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# Universal Asymptotics of the Thermodynamic Characteristics of the Nucleation on Small Macroscopic Nuclei of Soluble Surfactants

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**Abstract**—Asymptotic behavior of thermodynamic characteristics of nucleation on small macroscopic nuclei of soluble surfactants at their complete dissolution in a nucleating droplet is studied. It is taken into account that, in the region of small sizes of nuclei and corresponding small sizes of critical nuclei of liquid phase, the chemical potential of condensate and the work of droplet formation are affected by the presence of dense surfactant adsorption monolayer on the droplet surface. It is shown that, as the limiting surface area per surfactant molecule in adsorption monolayer increases, the behavior of thermodynamic characteristics of nucleation in the region of small nucleus sizes is characterized by the transition from asymptotics at the adsorption of almost all substance comprising nucleus in a monolayer to the asymptotics at constant adsorption. The study performed is not limited by the selection of specific adsorption isotherms; therefore, the obtained asymptotic dependences of thermodynamic characteristics on the nucleus size can be considered as universal for the heterogeneous nucleation on the nuclei of soluble surfactants.

## INTRODUCTION

During last decade, interest aroused in the problem of heterogeneous condensation of vapor on the atmospheric nuclei containing soluble surfactants formed due to natural processes [1–6]. To interpret experimental data, it should be realized how the solubility and surface activity of such nuclei can be manifested in the kinetics of heterogeneous nucleation. For this purpose, one needs to know the explicit dependence of the characteristics of barrierless and barrier nucleation such as the threshold value of vapor supersaturation, height of activation barrier of nucleation, and characteristic times of the establishment of steady-state rate of nucleation at a given vapor supersaturation below its threshold value on the nucleus size and nature.

The study of the effect of the surface activity of substance comprising soluble nucleus on the thermodynamic characteristics of heterogeneous nucleation was performed in [7–12]. It was established how the dependence of the chemical potential of condensate and the work of droplet formation on the nucleus size, parameters of surfactant and condensate are related to the adsorption isotherm (or the equation of state of the adsorption monolayer of substance comprising nucleus on the droplet surface). However, there are various models of adsorption and equations of monolayer state often applied only in a certain range of solution concentration. At the same time, as was shown earlier [10, 13], in the region of small nucleus sizes (with the number of molecules beginning with $10^3$), the general asymptotics for thermodynamic characteristics can be constructed irrespective of the specific pattern of adsorption isotherm. For the region of larger nucleus sizes, one can also construct nearly universal asymptotics [10] responsible for the limiting situation when the adsorption of substance comprising soluble nucleus can be neglected; however, we will not discuss these asymptotics in the present work. The region of small nucleus sizes is most interesting, because the chemical potential of condensate and work of droplet formation in this region are mostly affected by the presence of dense adsorption monolayer of substance comprising soluble nucleus on the droplet surface. In [10, 13], the asymptotics of thermodynamic characteristics of nucleation in the initial region of nucleus sizes were constructed under the assumption that almost all amount of substance comprising nucleus is adsorbed on the droplet surface. It can be expected that, with definite values of external parameters of a problem related to surfactant and condensate, the domain of applicability is sharply narrowed or even vanishes. What are the boundaries of applicability of asymptotics obtained in [10, 13] and do the other universal asymptotics of thermodynamic characteristics of nucleation exist beyond these boundaries in the region of small nucleus sizes, which can be used to perform sufficiently simple analytical calculations for practical situations? How are they related to the known model adsorption isotherms of surfactant in a monolayer? These questions are answered in this work.

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## 1. BASIC THERMODYNAMIC CHARACTERISTICS OF NUCLEATION WITH ALLOWANCE FOR ADSORPTION OF SUBSTANCE COMPRISING NUCLEUS

We denote the number of condensate molecules in a droplet by $\nu$, and the number of surfactant molecules in a nucleus by $\nu_n$. It is assumed that the nucleus is completely dissolved in a condensate, and the solution in the bulk phase of a droplet is a molecular (but not micellar) system. Let us introduce the dimensionless adsorption, which is related to the dimension adsorption $\Gamma_n$ (the excess number of molecules of dissolved substance; for electrolyte, it is the sum of excess quantities of all ions per unit area) by the relation

$$s = 4\pi\left(\frac{3v_l}{4\pi}\right)^{2/3}\Gamma_n, \qquad (1.1)$$

where $v_l$ is the molecular volume of condensate and coefficient at $\Gamma_n$ is equal to the surface area of a sphere with volume $v_l$ (this coefficient equals 0.4656 nm$^2$ for water with density of 1000 kg m$^{-3}$).

We denote the value of dimension adsorption by $\Gamma_\infty$ and dimensionless adsorption at the limiting coverage of a monolayer of substance comprising nucleus on the droplet surface, by $s_\infty$. Since only parameter $v_l$ that is practically independent of solution concentration at low concentrations typical of surfactant solutions enters into expression (1.1), it can be seen that the adsorption capacity of monolayer $s_\infty$ is determined as the ratio of total surface area of condensate molecule to the limiting area (the cross-sectional area of surfactant molecule in the case of maximally packed monolayer) of surfactant molecule in the adsorption monolayer. The value $s_\infty = 1$, for which the thermodynamic characteristics of nucleation were calculated [11, 12], corresponds to the situation when the limiting area of a molecule of substance comprising nucleus coincides with the surface area of condensate molecule. However, together with the situation when $s_\infty \approx 1$, the situation when the limiting area of a molecule of substance comprising the nucleus is much larger than the surface area of condensate molecule is also of interest. As can be seen below, the effect of parameter $s_\infty$ on the thermodynamic characteristics of nucleation turns out to be dominant in the region of small sizes of condensation nuclei.

Let us define the dimensionless surface tension of droplet, $a$, via the dimension surface tension $\sigma$ as

$$a = 4\pi(3v_l/4\pi)^{2/3}\sigma/kT, \qquad (1.2)$$

where $k$ is Boltzmann's constant, $T$ is the temperature of the vapor–gas medium assuming that the temperature of a medium and a droplet is identical. In terms of dimensionless values of $a$ and $s$, the Gibbs adsorption equation (under the assumption that dilute surfactant solution is ideal) can be written in the form

$$\partial a/\partial \ln x = -s, \qquad (1.3)$$

where $x$ is the ratio of surfactant and condensate concentrations in the droplet bulk phase (for brevity, this relative concentration we call simply the solution concentration).

