

# THERMODYNAMICS OF CONDENSATION ON SOLUBLE SURFACTANT NUCLEI WITH CONSTANT ADSORPTION

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UDC 536.421.3:541.183

*A study is made of a model of a drop in the case of constant adsorption of a surfactant which is present in the drop as a result of dissolution of the condensation nucleus. This model, corresponding to the limiting situation of complete saturation of adsorption, makes it possible to establish the entire thermodynamic pattern of behavior of the chemical-potential extrema of the substance which condenses in the drop from the vapor phase. A restriction is placed on the size of the nucleus of the surfactant, this being the size at which only extrema exist. It is shown that there are two extrema: one maximum and one minimum. The threshold value of the chemical potential of the vapor is determined. The range of application of the model in the thermodynamics of condensation on soluble surfactant nuclei is also established. The results of the analytical theory are illustrated by direct numerical calculations of the chemical potential of the condensing substance as a function of the number of molecules of the latter.*

The principles of the thermodynamics of condensation on soluble nuclei were presented in [1] with allowance for adsorption of the substance on the surface of a drop. A closed system of equations linking the thermodynamic characteristics of a drop in which the chemical potential of the condensate (the substance which condenses in the drop from the vapor phase) has an extremum was constructed for the general case of an arbitrary degree of saturation of adequate. The study of this system of equations in the model of a drop with constant adsorption will be the goal of the present article.

Although the assumption of constant adsorptions — corresponding to the limiting situation of complete saturation of adsorption — makes our investigation quite a bit easier, it nonetheless remains challenging. In fact, with constant adsorption, there continues to be an effect on the surface tension of the drop. In accordance with the Gibbs adsorption equation, this in turn causes surface tension to be dependent on the concentration of the solution inside the drop. Thus, even in a drop model with constant adsorption, the thermodynamics of condensation on soluble surfactant nuclei remains nonlinear.

At the same time, the model makes it possible to not only quantitatively describe the thermodynamics of condensation on soluble surfactant nuclei in the case of complete saturation of adsorption, but it allows us to describe the laws characteristic of the thermodynamics of condensation on such nuclei in general.

**Initial System of Equations.** The closed system of equations constructed in [1] — which, with allowance for adsorption, connects the thermodynamics characteristics of a drop in which the chemical potential of the condensation has an extremum — is written as follows in the limiting situation of complete saturation of adsorption:

$$(1 + 2v)z^2 - 2(v + 3)z + 9 = 0 \quad (1)$$

$$v = w - \ln \xi \quad (2)$$

(see relations (40), (55-57) from [1]). Here,

$$z = s_{\infty} \nu_0^{2/3} / \nu_n \quad (0 \leq z \leq 1) \quad (3)$$

$$v \equiv a/s_{\infty} \quad (4)$$

$$w \equiv \bar{a}/s_{\infty} \quad (5)$$

$$\xi \equiv x/x_{\alpha} \quad (6)$$

([1], definitions (32), (46-48), with allowance for Eq. (53)). In turn,  $\nu_0$  is the total number of condensate molecules;  $\nu_n$  is the number of molecules or ions of the condensation nucleus;  $x$  is the relative concentration of the substance of the nucleus in the solution within the bulk phase of the drop;  $x_{\alpha}$  is a characteristic value of concentration such that filling of the adsorption monolayer of surfactant only begins at  $x \ll x_{\alpha}$  and ends at  $x \gg x_{\alpha}$  (the characteristic value of  $x_{\alpha}$  is determined quantitatively by Eq. (13) from [1]);  $s_{\infty}$  is the dimensionless adsorption in the case of complete saturation of adsorption (dimensionless adsorption  $s$  with an arbitrary degree of filling of the monolayer is given by Eq. (4) from [1]);  $a$  is the dimensionless surface tension of the drop (determined by Eq. (4) from [2]);  $\bar{a}$  is the dimensionless surface tension of the drop in the absence of adsorption. The quantities  $\nu_n$ ,  $x_{\alpha}$ ,  $s_{\infty}$ , and  $w$  are external parameters of the problem.

