

On the Conditions Imposed on the Spreading Coefficient and the Nucleus Size in the Theory of Nucleation on Wettable Insoluble Nuclei

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Abstract—Based on the analysis of the characteristic pattern of the disjoining pressure isotherm in thin wetting film on a macroscopic solid insoluble condensation nucleus, the conditions imposed on the initial value of the coefficient of condensate spreading over the nucleus surface and the conditions imposed on the nucleus size are formulated. When these conditions are fulfilled, the droplet emergence on a nucleus occurs via the formation of the liquid film with a uniform thickness surrounding the nucleus.

INTRODUCTION

As was shown in [1], the stage of the creation of condensate thin films with overlapping surface layers at the nucleus–film and the film–vapor interfaces plays an important role in the theory of the nucleation of supersaturated vapors on insoluble wettable nuclei. Special properties of thin films related to their essential inhomogeneity can be described, for example, using the disjoining pressure isotherm or the isotherm of adsorption from the gaseous phase on a solid substrate. These isotherms are interrelated, and if we know one of them, we can obtain the other one.

The disjoining pressure was originally determined for plane-parallel films [2]. This notion can also be applied to the uniformly thick films on a curved substrate, for example, on a spherical solid nucleus, provided that its curvature is not very large [1].

Generalization to the case of nonuniformly thick films is also possible: the disjoining pressure at each point at the substrate surface is equal to its value corresponding to the local film thickness [2, 3]. In this case, it is important that the film thickness should vary rather slowly along the surface; i.e., the absolute value of the local angle of thickness profile tilt should be small.

Whether the film is uniform or not depends on the wetting conditions of the surface and the nucleus size. In the case of partial wetting of a uniform nucleus surface, the film is separated into the thin wetting film and the sessile droplet representing small lens. Naturally, the disjoining pressure isotherm or the adsorption isotherm completely determine both the wetting conditions and the precise profile of the thickness of such a nonuniform film [3, 4], provided that the substrate curvature is preset. However, the entire disjoining pressure isotherm is not easily measured, and its theoretical description is rather complicated because surface

forces are governed by many factors that are significant within different thickness ranges [2]. At the same time, knowledge of the entire disjoining pressure isotherm is not required at all in the theory of heterogeneous nucleation to discuss the conditions of the creation of droplets in the form of uniform films. Therefore, it seems useful to formulate, via a relatively small number of characteristic parameters, the wetting conditions of the uniform surface of an insoluble nucleus and the formation conditions for a uniformly thick film formed as a result of adsorption from vapor, which is transformed into the condensation on a nucleus. The significance of these conditions is stipulated by the existence of the developed analytical theory [1, 5, 6] describing thermodynamics and the kinetics of condensation and determining the possibility of barrierless nucleation.

1. RELATIONSHIP BETWEEN THE DISJOINING PRESSURE ISOTHERM AND THE WORK OF WETTING FOR UNIFORMLY THICK FILM ON A NUCLEUS

Let us recall some relations connecting the work of nucleus wetting and the disjoining pressure, which are important for further discussion. According to [1], the isotherm of disjoining pressure Π (in the case when this concept can be used) in a thin condensate film with radius R on a solid wettable nucleus with radius R_n can be related to the depending on the film thickness $R - R_n$ dimensionless work of nucleus wetting in the following manner:

$$f = -\frac{4\pi}{kT} \int_{R_n}^R d\tilde{R} \tilde{R}^2 \Pi(\tilde{R} - R_n) - \frac{4\pi R_n^2}{kT} \sigma^{\gamma\alpha}, \quad (1.1)$$

where k is Boltzmann's constant, T is the temperature, and $\sigma^{\gamma\alpha}$ is the surface tension at the vapor–condensate interface.

As follows from (1.1), the work of wetting f_* at $R \rightarrow \infty$ is equal to

$$f_* = -\frac{4\pi}{kT} \int_{R_n}^{\infty} d\tilde{R} \tilde{R}^2 \Pi(\tilde{R} - R_n) - \frac{4\pi R_n^2}{kT} \sigma^{\alpha\beta}. \quad (1.2)$$

On the other hand, at $R \rightarrow \infty$, the expression for the work of wetting tends to a quite definite limit:

$$f_* = \frac{4\pi R_n^2 (\sigma^{\alpha\beta} - \sigma^{\gamma\beta})}{kT}, \quad (1.3)$$

where $\sigma^{\gamma\alpha}$ and $\sigma^{\gamma\beta}$ are the surface tensions at the nucleus–condensate and the nucleus–vapor interfaces, respectively. Formula (1.3) is known as the Dupré formula. Let us introduce designation $\Delta\sigma \equiv \sigma^{\gamma\alpha} - \sigma^{\gamma\beta}$. Inequality $\Delta\sigma < 0$ corresponds to the film that wets the substrate.

