An influence of expressions for thermophysical parameters on calculation results of melting and detonation combustion of aluminum suspensions

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Abstract. The influence of the method for determining the specific heat coefficient on the processes of aluminium melting and propagation of heterogeneous detonation in a mixture of gas and ultrafine aluminum particles is analyzed. Melting process is described within the phenomenological approach for particles with a radius of 6 and 15 nm. An insignificant effect of the relation between the heat capacity and the particle temperature and radius on melting time and temperature distribution inside the particle has been established. The detonation process is studied for stoichiometric suspensions of 50-nm and 1-μm aluminum particles, taking into account the transition from diffusion to kinetic regime of combustion with decreasing particle size. An insignificant influence of the specific heat coefficient representations on the results of detonation structure calculations is established for nanoparticles. For micron aluminum particle suspensions, the 20% difference in the Chapman-Jouguet pressure has been obtained.

1. Introduction
Aluminum dusts are widely used in various industries in view of high-energy characteristics of aluminum particles. Ultrafine aluminum has a potential to be considered as one of the components of fuel. As a result the influence of the thermophysical characteristics of aluminum on the processes of melting and combustion of micro and nanoparticles is of interest. As is known, with a decrease in the size of nanoparticles, it is possible to change some of the thermophysical properties, the so-called scale effect [1].

There are several approaches to modeling the processes taking place in nanoparticles. One way is the molecular dynamics method [2, 3]. Another way of modeling the processes of interaction with nanoscale particles is the phenomenological approach [4, 5]. Previously [4], the description of the melting process of a nanoparticle was carried out using a non-classical one-phase Stefan problem, however, in solving this problem, the bulk parameters of the particle were used. Melting studies in a similar formulation for a two-phase medium were carried out in [5, 6]. Since the thermophysical parameters of the metal nanoparticles depend on the particle size and temperature, it is interesting to investigate the effect of these dependences on the melting process.

As for the detonation combustion of aluminum particles, a strong influence of method of specifying the heat capacity on temperature and pressure was shown in [7]. In work [8], the analysis of structures of detonation waves in gas suspensions of micro- and nanoparticles was carried out. However, the effect of representation of thermophysical parameters on the melting processes and the role of these
processes in the propagation of detonation are not analyzed. This paper studies the effect of method of specifying of the specific heat coefficient on the stationary structures of plane detonation waves.

Simulation was carried out in two stages. At the first stage, a phenomenological approach was used to describe and analyze characteristics of the melting process of a single aluminum nanoparticle. The second stage was the investigation of the influence of representation of the specific heat coefficient on the detonation wave structure for the gas suspension of micron and nanosized aluminum particles.

2. Analysis of the melting process of a single aluminum particle

Consider a nano-crystal of aluminum, which is placed in a high-temperature field. It is assumed that the temperature distribution in the core of the particle is determined from the energy conservation equation [4-6]

\[ \rho c_p \frac{\partial T}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left( \frac{\partial}{\partial r} \left( \lambda \rho \nu \frac{\partial T}{\partial r} \right) \right), \] (1)

in the area \( 0 \leq r \leq r_{p0} \) with boundary conditions

\[ r = r_{p0}, \quad T = T_c \] (2)

and initial conditions

\[ T(0, r) = T_0, \quad 0 \leq r < r_{p0}. \] (3)

At the center of the particle the symmetry condition is set. Here \( \rho, \lambda, c_p, r_{p0} \) are the density, thermal conductivity, heat capacity and initial radius of the nanoparticle, \( \nu \) is the symmetry index, equal to 0, 1, 2 for Cartesian, polar and spherical coordinates, respectively. Thermophysical parameters of the solid-melt system are given in [5]. Dimensionless quantities are determined by characteristic time \( t_0 = \rho c_p r_{p0}^2 / \lambda \), \( r_{p0} \) the is initial particle radius, and \( T_0 \) is the particle temperature at the normal condition.

The Stefan problem (1) - (3) considered above was solved to determine the influence of method of specifying of the specific heat coefficient on the melting process of aluminum particles. The initial-boundary value problem was solved by the direct method [9].