Written in thermodynamic form, Eq. (1) solves the following equation when  $s = s_{\infty}$ .

$$(\partial b_{\nu} / \partial \nu)_0 = 0 \quad (7)$$

where  $b_{\nu}$  is the chemical potential of the condensate inside the bulk phase of the drop. The zero subscript characterizes values of quantities at the extremum of the chemical potential (for simplicity, this subscript is indicated in (3-6) only for the quantity  $\nu$ ). Equation (2) is a consequence of the Gibbs adsorption equation at  $s = s_{\infty}$ .

Following [1], we choose the quantity  $z$  defined by (3) as the independent variable to describe a drop in which the chemical potential of the condensate has an extremum. This quantity is the fraction of the total amount of the substance of the nucleus that is adsorbed. In this case, the parameter  $\nu_n$  (an external parameter of the problem) will be a function of  $z$ . As will be seen below, the variable  $z$  also makes it possible to see the entire thermodynamic pattern of behavior of the extrema of condensate chemical potential. No special problems are encountered in changing over from the independent variable  $z$  to the independent variable  $\nu_n$  in the final formulas.

**Concentration of the Solution Inside a Drop with Constant Adsorption.** Solving system (1-2) for  $\xi$ , we have

$$\xi = \exp(w) \exp \left[ - \frac{(3-z)^2}{2z(1-z)} \right] \quad (8)$$

Expression (8) shows that

$$\partial \xi / \partial z > 0 \quad (z < z_m) \quad (9)$$

$$\partial \xi / \partial z = 0 \quad (z = z_m) \quad (10)$$

$$\partial \xi / \partial z < 0 \quad (z > z_m) \quad (11)$$

where

$$z_m = 3/5 \quad (12)$$

We will use the subscript  $m$  to denote quantities at the point  $z = z_m$ . Here, in accordance with (9-11), the concentration of the solution  $\xi$  inside a drop having a maximum of chemical potential is itself maximal. We obtain the following from (8) and (12) for the maximum value  $\xi_m$  of concentration  $\xi$

$$\xi_m = \exp(w - 12) \quad (13)$$

The dependence of concentration  $\xi$  on the variable  $z$  described by Eq. (8) is shown in Fig. 1 in the physical region of the variable  $0 \leq z \leq 1$ .

Observance of the condition  $\xi \gg 1$  in the constant-adsorption model for the solution concentration  $\xi$  implies that the same condition is at least also observed for the maximum value of concentration  $\xi_m$ . In light of (12), this means that

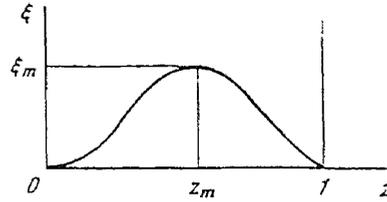


Fig. 1. Dependence of the concentration of the solution  $\xi$  inside a drop on the variable  $z$  describing the drop with constant adsorption.

$$\exp(w - 12) \gg 1 \quad (14)$$

Inequality (14), imposing a lower bound on the initial parameter  $w$ , is in principle necessary because the extremum of the condensate chemical potential can be reached with constant adsorption on the drop surface — with complete saturation of adsorption.

In accordance with inequality (14), the parameter  $w$  should be at least 2-3 units greater than 12. As is clear from (5), however, this would require the surface tension  $\bar{a}$  in the absence of adsorption to be relatively large and, conversely, would require adsorption  $s_\infty$  to be relatively small in the case of complete saturation.

In accordance with (2), the greater  $\xi$ , the smaller  $v$ . The value of  $v_m$  is thus minimal for  $v$ . It follows from (2) and (13) that

$$v_m = 12 \quad (15)$$

Thus, regardless of the degree to which inequality (14) is observed, the value of  $v$  found from (4) has the same minimum value of 12 at the maximum of solution concentration. When inequality (14) is observed, the solution concentration inside a drop in which condensate chemical potential has a extremum stabilizes the surface tension of the drop  $a$  at the point of its minimum (at the point of the concentration maximum). The minimum value of surface tension  $a$  is always equal to  $12s_\infty$ .