Comparing (1.2) and (1.3), we conclude that

$$\frac{1}{R_n^2} \int_{R_n}^{\infty} d\tilde{R} \tilde{R}^2 \Pi(\tilde{R} - R_n) = \sigma^{\gamma\beta} - \sigma^{\gamma\alpha} - \sigma^{\alpha\beta}. \quad (1.4)$$

Difference $s \equiv \sigma^{\gamma\beta} - \sigma^{\gamma\alpha} - \sigma^{\alpha\beta} = |\Delta\sigma| - \sigma^{\alpha\beta}$ is called the spreading coefficient. For the case of complete wetting, when the film covers the substrate uniformly and completely, $s > 0$. Note that since the evidently non-equilibrium (for the given system) value of surface tension $\sigma^{\gamma\beta}$ for a “dry” nucleus surface is present in the definition of this parameter, the spreading coefficient thus determined is the non-equilibrium magnitude corresponding to the spreading of a liquid over the “dry” surface. Therefore, unlike equilibrium spreading coefficient $s_e = \sigma_e^{\gamma\beta} - \sigma^{\gamma\alpha} - \sigma^{\alpha\beta}$, which is determined at the equilibrium surface tension $\sigma_e^{\gamma\beta}$, this parameter can be both negative or positive. The equilibrium spreading coefficient is always negative or equal to zero, $s_e \leq 0$.

We can derive expressions connecting the equilibrium surface tension and the spreading coefficient with their non-equilibrium values obtained for a flat “dry” surface. The work of wetting (it is convenient here not to use its dimensionless value) of the unit area of a “dry” substrate surface by the liquid phase (i.e., by the infinitely thick film) is written similarly to (1.2) as $-\int_0^{\infty} \Pi(h)dh - \sigma^{\alpha\beta}$. The work of wetting of the unit area of the “equilibrium” surface of a flat substrate, i.e., the substrate already covered with the film of a certain thickness, is then equal to $-\int_{h_e}^{\infty} \Pi(h)dh - \sigma^{\alpha\beta}$. Hence, using (1.4), for the flat surface, we obtain the following relationships:

$$s = \int_0^{\infty} \Pi(h)dh, \quad (1.5)$$

$$s_e = \int_{h_e}^{\infty} \Pi(h)dh, \quad s_e = s - \int_0^{h_e} \Pi(h)dh, \quad (1.6)$$

and

$$\sigma_e^{\gamma\beta} = \sigma^{\gamma\beta} - \int_0^{h_e} \Pi(h)dh. \quad (1.7)$$

2. ADSORPTION AND EXPONENTIAL ASYMPTOTICS OF THE WORK OF WETTING AND DISJOINING PRESSURE

As is seen from the above discussion, it is important to know the initial part of the disjoining pressure isotherm in order to estimate the conditions for the formation of a uniformly thick film. For a sufficiently thin film, the disjoining pressure isotherm is determined by the surface adsorption properties. Note that we are dealing here with polymolecular adsorption, which always precedes the condensation in systems with complete or partial wetting. In fact, there is no distinct difference between these phenomena, and the adsorption of several tens of molecular layers can already be considered to be the condensation. For flat adsorption films, the dependence of adsorption Γ on concentration n^β of vapor molecules at the initial part of an adsorption isotherm can be represented [7] as

$$\Gamma = K_\Gamma (n^\beta)^{1/m}, \quad (2.1)$$

where K_Γ is a certain constant, which can be determined experimentally; parameter m is equal to unity for the energy-homogeneous adsorbing surface (the Henry isotherm), whereas for the energy-heterogeneous surface its value does not exceed five (the Freundlich isotherm). These isotherms are rather universal (the powers depend on the energy homogeneity of the surface), and constant K_Γ depends on the types of surface and adsorbate.

Naturally, in the case of polymolecular adsorption, the real adsorption isotherm differs from isotherm (2.1) in the range of thicknesses corresponding to the equilibrium with almost saturated and, even more so, with supersaturated vapor. This difference is to be discussed below and, as will be shown, does not affect the final result.

