Simulation of thermal explosion on the base of solution of the equation for the probability density function of particle temperature fluctuations

I V Derevich and A K Klochkov
Faculty of Fundamental Sciences, Department of Applied Mathematics, Moscow State Technical University by N.E. Bauman (MSTU), 2-ya Baumanskaya Str. 5 (main Building), Moscow, Russian Federation 105005
DerevichIgor@bmstu.ru (I V Derevich)

Abstract. The influence of temperature fluctuations of gas on the thermal explosion of particles with internal exothermic reactions is considered. The dependence of the rate of a chemical reaction on the concentration of a gas reagent is taken into account. Based on a rigorous system of heat and mass transfer equations, equations for the average temperature and concentration of the reagent inside the particle are obtained. A study of the dynamics of changes in the concentration of reagents and temperature inside the particle in a random field of temperature is carried out on the basis of the probability density function. Based on the solution of the systems of stochastic ordinary differential equations, a method of direct numerical simulation of random temperatures and reagent concentration in a particle is developed. A method for solving the equation for the probability density function is created. The results of comparing the empirical probability density function obtained by direct numerical simulation and the results of solving the equation for the probability density function are presented.

1. Introduction
In many technical applications, for example, in the combustion chambers of aircraft engines, thermal power plants, catalytic chemical reactors, as well as in natural phenomena, disperse systems of chemically reacting particles with significantly random temperature fluctuations have been found. Compared to the deterministic behaviour of systems, the presence of fluctuations in the parameters of the medium introduces fundamentally new effects in the physics of combustion and thermal explosion. The deterministic theory of combustion is fully developed [1, 2]. The problem of the influence of temperature fluctuations on the rate of chemical transformations is not entirely clear. In the Arrhenius model of a chemical reaction, the reaction rate depends exponentially on temperature. Therefore, one should expect a significant effect of fluctuations in the temperature of medium on the intensity of chemical transformations [3].

In the deterministic theory of combustion and explosion, the conditions of thermal explosion are determined by the critical temperature, the value of which depends on the geometry of the object and chemical kinetics [1-3]. The significant temperature dependence of the chemical reaction rate and the
extreme properties of random processes lead to fundamentally new effects, the study of which is of interest from the scientific and practical points of view [4].

Two methods of theoretical research are used. First, the method of direct numerical simulation of Lagrange. The Lagrange method is based on the calculation of the trajectories of random particles in the phase space of temperature and concentration. Modern methods of numerical solution of stochastic ordinary differential equations (SODE) are used. Averaging over an ensemble of random trajectories leads to an empirical probability density function (PDF). The second method is based on the Euler approach. In this case, a closed equation for the PDF of a random temperature and reagent concentration in a particle is constructed. We have developed an original method for the numerical solution of the equation for PDF.

2. Main equations

The equation for the temperature of particle \( \Theta_p (r, t) \) with internal heat release as a result of an exothermic chemical reaction has the form

\[
\rho_p c_p \frac{\partial \Theta_p}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( \lambda_p r^2 \frac{\partial \Theta_p}{\partial r} \right) + QA \left( \frac{Z_p}{Z_g} \right)^m \left( \frac{\Theta_p}{\Theta_g} \right)^n \exp \left( - \frac{E}{R' \Theta_p} \right)
\]  

(1)

Here \( \rho_p, c_p, \lambda_p \) are the density, heat capacity and heat conduction of the particle material; \( Q \) is thermal effect of the reaction; \( R' \) is universal gas constant; \( E \) is activation energy; \( A \) is the rate of chemical reaction; \( Z_p, Z_g \) are concentrations of gaseous reagent inside the particle and in the surrounding medium; \( m, n \) reaction order and empirical accounting of the combustion of a reactive particle material.

The equation for the concentration of the reagent inside the porous particle has the form

\[
\frac{\partial Z_p}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( D_p r^2 \frac{\partial Z_p}{\partial r} \right) - A \left( \frac{Z_p}{Z_g} \right)^m \left( \frac{\Theta_p}{\Theta_g} \right)^n \exp \left( - \frac{E}{R' \Theta_p} \right)
\]  

(2)

Here \( D_p \) is reagent diffusion coefficient in a porous particle.

Boundary conditions on the particle surface describe heat transfer and mass transfer

\[
\frac{\partial \Theta_p}{\partial r} \bigg|_{r=d_p/2} = \alpha_p \left( \Theta_p \bigg|_{r=d_p/2} - \Theta_s \right), \quad \frac{\partial Z_p}{\partial r} \bigg|_{r=d_p/2} = \beta_p \left( Z_p \bigg|_{r=d_p/2} - Z_g \right)
\]  

(3)

Here \( \alpha_p, \beta_p \) are heat and mass transfer coefficients; \( d_p \) is particle diameter.

