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INFLUENCE OF FOREIGN GASES ON PHASE TRANSITIONS IN NANOSIZED CAPILLARIES

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The influence of foreign adsorbable gases on evaporation of a liquid from nanosized capillaries, as well as on the thickness of a polymolecular film which is formed on their walls, is considered theoretically.

In recent years, investigators have been increasingly attracted to questions of transfer in nanosized systems. This is associated, in particular, with the development of nanoelectromechanical systems (NEMS), manufacture of nanoparticles and nanotubes of different composition, drying of materials with nanosized pores, and so on. The present paper considers questions on the influence of a foreign gas adsorbable on the phase-transition surface on evaporation–condensation processes in nanosized capillaries, where a correction in a saturation vapor pressure connected with the Kelvin effect becomes essential.

In an isothermal case, the flux density of the gas molecules which pass through a cylindrical capillary with impermeable walls in a free-molecule regime of flow, with the surface diffusion of adsorbed gas molecules being neglected, can be written as [1]

$$I = \left[\frac{P_0}{(2\pi mkT)^{1/2}} - \frac{P_1}{(2\pi mkT)^{1/2}} \right] W \, . \tag{1}$$

The probability W that the molecules will pass through the capillary at arbitrary ratios of the length of the capillary to its diameter should be found from the solution of the Clausing equation [1]. For $L/d >> 1$ and diffusive scattering of molecules by the walls, the relation $W = 4d/(3L)$ was obtained [1], and at rather low values of L/d the following expression was obtained for W [2]:

$$W = (1 + L/d)^{-1} \, . \tag{2}$$

If the capillary is restricted on one side by a meniscus (heated, for definiteness, at $X = 0$), the flux of vapor molecules entering the capillary after they evaporated from the meniscus depends, in principle, on the geometry of the latter. First, for simplicity we consider the case where a cylindrical capillary is filled to a certain level with a liquid and its walls above the meniscus are not covered with a layer of condensed phase (a polymolecular film). The influence exerted by the polymolecular film attached to the capillary wall on mass transfer in it will be considered below. We assume that the liquid is wetting and that the meniscus can be approximated by a hemisphere of radius equal to the capillary radius. Next, for simplicity we can let the coefficients of condensation and evaporation of molecules for the clean liquid surface be equal to unity. In [3], the conductivity of a capillary with an evaporating meniscus was found by the Monte Carlo method, with menisci of convex, flat, and concave shapes. It is shown that at a condensation coefficient equal to unity the conductivity of a capillary with a flat meniscus and with a concave one is the same. The reason is that the advantage in the area of an evaporating surface in the second case is compensated by a higher probability that molecules will hit the surface and be subsequently condensed. With allowance for the foregoing, further for simplicity of the calculations we replace the concave hemispherical meniscus by a flat disk of radius equal to

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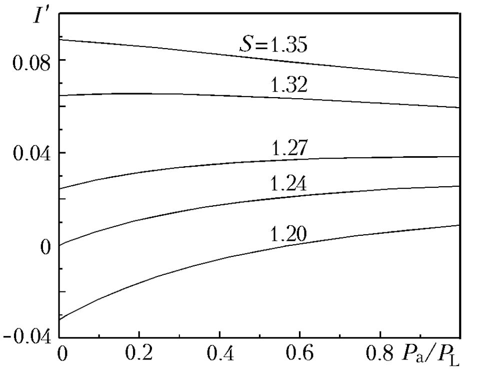

Fig. 1. Dependence of the dimensionless density of a flux of water molecules escaping from a capillary I' on dimensionless pressure of an adsorbing gas P_a/P_L at $d = 10^{-6}$ cm, $n_a = 6 \cdot 10^{14}$ cm^{-2}, $T = 293$ K, and different values of S.

that of the capillary. We also assume that molecules escape from the given plane according to the cosine law. With the assumptions listed, Eq. (1) also remains valid in the case where the above-mentioned meniscus is located at one of the ends of the capillary. Here, the quantity $N_0 = P_0/(2\pi mkT)^{1/2}$ describes the flux density of molecules escaping from the meniscus surface and, under the assumptions mentioned, can be represented as

$$N_0 = \frac{P_e}{(2\pi mkT)^{1/2}} \exp\left(-\frac{4\sigma V_m}{dkT}\right). \tag{3}$$

The molecules of a foreign (buffer or admixture) gas adsorbed on the phase-transition surface can influence the intensity of phase transition in two ways [4]. In the first place, they hamper the phase-transition surface, decreasing the density of the resulting flux of molecules; second, their adsorption can diminish the surface tension, which, according to (2), increases the flux density of molecules that evaporate from the meniscus. In [5], the following expression was obtained for the dependence of the surface-tension coefficient on the pressure of a foreign adsorbing gas P_a with regard for the Langmuir adsorption isotherm:

$$\sigma(P_a) = \sigma' - n_a kT \ln\left(\frac{P_a + P_L}{P_L}\right). \tag{4}$$

