

THEORY OF NUCLEATION ON CHARGED NUCLEI.

3. EXPANSION IN THE CURVATURE PARAMETER OF A DROP IN A STRONG FIELD OF A CHARGED NUCLEUS

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An iteration method with respect to the curvature parameter of a drop in a strong field of a charged nucleus has been developed. It has been shown that among the nonlinear electrical effects already described by the second iteration, there are some which are odd relative to the sign of the charge of the nucleus.

Expansion in the curvature parameter of a drop (the ratio of the thickness of its surface layer to its radius) is one of the most effective methods in the thermodynamics of homogeneous nucleation. The generalization of this method to nucleation in the presence of charged nuclei is the subject of the present work. The main purpose was to include strong electric fields, whose contributions can noticeably compete with the usual nonelectrical contributions and thereby significantly influence both the state of the drop and the entire nucleation process, in the description.

For the surface tension γ of a drop (on its boundary with a vapor), we shall use the generalized adsorption equation {[1], Eq. (27)}:

$$d\gamma = -\Gamma d\mu + Dd\mathcal{P} \quad (1)$$

and the equation of mechanical equilibrium {[1], Eq. (15)}:

$$p_N^\alpha(r) - p_N^\beta(r) = 2\gamma/r. \quad (2)$$

The temperature T is assumed to be fixed (accordingly, we shall not indicate the dependence on it), and the substance surrounding the insoluble nucleus will be considered a one-component substance. In the case under consideration of an equilibrium drop, it has a unique chemical potential μ . The notation is the same as in [1]: r is the radius of tension surface, Γ and \mathcal{P} are the specific adsorption and excess polarization (relative to the tension surface), $D \equiv q/r^2$ is the induction,* q is the charge of the nucleus, $p_N(r)$ is the normal component of the pressure tensor, and the superscripts α and β correspond to the bulk properties of the liquid (composing the drop) and the vapor.

As the two independent variables corresponding to the two degrees of freedom of the system at a fixed temperature, we take μ and D . Introducing $\sigma \equiv \gamma - D\mathcal{P}$ (the thermodynamic surface tension), we rewrite (1) as[†]

$$d\sigma = -\Gamma d\mu - \mathcal{P} dD. \quad (3)$$

Integrating this with respect to D at a constant μ , we have

$$\sigma(\mu, D) = \sigma_0(\mu) - \int_0^D \mathcal{P}(\mu, D') dD' \quad (4)$$

*We shall consider the positive directions emerging from the center of the drop.

[†]The influence of an electric field on the surface tension was considered for the first time in [2].

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where the subscript 0 corresponds to the value at the same chemical potential in the absence of a field. Then differentiating (4) with respect to μ at constant D and comparing the result with (3), we obtain

$$\Gamma(\mu, D) = \Gamma_0(\mu) + \int_0^D \frac{\partial \mathcal{F}(\mu, D')}{\partial \mu} dD'. \quad (5)$$

Returning to $\gamma \equiv \sigma + D\mathcal{F}$ in (4) and taking into account that $\gamma_0(\mu) \equiv \sigma_0(\mu)$, we find

$$\gamma(\mu, D) = \gamma_0(\mu) + D\mathcal{F}(\mu, D) - \int_0^D \mathcal{F}(\mu, D') dD'. \quad (6)$$

The electrical contributions to the left-hand side of Eq. (2) are easily isolated {[3], Eq. (11)}. After this, Eq. (2) can be written as

$$\Delta p_0^\alpha(\mu) - \Delta p_0^\beta(\mu) + u(\mu) D^2 = 2\gamma(\mu, D)/r, \quad (7)$$

where $\Delta p_0^{\alpha, \beta}$ is the deviation of the pressure in the presence of a field from its value when $r = \infty$,

$$u \equiv (1/\varepsilon^\beta - 1/\varepsilon^\alpha)/8\pi \quad (8)$$

and $\varepsilon^{\alpha, \beta}$ is the dielectric constant. For polar liquids, in which we are interested, $\varepsilon^\beta \approx 1 \ll \varepsilon^\alpha$, so that $u \approx 1/8\pi$.