Using (8), (12), and (13), we obtain

$$(\partial^2 \xi / \partial z^2)|_{z=z_m} = - (625/6) \xi_m \quad (16)$$

where the coefficient with  $\xi_m$  is independent of the initial parameters of the problem. The minus sign in the right side of (16) corresponds to the maximum of concentration  $\xi$  at the point  $z = z_m$ .

**Thermodynamics of a Drop with Constant Adsorption.** In accordance with general thermodynamic expressions (34) and (35) from [1] and with allowance for the equality  $s = s_\infty$  and definition (6), we have:

$$v_n^{1/2} = \frac{s_\infty^{3/2}}{x_\alpha} \frac{1-z}{z^{3/2}} \frac{1}{\xi} \quad (17)$$

$$v_0^{1/3} = \frac{s_\infty}{x_\alpha} \frac{1-z}{z} \frac{1}{\xi} \quad (18)$$

Inserting (8) into (17) and (18), we find

$$v_n^{1/2} = \frac{s_\infty^{3/2}}{x_\alpha} \exp(-w) \frac{1-z}{z^{3/2}} \exp \left[ \frac{(3-z)^2}{2z(1-z)} \right] \quad (19)$$

$$v_0^{1/3} = \frac{s_\infty}{x_\alpha} \exp(-w) \frac{1-z}{z} \exp \left[ \frac{(3-z)^2}{2z(1-z)} \right] \quad (20)$$

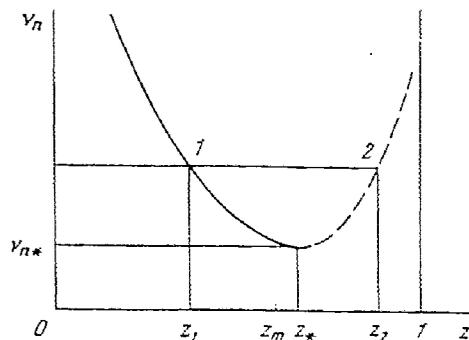


Fig. 2. Dependence of  $\nu_n$  on the variable  $z$  describing a drop in the case of constant adsorption.

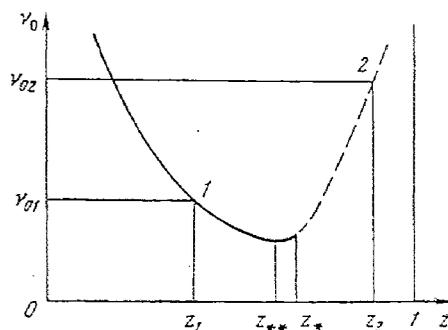


Fig. 3. Dependence of  $\nu_0$  on the variable  $z$  describing a drop in the case of constant adsorption.

which in addition to the already-determined concentration  $\xi$  determines the thermodynamic characteristics of a drop with an extreme chemical potential as a function of the variable  $z$ .

Let us examine the dependence of  $\nu_n$  on  $z$ . In accordance with (19), we have

$$\frac{\partial \nu_n^{1/2}}{\partial z} = \frac{s_\infty^{3/2}}{2x_\alpha} \exp(-w) \frac{(3-z)(z^2+4z-3)}{z^{7/2}(1-z)} \exp\left[\frac{(3-z)^2}{2z(1-z)}\right] \quad (21)$$

The partial derivatives are taken with fixed  $x_\alpha$ ,  $s_\infty$ , and  $w$ .