The barrierless nucleation on soluble nuclei is characterized by the largest extremum of condensate chemical potential in a droplet, which is equal to the threshold value of chemical potential in a vapor. Further, the chemical potential is expressed in $kT$ units and calculated from its equilibrium value for the flat liquid–vapor interface. We denote given chemical potential of a substance condensing in vapor by $b$, and the chemical potential of condensate in a droplet dependent on the number of molecules in a droplet, by $b_\nu$. Correspondingly, the largest extremum $b_\nu$ at $\nu = \nu_{\mathrm{th}}$ is denoted by $b_{\mathrm{th}}$ (subscript th refers to the threshold value).

The intensity of nucleation on soluble nuclei at $b < b_{\mathrm{th}}$ is determined by the height of activation barrier of nucleation. For the height $\Delta F$ of activation barrier expressed in $kT$ units, we have [10, 13]

$$\Delta F = \frac{4}{3}(b_{\mathrm{th}} - b)^{3/2}\left[2/\left|\partial^2 b_\nu/\partial\nu^2\right|_{\nu=\nu_{\mathrm{th}}}\right]^{1/2}. \qquad (1.4)$$

The characteristic time $\Delta t_0$ of the establishment of equilibrium droplet distribution over the entire region of subcritical droplet sizes and the characteristic time $\Delta t_1$ of the establishment of steady-state nucleation rate during the incubation stage in the limit of large $\Delta F$ values are found as [14]

$$\Delta t_0 = (16/11W^{+}_{\mathrm{th}})\left(3/2\left|\partial^2 b_\nu/\partial\nu^2\right|_{\nu=\nu_{\mathrm{th}}}\right)^{2/3}\Delta F^{2/3}, \qquad (1.5)$$

$$\Delta t_1 = (2/3W^{+}_{\mathrm{th}})\left(3/2\left|\partial^2 b_\nu/\partial\nu^2\right|_{\nu=\nu_{\mathrm{th}}}\right)^{2/3}\Delta F^{-1/3}, \qquad (1.6)$$

where $W^{+}_{\mathrm{th}} = \alpha_C v_T n_1 \pi(3v_l/4\pi)^{2/3}\nu_{\mathrm{th}}^{2/3}$ is the number of vapor molecules attached by the droplet from $\nu_{\mathrm{th}}$ molecules per unit time, $\alpha_C$ is the coefficient of condensation of vapor molecules, $v_T$ is the mean thermal velocity of vapor molecules, and $n_1$ is the concentration of vapor molecules. Hence, in order to estimate the role of surfactant comprising nucleus in the nucleation on soluble nuclei, it is necessary to describe the effect of surfactant on the $b_{\mathrm{th}}$ and $|\partial^2 b_\nu/\partial\nu^2|_{\nu=\nu_{\mathrm{th}}}$ values.

## 2. GENERAL RELATIONS IN THE EXTREME POINTS OF CONDENSATE CHEMICAL POTENTIAL

According to [7], let us introduce the value

$$z \equiv s\nu_0^{2/3}/\nu_n \quad (0 \le z \le 1), \qquad (2.1)$$

representing the fraction of adsorbed substance comprising nucleus of its total amount in the extreme points of condensate chemical potential at $\nu = \nu_0$ (here, the $s$ value is not arbitrary, but corresponds to the extremum of condensate chemical potential at a given value of $\nu_n$). It follows from the balance of the substance comprising the nucleus between the adsorption monolayer and the droplet volume that $z = 1 - x\nu_0/\nu_n$. The equation determining the extrema of condensate chemical potential $b_\nu$ is written in terms of variables $z$ and $s$ as [10]

$$[2(a/s)z(1-z) - (3-z)^2]\partial a/\partial s = 2(a/s)z^2. \tag{2.2}$$

In Eq. (2.2), adsorption $s$ can be chosen as an independent variable. Then, in the extreme points of condensate chemical potential, $z$ and $\nu_n$ values (as well as concentration $x$) are the function of $s$. Because relation (2.2) is reduced to the quadratic equation with respect to $z$, we can conclude that the dependence of $z$ on $s$ [at a given equation of state $a(s)$] is not a single-valued, and one value of $s$ corresponds to two values of $z$. Therefore, it is convenient further to pass to inverse single-valued dependence $s(z)$.

As was demonstrated in [10], relations for the extrema $(b_\nu)_0$ of condensate chemical potential and for the second derivative of $b_\nu$ with respect to $\nu$ at $\nu = \nu_0$ have the form

$$(b_\nu)_0 = (s/z)^{3/2}\nu_n^{-1/2}(2az/3s + z - 1), \tag{2.3}$$

$$\begin{aligned}\left(\frac{\partial^2 b_\nu}{\partial \nu^2}\right)_0 = \left(\frac{s}{z}\right)^{9/2}\frac{\nu_n^{-7/2}}{27(3-z)^3}\Bigg\{&8\left(\frac{a}{s}\right)^3 z^2(1-z) \\ &-4\left(\frac{a}{s}\right)^2 z(1-z)(3-z)(6+z) \\ &-6\frac{a}{s}(3-z)^2(z^2+4z-3) \\ &-\left[2\frac{a}{s}z(1-z)-(3-z)^2\right]^3\frac{s}{z^2}\frac{\partial^2 a}{\partial s^2}\Bigg\},\end{aligned} \tag{2.4}$$

where the number $\nu_n$ of surfactant molecules in a droplet at any given $z$ and corresponding values of $s$ and $x$ can be presented as

$$\nu_n^{1/2} = \frac{s^{3/2}}{x}\frac{1-z}{z^{3/2}}. \tag{2.5}$$

For the derivative $\partial s/\partial z$ characterizing the dependence of $s$ on $z$ in the extreme points of chemical potential, from Eq. (2.2) we find

$$\frac{\partial s}{\partial z} = \frac{(a/s+3)z - 9}{\frac{z}{2}\left[(3-z)^2\left(\frac{\partial \ln a}{\partial s} - \frac{1}{s}\right) + 2\frac{a}{s}z^2\frac{\partial^2 a/\partial s^2}{(\partial a/\partial s)^2}\right]}. \tag{2.6}$$

We denote the point at the $z$-axis, where the maximal value of adsorption $s_m$ is reached at the extreme values of condensate chemical potential by $z_m$. In this point, $(\partial s/\partial z)_m = 0$; hereafter, the values at $z = z_m$ or $s = s_m$ are denoted by subscript $m$.