In order to find the disjoining pressure isotherm $\Pi(h)$ corresponding to the adsorption isotherm (2.1), let us derive the expression for the chemical potential of a film. To this end, we consider the vapor, which is in equilibrium with a flat thin film. Chemical potentials of vapor and film are identical and equal to $b = b_\infty +$

$\ln(n^\beta/n_\infty^\beta)$, where b_∞ and n_∞^β are the dimensionless chemical potential (expressed in kT units) and the saturated vapor concentration, respectively. Using (2.1), we specify this formula as $b = b_\infty + m \ln(h/l_A)$, where $l_A \equiv K_\Gamma(n_\infty^\beta)^{1/m}/n^\alpha$ is a certain characteristic film thickness, and n^α is the number of molecules per unit volume of a liquid phase. Then, for the chemical potential b_R of the spherical film with the outer radius R formed around the spherical nucleus with radius R_n with allowance for the capillary pressure we have:

$$b_R = \frac{2\sigma^{\alpha\beta}}{kTn^\alpha R} + m \ln \frac{h}{l_A}, \quad (2.2)$$

where $h \equiv R - R_n$. On the other hand, it is known from the theory of heterogeneous condensation of completely wettable nuclei [1] that

$$b_R = \frac{2\sigma^{\alpha\beta}}{kTn^\alpha R} - \frac{\Pi(h)}{kTn^\alpha}. \quad (2.3)$$

From this expression, we obtain asymptotics for $\Pi(h)$ in the region of low thicknesses (or, for brevity, the adsorption asymptotics):

$$\Pi(h) = -mn^\alpha kT \ln(h/l_A), \quad (2.4)$$

In spite of sign “-”, this value is positive, because this asymptotics is true at $h < l_A$ when the logarithm is negative.

Using (1.1), we find the following expression for the adsorption asymptotics of the work of nucleus wetting at $h \ll R_n$:

$$f(h) = -4\pi R_n^2 h n^\alpha m \left(1 - \ln \frac{h}{l_A}\right) - \frac{4\pi R_n^2}{kT} \sigma^{\alpha\beta}. \quad (2.5)$$

Such an asymptotics of the work of wetting operates in the region of very thin films with thicknesses of units of Angströms, whereas for thicker films (with the thickness of dozen of angströms or thicker) the exponential asymptotics of the work of wetting, which results from the structural forces, is in operation:

$$f(h) = f_* [1 - C \exp(-h/l_s)], \quad (2.6)$$

where l_s is the parameter with a meaning of the correlation length, and C is a certain positive constant. Formula (2.6) suggests the monotonic achievement of the limiting value of the work of wetting f_* . As follows from (1.1) and (1.4), in this case, $\Pi(h) \geq 0$ and $s > 0$.

If it is assumed that the exponential asymptotics is true up to the thinnest films, just as was done in [1], we can formulate the condition required for the maximum to exist at the curve of the chemical potential of a condensate in a nucleus. Indeed, as follows from (1.1) and

(2.6), the derivative of disjoining pressure $\Pi'(h)$ with respect to film thickness is equal to:

$$\Pi'(h) = \frac{kT}{4\pi R_n^2} \frac{f_* C}{l_s^2} \exp\left(-\frac{h}{l_s}\right). \quad (2.7)$$

With allowances for (2.3), (2.7), and (1.3), the equation for radius R_0 corresponding to the maximal chemical potential has the following form:

$$\frac{2\sigma^{\alpha\beta}}{R_0^2} = \frac{|\Delta\sigma|C}{l_s^2} \exp\left(-\frac{R_0 - R_n}{l_s}\right). \quad (2.8)$$

Constant C can be determined, if we assume that the work of the formation of a zero-thick film is equal to zero. Then

$$f_*(1 - C) + \frac{4\pi R_n^2}{kT} \sigma^{\alpha\beta} = 0. \quad (2.9)$$

Expressing f_* from (1.3), we obtain

$$C = \frac{|\Delta\sigma| - \sigma^{\alpha\beta}}{|\Delta\sigma|} \equiv \frac{s}{|\Delta\sigma|}. \quad (2.10)$$

Finally, substituting C from (2.10) into equation (2.8) and ignoring the difference between R_0 and R_n (assuming that $l_s \ll R_n$) in the left-hand side of this equation, we find:

$$R_0 - R_n = l_s \ln \frac{s R_n^2}{2 l_s^2 \sigma^{\alpha\beta}}. \quad (2.11)$$

To provide inequality $R_0 > R_n$, it is necessary to fulfill the condition

$$s > \frac{2 l_s^2 \sigma^{\alpha\beta}}{R_n^2}, \quad (2.12)$$

which can definitely be violated at a sufficiently low (albeit positive) spreading coefficient s . If this inequality is violated, the maximal chemical potential is not realized at physically correct (positive) values of the film thickness.

However, this inequality should be understood as the limitation on the applicability of the exponential asymptotics of the work of wetting (2.6) at low film thicknesses, rather than the real limitation on the spreading coefficient, because it is related to the finite value of $\Pi'(h)$ for the exponential asymptotics at $h \rightarrow 0$.

Because, in reality, $\Pi'(h) \rightarrow -\infty$, the equation for the maximum chemical potential of the condensate in a nucleus has always a physically correct root. If it falls into the range of very thin films, the exponential asymptotics cannot be used.