Whether the extremum of condensate chemical potential  $b_\nu$  is maximal or minimal is determined by the sign of the second derivative  $(\partial^2 b_\nu / \partial \nu^2)_0$ . In contrast to the derivatives in which  $z$  is an independent variable and  $\nu_n$  is thus a function of  $z$ , the derivative just written (as the derivative in Eq. (7)) should be taken with all of the external parameters  $\nu_n$ ,  $x_\alpha$ ,  $s_\infty$ , and  $w$  fixed. Considering this, differentiating thermodynamic expression (30) from [1] for  $\partial b_\nu / \partial \nu$  with respect to  $\nu$  with the use of (2-4), (6), and (17-18) and the equality  $s = s_\infty$ , and taking (7) into account, after some simple but very lengthy calculations we obtain

$$\left(\frac{\partial^2 b_\nu}{\partial \nu^2}\right)_0 = \frac{2\nu_n}{27\nu_0^3} \frac{(3-z)(z^2+4z-3)}{(1-z)^2} \quad (22)$$

Using (21) and (22), we determine

$$\partial \nu_n / \partial z < 0, \quad (\partial^2 b_\nu / \partial \nu^2)_0 < 0 \quad (z < z_*) \quad (23)$$

$$\partial \nu_n / \partial z = 0, \quad (\partial^2 b_\nu / \partial \nu^2)_0 = 0 \quad (z = z_*) \quad (24)$$

$$\partial \nu_n / \partial z > 0, \quad (\partial^2 b_\nu / \partial \nu^2)_0 > 0 \quad (z > z_*) \quad (25)$$

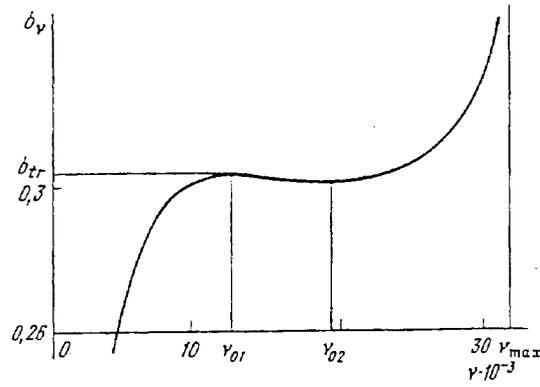


Fig. 4. Chemical potential  $b_\nu$  as a function of  $\nu$  with  $\nu_n = 1000$ ,  $x_\alpha = 10^{-5}$ ,  $s_\infty = 1$ ,  $w = 20$ , and constant adsorption.

where

$$z_* = -2 + \sqrt{7} \approx 0.65 \quad (26)$$

In accordance with (23-25), the value of  $\nu_n$  at  $z = z^*$  is minimal at the extremum of the chemical potential of the condensate. Using  $\nu_{n*}$  to represent the minimum value of  $\nu_n$ , we find from (19) and (26) that

$$\nu_{n*} \approx 1.25 \cdot 10^5 \frac{s_\infty^{3/2}}{x_\alpha} \exp\left(-\frac{\bar{a}}{s_\infty}\right) \quad (27)$$

(where we have taken (5) into account in order to show the sensitivity of the exponent to the parameter  $s_\infty$ ). It should be noted that the common factor  $z^2 + 4z - 3$  in Eqs. (21-22) is responsible for (23-26), this factor also determining the sign of the right sides of these expressions at  $0 \leq z \leq 1$ . We also note that, in accordance with (12) and (26), the value of  $z_*$  is slightly greater than  $z_m$ .

We can make the following conclusions on the basis of (23-25).

The minimum of  $\nu_m$  is reached at  $z = z_n$ . This minimum is equal to the value of  $\nu_{n*}$  determined by (27).

In the regions  $z < z_*$  and  $z > z_*$  on the axis of  $z$  up to and beyond the minimum of  $\nu_n$ , the extremum of the chemical potential of the condensate is a maximum and a minimum, respectively.

The maximum and minimum of condensate chemical potential merge at the point  $z = z_*$ .

