Composition of vapor around a refractory particle under the action of laser radiation

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The processes leading to expansion of a vapor-gas cloud produced by the action of laser radiation on a refractory particle are considered. Cooling of the vaporized substance due to the expansion causes the overcooling of vapor and its partial condensation. However, the overcooling does not disappear completely and differs somewhat from zero value that corresponds to the saturation state. This difference is most significant in the case with small particles. We propose a criterion for determining the starting point at which an essential deviation from the saturation state occurs.

The action of high-power laser radiation on a refractory aerosol particle can be accompanied by warming up of the particle substance to temperatures of several thousand degrees as high. At such temperatures the vaporization completely suppresses heterogeneous combustion, because of the displacement of the oxidizer from the particle surface, and thus it mainly governs the changes in the particle size. The vaporized substance spreads at a high speed (of the order of local speed of sound in the vapor) and forms a vapor-gas halo around the particle. If we ignore the processes of homogeneous combustion at the edges of the halo or consider the case of expansion of a substance into the inert atmosphere or vacuum, then we should consider recondensation of the vaporized substance that takes place due to cooling of the vapor because of its almost adiabatic expansion as the basic process which can cause a change of the composition of expanding vapor-gas cloud. Two tendencies can be considered in the formation of secondary aerosol. First, it can be considered as a way to form aerosol particles of very small sizes in the nanometer range. Second, we can consider it as a process causing dissipation of energy added from a laser beam owing to the attenuation of radiation by secondary particles.

Earlier such a problem was solved by use of the thermodynamic approximation[1] that, as it will be shown below, is quite rough approximation for particles of natural atmospheric aerosols, i.e., for particles with the sizes up to 50 μm.

As numerical estimations for the regimes of developed vaporization show the concentration of atmospheric gases near the surface of a particle practically equals to zero, and the high-speed expansion can be accompanied by the appearance of a shock wave (abrupt difference of thermodynamic parameters[2]) at certain distance from a particle. This allows one to divide the space around a particle in two regions, in the case of the substance expansion into the atmosphere. The solution in the region between the particle surface and the shock wave front can be constructed using the same equations as in the case of expansion into vacuum. Considering the expanding cloud to be a single-component substance in a biphase state (with the possibility of interphase transitions) and ignoring the heat conduction of the mixture, as well as viscosity and pressure diffusion, and reducing the heat transfer to the stirring (that does not distort the result too much), and also using the well-grounded approximations of quasi-stationarity and spherical symmetry[3] we obtain the following system of first-order differential equations:

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(-r^2\rho_{\mathrm{v}} v\right) = J; \tag{1}$$

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\rho_{\mathrm{c}} v\right) = J; \tag{2}$$

$$v\frac{\partial v}{\partial r} = -\frac{1}{m_0(\rho_{\mathrm{c}}+\rho_{\mathrm{v}})}\frac{\partial P}{\partial r}; \tag{3}$$

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2 v\Big((\rho_{\mathrm{v}}C_V^{\mathrm{v}} + \rho_{\mathrm{c}}C_V^{\mathrm{c}})T + P + (\rho_{\mathrm{c}}+\rho_{\mathrm{v}})m_0 v^2/2\Big)\right] = \Big[L + (C_V^{\mathrm{c}} - C_V^{\mathrm{v}})T\Big]J; \tag{4}$$

$$J = \frac{\mathrm{d}}{\mathrm{d}t}\left(\int\limits_a^r I(r')g(r, r')\,\frac{\mathrm{d}r'}{v'}\right), \tag{5}$$

here ρ_{c} and ρ_{v} are the densities of the substance in condensed and vapor phases, r if the radial variable, v is the average mass rate of expansion, J is the velocity of interphase exchange, m_0 is the mass of atom, P is the pressure, T is the temperature, C_V^{c} and C_V^{v} are the heat capacity of condensed and vapor phases for constant volume, L is the specific heat of condensation, $I(r)$ is the number of nuclei arising in a unit of volume per unit time, $g(r, r')$ is the number of molecules in a secondary particle formed at a point with the coordinate r' and reached up the point with the coordinate r.

