HEAT TRANSFER IN LASER PULSE INTERACTION
WITH REACTIVE SUBSTANCES

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ABSTRACT

The purpose of this paper is to analyze thermal regime of a laser-pulse interaction with a substance reacting in bulk and on the surface. Emphasis is on the critical phenomena in non-resonant interaction of substance with laser beam, and how they depend on thermo-chemical and optical characteristics of system. It is shown that irradiation of exothermically reacting substance can induce its ignition, if the laser-beam diameter exceeds a critical one. This critical diameter depends on the pulse intensity and duration, as on the thermo-chemical characteristics of system. The cases of short-pulse and quasi-steady irradiation are considered in details.

A role of soot particles or other absorbing micro-inclusions in the interaction is investigated. In certain field of the system parameters such micro-inclusions cause local heat explosion, due to exothermic reaction in environment.

In the case of quasi-steady irradiation the explosion is induced if the particle diameter exceeds a critical one. This critical diameter depends on the initial temperature, reaction rate constants, as on radiation intensity. It is directly proportional to the characteristic space-scale of reaction in the system. The product of the particle critical diameter and the radiation intensity is approximately constant.

In the case of short-pulse irradiation the highest temperature disturbance in the substance is caused by particles having certain medium diameter. This critical diameter increases with pulse duration and with heat-conductivity of the substance.

The main results of consideration are illustrated by instances with reacting gas, condensed fuels, and explosives. The results application to typical problems of laser based diagnostics are also demonstrated.

INTRODUCTION

Development of laser based technologies needs deep understanding of specific features of laser-beam interaction with chemically reacting substances. Numerous experimental and theoretical data point to influence of geometric- and time- scales of irradiation on thermal regime of the interaction process. Among them, the phenomenon of anomaly high sensitivity of some propellants and explosives to IR-radiation (see, for example, Mikheev & Levashov, 1973; Karabanov & Bobolev, 1981), which is generally associated with presence of absorbing particles or other optical discontinuities.

Besides, the widespread application of laser-based diagnostic techniques to study chemical processes (Kuo & Parr, 1994) demands to analyze the temperature and other disturbances in the reactive medium, induced by laser-irradiation. One of the main questions of this problem is influence of soot particles or other absorbing micro-inclusions on thermal regime of the laser-matter interaction.

That is why the focus of this paper is a successive theoretical analysis of thermal regimes of reactions going in substances exposed by monochromatic or polychromatic radiation. Emphasis is placed on the critical conditions of non-resonant interaction and how they depend on the thermo-chemical and optical characteristics of substances.

This problem has many aspects, especially being applied to optically non-uniform substances (containing soot or metallic particles). Therefore it needs to simplify reasonably the mathematical formulation to find main criteria governing the interaction process, and find solutions of mathematical problem in clear analytical form. To reach this purpose we consider here some limit cases of the interaction, corresponding to limit relationship between spatial and time scales of the process.

QUASI-STEADY THERMAL REGIME.

In many cases the thermal relaxation time of irradiated volume is much less than pulse duration or other characteristic time of irradiation. Such limit cases correspond to quasi-steady thermal conditions of the interaction.

Critical Diameter of Laser Beam

If the radiation absorption depth is sufficiently large and the beam diameter is small enough, the heat release in irradiated volume is compensated by the heat losses to adjacent cool layers of substance. In such a case, there exists a quasi-steady thermal regime of the interaction with small difference between temperatures of irradiated and non-irradiated volumes. This low-temperature thermal equilibrium may be made impossible by increasing the bunch diameter or flux intensity. The situation is similar to the existence of critical size of the chemical reactor, which results in thermal explosion (Frank-Kamenetskii, 1969).

It is assumed that the laser-beam dispersion in the substance can be neglected. In such a case the problem of thermal regime in lighted cylindrical volume ($x \leq 0$, $0 \leq r \leq R$), Fig. 1, may be formulated using the one-dimensional equation of heat conductivity (1.1) (where $T(x, t)$ is the temperature averaged by the cross section of cylinder), with the boundary condition on the front surface ($x=0$), Eq. (1.2), and with a homogeneous initial distribution, Eq. (1.3):

$$\rho c \partial T/\partial t = \lambda \partial^2 T/\partial x^2 + \rho q_0 F_0(T) +$$