From the expression for $z$, which can be derived by solving Eq. (2.2) with respect to $z$, and Eq. (2.6), we obtain that, in the point of maximum adsorption $s_m$, equalities

$$a_m = 12s_m + 18s_m/(\partial a/\partial s)_m, \tag{2.7}$$

$$z_m = 9s_m/(a_m + 3s_m) \tag{2.8}$$

are valid.

Eliminating $a_m$ and $s_m$ values from Eqs. (2.7) and (2.8), we find

$$\left(\frac{\partial a}{\partial s}\right)_m = \frac{6z_m}{3 - 5z_m}. \tag{2.9}$$

As adsorption $s$ approaches its limiting value $s_\infty$, the absolute value of derivative $(\partial a/\partial s)$ rises and, in accordance with the van Laar and Frumkin model equations of state of a monolayer, even tends to infinity. Correspondingly, if $s_m \longrightarrow s_\infty$, derivative $|\partial a/\partial s|_m$ also tends to infinity. Then, from Eqs. (2.7)–(2.9), we have

$$\begin{aligned}&|\partial a/\partial s|_m \longrightarrow \infty, \quad z_m \longrightarrow 3/5, \\ &a_m \longrightarrow 12s_m \quad \text{at} \quad s_m \longrightarrow s_\infty,\end{aligned} \tag{2.10}$$

that was mentioned earlier [8].

Differentiating equality (2.6) with respect to $z$ and considering Eq. (2.8), for the second derivative $(\partial^2 s/\partial z^2)$ at $s = s_m$, we obtain

$$\left(\frac{\partial^2 s}{\partial z^2}\right)_m = \frac{a_m/s_m + 3}{\frac{z_m}{2}\left\{(3-z_m)^2\left[\left(\frac{\partial \ln a}{\partial s}\right)_m - \frac{1}{s_m}\right] + 2\frac{a_m}{s_m}z_m^2\frac{(\partial^2 a/\partial s^2)_m}{(\partial a/\partial s)_m^2}\right\}}. \tag{2.11}$$

With allowance for asymptotics (2.10), the right-hand side of equality (2.11) tends to zero at $s_m \longrightarrow s_\infty$. Hence, we have

$$(\partial^2 s/\partial z^2)_m \longrightarrow 0, \quad (s_m \longrightarrow s_\infty). \tag{2.12}$$

Similarly, we can be convinced that higher derivatives with respect to $s$ over $z$ at $s = s_m$ and $s_m \longrightarrow s_\infty$ also tend to zero in the points of extrema of condensate chemical potential.

## 3. ASYMPTOTICS IN THE VICINITY OF THE SATURATION OF ADSORPTION MONOLAYER ON THE DROPLET SURFACE

As was already mentioned above, Eq. (2.2) has two roots. The first root describes the variation in variable $z$ from zero to $z_m$ at the corresponding variation in adsorption $s$ from zero to $s_m$. The second root corresponds to a decrease in adsorption from its maximal value to a certain value $z_1$; in this case, the $z$ value rises from $z_m$ to unity. As is seen from Eq. (2.1), equality $z = 1$ corresponds either to the limiting case (at finite $\nu_0$ and $\nu_n$) when all of the substance comprising the nucleus is completely distributed over the droplet surface (then $x = 0$) or to the case when $\nu_0$ and $\nu_n$ tend to zero (then $x$ is finite). In this consideration, the second case is realized, because we assume that the surfactant is soluble; in this case, surfactant concentration in a droplet always differs from zero. In the vicinity of $z = 1$, provided that equality $1 - z \ll 1$ is fulfilled, the following asymptotics can be constructed for the number of molecules in a nucleus, $\nu_n$, number of condensate molecules in a droplet, $\nu_0$, for the extrema $(b_\nu)_0$ of chemical potential of condensate and the second derivative $(\partial^2 b_\nu/\partial\nu^2)_0$ as functions of $z$ [10]:

$$\nu_n^{1/2} = (s_1^{3/2}/x_1)(1 - z), \tag{3.1}$$

$$\nu_0 = (\nu_n/s_1)^{3/2}, \tag{3.2}$$

$$(b_\nu)_0 = \frac{2}{3}a_1\left(\frac{s_1}{\nu_n}\right)^{1/2}\left[1 + \frac{1}{2}\left(1 - \frac{3s_1}{a_1}\right)(1 - z)\right], \tag{3.3}$$

$$\left(\frac{\partial^2 b_\nu}{\partial\nu^2}\right)_0 = -\frac{2}{9}a_1\left(\frac{s_1}{\nu_n}\right)^{7/2}\left[1 - \frac{4s_1^2}{3a_1}\left(\frac{\partial^2 a}{\partial s^2}\right)_1\right], \tag{3.4}$$

where $a_1 \equiv a(s_1)$, $(\partial^2 a/\partial s^2)_1 \equiv (\partial^2 a/\partial s^2)_{s = s_1}$, and $x_1 \equiv x(s_1)$ are the values of surface tension, its second derivative with respect to $s$, and the solution concentration in a droplet at $z \longrightarrow 1$, respectively. The value of adsorption $s_1$ is found by substituting $z = 1$ into Eq. (2.2) and the numerical solution of equation thus obtained for the specific form of adsorption equation $x(s)$ or the equation of state $a(s)$. The sign of Eq. (3.4) indicates that the extremum of condensate chemical potential set by asymptotics (3.3) is a maximum within the entire domain of applicability of asymptotics (3.1)–(3.4).