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A question on the correct statement of the boundary conditions for the flux of expanding substance is very complex within the given problem. The difference between the thermodynamic parameters, which occurs near the surface of a particle that is intensely vaporized and is connected with the "Maxwellization" of the flux,[4] causes significant overcooling in the flux and, as a result, recondensation of the vaporized substance can occur. Under that strong overcooling $\theta = (T_p - T)/T_p \approx 0.3$ (T_p is the temperature of vapor saturated at a given density) it is only time that is needed to remove it by the formation of nuclei

$$\Delta t \sim (an_0)/(\bar{v}I(\theta)g_*) \sim 10^{-9}\ \text{s}, \tag{6}$$

here a is the radius of the initial particle, n_0 is the number of molecules that constitute the secondary particles, $\bar{v}$ is the mean velocity of vapor molecules, g_* is the number of molecules in the critical nucleus. This allows one to judge on the rate of the given process in a globular layer with the thickness $\delta x \sim (\Delta t\bar{v}) \sim 0.1a$.

A smallness of thickness of the layer of nucleus formation allows one again to reformulate the boundary conditions of the problem relative to the surface of a particle

$$\begin{gathered} T = 0.92T_\text{s},\ j = 0.82j_\text{s}, \\ \rho_\text{v} = 0.295\rho_\text{s},\ \rho_\text{c} = 0.015\rho_\text{s}, \end{gathered} \tag{7}$$

where j is the flux of vaporized substance, and the index s points the magnitudes of values near the surface.

Refining the boundary conditions, which decreases the initial supersaturation down to zero, allows us to write the expression (5) for the rate of substance condensation under expansion in a more simple form. It is supposed within the framework of the approximation of monodisperse composition (N identical nuclei of solid phase are formed) that the nucleus-formation occurs at the initial stage only

$$J = N\frac{\mathrm{d}g}{\mathrm{d}t} \approx N4\pi\, a_0^2\, g^{2/3}\rho_\text{v}\bar{v}\left[1 - \frac{T_p}{T}\exp\left(\frac{L}{kT_p} - \frac{L}{kT}\right)\right]. \tag{8}$$

Here a_0 is the size of a vapor molecule, k is the Boltzmann constant.

Completing the system (1)–(5) with the characteristic equation for gas phase $P = \rho_\text{v}kT$ along with the boundary conditions, we obtain a mathematical simulation of the problem.

Let us sum and integrate two first equations from the system (1)–(5), thus obtaining the law of conservation of flux $j = 4\pi r^2(\rho_\text{v} + \rho_\text{c})$. In the penultimate equation for energy (4) we can neglect in its right-hand side the difference between the specific heat capacities of vapor and condensed phase, then the equation can easily be integrated

$$\rho_\text{v}\left[(C_V^\text{v}T + m_0v^2/2) + P + \rho_\text{c}(C_V^\text{c}T + m_0v^2/2)\right] = \frac{q}{4\pi r^2 v} + \rho_\text{c}L, \tag{9}$$

here q is the total flux of energy from a particle.

The relationship between the volume of a single molecule (ω) and the volume of a secondary particle with the radius a_sec, and also between the concentration and condensation degree $[\beta = \rho_\text{c}/(\rho_\text{c} + \rho_\text{v})]$ is

$$g\omega = 4\pi a_\text{sec}^3/3,\quad Ng = \rho_\text{c} = \beta(\rho_\omega + \rho_\text{c}). \tag{10}$$

Also for the pressure of saturated vapor we can use the expression

$$P = P_\infty \exp[-L/(kT)], \tag{11}$$

where P_∞ is the constant value.

Then the expression (8) for the condensation rate takes the form

$$J = \frac{3\omega}{a_\text{sec}}\beta(1-\beta)(\rho_\text{v} + \rho_\text{c})^2\,\bar{v}\left[1 - \frac{P_\infty}{P}\exp\left(-\frac{L}{kT}\right)\right]. \tag{12}$$

Performing a substitution of variables as follows below

$$\breve{T} = T(r)/T_0,\ \breve{P} = P/P_A,\ x = -a/r,\ \breve{v} = v/v_0, \tag{13}$$

we obtain two algebraic equations and two differential equations of the first-order

$$\frac{m_0\, v_0^2}{kT_0}\, x^2\, \frac{\mathrm{d}\breve{v}}{\mathrm{d}x} = -\frac{\mathrm{d}\breve{P}}{\mathrm{d}x}\,; \tag{14}$$

$$\breve{T} + \frac{m_0\, v_0^2}{2C_p^\text{v}T_0}\,\breve{v}^2 = \frac{q}{jC_p^\text{v}T_0} + \beta\left(\frac{L}{C_p^\text{v}T_0} + \frac{k}{C_p^\text{v}}\,\breve{T}\right); \tag{15}$$

$$\breve{P}\breve{v} = (1-\beta)x^2T; \tag{16}$$

$$\frac{\mathrm{d}\beta}{\mathrm{d}x} = H\,\frac{\beta(1-\beta)\sqrt{\breve{T}}}{\breve{v}^2}\left[1 - \frac{P_\infty}{P_A\breve{P}}\exp\left(-\frac{L}{kT_0\breve{T}}\right)\right], \tag{17}$$

where T_0 and P_A are the temperature and pressure of the environment at the infinity or the characteristic temperature and pressure, $v_0 = jkT_0/(4\pi a^2P_A)$ is the characteristic velocity, $H = \omega\bar{v}(T_0)j/(4\pi a a_\text{sec}v_0^2)$.