$$J(t)e^{x/h}/h - 4Q/D, \qquad (1.1)$$

$$(\partial T/\partial x)_0 = \beta(T_2 - T_1) + q_s F_s(T_1),$$

$$T_1 = T(0,t), \qquad (1.2)$$

$$T(x, 0) = T_0 = T(x \rightarrow -\infty, t). \qquad (1.3)$$

Here ρ, c and λ are the density, heat capacity and thermal conductivity of the substance, respectively; $q_0 F_0$ and $q_s F_s$ are the heat release rates of bulk and heterogeneous reactions (it is supposed that reactions go in the kinetic regime (Frank-Kamenetskii, 1969)); J is the density of absorbed light flux; h is the characteristic absorption's depth; Q is the density of heat-flux going through the side of the irradiated cylindrical volume; β and T_2 represent the coefficient of heat exchange and the temperature of the surrounding medium at the end of the cylinder; D and R are the diameter and radius of laser beam.
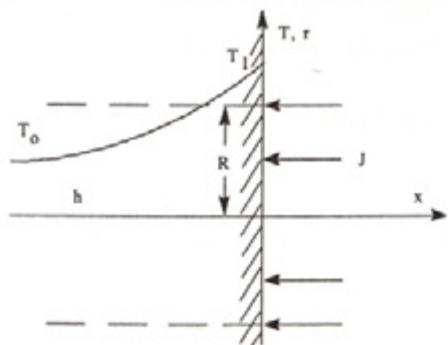
Fig. 1. Schematic sketch of laser-matter interaction. and temperature distribution in depth of semi-transparent substance.

An asymptotic analysis of the temperature distribution outside of irradiated volume (under condition h>>D) shows that the intermediate asymptote for the heat-flux Q (on times t~ $D^2 \rho c/\lambda$) has the form (Assovskiy, 1994):

$$Q \approx 2\lambda(T(x, t) - T_0)/D. \qquad (1.4)$$

The activation energy E_0 of bulk reaction is assumed to be large enough; therefore the reaction takes place mainly in the thin layer (thickness $l_0 \ll h$) located near the position of maximum temperature (Frank-Kamenetskii, 1969). Resulting rate of heat release in the reaction zone is positive if $T>T^*$, where T^* is the temperature of non-stable heat equilibrium of the homogeneously heated cylinder with environment (Assovskiy & Leipunskiy, 1980):

$$\rho q_0 F_0(T^*) = 8\lambda(T^* - T_0)/D^2. \qquad (1.5)$$

Homogeneous Heating. When $T>T^*$ throughout the cylinder, it results in self-heating (thermal explosion) of substance. Whether $T>T^*$ only in a small part of the irradiated volume, possibility of the thermal explosion depends on parameters of the temperature distribution, on characteristics of the bulk reaction, and on the heat-release due to radiation absorption's.

We assume further the reaction rates are varying with temperature according to the Arrhenius law:

$$F_0 = k_0 \exp(-E_0/R_g T); \quad F_s = k_s \exp(-E_s/R_g T). \quad (1.6)$$

Using (1.5), (1.6) and Frank-Kamenetskii expansion (Frank-Kamenetskii, 1969), a relationship between T^* and D may be presented in the form:

$$D^2/l_0^2(T_0) = 8x \exp(-x), \qquad (1.7)$$

where l_0 is characteristic scale of thickness of bulk reaction zone, and x is a relative temperature of irradiated volume.

$$l_0^2(T) = \lambda R_g T^2/E_0 \rho q_0 F_0(T),$$

$$x = (T^* - T_0)E_0/R_g T_0^2 \qquad (1.8)$$

The plot of function (1.7) is presented on Fig. 2. This figure shows the existence of a critical diameter D^* of laser beam, which corresponds to the maximum of function (1.7) (at x = 1).

$$D^* = 2(2/e)^{1/2} l_0(T_0). \qquad (1.9)$$

According to (1.9), D^* has an order of magnitude equal to lo(To). Figure 3 shows plots of lo as a function of temperature for some exothermically reacting substances which thermochemical characteristics are presented in Tab. 1.
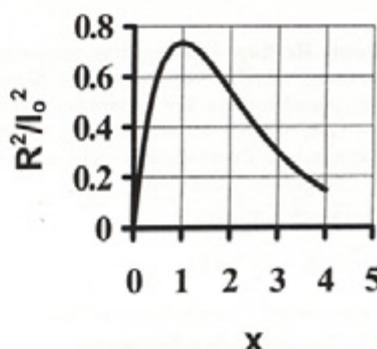
Fig. 2. Dependence of the relative radius R/l_0 on the relative temperature x of irradiated cylindrical volume.