Assuming that $\gamma_0(\mu)$, $\mathcal{F}(\mu, D)$, $\Delta p_0^{\alpha, \beta}(\mu)$, and $u(\mu)$ are assigned functions, we can find the function $\gamma(\mu, D)$ from (6). Then treating (7) as an algebraic equation with respect to μ , we find $\mu = \mu(r, D)$ and consequently $\gamma(r, D) \equiv \gamma[\mu(r, D), D]$.

This procedure is especially simpler in the case under consideration here of a small curvature parameter

$$\delta_1 \equiv \lambda_\infty/r, \quad (9)$$

where λ_∞ is the difference between the radii of an equimolecular surface and the tension surface ($\lambda_\infty > 0$), and the subscript ∞ (here and in the following) indicates that the quantity refers to the case of a flat layer in the absence of a field. In fact, when $\delta_1 \ll 1$, the value of γ on the right-hand side of (7) can be approximated in order of magnitude with respect to δ_1 by its value γ_∞ when $\delta_1 = 0$. Identifying the number of the approximation with the order of the relative error with respect to the parameter δ_1 , we shall call γ_∞ the first approximation for γ . Solving Eq. (7) at $\gamma = \gamma_\infty$ and setting $\mu_\infty = 0$ (computing μ relative to μ_∞), for μ we find the first approximation $\mu^{(1)}(r, D)$. Then substituting $\mu^{(1)}(r, D)$ into the function $\gamma(\mu, D)$ defined by equality (6), for γ we find the second approximation $\gamma^{(2)}(r, D) \equiv \gamma[\mu^{(1)}(r, D), D]$. The further performance of the iterations is already obvious. Of course, the transition to each successive approximation requires increasingly more accurate knowledge of the functions $\gamma_0(\mu)$, $\mathcal{F}(\mu, D)$, $\Delta p_0^{\alpha, \beta}(\mu)$, and $u(\mu)$, which play the role of the assigned equations of state.

An additional facilitating circumstance when $\delta_1 \ll 1$ is the clear fulfillment of the inequality $\Delta p_0^\beta/\Delta p_0^\alpha \ll 1$, which permits the neglect of the second term on the left-hand side of (7) in comparison to the first. The fulfillment of the inequality $\rho^\beta/\rho^\alpha \ll 1$, where ρ is the density of the number of molecules, is scarcely weaker. The latter permits the neglect of ρ^β in comparison to ρ^α . These two simplifications will be made in the following without any additional stipulations.

The corrections with respect to δ_1 may be of the same order of magnitude as the corrections for the compressibility of the liquid.* As the tabulated data show, in the range of pressures of interest to us the compressibility of the liquid χ may be assumed constant: $\chi = \chi_\infty$. For the density of the liquid we then have

$$\rho_0^\alpha = \rho_\infty^\alpha (1 + \rho_\infty^\alpha \chi_\infty \mu) \quad (10)$$

*The combined determination of these corrections in the absence of a field was carried out in [4].

(the chemical potential is determined relative to the value of μ_∞). Then integrating the thermodynamic relation $d\Delta p_0^\alpha/d\mu = \rho_0^\alpha$ with respect to μ , we obtain

$$\Delta p_0^\alpha = \rho_\infty^\alpha \mu \left(1 + \frac{1}{2} \rho_\infty^\alpha \chi_\infty \mu \right). \quad (11)$$

Assuming for a time that the equalities $\Delta p_0^\alpha = \rho_\infty^\alpha \mu$ and $u = u_\infty$ are valid in a first approximation, from (7) we obtain in the same approximation

$$\mu \equiv \mu^{(1)} = 2\gamma_\infty/\rho_\infty^\alpha r - u_\infty D^2/\rho_\infty^\alpha. \quad (12)$$

Taking into account (12), we have

$$\rho_\infty^\alpha \chi_\infty \mu = \delta_2 - \delta_3 \quad (13)$$

where

$$\delta_2 \equiv 2\chi_\infty \gamma_\infty / r, \quad \delta_3 \equiv \chi_\infty u_\infty D^2. \quad (14)$$

