Journal of Engineering Physics and Thermophysics, Vol. 78, No. 1, 2005

INFLUENCE OF SURFACE PROCESSES AND EXTERNAL FIELDS ON TRANSFER PHENOMENA AND PHASE TRANSITIONS IN AEROSOL SYSTEMS WITH NANO-SIZE PARTICLES

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UDC 541.182

The influence of dimensional effects, surface phenomena, and resonance radiation on the transfer processes and phase transitions in aerosol systems with nano-size particles is theoretically investigated.

In recent years, transfer phenomena in two-phase systems, where one phase represents nano-size objects, in particular, nanoparticles, nanotubes, and fullerenes, have attracted the increasing attention of researchers. It is well known that the influence of surface processes occurring on the interfaces increases with decrease in the size of the objects. If the nano-size objects are in the gas phase, the mean free path of gas molecules in a number of cases is larger than the characteristic dimension of the objects or comparable to it. This leads to the necessity of considering transfer processes in a wide range of variation of the Knudsen number, determined by the ratio of the mean free path to the characteristic dimension. Furthermore, new regularities arise in the course of phase and chemical transformations on the particle surface with decrease in the characteristic dimension, for example, in the radius of a spherical nanoparticle. These regularities are, in particular, due the dependence of the condensation (sticking) coefficient on the particle size. Phase transitions and chemical reactions on the particle surface can also depend on the influence of the external fields (for example, of resonance laser radiation). In this work, the influence of dimensional effects, surface phenomena, and resonance radiation on the transfer processes in aerosol systems is studied theoretically using the growth of a small aerosol particle in physical deposition from a gas phase as an example.

It is well known that an authentic description of the transfer processes in a gas–aerosol particle system with arbitrary Knudsen numbers and phase transitions on the particle surface can be performed only by solving the Boltzmann kinetic equation [1]. However, the arising mathematical difficulties do not enable one to obtain fairly simple expressions for the resulting molecular flux into the particle. Such relations can be found either from an approximate solution of the Boltzmann equation or by the use of simpler models based on the diffusion equation. Thus, for example, in [2] the possibility of using the diffusion equation was discussed, including the case where the particle radius is smaller than the mean free path of the gas molecules.

We will not dwell on the numerous theoretical approaches available in the literature that enable us to obtain an approximate expression for the resulting flux of vapor molecules into the particle. Based on what has been said above, we will describe the problem of mass transfer in the vapor–buffer gas–particle system by the diffusion equation with boundary conditions set at $r = R$ and $r \to \infty$. The distribution of the number density of vapor molecules in the vicinity of a spherical particle in the quasisteady approximation has the form [1]

$$n = A - \frac{B}{r}\,, \tag{1}$$

where A and B are the integration constants determined from the boundary conditions.

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We suppose that $n = n_\infty$ at $r \to \infty$; whence it follows that $A = n_\infty$. The second boundary condition with the Maxwell velocity distribution function of vapor molecules can be written, in view of [3], as

$$D \left. \frac{dn}{dr} \right|_{r=R} = (1 - \theta) \left(\frac{kT}{2\pi m} \right)^{1/2} \left[\alpha n (R) - \alpha_e n_e \exp \left\{ \frac{2\sigma V_m}{RkT} \right\} \right] . \tag{2}$$

We note that the condensation coefficient for fairly small aerosol particles generally depends on their size [4, 5]. When the radiation, which is resonant relative to vapor molecules, acts on the vapor–particle system, the condensation coefficient with the two-level model of molecular transitions from one state to another is determined by the expression [6]

$$\alpha = \alpha_1 - \gamma (\alpha_1 - \alpha_2) . \tag{3}$$

Here, the quantity $\gamma = n_2/(n_1 + n_2)$, which characterizes a part of the excited molecules, in the steady case can be found from the system of equations describing molecular transitions from one state to another [7]:

$$\frac{dn_1}{dt} = \frac{I\sigma'}{h\nu} (n_2 - n_1) + \frac{n_2}{\tau_r} , \tag{4}$$

$$\frac{dn_2}{dt} = \frac{I\sigma'}{h\nu} (n_1 - n_2) - \frac{n_2}{\tau_r} . \tag{5}$$

