TO THE THEORY OF IGNITION, COMBUSTION AND DETONATION OF MICRO- AND NANOPARTICLES

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This work is devoted to the review of some papers which were done in the domain of mechanics of reacting heterogeneous media (MRHM) of micro- and nano- structure. The review consists of some parts.

In the first part we were investigated the problems of physical and mathematical modeling of melting of nanoparticles of Al, Fe. We use the methods of molecular dynamics to describe the problems. This allows to determine the melting temperature, the heat capacity and some other parameters of the melting nanoparticles. Numerical data were compared with experimental one. We got a good correspondence between melting temperature vs particles radius dependences. Then new physical and mathematical phenomenological models were proposed to describe the process of melting of metal nanoparticles. These models took into account the experimentally observed fact of reduction of the melting temperature with decreasing particle radius. Two-front modes of melting were found for the first time for thermal fields of plane, cylindrical, and spherical

particles. The melting times for different types of symmetry were found to be ordered, and the corresponding approximation dependences of this parameter on the particle size were derived.

The second part of the paper was devoted to mathematical modeling of the burning of micro- and nano- particles from the point of view of MRHM. The hierarchy of the models for describing the ignition, burning of these physical objects was presented. This allowed us to describe the time of ignition and combustion of the particles of different sizes at different temperatures and pressures of the environment. Comparison with some of the available experimental data has shown the adequacy of the models. We pay also attention to the problems of detonation suppression by the clouds of inert solid particles.

Keywords: mathematical modeling, nanoparticles, molecular dynamics, heterogeneous detonation, suppression, mixture of a gas and reactive particles.

The mathematical modeling of nanoparticles heating. The problem of physical and mathematical modeling of various processes in nanoparicles during their heating is of significant interest owing to certain unique properties manifested by these objects. There are several approaches to simulating the behavior of such objects under various types of loading. We used two of them: molecular dynamics method and phenomenological approach of mechanics of heterogeneous media. Really, it seems of interest to apply the molecular dynamics method for obtaining characteristic thermodynamic parameters of nanosystems reflecting their dependences on the state parameters and size, which are necessary for

phenomenological models, in order to use them later on in less computationally expensive phenomenological models.

In [1], we proposed a model of melting of metal nanoparticles within the framework of a single-phase Stefan problem which permit one to describe the experimentally established fact the melting temperature reduction with decreasing particle radius. The dynamics of the temperature fields in the cases of melting of aluminum and gold nanoparticles calculated on the basis of the single-phase and two-phase approaches was demonstrated to be in reasonable agreement. The dependences of the melting time of aluminum and gold nanoparticles on the particle radius and ambient temperature were obtained. In our later study of aluminum nanoparticle melting [2], we proposed and verified a semi-empirical model of molecular dynamics with a glue potential, which provided an adequate description of the thermal history of particles 2–8 nm in size. Based on this model, the specific heat of the particles and the latent phase transition heat were found as functions of the particle size and temperature. With increasing particle size, this dependence was found to tend to a limiting function, which describes the specific heat of the particle in a massive sample. A comparison of the characteristics of aluminum nanoparticle melting calculated by the molecular dynamics method and phenomenological model revealed their reasonable agreement in terms of the melting time. In [3], we described the procedure of calculating the melting process of an aluminum nanocrystal with a size 2–8 nm within the framework of the molecular dynamics method with the use of the embedded atom potential of the

DL POLY Classic software package [4] and with H.Sheng's parametrization [5]. Among other aspects, in [3] we justified our previous semiempirical model [2] developed for describing the dependence of the crystal melting temperature on the crystal size. The resultant specific heats ensure a qualitatively correct description of their dependences on the temperature and crystal size.

Now, let us consider a metal nanocrystal located into the Evans thermostat [6, 7]. Some numerical data presented below. Figure 1 shows the results of calculations of heat capacity. As the particle size increases, the peak of the heat capacity curve corresponding to the melting point decreases, and the heat capacity tends to the value corresponding to the bulk sample. For determining the thermal conductivity λ, we use the equilibrium method based on the Green–Kubo formalism [8, 9, 10]:

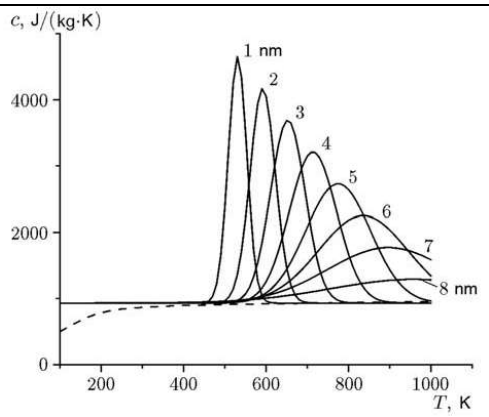

Fig. 1. Approximation (5) of the specific heat as a function of the temperature and particle size: the nanoparticle sizes are indicated by the numbers at the corresponding curves; the dashed curve show the specific heat of the massive sample.

