inset shows the dependence of shaping parameter a on the stoichiometry x used in calculation; dashed lines are the combustion limits.

monotonic dependence of the burning rate on burning temperature. However, the behavior of the burning rate in the range $x = [1, 1.4]$ differs essentially from this trend: The burning rate decreases in this although the adiabatic temperature is constant. This means that the adiabatic temperature is not the only governing parameter for the burning rate. Such a situation occurs in the combustion of heterogeneous mixtures such as $\text{Ti} + x\text{Si}$ for which combustion is accompanied by complex microstructural and phase transformations. At present there are no combustion models that could quantitatively describe the change of the burning rate of heterogeneous systems at a constant burning temperature. The developed model above for the combustion of a system with randomly distributed reaction cell allows giving such a description. According to the developed model, the dimensionless burning rate depends on the dimensionless ignition temperature of reaction cells and the structure of the mixture, which is described by the shaping parameter a . Thus, the shaping parameter a is an additional “degree of freedom” for the burning rate of heterogeneous systems: A change of the shaping parameter can result in changing in the burning rate, even at a constant nondimensional ignition temperature ε . This allows explaining a change of burning rate of heterogeneous mixtures $\text{Ti} + x\text{Si}$ in the range $x = [1, 1.4]$, where its adiabatic temperature is constant. It is enough to assume that the shaping parameter a depends on the stoichiometry x . Calculations of the burning rate of the mixture $\text{Ti} + x\text{Si}$ were carried out by using dependencies

$$r = r_0 \omega_r(\varepsilon, a), \quad (25)$$

$$\varepsilon = \frac{T_{\text{ign}} - T_{\text{in}}}{T_B - T_{\text{in}}}, \quad (26)$$

where T_{ign} , r_0 are the constants; $\omega_r(\varepsilon, a)$ was calculated according to Eqs. (13) and (10) with $\varphi = 1$; $\omega_p(\varepsilon)$ was calculated according to Eqs. (4) and (5), obtained in [35] for

a periodic system; $T_B(x)$ was determined by using data [9] (Fig. 10); $T_{\text{in}} = 300$ K. As described above, in the developed model it is impossible to organize a stable combustion process at $\varepsilon > 0.45$ under any initial conditions for the whole range of parameter a . This should be seen as a natural inflammability limit for the combustion model under consideration. In the experiments [9], the inflammability limits $x = 0.3$ and $x = 1.5$ were obtained for heterogeneous mixtures $\text{Ti} + x\text{Si}$. The developed model allows explaining these inflammability limits, if we assume that $\varepsilon > 0.45$ outside the range $x = [0.3, 1.5]$. Thus, our calculations assumed that $\varepsilon = 0.45$ on the both inflammability limits, obtained in the experiments; this allowed the determined the value of $T_{\text{ign}} = 950$ K. The dependence of the shaping parameter on the stoichiometry x , $a(x)$ was matched to obtain the best fit with the experimental data on burning rate. For definiteness, it is assumed that $a = 1$ at the inflammability limits. The matched dependence $a(x)$ is shown in the inset of Fig. 10. The calculated dependence of the burning rate on the stoichiometry x for $\text{Ti} + x\text{Si}$ is also shown in Fig. 10 by the solid line. We assumed in the calculations $r_0 = 12$ mm/s. Thus, the variations in shaping parameter a can completely describe the dependence of the burning rate on the stoichiometry x at a constant burning temperature. An analysis of dependence $a(x)$ (Fig. 10) shows that the shaping parameter a reaches a maximum value $a \approx 94$ at $x = 0.8$. As shown above, the more $a \gg 1$ the more ordered is the system: as $a \rightarrow \infty$ the system tends to be periodic. The obtained dependence $a(x)$ (Fig. 10) shows that the $\text{Ti} + x\text{Si}$ mixture becomes more ordered at $x \rightarrow 0.8$, while, by contrast, the mixture becomes disordered if it moves away from $x = 0.8$. Such a behavior of the structure of the mixture can be connected with the peculiarities of the packing of Ti and Si particles in the volume of the mixture during the mixing process at different concentrations of the components.