Let us examine the dependence of  $\nu_0$  on  $z$ . In accordance with (20), we have

$$\frac{\partial \nu_0^{1/3}}{\partial z} = -\frac{s_\infty}{2x_\alpha} \exp(-w) \frac{3z^2 - 16z + 9}{z^3(1-z)} \exp\left[\frac{(3-z)^2}{2z(1-z)}\right] \quad (28)$$

(the partial derivative is taken with fixed  $x_\alpha$ ,  $s_\infty$ , and  $w$ ). Using (28), we establish

$$\partial \nu_0 / \partial z < 0 \quad (z < z_{**}) \quad (29)$$

$$\partial \nu_0 / \partial z = 0 \quad (z = z_{**}) \quad (30)$$

$$\partial \nu_0 / \partial z > 0 \quad (z > z_{**}) \quad (31)$$

where

$$z_{**} = (8 - \sqrt{37})/3 \approx 0.64 \quad (32)$$

It follows from (29-31) that the value  $z = z_*$  gives a minimum of  $\nu_0$ . In accordance with (12), (26), and (32), this value is much greater than  $z_m$  and slightly less than  $z_*$ .

**Extrema of Condensate Chemical Potential with Constant Adsorption.** If  $\nu_n$  is given (which is usually the case in experiments), then it follows from the conclusions reached in the previous section on the basis of (23-25) that at  $\nu_n < \nu_{n*}$  there are no drops in which the condensate has an extremum of chemical potential, while at  $\nu_n > \nu_{n*}$  there are two drops having such an extremum. One of them (which we will call the first drop) has a maximum, while the other (the second drop) has a minimum. The values  $z_1$  and  $z_2$  of the variable  $z$  corresponding to these drops satisfy the inequalities

$$z_1 < z_*, z_2 > z_* \quad (33)$$

When  $\nu_n = \nu_{n*}$ , the drops having potential extrema become identical. They then correspond to the value  $z_*$  of  $z$ .

The above is illustrated by Fig. 2. The curve shows the dependence of  $\nu_n$  on  $z$  in the interval  $0 \leq z \leq 1$  as described by (19) and (21). The part of the curve represented by the solid line at  $0 \leq z \leq z_*$  corresponds to a maximum of condensate chemical potential, while the part shown by the dashed line at  $z_* < z \leq 1$  corresponds to a minimum of chemical potential. Points 1 and 2 on the curve and the corresponding values  $z_1$  and  $z_2$  correspond to drops which, at the specified  $\nu_n$ , have a maximum and minimum of chemical potential. Indicated on the  $z$  axis is the value  $z_m$  that gives the maximum of solution concentration inside the drop. It is evident that this value lies within a region in which the extremum of condensate chemical potential is a maximum.

Thus, at  $\nu_n > \nu_{n*}$ , Eq. (7) has two roots  $\nu_{01}$  and  $\nu_{02}$ . The subscripts 1 and 2 denote (as in  $z_1$  and  $z_2$ ) values of thermodynamic quantities in drops in which the condensate has a chemical potential with a maximum and a minimum, respectively.

Let us see how the roots  $\nu_{01}$  and  $\nu_{02}$  are positioned relative to one another on the axis of  $\nu$  for the given  $\nu_n$ . Here, we have

$$\nu_{n1}^{1/2} = \nu_{n2}^{1/2} \quad (34)$$

It follows from (17-18) that

$$\nu_0^{1/3} / \nu_n^{1/2} = z^{1/2} / s_\infty^{1/2} \quad (35)$$

Applying Eq. (35) to a drop characterized by the values  $z_1$ ,  $\nu_{01}$ , and  $\nu_{n1}$  and to another drop characterized by the values  $z_2$ ,  $\nu_{02}$ , and  $\nu_{n2}$  and then taking (34) into account, we obtain

$$\nu_{01}^{1/3} / \nu_{02}^{1/3} = (z_1 / z_2)^{1/2} \quad (36)$$

In light of (33), we will have

$$z_1 < z_2 \quad (37)$$

We can use (36-37) to establish

$$\nu_{01} < \nu_{02} \quad (38)$$

Thus, with  $\nu_n$  given, the root  $\nu_{01}$  ensuring the location of the maximum of chemical potential  $b_p$  on the  $\nu$  axis is to the left of the root  $\nu_{02}$  ensuring the minimum of chemical potential  $b_p$ .