We substitute the pressure in the first equation with the third one then differentiate the second equation (15) (to exclude the derivative of temperature) and obtain the system prepared for calculations, which is formed from the equations (16), (17), and two equations that follow:

$$\breve{T} = \left(\frac{q}{jC_p^\text{v}T_0} + \frac{\beta L}{C_p^\text{v}T_0} - \frac{m_0v_0^2}{2C_p^\text{v}T_0}\,\breve{v}^2\right)\Big/\left(1 - \frac{\beta k}{C_p^\text{v}}\right); \tag{18}$$

$$\frac{\mathrm{d}\breve{v}}{\mathrm{d}x} = \\ = \frac{-\dfrac{1}{x}(1-\beta) + \dfrac{\mathrm{d}\beta}{\mathrm{d}x}\left[-1 + \dfrac{C_p^\text{v}(1-\beta)}{C_p^\text{v} - \beta k}\left(\dfrac{L}{C_p^\text{v}T_0\breve{T}} + \dfrac{k}{C_p^\text{v}}\right)\right]}{\dfrac{m_0\, v_0^2}{kT_0}\,\dfrac{C_V^\text{v} - \beta k}{C_p^\text{v} - \beta k} - (1-\beta)\,\dfrac{\breve{T}}{\breve{v}^2}}\,\frac{\breve{T}}{\breve{v}}\,. \tag{19}$$

Solution of this system which is sought over the whole space of values of the coordinate [−1; 0] is the solution of the problem on the quasi-stationary dispersal of a vaporized substance into the vacuum and allows us to take into account more correctly the change of the condensation rate which occurs due to the decrease of vapor density under the expansion. Solution presented in Ref. 1 has a disadvantage in the sense that the pressure is assumed to be equal to the pressure of a saturated vapor.

However, at a certain distance from the surface of a particle the process of condensation ceases and "hardening"[5] process starts. As a criterion of the condensation cessation we can use the point, at which in the stage of the still going on expansion the effective number of collisions among the vapor molecules reaches unity

$$N_{\mathrm{eff}} = \int\limits_{t_0}^{\infty} \frac{v\,\mathrm{d}t}{l} = 1, \tag{20}$$

where $l = (\sqrt{2}\pi d^2 \rho_0)^{-1}$ is the free path. If we pass from the integration over time to the integration over the a spatial coordinate we obtain

$$N_{\mathrm{eff}} = \sqrt{2} j a_0^2 \int\limits_{r_{\mathrm{cr}}}^{\infty} \frac{\mathrm{d}r}{r^2 v} = 1. \tag{21}$$

Ignoring the change in the rate after the onset of "hardening", what is physically justified, we obtain

$$x_{\mathrm{cr}} = -\frac{\sqrt{2\pi m_0/kT_{\mathrm{s}}}}{4.64\pi a_0^2\, \rho_p(T_{\mathrm{s}})} \frac{v}{a}. \tag{22}$$

To compare the results, we construct the solution of the system (1)–(5) assuming the pressure to be equal to the pressure of saturated vapor. Consecutively excluding from the equations the pressure and both concentrations (with the characteristic equation and Eq. (11)) we obtain one algebraic equation and one first-order differential equation

$$\frac{j m_0}{4\pi r^2} \frac{\mathrm{d}v}{\mathrm{d}r} = -\frac{L P_\infty}{kT^2} \exp\left(-\frac{L}{kT}\right) \frac{\mathrm{d}T}{\mathrm{d}r}; \tag{23}$$

$$\left(1 + \frac{L}{kT}\right) \exp\left(-\frac{L}{kT}\right) = \frac{j}{4\pi r^2 v P_\infty} \left(\frac{q}{j} + L - C_V^{\mathrm{c}} T - \frac{m_0 v^2}{2}\right). \tag{24}$$

One can see from the equations (23) and (24) that their product enables one to exclude the spatial variable and to obtain the differential first-order equation that relates the rate to temperature

$$\left(1 + \frac{L}{kT}\right) m_0 v \frac{\mathrm{d}v}{\mathrm{d}T} = -\left(\frac{q}{j} + L - C_V^{\mathrm{c}} T - \frac{m_0 v^2}{2}\right) \frac{L}{kT^2}\cdot \tag{25}$$

Hence, integrating the equation (25) in the sense of decreasing the temperature, that is physically correct under conditions of expansion, we can construct the dependence $v(T)$ from which we can directly determine the corresponding dependences $v(r)$ and $T(r)$ using the equation (24).