B. Thermite systems

Here we compare the experimental data for dilute thermite systems [47], which consist of powder components capable of exothermic transformation, mixed with some inert diluter, with the theoretical model developed in the earlier sections. The burning temperature of the system and its burning rate can be changed over a wide range by changing the amount of the inert diluter; in doing so the mechanism of heat release in combustion is not changed. In such systems, the groups of active particles, which are capable of chemical transformations, play the role of heat sources, while the T_{ign} is either the melting point of a powder component or a temperature of eutectic [8,28] at which the initial solid components are capable of chemical reactions with one another. The values of the burning rate and burning temperature of several thermite systems which contain different amounts of the inert diluter are collected in the work of the authors of [47]. Neglecting the heat losses, the measured burning temperature of the system will be identified with the adiabatic temperature of the system T_{ad} . Figure 10 contains the data of the authors of [47], processed in the coordinates of the burning rate versus a burning temperature. The amount of inert diluter n in these systems is equivalent to the change in the range from 0 to 70%, in doing so the burning rate could be reduced by a factor of 20 within one system

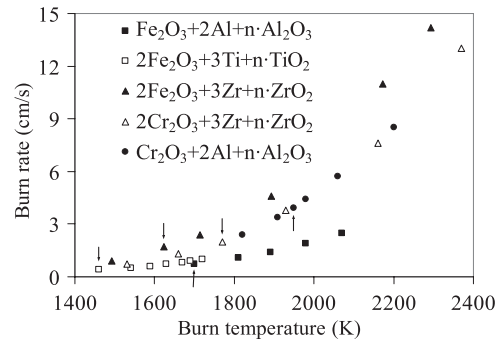


FIG. 11. Correlation of burning rate and burning temperature for several thermite systems, based on data of the authors of [47]. The arrows show the critical points, which correspond to the beginning of oscillatory combustion modes.

while a reduction of a burning temperature can be reached by 1000 K. It is necessary to note that starting systems without a diluter are distinguished by the levels of the burning rate and burning temperature: the burning rate of the systems without an inert diluter are different by a factor of 30 while their burning temperatures are different by 700 K. At a relatively low concentration of inert diluter the combustion of the thermite systems [47] occurs in steady-state mode without oscillations. At a certain concentration of the inert diluter a steady-state combustion loses its stability and the combustion of the system is accompanied by oscillations of the burning rate (pulsating regime of combustion) or by periodic flashes of separated hot spots (hot-spot regime of combustion); further increasing in the concentration of the diluter intensifies these oscillations and at some limited concentrations of the diluter the combustion of the system becomes impossible: extinguishing occurs for any condition of initial inflammation of the system. The mean burning rate during the whole time of the combustion of several systems has been determined by the authors of [47] for steady-state and pulsating combustion regimes; this one can correspond to the theoretical mean burning rate Eq. (13) (Fig. 5). The arrows in Fig. 11 show the dots corresponding to a beginning of the pulsating regimes of combustion of different systems. The treatment of the data [47] has been carried out in the coordinates $\varepsilon - \omega$. In doing so it is considered that a beginning of the pulsating regime of combustion, observed in the experiments, corresponds to the theoretical critical values of the parameters ε_{cr} and ω_{cr} . As we have established above the detectable oscillations in such a system begin at $\varepsilon_{\text{cr}} = 0.4$; these parameters we consider as the critical parameters for disordered systems. Assume that burning rate r_{cr} and burning temperature $T_{\text{ad,cr}}$, determined in the experiments, correspond to the beginning of the pulsating regime of combustion for a real system. Then we can define the ignition temperature of heat sources for this system, using the recommendations of the theory above as $T_{\text{ign}} = T_{\text{in}} + \varepsilon_{\text{cr}}(T_{\text{ad,cr}} - T_{\text{in}})$. Hereafter we assume that the ignition temperature, defined in such a manner, is a constant characteristic of the system and does not depend on the dilution degree of the system by inert diluters. Then

$$\varepsilon = \varepsilon_{\text{cr}} \frac{T_{\text{ad,cr}} - T_{\text{in}}}{T_{\text{ad}} - T_{\text{in}}}. \quad (27)$$