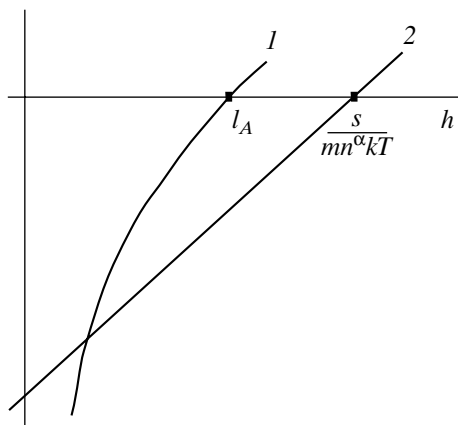


Fig. 1. Dependence of (1) the left-hand and (2) the right-hand sides of equation (3.3) on film thickness.

Thus, to determine thermodynamic characteristics at sufficiently small film thicknesses, it becomes necessary to use some other approximations, say the Henry or the Freundlich isotherms.

3. SEWING OF ADSORPTION AND EXPONENTIAL ASYMPTOTICS OF THE WORK OF WETTING

Let us assume that the work of wetting for very thin films is determined by the adsorption asymptotics (2.5), while for rather thick films, it is determined by the exponential asymptotics (2.6). Let us sew these two asymptotics: we assume that there is a thickness h_p at which adsorption approximation (2.5) is valid at $h < h_p$, whereas exponential approximation (2.6) of the work of wetting with constant C' (which is, in general, different than C) operates at $h > h_p$. Let us require that the sewing process be smooth, i.e., the work of wetting and its derivative should be characterized by the continuity in the point h_p (the requirement of continuity of the derivative is equivalent to that of the disjoining pressure isotherm or the curve of the chemical potential for the condensate). These requirements are expressed mathematically by the set of equations:

$$\begin{cases} f_* \left[1 - C' \exp\left(-\frac{h_p}{l_s}\right) \right] \\ = -4\pi R_n^2 mn^\alpha h_p \left(1 - \ln \frac{h_p}{l_A} \right) - \frac{4\pi R_n^2}{kT} \sigma^{\alpha\beta}, \\ f_* \frac{C'}{l_s} \exp\left(-\frac{h_p}{l_s}\right) = 4\pi R_n^2 mn^\alpha \ln \frac{h_p}{l_A}. \end{cases} \quad (3.1)$$

Thickness h_p corresponding to sewing and constant C' are unknown variables in this set of equations. After the substitution of the value of f_* from (1.3) and some simplifications, the set acquires the following form:

$$\begin{cases} |\Delta\sigma| C' \exp\left(-\frac{h_p}{l_s}\right) = -mn^\alpha kT h_p \left(1 - \ln \frac{h_p}{l_A} \right) + s, \\ |\Delta\sigma| C' \exp\left(-\frac{h_p}{l_s}\right) = -mn^\alpha kT l_s \ln \frac{h_p}{l_A}. \end{cases} \quad (3.2)$$

Let us analyze the conditions of the solution of this set of equations. Using the second equation, we can exclude constant C' . Then, the first equation in (3.2) is transformed into:

$$(l_s + h_p) \ln \frac{h_p}{l_A} = h_p - \frac{s}{mn^\alpha kT}. \quad (3.3)$$

Taking into account that approximation (2.5) is true at $h < l_A$, we can conclude that physically correct solutions correspond to the negative values of the left-hand side of equation (3.3). Thus, condition (see Fig. 1) of the physically correct solution of equation (3.3) and simultaneously that of set (3.2) appear in the following form:

$$s > mn^\alpha kT l_A. \quad (3.4)$$

By the construction of sewing procedure, equality (1.5) for the initial spreading coefficient is automatically fulfilled if the sewing is possible, i.e., if system (3.2) has a physically correct solution. The case, when $h_p > l_A$ and $C' < 0$, cannot be regarded as physically correct.