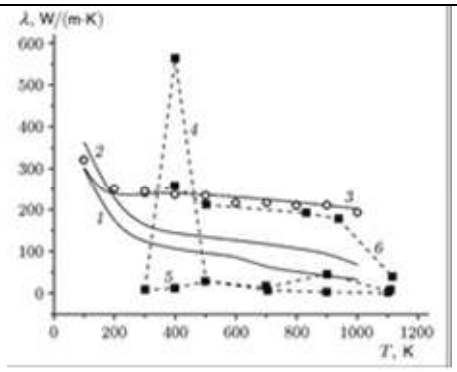

Fig. 2. Thermal conductivity versus temperature: curves *1–3* show the authors' data for particles 3 (*1*) and 7 nm (*2*) and for a massive sample (*3*); curves *4–6* show the authors' data [12] for clusters composed of 500 (*4*) and 256 articles (*5*) and for a massive sample (*6*).

Fig. 2 shows the results of our calculations for the thermal conductivity as a function of temperature for aluminum nanoparticles 3 and 7 nm in size (curves 1

and 2), and also for a massive sample (circles). As the temperature increases, the thermal conductivity tends to decrease, which can be attributed to scattering of phonons in metals [11]. On the other hand, as the nanoparticle size increases, the thermal conductivity approaches the value typical for the massive sample from below. The results of modeling of the thermal conductivity of the massive sample agree well with experimental data (curve 3). The difference between our results and those obtained in [12] can be explained by the fact that Taherkhani and Rezania [12] used the Sutton–Chen potential, which provides an inadequate description of the melting temperature as a function of the particle size, as was demonstrated in [13].

Iron particles. In [14–16] molecular dynamics models of iron, nickel and others metals heating was presented. In [17] iron spherical nanoparticle heating was investigated. Amount of atoms in these particles varies from 2000 to 56781 atoms, moreover the investigation of heat capacity and heat conductivity coefficients were found too. Some results concerning the melting temperatures were presented in this paper. It was found an empirical coefficient in the dependence between melting temperature Tm and particle radius r . The heat capacity and thermal conductivity of iron particles were found too and presented in analytical form.

Problem of nanoparticle melting in the phenomenological formulation was described in the non-classical single-phase Stefan problem in [18, 19]. Based on the phenomenological approach, the thermal history of the melting particle was

determined within the framework of the model with thermophysical parameters depending on the particle size and temperature *T*. The influence of these parameters was analyzed. Among other phenomena, a two-front mode of nanoparticle melting ("layered cake") induced by scaling was reveal.

Ignition, burning and detonation of micro- and nano- particles and its mixtures with air. We present a point wise mathematical model to describe the burning of Al nanoparticle in oxygen and air in [20]. The paper describes this process for the nano-size aluminum particles (80 nm), which provides an adequate description of the burning time in the range of initial pressures $p0 \in (8, 32)$ atm and temperatures $Ten \in (1200, 2200)$ K with variations of the fraction of oxygen in the mixture from 10 to 50%. A physicomathematical model of ignition of suspensions of aluminum particles under dynamic conditions including melting, low-temperature oxidation of aluminum, and polymorphic transformation of the oxide film was presented in [21]. Model verification is based on experimental data

on the limit temperatures and delays of ignition of suspensions of aluminum particles in shock and detonation waves. Applicability of reduced models (without melting and pre-frame oxidation) at an adequate temperature criterion that ensures identical ignition delays is demonstrated, based on the analysis of thermal dynamics of the mixture. Dependences of the ignition temperature on the shock wave parameters, particle size and concentration, and oxidizer concentration are obtained. Formulas for an invariant (with respect to concentrations) criterion are derived, which express the dependence of the ignition temperature on the current temperature of the gas. The governing constants are found for suspensions of particles in air and oxygen. The problems of diffraction of detonation waves in the mixture of a gas and aluminum particles were investigated in [21, 22, 23]. Propagation of heterogeneous detonation in a mixture of oxygen and fine aluminum particles in a plane channel with a backward-facing step was studied numerically. Possible scenarios of evolution of this flow after its passage to the expanded part of the channel were analyzed. The effect of the particle size and channel geometry on detonation propagation/failure was found. Cellular detonation was formed in the wide part of the channel, with a subsequent change in the cell size in the course of establishment of a steady propagation regime. The cell size in steady regimes was invariant with respect to the flow formation process. The problems of mathematical modeling of detonation suppression were discussed in [24]. These investigations were partly supported by the projects RSF 16-19-00010, RFBR – 15-08-01947.

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