Thermodynamics of a Dielectric Droplet with Charged Nucleus in an External Electric Field

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Abstract—The equilibrium profile of a dielectric droplet originating on an insoluble charged nucleus in an external uniform electric field was found. The relationships obtained in three orders of the perturbation theory with respect to small deviation from the non-sphericity describe combined field effects of the charged nucleus and the external field in the coordinate system related to the mass center of the droplet. The dependences of the chemical potential and the work of droplet formation on the number of molecules in the droplet, the surface tension, the permittivity, the nuclear charge, and the strength of the external electric field were determined in analytical forms. The influence of the resultant electric field on the threshold value of vapor supersaturation and the activation energy of heterogeneous nucleation was considered. Thermodynamic relationships that allow us to verify theoretical self-consistency were discussed.

INTRODUCTION

Earlier [1], using a dielectric droplet induced by the dipole condensation center as an example, we formulated an iterative procedure for finding the equilibrium shape of the surface, the chemical potential, and the work of the droplet formation in an axisymmetrical electric field. The results of [1] may be extended to the essentially more complex case of droplet nucleation on a charged nucleus in an external uniform electric field. This case is of great practical importance, because an external uniform electric field is often used to divide centers according to their charge sign in the study of nucleation on charged centers [2, 3]. In an axisymmetrical electric field that is presented by the superposition of the external uniform electric field and the field of the charged condensation nucleus, the surface of a droplet of a dielectric liquid originating on a nucleus will deviate from the spherical shape. The difference in droplet shape from sphericity at a given number of condensate molecules in the droplet affects the values of the chemical potential of the condensate and the work of droplet formation, and hence the height of the nucleation barrier and the value of the vapor supersaturation beginning with which the nucleation of a new phase becomes barrierless.

A great number of studies are devoted to the separate effects of the central field of the charged condensation nucleus and the external electric field on the thermodynamic characteristics of droplets. For example, thermodynamics of ion-induced nucleation was considered in [4–6] with the impact on the polarization effects of the surface layer of a spherical droplet. The influence of the external uniform electric field on the critical size and the work of formation of neutral droplets in a supersaturated vapor was studied elsewhere [7]. In that

case, it was assumed that the droplet is represented by a spheroid with a small eccentricity and that is elongated along the field. The deviation of the equilibrium shape from sphericity was studied in [8, 9] for conductive and dielectric droplets. It was shown [10] that, for calculations carried out with an accuracy up to the terms proportional to the squared eccentricity, the equilibrium shape of a surface-charged droplet of an ideal incompressible conductive liquid in a uniform electric field and in the gravitational field may be assumed to be spheroidal. The nonlinear problem of the shape and stability of a surface-charged droplet of an ideal incompressible conductive liquid in an external uniform electric field was solved numerically in [11]. The Monte Carlo simulation of the formation of a dielectric droplet in an external uniform electric field was performed in [12]. The correlation between the shape of the droplet, its chemical potential, and the work of formation in the external uniform electric field was analytically established in [13, 14].

However, combined (nonadditive) effects of the external electric field and the field of the charged condensation nucleus were not considered at all in the thermodynamics of heterogeneous nucleation. Meanwhile, it is clear that such effects should take place, and we discuss below the mechanism of their appearance.

1. INITIAL EQUATIONS

Let us place a droplet with a insoluble nucleus that is charged and solid at its center in an external uniform electric field; the size of the nucleus is negligible compared to that of the droplet. The droplet contains ν molecules of an incompressible dielectric liquid (the α phase) and is surrounded by a vapor (the β phase).

Hereafter, the α and β indices denote the values that refer to the liquid and vapor phases, respectively. The α and β phases are assumed to be single-component; the effect of the gravitational field on the droplet is neglected.