For the activation energy $\Delta F$ at relative deviation $\varepsilon \equiv (b_{\text{th}} - b)/b_{\text{th}}$ below the threshold value of vapor chemical potential within the prethreshold region [10, 13], we have

$$\Delta F = \frac{16\varepsilon^{3/2}\nu_n a_1}{6^{1/2}3s_1}\left[1 - \frac{4s_1^2}{3a_1}\left(\frac{\partial^2 a}{\partial s^2}\right)_1\right]^{-1/2}. \tag{3.5}$$

Substituting equalities (3.2) and (3.4) into Eq. (1.6), for the time of the establishment of steady-state nucleation rate $\Delta t_1$, we arrive at the following expression:

$$\Delta t_1 = \frac{3}{2^{1/3}\alpha_C v_T n_1 \pi\left(\frac{3v_l}{4\pi}\right)^{2/3}} \times \frac{\nu_n^{4/3}}{a_1^{2/3}s_1^{4/3}\left[1 - \frac{4s_1^2}{3a_1}\left(\frac{\partial^2 a}{\partial s^2}\right)_1\right]^{2/3}}\Delta F^{-1/3}. \tag{3.6}$$

Let us now consider the region of the variation in variable $s$ in the vicinity of its maximal value $s_m$. We represent adsorption $s$ in the form of expansion in terms of $z$ in the vicinity of $z = z_m$:

$$s = s_m + \frac{1}{2}\left(\frac{\partial^2 s}{\partial z^2}\right)_m (z - z_m)^2 + \frac{1}{3!}\left(\frac{\partial^3 s}{\partial z^3}\right)_m (z - z_m)^3 + \dots. \tag{3.7}$$

Because, as was already mentioned at the end of previous section, the derivatives of $s$ with respect to $z$ at $s = s_m$ and $s_m \longrightarrow s_\infty$ tend to zero, we have $s \approx s_m$; i.e., the adsorption remains almost constant in a certain region of variations in variable $z$, this region being the wider the closer $s_m$ to $s_\infty$.

The region of variation in variable $z$ in which $s \approx s_m$ is determined by equation

$$2(a/s_m)z(1 - z) - (3 - z)^2 = 0, \tag{3.8}$$

because, at $s \approx s_m$, derivative $|\partial a/\partial s| \approx \infty$.

At $s \approx s_m$, Eq. (1.3) for $a$ has the form

$$\partial a/\partial x = -s_m/x. \tag{3.9}$$

In this case, we can take advantage of the results obtained for the model of droplet with constant adsorption discussed in [8]. The following equation of state:

$$a = a_m - s_m \ln(x/x_m) \tag{3.10}$$

satisfies differential equation (3.9).

From Eqs. (3.8) and (3.10), we find

$$x = x_m \exp\left(\frac{a_m}{s_m}\right)\exp\left[-\frac{(3 - z)^2}{2z(1 - z)}\right]. \tag{3.11}$$

Equation (3.11) differs from formula (8) in [8] by that the constant value of adsorption is equal to $s_m$, but not to $s_\infty$. Evidently, corresponding values $a_m$ and $x_m$ can be readily calculated by the model or experimental adsorption isotherms for surfactant comprising nucleus, using Eq. (2.7).

For the asymptotics of the number $\nu_0$ of condensate molecules, condensate chemical potential and its second derivative with respect to $\nu$ at $\nu = \nu_0$ and number of molecules comprising nucleus, from Eqs. (2.1) and (2.3)–(2.5), at constant adsorption $s \approx s_m$ with allowance for Eqs. (3.8) and (3.11), we derive expressions

$$\nu_0^{1/3} = \left(\frac{z}{s_m}\right)^{1/2}\nu_n^{1/2}, \tag{3.12}$$

$$(b_\nu)_0 = \frac{2}{3}s_m^{3/2}\nu_n^{-1/2}\frac{3-z^2}{z^{3/2}(1-z)}, \tag{3.13}$$

$$\left(\frac{\partial^2 b_\nu}{\partial \nu^2}\right)_0 = \frac{2}{27}\left(\frac{s_m}{z}\right)^{9/2}\frac{(3-z)(z^2+4z-3)}{(1-z)^2}\nu_n^{-7/2}, \tag{3.14}$$

$$\nu_n^{1/2} = \frac{s_m^{3/2}}{x_m}\exp\left(-\frac{a_m}{s_m}\right)\exp\left(\frac{(3-z)^2}{2z(1-z)}\right)\frac{1-z}{z^{3/2}}. \tag{3.15}$$

Equation (3.15) can be considered as a relation determining the dependence of $z$ on $\nu_n$. Then, setting $\nu_n$, we find $z$ from Eq. (3.15) and, using equalities (3.12)–(3.14), all other remaining thermodynamic characteristics as functions of $\nu_n$ in the extreme points of condensate chemical potential.

Substitution of Eqs. (3.13) and (3.14) into Eq. (1.4) at the largest $(b_\nu)_0 = b_{\rm th}$ value yields

$$\Delta F = \frac{4}{3}\varepsilon^{3/2}\frac{2^{3/2}(3-z^2)^{3/2}}{(1-z)^{1/2}(3-z)^{1/2}|z^2+4z-3|^{1/2}}\nu_n. \tag{3.16}$$

In view of relation (3.15), from Eq. (3.16) follows the dependence of the height $\Delta F$ of activation barrier of nucleation on the relative deviation $\varepsilon$ of vapor chemical potential from the threshold value $b_{\rm th}$ and on the nucleus size $\nu_n$. For the time of the establishment of steady-state nucleation rate, $\Delta t_1$, with allowance for Eqs. (3.12) and (3.14), we find using Eq. (1.6)

$$\Delta t_1 = \frac{3^{5/2}\nu_n^{4/3}}{2^{1/3}\alpha_C v_T n_1 \pi(3v_l/4\pi)^{2/3}} \times \frac{z^2(1-z)^{4/3}}{s_m^2(3-z)^{2/3}|z^2+4z-3|^{2/3}}\Delta F^{-1/3}. \tag{3.17}$$

In view relation (3.15), Eq. (3.17) determines the dependence of time $\Delta t_1$ on $\Delta F$ and $\nu_n$.