As a result of averaging the equations (1)-(3) over the particle volume, we obtain equations for the average temperature and average concentration of the reagent inside the particle

\[
\frac{d\Theta_p (t)}{dt} = \frac{1}{\tau_\Theta} \left[ \Theta_s (t) - \Theta_p (t) \right] + QW \left( \Theta_p (t), Z_p (t) \right)
\]  

(4)

\[
\frac{dZ_p (t)}{dt} = \frac{1}{\tau_Z} \left( Z_s (t) - Z_p (t) \right) - W \left( \Theta_p (t), Z_p (t) \right)
\]  

(5)

Here \( \tau_\Theta, \tau_Z \) are thermal and diffusion relaxation times of the particle; rate of chemical reaction is

\[
W \left( \Theta_p, Z_p \right) = A \left( \frac{Z_p}{Z_g} \right)^m \left( \frac{\Theta_p}{\Theta_g} \right)^n \exp \left( - \frac{E}{R' \Theta_p} \right)
\]  

(6)

3. Equation for PDF of temperature and concentration in a particle

The temperature of the medium fluctuates near a certain average value

\[
\Theta_s (t) = \langle \Theta_s \rangle + \theta_s (t), \quad \langle \theta_s (t) \rangle = 0
\]
Here \( \langle \ldots \rangle \) denotes averaging over ensemble of random realization.

We simulate temperature fluctuations as a stationary random process with a given autocorrelation function

\[
\langle \theta_k(t')\theta_k(t^*) \rangle = \langle \theta_k^2 \rangle \Psi_{\theta}(t'-t^*)
\]

In accordance with the axioms of A.N. Kolmogorov we define an indicator function that cuts out random trajectories in phase space (see, for example, [5])

\[
\phi(\Theta_p, Z_p, t) = \delta(\Theta_p - \Theta_p(t))\delta(Z_p - Z_p(t))
\]

Here \( \Theta_p, Z_p \) are coordinates in the phase space; \( \delta(x) \) is Dirac delta function.

Applying the equations (4) and (5), we obtain a closed equation for the indicator function (Liouville equation)

\[
\frac{\partial}{\partial t} \Phi(\Theta_p, Z_p, t) + \frac{\partial}{\partial \Theta_p} \left[ \frac{1}{\tau_\theta} \langle \theta_k \rangle - \Theta_p \right] + QW(\Theta_p, Z_p) \Phi(\Theta_p, Z_p, t)
\] +
\[
+ \frac{\partial}{\partial Z_p} \left[ \frac{1}{\tau_z} \langle Z_k \rangle - Z_p \right] - W(\Theta_p, Z_p) \Phi(\Theta_p, Z_p, t) \right] = -\frac{1}{\tau_\theta} \frac{\partial}{\partial \Theta_p} \langle \theta_k(t) \rangle \Omega(\Theta_p, Z_p, t)
\]

PDF is obtained by averaging the indicator function \( \Phi(\Theta_p, Z_p, t) = \langle \phi(\Theta_p, Z_p, t) \rangle \). However, the equation for PDF is not closed

\[
\frac{\partial}{\partial t} \Phi(\Theta_p, Z_p, t) + \frac{\partial}{\partial \Theta_p} \left[ \frac{1}{\tau_\theta} \langle \theta_k \rangle - \Theta_p \right] + QW(\Theta_p, Z_p) \Phi(\Theta_p, Z_p, t)
\] +
\[
+ \frac{\partial}{\partial Z_p} \left[ \frac{1}{\tau_z} \langle Z_k \rangle - Z_p \right] - W(\Theta_p, Z_p) \Phi(\Theta_p, Z_p, t) \right] = -\frac{1}{\tau_\theta} \frac{\partial}{\partial \Theta_p} \langle \theta_k(t) \rangle \Phi(\Theta_p, Z_p, t)
\]

In a turbulent flow, fluctuations in the temperature of the medium along the particle trajectory are random Gaussian process. To identify the correlation \( \langle \theta_k(t) \rangle \Phi(\Theta_p, Z_p, t) \), we use the Furutsu-Novikov formula [5]. In the diffusion approximation, a closed equation is obtained for PDF fluctuations of temperature and reagent concentration in a particle

\[
\frac{\partial}{\partial t} \Phi(\Theta_p, Z_p, t) + \frac{\partial}{\partial \Theta_p} \left[ \frac{1}{\tau_\theta} \langle \theta_k \rangle - \Theta_p \right] + QW(\Theta_p, Z_p) \Phi(\Theta_p, Z_p, t)
\] +
\[
+ \frac{\partial}{\partial Z_p} \left[ \frac{1}{\tau_z} \langle Z_k \rangle - Z_p \right] - W(\Theta_p, Z_p) \Phi(\Theta_p, Z_p, t) \right] = \frac{Q^2}{\tau_\theta} \frac{\partial}{\partial \Theta_p} \left[ f_\theta(\Theta_p, Z_p, t) \frac{\partial}{\partial \Theta_p} \Phi(\Theta_p, Z_p, t) \right]
\]