The equilibrium shape of the droplet in the electric field is determined by the balance of pressures at any point on its surface [15]:

$$P^{\alpha}_{NN} - P^{\beta}_{NN} = P_{\gamma}, \qquad (1.1)$$

where P_{γ} is the capillary pressure under the curved surface of the droplet, and P^{α}_{NN} and P^{β}_{NN} are the normal components of the pressure tensor of the liquid and vapor, respectively. In the case under consideration, the external uniform electric field will accelerate the condensation nucleus together with the entire droplet. Assuming that the droplet as a whole is dragged by the nucleus, in the noninertial reference system related to the nucleus we have

$$P^{\alpha}_{NN} = P^{\alpha}_{0} - \sigma^{\alpha}_{N} + P_{w}, \quad P^{\beta}_{NN} = P^{\beta}_{0} - \sigma^{\beta}_{N}. \qquad (1.2)$$

Here, P_{0} is the pressure in the corresponding phase in the absence of the electric field but under the condition that the chemical potential of the droplet (the chemical potential of a liquid molecule in the droplet) is equal to the potential in the presence of the external field; σ_{N} is the normal component of Maxwell's stress tensor at the surface of the droplet:

$$\sigma^{\alpha,\beta}_{N} = \frac{\varepsilon^{\alpha,\beta}(E^{\alpha,\beta}_{N})^{2}}{4\pi} - \frac{\varepsilon^{\alpha,\beta}(\mathbf{E}^{\alpha,\beta})^{2}}{8\pi}, \qquad (1.3)$$

where ε is the permittivity, and $\mathbf{E}$ and E_{N} are the vector of the electric field strength and its component that is normal to the surface of the droplet, respectively. The contribution of P_{w} to P^{α}_{NN} is related to the uniformly accelerated motion of the droplet in the external uniform electric field and is equal to (provided that the density of gas compared to that of liquid is ignored)

$$P_{w} = -m\rho^{\alpha}wz, \qquad (1.4)$$

where m is the molecular mass of the liquid, ρ^{α} is the number of molecules per unit volume of the liquid, and w is the modulus of the droplet acceleration; the z coordinate is taken from the droplet center along the direction of its motion. The gravitational field, which would balance the droplet at its particular size, could be introduced into consideration. Then, instead of (1.4) we would have the equation $P_{w} = -m\rho^{\alpha}gz$ (g is the acceleration of gravity), and the condition of a balance of pressures (1.1) would refer to a droplet of a given size in the inertial coordinate system.

Evidently, the larger the mass of the droplet, the lower the acceleration w. Hereafter, we neglect the droplet velocity compared to the mean thermal velocity of vapor molecules. This allows us to ignore the non-

equilibrium effects related to the flux of vapor molecules that condense on the droplet as a function of the velocity of its motion. Estimation of the characteristic times of relaxation processes demonstrates that the droplet has a chance to come into the equilibrium state between two single acts of attachment or loss of a molecule. Thermodynamic relationships obtained in this work are precisely those that will be applied to this state of equilibrium.

In the axisymmetrical electric field, the equation for the equilibrium profile of the droplet surface may be written in the following form:

$$r(\theta) = R + f(\theta), \qquad (1.5)$$

where R is the radius of a sphere that has the same volume as the droplet, and the $f(\theta)$ function makes allowance for the deviation of the droplet surface from the spherical shape. Polar angle θ is taken from the z axis. Hence, denoting the volume of the droplet by V_{v}, we may write

$$V_{v} = (4\pi/3)R^{3}. \qquad (1.6)$$

Note that the volume V_{v} of a droplet that contains v molecules of an incompressible liquid is equal to $V_{v} = v/\rho^{\alpha}$. It is evident that

$$R = (3/4\pi\rho^{\alpha})^{1/3}v^{1/3}. \qquad (1.7)$$

Hereafter, we will consider only such strengths of the external field and dimensions of the resultant droplets for which

$$|f(\theta)| \ll R, \qquad (1.8)$$

accordingly, the $f(\theta)$ function will be referred to as the correction for the non-sphericity of the droplet. In this case, we have

$$V_{v} = \frac{2\pi}{3}\int_{0}^{\pi} r^{3}(\theta)\sin\theta \, d\theta$$

$$= \frac{2\pi R^{3}}{3}\int_{0}^{\pi}\left(1 + 3\frac{f}{R} + 3\left(\frac{f}{R}\right)^{2}\right)\sin\theta \, d\theta \qquad (1.9)$$

with an accuracy up to terms of the $(f/R)^{2}$ order.