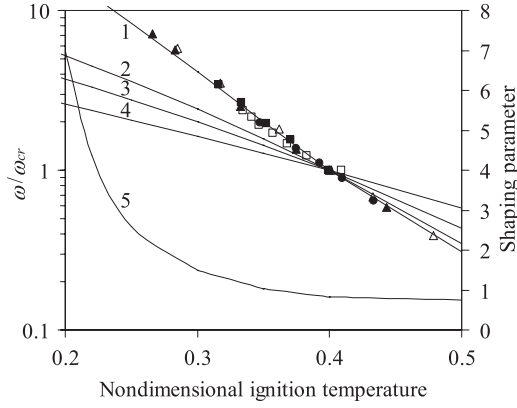


FIG. 12. Comparing of experimental and theoretical dependencies $\omega(\varepsilon)$. Dots are the treated experimental data [47] (see the text for details; the designations correspond to those for Fig. 11); solid lines 1 to 4 are the theoretical dependence (10) and (13) for gamma distribution: line 1 corresponds to calculation for variable $a(\varepsilon)$; lines 2 to 4 correspond to calculations for $a = \text{const}$: (2) $a = 0.7$; (3) $a = 2$; (4) $a = 20$. Line 5 is the dependence of shaping parameter a on nondimensional ignition temperature ε used in calculation for line 1.

In accordance with Fig. 5, critical nondimensional burning rate $\omega_{\text{cr}} = \omega(\varepsilon_{\text{cr}})$ depends on the shaping parameter a ; this means that ω_{cr} depends on the system's internal structure. Taking into account that $\omega = rl_0/\kappa$, a nondimensional burning rate of thermite systems satisfies the expression

$$\omega/\omega_{\text{cr}} = (r/r_{\text{cr}})(l_0/l_{0\text{cr}}), \quad (28)$$

where r is the burning rate of the system; index "cr" marks the parameters of a dilute system, which corresponds to a beginning of the pulsating regime of the combustion in the system. Assuming that the quantity of heat sources in the system does not depend on the amount of diluter, we can write

$$\left(\frac{l_0}{l_{0\text{cr}}}\right)^3 = \frac{1 - n_{\text{cr}}}{1 - n}, \quad (29)$$

where n is the mass fraction of inert diluter in the system. Experimental data [47] treated by using expressions (27) to (29) are shown in Fig. 11. Lines 2-4 (Fig. 12) show the theoretical dependence (13) and (10), with $\varphi = 1$ for different values $a = \text{const}$. In these cases we assumed $\omega_{\text{cr}} = \omega_r(\varepsilon_{\text{cr}})$ for each a . One can see that theoretical dependencies $\omega_r(\varepsilon)$ for $a = \text{const}$ give only a qualitative agreement with the experimental data, but not a quantitative one: the theoretical sensitivity $K = -\frac{\partial \ln \omega}{\partial \varepsilon}$ is less essential than the experimental one. To explain this difference we made the natural assumption that the dilution of the thermite system results in the changing of its structure. We assume that the changing of ε in the dilution of the system is accompanied with the changing of the shaping parameter a , which describes the system's structure. Moreover we consider that all thermite systems under consideration can be described by the same dependence $a(\varepsilon)$. The dependence $a(\varepsilon)$ is matched from the condition of coincidence of theoretical dependence $\omega(\varepsilon)$ with the experimental data [47] (Fig. 12). Such a dependence $a(\varepsilon)$ is shown in Fig. 12 (line 5). Theoretical dependence $\omega(\varepsilon)$, calculated by using expressions Eqs. (10) and (13), taking into account the matched dependence $a(\varepsilon)$, is shown in Fig. 12

(line 1); it describes correctly the experimental data [47] for a wide class of thermite systems. The value $\omega_{\text{cr}} = 0.25$ was used in these calculations. The experimental data [47] allows estimating a limiting value of parameter ε for each system, above which a self-sustained combustion is impossible. The data [47], processed in variables $\varepsilon - \omega$, show that combustion becomes impossible at $\varepsilon = 0.45 \dots 0.5$; this fact correlates well with the theoretical results obtained above.