Under the stationarity condition, we have for γ

$$\gamma = \frac{(I\sigma'/h\nu)\, \tau_r}{1 + (2I\sigma'/h\nu)\, \tau_r} . \tag{6}$$

It should be noted that the surface tension generally depends on the pressure of a foreign gas, the molecules of which can adsorb on the particle (drop) surface, resulting in a decrease in this coefficient. In [8], the expression for the dependence of the surface tension on the pressure of the adsorbing gas P_a with consideration for the Langmuir adsorption isotherm was obtained:

$$\sigma (P_a) = \sigma_0 - n_0 kT \ln \left(\frac{P_a + P_0}{P_0} \right) , \tag{7}$$

where P_0 can be represented as

$$P_0 = \frac{n_0 (2\pi m_a kT)^{1/2}}{\beta\tau} . \tag{8}$$

Taking (1)–(8) into account, with allowance for [3, 5], we can obtain the expression for the critical diameter of the particle (drop) d_{cr}, which is determined by the condition of equality of the resulting molecular flux into the particle to zero:

$$d_{cr} = \frac{4}{\ln (\alpha s/\alpha_e)} \left[\frac{\sigma_0 V_m}{kT} - V_m n_0 \ln \left(1 + \frac{P_a}{P_0} \right) \right] . \tag{9}$$

As follows from (9), the critical diameter depends on the ratios P_a/P_0 and $\alpha s/\alpha_e$. These quantities can change both with excitation of vapor molecules due to the change in the condensation coefficient α and with excitation of the

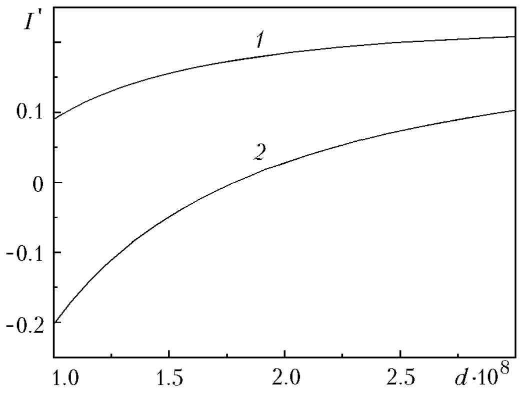

Fig. 1. Dependence of the dimensionless density of the resulting flux I' of vapor molecules into a water drop on its diameter at T = 273 K, s = 1.4: 1) $\alpha = \alpha_e = 1$; 2) $\alpha' = \alpha_e = 1$, $\alpha = \alpha' \exp\left\{-6\sigma V_m/(dkT)\right\}$. d, m.

molecules of the foreign gas because of the change in the sticking coefficient β and, correspondingly, in P_0. It is worth noting that the value of the critical particle diameter determined by the classical expression of Kelvin $d_{cr} = 4\sigma V_m/(kT \ln s)$ [9] does not contain the condensation coefficient of vapor molecules.

It is well known that the rate of homogeneous nucleation substantially depends on the critical dimension of the clusters formed [9]. Therefore, change in this critical dimension related to the surface effects has a fairly strong influence on the rate of homogeneous nucleation and the growth of the arising clusters. This can be used for control of the process of formation and growth of nano-size particles. It should be noted that the initiation (observed experimentally) of a nucleation process in the field of electromagnetic radiation can be associated with the increase in the condensation coefficient of vapor molecules in the radiation field.