Considering (1.6) and (1.9), we obtain a relationship for the non-sphericity correction f, which is important for further analysis:

$$\int_{0}^{\pi}(Rf + f^{2})\sin\theta \, d\theta = 0. \qquad (1.10)$$

An additional constraint on the f function follows from the fact that center of the nucleus should coincide with the mass center of the droplet (in the reference system related to the nucleus, the droplet is quiescent). Accordingly, the shape of the droplet should be such as

to fulfill condition $\int_0^\pi r^4(\theta)\cos\theta\sin\theta d\theta = 0$. Neglecting the terms that are higher than $(f/R)^2$ in the integrand of this expression, we obtain

$$\int_0^\pi (2Rf + 3f^2)P_1\sin\theta d\theta = 0, \qquad (1.11)$$

where of $P_1 = P_1(\cos\theta)$ is the Legendre polynomial of the first degree. It is condition (1.11) that will determine the value of acceleration modulus w for the non-inertial coordinate system or the droplet size R for the inertial coordinate system in the presence of compensating gravitational field.

2. EQUATIONS FOR THE PROFILE OF A DROPLET AND THE ELECTRIC POTENTIAL

The capillary pressure P_γ under the curved surface of a droplet is determined by the equality $P_\gamma = \gamma(1/R_1 + 1/R_2)$, where γ is the surface tension, and R_1 and R_2 are the principal radii of the surface curvature at a given point. Writing $1/R_1$ and $1/R_2$ in spherical coordinates, we obtain that the capillary pressure P_γ assumes the form

$$P_\gamma = \frac{\gamma}{(r^2 + r_\theta^2)^{1/2}}\left\{2 + \frac{r_\theta^2 - rr_{\theta\theta}}{r^2 + r_\theta^2} - \frac{r_\theta}{r}\cot\theta\right\}, \qquad (2.1)$$

where $r_\theta \equiv dr/d\theta$ and $r_{\theta\theta} = d^2r/d\theta^2$. Substituting (1.2), (1.3), and expression (2.1) for P_γ written with an accuracy up to terms of the $(f/R)^2$ order into the left-hand and right-hand parts of equality (1.1), respectively, we arrive at a differential equation with respect to the correction f for non-sphericity

$$\frac{2\gamma}{R} - \frac{\gamma}{R^2}\left\{2f + \frac{1}{\sin\theta}\frac{d}{d\theta}(\sin\theta f_\theta)\right\}$$

$$+ \frac{2\gamma}{R^3}\left\{f^2 + \frac{f}{\sin\theta}\frac{d}{d\theta}(\sin\theta f_\theta)\right\} = P_0^\alpha - P_0^\beta \qquad (2.2)$$

$$+ \frac{\varepsilon^\alpha(\mathbf{E}^\alpha)^2}{8\pi} - \frac{\varepsilon^\beta(\mathbf{E}^\beta)^2}{8\pi} + \frac{\varepsilon^\beta(E_N^\beta)^2}{4\pi} - \frac{\varepsilon^\alpha(E_N^\alpha)^2}{4\pi} + P_w,$$

where the $(\mathbf{E}^\alpha)^2$, $(\mathbf{E}^\beta)^2$, $(E_N^\alpha)^2$, and $(E_N^\beta)^2$ values are determined for a point at the droplet surface described by equation (1.5). The boundary conditions for a freely suspended droplet are written in the form

$$(df/d\theta)|_{\theta=0} = (df/d\theta)|_{\theta=\pi} = 0. \qquad (2.3)$$

To specify the right-hand side of equation (2.2) in an explicit form, we should solve Laplace's electrostatic equation for the potential Φ in the droplet–vapor two-phase system with the boundary conditions

$$\Phi^\alpha\big|_{r=r(\theta)} = \Phi^\beta\big|_{r=r(\theta)},$$

$$\varepsilon^\alpha(\nabla\Phi^\alpha, \mathbf{n})\big|_{r=r(\theta)} = \varepsilon^\beta(\nabla\Phi^\beta, \mathbf{n})\big|_{r=r(\theta)}, \qquad (2.4)$$

$$\Phi^\alpha \xrightarrow[r\to 0]{} q/\varepsilon^\alpha r, \quad \Phi^\beta \xrightarrow[r\to\infty]{} -E_\infty r\cos\theta, \qquad (2.5)$$

where q is the charge of the condensation nucleus and E_∞ is the modulus of the strength of the external uniform electric field at $r \longrightarrow \infty$. The boundary conditions (2.4) are set at the surface of the droplet; the relationship determining the normal vector $\mathbf{n}$ to this surface at each of its points is known from differential geometry:

$$\mathbf{n} = \frac{r\mathbf{e}_r - r_\theta\mathbf{e}_\theta}{(r^2 + r_\theta^2)^{1/2}}, \qquad (2.6)$$

where $\mathbf{e}_r$ and $\mathbf{e}_\theta$ are the unit vectors in the radial and azimuthal directions at each point of the surface. The applicability of the first boundary condition in (2.5) is ensured by the above assumption that the size of the nucleus is negligible compared to that of the droplet.