The dimensionless parameter δ_2 also plays the role of a curvature parameter. Since the quantity $2\chi_\infty \gamma_\infty$ is on the order of fractions of an angstrom under ordinary conditions, we may expect $2\chi_\infty \gamma_\infty \lesssim \lambda_\infty$ and thus $\delta_2 \lesssim \delta_1$. Assuming in addition that $\delta_3 \lesssim \delta_1$ (this places an upward restriction on $|q|$), the neglect of the term $\rho_\infty^\alpha \chi_\infty \mu / 2$ in (11) during the determination of $\mu^{(1)}$ is justified. If it is found for some substance that $2\chi_\infty \gamma_\infty \geq \lambda_\infty$ and thus $\delta_1 \lesssim \delta_2$, the major parameter in all subsequent evaluations will be δ_2 , which should then be small ($\delta_2 \ll 1$), rather than δ_1 . Accordingly, instead of $\delta_3 \lesssim \delta_1$, it should then be required that $\delta_3 \lesssim \delta_2$.

Next, after obtaining the equality

$$\frac{1}{u_\infty} \frac{du}{d\mu} \simeq \frac{1}{(\epsilon^\alpha)^2} \frac{d\epsilon^\alpha}{d\mu} - \frac{1}{(\epsilon^\beta)^2} \frac{d\epsilon^\beta}{d\mu} \quad (15)$$

(where it has been taken into account that $u_\infty \simeq 1/8\pi$) from (8), for the evaluation of the first term on its right-hand side we use the relation

$$\frac{1}{\epsilon^\alpha} \frac{d\epsilon^\alpha}{d\mu} \lesssim \frac{1}{\rho_0^\alpha} \frac{d\rho_0^\alpha}{d\mu} \simeq \rho_\infty^\alpha \chi_\infty \quad (16)$$

and for the evaluation of the second term we use the equality

$$\epsilon^\beta \simeq 1 + 3\rho_0^\beta/\rho_\infty^\alpha \quad (17)$$

(which follows from the Langevin-Debye equation) and the equation of an ideal gas $d\rho_0^\beta/d\mu = \rho_0^\beta/kT$ (k is Boltzmann's constant). As a result, we obtain

$$\frac{1}{u_\infty} \frac{du}{d\mu} \lesssim \frac{\rho_\infty^\alpha \chi_\infty}{\epsilon^\alpha} - \frac{3\rho_0^\beta}{kT\rho_\infty^\alpha}. \quad (18)$$

The second term on the right-hand side of (18) almost never exceeds the first term. Thus,

$$\frac{1}{u_\infty} \frac{du}{d\mu} \lesssim \rho_\infty^\alpha \chi_\infty / \epsilon^\alpha. \quad (19)$$

Along with (13) this allows us to write

$$\left| \frac{1}{u_\infty} \frac{du}{d\mu} \mu \right| \lesssim |\delta_2 - \delta_3| / \epsilon^\alpha \lesssim \delta_1 / \epsilon^\alpha. \quad (20)$$

According to (20), the relative change in the value of u does not exceed δ_1/ϵ^α . In view of the fact that $1/\epsilon^\alpha \ll 1$, this justifies the relation $u = u_\infty$ not only in the first, but also in the second approximation. In addition, this also justifies the linearity of the equation of the electrostatics of the α and β phases used in isolating the electrical contributions to the left-hand side of (7).

Unlike the α and β phases, the surface layer of a drop displays nonlinearity in its electrical properties. As the simplest approximation taking into account this nonlinearity we can use

$$\mathcal{P}(\mu, D) = \mathcal{P}_0(\mu) + \mathcal{P}_e, \quad \mathcal{P}_e = k_1 D + k_2 D^2, \quad (21)$$

where $\mathcal{P}_0(\mu)$ and \mathcal{P}_e are the spontaneous and excess induced polarizations, and the coefficients k_1 and k_2 in the principal approximation are assumed constant. Equations (5) and (6) then give

$$\Gamma(\mu, D) = \Gamma_0(\mu) + D d\mathcal{P}_0/d\mu \quad (22)$$

$$\gamma(\mu, D) = \gamma_0(\mu) + \frac{1}{2} k_1 D^2 + \frac{2}{3} k_2 D^3. \quad (23)$$