## 4. DOMAINS
## OF ASYMPTOTICS APPLICABILITY

It can be expected that, at small values of $\nu_n$, there is a region where only asymptotics (3.1)–(3.6) are realized during the adsorption of almost all of the substance comprising the nucleus on the droplet surface, and there is a region where the maxima of chemical potential corresponding to Eqs. (3.3) and (3.13) exist simultaneously. Let us equate the asymptotics of chemical potential $(b_\nu)_0$ set by relation (3.3) in the principal order with respect to small parameter $1 - z \ll 1$ and relation (3.13). We denote the point, where these asymptotics are equal, by $z_a$. Let us introduce function $f(z)$

$$f(z) = \frac{3-z^2}{z^{3/2}(1-z)}. \tag{4.1}$$

As follows from Eqs. (3.3) and (3.13), the value of $z_a$ is determined by the solution of equation

$$f(z) = \frac{a_1}{s_1}\left(\frac{s_1}{s_m}\right)^{3/2}. \tag{4.2}$$

The dependence of function $f$ on $z$ has the form of oblate parabola at $0 < z < 1$. The straight line set by the right-hand side of Eq. (4.2) intersects this parabola in two points. The root $z_a$ of Eq. (4.2), which is of interest to us, is determined by the smaller value of the intersection point of straight line $(a_1/s_1)(s_1/s_m)^{3/2}$ and curve $f$ [the right-hand intersection point corresponds to the minimum of condensate chemical potential in Eq. (3.13)]. Substituting $z_a$ into Eq. (3.13) for asymptotic $\nu_n$ at constant adsorption, we arrive at corresponding value of $\nu_n^{(a)}$

$$\nu_n^{(a)} = \nu_n|_{z = z_a}. \tag{4.3}$$

The $\nu_n^{(a)}$ value allows us to conclude which asymptotics (at the adsorption of almost all of the substance comprising the nucleus or at constant adsorption) are realized in practice, because, in fact, the number $\nu_n$ of surfactant molecules in nucleus is the external parameter of a problem. Let us assume that all the nuclei considered in this work are macroscopic, if they contain more than $10^3$ molecules; i.e., the inequality $\nu_n > 10^3$ should take place. Then, if $\nu_n^{(a)} > 10^3$, both asymptotics can exist: at $10^3 < \nu_n < \nu_n^{(a)}$, the maximum of condensate chemical potential set by formula (3.3) turned out to be larger than that set by formula (3.13) and, consequently, asymptotics (3.1)–(3.6) are realized upon the adsorption of almost all of the substance comprising the nucleus; at $\nu_n > \nu_n^{(a)}$, chemical potential set by formula (3.13) becomes larger than that set by formula (3.3) and asymptotics (3.12)–(3.17) are then realized at the constant value of adsorption. However, if turned out that, at given values of external parameters $\nu_n^{(a)} < 10^3$, only asymptotics (3.12)–(3.17) are realized at $\nu_n > 10^3$. The role of external parameter $s_\infty$ of a problem is now easily understood. Because it is the parameter $s_\infty$ that determines the characteristic values of adsorption $s_m$ and $s_1$, we define the $(a_1/s_1)(s_1/s_m)^{3/2}$ value (at given dimensionless surface tension of pure condensate $\bar{a}$) and, in a final analysis, the $\nu_n^{(a)}$ value. Hence, the domains of applicability of asymptotics (3.1)–(3.6) upon the adsorption of most of the substance comprising the nucleus in the initial region of nucleus sizes and

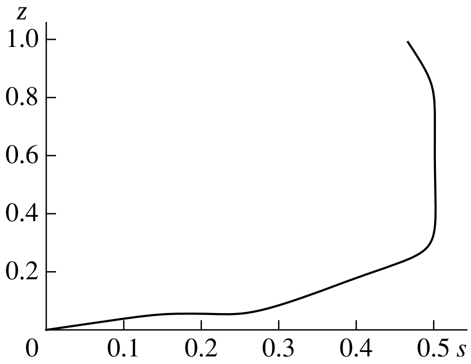

**Fig. 1.** Dependence of value $z$ on $s$ at $s_\infty = 0.5$, $\kappa = 1.95$, $\bar{a} = 10$, and $x_\alpha = 10^{-5}$.

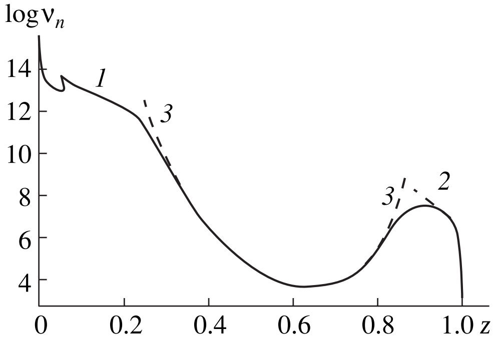

**Fig. 2.** Dependences of value $\log \nu_n$ on $z$ for the case $s_\infty = 0.5$ at $\kappa = 1.95$, $\bar{a} = 10$, and $x_\alpha = 10^{-5}$. Curve *1* corresponds to the exact value of $\log \nu_n$; curve *2*, to the asymptotics upon the adsorption of most of the substance comprising the nucleus; and curve *3*, to asymptotics at constant adsorption.

asymptotics at constant adsorption (3.12)–(3.17) depend on the $s_\infty$ value.

## 5. NUMERICAL CALCULATIONS OF THERMODYNAMIC PARAMETERS FOR MODEL ADSORPTION ISOTHERMS

Let us now set the specific pattern of adsorption isotherm in order to compare the results of exact calculations with those given by asymptotics (3.1), (3.3), (3.5), (3.6), (3.13), and (3.15)–(3.17). Unfortunately, up to now there are no direct measurements of threshold supersaturation (and, respectively, chemical potential) as a function of the size of condensation nuclei composed of surfactants. Therefore, comparison can be performed only with the results of direct numerical calculations by Eqs. (2.1)–(2.5), using representative model adsorption isotherms. Such a representative adsorption isotherm is the Frumkin isotherm that, which takes into account lateral interactions in a surfactant monolayer and in our designations has the form

$$x = (x_\alpha s/(s_\infty - s))\exp(-2\kappa s/s_\infty), \qquad (5.1)$$

where $x_\alpha$ is the characteristic solution concentration such that the $x_\alpha/s_\infty$ ratio is the Henry constant and $\kappa$ is the parameter of lateral interactions in a monolayer. At $\kappa = 0$, isotherm (5.1) is transformed into the Langmuir adsorption isotherm. The integration of Gibbs adsorption isotherm (1.3) with allowance for Eq. (5.1) yields the equation of state of surfactant adsorption layer

$$a = \bar{a} + s_\infty[\ln(1 - s/s_\infty) + \kappa(s/s_\infty)^2]. \qquad (5.2)$$

In further calculations, we assume that $\bar{a} = 10$ (that corresponds to water as condensate at $T = 273$ K), $x_\alpha = 10^{-5}$, and $\kappa = 1.95$.