We will search for the solution of Laplace's equation with the boundary conditions (2.4) and (2.5) in the form

$$\Phi = \Phi_0 + \delta\Phi, \quad |\delta\Phi| \ll |\Phi_0|, \qquad (2.7)$$

where the Φ_0 potential satisfies Laplace's equation in the droplet–vapor system having a spherical droplet with the radius R. In this case, the boundary conditions at the surface of the droplet are transformed for the Φ_0 potential into

$$\Phi_0^\alpha\big|_R = \Phi_0^\beta\big|_R, \quad \varepsilon^\alpha(\partial\Phi_0^\alpha/\partial r)\big|_R = \varepsilon^\beta(\partial\Phi_0^\beta/\partial r)\big|_R. \qquad (2.8)$$

The boundary conditions for the Φ_0 potential at the origin of the coordinate system and at infinity are identical to the boundary conditions (2.5).

Let us now take into account the deviation of the droplet from spherical shape. In the second order approximation with respect to deviations of f and $\delta\Phi$, the $\Phi^{\alpha,\beta}$ potential and its gradient at the surface of the droplet are written as

$$\Phi^{\alpha,\beta}\big|_{R+f} = \Phi_0^{\alpha,\beta}\big|_R + \delta\Phi^{\alpha,\beta}\big|_R$$

$$+ f\frac{\partial\Phi_0^{\alpha,\beta}}{\partial r}\bigg|_R + f\frac{\partial\delta\Phi^{\alpha,\beta}}{\partial r}\bigg|_R + \frac{f^2}{2}\frac{\partial^2\Phi_0^{\alpha,\beta}}{\partial r^2}\bigg|_R, \qquad (2.9)$$

$$\nabla\Phi^{\alpha,\beta}\big|_{R+f} = \nabla\Phi_0^{\alpha,\beta}\big|_R + \nabla\delta\Phi^{\alpha,\beta}\big|_R \qquad (2.10)$$

$$+ f\frac{\partial(\nabla\Phi_0^{\alpha,\beta})}{\partial r}\bigg|_R + f\frac{\partial(\nabla\delta\Phi^{\alpha,\beta})}{\partial r}\bigg|_R + \frac{f^2}{2}\frac{\partial^2(\nabla\Phi_0^{\alpha,\beta})}{\partial r^2}\bigg|_R.$$

In the same approximation with allowance for (2.6) and (2.7), we have for the $(\mathbf{E}^{\alpha,\beta})^2|_{R+f} = (\nabla\Phi^{\alpha,\beta})^2|_{R+f}$ and $(E_N^{\alpha,\beta})^2\big|_{R+f} = (\nabla\Phi^{\alpha,\beta}, \mathbf{n})^2\big|_{R+f}$ values

$$(\mathbf{E}^{\alpha,\beta})^2\big|_{R+f} = \left\{\left(\frac{\partial\Phi_0^{\alpha,\beta}}{\partial r}\right)^2 + \frac{1}{R^2}\left(\frac{\partial\Phi_0^{\alpha,\beta}}{\partial\theta}\right)^2\right.$$

$$+2\frac{\partial\Phi_0^{\alpha,\beta}}{\partial r}\frac{\partial\delta\Phi^{\alpha,\beta}}{\partial r} + \frac{2}{R^2}\frac{\partial\Phi_0^{\alpha,\beta}}{\partial\theta}\frac{\partial\delta\Phi^{\alpha,\beta}}{\partial\theta}$$

$$+f\frac{\partial}{\partial r}\left(\frac{\partial\Phi_0^{\alpha,\beta}}{\partial r}\right)^2 + f\frac{\partial}{\partial r}\left(\frac{1}{r}\frac{\partial\Phi_0^{\alpha,\beta}}{\partial\theta}\right)^2 \qquad (2.11)$$

