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INFLUENCE OF SIZE EFFECTS ON THE CRITICAL DIAMETER AND GROWTH OF NANOPARTICLES

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

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The effect exerted by the dependence between the condensation and surface-tension coefficients and the size of an aerosol nanoparticle on its growth and critical diameter is investigated theoretically.

Investigation of the characteristic features of transfer processes in aerosol systems with nanosized particles is of interest both for description of the atmospheric phenomena related to the formation and growth of water drops in the atmosphere [1] and for the technological processes where nanoparticles are obtained (or used) [2].

It is well known that, when the size of a particle decreases, the processes occurring on its surface begin to play an increasing role. As this takes place, in a number of cases an investigation of the processes in aerosol systems with nanoparticles necessitates taking account of the specific features in the progression of these processes due to the size effects. Thus, for example, the frequent (in phase transitions) assumption that the condensation coefficient is equal to the evaporation coefficient can lead to qualitatively incorrect results in the case of nanoparticles.

The saturated vapor pressure over a small particle (drop) depends on its size [1]. The sticking (condensation) and surface-tension coefficients of nanoparticles also become functions of their size [3–5]. It should be noted that small particles can arise in a gas phase only at sufficiently high values of the saturation ratio of vapor. The condition of the equilibrium of such particles with a gas phase is determined by the so-called critical size of a particle. In [4], the influence exerted by the dependence between the condensation coefficient and the size of particles on their critical diameter and growth rate was discussed, with the surface-tension coefficient being supposed constant. In the present paper, we consider the joint effect of the condensation and surface-tension coefficients influenced by the size of aerosol nanoparticles on the phase transitions occurring on their surfaces.

The particle growth rate v_{p} in vapor condensation can be written as

$$v_{\text{p}} = n_{\text{c}}^{-1} \, (j_{\text{c}} - j_{\text{e}}) \, . \tag{1}$$

We shall analyze the dependence of j_{e} and j_{c} on the particle size. The flux density of the molecules that evaporate from the surface of a small aerosol particle, with consideration for the Kelvin correction for the saturated vapor pressure over the particle, takes the form

$$j_{\text{e}} = \alpha_{\text{e}} \frac{P_{\text{e}}}{(2\pi mkT_{\text{s}})^{1/2}} \exp \left\{ \frac{4\sigma V_{\text{m}}}{dkT_{\text{s}}} \right\} . \tag{2}$$

According to [6], the evaporation coefficient α_{e} is defined as a coefficient of proportionality between the actual (measured) flux density of evaporating molecules for a flat massive sample and the greatest possible, during evaporation into vacuum, flux density, which is equal to $P_{\text{e}}/(2\pi mkT_{\text{s}})^{1/2}$. In other words, the evaporation coefficient is a measure of the deviation of an actual evaporation rate from the greatest possible one for a flat massive sample. With such a definition, the evaporation coefficient is independent of the particle size (the size dependence of the evaporation rate is taken into account by the exponential term in (2), which describes, according to the Kelvin formula, an increase

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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; email: vlev5@yahoo.com; [b] Institute of Chemical Process Fundamentals AS CR, Prague. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 79, No. 2, pp. 14–18, March–April, 2006. Original article submitted February 22, 2005.

in the saturated vapor pressure over a spherical surface). We note that if the evaporation coefficient is defined as a coefficient of proportionality between the actual flux density of the molecules evaporating from a particle and the quantity $P_e/(2\pi mkT_s)^{1/2}$, it will increase with a decreasing particle size. The quantity P_e has the form

$$P_e = P_0 \exp\left\{-\frac{Q}{kT_s}\right\}. \tag{3}$$

Here, expression (2) can be written as follows:

$$j_e = \alpha_e \frac{P_0}{(2\pi mkT_s)^{1/2}} \exp\left\{-\frac{Q_{\text{eff}}}{kT_s}\right\}, \tag{4}$$

where $Q_{\text{eff}} = Q - \dfrac{4\sigma V_m}{d}$ is the effective energy of the evaporation of molecules from the particle which decreases with the size of the latter.

For sufficiently small particles, the surface-tension coefficient σ also depends on their size. According to the Tolman formula [5], this dependence has the form

$$\sigma(d) = \frac{\sigma_f}{1 + \dfrac{4\delta}{d}}, \tag{5}$$

where σ_f is the surface tension coefficient for a flat surface; δ is the so-called Tolman length. According to [5], the variation range of δ is 0.96–3.5 Å. Further we will take that $\delta = 3.5$ Å. Some questions connected with the influence of the curvature of the liquid-phase surface on the equilibrium conditions in the liquid–vapor system are considered in [7].

Paper [8] gives a correlation between the results of calculations by the Tolman formula and the results obtained by computer simulation. The values of the surface-tension coefficient obtained by both methods fall sufficiently close together (including the case of very small diameters of particles). It follows from (2) that introducing a correction for the dependence of the surface-tension coefficient on the particle size does not alter the form of the expression for j_e if we use the quantity $d_{\text{eff}} = d + 4\delta$ in it instead of d and consider that $\sigma = \sigma_f$.