Figure 1 shows the dependence of $z$ on $s$ followed from Eq. (2.2) at $s_\infty = 0.5$ that corresponds to the situation when the limiting area of surfactant molecule in a monolayer twice as large as the surface area of water molecule. Because Eq. (2.2) has two roots, Fig. 1 shows two branches of the $z(s)$ dependence, which are merged in point $z_m \approx 3/5$ at $s = s_m$. As is seen from Fig. 1, the $z$ value varies within wide range upon the variation of adsorption $s$ over a very narrow range in the vicinity of maximal $s_m$ value; hence, it can be expected that, in this range, asymptotics (3.12)–(3.17) provide for good approximation to the corresponding exact values. Let us consider first the dependence of the number of surfactant molecules in a nucleus on $z$. Figures 2 and 3 present the dependences of $\log \nu_n$ on $z$ for two cases: $s_\infty = 0.5$ and 0.1, respectively. Solid lines (curves *1* in Figs. 2 and 3) correspond the $\log \nu_n$ value calculated by Eqs. (5.1) and (5.2) upon their substitution into Eqs. (2.1)–(2.5) using the algorithm described in [11]. It is seen that, in the case of not so large limiting area for surfactant molecule ($s_\infty = 0.5$), there are regions at the $z$-axis where asymptotic (3.15) at constant adsorption (corresponding to curve *3*, Fig. 2) and asymptotic (3.1) at the adsorption of almost all of the substance comprising the nucleus on the droplet surface (curve *2*, Fig. 2) are both valid. In addition, it is seen that asymptotic (3.15) is valid within the wide range of values of variable $z$ and the number of molecules $\nu_n$. In the case of larger limiting area of surfactant molecule (at $s_\infty = 1$) and restraint to the number of surfactant molecules in a nucleus ($\nu_n > 10^3$), asymptotic (3.1) is no longer realized. At $\nu_n > 10^3$, only one branch of $z(s)$ dependence is used for the exact calculation of $\log \nu_n(z)$ function (in Fig. 1, it corresponds to the lower branch), whereas asymptotic (3.15) is valid within a narrow range of variable $z$. However, asymptotic at constant adsorption still leads to good agreement with the exact value of $\log \nu_n$ within a wide range of the sizes of surfactant nuclei.

The fact that, at $s_\infty = 0.1$ and $s_\infty = 0.5$, the situations turned out to be different from the standpoint of the applicability of asymptotics is explained by that they are characterized by the different values of $\nu_n^{(a)}$. Figure 4 shows the dependence of $\nu_n^{(a)}$ on parameter $s_\infty$ calculated for the case of the Frumkin adsorption isotherm and other external parameters set above. As is seen from Fig. 4, at $s_\infty = 0.1$, we obtain $\nu_n^{(a)} < 10^3$ (and even $\nu_n^{(a)} < 1$), whereas at $s_\infty = 0.5$, we have $\nu_n^{(a)} > 10^3$. In accordance with what have been said in Section 4, this explains why, at $s_\infty = 0.5$, there is a region of nucleus sizes, where asymptotics are applicable upon the adsorption of almost all of the substance comprising the nucleus on the droplet surface; at $s_\infty = 0.1$, such a region does no longer exist.

Let us introduce the renormalization factor $f^{(b)}$ via relation

$$f^{(b)} = (b_\nu)_0/(\bar{b}_\nu)_0, \tag{5.3}$$

where $(\bar{b}_\nu)_0 = 2(2\bar{a}/9)^{3/2}\nu_n^{-1/2}$ is the chemical potential in the point of maximum for the case of surface-inactive substance comprising nucleus (other parameters being equal) [10, 13]. Renormalization adsorption factor $f^{(b)}$ can be calculated as a function of $\nu_n$ using relations (2.1)–(2.5) with the algorithm described in [11]. Dependence of $f^{(b)}$ on $\log\nu_n$ is shown in Fig. 5 for two values of parameter $s_\infty$: 0.5 and 0.1. Curve *1* at $s_\infty = 0.5$ was calculated only for the Frumkin adsorption isotherm with the parameter of lateral interactions $\kappa = 1.95$, whereas curves *2* and *3* at $s_\infty = 0.1$ were obtained for the Frumkin ($\kappa = 1.95$) and Langmuir ($\kappa = 0$) adsorption isotherms, respectively. Solid lines in Fig. 5 correspond to exact calculations [in the region of sizes, where each $\nu_n$ value corresponds to the three values of $z$ in Fig. 2, calculations lead to three branches of $f^{(b)}$]; dashed lines depict asymptotics upon the adsorption of almost all of the substance comprising the nucleus (curve *1*') and at constant adsorption (curves *1*", *2*", *3*"). As is seen from Fig. 5, at $s_\infty = 0.1$, the asymptotic corresponding to the adsorption of almost all of the substance comprising the nucleus on the droplet surface is not realized for both adsorption isotherms. The dependence of adsorption factor $f^{(b)}$ for the Langmuir adsorption isotherm is distinguished by the absence of the ambiguity region at large nuclei and does not exceed unity within the entire range of surfactant nucleus sizes. Asymptotics at constant adsorption in both cases ($s_\infty = 0.5$ and $s_\infty = 0.1$) provide for a good approximation of the exact value of renormalization adsorption factor $f^{(b)}$ in a wide range of the variation in the number of molecules $\nu_n$.

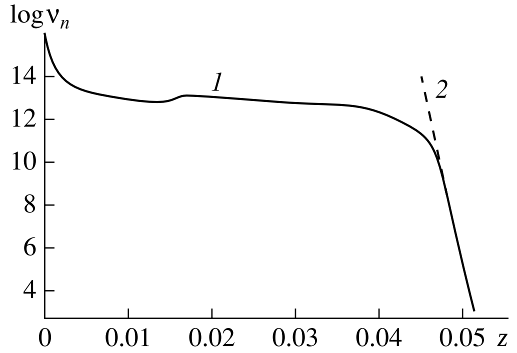

**Fig. 3.** Dependences of value $\log\nu_n$ on $z$ for the case $s_\infty = 0.1$ at $\kappa = 1.95$, $\bar{a} = 10$, and $x_\alpha = 10^{-5}$. Curve *1* corresponds to the exact value of $\log\nu_n$; curve *2*, to the asymptotics at constant adsorption.