Approximation of the dependence of the heat capacity coefficient of \( c_p(T) \) for aluminum is presented below.

1. Specific heat of particles with allowance for scale effects. Earlier in [10], the method for determining the heat capacity and thermal conductivity of aluminum nanoparticles is described. The results obtained are approximated. Approximation of the specific heat coefficient was carried out using the formula:

\[ c_p = \alpha_2 + \beta_2 \left( T_0 \right) \exp \left( -\gamma_2 \left( T_0 \right) \left( T - T_c \left( r_{p0} \right) \right)^2 \right), \] (4)

2. Bulk material heat capacity. To approximate the dependence of \( c_p(T) \) or bulk aluminum, we used a piecewise linear function:

\[ \begin{align*}
    c_p &= 0.55T + 737, \quad T \leq 933^\circ K \\
    c_p &= 1176 J / (kg \cdot ^\circ K), \quad T > 933^\circ K
\end{align*} \] (5)

3. The description of specific heat with constant value \( c_p=128 J/(kg \cdot ^\circ K) \) at \( T=300 K \)

The simulation was realized for particles with a diameter of 12 nm and 30 nm.

The simulation results are shown in Fig. 1. Figures 1a and 1b show calculations for a particle with a diameter of 12 nm and 30 nm, respectively. In general, the melting process proceeds as follows. At the external boundary, the temperature is constant and equal to \( T_c=1200 K \). As can be seen, within the framework of the single-phase Stefan problem, the distribution of the phase temperature is as follows. In solid phase, the temperature is constant and equal to the melting point, while in liquid phase it changes from a temperature equal to that at the outer boundary of the particle to the melting temperature at the interface between the liquid and solid phases. In accordance with the mechanism of
melting of nanoscale objects, as this boundary moves into the solid core, the melting point temperature decreases [4-6].

From the temperature distribution in the particle, it can be seen that for the same instant of time, the particle with a constant specific heat value (Figure 1) is heated most rapidly, both for a 12 nm particle and for a particle with a diameter of 30 nm. At time \( t=0.01 \), the temperature distributions in the particle are close, regardless of the heat capacity. In Fig. 1a, one can clearly see that the particle with constant heat capacity melts most rapidly (dot-dashed curve, \( t=0.38 \)), then for the particle where specific heat is specified with formula (5) for bulk material (dashed line, \( t=0.4 \)). The melting time for the particle where the heat capacity specified for nanoparticles according to formula (4) is about 0.5, and the phase transition point coincides for all the considered cases. A similar effect of method of specifying of the specific heat on the process of melting of larger particle is observed in Fig. 1b.

For 12 nm particles, nonlinear effects in the region of complete melting of the particle are practically invisible. For a 30-nm particle it is seen that in the region of complete penetration of the particle, the function is smoothed (Fig. 1b). It is also clear that thermograms of melting are fairly close for all the time segments considered. The melting times are also commensurable. For a particle with a diameter of 30 nm, the greatest difference in the melting times is \( \Delta t=0.2 \), and for a particle with a diameter of 12 nm, \( \Delta t=0.12 \).

![Figure 1](image_url)

**Figure 1.** Thermograms of melting of aluminum particles with diameters a) 12 nm and b) 30 nm. Dotted lines - the heat capacity value according to the formula (4), solid lines - the heat capacity value according to the formula (5), the dash-dotted line - using the constant value of heat capacity, and the dot curve - the melting temperature dependence on the particle radius for aluminum.

On the whole, the obtained results prove that the use of different approaches for describing the specific heat coefficient has little effect on the determination of the melting time and temperature distribution.