Here, P_L may be represented as

$$P_L = \frac{n_a (2\pi m_a kT)^{1/2}}{\alpha_a \tau}. \tag{5}$$

Based on (3) and (4) and the expression for the surface coverage by adsorbed molecules of a buffer (admixture) gas $\theta = P_a/(P_a + P_L)$, for the density of the resulting flux of molecules escaping from the capillary in evaporation of molecules from the hemispherical meniscus we may write the expression

$$I = \frac{P_1}{(2\pi mkT)^{1/2}} \frac{P_L}{P_a + P_L}\left[S \exp\left\{-\frac{4\sigma' V_m}{dkT}\right\}\left(\frac{P_L}{P_a + P_L}\right)^{-G} - 1\right] W, \tag{6}$$

where $G = 4V_m n_a/d$ and $S = P_e/P_1$.

Figure 1 presents the dependence of the dimensionless density of the resulting flux of water molecules $I' = I/(N_1 W)$, where $N_1 = P_1/(2\pi mkT)^{1/2}$, on the dimensionless pressure of an adsorbing foreign gas P_a/P_L at $d = 10^{-6}$ cm and $T = 293$ K. It is seen from the figure that the presence of adsorbed molecules on the meniscus surface can lead both to an increase in the resulting flux of escaping vapor molecules (at sufficiently low values of the parameter S) and to a decrease in this flux (at higher values of S).

A drop in the surface-tension coefficient during adsorption of molecules of a foreign gas on the meniscus surface results in a correction to the Laplace pressure. For example, if a liquid column with two hemispherical menisci is present in a capillary and an adsorbing gas, while decreasing the surface tension, is available at one of its ends, then with regard for (4) for the difference between the pressures acting on the opposite ends of the fluid column we can write the expression

$$\Delta P = \frac{4n_{\mathrm{a}}kT}{d} \ln \left(1 + \frac{P_{\mathrm{a}}}{P_{\mathrm{L}}} \right). \tag{7}$$

We note that actually the capillary surface from the meniscus to the exit section is generally covered with a liquid polymolecular film, whose thickness depends on the capillary diameter, the surface-tension coefficient, and the interaction of molecules in the film with regard for the influence of the capillary wall [6], as well as the adsorption of molecules of a foreign gas on the film surface. Next, the distribution of the foreign gas molecules adsorbed on the film surface is assumed to be uniform. As previously, the influence of adsorption of a foreign gas on phase transitions will be taken into account in terms of the change in the surface-tension coefficient, as well as through the blocking effect of the molecules adsorbed. We note that with the adsorbed molecule being nonuniformly distributed over the film surface, the mass transfer in the film will depend on the change in the surface-tension coefficient along the surface due to the nonuniform distribution of the adsorbate. Subject to [6] and expressions (3) and (4), for the flux densities of molecules which evaporate from a film of nonpolar and polar (for example, water) substances, respectively, we can write the relations

$$j_1 = \frac{P_{\mathrm{e}}}{(2\pi mkT)^{1/2}} \left(\frac{P_{\mathrm{L}}}{P_{\mathrm{a}} + P_{\mathrm{L}}} \right)^{-G} \exp \left\{ - \frac{V_{\mathrm{m}}}{kT} \left[\frac{2\sigma'}{d + 2h} + \frac{A}{6\pi h^3} \right] \right\}, \tag{8}$$

$$j_2 = \frac{P_{\mathrm{e}}}{(2\pi mkT)^{1/2}} \left(\frac{P_{\mathrm{L}}}{P_{\mathrm{a}} + P_{\mathrm{L}}} \right)^{-G} \exp \left\{ - \frac{V_{\mathrm{m}}}{kT} \left[\frac{2\sigma'}{d + 2h} + \varphi \exp \left(- \frac{h}{\lambda} \right) \right] \right\}. \tag{9}$$

According to [6], the quantity φ for polymolecular water films on quartz, glass, and mica has an order of 10^7 N·m^{-2}, and the parameter λ changes from 2.3 to 3.3 nm; Eq. (9) was written on the assumption that a polymolecular film is in a stable form (the so-called α-film [6]).

Provided that the thickness of an equilibrium film is much less than the capillary radius and that it is determined by phase transitions, whereas the influence of the film flow can be neglected, the distribution of its thickness in the case of a nonpolar substance can be found, with consideration for [7, 8], from the equation

$$j \exp(-\beta h^{-3}) = \int_0^1 j \exp(-\beta h^{-3}) K_1(|x - x'|)\, dx + N_0 K(x) + N_1 K(1 - x), \tag{10}$$

where $\beta = AV_{\mathrm{m}}/(6\pi kT)$. The functions K and K_1 characterize the probabilities of transition of molecules from one element of the surface to another (the spatial distribution of the molecules both entering into the channel and escaping from its surface will be further considered corresponding to the cosine law) and for a cylindrical channel are determined by the expressions [1, 8–10]

$$K(x) = \frac{l^2 x^2 + 2}{2(l^2 x^2 + 4)^{1/2}} - \frac{l}{2} x, \quad K_1(x) = - \frac{dK(x)}{dx}, \quad l = \frac{2L}{d}. \tag{11}$$