There are two states of the heat equilibrium for each D < D^* (low-temperature x_1 and high temperature x_2), Fig.2. The value x_1 corresponds to a small deviation of the irradiated volume's temperature T_1 from the environment's temperature T_0:

$$T_1 - T_0 < R_g T_0^2/E_0 .$$
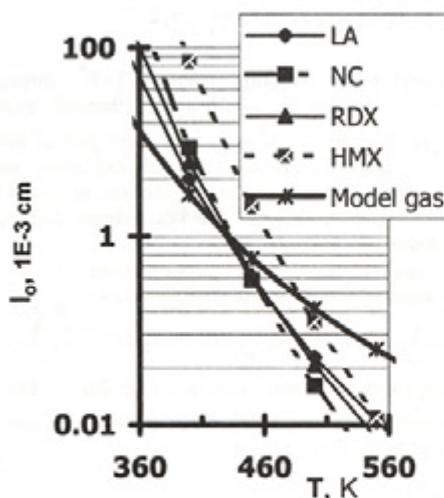
Fig. 3. Scale of reaction zone thickness l_o vs. reaction zone temperature T.

The high temperature x_2 defines the upper limit of homogeneous heating of the lighted volume, not exciting the heat explosion:

$$T^*(D) = T_0 + x_2 R_g T_0^2/E, \quad (x_2 > 1). \qquad (1.10)$$

The value of critical temperature, Eq.(1.10), increases rapidly with decreasing the radiation beam's diameter (due to increase of x_2, Fig. 2). So, it may considerably exceed the minimal temperature corresponding to $D = D^*$: $T^*(D^*) = T_0 + R_g T_0^2/E_0$, that is usually considered as the pre-explosion temperature (Semenov, 1940). Typical values of the critical temperature T^* for some exothermically reacting substances are presented in Tab. 2.

Non-Homogeneous Heating. The reaction zone temperature may far exceed the value (1.10), under non-homogeneous heating of the irradiated volume. The asymptotic analysis of the system (1.1) - (1.4) (made in condition: $l_o \ll h$) shows possibility of the quasi-steady interaction with the reaction zone temperature T_1 determined by equation:

$$Q_l(T_1) = 2\sqrt{2}\,\lambda(T_1 - T_0)/D,$$
$$T_1 = T_0 + JD^2/8(h + D/2\sqrt{2}) \qquad (1.11)$$

Table 1. Thermochemical Characteristics of Some Exothermically Reacting Substances.

Substances	$\lg(\rho q_o k_o)$	E, kJ/mol	λ, 10^{-3} W/cmK
Lead azide (LA)	16.83	152	1.76
Nitro cellulose (NC)	22.56	201	2.35
Hexogen (RDX)	19.01	172	1.67
Octogen (HMX)	23.26	220	2.90
Model gas-mixture (MG)	10.00	100	0.50

Table 2. Critical Temperatures T^* for the Thermal Explosion of Uniformly Irradiated Volume, °C.

Substance	HMX	RDX	NC
R = 2.0 mm	250	220	200
R = 5.0 mm	200	185	180

Here Q_l is the heat flux from the reaction zone to colder layers of the irradiated volume:

$$Q_l^2(T) = (\beta(T_2 - T) + q_s F_s(T))^2 +$$
$$2\lambda R_g T^2 E^{-1}(\rho q_0 F_0(T) - 8\lambda(T - T_0)/D^2). \quad (1.12)$$

The maximum diameter of the radiation beam, such that the quasi-steady thermal regime is yet possible, can be defined similar to the Semenov's theory of thermal-explosion (Semenov, 1940). The critical condition correlates with the contact of curves corresponding to the left (Eq.(1.12)) and right parts of Eq.(1.11), see Fig. 4.