VI. DISCUSSION

A. Effect of system structure

The obtained agreement of the theoretical and experimental dependencies $\omega(\varepsilon)$ (Figs. 10 and 12) augurs well for the discrete combustion model of heterogeneous systems under consideration. We have shown that the random structure of the powder system can play a crucial role in the combustion process and should be taken into account in the modeling of the combustion of microheterogeneous systems. This is a consequence of the nonlinear interaction of the system structure and the thermal wave, which creates the features in the propagation of the combustion wave. This is an important result of this study. We concluded that the structure of the system cannot be considered as an unchanged one, and it can vary with changes in the size of the particles of dispersed components or their concentrations, which results in the changing in the nature of the combustion process and in the burning rate, even at a constant burning temperature. This is confirmed by the experimental data [9]. We found that some features of the combustion of actual powder systems can be described by the regularization or stochastization of the system when the structure of the system becomes more ordered, or, on the contrary, disordered due to the changing of concentration of disperse components. The limiting case of the stochastization of the mixture is its clustering when individual hot spots are collected into the compact groups (clusters) and act as the larger hot spots in the combustion process. Thus, the results of experiments with the Ti-xSi system [9] can be explained by assuming that a relative regularization of the system occurs ($a \rightarrow 94$) at $x \rightarrow 0.8$ while the system approaches the concentration inflammability limits $x = 0.3$ and $x = 1.5$ the stochastization of the system ($a \rightarrow 1$) occurs. Experimental data on the combustion of a wide class of thermite systems with inert diluters [47] can also be explained with a change in the structure of the powder mixture due to the change of the concentration of the diluter. Thus, in the range $\varepsilon = 0.25, \dots, 0.35$ the system should have a random structure with an almost uniform random distribution of hot spots ($a = 1, \dots, 3$), while a weak clustering of hot spots ($a = 0.75$) should occur near the concentration inflammability limit. These results are of fundamental importance because earlier the effect of the structure of system on the combustion process either was neglected, or assumed that the structure of the system does not change with the changing in the concentration and dispersion of the components [9]. The analysis of Fig. 3 shows that the combustion process becomes very sensitive to the structure of the system at high ignition temperatures: The higher the ignition temperature, the higher the sensitivity. Thus, the presence of random heterogeneities in the system can

have a weak affect on the combustion process at low ignition temperatures, but can result in significant fluctuations of the burning rate and even long periods of stopping of the burning front (big ignition delays) at high ignition temperatures. We can say that the heterogeneities of the system are precisely that obstacle on which a termination of combustion occurs at suprathreshold ignition temperatures.

B. Quasi-Arrhenius' macrokinetics

The experimental data for all termite systems considered [47] (Fig. 12) can be approximated (fitted) by the single dependence

$$\omega = 67.6 \exp(-14\varepsilon), \quad (30)$$

although these systems essentially differ not only from one another by their properties, but also they are different by the contents of the diluter within a system. Taking into account that, usually, $T_{\text{ad}} \gg T_{\text{in}}$, the dependence Eq. (30) can be considered as the Arrhenius' one, that is, $\omega \sim e^{-E_{\text{ef}}/RT_{\text{ad}}}$, with an effective activation energy of macroprocess $E_{\text{ef}} \approx 9.08R(T_{\text{ign}} - T_{\text{in}})$, where R is the universal gas constant. A similar dependence of the macroscopic burning rate on burning temperature can be obtained theoretically in a homogeneous combustion model with Arrhenius' microkinetics [40,44]. Note that the obtained Arrhenius' dependence of the macroscopic burning rate of the system on its adiabatic temperature is not connected with Arrhenius' microkinetics of chemical reactions in heat sources. The obtained result shows that Arrhenius' macrokinetics, which is usually detected in experiments, can be connected with an existence of threshold temperature T_{ign} and a heterogeneous nature of the system under consideration and it can have purely a thermal nature.