Here, the response function \( f_\theta(\Theta_p, Z_p, t) \) takes into account not only the participation of particles in gas temperature fluctuations, but also the additional generation of temperature fluctuations as a result of a random change in the rate of a chemical reaction

\[
f_\theta(\Theta_p, Z_p, t) = \frac{1}{1 + (\tau_\theta/T_E)(1 - T_E/T_0(\Theta_p, Z_p))} \left[ 1 - \exp \left\{ -\frac{1 + (\tau_\theta/T_E)(1 - T_E/T_0(\Theta_p, Z_p))}{T_\theta}(t/\tau_\theta) \right\} \right]
\]

Here \( T_E \) is integral time scale of fluctuations in the temperature of the medium along the particle trajectory; \( \tau_0(\Theta_p, Z_p) \) is the so-called chemical time, which characterizes the time of the particle temperature changes due to an exothermic chemical reaction (equation (6))

\[
\tau_0(\Theta_p, Z_p) = Q \frac{\partial W(\Theta_p, Z_p)}{\partial \Theta_p}
\]
If the chemical time exceeds significantly the integral time scale \( T_E/T_Q \ll 1 \), then the response function coincides with the function of the passive impurity \( T \gg \tau \) \( \approx 1 \):

\[
0 \approx 1 \quad E_f T_\Theta \Theta \approx + \tau
\]

If the chemical time is comparable to the integral time scale \( T_E/T_Q \approx 1 \), then this leads to a significant increase in the response function. This is due to the contribution of fluctuations in the rate of a chemical reaction to particle temperature fluctuations.

4. Direct numerical simulation

The calculation of the random temperature and concentration of the reagent in a particle (equations (4)-(6)) is carried out by the modernized Runge-Kutta method, generalized to solve SODE. Modeling of temperature fluctuations of the medium with a given autocorrelation function is also carried out based on the solution of SODE

\[
\frac{d \eta_\Theta(t)}{dt} = \frac{1}{T_E} \left[ \eta_\Theta(t) - \Theta(t) \right], \quad \langle \eta_\Theta(t) \eta_\Theta(t') \rangle = 2 \tau_\Theta \langle \eta_\Theta^2 \rangle \delta(t' - t) \tag{9}
\]

Here \( \eta_\Theta(t) \) is a time-correlated random Gaussian process, generated by a computer; \( \eta_\Theta^2 \) is dispersion; \( \tau_\Theta \) is time micro scale. The general form of the system of equations (4)-(6), (9) is as follows

\[
\frac{dX(t)}{dt} = A(X(t),t) + B(X(t),t)\xi(t) \quad X(0) = X_0
\]

The two-step Runge-Kutta method of integration with \( s \)-stage has the form [6-8]

\[
x_j = X_j + \Delta t \sum_{i=1}^s R_{ij} A(x_j, t_j) + \sum_{i=1}^s \hat{R}_i B(x_j, t_j), \quad X_{j+1} = X_j + \Delta t \sum_{i=1}^s R_{ij} A(x_j, t_j) + \sum_{i=1}^s \hat{R}_i B(x_j, t_j)
\]

Here \( \xi = \sqrt{\Delta t} \xi, \xi \sim N(0,1) \) is random variable with Gauss distribution (computer), matrices \( R, \hat{R}, r, \hat{r} \) can be found elsewhere.

5. Numerical solution of the PDF equation

We constructed a conservative scheme for numerical integration of a closed equation for PDF (8) using the “method of lines”. We demonstrate the basic idea of solving the PDF equation (8) in the one-dimensional case. We used the idea of the paper [9]. General view of the equation for PDF in the diffusion approximation is

\[
\frac{\partial}{\partial t} \Phi(\Theta,t) + \frac{\partial}{\partial \Theta} \left[ F(\Theta) \Phi(\Theta,t) \right] = \frac{\partial}{\partial \Theta} \left[ D(\Theta,t) \frac{\partial}{\partial \Theta} \Phi(\Theta,t) \right]
\]

The equation for the PDF in a transformed form is

\[
\frac{\partial \Phi(\Theta,t)}{\partial t} + \frac{\partial W(\Theta,t)}{\partial \Theta} = 0 \quad F'(\Theta) = F(\Theta) + \frac{\partial D(\Theta,t)}{\partial \Theta}
\]

\[
W(\Theta,t) = F'(\Theta) \Phi(\Theta,t) - \frac{\partial}{\partial \Theta} \left[ D(\Theta,t) \Phi(\Theta,t) \right]
\]