$$+f^2\frac{\partial}{\partial r}\left(\frac{\partial\Phi_0^{\alpha,\beta}}{\partial r}\frac{\partial^2\Phi_0^{\alpha,\beta}}{\partial r^2}\right) + 2f\frac{\partial}{\partial r}\left(\frac{\partial\Phi_0^{\alpha,\beta}}{\partial r}\frac{\partial\delta\Phi^{\alpha,\beta}}{\partial r}\right)$$

$$+\left.\left(\frac{\partial\delta\Phi^{\alpha,\beta}}{\partial r}\right)^2 + \frac{1}{R^2}\left(\frac{\partial\delta\Phi^{\alpha,\beta}}{\partial\theta}\right)^2\right\}\Bigg|_R,$$

$$(E_N^{\alpha,\beta})^2\big|_{R+f} = \left\{\left(\frac{\partial\Phi_0^{\alpha,\beta}}{\partial r}\right)^2 + 2\frac{\partial\Phi_0^{\alpha,\beta}}{\partial r}\frac{\partial\delta\Phi^{\alpha,\beta}}{\partial r}\right.$$

$$+f\frac{\partial}{\partial r}\left(\frac{\partial\Phi_0^{\alpha,\beta}}{\partial r}\right)^2 - \frac{2}{R^2}f_\theta\frac{\partial\Phi_0^{\alpha,\beta}}{\partial r}\frac{\partial\Phi_0^{\alpha,\beta}}{\partial\theta}$$

$$+f^2\frac{\partial}{\partial r}\left(\frac{\partial\Phi_0^{\alpha,\beta}}{\partial r}\frac{\partial^2\Phi_0^{\alpha,\beta}}{\partial r^2}\right) + 2f\frac{\partial}{\partial r}\left(\frac{\partial\Phi_0^{\alpha,\beta}}{\partial r}\frac{\partial\delta\Phi^{\alpha,\beta}}{\partial r}\right) \qquad (2.12)$$

$$-\left.\frac{2}{R^2}f_\theta\frac{\partial\Phi_0^{\alpha,\beta}}{\partial r}\frac{\partial\delta\Phi^{\alpha,\beta}}{\partial\theta} - \frac{1}{R^2}f_\theta^2\left(\frac{\partial\Phi_0^{\alpha,\beta}}{\partial r}\right)^2 + \left(\frac{\partial\delta\Phi^{\alpha,\beta}}{\partial r}\right)^2\right\}\Bigg|_R.$$

The contributions of the order of f^2, $f\delta\Phi$, and $(\delta\Phi)^2$ having the expression $(\partial\Phi_0/\partial\theta)\big|_R$ as a coefficient are omitted in the right-hand parts of relationships (2.11) and (2.12) for the reasons that will be explained below.

The small addend $\delta\Phi$ to the Φ_0 potential entering into the right-hand parts of relationships (2.9)–(2.12) satisfies, as follows from (2.7), Laplace's equation. The boundary conditions for $\delta\Phi$

$$\delta\Phi^\alpha \xrightarrow[r\to 0]{} 0, \quad \delta\Phi^\beta \xrightarrow[r\to\infty]{} 0 \qquad (2.13)$$

follow from (2.7) and the coincidence of the boundary conditions for the Φ_0 and Φ potentials at the origin of the coordinate system and at infinity.

In order to write the boundary conditions for $\delta\Phi$ at the surface of the droplet, we substitute (2.9) and (2.10) into (2.4). Using (2.6) in the second order approximation with respect to f and taking into account (2.8), we obtain

$$(\delta\Phi^\alpha - \delta\Phi^\beta)\big|_R = \left(1 - \frac{\varepsilon^\beta}{\varepsilon^\alpha}\right)f\frac{\partial\Phi_0^\beta}{\partial r}\Bigg|_R \qquad (2.14)$$

$$+f\frac{\partial}{\partial r}(\delta\Phi^\beta - \delta\Phi^\alpha)\big|_R + \frac{f^2}{2}\frac{\partial^2}{\partial r^2}(\Phi_0^\beta - \Phi_0^\alpha)\big|_R,$$