This is illustrated by Fig. 3. The curve shows the dependence of  $\nu_0$  on  $z$  in the interval  $0 \leq z \leq 1$  as determined by Eqs. (20) and (28). The part of the curve represented by the solid line at  $0 \leq z \leq z_*$  corresponds to the maximum of chemical potential of the condensate, while the part represented by the dashed line at  $z_* < z \leq 1$  corresponds to the minimum of condensate chemical potential in the drop. Points 1 and 2 on the curve and the corresponding values  $z_1$  and  $z_2$  of  $z$ , as well as the values  $\nu_{01}$  and  $\nu_{02}$  of  $\nu_0$ , correspond to drops in which, for the given  $\nu_n$ , the chemical potential of the condensate has a maximum and a minimum. The figure also shows the relative location of the coordinates  $z_*$  and  $z_{**}$  on the  $z$  axis as determined by (26) and (32) and the same for the coordinates  $z_1$  and  $z_2$  on the  $z$  axis as determined by (37). It is apparent that inequality (38) is satisfied.

**Threshold Value of the Chemical Potential of the Vapor. Limits of Applicability of the Theory.** In accordance with general thermodynamic formula (41) from [1], the following is valid for the extreme value  $(b_\nu)_0$  of condensate chemical potential  $b_\nu$ ,

$$(b_\nu)_0 = x \left[ \frac{2zv}{3(1-z)} - 1 \right] \quad (39)$$

where we have taken into account relation (57) from [1], corresponding to the given case of complete saturation of adsorption:  $s = s_\infty$ . The chemical potential of the condensate  $b_\nu$  is expressed in thermal energy units and is reckoned from the value corresponding to equilibrium between the vapor and the condensing liquid when their contact surface is planar.

In the thermodynamics of condensation on soluble surfactant nuclei with constant adsorption of the surfactant on the surface of the drops, at  $\nu_n > \nu_{n*}$  Eq. (7) has only one root  $\nu_0 = \nu_{01}$  which yields a maximum of condensate chemical potential  $b_\nu$  (the second root gives a minimum of  $b_\nu$ ). Thus, we have the following for the threshold value  $b_{tr}$  of the chemical potential of the vapor, determined by the maximum chemical potential of the condensate (or the greatest of its maxima, if it has more than one)

$$b_{tr} = (b_\nu)_{01} \quad (40)$$

where, by virtue of (39) and (6),

$$(b_\nu)_{01} = x_\alpha \xi_1 \left[ \frac{2z_1 v_1}{3(1-z_1)} - 1 \right] \quad (41)$$

( $\xi_1$  and  $v_1$  correspond to the value  $z_1$  of the variable  $z$ ). The threshold value  $b_{tr}$  of the chemical potential of the vapor (as  $b_\nu$ ) is expressed in thermal energy units and is reckoned from the value corresponding to equilibrium between the vapor and the condensing liquid when their contact surface is planar.

The previous sections of this article described an algorithm for finding the quantities in the right side of (41) with assigned external parameters  $\nu_n$ ,  $x_\alpha$ ,  $s_\infty$ , and  $w$ .

Let us discuss the physical validity of the above thermodynamic study of condensation on soluble nuclei in a drop model with constant adsorption. The method of investigation was rigorous and thus places no restrictions on the results. The only limitations are due to the model itself, in which it is assumed that  $\xi \gg 1$ .

At  $\nu_n^{1/2} < \nu_{n*}^{1/2}$ , Eq. (7) in general has no roots — the condensate in drops cannot have an extremum of chemical potential. However, if the inequality  $\nu_n^{1/2} > \nu_{n*}^{1/2}$  is satisfied sufficiently weakly, then the values  $z_1$  and  $z_2$  of the variable  $z$  for drops in which the condensate has a maximum and minimum of chemical potential will be close to  $z_*$  and, because  $z_* \approx z_m$ , will also be close to  $z_m$  (see Fig. 2). In this case, the concentrations  $\xi_1$  and  $\xi_2$  of the solution inside these drops will be close to the maximum value  $\xi_m$ . Since the condition for maximum concentration  $\xi_m$  is observed with restriction (14), the conditions  $\xi_1 \gg 1$ ,  $\xi_2 \gg 1$  will also be observed with the same restriction.