### 3. Detonation combustion of gas suspensions of aluminum particles

It is known, that for particles with the size below 2 – 3 nm the combustion regime changes from the diffusion one, when burning time is proportional to the particle diameter \( \tau_b \sim d^2 \), to the kinetic regime, when \( \tau_b \sim d^{0.3} \) [11]. The effect of using the actual value of the specific heat coefficient for aluminum particles was also analyzed, when the specific heat was determined using the approximating function \( c_p(T) \), taking into account the phase transition processes in aluminum particles (melting and evaporation of aluminum particles). The basic equations express the laws of conservation of mass, momentum, and energy for each of the phases and components, the system is closed by the equations of state and relations for the processes of mass transfer between components (evaporation, condensation, combustion), pulse exchange (resistance forces), and heat exchange between gas and particles. More detailed information about the model is presented in the works [8, 12].
More detailed description of burning of aluminum particles is expedient. We take into account the transition from the diffusion to the kinetic regime of combustion for particles smaller than 3.5 μm. The equation of reduced kinetics is characterized by the Arrhenius dependence. In the range from 500 nm to 3.5 μm, the activation energy was 32 kJ/mol as in [8, 12-15]. Dependence between characteristic burning time of the particles and their diameter considering data [11, 16] is:

\[ \tau_\psi = \tau_0 (d / d_0)^{0.3} \exp \left( E_a / RT \right) \]

where \( d_0 = 3.5 \mu m \) and \( \tau_0 = 0.294 \, ms \).

Burning model of the nanoparticles is described by based on generalization of the data [11, 17] for stoichiometric suspension of the aluminum in oxygen, where \( d_0 \leq 250 \, nm \),

\[ \tau_\psi = \tau_0 (d / d_0)^{0.3} \exp \left( E_a / RT \right)(p / p_0)^{m} \]

where \( d_0 = 80 \, nm \), \( p_0 = 8 \, atm \); \( E_a = 60 \, kJ/mole \), \( m = 0.5 \), and \( \tau_0 = 0.25 \, ms \).

In [8, 12-16] the value of \( c_{v,2} = 880 \, J/kg-K \) was used as heat capacity. To refine the model, it was suggested to use the heat capacity approximation, which is described by formula (5). Using the coefficient of heat capacity obtained for aluminum nanoparticles is inadvisable when considering particles larger than 30 nm in diameter, where, due to insignificant scale effects, it is possible to use thermophysical parameters for a bulk material (5).

For nanoparticles with 50 nm diameter the parameters behind the front of the detonation wave are shown in Fig. 2. Calculations were made considering the particle diameter \( d < 250 \, nm \) using (7). Three heat capacity models were used: \( c_{v,2} = 880 \, J/kg-K \) - black curves, \( c_{v,2} \) according to the formula (5) - red curves, and \( c_{v,2} = 1176 \, J/kg-K \) - blue curves. Fig. 2a shows the distribution of temperatures and particle velocities behind the front of the detonation wave for the gas (solid lines) and for particles (dashed lines). It can be seen that the initial growth of the gas temperatures for both considered representations for \( c_{v,2} \) proceeds according to a similar scenario. Temperatures grow up to approximately 2100K, after which their values begin to fall until reaching the equilibrium temperature between the gas and the particles. For the function \( c_{v,2}(T_2) \), initial increase in the gas temperature, a slightly higher peak value, about 100 K, is observed, after which the temperature also decreases, until the temperature equilibrium of the system occurs.

The particle temperature for all the considered cases increases similarly, however, it is worth noting that the blue and red curves occur later than in the case of the black curve, both in time and in temperature. Similar behavior was observed in the study of the phenomenological problem of nanoparticle melting, when using different approaches to the description of the specific heat coefficient, close melting times were obtained, but there was a slight discrepancy in the particle temperatures. In general, it is also evident that the melting time for all three cases is approximately the same and does not depend on the method of specifying the heat capacity.

Despite these differences, in the melting zone of particles the equilibrium temperature occurs approximately at the same time, at \( t = 6 \times 10^{-6} \, ms \). Rapid equilibrium is also achieved in the same period of time. It is worth noting that the temperature equilibrium is achieved for the red and black curves at about the same temperature below 1400 K, and for the blue curve, the temperature equilibrium is reached at a lower temperature of 1200 K. The latter can be caused by the large value of the heat capacity coefficient for the same amount of spent energy.