$$\frac{\partial}{\partial r}(\varepsilon^\alpha\delta\Phi^\alpha - \varepsilon^\beta\delta\Phi^\beta)\Bigg|_R = f\frac{\partial^2}{\partial r^2}(\varepsilon^\beta\Phi_0^\beta - \varepsilon^\alpha\Phi_0^\alpha)\Bigg|_R$$

$$+\frac{(\varepsilon^\alpha - \varepsilon^\beta)}{R^2}f_\theta\frac{\partial\Phi_0^\beta}{\partial\theta}\Bigg|_R + f\frac{\partial^2}{\partial r^2}(\varepsilon^\beta\delta\Phi^\beta - \varepsilon^\alpha\delta\Phi^\alpha)\Bigg|_R \qquad (2.15)$$

$$+\frac{f^2}{2}\frac{\partial^3}{\partial r^3}(\varepsilon^\beta\Phi_0^\beta - \varepsilon^\alpha\Phi_0^\alpha)\Bigg|_R + \frac{1}{R^2}f_\theta\frac{\partial}{\partial\theta}(\varepsilon^\alpha\delta\Phi^\alpha - \varepsilon^\beta\delta\Phi^\beta)\Bigg|_R.$$

The boundary conditions (2.14) and (2.15) complete the formulation of the problem of finding $\delta\Phi$.

3. THE PROFILE OF THE DROPLET AND ELECTRIC POTENTIAL IN THE FIRST APPROXIMATION IN THE DEVIATION FROM SPHERICITY SHAPE

Retaining the summands of the order of f in the left-hand part of equation (2.2) and substituting relationships (1.4) at $z = (R + f)\cos\theta$, (2.11), and (2.12) written with an accuracy on the order of f and $\delta\Phi$ into the right-hand part of equation (2.2), we obtain a linear differential equation with respect to f:

$$\frac{2\gamma}{R} - \frac{\gamma}{R^2}\left\{2f + \frac{1}{\sin\theta}\frac{d}{d\theta}(\sin\theta f_\theta)\right\} = P_0^\alpha - P_0^\beta$$

$$+\frac{(\varepsilon^\alpha - \varepsilon^\beta)}{8\pi}\left\{\frac{1}{R^2}\left(\frac{\partial\Phi_0^\beta}{\partial\theta}\right)^2 + \frac{\varepsilon^\beta}{\varepsilon^\alpha}\left(\frac{\partial\Phi_0^\beta}{\partial r}\right)^2\right\}\Bigg|_R$$

$$+\frac{1}{8\pi}\left\{\frac{2}{R^2}\frac{\partial\Phi_0^\beta}{\partial\theta}\frac{\partial}{\partial\theta}(\varepsilon^\alpha\delta\Phi^\alpha - \varepsilon^\beta\delta\Phi^\beta)\right. \qquad (3.1)$$

$$-2\varepsilon^\beta\frac{\partial\Phi_0^\beta}{\partial r}\frac{\partial}{\partial r}(\delta\Phi^\alpha - \delta\Phi^\beta)$$

$$\left.-2f\varepsilon^\beta\frac{\partial\Phi_0^\beta}{\partial r}\frac{\partial^2}{\partial r^2}(\Phi_0^\alpha - \Phi_0^\beta)\right\}\Bigg|_R - m\rho^\alpha w(R + f)\cos\theta.$$

We also excluded the summand with the $f f(\partial\Phi_0^\beta/\partial\theta)^2\big|_R$ coefficient from the right-hand part of (3.1), because it was beyond the limits of the first approximation. The solution of equation (3.1) should satisfy conditions (1.10) and (1.11), which in the first approximation in terms of the deviation from the sphericity have the following form:

$$\int_0^\pi f \sin\theta \, d\theta = 0, \quad \int_0^\pi f P_1 \sin\theta \, d\theta = 0. \tag{3.2}$$