Let us make estimates for water under standard conditions. Surface tension $\sigma^{\alpha\beta} = 70 \text{ dyne cm}^{-1}$, and $n^\alpha = 3.3 \times 10^{22} \text{ cm}^{-3}$. At room temperature, $kT = 4.2 \times 10^{-14} \text{ erg}$. Then, we have $s/n^\alpha kT = (s/\sigma^{\alpha\beta}) \times 5.0 \times 10^{-8} \text{ cm}$. Substituting this estimate into (3.4), we find

$$l_A < \frac{s}{m\sigma^{\alpha\beta}} \times 5 \text{ \AA}. \quad (3.5)$$

Let be $h_p \ll l_A$; then in the first equation of system (3.2) we can neglect unity compared with $\ln(h_p/l_A)$. Further, using the second equation, the first equation in (3.2) can be rewritten as:

$$-mn^\alpha kT (l_s + h_p) \ln \frac{h_p}{l_A} = s. \quad (3.6)$$

At $h_p \ll l_s$, the approximate solution of this equation has the following form:

$$h_p = l_A \exp\left(-\frac{s}{mn^\alpha kT l_s}\right). \quad (3.7)$$

Now we rewrite equality (3.6) as follows:

$$-mn^\alpha kT l_s \ln \frac{h_p}{l_A} \cong (|\Delta\sigma| - \sigma^{\alpha\beta}) \left(1 - \frac{h_p}{l_s} \right). \quad (3.8)$$

Hence, using the second equation of system (3.2), we obtain

$$C' = \frac{|\Delta\sigma| - \sigma^{\alpha\beta}}{|\Delta\sigma|} \left(1 - \frac{h_p}{l_s}\right) \exp\left(\frac{h_p}{l_s}\right) \quad (3.9)$$

$$\cong \frac{s}{|\Delta\sigma|} \left[1 - \frac{1}{2}\left(\frac{h_p}{l_s}\right)^2\right].$$

Comparing (3.9) and (2.10), we can see that the correction to constant C related to the correction to the exponential asymptotics for thin films is characterized only by the second order of smallness with respect to h_p/l_s :

$$C' \cong C \left[1 - \frac{1}{2}\left(\frac{h_p}{l_s}\right)^2\right], \quad (3.10)$$

i.e., it is relatively small.

4. PHYSICAL MEANING OF THE CONSTRAINT ON SPREADING COEFFICIENT

The meaning of the constraint (3.4) can be understood, if we take into account equality (1.5). Setting the behavior of curve $\Pi(h)$ at a sufficiently low thickness h by adsorption asymptotics (2.4), we thereby set the value of integral $\int_0^h \Pi(\xi) d\xi$ for the small values of h . In our case, this integral is positive, because the approximation (2.4) is true at $h < l_A$ where the integrand is positive. It is important that the behavior of integral $\int_0^h \Pi(\xi) d\xi$ within this thickness range be determined by the adsorption properties of a surface:

$$\int_0^h \Pi(\xi) d\xi = -mn^\alpha kTh \ln \frac{h}{l_A} + mn^\alpha kTh. \quad (4.1)$$

In fact, the disjoining pressure isotherm becomes different from (2.4) as h approaches l_A , this difference being mostly pronounced for complete wetting. Figure 2a illustrates the disjoining pressure isotherm for the case of complete wetting; Fig. 2b shows the isotherm obtained by the sewing procedure described above (also corresponding to complete wetting), and Fig. 2c represents the case of incomplete wetting. Dotted lines in Figs. 2a and 2c show curves (2.4) of the adsorption asymptotics of the disjoining pressure in the range where it noticeably differs from the real isotherm.

Even if it is not assumed that the exponential asymptotics operates at rather large film thicknesses, we can nonetheless obtain constraint (3.4). This allows us to consider the cases of both complete and incomplete wetting. In the case of complete wetting, the estimate

$$\int_0^h \Pi(\xi) d\xi > \int_0^{l_A} \Pi(\xi) d\xi > mn^\alpha kTl_A \quad (4.2)$$

is true for all $h > l_A$.