From Fig. 2b it can be seen that the use of different approaches to the description of heat capacity practically does not affect pressure distribution behind the detonation wave front. The pressure increase occurs almost immediately behind the front of the detonation wave, after which a chemical reaction of the combustion of aluminum particles occurs. Because of the higher heat capacity, in the model corresponding to the blue curve, the burning reaction takes a little longer than for the other models. As a result, the pressure retains an increased value for a longer period of time. Reducing the pressure on the black and red curves occurs according to a similar scenario.
Figure 2. Parameters of the detonation wave ($c_{v,2}=880$ J/kg·K - black curves, $c_{v,2}$ according to the formula (5) - red curves, $c_{v,2}=880$ 1176 J/kg·K - blue curves). a) parameters for achieving the speed and thermal equilibrium of the system (solid line-gas, dotted line-particles), b) pressures behind the front of the detonation.

Consider the structure of the detonation wave for particles with a diameter of 1 μm. Calculation of the kinetics was carried out taking into account the transition combustion regime by formula (6). The temperature distributions are shown in Fig. 3. The heating rate of micro and nanoparticles differs by orders of magnitude (Figures 2 and 3). For micron particles, the thermal equilibrium is reached at about $t=0.04$ ms. Particle burning using model (5) (red curve) occurs at a lower temperature at initial instants of time, but equilibrium temperature is reached at the same time as for the models with constant heat capacity (black and blue curves). The difference in equilibrium temperatures for the blue and black curves is about 30K. It is worth noting that the temperature of micron particles does not exceed the evaporation temperature, in contrast to the detonation combustion of aluminum nanoparticles.

The pressure distributions determined for the suspension of particles of 1 μm in size are shown in Fig. 3b. It is seen that the pressure for $c_{v,2}=1176$ J/kg·K (blue curve) and $c_{v,2}$ by formula (5) (red curve) exceeds the value determined in [14, 15] with $c_{v,2}=880$ J/kg·K (black curve) by 10 and 15 atm, respectively. It is also clear that the peak pressure falls on different periods of time.

Figure 3. The parameters behind the detonation wave for a particle suspension of 1 μm. ($c_{v,2}=880$ J/kg·K - black curves, $c_{v,2}$ according to the formula (5) - red curves, $c_{v,2}=880$ 1176 J/kg·K - blue curves). a) parameters for achieving the thermal equilibrium of the system (solid line-gas, dotted line-particles), b) pressures behind the front of the detonation.
From the obtained results, it can be concluded that the heat capacity models considered do not lead to significant differences in the results of calculations of detonation combustion of aluminum particles. The use of the function (5) to describe the specific heat gives rise to an elevated temperature behind the shock wave front both for gas and for micro- and nanoparticles. In this case, the influence of models on the description of ignition delay processes and the times for achieving temperature and velocity equilibrium are negligible. After reaching the temperature equilibrium, there is a slight decrease in temperature by 10-30 K for micron and nanoparticles. For micron particles, the pressure in the Chapman-Jouguet plane is increased by 10 atm, which is caused by increased energy release during the combustion reaction. It should be noted that the authors of [7] observed a considerable decrease in temperature (about 200 K) when the heat capacity of type (5) was used to describe the detonation combustion of particles.

4. Conclusions
The study has shown that the use of the considered approaches for describing the specific heat coefficient: in the form of a constant value and approximation by exponential representations, taking into account the dependence on temperature and particle radius, has little effect on the determination of the melting and temperature distribution times.

In detonation combustion, the use of the function (5) to describe the specific heat gives increased by 10% temperature behind the shock front for the gas, both for micro- and nanoparticles. At the same time, the effect on the processes of ignition delay and the achievement of temperature and velocity equilibrium are negligible. For micron particles, the use of formula (5) leads to somewhat higher values of pressure in the Chapman-Jouguet plane (by no more than 10 atm), due to the increase in energy release in chemical reaction. Using bigger value of the heat capacity leads to increase of the releasing energy.

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