Setting

$$\Gamma \equiv [\rho^\alpha(r) - \rho^\beta(r)] \lambda \simeq \rho^\alpha(r) \lambda, \quad (24)$$

we relate λ to the radius R of an equimolecular surface {[3], Eq. (25)}

$$R^3 = r^3 + 3\lambda r^2 - 3 \left(\frac{1}{r} - \frac{1}{R} - \frac{\lambda}{r^2} \right) \frac{du}{d\mu} \frac{q^2}{\rho_0^\alpha} \quad (25)$$

[the inequality $\rho_0^\beta \ll \rho_0^\alpha$ and definition (8) have been taken into account]. As is clear from (19), (14), and (9), the last term on the right-hand side of (25) does not exceed a value of $-\lambda r^2 \delta_1 \delta_3 / \epsilon^\alpha$, which (in view of the fact that $\delta_3 \leq \delta_1$ and $1/\epsilon^\alpha \ll 1$) is smaller by more than two orders of magnitude with respect to δ_1 , than the second term on the right-hand side of (25). Relation (25) then gives the equation

$$R = r(1 + \lambda/r), \quad (26)$$

in which the quantities which are small by two orders of magnitude with respect to δ_1 were neglected.

For the density $\rho^\alpha(r)$ we may write {[3], Eq. (19)}:

$$\rho^\alpha(r) = \rho_0^\alpha(\mu) + \frac{D^2}{8\pi} \frac{1}{(\epsilon^\alpha)^2} \frac{d\epsilon^\alpha}{d\mu}. \quad (27)$$

According to (16) and (14), the second term on the right-hand side of (27) has a smallness factor δ_3/ϵ^α in comparison to ρ_∞^α . Recalling (10) and (13) and again taking into account that $1/\epsilon^\alpha \ll 1$, we conclude

$$\rho^\alpha = \rho_0^\alpha = \rho_\infty^\alpha (1 + \delta_2 - \delta_3), \quad (28)$$

where the second-order quantities have been neglected.

Using (28), we write (24), respectively, in the presence and absence of a field as

$$\Gamma = \rho_0^\alpha \lambda, \quad \Gamma_0 = \rho_0^\alpha \lambda_0. \quad (29)$$

Substituting this into (22), we obtain

$$\lambda = \lambda_0 + \Delta_q \lambda, \quad \Delta_q \lambda \equiv \frac{D}{\rho_0^\alpha} \frac{d\mathcal{P}_0}{d\mu}. \quad (30)$$

We can now explain the appearance of the nonlinearity in expression (21) for \mathcal{P}_e . From the result previously obtained {[5], Eq. (51)}, it follows that in the principal approximation with respect to the curvature parameter

$$\mathcal{P}_e = 2u_\infty \eta D, \quad (31)$$

where η is the difference between the surface relative to which the excess polarization \mathcal{P}_e is equal to zero and the tension surface. Since the dielectric constant is determined mainly by the density of the substance, it is reasonable to assume that $\eta = \lambda$. In view of (30) we then have

$$\mathcal{P}_e \sim 2u_\infty \lambda_0 D + \frac{2u_\infty}{\rho_0^\alpha} \frac{d\mathcal{P}_0}{d\mu} D^2. \quad (32)$$

This formula is characterized by the same structure as expression (21) for \mathcal{P}_e with the μ -independent coefficients

$$k_1 \sim 2u_\infty \lambda_\infty, \quad k_2 \sim \frac{2u_\infty}{\rho_\infty^\alpha} \left(\frac{d\mathcal{P}_0}{d\mu} \right)_\infty, \quad (33)$$

where we have replaced λ_0 , ρ_0^α , and $d\mathcal{P}_0/d\mu$ by their first approximations λ_∞ , ρ_∞^α , and $(d\mathcal{P}_0/d\mu)_\infty$ since \mathcal{P}_e will appear in all the final expressions (for γ ; μ , and the work of formation of a drop) as first-order corrections with respect to δ_1 .