C. Relay-race mode versus quasihomogeneous mode

For a long time there has been a discussion in the literature [1–9,28] on what is the mode in which the combustion of disperse (powder) systems, in particular gasless combustion, occurs: in a quasihomogeneous mode or in a microheterogeneous (relay-race) mode. This question is of fundamental importance for the simulation of the combustion of such systems because the well-mastered and widely used quasihomogeneous combustion model [48,49], which historically goes back to the founders of the combustion theory (Zeldovich, Frank-Kamenetsky, Schwab *et al.*), are based on the assumption about smooth and continuous distribution of temperature and other parameters in the combustion wave, and they need a justification as applied to combustion of microheterogeneous systems. It is easy to introduce a criterion of the "homogeneity" of the combustion wave as applied to disperse systems. Let the characteristic thickness of the thermal layer in the combustion wave be λ . According to the combustion theory of homogeneous systems [40–44], this thickness is connected with the burning rate r by expression

$$\lambda = \frac{\kappa}{r}. \quad (31)$$

Obviously, the combustion wave in the powder system can be considered as a quasihomogeneous one, if the condition

$$\lambda \gg d \quad (32)$$

is satisfied or

$$\lambda \gg l_0, \quad (33)$$

where d is the characteristic size of the particles. The criterion in Eq. (32) is applicable to the combustion models that take into account the finite size of the particles. In our model of point hot spots one should use the criterion Eq. (33), which, with taking into account Eq. (31), takes the form

$$\frac{r l_0}{\kappa} \ll 1, \quad (34)$$

or, by the definition of the nondimensional burning rate ω

$$\omega \ll 1. \quad (35)$$

Thus, only if the nondimensional burning rate is much less than unity, one can consider that the combustion of microheterogeneous system occurs in a quasihomogeneous mode. In practice, one can speak about a quasihomogeneous mode when at least the condition $\omega < 0.1$ is satisfied. According to the theory under consideration, the less the shaping parameter a the less the burning rate at the same nondimensional ignition temperature ε . Using the expression Eqs. (13) and (10) (Fig. 5), we find that the nondimensional burning rate $\omega > 0.2$ even for $a = 0.7$ at $\varepsilon < 0.45$ while the nondimensional burning rate $\omega > 0.5$ for $\varepsilon < 0.3$. Thus, we conclude that the combustion of disperse systems occurs always in microheterogeneous mode according to the relay-race mechanism and the application of quasihomogeneous combustion models for such systems is unfounded. This conclusion is also confirmed by experimental observations [5–9].

VII. CONCLUDING REMARKS

The results show that the use of the gamma distribution for the modeling of microheterogeneous systems allows describing the peculiarities of the combustion of solid mixtures with wide variations in their internal structure, from periodic, which correspond to $a = \infty$ (they were separately investigated in detail in [35,38]) to random homogeneous disordered systems, which correspond to $a = 1$ (they were separately investigated in detail in [38]), and ending with clustered systems which correspond to $0.5 < a < 1$. The burnfront moves linearly for a system with larger a and acquires a jump hesitate for lower a . The generalized theoretical dependence obtained for random system burn rates normalized to a periodic system show a complete agreement with the numerical results. Self-similarity in burning front propagation is observed for different ignition temperatures for the same random realization of system structures. The relative standard deviation of burning rates was found to be approximately equal to the relative standard deviation of the burning time of same sample. An aalysis shows that the controlling factor affecting burn front propagation is the dispersion of the ignition delay between adjacent reaction cells. An additional "degree of freedom," the shaping parameter a , introduced in the model allowed reproducing theoretically the experimental data for a wide range of pyrotechnic mixtures, as well as explained the previously unexplained from the point of view of the theory of the combustion of homogeneous systems the experimental data on combustion of Ti + xSi mixtures. Only the assumption

that the burning rate depends on the structure of the mixture and can change with the changing of the structure of mixture even at a constant burning temperature allowed describing the dependence of the burning rate on stoichiometry x , including, in the range with a constant burning temperature.

Of course, we understand that the one-dimensional model and the gamma distribution is an approximation describing the combustion of actual microheterogeneous systems. The actual powder systems are the three-dimensional ones, the particles in them have finite sizes, and the internal structure of the mixtures is automatically formed in the process of their preparation, depending on the sizes and concentrations of the components. Accordingly, if the regularization or a clusterization of the system occurs, it must be a result of the system composition, but not specified as an input data. For this reason, a more natural way is the direct simulation of the structure of the system, based on one of the methods of packing of particles, e.g., [50,51], and the subsequent direct calculation of the combustion process [37,39], which automatically takes into account the actual structure of the system, including its possible regularization or clustering. As applied to actual powder mixtures this work is planned in the next stage of this research. In addition, the undoubted theoretical interest is the investigation of non-Markovian random process (2). This problem belongs to the fundamental problems of the theory of random processes.

