Journal of Engineering Physics and Thermophysics, Vol. 77, No. 5, 2004

POLYMOLECULAR FILMS ON THE SURFACE OF AEROSOL PARTICLES

V. V. Levdanskii,[a] **J. Smolik,**[b]
and P. Moravec[b]

UDC 541.182

The influence of the size of aerosol particles and their heating by incident radiation on the critical thickness of polymolecular films on the particle surface is theoretically investigated.

Investigation of the regularities of deposition of thin films on aerosol particles is extremely important for both the atmospheric processes related to the formation of polymolecular water films on the particles and in the processes of modern technology, for example, in obtaining nanoparticles coated with a film of another substance (in particular, such coatings are used in heterogeneous catalysis to increase the catalytic efficiency of particles). The thickness of the resulting film depends on the particle size, the saturation ratio of the substance deposited, the presence of foreign-gas molecules, which can adsorb on the film surface and change the surface tension, in the gas phase, and on the influence of external fields (for example, of resonance radiation). It should be noted that the formation of a substance layer on the aerosol particle can occur both in chemical deposition and by ordinary vapor condensation (physical deposition). Below are considered some problems connected with determination of the thickness of a liquid polymolecular wetting film on the aerosol particle in physical vapor deposition. It is pertinent to note that, as the saturation ratio of the vapor increases, a state can be reached where spontaneous vapor condensation begins on the interface and the particle–film system transforms to a drop–nucleus system. Determination of the parameters for which this transformation occurs is important both for atmospheric processes and in a number of technological processes when phase transitions in the presence of aerosol particles take place.

We consider the problem on the critical (equilibrium) thickness of a film on an aerosol particle. The particle–film–gas system is considered to be isothermal. Taking account of [1–3] and assuming the Langmuir mechanism of adsorption of a foreign gas on the film surface, we can write the following equation for the rate of growth of the film thickness in the quasistationary approximation:

$$n\,\frac{dh}{dt}=\frac{\dfrac{\alpha P_\infty}{(2\pi mkT)^{1/2}}\,\dfrac{P_{\mathrm{L}}}{P_{\mathrm{a}}+P_{\mathrm{L}}}-\dfrac{\alpha_{\mathrm{e}}P_{\mathrm{e}}}{(2\pi mkT)^{1/2}}\exp\left\{\dfrac{1}{kT}\left(\dfrac{4\sigma_0 V_{\mathrm{m}}}{d+2h}-Q_i\right)\right\}\left(\dfrac{P_{\mathrm{L}}}{P_{\mathrm{a}}+P_{\mathrm{L}}}\right)^{G+1}}{1+\alpha\,\dfrac{P_{\mathrm{L}}}{P_{\mathrm{a}}+P_{\mathrm{L}}}\,\dfrac{3\,(d+2h)}{8\lambda}}\,. \tag{1}$$

Here, $G = 4V_{\mathrm{m}}n_0/d$; the quantity Q_i characterizes the change in the energy of evaporation from a flat film as compared to that for a flat massive sample; the values of Q_i for liquid films of polar (for example, water) and nonpolar substances respectively (Q_1 and Q_2) with allowance for [3] can be written as

$$Q_1 = K\exp\{h/\beta\}\,V_{\mathrm{m}}\,, \tag{2}$$

$$Q_2=\frac{A}{6\pi h^3}\,V_{\mathrm{m}}\,. \tag{3}$$

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[a] A. V. Luikov Heat and Mass Transfer Institute, National Academy of Sciences of Belarus, 15 P. Brovka Str., Minsk, 220072, Belarus; [b] Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic; email: vlev5@yahoo.com. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 77, No. 5, pp. 41–45, September–October, 2004. Original article submitted October 21, 2003.

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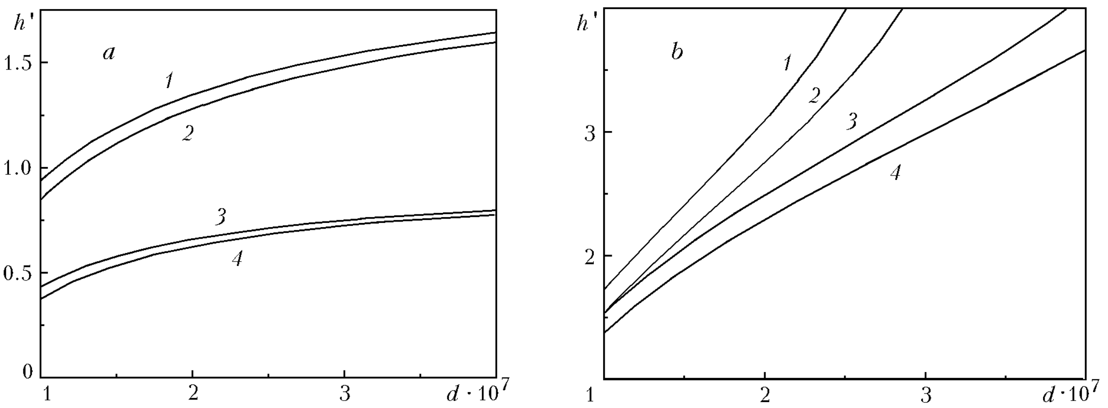