The $\delta\Phi$ function entering into the right-hand part of equation (3.1) satisfies Laplace's equation with the boundary conditions (2.14) and (2.15) at the surface of the droplet, which in the linear approximation with respect to f are transformed into

$$(\delta\Phi^\alpha - \delta\Phi^\beta)|_R = (1 - \varepsilon^\beta/\varepsilon^\alpha) f(\partial\Phi_0^\beta/\partial r)|_R, \tag{3.3}$$

$$\frac{\partial}{\partial r}(\varepsilon^\alpha \delta\Phi^\alpha - \varepsilon^\beta \delta\Phi^\beta)\Big|_R$$

$$= f\frac{\partial^2}{\partial r^2}(\varepsilon^\beta \Phi_0^\beta - \varepsilon^\alpha \Phi_0^\alpha)\Big|_R + \frac{(\varepsilon^\alpha - \varepsilon^\beta)}{R^2} f_\theta \frac{\partial\Phi_0^\beta}{\partial\theta}\Big|_R. \tag{3.4}$$

Let us represent the Φ_0 potential entering into the right-hand parts of equations (3.1), (3.3), and (3.4) as the superpositions of the Φ_{0q} and Φ_{0E} electric potentials

$$\Phi_0 = \Phi_{0q} + \Phi_{0E}, \tag{3.5}$$

which satisfy Laplace's equation with the boundary conditions (2.8) at the surface of the droplet and, correspondingly, the boundary conditions (2.5) at the origin of the coordinate system, and at infinity and are written as

$$\Phi_{0q}^\alpha = \left(\frac{1}{\varepsilon^\beta} - \frac{1}{\varepsilon^\alpha}\right)\frac{q}{R} + \frac{q}{\varepsilon^\alpha r} \quad (r < R),$$

$$\Phi_{0q}^\beta = \frac{q}{\varepsilon^\beta r} \quad (r > R). \tag{3.6}$$

and

$$\Phi_{0E}^\alpha = -\frac{3\varepsilon^\beta E_\infty r}{(\varepsilon^\alpha + 2\varepsilon^\beta)}\cos\theta \quad (r < R),$$

$$\Phi_{0E}^\beta = \frac{(\varepsilon^\alpha - \varepsilon^\beta)E_\infty R^3 \cos\theta}{(\varepsilon^\alpha + 2\varepsilon^\beta)r^2} - E_\infty r\cos\theta \quad (r > R). \tag{3.7}$$

Similarly to the case of a spherical interface, the potential of electric field in the vapor and the droplet, whose profile is set by relationship (1.5), may be represented as the superposition

$$\Phi = \Phi_q + \Phi_E, \tag{3.8}$$

where

$$\Phi_q = \Phi_{0q} + \delta\Phi_q, \quad |\delta\Phi_q| \ll |\Phi_{0q}|, \tag{3.9}$$

$$\Phi_E = \Phi_{0E} + \delta\Phi_E, \quad |\delta\Phi_E| \ll |\Phi_{0E}|, \tag{3.10}$$

and

$$\delta\Phi = \delta\Phi_q + \delta\Phi_E. \tag{3.11}$$

The $\delta\Phi_q$ and $\delta\Phi_E$ correction potentials, satisfy Laplace's equation, exactly as does $\delta\Phi$. It follows from the identical boundary conditions for the Φ_q, Φ_{0q}, Φ_E, and Φ_{0E} potentials at the origin of the coordinate sys-

tem and at infinity that $\delta\Phi_q$ and $\delta\Phi_E$, exactly like $\delta\Phi$, are equal to zero at the origin of the system and at infinity. The boundary conditions (3.3) and (3.4) at the surface of the droplet with allowance for (3.9)–(3.11) and (3.6), (3.7) may be conveniently divided for the $\delta\Phi_q$ and $\delta\Phi_E$ functions as

$$(\delta\Phi_q^\alpha - \delta\Phi_q^\beta)|_R = \left(1 - \frac{\varepsilon^\beta}{\varepsilon^\alpha}\right)f\left(\frac{\partial\Phi_{0q}^\beta}{\partial r}\right)\Big|_R,$$

$$\frac{\partial}{\partial r}(\varepsilon^\alpha \delta\Phi_q^\alpha - \varepsilon^\beta \delta\Phi_q^\beta)\Big|_R = 0, \tag{3.12}$$

$$(\delta\Phi_E^\alpha - \delta\Phi_E^\beta)|_R = \left(1 - \frac{\varepsilon^\beta}{\varepsilon^\alpha}\right)f\left(\frac{\partial\Phi_{0E}^\beta}{\partial r}\right)\Big|_R,$$

$$\frac{\partial}{\partial r}(\varepsilon^\alpha \delta\Phi_E^\alpha - \varepsilon^\beta \delta\Phi_E^\beta)\Big|_R \tag{3.13}$$

$$= \varepsilon^\beta f\frac{\partial^2\Phi_{0E}^\beta}{\partial r^2}\Big|_R + \frac{(\varepsilon^\alpha - \varepsilon^\beta)}{R^2} f_\theta \frac{\partial\Phi_{0E}^\beta}{\partial\theta}\Big|_R.$$