We consider the question on the resulting flux of vapor molecules into the particle. For the sake of simplicity, we assume that the dependence of the condensation coefficient on the particle size is the same for excited and unexcited molecules and is determined as [4]

$$\alpha = \alpha' \exp\left\{-\frac{6\sigma V_m}{dkT}\right\}, \tag{10}$$

and the condensation coefficient of unexcited vapor molecules for the plane surface and the evaporation coefficient are equal to unity.

Molecules of the foreign gas, adsorbed on the particle (drop) surface, can both increase the resulting flux of vapor molecules into the particle due to the lowering surface tension and decrease it because of the interface blocking. Based on what has been said above and on [3, 5], we obtain in the isothermal case the following expression for the resulting flux of vapor molecules into the particle, which allows for the dependence of the condensation coefficient on the particle size, the influence of resonance radiation, and the presence in the system of the foreign-gas molecules adsorbing on the particle surface:

$$I = \frac{\dfrac{[1-\gamma(1-\alpha_2')]\,P_\infty}{(2\pi mkT)^{1/2}} \exp\left\{-\dfrac{6\sigma_0 V_m}{dkT}\right\}\left(1+\dfrac{P_a}{P_0}\right)^{3G/2} - \dfrac{P_e}{(2\pi mkT)^{1/2}} \exp\left\{\dfrac{4\sigma_0 V_m}{dkT}\right\}\left(1+\dfrac{P_a}{P_0}\right)^{-G}}{1+\dfrac{P_a}{P_0}+\dfrac{3\,[1-\gamma(1-\alpha_2')]}{4\mathrm{Kn}} \exp\left\{-\dfrac{6\sigma_0 V_m}{dkT}\right\}\left(1+\dfrac{P_a}{P_0}\right)^{3G/2}}\,. \tag{11}$$

Here $G = 4V_m n_0/d$ and $\mathrm{Kn} = 2\lambda/d$, λ is the mean free path of vapor molecules.

Figure 1 compares the dimensionless densities of the resulting flux of vapor molecules into a water drop $I' = I(2\pi mkT)^{1/2}/P_\infty$ both in the case where the condensation coefficient is assumed to be independent of the drop size and with the dependence according to (10) (the values of γ and P_a are assumed to be zero, for the sake of simplicity, and

$Kn \gg 1$). As follows from the results presented, a decrease in the condensation coefficient of vapor molecules with decrease in the particle size reduces the value of the resulting flux of these molecules into the particle and, correspondingly, the rate of its growth. Consideration of the dependence of the condensation coefficient on the particle size can lead to a qualitative change in the course of the process (transition from the regime of growth of particles to their evaporation). The change of sign in the resulting molecular flux into the particle may also be due to the adsorption of molecules of the foreign gas on the particle surface [10] and to the change in the condensation coefficient in the field of electromagnetic radiation [6]. These regularities can be used for control of phase-transition processes in aerosol systems with nano-size particles.

It should be noted that, when the excitation of vapor molecules in the field of resonance radiation takes place with the difference in the condensation coefficients for excited and unexcited molecules and if the dependence of the condensation coefficient on the particle size is allowed for, the assumption on equality of the evaporation and condensation coefficients, which is commonly taken (and was used in [4]), becomes incorrect and can lead to qualitatively incorrect results.

With decrease in the condensation coefficient of vapor molecules in the field of resonance radiation, thermal and resonance effects (heating of particles by radiation and molecular excitation) reduce the rate of particle growth. When the radiation-excited molecules are characterized by a larger condensation coefficient than unexcited ones, thermal and resonance effects act in different directions and their partial compensation can be realized.

It is worth noting that in nanotechnologies, in addition to the problems related to the formation and growth of nano-size systems, the problems of control of nanoparticle motion are pressing. In particular, this is important in deposition of thin films used for creation of different devices in microelectronics. In some cases, it is necessary to keep the nanoparticles from arriving at the film (for example, in obtaining films of a high-purity substance); in others, it is necessary to deposit nanoparticles (in particular, for modification of the physicochemical properties of the film obtained). Control of the particle motion is possible by phoretic forces acting on the aerosol particles.