For the temperature range \( \Theta_{\text{min}} \leq \Theta \leq \Theta_{\text{max}} \), the PDF balance condition is satisfied if \( W(\Theta_{\text{min}}) = 0, \quad W(\Theta_{\text{max}}) = 0 \). We write the system of non-stationary, conservative finite-difference equations in the form of a system of ODE

\[
\frac{d\Phi_i^0}{dt} = \frac{2}{h_i} \left\{ -F_{i+1/2}^0 \Phi_{i+1/2}^0 + \frac{D_{i+1}^0 \Phi_i^0 - D_i^0 \Phi_i^0}{h_i} \right\}, \quad i = 1, \quad \Theta_i = \Theta_{\text{min}}
\]

\[
\frac{d\Phi_i}{dt} = -\frac{F_{i+1/2}^i \Phi_{i+1/2}^i - F_{i-1/2}^i \Phi_{i-1/2}^i}{h_i} + \frac{1}{h_i} \left\{ \frac{D_{i+1}^i \Phi_i^i - D_i^i \Phi_i^i}{h_i} + \frac{D_{i-1}^i \Phi_{i-1}^i - D_{i-1}^i \Phi_{i-1}^i}{h_{i-1}} \right\}, \quad i = 2 \ldots N-1 \tag{10}
\]

4
Here the coordinates of the grid nodes are equal
\[ h_i = x_{i+1} - x_i, x_{i+1/2} = \left(x_{i+1} + x_i\right)/2, \]
PDF approximation at intermediate points has the form
\[ \Phi^e_{i+1/2} = \theta_{i+1/2} \Phi^e_i + (1-\theta_{i+1/2}) \Phi^e_{i+1}, \theta_{i+1/2} = \left(1 + \left|F^e_{i+1/2}/F^e_{i+1/2}\right|\right)/2. \]
Note that the difference scheme (10) has a second order of approximation with respect to spatial variables. The initial distribution of PDF is \( \Phi(\Theta, t)_{t=0} = \Phi(\Theta). \) The ODE system (10) is numerically integrated with Runge-Kutta method with automatic step selection.

6. Calculation results
We present the results in dimensionless variables, which are used in papers on the theory of combustion and explosion. Dimensionless temperature \( \Theta_p' = E'(\Theta_p - \langle \Theta_s \rangle)/\langle \Theta_s \rangle, \) dimensionless activation energy \( E' = E/R \), dimensionless time \( t' = tA \exp(-E') \). The dimensionless equations for temperature and concentration are as follows
\[ \frac{d\Theta_p'}{dt'} = \frac{1}{\tau_{\Theta}} \left( \langle \Theta_s' \rangle - \Theta_p' \right) + Q' Z_p^m \left(1 + \Theta_p'/E'\right)^m \exp\left\{ \Theta_p'/\left(1 + \Theta_p'/E'\right) \right\} \]  
\[ \frac{dZ_p'}{dt'} = \frac{1}{\tau_Z} \left(1 - Z_p' - Z_p^m \left(1 + \Theta_p'/E'\right)^m \exp\left\{ \Theta_p'/\left(1 + \Theta_p'/E'\right) \right\} \right) \]
At a stationary temperature of the medium, the equations (11), (12) have (in the general case) three roots. Figure 1 shows a diagram of N.N. Semenov [2] with a fixed concentration of the reagent \( Z_p' \) in the particle. Here \( W_p' \langle \Theta_p' \rangle = \Theta_p'/\tau_{\Theta} \) is heat transfer generation. It can be seen from the figure that there is a critical temperature \( \Theta_{cr}' \), an infinitely small excess of which leads to a thermal explosion. The dynamics of thermal explosion in random media is illustrated in figure 2. It can be seen that a thermal explosion will occur even at a low initial temperature equal to the average temperature of the medium (figure 3). Due to fluctuations in the rate of a chemical reaction, fluctuations in the temperature of inertial particles reach high values. Here \( \Omega_{\Theta} = \tau_{\Theta}/T_E \) is parameter of thermal inertia of particles. We emphasize that in the deterministic case (see figure 1) thermal explosion at such initial particle temperatures is impossible in principle.
7. Main conclusions
The paper presents two methods for studying the loss of thermal stability of a particle during internal exothermic reactions at a random temperature of the surrounding medium. The calculation results are presented for the case when in the deterministic case there is a critical temperature, the excess of which leads to a thermal explosion. In this situation, temperature fluctuations always lead to a thermal explosion, even if the initial particle temperature is much lower than the critical temperature.

It is seen (figure 3) that the probability of a thermal explosion is high even at a low initial temperature of particles entering the medium with temperature fluctuations. It is also seen that in the deterministic theory a thermal explosion at such initial particle temperatures is impossible.

Acknowledgments
This work was supported by the Russian Foundation for Basic Research (project code No. 17-08-00376).

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