The quantity j has the form

$$j = \frac{P_\mathrm{e}}{(2\pi mkT)^{1/2}} \left(\frac{P_\mathrm{L}}{P_\mathrm{a} + P_\mathrm{L}} \right)^{-G} \exp\left\{ -\frac{2\sigma' V_\mathrm{m}}{dkT} \right\}. \qquad (12)$$

With exponential approximation of the functions K and K_1 in (10) [9, 10], we can obtain the expression for the thickness of film of a nonpolar substance [7, 8]:

$$h\,(x) = \left\{ \frac{\beta}{\ln\,[j/(a + bx)]} \right\}^{1/3}, \qquad (13)$$

where $a = \dfrac{l+1}{l+2} N_0 + \dfrac{1}{l+2} N_1$; $b = \dfrac{l}{l+2} (N_1 - N_0)$.

An equation analogous to (10) also holds for the case where a film consists of polar molecules and the flux density of molecules evaporating from it can be represented in the form of (9). With assumptions identical to those used in the derivation of (10), we can find the distribution of the thickness of an equilibrium film for a nonpolar substance:

$$h = \lambda \ln \left\{ \frac{\varphi V_\mathrm{m}}{kT \ln\,[j/(a + bx)]} \right\}. \qquad (14)$$

It is seen from (12)–(14) that the film thickness decreases from the mouth which faces the side of a higher pressure of the condensing-substance vapor to the mouth which contacts the gas phase, where the vapor pressure is lower. It is also evident that, when the pressure of an adsorbing gas increases, the film thickness diminishes.

Thus, the presence of adsorbed molecules of a foreign gas on the surface of a liquid polymolecular film under the above-made assumptions leads to a decrease in the film thickness and correspondingly in the amount of the moisture contained in the capillary in the form of a polymolecular film.

In the case where a system represents a meniscus that passes into a liquid polymolecular film, the presence of adsorbed molecules on the surface of a liquid phase can manifest itself in a more complicated manner. As is indicated above, in some cases the presence of adsorbed molecules of a foreign gas on the meniscus surface leads to an increase in the flux of molecules evaporating from the meniscus. This shows up as an increase in the value of N_0 in (10), which results in a thicker polymolecular film. At the same time, adsorption of foreign molecules on the surface of the film decreases the surface tension and as a result initiates a decrease in the film thickness. This is connected with the increase in the flux density of molecules evaporating from the film.

It should be noted that analogously to the case of nanosized aerosol particles [11], in capillaries of a rather small diameter one can observe size effects connected with the influence of the surface curvature on coefficients of the condensation of vapor and sticking of adsorbing molecules of a foreign gas, as well as on the evaporation and adsorption energies. Generally the surface tension is also a function of the surface curvature. This dependence for a concave surface was considered in [12–14].

Thus, in the paper we have analyzed the influence of the molecules of a foreign gas adsorbed on the phase-transition surface on the evaporation–condensation processes in nanosized capillaries, where the Kelvin correction to the saturated vapor pressure is essential. It is shown that the presence of a foreign gas can lead both to an increase in the resulting flux of vapor molecules outgoing from a capillary and to its decrease (depending on the value of the relationship between the vapor pressure near the exit section of the capillary and the saturated vapor pressure). This is related to the fact that the presence of adsorbed molecules at the phase-transition front influences this transition in two ways. On the one hand, adsorbed molecules can decrease the surface tension, which for a concave meniscus increases the probability of evaporation of molecules from the meniscus. On the other hand, adsorption of the molecules of a foreign gas initiates a blocking effect relative to evaporation–condensation processes, which decreases the resulting flux of molecules outgoing from the capillary.

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NOTATION

A, Hamaker constant; d, capillary diameter; I, density of the resulting flux of molecules passing through a capillary; I', dimensionless density of the resulting flux of molecules; j_1 and j_2, densities of the fluxes of molecules evaporating from a film of a nonpolar and polar substance, respectively; h, film thickness; k, Boltzmann constant; L, capillary length; m, mass of a vapor molecule; m_a, mass of an adsorbed molecule; n_a, number of molecules in a fully filled monolayer; N, density of the film of vapor molecules entering a capillary; P, vapor pressure; P_a, pressure of adsorbing foreign gas; P_e, saturated vapor pressure over a flat surface; Q_a, adsorption energy; T, temperature; V_m, volume per molecule in a film; W, probability of passage of molecules through a capillary; $x = X/L$; X, coordinate directed along the capillary axis; α_a, coefficient of sticking of molecules of a foreign (buffer or admixture) gas to the part of the surface free of adsorbed molecules; σ, surface-tension coefficient; σ', surface-tension coefficient of clean liquid; τ, time of adsorption of molecules of a foreign gas; φ and λ, constants characterizing the interaction of molecules in the film of a polar substance. Subscripts: a, adsorption; L, Langmuir; m, molecule; e, saturated vapor; 0 and 1, values at $x = 0$ and $x = 1$, respectively.

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