Fig. 1. Dependence of the dimensionless critical thickness h' of a water film on the diameter d of an aerosol particle at $K = 10^7$ N·m^{-2}, $T = 273$ K, $P_a/P_L = 0.5$ (curves 1 and 3), and $P_a/P_L = 0$ (curves 2 and 4): a) $s' < 1$ (1 and 2 for $s' = 0.99$; 3 and 4 for $s' = 0.97$); b) $s' > 1$ (1 and 2 for $s' = 1.007$; 3 and 4 for $s' = 1.004$). d. m.

According to [3], the value of K for polymolecular water films on quartz, glass, and mica is of the order of 10^7 N·m^{-2} and the parameter β changes from 2.3 to 3.3 nm; it was assumed in the derivation of (2) that the polymolecular film was in stable form (so-called α-film [3]). The quantity P_L can be represented as follows:

$$P_L = \frac{n_0 (2\pi m_a kT)^{1/2}}{\alpha_1 \tau} . \tag{4}$$

Equation (1) makes it possible to calculate the growth rate of polymolecular film with account for the diffusion resistance and the effects related to surface processes and to find critical values of the quantities for which the particle–film–gas system is in equilibrium. We consider the problem on the critical film thickness on a small spherical particle. Setting $dh/dt = 0$ and $h << d$ in (1) and disregarding, in the first approximation, the term $2h$ in the sum $d + 2h$, which enters into the exponent, we obtain from (1)–(3) the following expressions for the critical film thickness of polar (h_1) and nonpolar (h_2) substances respectively:

$$h_1 = \beta \ln \left\{ \frac{kT}{KV_m} \left[\frac{4\sigma_0 V_m}{dkT} - \ln \left(s' \left(\frac{P_a + P_L}{P_L} \right)^G \right) \right] \right\}^{-1} , \tag{5}$$

$$h_2 = \left\{ \frac{AV_m}{6\pi kT} \left[\frac{4\sigma_0 V_m}{dkT} - \ln \left(s' \left(\frac{P_a + P_L}{P_L} \right)^G \right) \right]^{-1} \right\}^{1/3} . \tag{6}$$

Here, $s' = \alpha s/\alpha_e$; s is the vapor-saturation ratio which characterizes the ratio of the partial vapor pressure to the saturated-vapor pressure above the flat surface of a massive sample.

As follows from (5) and (6), the value of the critical film thickness increases with particle diameter and pressure of the foreign adsorbable gas which decreases the surface tension (it is assumed, for the sake of simplicity, to be identical to that for the volumetric phase). The film thickness also depends on the change in the condensation coefficient that can be realized with the influence of external fields on the system, for example, with excitation of internal degrees of freedom of vapor molecules under the effect of resonance laser radiation.

In Fig. 1 are shown the dependences of the dimensionless critical thickness of a water film $h' = h_1/\beta$ on the particle diameter for the quantities s', which are respectively larger and smaller than unity, in the presence of a foreign adsorbable gas in the system. It follows from the results of calculations that at $s' < 1$ the film thickness increases with particle diameter and tends to the limiting value corresponding to a flat surface. The film thickness decreases with s'.

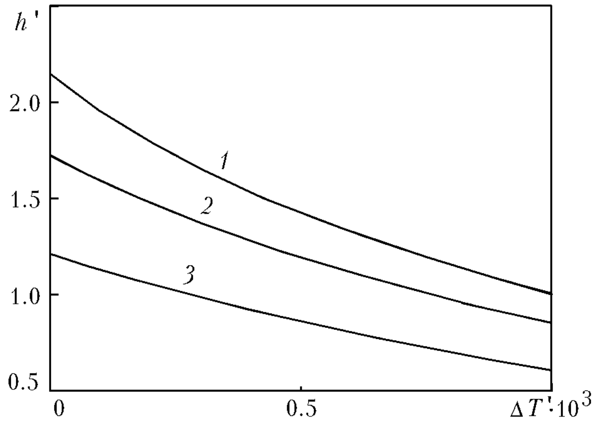

Fig. 2. Dependence of the dimensionless critical thickness h' of a water film on an aerosol particle on the dimensionless temperature drop $\Delta T'$ at $K = 10^7$ N·m^{-2}, $d = 10^{-7}$ m, and $T_g = 273$ K: 1) $s_0 = 1.015$, 2) 1.01; 3) 1.005.

