

sible; and further decrease in the foam volume, although it proceeds from the surface, occurs in the form of simultaneous disintegration of large volumes of foam. For such an avalanche-like process, it is probably sufficient that only some of the bubbles achieve "critical" sizes. For this mechanism of disintegration of the foam column, the foam lifetime is the time for achievement of the "critical" dispersion. This is determined by the rate of internal disintegration, the initial dispersion, and the value of the "critical" dispersion itself. Between these two different mechanisms for disintegration of the foam column, different intermediate variants are possible: in particular, ones with gradual disintegration of the column, which is explained by the polydispersion of the foam and other factors.

#### LITERATURE CITED

1. H. W. Schwarz, *Fette, Seifen, Anstrichmittel*, 66, No. 5, 380 (1964).
2. A. V. Pertsov, V. F. Borachuk, B. E. Chistyakov, and E. D. Shchukin, *Summaries of Reports, Seventh Conference on Surface Forces [in Russian]*, Nauka, Moscow (1980), p. 36.
3. E. Manegold, *Foam [in German]*, Strassenbau, Chemie und Technik Verlag, Heidelberg (1953).
4. E. M. Savitskaya and P. A. Rebinder, *Kolloidn. Zh.*, 13, No. 3, 200 (1951).
5. Khr. Khristov, P. M. Kruglyakov et al., *Colloid Polym. Sci.*, 257, No. 5, 506 (1979).
6. Kh. I. Khristov, D. R. Ekserova, et al., *Kolloidn. Zh.*, 43, No. 1, 101, 195 (1981).
7. V. K. Tikhomirov, *Foams [in Russian]*, Khimiya, Moscow (1973).
8. N. O. Clark and M. Blackman, *Trans. Faraday Soc.*, 44, No. 1, 1 (1948).
9. P. M. Kruglyakov and P. R. Taube, *Zh. Prikl. Khim.*, 38, No. 10, 2258 (1965).
10. L. L. Kuznetsova and P. M. Kruglyakov, *Kolloidn. Zh.*, 41, No. 4, 673 (1979).
11. A. A. Trapeznikov, in: *Foams. Production and Use [in Russian]*, Reports of the Scientific and Technical Conference, VNIPO, Moscow (1974), p. 6.
12. A. J. de Vries, *Rec. Trav. Chem. Pays-Bas*, 77, No. 1, 81 (1958).
13. L. L. Kuznetsova and P. M. Kruglyakov, *Dokl. Akad. Nauk SSSR*, 260, No. 4, 928 (1981).
14. P. M. Kruglyakov and Yu. G. Rovin, *Physical Chemistry of Black Hydrocarbon Films [in Russian]*, Nauka, Moscow (1978).
15. A. F. Sharovarnikov, V. N. Tsan, et al., *Kolloidn. Zh.*, 43, No. 4, 808 (1981).

#### THEORY OF NUCLEATION ON CHARGED NUCLEI.

#### 4. CALCULATION OF THE WORK OF FORMATION FOR A DROPLET IN THE STRONG FIELD OF A CHARGED NUCLEUS

F. M. Kuni, A. K. Shchekin, and A. I. Rusanov

UDC 536.423.4.001

We have determined in analytical form the work of formation for a droplet not in equilibrium with the vapor as a function of the number of molecules in the droplet and the charge of the nucleus, in the strong field of which the droplet grows.

The most important item which nucleation theory obtains from thermodynamics is the work of formation for a droplet. The general thermodynamic expression for the work of formation for a droplet growing on a charged nucleus and not in equilibrium with the vapor was obtained in [1]. Based on the method developed in [2] for the expansion with respect to the curvature parameter for a droplet in the strong field of a charged nucleus, we calculate the thermodynamic parameters entering into this expression. Based on the assumption that the escape of vapor molecules in the droplets is independent of vapor density, we extend it to droplets which are not found in equilibrium with the vapor.