As was noted in [6], when the values of α_e and P_∞ are unknown, the flux density of evaporating molecules can be obtained with the aid of kinetic expressions which do not include these parameters. For example, in the simplest case for j_e we can write [9]

$$j_e = n_c \left(\frac{kT_s}{2\pi m}\right)^{1/2} \exp\left\{-\frac{Q}{kT_s}\right\}. \tag{6}$$

Some other kinetic expressions for α_e are presented in [6]. Further we shall restrict ourselves, for simplicity, to an isothermal approximation, when the temperature of the phase-transition surface T_s can be assumed equal to the gas temperature T_g ($T_s = T_g = T$). We consider the influence of the size effects on the value of j_c. Under the assumption of the Maxwell velocity distribution function for incident molecules, the latter quantity takes the form

$$j_c = \alpha \frac{P(0)}{(2\pi mkT)^{1/2}}, \tag{7}$$

where $P(0)$ is the partial vapor pressure near a particle which depends on the vapor mass transfer (through a buffer gas) to it and on the phase-transition kinetics on its surface. Generally, the condensation coefficient α, which is defined as the probability that the molecule incident on the surface will not reflect elastically back to the gas phase, depends on the particle size due to the decrease in the number of particle molecules that interact with the gas molecule incident on the particle. Here, the value of α decreases with the particle size as well [3, 4]. On the basis of the ex-

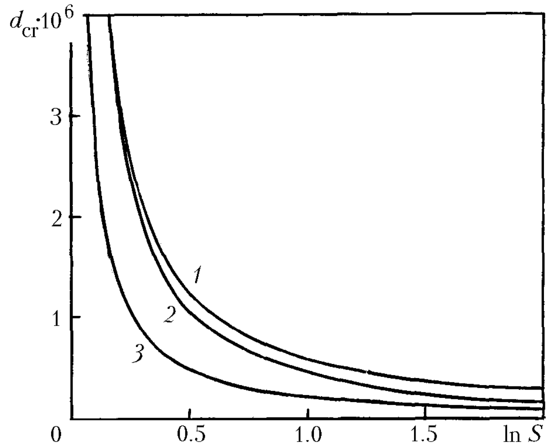

Fig. 1. Dependence of the critical diameter of a water drop on ln S at T = 273 K, Kn >> 1: 1) $\alpha = \alpha(d)$, $\sigma = \sigma_f$; 2) $\alpha = \alpha(d)$, $\sigma = \sigma(d)$; 3) Kelvin formula. d_{cr}, cm.

pression for the dependence of the condensation coefficient on the particle size given in [3] and formula (5), the dependence of α on the particle (drop) diameter can be presented as

$$\alpha = \alpha_f \exp\left\{-\frac{6\sigma_f V_m}{(d+4\delta)\,kT}\right\}, \tag{8}$$

where further, for simplicity, we suppose that $\alpha_f = \alpha_e = 1$.

According to (8), the condensation coefficient decreases with the particle size, as differentiated from the evaporation coefficient (in both of the above variants of the definition of the latter). Thus, the assumption on the equality of the condensation and evaporation coefficients in the range of nanosized particles, where the dependence of the condensation coefficient on the particle size can be appreciable, becomes incorrect.

Based on the foregoing and [4], we can write the following expression for the resulting flux of molecules into the particle:

$$I = \frac{\dfrac{P_\infty}{(2\pi mkT)^{1/2}}\left[\exp\left\{-\dfrac{6\sigma_f V_m}{(d+4\delta)\,kT}\right\} - \dfrac{1}{S}\exp\left\{\dfrac{4\sigma_f V_m}{(d+4\delta)\,kT}\right\}\right]}{1 + \exp\left\{-\dfrac{6\sigma_f V_m}{(d+4\delta)\,kT}\right\}\dfrac{vd}{8D}}, \tag{9}$$

where

$$S = \frac{P_\infty}{P_e}; \qquad \frac{vd}{8D} = \frac{3}{4\mathrm{Kn}}.$$

At I = 0, relation (9) yields the value of the critical (equilibrium) drop diameter d_{cr} provided account is taken of the dependence of the condensation and surface-tension coefficients on the particle (drop) size:

$$d_{cr} = \frac{10\sigma_f V_m}{kT \ln S} - 4\delta\,. \tag{10}$$

Naturally, the area of applicability of (10) is limited by the values of the parameters at which the right-hand side is higher than zero.