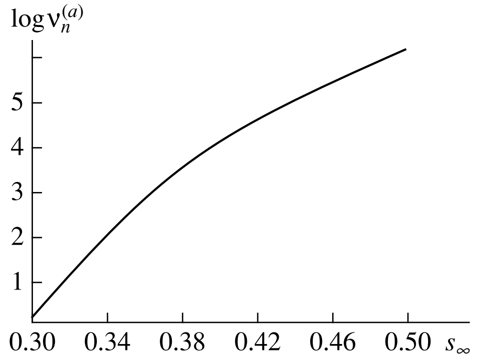

**Fig. 4.** Dependence of the number of molecules $\nu_n^{(a)}$ on parameter $s_\infty$ at $\kappa = 1.995$, $\bar{a} = 10$, and $x_\alpha = 10^{-5}$.

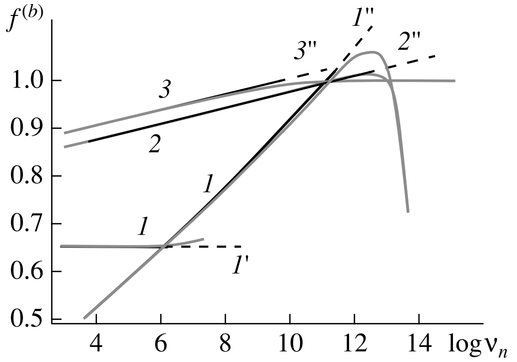

**Fig. 5.** Dependences of value $f^{(b)}$ on $\log\nu_n$ for the cases (*1*, *1*', and *1*") $s_\infty = 0.5$, $\kappa = 1.95$ and (*2*, *2*" and *3*, *3*") $s_\infty = 0.1$, $\kappa = 1.95$ and $\kappa = 0$ at $\bar{a} = 10$ and $x_\alpha = 10^{-5}$. Curves *1*, *2*, and *3* correspond to the exact value of $f^{(b)}$; curve *1*', to the asymptotic upon the adsorption of most of the substance comprising the nucleus; and curves *1*", *2*", *3*", to the asymptotic at constant adsorption.

Note once more that, although the range of variable $z$, where asymptotics at constant adsorption are valid, changes, depending on parameter $s_\infty$, it always corresponds to the wide range of the number of surfactant molecules in a nucleus. Such a good agreement between the exact values and asymptotic expressions at constant adsorption, which is seen in Figs. 2, 3, and 5, is due to the fact that the value of $s_m$ and corresponding values $x_m$ and $a_m$ entering into Eqs. (3.9) and (3.10) are exactly calculated using Eqs. (2.7), (5.1), and (5.2). In

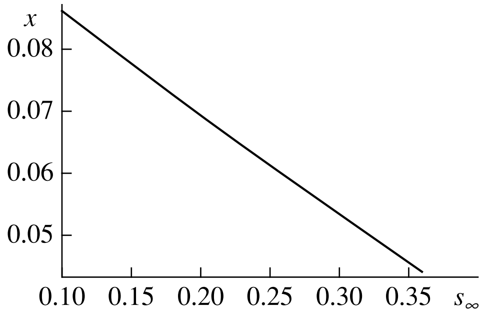

**Fig. 6.** Dependence of the estimate from above for concentration $x$ on parameter $s_\infty$.

addition, the value of $s_m$ can always be calculated for a given adsorption isotherm or chosen from the experiment, thus ensuring good agreement between the approximated and exact values.

As is seen from Figs. 2 and 3 by comparing the dependences of $\log\nu_n$ on $z$ at $s_\infty = 0.5$ and 0.1, the region of variable $z$, where asymptotic expressions at constant adsorption are applicable and the exact calculations are performed and inequality $\nu_n > 10^3$ is fulfilled, is the narrower the smaller parameter $s_\infty$ (other parameters being equal). Formally, all the values can be calculated using the algorithm given in [11] for any value of variable $z$; however, at small values of $s_\infty$, the ambiguity region for small nuclei and corresponding transition point from one branch of the dependence of the extrema of condensate chemical potential to the other shifts at the $\log\nu_n$-axis to the left to the region $\nu_n < 10^3$ (and even to $\nu_n \ll 1$). In this case, concentration $x_m$ calculated by Eq. (5.1) in the point of adsorption maximum $s_m$ becomes so high that the inequality $x \ll 1$ is violated. The latter is attributed to the fact that the Frumkin isotherm does not involve restraint from above on the value of concentration (in fact, there is a limiting solution concentration set by the solubility of substance comprising nucleus) and Eq. (5.1) provides for as high a concentration at $s \longrightarrow s_\infty$ as needed. From the standpoint of the applicability of the whole theory, the corresponding values of the number of molecules $\nu_n$ in a nucleus and concentration $x$ should be excluded from consideration. In such a situation, values $s_m$, $a_m$, and $x_m$ entering into Eqs. (3.12)–(3.17) for the asymptotics at constant adsorption should also be considered only as reference parameters that make it possible to describe thermodynamic characteristics in the region of constant adsorption where conditions $x \ll 1$ and $\nu_n > 10^3$ are fulfilled.

Let us demonstrate that condition $\nu_n > 10^3$ is stronger and automatically provides for the fulfillment of condition $x \ll 1$. We consider the values of parameter $s_\infty < 0.36$. At these $s_\infty$ values, $\nu_n^{(a)} < 10^3$ (see Fig. 4), and the region of small nucleus sizes is described by asymptotics (3.9)–(3.14) (asymptotics upon the adsorption of almost all of the substance comprising the nucleus on the droplet surface are not realized). In this case, the values of limiting adsorption $s_m$ turned out to be so close to the corresponding values of $s_\infty$ that the values of maximal concentration $x_m$ determined by Eq. (5.1) do not satisfy condition $x \ll 1$. As the adsorption increases, variable $z$ (here, only the lower branch of $z(s)$ dependence operates) and concentration $x$ presented by Eq. (3.11) rise, while the number of molecules in a nucleus $\nu_n$ calculated by Eq. (3.15) decreases. According to Eqs. (3.11) and (3.15). the condition to the macroscopicity of condensation nucleus $\nu_n > 10^3$ can be written as

$$x < s_m^{3/2}(1-z)/(10z)^{3/2}. \tag{5.4}$$

We consider how the right-hand side of inequality (5.4). Finding numerically the value of variable $z$, at which $\nu_n = 10^3$, for each value of parameter $s_\infty$ with the aid of Eq. (3.15), and substituting the thus obtained value of $z$ into the right-hand side of Eq. (5.4), we obtain the estimate from above for concentration $x$. Figure 6 shows the dependence of this estimate on parameter $s_\infty$. It is seen that, under condition $\nu_n > 10^3$, the concentration is estimated from above by the value much smaller than unity.