In the method of expanding in the curvature parameter, we used six dimensionless parameters ([2], Eqs. (9), (14), and (35))

---

Leningrad University. Translated from *Kolloidnyi Zhurnal*, Vol. 45, No. 5, pp. 901-907, September-October, 1983. Original article submitted July 19, 1982.

$$\begin{aligned} \delta_1 &\equiv \lambda_\infty / r, \quad \delta_2 \equiv 2\chi_\infty \gamma_\infty / r, \quad \delta_3 \equiv \chi_\infty \mu_\infty q^2 / r^4, \\ \delta_4 &\equiv \frac{k_1}{2\mu_\infty r}, \quad \delta_5 \equiv \frac{q}{\rho_\infty^\alpha r^3} \left( \frac{d\mathcal{P}_0}{d\mu} \right)_\infty, \quad \delta_6 \equiv \frac{k_2 q}{2\mu_\infty r^3}, \end{aligned} \quad (1)$$

where we expressed the induction in terms of  $q$  and  $r$  ( $D \equiv q/r^2$ ). All the symbols from [1, 2] are completely retained. The results obtained in the second approximation of the method are reduced to the following: ([2], Eqs. (28), (36), (38), (40), and (43)):

$$\rho^\alpha = \rho_\infty^\alpha (1 + \delta_2 - \delta_3) \quad (2)$$

$$q^{\mathcal{P}} = q^{\mathcal{P}_0\infty} + 2\gamma_\infty r^2 \delta_5 + \frac{2\mu_\infty q^2}{r} \left( \delta_4 - \frac{1}{2} \delta_5 + \delta_6 \right) \quad (3)$$

$$R = r(1 + \delta_1 + \delta_5) \quad (4)$$

$$\gamma = \gamma_\infty (1 - 2\delta_1) + \frac{\mu_\infty q^2}{r^3} \left( \delta_1 + \delta_4 + \frac{4}{3} \delta_6 \right) \quad (5)$$

$$\mu = \frac{2\gamma_\infty}{\rho_\infty^\alpha r} \left( 1 - 2\delta_1 - \frac{1}{2} \delta_2 \right) - \frac{\mu_\infty q^2}{\rho_\infty^\alpha r^4} \left[ 1 - 2(\delta_1 + \delta_4) - \delta_2 + \frac{1}{2} \delta_3 - \frac{8}{3} \delta_6 \right], \quad (6)$$

where we again expressed the induction in terms of  $q$  and  $r$ .

To the accuracy assumed in Eqs. (2)-(6), in all further calculations we will neglect the derivatives of the parameter  $\delta_1, \dots, \delta_6$  higher-order terms without additionally stipulating this.

For nucleation theory, another characteristic of the droplet — the number of molecules in the droplet,  $\nu$  — proves to be more convenient than the radius  $r$  of its surface of tension. It is specifically this number  $\nu$  which, as an independent variable characterizing the droplet, enters into the original Zeldovich nucleation equation which has a finite-difference form with respect to this number. Being dimensionless, the number  $\nu$  is more convenient than the radius  $r$  for formulating the degree of approximation and the region of applicability for this theory.

In order to determine  $\nu$ , we may arbitrarily assume that the bulk properties achievable by the liquid inside are retained from the surface layer right down to the center of the droplet. In fact, inside the droplet we find a nucleus (material of a different nature) and, furthermore, at very small distances from the nucleus the density of the liquid begins to depend on this distance. This leads only to a difference between  $\nu$  and the true number of molecules of the material condensed in the droplet by some relatively small value (for low small curvature parameter)  $\nu_n$  which can be calculated; this difference may be assumed to be constant (not depending on  $\nu$ ). The existence of  $\nu_n$  only means a shift in the scale of the variable  $\nu$ , selected as an independent functional argument. This shift, in the case of an insoluble nucleus, does not have physical meaning. It is not apparent in calculation of the amount of vapor condensed in the droplets: The decrease in saturation of the vapor begins to be appreciable only when the droplets attain large sizes, when the shift  $\nu_n$  becomes in general vanishingly small in relative magnitude.