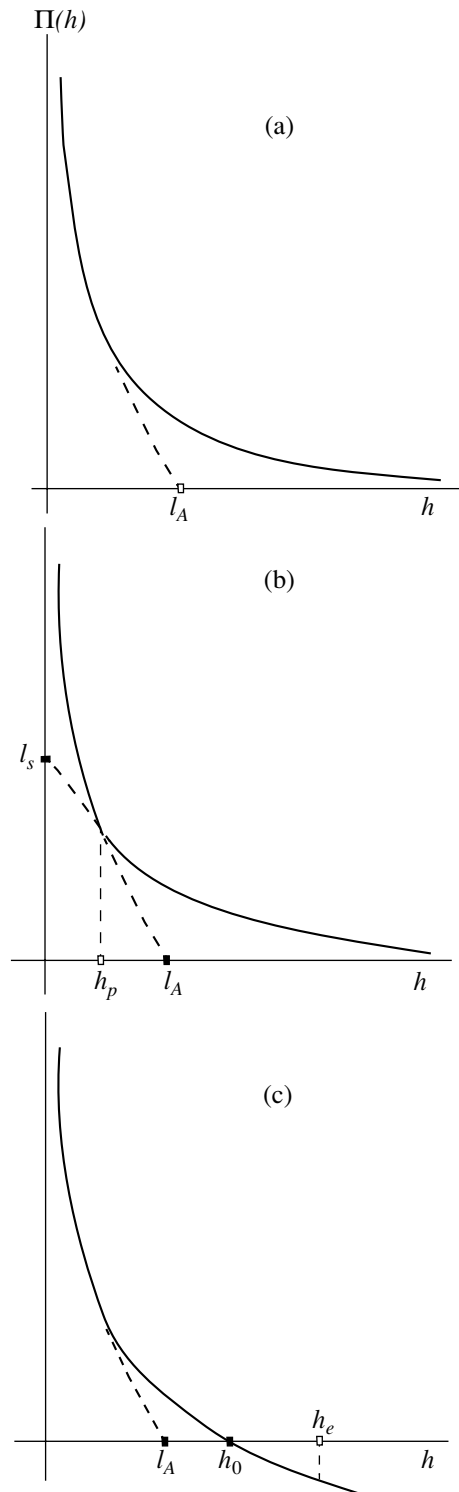


Fig. 2. Disjoining pressure isotherms for (a, b) complete and (c) incomplete wetting. Isotherm shown in Fig. 2b was obtained by the sewing method.

A sufficient condition for the incomplete wetting is the existence of such film thickness h_e at which

$$\int_{h_e}^{\infty} \Pi(\xi) d\xi < 0, \quad (4.3)$$

i.e., the thickness at which the spreading coefficient becomes negative. The same condition can be rewritten using the initial spreading coefficient s and the integral over the initial part of the disjoining pressure isotherm:

$$\int_0^{\infty} \Pi(\xi) d\xi - \int_0^{h_e} \Pi(\xi) d\xi \equiv s - \int_0^{h_e} \Pi(\xi) d\xi < 0. \quad (4.4)$$

Then it can be concluded that the sufficient condition of incomplete wetting is the existence of such a film thickness h_e at which

$$s < \int_0^{h_e} \Pi(\xi) d\xi, \quad (4.5)$$

and, hence, the necessary condition of complete wetting is the fulfillment of condition

$$s > \int_0^h \Pi(\xi) d\xi \quad (4.6)$$

for any film thickness h . Hence, using estimate (4.2), we obtain (3.4) as the necessary condition for complete wetting.

As is seen from the above discussion, the condition of (3.4) type is not bounded by the concrete choice of the approximation for the initial part of the $\Pi(h)$ isotherm but is the generally known fact. The specific pattern of the adsorption isotherm affects only the value of the right-hand side of condition (3.4). The general fact is that, even at the positive initial spreading coefficient, the forming adsorbate (condensate) film can substantially change the wetting conditions.

It is the spreading coefficient that precisely characterizes the wetting. We can introduce the current spreading coefficient, which is dependent on film thickness:

$$s_{ne}(h) = \int_h^{\infty} \Pi(\xi) d\xi. \quad (4.7)$$

Subscript "ne" reminds us that this value is generally the non-equilibrium parameter.

The behavior of the disjoining pressure isotherm and the work of wetting at low film thicknesses is unambiguously determined by the (2.1) type expression or other similar isotherms of polymolecular adsorption. The behavior of the value of $s - s_{ne}(h) = \int_0^h \Pi(\xi) d\xi$ in the range of low h is also determined. If appears that condition $\int_0^h \Pi(\xi) d\xi > s$ is fulfilled for a certain h falling into the domain of the applicability of approximation (2.4), it means that $s_{ne}(h) < 0$. In this case, upon further condensation, the surface will act as though it is partially wetted, even if the initial spreading coefficient $s \equiv s_{ne}(0)$ was positive.

Note that the use of thickness to describe adsorption films is to some extent formal; the adsorption determined correctly both for very thin and thicker adsorption films has the physical meaning. However, we use the thickness, considering it to always be proportional to the adsorption. All the procedures performed above can be rewritten in terms of the dependence of the chemical potential of condensate on adsorption using expression (2.3) that relates the disjoining pressure with the chemical potential. The sewing procedure described above can be physically understood to be the sewing of the asymptotics of the condensate with respect to adsorption.

5. FORMATION OF NONUNIFORMLY THICK FILM AND THE CONSTRAINT ON NUCLEUS SIZE

The equation of the droplet profile expressing the constancy of chemical potential in a film has the following form:

$$P_L - \Pi = \Delta P \equiv P^\alpha - P^\beta = \text{const}, \quad (5.1)$$

where P_L and Π are the local values of Laplacian and disjoining pressures, respectively.