According to the classical Kelvin formula (where it is generally supposed that $\sigma = \sigma_f$), the critical diameter of the particle is determined as [1]

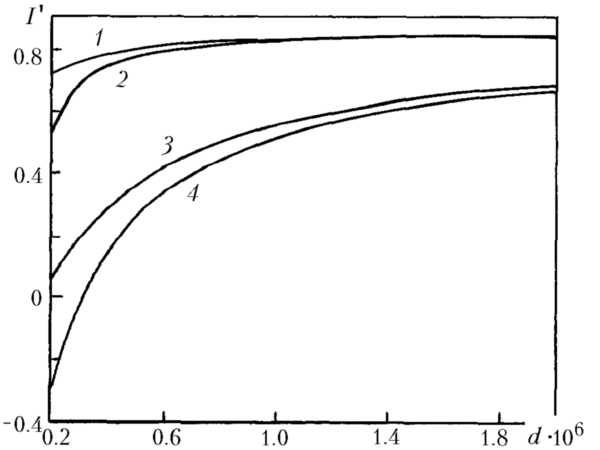

Fig. 2. Dependence of the dimensionless density of the resulting flux of vapor molecules into a water drop on its diameter at T = 273 K, S = 7: 1, 2) α = 1; 3, 4) $\alpha = \alpha(d)$; 1, 3) $\sigma = \sigma(d)$; 2, 4) $\sigma = \sigma_f$. d_{cr}, cm.

$$d_{cr} = \frac{4\sigma V_m}{kT \ln S}. \tag{11}$$

A correlation of the dependences of the critical diameter of a water drop at 273 K on the value of ln S calculated both with the size effects taken into account and by the Kelvin formula is presented in Fig. 1. It follows from the figure that allowance for the dependence of the condensation and surface-tension coefficients on the particle size in the studied range of the value of S leads to higher values of the critical diameter of the particle as compared to the value calculated by the Kelvin formula. At sufficiently small values of the parameter S, the dependence of the surface-tension coefficient on the particle size practically does not influence its critical size deduced with taking account of the size effect for the condensation coefficient at $\sigma = \sigma_f$. When ln S = 2, the magnitude of the critical diameter is close to its value calculated on the basis of the Kelvin formula.

We will analyze the influence of the size effects on the resulting flux of molecules into a particle (drop). Figure 2 gives the values of the dimensionless flux density of molecules $I' = I(2\pi mkT)^{1/2}/P_\infty$ as a function of the diameter of a water drop at 273 K and Kn >> 1 with the dependence of the condensation and surface-tension coefficients on the drop size taken into account and ignored. The value of the parameter S was taken equal to 7. It is seen from Fig. 2 that, when the condensation coefficient depends on the particle size, the resulting flux of molecules into it decreases. Here, the dependence of the surface-tension coefficient on the particle diameter in the range of sufficiently small particle sizes is responsible for the rise in the value of the resulting flux of molecules into the particle and can even result in transition from evaporation to growth of the particle.

Thus, the dependence of the condensation and surface-tension coefficients on the size of the particle influences both its critical size and the resulting flux of vapor molecules into the particle and correspondingly the rate of its growth. Here, for some values of the parameters, consideration of the above-mentioned size effects can lead to a change in the sign of the resulting flux of vapor molecules into the particle.

It should be noted that the size effects related to the dependence of the condensation and surface-tension coefficients on the particle size can also influence the rate of homogeneous nucleation J, which can be presented in general form as [10, 11]

$$J = A \exp\left\{-\frac{G}{kT}\right\}, \tag{12}$$

where A is the pre-exponential factor which generally is proportional to the condensation coefficient; G is the free energy of cluster formation, which in the classical theory of nucleation is expressed as $G = \frac{1}{3}\sigma\pi d_{cr}^2$.

The rate of homogeneous nucleation J is very sensitive to a change in the critical cluster diameter. For example, [11] gives the results of calculation of the value of J for water at $\alpha = 1$, $T = 273$ K, $\sigma = 76.1$ dyn/cm, and $P_e = 4.58$ mmHg. From them, in particular, it follows that a change in the saturation ratio from 4 to 5 leading to a decrease in the critical diameter from $1.74 \cdot 10^{-7}$ to $1.5 \cdot 10^{-7}$ cm (approximately by 14%) corresponds to an increase in the nucleation rate from $5.78 \cdot 10^{-2}$ to $1.1 \cdot 10^{6}$ $\text{cm}^{-3} \cdot \text{sec}^{-1}$ (i.e., by almost 8 orders of magnitude). A change in the critical cluster size related to the dependence of the condensation and surface-tension coefficients on the particle (cluster) size can also substantially influence the rate of homogeneous nucleation.

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NOTATION

D, diffusivity of vapor molecules; d, diameter of a particle; I, resulting flux of molecules into a particle; J, rate of homogeneous nucleation; j_c, density of a flux of vapor molecules condensing on particle surface; j_e, density of a flux of molecules evaporating from a particle; k, Boltzmann constant; Kn, Knudsen number; m, mass of a vapor molecule; n_c, number density of molecules in the condensed phase; P, partial pressure of a vapor; P_e, saturated vapor pressure over a flat surface; P_0, pre-exponential factor in (3); Q, evaporation energy; S, saturation ratio; T_s, temperature of the surface of phase transition; t, time; V_m, volume per molecule in the particle; v, rate of particle growth; α, condensation coefficient; α_e, evaporation coefficient; σ, surface-tension coefficient. Subscripts: c, condensation; cr, critical; e, evaporation; eff, effective; f, flat; g, gas; m, molecule; p, particle; s, surface; ∞, infinite distance from a particle.

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