Bearing in mind what has been said above, and also taking into account the definition of equimolecular surface and the fact that on the outside at distances on the order of the surface layer, the material is close in density to a homogeneous vapor, we will have  $\nu = (4\pi R^3/3) \cdot \rho^\alpha$  ( $\rho^\alpha$  is the number density of the molecules in the liquid). Solving this relative to  $R$ , we obtain

$$R = (3/4\pi\rho^\alpha)^{1/3} \nu^{1/3}. \quad (7)$$

Since the parameters  $\delta_1, \dots, \delta_6$  themselves are small, they may be expressed in terms of  $\nu$  using a first-approximation formula

$$r = (3/4\pi\rho_\infty^\alpha)^{1/3} \nu^{1/3} \quad (8)$$

which obviously follows from Eqs. (2), (4), and (7). Substituting Eq. (8) into Eq. (1), we obtain

$$\delta_1 = c_1 \nu^{-1/3}, \quad \delta_2 = c_2 \nu^{-1/3}, \quad \delta_3 = c_3 \nu^{-4/3}, \quad \delta_4 = c_4 \nu^{-1/3}, \quad \delta_5 = c_5 \nu^{-1}, \quad \delta_6 = c_6 \nu^{-1}, \quad (9)$$

where

$$\begin{aligned}
c_1 &\equiv (4\pi\rho_\infty^\alpha/3)^{1/3} \lambda_\infty, \quad c_2 \equiv 2(4\pi\rho_\infty^\alpha/3)^{1/3} \gamma_\infty \gamma_\infty, \quad c_3 \equiv (4\pi\rho_\infty^\alpha/3)^{1/3} \gamma_\infty u_\infty q^2, \\
c_4 &\equiv (4\pi\rho_\infty^\alpha/3)^{1/3} k_1/2u_\infty, \\
c_5 &\equiv \frac{4\pi}{3} q \left( \frac{d\mathcal{P}_0}{d\mu} \right)_\infty, \quad c_6 \equiv \frac{2\pi}{3} \frac{\rho_\infty^\alpha k_2 q}{u_\infty}.
\end{aligned} \tag{10}$$

Substituting Eq. (9) into Eq. (2), and then the obtained result into Eq. (7), we find that

$$R = (3/4\pi\rho_\infty^\alpha)^{1/3} v^{1/3} \left( 1 - \frac{1}{3} c_2 v^{-1/3} + \frac{1}{3} c_3 v^{-4/3} \right). \tag{11}$$

In turn, substituting Eq. (11), together with Eq. (9), into Eq. (4) and then solving Eq. (4) relative to  $r$ , we will have

$$r = (3/4\pi\rho_\infty^\alpha)^{1/3} v^{1/3} \left[ 1 - \left( c_1 + \frac{1}{3} c_2 \right) v^{-1/3} + \frac{1}{3} c_3 v^{-4/3} - c_5 v^{-1} \right]. \tag{12}$$

As is well known in nucleation theory, an especially important role is played by the chemical potential as a function of  $v$ . It is more convenient to deal with the dimensionless chemical potential expressed in thermal units  $kT$ :

$$b_v \equiv \mu/kT, \tag{13}$$

where we have indicated by the subscript its dependence on  $v$  (let us furthermore recall that the chemical potential is reckoned from the value for a flat interface in the absence of a field). Directing our attention to determining  $b_v$ , let us first of all introduce two dimensionless parameters

$$a \equiv \frac{3}{2} \frac{2\gamma_\infty}{kT\rho_\infty^\alpha} \left( \frac{4\pi\rho_\infty^\alpha}{3} \right)^{1/3} \equiv \frac{4\pi\gamma_\infty}{kT} \left( \frac{3}{4\pi\rho_\infty^\alpha} \right)^{2/3}, \tag{14}$$

$$a_q \equiv 3 \frac{u_\infty q^2}{kT\rho_\infty^\alpha} \left( \frac{4\pi\rho_\infty^\alpha}{3} \right)^{1/3} \equiv \frac{4\pi u_\infty q^2}{kT} \left( \frac{4\pi\rho_\infty^\alpha}{3} \right)^{1/3}, \tag{15}$$

where  $a_q$  (in contrast to  $a$ ) depends on  $q$ . From Eqs. (10), (14), and (15) follows identity  $a_q/a \equiv 2c_3/c_2$ , which may be written as

$$ac_3 = \frac{1}{2} a_q c_2. \tag{16}$$

Determining (13) with the use of (6), (9), and (12), taking into account in this case (14) and (15), and then using the identity (16) in the result obtained, we arrive at

$$\begin{aligned}
b_v &= \frac{2}{3} a v^{-1/3} \left[ 1 - \left( c_1 + \frac{1}{6} c_2 \right) v^{-1/3} + c_5 v^{-1} \right] \\
&- \frac{1}{3} a_q v^{-1/3} \left[ 1 + 2 \left( c_1 + \frac{1}{3} c_2 - c_4 \right) v^{-1/3} - \frac{5}{6} c_3 v^{-4/3} + 4 \left( c_5 - \frac{2}{3} c_6 \right) v^{-1} \right].
\end{aligned} \tag{17}$$