Let us assume now that, in the case of incomplete wetting, the profile of nonuniformly thick film on the curved substrate (i.e., on the solid nucleus) has, similarly to the case of a flat substrate, the form of a uniform thin film contacting with the droplet-small lens. The top of this droplet represents almost a spherical segment with a certain radius of curvature R_d ; the Laplacian pressure in this part of a droplet is much higher than the disjoining pressure; hence, $R_d \equiv 2\sigma^{\alpha\beta}/\Delta P$. More exactly

$$\frac{2\sigma^{\alpha\beta}}{R_d} - \Pi(H) = \Delta P, \quad (5.2)$$

where H is the thickness of a liquid layer at the top of a small lens.

However, in the bottom part of this droplet there is a transition zone from the meniscus to the uniformly thick film where both Laplacian and disjoining pressures are significant. For the uniform film with thickness h_e at the nucleus surface with radius R_n , we can write:

$$\frac{2\sigma^{\alpha\beta}}{R_n + h_e} - \Pi(h_e) = \Delta P. \quad (5.3)$$

Hence

$$\frac{2\sigma^{\alpha\beta}}{R_d} - \frac{2\sigma^{\alpha\beta}}{R_n + h_e} = \Pi(H) - \Pi(h_e). \quad (5.4)$$

In the case under consideration, the left-hand side of this equation is positive; hence, the right-hand side should also be positive. This condition imposes certain constraints on a possible pattern of the disjoining pres-

sure isotherm. For example, we can see at once that the monotonically decreasing isotherm $\Pi(h)$ cannot satisfy equation (5.4).

Considering the limiting case of a flat substrate ($R_n \rightarrow \infty$), we can see that, in this case, the $\Pi(h)$ curve should have the negative part in order to form a droplet-small lens. Indeed, during the unlimited growth of R_d , the contact angle tends to a constant value, and, hence, thickness H is directly proportional to R_d . In this case, the $\Pi(H)$ value decreases rather quickly (usually in an exponential manner with the power larger than two), thus resulting in condition $\Pi(h_e) < 0$ derived from (5.4).

Figure 3 illustrates the typical pattern of the disjoining pressure isotherm for the case of incomplete wetting. The case is also possible when the isotherm has no positive β -branch. For the curve shown in Fig. 3, equation (5.4) results in two important constraints. Let us consider them below.

Nuclei of Small Sizes. If the film thickness h is so small that falls on the α -branch of the disjoining pressure isotherm and $\Pi(h) > \Pi(h_{\max})$, then such a film cannot be separated into a still thinner film and droplet-small lens, because it should contradict equation (5.4). In the absence of the positive β -branch, the separation does not occur under the condition $\Pi(h) > 0$. However, the values of the disjoining pressure at the α -branch are usually so large that the constraints $\Pi(h) > \Pi(h_{\max})$ and $\Pi(h) > 0$ on the film thickness are practically identical. Therefore, for simplicity, hereafter we assume that such a constraint is the inequality $\Pi(h) > 0$.

If the nucleus is so small that the nucleating center corresponding to the maximum chemical potential falls into the indicated region of very thin films, the separation can occur only during the further growth of the nucleus. In this case, the threshold supersaturation resulting in the condition of barrierless nucleation, as well as the curve of the chemical potential and the work of nucleus formation in the vicinity of the critical size in the subthreshold region of supersaturations are determined in the same manner as in the case of condensation on completely wettable nuclei.

Let us find the quantitative solution corresponding to this case. According to (2.3), film thickness h_{th} for the nucleus with the maximum (threshold) value of chemical potential will be determined by the equality:

$$\Pi'(h_{th}) = -\frac{2\sigma^{\alpha\beta}}{(R_n + h_{th})^2}. \quad (5.5)$$

Assuming that derivative $\Pi'(h)$ is monotonically increasing function on the α -branch, let us write the condition indicating that critical nucleus falls into the given region of low film thicknesses in the form of $\Pi'(h_{th}) < \Pi'(h_0)$, where h_0 is the smallest root of equation $\Pi(h) = 0$, i.e.,

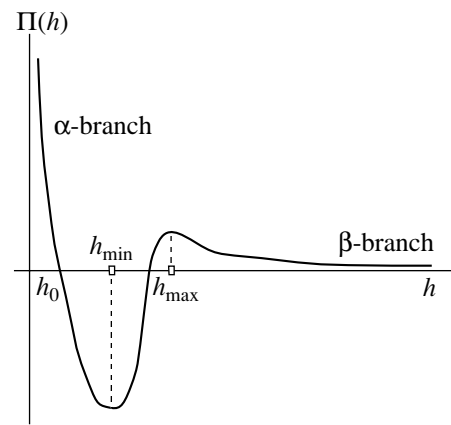


Fig. 3. Typical disjoining pressure isotherm for the case of incomplete wetting.

$$\frac{2\sigma^{\alpha\beta}}{(R_n + h_{th})^2} > -\Pi'(h_0). \quad (5.6)$$

This condition is reduced to the upper bound of the value of R_n :

$$R_n + h_{th} < \sqrt{\frac{2\sigma^{\alpha\beta}}{\Pi'(h_0)}}. \quad (5.7)$$

Such a constraint does not arise when conditions (2.12) and (3.4) of the applicability of exponential approximation (2.6) for completely wetting films are fulfilled.