INITIATION OF EXOTHERMIC REACTION BY POLYCHROMATIC PULSE-IRRADIATION

The problem of thermal regime of chemical reaction exposed by polychromatic pulse-radiation can be solved using results of previous consideration of monochromatic irradiation. We assume that the absorption of each mode, having a wave-length m, does not depend on other one. Taking into account Eq. (1.1), the heat-conductivity equation can be presented in the form:

$$\rho c \partial T/\partial t = \lambda \partial^2 T/\partial x^2 + \rho q_0 F_0(T) +$$
$$\int_0^\infty j(t,m)h^{-1}\exp(x/h)\,dm - 4Q/D. \qquad (1.13)$$

A parametric analysis of Eqs. (1.13), (1.2), (1.3) shows that the thermal regime of interaction depends significantly on relationship between following time-scales (designation corresponds to Assovskiy & Leipunskiy, 1980):
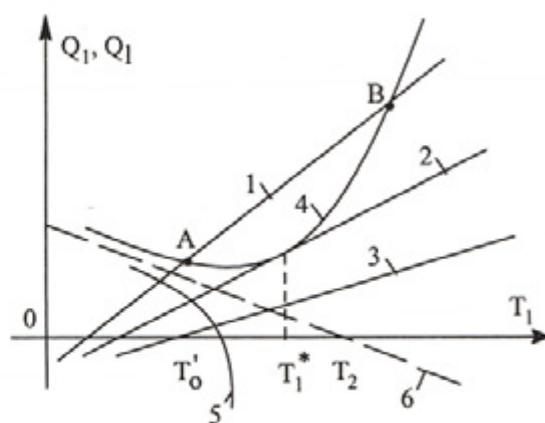
Fig. 4. The relation between heat removal Q_l (lines: 1,2, and 3) and heat flux from the reaction zone Q_l (curves: 4,5, and 6) for exothermic (4), endothermic (5), and neutral (6) reactions at different values of the laser beam diameter: (1) $D < D^*$, (2) $D = D^*$, (3) $D > D^*$.

the pulse duration t_J, the characteristic scales of thermal relaxation of irradiated volume $t_1 = h^2_m/\chi$ and $t_2 = R^2/\chi$, and the time-scale of volume's self-heating due to reaction $t_3 = c(T_1 - T_o)/q_o F_o$. Here h_m is a characteristic depth of absorption.

If the pulse duration t_J is much smaller than other time-scales, the volume temperature distribution depends (during irradiation) only on spectrum of absorbed radiation and on function $h(m)$:

$$T(x,t) = T_o + \int_0^t \int_0^\infty j(t,m)\, h^{-1} \exp(x/h)\, dm\, dt.$$

Transformation of this distribution after irradiation depends on a ratio of time-scales t_1, t_2, t_3. In limit cases of such a ratio, it is possible to find the solutions in analytical form.

For example, the critical relationship between characteristics of igniting pulse, under assumption $t_J \ll t_1, t_2$, has a form:

$$a = Q_1(T_1) h_m / \lambda (T_1 - T_o) > a^*. \tag{1.14}$$

Here a criterion a is a ratio of the total heat-release in reaction-zone $Q_1(T_1)$, Eq. (1.12), at the end of irradiation, to the heat-flux from the front-surface to colder layers of irradiated cylindrical volume.

The critical value a^* is a function of ratio h_m/D. If $D \gg h_m$, then $a^* < 1$, and there exists a region of parameters $1 > a > a^*$, where the system self-ignition takes place later a time-delay after irradiation. If $D < h$, then $a^* > 1$, and there exists a region $1 < a < a^*$, where the initial self-heating of system, after irradiation, changes then to the cooling due to heat-losses.

INFLUENCE OF OPTICAL MICRODISCONTINUITY

Optical discontinuity as absorbing microparticles being present in the reacting substance may essentially influence not only optical characteristics but the macrokinetics of chemical process as well. That is why the phenomenon of anomalously low threshold for laser-pulse initiation of some explosives is usually explained by the presence of absorbing microparticles (see, for example, Karabanov & Bobolev, 1981).

Common physical considerations make clear that large sooty or metallic particles heated by irradiation may considerably intensify the reaction in adjacent matter and, in particular, initiate a local thermal explosion of exothermic reaction. Evaluation of possible temperature disturbances is necessary to analyze this phenomenon.

This paper presents an asymptotic analysis of the thermal regime of an optically dense spheroid particle located in transparent reagent, Fig. 5.