Let us designate as  $\xi_v$  the dimensionless density (degree of supersaturation) in the vapor, found in equilibrium with the droplet of  $v$  molecules. From the formula for an ideal gas, we have  $b_v = \ln \xi_v$ . Substituting this into the left-hand side of (17), we obtain a relationship which defines in explicit form the dependence of  $\xi_v$  on  $v$  (and  $q$ ). This relationship generalizes, by means of corrections with coefficients  $c_1, \dots, c_6$ , the familiar Kelvin-Thomson relationship. If the electric field of the nucleus is strong, then the corrections are substantial. It is evident that the existence of a charge on the nucleus for each  $v$  decreases the density of the vapor found in equilibrium with the droplet. In proportion to the decrease in  $v$ , in expression (17) the term with the coefficient  $a_q$  begins to increase more rapidly than the term with the coefficient  $a$ ; so that  $b_v$ , after achieving a maximal value  $b_{\max}$  (depending on the magnitude of the charge and its size), then decreases, rapidly passing through zero.

For the number of molecules  $v$  in a droplet which is found in equilibrium with the vapor, having a given dimensionless density  $\xi$  and correspondingly a given dimensionless chemical potential  $b = \ln \xi$ , we have the equation  $b = b_v$  [where  $b_v$  is defined by Eq. (17)]. Obviously, if  $b > b_{\max}$ , then the equation  $b = b_v$  does not have positive solutions; if  $b < b_{\max}$  (and  $b > 0$ ), then there will be two positive solutions. The greater of these solutions corresponds to unstable equilibrium of the droplet with the vapor (the critical droplet); and the smaller of

These solutions corresponds to stable equilibrium. It is important that, for a sufficiently high value of the ratio  $a_q/a$ , the stable solution falls within the region of  $\nu$  values achieved by our method.

Another important parameter in nucleation theory is the work of formation for the droplet  $W$ . In the case we have considered so far, when the droplet is found in equilibrium with the vapor (unstable or stable), the work  $W$  (which in this case will be designated as  $W^e$ ) coincides with the change in the grand thermodynamic potential of the system  $\Delta\Omega$ , occurring in the system upon formation of the droplet. The general thermodynamic expression for  $W^e \equiv \Delta\Omega$  has already been obtained ([1], Eq. (50)). We give it as:

$$W^e = \frac{4\pi}{3} \gamma r^2 - 4\pi \rho q + \frac{16\pi}{3} \frac{uq^2}{r} + \Delta\Omega_n, \quad (18)$$

where we have omitted the subscripts  $\alpha$  and  $\beta$  for the surface layer of the droplet on the boundary with the vapor; also, we have expressed the area of the surface of tension in terms of its radius  $r$ , and we have used the abbreviations  $u \equiv (1/\epsilon^\beta - 1/\epsilon^\alpha)/8\pi$  ([2], definition (8)). The work  $\Delta\Omega_n$  for introducing a nucleus from the vapor into the liquid which is found at the same chemical potential  $b_\nu$  (and temperature  $T$ ) depends on  $b_\nu$  (and  $T$ ).