The inequality  $\nu_n^{1/2} > \nu_{n*}^{1/2}$  becomes stronger with an increase in  $\nu_n^{1/2}$ . Accordingly, the concentrations  $\xi_1$ ,  $\xi_2$  come to be significantly less than the maximum concentration  $\xi_m$ . As is clear from (17), however, the concentrations  $\xi_1$ ,  $\xi_2$  will continue to satisfy the conditions  $\xi_1 \gg 1$ ,  $\xi_2 \gg 1$  defining the range of application of the model as long as the following restriction holds

$$\nu_n^{1/2} \ll \frac{s_\infty^{3/2}}{x_\alpha} \frac{1-z}{z^{3/2}} \quad (42)$$

where  $z = z_1$  or  $z = z_2$ . In accordance with (13), restriction (42) is equivalent to restriction (14) at  $z = z_m$ , when  $\xi = \xi_m$ . However, (42) is stricter than (14) when  $z \neq z_m$ .

In the drop model with constant adsorption, the variable  $z$  cannot reach the limiting values  $z = 0$  and  $z = 1$  — values at which, in accordance with (8) (Fig. 1), we would have  $\xi = 0$ .

**Direct Calculations of the Chemical Potential of the Condensate with Constant Adsorption.** We will illustrate the above analytical study of extrema of condensate chemical potential  $b_\nu$  by calculating  $b_\nu$  directly as a function of the variable  $\nu$  with assigned external parameters  $\nu_n$ ,  $x_\alpha$ ,  $s_\infty$ , and  $w$ .

We will proceed on the basis of the general thermodynamic expression for  $b_\nu$  obtained in [1]:

$$b_\nu = -x + (2/3)av^{-1/3} \quad (43)$$

([1], expression (9)). In the given case of constant adsorption, besides  $s = s_\infty$  we have Eq. (2). As is clear from definitions (4-6), this equation gives the dependence of the surface tension of the drop  $a$  on concentration  $x$ . We also take into account the material balance equation ([1], Eq. (5)), which at  $s = s_\infty$  reduces to

$$x = \nu_n \nu^{-1} - s_\infty \nu^{-1/3} \quad (44)$$

In accordance with (44) and (2), we obtain:  $x \rightarrow \infty$ ,  $a \rightarrow -\infty$  as  $\nu \rightarrow 0$ . While having purely formal significance, this result (in accordance with (43)) nonetheless ensures the correct final result:  $b_\nu \rightarrow -\infty$  as  $\nu \rightarrow 0$ . The latter is not influenced by the necessity of having to replace the first term in the right side of (43) by  $-\ln x$  as  $x \rightarrow \infty$ .

In accordance with (44), (2) and (43), we also obtain

$$x = \frac{2}{3} s_\infty \nu_{\max}^{-4/3} (\nu_{\max} - \nu) \rightarrow 0 \quad (\nu \rightarrow \nu_{\max} - 0) \quad (45)$$

$$a = -s_\infty \ln(\nu_{\max} - \nu) \rightarrow \infty \quad (\nu \rightarrow \nu_{\max} - 0) \quad (46)$$

$$b_\nu = -\frac{2}{3} s_\infty \nu_{\max}^{-1/3} \ln(\nu_{\max} - \nu) \rightarrow \infty \quad (\nu \rightarrow \nu_{\max} - 0) \quad (47)$$

$$\partial b_\nu / \partial \nu = \frac{2}{3} s_\infty \nu_{\max}^{-1/3} (\nu_{\max} - \nu)^{-1} \rightarrow \infty \quad (\nu \rightarrow \nu_{\max} - 0) \quad (48)$$

where

$$\nu_{\max} = (\nu_n / s_\infty)^{3/2} \quad (49)$$

and  $\nu \rightarrow \nu_{\max} - 0$  means that  $\nu$  approaches  $\nu_{\max}$  from the left.