It is well known that the effect of electromagnetic radiation on aerosol systems can lead to the occurrence of thermophoretic and (or) photophoretic forces experienced by the particles due to the arising temperature drop in the gas phase or in the particles themselves, respectively. New characteristic features of momentum transfer to the aerosol particles by gas molecules (which lead to the occurrence of new components of the phoretic force acting on the particles) can take place in the case where radiation is resonant relative to the gas molecules. This is connected with the difference in the interaction of the gas molecules excited by resonance radiation and unexcited ones with the particles, which results in a change in the parameters, such as, in particular, the indicatrix of molecular scattering by the surface and the condensation (sticking) coefficient of molecules. Let a nonuniform illumination of the aerosol particles or detuning of the radiation frequency from the resonance frequency of the gas molecules, which leads to the excitation of molecules, flying in a certain direction, due to the Doppler effect (velocity-selective excitation), take place. Then the parameters characterizing the molecular–particle interaction can change along the particle surface, which is capable of causing the occurrence of new components of the force acting on the aerosol particles [11, 12]. Here, the new components of the phoretic force differ from zero, even though the temperature gradients in the particles and in the gas phase are equal to zero, which is of crucial importance in cases where the forces related to the occurrence of temperature gradients can be neglected.

Thus, the study conducted enabled us to analyze the influence of dimensional effects, surface phenomena, and resonance radiation on the formation of nano-size aerosol particles in the process of condensation of vapor molecules. Factors like the dependence of the condensation coefficient on the particle size, excitation of vapor molecules in the field of resonance radiation, and the presence of a foreign gas in the system that adsorbs on the particle surface are shown to result in a change in the critical dimension of a particle. This, in particular, affects the rate of homogeneous nucleation. If the dependence of the condensation coefficient on the particle size is allowed for, the assumption of equality of the condensation and evaporation coefficients, which is commonly taken, collapses. The resonance-radiation effect on the aerosol system leads to the occurrence of new components of the phoretic force acting on the aerosol particles, which opens up new possibilities of controlling their motion by resonance radiation.

This work was carried out with partial support from GACR, project No. 104/02/1079, and GAASCR, project No. IAA2076203.

NOTATION

D, diffusion coefficient of vapor molecules, m^2/sec; d, particle diameter, m; h, Planck constant, J·sec; I, density of the radiation flux, J/(m^2·sec); k, Boltzmann constant, J/K; Kn, Knudsen number; m, mass of a vapor molecule, kg; m_a, mass of a molecule of the adsorbing gas, kg; n, number density of vapor molecules, m^{-3}; n_e, number density of molecules of a saturated vapor above the plane surface of phase transition, m^{-3}; n_0, number of adsorption centers per unit surface, m^{-2}; P_a, pressure of the foreign adsorbing gas, N/m^2; P_e, saturation-vapor pressure above the plane surface, N/m^2; P_∞, vapor pressure at an infinite distance from the particle, N/m^2; Q_a, adsorption energy of a molecule of the foreign gas, J; R, particle radius, m; r, radial coordinate counted from the particle center, m; s, saturation ratio; T, temperature, K; t, time, sec; V_m, volume per molecule in the particle, m^3; α, condensation coefficient; α', condensation coefficient for the plane surface; α_e, evaporation coefficient; β, coefficient of sticking of molecules of the foreign gas to the surface's part free from adsorbed molecules; θ, surface coverage by the adsorbed molecules of the foreign gas; ν, radiation frequency, sec^{-1}; σ, surface tension, N/m; σ', resonance-absorption cross section, m^2; σ_0, surface tension of a pure liquid, N/m; τ, adsorption time of molecules of the foreign gas, sec; τ_r, relaxation time of excited molecules, sec. Subscripts: a, adsorption; cr, critical; e, evaporation; m, molecule; r, relaxation; 1 and 2, nonexcited and radiation-excited molecules.

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