Let us determine the explicit dependence of  $W^e$  on  $\nu$ . Setting  $u = u_\infty$  (as was shown in [2], the relative error in this case is much less than the curvature parameter) and also taking into account Eqs. (3) and (5), we reduce Eq. (18) to

$$W^e = \frac{4\pi}{3} \gamma_\infty r^2 (1 - 2\delta_1 - 6\delta_5) + \frac{16\pi}{3} \frac{u_\infty q^2}{r} \left[ 1 + \frac{1}{4} \delta_1 - \frac{5}{4} \delta_4 + \frac{3}{4} \delta_5 - \frac{7}{6} \delta_6 \right] + \Delta\Omega_n - 4\pi \rho_{0\infty}. \quad (19)$$

It is more convenient to deal with the dimensionless work of formation expressed in thermal kT units:

$$\mathcal{F}_\nu^e \equiv W^e/kT. \quad (20)$$

where we have indicated its dependence on  $\nu$  by the subscript. Substituting Eq. (19) into Eq. (20), using in this case Eqs. (9), (12), (14)-(16), we obtain

$$\mathcal{F}_\nu^e = \frac{1}{3} a \nu^{1/3} \left[ 1 - 4 \left( c_1 + \frac{1}{6} c_2 \right) \nu^{-1/3} - 8c_5 \nu^{-1} + \frac{4}{3} a_q \nu^{-1/3} \left[ 1 + \frac{5}{4} \left( c_1 + \frac{1}{3} c_2 - c_4 \right) \nu^{-1/3} - \frac{1}{3} c_3 \nu^{-1/3} + \frac{7}{4} \left( c_5 - \frac{2}{3} c_6 \right) \nu^{-1} \right] \right] + f(b_\nu), \quad (21)$$

where

$$f(b_\nu) \equiv (\Delta\Omega_n - 4\pi q \rho_{0\infty})/kT \quad (22)$$

(we do not indicate the dependence on the fixed temperature  $T$ ).

If, as is indeed the case, we have not specified the number  $\nu$  of molecules in the droplet found in equilibrium with the vapor, but rather specify the chemical potential  $b$  of the vapor (or, which is the same thing, its density  $\xi \equiv \exp b$ ), then in Eq. (21) we must mean by  $\nu$  the root of the equation  $b = b_\nu$ . Correspondingly, the argument  $b_\nu$  of the function  $f(b_\nu)$  must be replaced by  $b$ . The difference between the values in expression (21) upon substitution into this equation of the largest (critical droplet) and the smallest roots is the activation barrier for nucleation. The exponent, which involves the activation barrier with a minus sign, just determines the rate of fluctuation nucleation on charged nuclei.

The importance of knowing the work of formation  $\mathcal{F}_\nu^e$  for the droplet\* not found in equilibrium with the vapor is explained by the fact that it is precisely the derivative with respect to this work  $\mathcal{F}_\nu^e \equiv (\partial \mathcal{F}_\nu^e / \partial \nu)_b$  which enters into the relationship

$$P_\nu^- / P_{\nu-1}^+ = \exp \mathcal{F}_\nu^e \quad (23)$$

(which stems from the Zeldovich nucleation equation), where  $P_{\nu-1}^+$  is the number of vapor molecules absorbed per unit time by droplets of  $\nu - 1$  molecules and  $P_\nu^-$  is the number of vapor molecules released per unit time by droplets of  $\nu$  molecules.

\*As before, we assume the work is expressed in thermal kT units.

If the vapor density  $\xi \equiv \exp b$  coincides with  $\xi_v \equiv \exp b_v$ , the droplets are found in equilibrium with the vapor. Then the release of vapor molecules by the droplets (as the result of which  $v$  goes to  $v - 1$ ) is compensated by absorption of vapor molecules by the droplet (as a result of which  $v - 1$  goes back to  $v$ ). In this case, we have  $P_v^-/P_{v-1}^+ = 1$ . If we now have that the vapor density  $\xi \equiv \exp b$  becomes different while the droplets retain the prior number of molecules, then the parameter  $P_{v-1}^+$  (being proportional to the vapor density) is increased by a factor of  $(\exp b)/(\exp b_v)$ ; the magnitude of  $P_v^-$  practically remains as before (the droplet, as a dense formation, is weakly sensitive to a change in the vapor). As a result, the left-hand side of Eq. (23) becomes equal not to unity but to  $\exp(b_v - b)$ . Taking the logarithm of Eq. (23), we then obtain

$$\mathcal{F}'_v = -b + b_v. \quad (24)$$

We use this relationship, based on physical considerations and the properties of  $\mathcal{F}_v$  (which are just the ones that are important in nucleation theory), to determine the work of formation for the droplet not found in equilibrium with its surrounding vapor. Collecting together all the assumptions of the theory in physically substantiated confirmation of the independence of  $P_v^-$  relative to vapor density, we thereby avoid the difficulties arising in direct computation of  $\mathcal{F}_v$  connected with the existence in the general case of a nonequilibrium layer of material between the droplet and the vapor.