The formulation of this problem differs from the well-known problem of thermal explosion of spherical reactor (Frank-Kamenetskii, 1969). In the case under consideration the reaction volume is out of sphere, and the reactor wall temperature is not known but the law of heat exchange is given. It is necessary to underline that initiation of thermal explosion of transparent reactive medium by continuous irradiation does not caused by the particle heat capacity. The reason for the thermal explosion is the effective absorption of radiant flux transferred by the particle to the surrounding medium.

The asymptotic analysis of this problem is carried out assuming that the activation energy of the bulk reaction is large enough. This analysis shows that quasi-steady temperature field around the particle can exist if the particle diameter D_1 does not exceed the critical one. The maximum temperature T_1 of adjacent layers is defined by

$$2R_g T_1^2 E_o^{-1} \rho q_o F_o(T_1) + \beta_1^2 (T_2 - T_1)^2 = 4\lambda^2 (T_1 - T_o)/D_1^2, \tag{2.1}$$
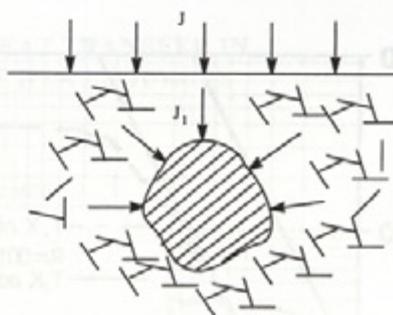
Fig. 5. Diagram of irradiation of particle enclosed in a scattering medium.

where $T_2 = T_0 + z\, J_1/\beta_1$ is an effective temperature; J_1 is density of radiative flux absorbed by particle; z is relative size of lighted part of particle surface, depending on light scattering in the substance ($1/4 \le z \le 1$); and β_1 is coefficient of heat exchange.

The equation (2.1) possesses the solution only in case $D_1 \le D_1^*$. Functional relations between critical values of particle diameter D_1, particle temperature T_1, and the radiation flux J_1 may be presented in parametric form (the asterisk indicating the critical values is omitted):

$$D_1 = 2\sqrt{2}\, l_0(T)/(e - 2\beta_1 l_0(T)/\lambda), \tag{2.2}$$

$$J_1 = e z \lambda (T - T_0)/\sqrt{2}\, l_0(T), \tag{2.3}$$

$$T_1 = T + 2R_g T^2/E, \quad e = 2.72.$$

Here T is an independent parameter, corresponding in the physical sense to the temperature of the particle (with diameter D_1^*) included in the inert substance ($q_o = 0$). The width of reaction zone at this temperature is the characteristic scale of the critical particle diameter.

THE SMALL PARTICLES PARADOX

Relationship between the critical diameter D_1^* and the characteristic width of the reaction zone l_0 is a function of the particle re-emission intensity. In a case of rather high reemission ($\beta_1 \ge e\lambda/\sqrt{2}l_0$), particles of any diameter do not induce the thermal explosion. If re-emission of the particle is negligibly small ($\beta_1 \ll \lambda/l_0$), the ratio of the critical diameter to the width l_0 is constant.

$$D1^*/l_0 = 2\sqrt{2}/e \cong 1.04. \tag{2.4}$$

In this case, the critical diameter D_1^* as a function of the particle temperature is similar to $l_0(T_1)$ (Fig.3), and the relationship is mutually unique. The explicit ratio between critical particle diameter and intensity of laser irradiation can be obtained from (2.3) and (2.4)

$$z J_1 = 2\lambda(T_1^o(D_1) - T_o)/D_1^*, \tag{2.5}$$

where T_1^o is the temperature of particle in inert medium:

$$T_1^o = T_o + z J_1 D_1/(2\lambda + \beta_1 D_1). \tag{2.6}$$

It follows from (2.5) that the product $J_1 D_1^*$ can be considered constant (when D_1 changes by one order of magnitude), since $T_1^o(D_1)$, (2.6), decreases insignificantly with increasing D_1.
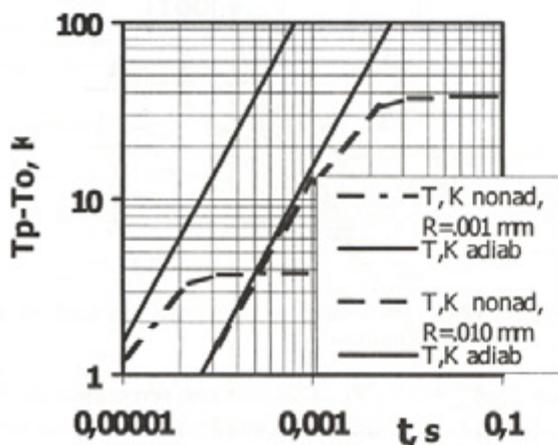
Fig. 6. Temperature of inert particle under irradiation in adiabatic and non-adiabatic cases.