Equation (47) and  $b_\nu \rightarrow -\infty$  ( $\nu \rightarrow 0$ ) lead to the same conclusion as above — that the maximum of chemical potential  $b_\nu$  in the model of a drop with constant adsorption can exist only together with its minimum.

The value  $\nu_{\max}$  determined by Eq. (49) is in principle the maximum for the variable  $\nu$  in the constant-adsorption drop model. Upon attainment of the given value, all of the condensed matter turns out to be adsorbed on the surface of the drop. The fact that we will have  $x = 0$  in this case naturally disturbs the condition  $x/x_\alpha \gg 1$  defining the region in which the model is valid. As long as the condition  $x/x_\alpha \gg 1$  is satisfied, the value of  $\nu_{\max}$  can only be approached from below.

As was explained above, the inequality  $\nu_n > \nu_{n*}$  (where  $\nu_{n*}$  is determined by (27)) is the condition for the simultaneous existence of a maximum and minimum of chemical potential  $b_\nu$ . If the inequality  $\nu_n > \nu_{n*}$  is not observed, then chemical potential  $b_\nu$  in general has no extrema. In this case, by virtue of (47) and  $b_\nu \rightarrow -\infty$  ( $\nu \rightarrow 0$ ), chemical potential  $b_\nu$  increases monotonically from  $-\infty$  to  $\infty$  with an increase in  $\nu$  in the interval  $0 < \nu < \nu_{\max}$ .

Figure 4 shows results from calculation of  $b_\nu$  as a function of  $\nu$  on the basis of (43), (2), (4-6), and (44). We put  $\nu_n = 1000$ ,  $x_\alpha = 10^{-5}$ ,  $s_\infty = 1$ ,  $\bar{a} = 20$ . In light of (5), this means that  $w = 20$ . The latter in turn ensures satisfaction of necessary condition (14) for a drop model with constant adsorption. Given the chosen values of the parameters, we have the following on the basis of (27):  $\nu_{n*} = 735$ . The inequality  $\nu_n > \nu_{n*}$  is thus satisfied. The relative location of the maximum and minimum in Fig. 4 agrees with (38).

Having decreased the parameter  $\nu_n$ , we weaken the inequality  $\nu_n > \nu_{n*}$ . This in turn causes the maximum and minimum of  $b_\nu$  to converge. They become the same when  $\nu_n = \nu_{n*}$ .

As is clear from (27), weakening of the inequality  $\nu_n > \nu_{n*}$  might also be due to a change in the parameters  $x_\alpha$ ,  $s_\infty$ , and  $\bar{a}$  for the chosen  $\nu_n$ .

The above analytical study of the extrema of condensate chemical potential was essential to discovering the above-described nontrivial effect of all four external parameters  $\nu_n$ ,  $x_\alpha$ , and  $s_\infty$  on  $b_\nu$  in relation to  $\nu$ , i.e. this could not have been determined simply by numerical calculation. Another point to be emphasized is that any numerical determination of  $b_\nu$  as a function of  $\nu$  applies in any case only to one value of the external parameter  $\nu_n$ , while the analytical relations found between

the thermodynamic characteristics of a drop with an extremum of condensate chemical potential embrace the entire range of possible values of  $\nu_n$ .

We also note the following in conclusion. Compared to the threshold chemical potential found here for the vapor on the basis of experimental data on heterogeneous condensation, the other thermodynamic characteristics of heterogeneous nucleation are less important [2, 3]. A thermodynamic method of finding all of these characteristics for the chosen threshold value  $b_{tr}$  was proposed in [2]. This method, used in [2] for the case when the adsorption of the substance of the soluble condensation nucleus is ignored, can also be used without difficulty (assuming a value is found for  $b_{tr}$ ) when allowance is made for adsorption. However, due to the cumbersome calculations that would be required, we have limited our study of the thermodynamics of heterogeneous nucleation to the central problem noted in [2] — study of the extrema of condensate chemical potential.

## REFERENCES

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