Substituting Eq. (17) into Eq. (24), we then integrate this relationship with respect to  $v$  (for constant  $b$ ). We obtain

$$\begin{aligned} \mathcal{F}_v = & -b_v + av^{1/2} \left[ 1 - 2 \left( c_1 + \frac{1}{6} c_2 \right) v^{-1/2} - 2c_5 v^{-1} \right] \\ & + a_q v^{-1/2} \left[ 1 + \left( c_1 + \frac{1}{3} c_2 - c_4 \right) v^{-1/2} - \frac{1}{6} c_3 v^{-1/2} + \left( c_5 - \frac{2}{3} c_6 \right) v^{-1} \right] + C(b), \end{aligned} \quad (25)$$

where  $C(b)$  is the constant of integration (a function of  $b$ ). In order to determine this, we must take into account the fact that when we know  $v$ , which is equal to the number of molecules in the droplet found in equilibrium with the vapor of a given chemical potential  $b$ , expression (25) should coincide with Eq. (21). On the other hand, obviously we may choose this value of  $v$  as the independent variable, and the parameter  $b$  in Eq. (25) may be replaced by  $b_v$ . Proceeding in this manner, and in this case taking into account Eq. (17), we obtain (after combining like terms) an expression which differs from Eq. (21) only in the replacement of  $f(b_v)$  by  $C(b_v)$ . Since in fact there should not be such a difference, we have  $C(b_v) = f(b_v)$ . By virtue of the arbitrariness of  $v$ , this means  $C(b) = f(b)$ ,\* which determines  $C(b)$  in Eq. (25).

According to Eqs. (17) and (21), the parameters  $b_v$  and  $\mathcal{F}_v^e$  do not depend on  $b$ . Differentiating Eq. (21) with respect to  $v$  for constant  $b$ , we obtain

$$\mathcal{F}_v'' = b'_v, \quad (26)$$

where  $\mathcal{F}_v'' \equiv (\partial^2 \mathcal{F}_v / \partial v^2)_b$ ,  $b'_v \equiv db_v/dv$ . Using Eqs. (17) and (21), we may represent Eq. (25) in the form

$$\mathcal{F}_v = -(b - b_v)v + \mathcal{F}_v^e - f(b_v) + f(b). \quad (27)$$

The work for introducing the nucleus from the vacuum into the liquid is equal to the difference between the grand thermodynamic potentials of the liquid around the insoluble nucleus and the pure liquid, when they have the same chemical potential  $b$  (and also the same volume and temperature). When we change  $b$  by the amount  $db$ , this difference changes by  $v_n db$ , where  $v_n$  is familiar to us as the difference between the number of molecules of pure liquid which would arrive at the region occupied by the nucleus and the adjacent surface layer and the true number of molecules in this region. In the case of the vapor, the analogous number  $v_n^\beta$  will be much less than  $v_n$ . Then integrating  $v_n db$  with respect to  $b$  and taking into account the fact that in the corrections induced by the deviation of  $b$  from the value  $b_\infty = 0$  we may neglect the compressibility of the liquid and the nucleus, we obtain for the function  $f(b)$ , defined by relationship (22), and the function  $C(b)$  equal to it,

\*For  $b > b_{\max}$  - only in the sense of analytical continuity.

$$f(b) = C(b) = f_{\infty} + v_n b, \quad (28)$$

where we have neglected (by virtue of the fact that  $v_n^{\beta} \ll v_n$ ) the work for introducing the nucleus into the vapor. Substituting Eq. (28) into Eq. (27), we find\*

$$\mathcal{F}_v = -(b - b_v)(v - v_n) + \mathcal{F}_v^e \quad (29)$$

where  $v - v_n$  is the true number of molecules of liquid in the droplet.