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APPENDIX

Let us calculate a mean burning rate of a disordered system when the time intervals between the ignition of neighboring sources and the distances between them are related by Eq. (12). Consider some time interval, during which some number of heat sources $N \gg 1$ are burned away. The duration of this time interval is

$$t_N = \sum_{i=1}^N \tau_i. \quad (\text{A1})$$

Taking into account Eq. (12), we obtain

$$t_N = \varphi \omega_p^{-1} \sum_{i=1}^N L_i^m,$$

or

$$t_N = \varphi \omega_p^{-1} N \langle L^m \rangle, \quad (\text{A2})$$

where

$$\langle L^m \rangle = \frac{1}{N} \sum_{i=1}^N L_i^m$$

is the mean value of the parameter L^m . Because

$$\langle L^m \rangle = \int_0^\infty L^m P(L) dL$$

one can easily obtain while taking into account Eq. (6)

$$\langle L^m \rangle = \frac{\Gamma(a+m)}{a^m \Gamma(a)}, \quad (\text{A3})$$

where

$$\Gamma(m+1) = \int_0^\infty z^m e^{-z} dz$$

is the gamma function.

The mean burning rate of the system under consideration as a whole

$$\omega_r = \frac{N}{t_N}$$

or with taking into account Eq. (A2)

$$\omega_r = \omega_p(\varepsilon) \frac{1}{\varphi \langle L^m \rangle}.$$

Taking into account Eq. (A3), we obtain

$$\omega_r / \omega_p = \frac{1}{\varphi} a^m \frac{\Gamma(a)}{\Gamma(a+m)}. \quad (\text{A4})$$

Let us estimate the fluctuations of the burning rate of the system as a whole. Consider the burning time of the system, consisting of N reaction cells (A1). The ignition delay times τ_i depend on the location of the hot spots in the system and for the system under consideration they are random. The discrete random process $L_i, i = \dots, 1, 2, 3, \dots$, by definition, is a Markovian one. Let us calculate a standard deviation of the system's burning time Eq. (A1) based on the assumption that discrete random process τ_i is also Markovian, that is, the ignition delay times τ_i relating to different hot spots are the statistically independent random quantities. In this case the burning time of the system consisting of N hot spots has the mean value

$$\langle t_N \rangle = N \langle \tau \rangle \quad (\text{A5})$$

and standard deviation

$$\sigma_t = \sqrt{\langle t_N^2 \rangle - \langle t_N \rangle^2} = \sqrt{N} \sqrt{\langle \tau^2 \rangle - \langle \tau \rangle^2}. \quad (\text{A6})$$

The relative standard deviation of the system's burning time together with Eq. (A5) is

$$\frac{\sigma_t}{\langle t_N \rangle} = \frac{1}{\sqrt{N}} \sqrt{\frac{\langle \tau^2 \rangle}{\langle \tau \rangle^2} - 1}. \quad (\text{A7})$$

Using the correlation Eq. (12) with $\varphi = 1$, we can write

$$\langle \tau \rangle = \omega_p^{-1} \langle L^m \rangle, \quad \langle \tau^2 \rangle = \omega_p^{-2} \langle L^{2m} \rangle, \quad (\text{A8})$$

where $\langle L^m \rangle$ is determined by the expression Eq. (A3) for any m . Using Eqs. (A8) and (A3), for the relative standard deviation of the system's burning time Eq. (A7) one obtains the expression

$$\frac{\sigma_t}{\langle t_N \rangle} = \frac{1}{\sqrt{N}} \sqrt{\frac{\Gamma(a)\Gamma(a+2m)}{\Gamma^2(a+m)} - 1}, \quad (\text{A9})$$

where the parameter m is determined by the correlation Eq. (10).

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