Since $\mathcal{P}_0 - \mathcal{P}_{0\infty}$ will also play the role of a first-order correction with respect to δ_1 , we can write $\mathcal{P}_0 - \mathcal{P}_{0\infty} = (d\mathcal{P}_0/d\mu)_\infty \mu$ after replacing μ here by the first approximation $\mu^{(1)}$. Taking into account (12), we then have

$$\mathcal{P}_0 = \mathcal{P}_{0\infty} + \frac{1}{\rho_\infty^\alpha} \left(\frac{2\gamma_\infty}{r} - u_\infty D^2 \right) \left(\frac{d\mathcal{P}_0}{d\mu} \right)_\infty. \quad (34)$$

We now introduce three dimensionless parameters

$$\delta_4 \equiv \frac{k_1}{2u_\infty r}, \quad \delta_5 \equiv \frac{D}{\rho_\infty^\alpha r} \left(\frac{d\mathcal{P}_0}{d\mu} \right)_\infty, \quad \delta_6 \equiv \frac{k_2 D}{2u_\infty r}. \quad (35)$$

According to (33), $\delta_4 \sim \delta_1$ ($\delta_4 > 0$), and $\delta_6 \sim \delta_5$ [the signs of the parameters δ_5 and δ_6 , which are identical, depend on the sign of q and the sign of the derivative $(d\mathcal{P}_0/d\mu)_\infty$]. From (21), (34), and (23) with consideration of definitions (35) we have

$$q\mathcal{P} = q\mathcal{P}_{0\infty} + 2\gamma_\infty r^2 \delta_5 + 2u_\infty r^3 D^2 \left(\delta_4 - \frac{1}{2} \delta_5 + \delta_6 \right) \quad (36)$$

$$\gamma = \gamma_0(\mu) + u_\infty r D^2 \left(\delta_4 + \frac{4}{3} \delta_6 \right). \quad (37)$$

Then, calculating the correction term to (26) with the aid of Eqs. (30), in which we can replace λ_0 , ρ_0^α , and $d\mathcal{P}_0/d\mu$ by their first approximations λ_∞ , ρ_∞^α , and $(d\mathcal{P}_0/d\mu)_\infty$, with consideration of (9) and the second of the definitions in (35) we obtain

$$R = r(1 + \delta_1 + \delta_5). \quad (38)$$

Below we shall assume that $|\delta_5| \sim |\delta_6| \lesssim \delta_1$ (this places an upward restriction on $|q|$ in addition to $\delta_3 \lesssim \delta_1$). The quantities discarded in (36) and (38) will then be second-order with respect to δ_1 , i.e., the parameter which is the upward major of the remaining parameters δ_2 , ... δ_6 of the theory.

In order to find $\gamma_0(\mu)$, we integrate Eq. (1) in the absence of a field with respect to μ . Since $\gamma_0(\mu) - \gamma_\infty$ plays the role of a correction to γ_∞ , in determining Γ_0 , with the aid of the second of the equalities in (29) we can replace the quantities ρ_0^α and λ_0 in it by their first approximations ρ_∞^α and λ_∞ . As a result we obtain

$$\gamma_0(\mu) = \gamma_\infty - \rho_\infty^\alpha \lambda_\infty \mu, \quad (39)$$

which provides an accuracy sufficient for constructing a second approximation to $\gamma(r, D)$ and $\mu(r, D)$.

We shall now proceed to its construction. Again taking into account the correction nature of the second term on the right-hand side of (39), we disclose it with the aid of the equation of the first approximation (12). Then substituting (39) into (37), with consideration of (9), we obtain

$$\gamma \equiv \gamma^{(2)} = \gamma_\infty (1 - 2\delta_1) + u_\infty r D^2 \left(\delta_4 + \delta_5 + \frac{4}{3} \delta_6 \right). \quad (40)$$

Next, substituting (40) into the right-hand side of (7) and noting that the equation of the first approximation (13) is adequate for determining the correction term in (11), as well as recalling that the relation $u = u_\infty$ along with the linearity of the electrostatics in the α and β phases remain valid in the second approximation, we find