When  $b < b_{\max}$  (and  $b > 0$ ), the equation  $b = b_v$  has two positive roots in which, according to (24), the condition  $\mathcal{F}_v' = 0$  is satisfied. The larger root provides the maximum for the function  $\mathcal{F}_v$  [otherwise, it would not decrease with an increase in  $v$  for large  $v$ , as is required for Eq. (25) when  $b > 0$ ] and the smaller root provides the minimum (there cannot be two maxima in succession). When  $b = b_{\max}$ , both positive roots to the equation  $b = b_v$  merge. In addition to  $\mathcal{F}_v' = 0$  we also have  $\mathcal{F}_v'' = 0$ , which follows from Eq. (26) and the relationship  $b_v' = 0$  (the necessary condition for the existence of a maximum at  $b_v$  for roots which coincide). Merging of the maximum and minimum for the function  $\mathcal{F}_v$  at its inflection point means that, when  $b$  attains the value  $b_{\max}$ , the nucleation of the droplet on a charged nucleus occurs not in a fluctuation manner but in a barrier-free manner. Finally, when  $b > b_{\max}$ , the equation  $b = b_v$  generally does not have positive roots. According to (24), the derivative  $\mathcal{F}_v'$  nowhere tends toward zero: The function  $\mathcal{F}_v$  monotonically decreases with an increase in  $v$ .

Thus, Eqs. (17), (21), (22), (25), and (28) in analytical form determine for the droplet in the field of a charged nucleus all the parameters, whose calculation is entrusted to the thermodynamics of nucleation by nucleation theory. The presence in  $\mathcal{F}_v$  of the "generating property" expressed by Eq. (24) gives Eq. (25) special significance: The other two formulas, (17) and (21), may be obtained from this one. In fact, differentiating (25) with respect to  $v$  (for constant  $b$ ) and comparing the result with (24), we arrive at (17). Substituting the parameter  $b$  in (25) by  $b_v$ , and then taking into account (17), we obtain (21). This makes formula (25) the major result of this work.

Let us express in terms of the variable  $v$  and the charge  $q$  the conditions for applicability of the theory, which (as was shown in [2]) reduce to

$$\delta_1 \ll 1, \delta_3 \leq \delta_1, |\delta_5| \leq \delta_1. \quad (30)$$

Then the fact that  $\delta_1$  dominates the rest of the parameters  $\delta_2$ ,  $\delta_4$ , and  $\delta_6$  follows from the relationships

$$\delta_2 \leq \delta_1, \delta_4 \sim \delta_1, \delta_6 \sim \delta_1 \quad (31)$$

substantiated in [2] (the last relationship implies that the sign of  $\delta_6$  and  $\delta_5$  is the same). Substituting (9) into (30) and separating out the charge dependence, we obtain

$$c_1 v^{-1/2} \ll 1, z^2 (c_3^0/c_1) v^{-1} \leq 1, |z| (|c_5^0/c_1) v^{-1/2} \leq 1, \quad (32)$$

where  $z \equiv q/q_0$ ,  $q_0$  is the elementary charge ( $q_0 > 0$ ),  $c_3^0 \equiv c_3/z^2$ ,  $c_5^0 \equiv c_5/z$ . From (10) it is evident that  $c_3^0$  and  $c_5^0$  are obtained from  $c_3$  and  $c_5$  by replacing  $q$  by  $q_0$ . Consequently, they do not depend on  $q$ . If for any material we have  $\delta_1 \leq \delta_2$ , then the role of the dominant parameter is played by  $\delta_2$  and not by  $\delta_1$ . Then, in (32) and the subsequent discussion we must replace  $c_1$  by  $c_2$ .

As is clear from (16), the parameter  $\Delta \equiv (c_3/c_2) v^{-1} \equiv z^2 (c_3^0/c_2) v^{-1}$  determines the relative weight of the electrical contributions compared with the nonelectrical contributions in Eq. (17). In Eqs. (21) and (25), the analogous weight is equal to  $8\Delta$  and  $2\Delta$ . Obviously, the parameter  $\Delta$  may be written as

$$\Delta = (c_1/c_2) z^2 (c_3^0/c_1) v^{-1}. \quad (33)$$

Conditions (32) impose on  $v$  a lower bound, and especially as  $|z|$  becomes greater. For

$$c_1 \leq [z^2 (c_3^0/c_1)]^{1/2} \quad (34)$$

\*We may obtain Eq. (29) by a purely thermodynamic route in analogy with the no-field case.