Let us introduce renormalization adsorption factors $f^{(\Delta F)}$ and $f^{(\Delta t)}$ using relations

$$f^{(\Delta F)} = \Delta F/\Delta\bar{F}, \tag{5.5}$$

$$f^{(\Delta t)} = \Delta t_1/\Delta\bar{t}_1, \tag{5.6}$$

where $\Delta\bar{F} = 16\varepsilon^{3/2}\nu_n/6^{1/2}$ is the activation energy and $\Delta\bar{t}_1$ is the time of the establishment of steady-state nucleation rate for the case of surface-inactive substance comprising nucleus (other parameters being equal). The $\Delta\bar{t}_1$ time is given by the expression similar to Eq. (1.6), where the number of condensate molecules $\nu_{\text{th}}$ and the second derivative $|\partial^2 b_\nu/\partial\nu^2|_{\nu = \nu_{\text{th}}}$ are replaced by the values corresponding to the case of the surface-inactive substance comprising the nucleus, $\bar{\nu}_{\text{th}} = (9/2\bar{a})^{3/2}\nu_n^{3/2}$ and $\overline{\left|\partial^2 b_\nu/\partial\nu^2\right|}_{\nu = \nu_{\text{th}}} = -(2/3)(2\bar{a}/9)^{9/2}\nu_n^{-7/2}$ [10]. Figures 7 and 8 show the dependences of renormalization factors $f^{(\Delta F)}$ and $f^{(\Delta t)}$ on $\log\nu_n$ for the Frumkin isotherm. The $f^{(\Delta F)}$ dependence is plotted for two values of parameter $s_\infty = 0.5$ and 0.1; solid lines correspond to exact calculations by Eqs. (2.1)–(2.5), (5.1), (5.2), and (1.4), dotted lines denote asymptotics upon the adsorption of almost all of the substance comprising the nucleus (curve *1*') and constant adsorption (curves *2*" and *3*"). Calculations of renormalization factor $f^{(\Delta F)}$ presented in Fig. 7 were performed under the assumption that relative deviation $\varepsilon$ in the subthreshold region of the vapor

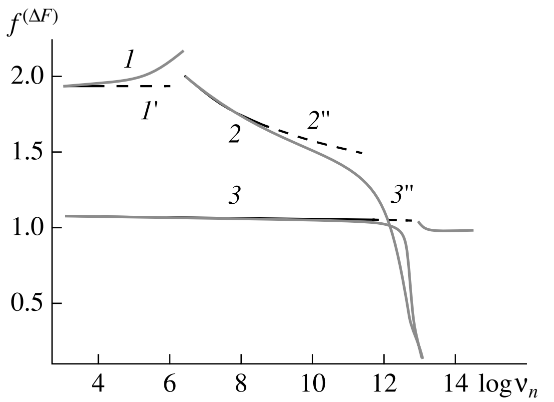

**Fig. 7.** Dependence of $f^{(\Delta F)}$ on $\log\nu_n$ for two values of parameter $s_\infty$: (*1*, *1'* and *2*, *2''*) 0.5 and (*3*, *3''*) 0.1 at $\kappa = 1.95$, $\bar{a} = 10$, and $x_\alpha = 10^{-5}$. Curves *1*, *2*, and *3* correspond to the exact value of $f^{(\Delta F)}$; curve *1'*, to the asymptotic upon the adsorption of most of the substance comprising the nucleus, and curves *2''*, *3''*, to the asymptotic at constant adsorption.

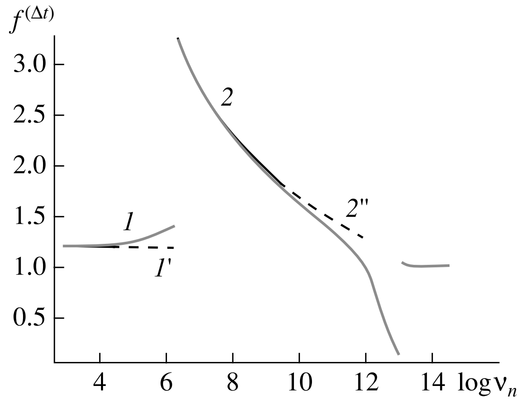

**Fig. 8.** Dependences of $f^{(\Delta t)}$ on $\log\nu_n$ for $s_\infty = 0.5$ at $\kappa = 1.95$, $\bar{a} = 10$, and $x_\alpha = 10^{-5}$. Curves *1* and *2* correspond to the exact value of $f^{(\Delta t)}$; curve *1'*, to the asymptotic upon the adsorption of most of the substance comprising the nucleus; and curve *2''*, to the asymptotic at constant adsorption.

metastability is identical for the cases of surface-active and surface-inactive substances comprising the nucleus.

Figure 8 demonstrates the dependence of $f^{(\Delta t)}$ on $\log\nu_n$ at $s_\infty = 0.5$. Solid lines correspond to the exact calculations by Eqs. (2.1)–(2.5), (5.1), (5.2), and (1.6), dotted lines denote asymptotics upon the adsorption of almost all of the substance comprising the nucleus (curve *1'*) and constant adsorption (curve *2''*). When constructing the dependences of renormalization factor $f^{(\Delta t)}$ on $\log\nu_n$, activation energies $\Delta F$ and $\Delta\bar{F}$ for the respective cases of surface-active and surface-inactive substances comprising nucleus were considered to be identical. This is attributed to the fact that, when varying the nucleus sizes, we should remain in the subthreshold region of vapor metastability whose boundaries are determined precisely by the $\Delta F$ value.

## ACKNOWLEDGMENT

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