In the case $s' > 1$, the condensate layer begins to grow for certain values of the particle diameter and thus the particle–film system transforms into a drop–nucleus system. When the values of s' increase, the particle diameter for which the stationary film ceases to exist decreases. The presence of a foreign gas adsorbing on the particle surface and decreasing surface tension in the system also decreases the particle diameter for which the condensate layer begins to grow.

It is well known that, when particles (drops) of different size are present in the supersaturated vapor, those with a size larger then the critical (equilibrium) one will grow, whereas particles with a smaller size than the critical one will evaporate. Thus, the system of drops of different size that is present in the supersaturated vapor tends in principle to a monodisperse system with particles whose size is equal to the critical one. However in the system of small particles coated with a polymolecular film and present in the supersaturated vapor, the equilibrium condition will hold for particles of different size too. Here, as follows from (5) and (6), the film thicknesses for particles of different diameter will be dissimilar.

We consider the case where electromagnetic radiation absorbed by the condensed phase acts on the particle coated with a film. The temperatures of the particle and the gas phase are different. For the sake of simplicity the mean free path of the gas molecules is considered to be much larger than the particle radius. If radiation is absorbed mainly in the particle (nucleus) and its absorption in the film is negligible, the film thickness under the assumption of uniform heating of the particle–film system is determined by expressions (5) and (6), in which the temperature of the considered system can be represented as

$$T_p = T_g + \frac{k_{\text{eff}} I}{4\alpha_h} = T_g + \Delta T \, , \tag{7}$$

where T_p and T_g are the temperatures of the particle–film system and the surrounding gas.

Conversely, when radiation is absorbed only in the film, the problem becomes more complicated. Here, the temperature of the particle–film system depends on the film thickness which in turn is acted upon by the system's temperature. Generally, in absorption of the optical radiation by the aerosol particle coated with a film, the distribution of absorbed power in the particle is rather complicated [4] and the temperature depends on the radiation absorption in both the particle (nucleus) and the film. Subsequently we restrict ourselves to an analysis of the situation where absorption is taken into account only in the particle and the temperature can be represented as (7).

Based on what has been said above, for the dependence of the dimensionless thickness of the water film on the aerosol particle $h' = h_1/\beta$ on the quantity ΔT at $\Delta T/T_g << 1$, $\alpha = \alpha_e$, and $P_a = 0$ we have

$$h' = \ln \left\{ \frac{4\sigma_0}{dK} - \frac{k\,(T_g + \Delta T)}{V_m K} \left[\ln s_0 - \frac{Q \Delta T}{k T_g^2} \right] \right\}^{-1} , \tag{8}$$

where s_0 is the vapor-saturation ratio for the temperature of the particle–film system equal to T_g.

Figure 2 shows the dependence of the dimensionless critical thickness of water film h' on the aerosol particle at T_g = 273 K on the drop in the dimensionless temperature $\Delta T' = (T_p - T_g)/T_g$. For the sake of simplicity, in this case we do not consider the change in the surface tension due to the possible influence of the adsorption of the foreign gas on the film surface. It follows from Fig. 2 that an increase in the particle temperature leads to a decrease in the film thickness.

We consider some problems related to the influence of polymolecular films on the coagulation and movement of the particles in the gas phase. It is well known that, when solid particles collide in a vapor whose partial pressure is below the saturated-vapor pressure, at the instant of their contact, conditions for realization of spontaneous capillary condensation in the contact zone and for formation of a liquid bridge between the particles arise [5]. The presence of a polymolecular film on the particles improves the conditions of formation of such a bridge. The appearance of the liquid bridge in turn promotes the formation of agglomerates consisting of particles which are interconnected by the liquid phase in the form of films and a capillary-condensed liquid.

When a particle coated with a polymolecular film is present in the gas phase, where there are molecules of the film substance, and the resonance radiation influences the gas–particle system, a new component of the force acting on the particle may in principle arise. The appearance of this force is due to the nonuniform process of evaporation and condensation of the molecules of the film substance along the particle surface and to the simultaneous transfer of the substance in the film from the region with a larger flux density of condensed vapor molecules to the region with a lower value of this quantity. Flow of the film can be caused by the change in its thickness along the particle surface, nonuniform heating of the film, and by the change in the surface tension along the film surface owing to the adsorption of the molecules of a surfactant on the surface.