in order to satisfy the first two conditions in (32), it is sufficient to satisfy the second condition. If at the allowed lower limit for the values  $v \sim z^2 c_3^0 / c_1$  the third condition in (32) is satisfied, i.e., if

$$|c_3^0| / |z|^{1/2} c_1^{1/2} (c_3^0)^{1/2} \lesssim 1, \quad (35)$$

then this limit will be the lower one for all three conditions in (32). Recalling that the left-hand side of the second inequality in (32) and hence the right-hand side of (33) in general take on maximum values equal, respectively, to 1 and  $c_1/c_2$ , we conclude from (33) that at the same limit  $v$  takes on its own maximum value  $\Delta_{\max}$  and  $\Delta$ . Obviously,  $\Delta_{\max} = c_1/c_2$ . Since from (31) and (9) it follows that  $c_2 \leq c_1$ ,  $\Delta_{\max}$  is somewhat greater than unity (the electrical contributions are greater than the nonelectrical contributions).<sup>\*</sup> Noting that at the lower limit for the values of  $v \sim z^2 c_3^0 / c_1$ , the radius  $r$  of the droplet increases with an increase in  $|z|$  as  $|z|^{2/3}$ , and assuming that, in this case, the radius  $r_n$  of the nucleus increases as  $|z|^{1/2}$  or  $|z|^{1/3}$  (the charge of the nucleus is distributed with constant density over its surface or volume) we conclude:  $r \gg r_n$ . This verifies the assumption that the field of the nucleus is spherical when the field is substantial.

Obviously, satisfying the inequalities in (34) and (35) requires a sufficiently high value for  $|z|$ . Using known data for water (temperature about 0°C), we have from (10):  $c_1 \approx 0.5$  [4, 5],  $c_2 \approx 0.36$ ,  $c_3^0 \approx 3$ ,  $c_5^0 \approx 2$ , where we take into account the fact that  $(d\mathcal{P}_0/d\mu)_\infty = -\kappa\mathcal{P}_\infty/kT$ ,  $\kappa \sim 1$  ( $\kappa > 0$ ) ([2], formula (44)) and we bear in mind that  $4\pi q_0 \mathcal{P}_\infty/kT \approx -4.2$  [6-9]. It is clear that when  $z = \pm 1$  (singly charged ion in the droplet), the strong inequality in (34) and the inequality in (35) are satisfied in practice. For  $\Delta_{\max}$  we obtain the value 1.7.

#### LITERATURE CITED

1. A. I. Rusanov and F. M. Kuni, *Kolloidn. Zh.*, 44, No. 5, 934 (1982).
2. F. M. Kuni, A. K. Shchekin, and A. I. Rusanov, *Kolloidn. Zh.*, 46, No. 4, 682 (1983).
3. A. I. Rusanov, *Phase Equilibria and Surface Phenomena* [in Russian], Khimiya, Leningrad (1967).
4. R. C. Tolman, *J. Chem. Phys.*, 17, No. 2, 118 (1949).
5. J. A. Wingrave, R. S. Schechter, and W. H. Wade, in: *Modern Capillarity Theory* [Russian translation], A. I. Rusanov and F. Ch. Gudrich, eds., Khimiya, Leningrad (1980).
6. A. Frumkin, Z. Iofa, and M. Gerovich, *Zh. Fiz. Khim.*, 30, No. 7, 1455 (1956).
7. A. N. Frumkin, *Zh. Fiz. Khim.*, 35, No. 9, 2163 (1961).
8. N. N. Kochurova, B. A. Noskov, and A. I. Rusanov, *Dokl. Akad. Nauk SSSR*, 227, No. 6, 1386 (1976).
9. V. L. Kuz'min and A. I. Rusanov, *Kolloidn. Zh.*, 39, No. 3, 455 (1977).

<sup>\*</sup>In this case,  $b_v < 0$ , so that the droplet is found in stable equilibrium with the incompletely saturated vapor, which corresponds to a single positive root to the equation  $b = b_v$  for  $b < 0$ .