According to Derjaguin and Zorin's data [8] for water films on the glass surface, $h_0 \approx 70 \text{ \AA}$, $\Pi'(h_0) \approx -7 \times 10^{13} \text{ dyne cm}^{-3}$, thus resulting in condition $R_n + h_{th} < 140 \text{ \AA}$. Since $h_{th} \leq h_0 = 70 \text{ \AA}$, this condition corresponds to very small nuclei, which are almost beyond the conditions of the applicability of the concept of the disjoining pressure for describing the properties of thin films on nuclei.

Nuclei of large sizes. Let us denote the difference between the values of the disjoining pressures in the maximum and minimum at the isotherm by $\Delta\Pi$. For the isotherm shown in Fig. 3 this means that $\Delta\Pi = \Pi(h_{\max}) - \Pi(h_{\min})$. When the positive β -branch is absent, $\Delta\Pi = -\Pi(h_{\min})$.

Since $\Pi(H) - \Pi(h_e) \leq \Delta\Pi$, it is possible, using (5.4), to write the following inequality:

$$\frac{2\sigma^{\alpha\beta}}{R_d} - \frac{2\sigma^{\alpha\beta}}{R_n + h_e} \leq \Delta\Pi. \quad (5.8)$$

Here, the sign of equality corresponds to the limiting case $h_e = h_{\min}$, $H = h_{\max}$.

Assuming that $h_e \ll R_n$, we can rewrite this inequality in the form

$$\frac{R_n}{R_d} - 1 \leq \frac{R_n \Delta\Pi}{2\sigma^{\alpha\beta}}. \quad (5.9)$$

Let us analyze this inequality. If the size of the droplet-small lens is sufficiently large, it can cover the noticeable part of a nucleus. Under the conditions when the radius of droplet-small lens R_d is larger than the radius of nucleus R_n , the droplet spreads over the entire nucleus, and the film thickness becomes uniform. Apparently, this corresponds to the situation when the Laplacian pressure suppresses the fine structure of the disjoining pressure. However, when $R_n \gg R_d$, from (5.9) we have

$$R_d \approx \frac{2\sigma^{\alpha\beta}}{\Delta\Pi} \quad (5.10)$$

and, correspondingly,

$$R_n \gg \frac{2\sigma^{\alpha\beta}}{\Delta\Pi}. \quad (5.11)$$

According to [2], for water films on quartz, $\Delta\Pi \approx 5 \times 10^3$ dyne cm^{-2} ; the surface pressure of water is equal to $\sigma^{\alpha\beta} = 70$ dyne cm^{-1} . Thus, ratio $\sigma^{\alpha\beta}/\Delta\Pi \approx 10^{-2}$ cm, and condition (5.11) imposed on R_n acquires the form $R_n \gg 10^{-2}$ cm.

However, when the radius R_d exceeds R_n , we arrive at the inequality:

$$R_n \lesssim \frac{2\sigma^{\alpha\beta}}{\Delta\Pi} \quad (5.12)$$

as the condition of the uniform spreading of the liquid film over the nucleus. Evidently, inequality (5.12) is only sufficient condition. Note that the larger $\Delta\Pi$, i.e., the deeper the minimum (the larger the contact angle), the smaller the range of nucleus sizes satisfying condition (5.12) is.

CONCLUSION

Hence, let us summarize the results of the study reported in this work. Once conditions (2.12) and (3.4) imposed on the initial spreading coefficient are fulfilled, the range of sizes of condensation nuclei appears, where the exponential approximation (2.6) of the work of nucleus wetting can be used in the theory

of nucleation. Once condition (2.12) is violated, the adsorption asymptotics (2.5) of the work of nucleus wetting can be used in calculations. When the condition (3.4) is violated, the range of the sizes of condensation nuclei, where the adsorption and exponential asymptotics for the disjoining pressure operate in the theory of nucleation of uniformly thick films, is significantly bounded by the constraint (5.7). Nonetheless, the heterogeneous nucleation occurring via the formation of uniform films on nuclei can still take place within the entire range of nucleus sizes that satisfies the sufficient condition (5.12) (even in the case of substances with finite contact angles). If the condition (3.4) is not fulfilled for nuclei whose sizes satisfy inequality (5.11), the emergence of droplets on these nuclei occurs in the form of small lenses.

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