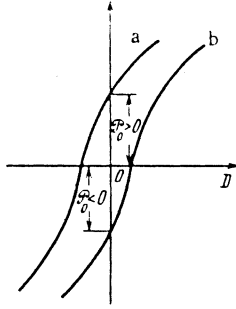


Fig. 1. Dielectric saturation curves in the surface layer: a) case of $\varphi_0 > 0$; b) case of $\varphi_0 < 0$.

$$\mu \equiv \mu^{(2)} = \frac{2\gamma_\infty}{\rho_\infty^\alpha r} \left[1 - 2\delta_1 - \frac{1}{2}(\delta_2 - \delta_3) \right] - \frac{u_\infty D^2}{\rho_\infty^\alpha} \left[1 - 2\left(\delta_1 + \delta_4 + \frac{4}{3}\delta_6\right) - \frac{1}{2}(\delta_2 - \delta_3) \right], \quad (41)$$

where the terms with products of the small parameters are neglected with the accuracy required for the second approximation. After obtaining the identity

$$\frac{2\gamma_\infty}{\rho_\infty^\alpha r} \delta_3 = \frac{u_\infty D^2}{\rho_\infty^\alpha} \delta_2 \quad (42)$$

directly from (14), we can reduce (41) to

$$\mu \equiv \mu^{(2)} = \frac{2\gamma_\infty}{\rho_\infty^\alpha r} \left(1 - 2\delta_1 - \frac{1}{2}\delta_2 \right) - \frac{u_\infty D^2}{\rho_\infty^\alpha} \left[1 - 2(\delta_1 + \delta_4) - \delta_2 + \frac{1}{2}\delta_3 - \frac{8}{3}\delta_6 \right]. \quad (43)$$

It is significant that while only one expansion parameter (the curvature parameter δ_1) is present, in (40) and (43) there are two independent variables: r and q (the dependence on q appears by means of $D \equiv q/r^2$). It may be stated that expansions (40) and (43) are uniform with respect to all q satisfying the conditions $\delta_3 \lesssim \delta_1$ and $|\delta_5| \sim |\delta_6| \lesssim \delta_1$. As is clear from (9), (14), and (35), the upward restrictions placed by these conditions on $|q|$ are weaker the greater is r (the smaller is δ_1). Just this allows us to assume that δ_3/δ_2 is not a small quantity when $\delta_1 \ll 1$. From (42) and from (40) and (43) it is seen that δ_3/δ_2 again determines the relative weight of the electrical contributions and the nonelectrical contributions to the values of $\gamma - \gamma_\infty$ and μ . Without requiring that δ_3/δ_2 is small in the theory, we maintain its applicability to strong electric fields, i.e., fields which have a significant effect on the drop. The correction terms in the second terms on the right-hand sides of (40) and (43) are also of interest in strong fields. Of course, in reality q takes on assigned values (whole numbers of the elementary charge q_0). Accordingly, the conditions $\delta_3 \lesssim \delta_1$ and $|\delta_5| \sim |\delta_6| \lesssim \delta_1$ place a lower restriction on r , which is stronger the larger is $|q|$.

The equation of the second approximation (43) for μ already contains a nonlinear electrical contribution, which is proportional to D^4 , in the correction term with the parameter δ_3 . It is due to electrostriction and is present even if $k_2 = 0$, i.e., \mathcal{P}_e has a form which is linear with respect to the field. The next approximations $\gamma^{(3)}(r, D)$, $\mu^{(3)}(r, D)$, ... also have the ability to generate nonlinear terms that are increasingly higher with respect to D . When $k_2 = 0$ ($\delta_6 = 0$), only terms which are even with respect to D appear, and when $k_2 \neq 0$ ($\delta_6 \neq 0$), odd terms also appear. The lowest of the odd terms are already represented by corrections with the parameter δ_6 in the equations of the second approximation (40) and (43). Of course, the subsequent iterations require the refinement of $\gamma_0(\mu)$ and $\mathcal{P}_0(\mu)$ [consideration of the derivative $(d\lambda_0/d\mu)_\infty$, consideration of the variation of the induction in the layer, etc.].