Let us normalize the system of equations (23)–(24) by analogy with the Eq. (13)

$$x = -\left[\frac{\dfrac{2kT_0 P_\infty}{m_0 v_0^2 P_A} \left(1 + \dfrac{L}{kT_0} \dfrac{1}{\breve{T}}\right) \exp\left(-\dfrac{L}{kT_0} \dfrac{1}{\breve{T}}\right)}{\dfrac{2q}{j m_0 v_0^2} + \dfrac{2L}{m_0 v_0^2} - \dfrac{2C_V^{\mathrm{c}} T_0}{m_0 v_0^2} \breve{T} - \breve{v}^2} \right]^{0.5}; \tag{26}$$

$$\frac{\mathrm{d}[\breve{v}^2]}{\mathrm{d}[1/T]} = \left(\frac{2q}{j m_0 v_0^2} + \frac{2L}{m_0 v_0^2} - \frac{2C_V^{\mathrm{c}} T_0}{m_0 v_0^2} \breve{T} - \breve{v}^2\right) \Big/ \left(\frac{1}{\breve{T}} + \frac{kT_0}{L}\right). \tag{27}$$

Basic results of the joint numerical solution of the systems of equations (16)–(19) and (26)–(27) for various sizes of the initial particles are presented in Figs. 1 and 2.

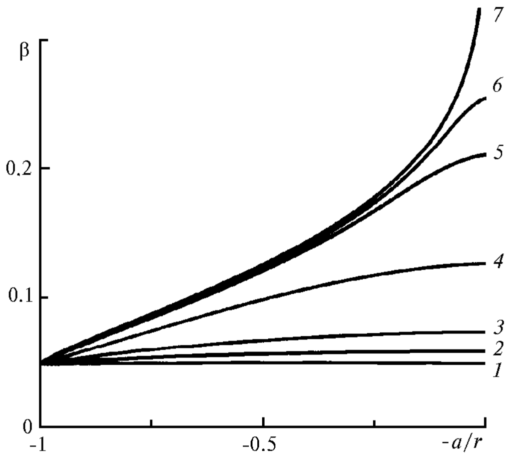

Fig. 1. Dependence of the condensation degree of vaporized substance (β) on the inverse distance to the initial particle (−a/r) for its various sizes: 10 (*1*); 50 (*2*); 100 (*3*); 200 μm (*4*); 0.5 (*5*); 1 mm (*6*); the saturated vapor (*7*).

The solutions show that in the flux of a gas, which is expanded from vaporized primary particles with the size $a \le 50$ μm practically no recondensation occurs, and the value of condensation degree at a large distance from a particle is a little bit larger than its initial value, i.e., the flux is practically a single-phase one. For large particles with the size $a \ge 250$ μm the condensation degree achieves 30%, and the vapor at a considerable distance has time "to watch" the supersaturation. These results are confirmed by the calculation of x_{cr} in accordance with the relation (22) too.

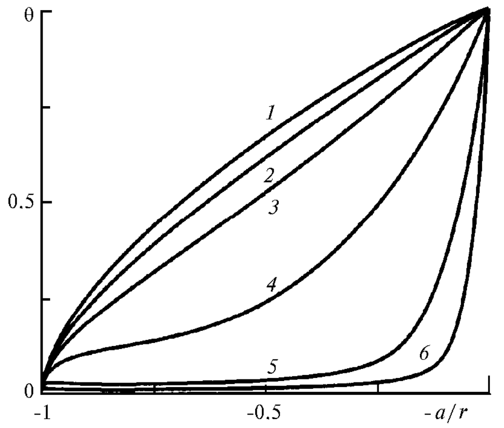

Fig. 2. Dependence of the overcooling in the flux (θ) on the inverse distance to initial particle ($-a/r$) for its various sizes: $a = 10$ (*1*); 20 (*2*); 50 (*3*); 100 (*4*); 200 (*5*); 500 μm (*6*).

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