Next, for the sake of simplicity, the isothermal case ($T_p = T_g = T$) will be considered in the absence of adsorbed molecules of a foreign gas on the film surface when we can restrict ourselves to only one mentioned factor capable of causing the film flow, namely, to a change in the film thickness. In particular, such a situation can arise in the aerosol system under the action of the resonance (for example, laser) radiation exciting the vapor molecules. If the sticking coefficients of excited and unexcited molecules are different and molecular excitation is asymmetric relative to the direction of the radiation flux (which can be due to both different degrees of illumination of the opposite particle sides and detuning of the radiation frequency from the resonant frequency of vapor molecules when most of the excited molecules fall on one side of a particle because of the Doppler effect), asymmetry is realized in molecular deposition on the particle sides which are opposite with respect to the incident radiation. This leads to a drop of the film thickness along the particle surface and accordingly to flow of the film in the direction of decrease in its thickness. In turn the flux density of molecules evaporating from the film surface and accordingly the recoil pressure of these molecules depend on the film thickness. For the case of a nonpolar film substance, the distribution of the film thickness (supposed to be much smaller than the particle diameter) with account for [6, 7] and the mentioned assumptions is described by the equation

$$\frac{4\rho A'}{\eta m d^2 \sin\theta}\,\frac{d}{d\theta}\left(\sin\theta \cdot h^{-1}\frac{dh}{d\theta}\right) = j\,(\theta) - \alpha\,(\theta)\,N\,, \tag{9}$$

where $A' = A/6\pi$, N is the flux density of vapor molecules incident on the film surface (the density is supposed to be independent of the angle θ), and η is the viscosity. As a result of symmetry, the condition $dh/d\theta = 0$ must hold at $\theta = 0$ and $\theta = \pi$. The expression for the flux density of molecules, evaporating from the film at $h \ll d$ has the form

$$j = \frac{\alpha_e P_e}{(2\pi m k T)^{1/2}} \exp\left\{\frac{V_m}{kT}\left(\frac{4\sigma_0}{d} - \frac{A'}{h^3}\right)\right\}. \tag{10}$$

The recoil pressure P_r of molecules escaping from the film surface is determined by the expression

$$P_r = \int\limits_{\xi_n > 1} \xi_n^2\, j\,\frac{m^3}{2\pi\,(kT)^2} \exp\left\{-\frac{m\xi^2}{2kT}\right\} d\xi\,, \tag{11}$$

where ξ is the molecular velocity and ξ_n is the projection of the velocity on the normal to the surface.

The resulting force acting on the particle due to different values of the recoil pressure for different parts of the particle surface takes the form

$$F = 2\pi R^2 \int_0^\pi P_r \sin\theta \cos\theta d\theta \, . \tag{12}$$

As follows from (9)–(12), the resulting force acting on the particle is related in the general case to the dependence of the quantities j and α on the angle θ. A change in the value of j can be due to both the nonuniform heating of the particle–film system and variation in surface tension owing to the adsorption of the molecules of the surfactant on the film surface.

It should be noted that, if the particle-film system is fixed in space (for example, in the case of a high-porosity body of globular structure), the above effects will lead to a light-induced mass transfer in the given system by analogy with the case of a capillary-porous body considered in [8].

Thus, as shown in the present work, the critical (equilibrium) thickness of a polymolecular film on a small aerosol particle depends on the particle diameter and the presence of molecules of a foreign gas in the system that can adsorb on the film surface and the change surface tension. The influence of resonance (in particular, laser) radiation on a particle coated with a polymolecular film can result in the nonuniformity of the processes of evaporation and condensation on the film surface, which in turn leads to a drop of the film thickness and film flow. The indicated phenomena can lead to the appearance of an additional force acting on the aerosol particle and the resulting mass flux in the case of a high-porosity body of globular structure.

This work was carried out with support from GAASCR, project No. IAA4072205 and GACR, project No. 104/02/1079.

NOTATION

A, Hamaker constant; *d*, diameter of a particle on which a film is deposited; *I*, density of the radiation flux incident on a particle; *k*, Boltzmann constant; k_{eff}, factor of efficiency of radiation absorption; *m*, mass of a vapor molecule; m_a, mass of adsorbed molecule; *h*, film thickness; n_0, number density of molecules in a filled monolayer; *n*, number density of molecules in a film; P_a, pressure of an adsorbable foreign gas; P_e, saturated-vapor pressure above the flat surface; P_∞, vapor pressure at an infinite distance from a particle; *T*, temperature; V_m, volume per molecule in the film; α and α_e, condensation and evaporation coefficients; α_1, coefficient of sticking of molecules of a buffer (admixture) gas to the portion of the surface free of adsorbed molecules; α_h, heat-transfer coefficient; θ, angle between the axis passing through the center of a particle in the direction parallel to the radiation flux and the normal to the particle surface; λ, mean free path of vapor molecules; ρ, mass density of a film; σ_0, surface tension of a pure liquid; τ, adsorption time of the molecules of a buffer gas. Subscripts: a, adsorption; c, critical; e, evaporation; eff, effective; h, heat transfer; g, gas; L, Langmuir; m, molecule; n, normal; p, particle; r, recoil.

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