The presence of terms which are odd with respect to q in (40) and (43) makes the disclosure of the sign of the coefficient k_2 appearing in them (by means of δ_6) important. The deviation of $\mathcal{P}_0(\mu)$ from zero is clearly caused by the difference between the properties of

the liquid and the vapor. Increasing μ at a constant temperature increases the supersaturation of the vapor and makes its properties more similar to the properties of the liquid, i.e., brings the state of the vapor and the liquid closer to the common critical state for them. We may, therefore, expect $(d|\mathcal{P}_0|/d\mu)_\infty < 0$ [a similar inequality is observed for the surface tension $\gamma_0(\mu)$], so that the sign of the derivative $(d\mathcal{P}_0/d\mu)_\infty$ and, according to (33), the sign of k_2 are opposite to the sign of \mathcal{P}_0 . In order to evaluate the absolute value of the derivative, it must be taken into account that the scale of variation characteristic of μ is kT . The foregoing allows us to write

$$(d\mathcal{P}_0/d\mu)_\infty = -\kappa\mathcal{P}_{0\infty}/kT, \quad \kappa \sim 1 \quad (\kappa > 0). \quad (44)$$

The same prediction of the sign can be attained on the basis of the data in Fig. 1, which presents plots of the dielectric saturation of $\mathcal{P}(\mu, D)$ due to the strong increase or decrease in D with constancy of μ in the cases of $\mathcal{P}_0 > 0$ and $\mathcal{P}_0 < 0$ [Eq. (21) describes only the part of the curves in the vicinity of the point $D = 0$]. In fact, Fig. 1 shows that the second derivative $\partial^2 \mathcal{P}(\mu, D) / \partial D^2$ at the point $D = 0$ is negative at the point $\mathcal{P}_0 > 0$ and positive in the case of $\mathcal{P}_0 < 0$. According to (21), this derivative is again equal (with accuracy to a factor of 2) to the coefficient k_2 .

LITERATURE CITED

1. A. I. Rusanov and F. M. Kuni, *Kolloidn. Zh.*, 44, No. 5, 934 (1982).
2. B. V. Deryagin, *Kolloidn. Zh.*, 1, No. 1, 217 (1935); *Acta Physiochim. URSS*, 2, 377 (1935).
3. F. M. Kuni, A. K. Shchekin, and A. I. Rusanov, *Kolloidn. Zh.*, 44, No. 6, 1062 (1982).
4. F. M. Kuni and A. I. Rusanov, *Teor. Mat. Fiz.*, 2, No. 2, 265 (1970).
5. A. I. Rusanov, *Kolloidn. Zh.*, 41, No. 5, 903 (1979).

DYNAMIC SURFACE ELASTICITY OF SURFACTANT SOLUTIONS AND THE STABILITY OF CAPILLARY WAVES

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On the basis of the thermodynamics of nonequilibrium processes, a general equation has been derived for the complex dynamic surface elasticity of surfactant solutions in the case of mass transfer across a phase interface or chemical reaction in a surface layer. The limits of applicability of the expression derived are examined.

According to a thermodynamic system departing from equilibrium, for example when the chemical affinity increases, a transition of the system from the thermodynamic branch is possible, i.e., a spontaneous formation of a spatial or space-time dissipative structure [1, 2]. In the physical chemistry of surface phenomena such structures, associated with the terms "spontaneous surface convection" and "surface turbulence," have been investigated many times in connection with problems of the acceleration of mass transfer across an interphase boundary and spontaneous emulsification [3-8].

Linear analysis of the stability of an interphase boundary reduces to an analysis of the dispersion relation (the relation between the frequency and the complex wave number) for superficial, usually capillary, waves, and the conditions for stability thus ensue from the boundary problem for the equations of the hydrodynamics of a viscous liquid. An analytical solution of the stability problem can be obtained only in some particular conditions [3-8]. The formal writing-down of the conditions of stability is simplified substantially if the concept of dynamic surface elasticity is introduced [4, 6-8]. The use of an independent general method for determining surface elasticity, therefore, offers a possibility of simplifying the problem and finding more general conditions for stability.

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