The heat transfer from particle to environment during irradiation is frequently neglected in the literature on laser pulse interaction with substances. In such a case, the particle temperature in result of irradiation is proportional to the specific surface area of the particle and to the pulse duration (Fig.6):

$$T_1^o - T_o = 6zJ \ t_j/D_1\rho_1c_1 \ , \qquad (2.7)$$

where c_1 is the heat capacity of the particle.

A paradoxical result follows from (2.7) considering the substance ignition by incandescent particles in framework of the thermal theory (Goldshleger, et al., 1973). The smaller the particle, the more dangerous it is with respect to the explosives sensitivity to irradiation.. For example, it was believed for lead azide that the particles which are smaller than 10^{-5} cm cause the thermal explosion (Karabanov & Bobolev, 1981).

Additional factors, for example, the impossibility of combustion propagation beyond the boundary of a small focus, are invoked in the literature to explain the existence of the low threshold. However, the paradox can be resolved in framework of the thermal explosion theory.

Actually, duration of a short laser-pulse in the experiments is usually equal to $(3 \div 5) \cdot 10^{-8}$ sec. It is comparable with or greater than characteristic time of formation of the quasi-stationary temperature distribution around a small particle (with diameter $D_1 < 10^{-5}$ cm) located in substance having the thermal diffusivity $k \sim 10^{-2}$ cm²/sec.

The Eq.(2.7) is thus not applicable for such a small particle. It is more accurate to use Eq. (2.6) for estimation of the particle temperature. According to Eq.(2.6) the increase in the particle temperature is proportional to the particle diameter. For this reason, the extremely small particles cannot induce the thermal explosion of environment.

Application of Eqs. (2.2)-(2.4) to the problems of ignition by pulse irradiation requires to verify the condition of quasi-stationary temperature distribution around the particle. For quite large critical diameter the thermal relaxation time $(\sim D_1^2/k)$ can be comparable with the pulse duration t_j. In such a case the thermal inertia of particle must be taken unto account.

Analysis of the non-steady temperature field around the particle is illustrated by Figs. 6,7. The particle temperature in adiabatic case can significantly exceed that one in non-adiabatic case, even during short pulse-irradiation, as it is shown on Fig.6.
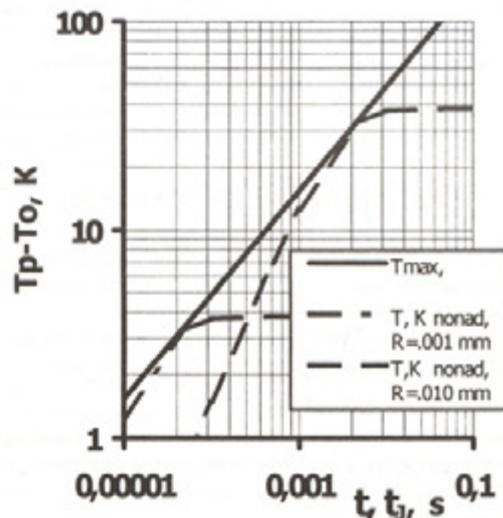
Fig. 7. The envelope $T_{max}(t_j)$ of the curves- family $T_1(t)$.

The maximum temperature disturbance is caused by particles of the medium size (Fig.7): $D_1 = 2(3t_j \ \lambda/\rho_1c_1)^{1/2}$

Only the particles of this size act as sensibilizators for the system irradiated during period t_j. Appropriate temperature disturbance induced by such a particle can be estimated using asymptotic formula: $T_1 - T_0 = zJ \ (3t_j/\lambda\rho_1c_1)^{1/2}$.

The critical condition of local explosion corresponds to a situation when appropriate characteristic thickness of reaction zone $l_0(T_1)$ is comparable with $D_1(\rho_1c_1/\rho \ c)^{1/2}$.

In conclusion we underline important role of the characteristic thickness of reaction zone l_0, Eq. (1.8), in non-isothermal processes. This thickness defines a scale for different critical sizes in the problem of laser pulse interaction with reactive substances.

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