The deviation of the droplet surface from spherical shape in the first order with respect to the small value f/R is attributed to the angle θ-dependent axisymmetrical contribution Φ_{0E} from (3.7) to the potential entering into the first braces in the right-hand part of (3.1). Therefore, in the first approximation concerning the deviation from sphericity, one should take into account contributions containing Φ_{0E} in the right-hand part of (3.1), while the summands containing $\delta\Phi_E$ should be omitted in view of inequality (3.10). Hence, in this approximation, $\delta\Phi_E^\alpha = \delta\Phi_E^\beta = 0$.

We will search for the deviation of the droplet surface from the spherical shape in the form of a series expansion in the Legendre polynomials:

$$f = R\sum_{n=0}^\infty C_n P_n, \tag{3.14}$$

where $P_n = P_n(\cos\theta)$ are the Legendre polynomials of the nth degree and C_n are coefficients of the series. The solution of Laplace's equation for the $\delta\Phi_q$ function, with the zeroth boundary conditions at the origin of the coordinate system and at infinity, and conditions (3.12) at the surface of the droplet with allowance for (3.14), may be written in the form

$$\delta\Phi_q^\alpha = -\left(\frac{1}{\varepsilon^\beta} - \frac{1}{\varepsilon^\alpha}\right)q\sum_{n=0}^\infty (n+1)\alpha_n C_n \frac{r^n}{R^{n+1}} P_n,$$

$$\delta\Phi_q^\beta = \left(\frac{1}{\varepsilon^\beta} - \frac{1}{\varepsilon^\alpha}\right)q\sum_{n=0}^\infty [1 - (n+1)\alpha_n]C_n \frac{R^n}{r^{n+1}} P_n, \tag{3.15}$$

where the notation

$$\alpha_n = \varepsilon^\beta / [n\varepsilon^\alpha + (n+1)\varepsilon^\beta] \qquad (3.16)$$

was introduced.

Substituting expressions (3.5)–(3.7), (3.11), (3.14), and (3.15) into the right-hand part of equation (3.1) and taking into account definition (3.16), we obtain the equality

$$\frac{2\gamma}{R} + \frac{\gamma}{R}\sum_{n=0}^{\infty}(n-1)(n+2)C_nP_n = P_0^\alpha - P_0^\beta$$

$$+\frac{3}{8\pi}(\varepsilon^\alpha - \varepsilon^\beta)\alpha_1 E_\infty^2 + \frac{1}{8\pi}\left(\frac{1}{\varepsilon^\beta} - \frac{1}{\varepsilon^\alpha}\right)\frac{q^2}{R^4}$$

$$+\left[\frac{3}{4\pi}(1-3\alpha_1)E_\infty\frac{q}{R^2} - m\rho^\alpha wR\right]P_1 + \frac{4\gamma}{3R}\epsilon_0^2 P_2 \qquad (3.17)$$

$$+\frac{1}{4\pi}\left(\frac{1}{\varepsilon^\beta} - \frac{1}{\varepsilon^\alpha}\right)\frac{q^2}{R^4}\sum_{n=0}^{\infty}[(n-1)-(2n+1)(n+1)\alpha_n]C_nP_n,$$

where the notation

$$\epsilon_0^2 = \frac{9(1-3\alpha_1)^2\varepsilon^\beta E_\infty^2 R}{16\pi\gamma} \qquad (3.18)$$

was introduced.

Comparing coefficients at identical Legendre polynomials in the right-hand and left-hand parts of equality (3.17), we find coefficients C_n

$$C_0 = -\frac{R}{2\gamma}\left\{ P_0^\alpha - P_0^\beta - \frac{2\gamma}{R} + \frac{3}{8\pi}(\varepsilon^\alpha - \varepsilon^\beta)\alpha_1 E_\infty^2 \right.$$

$$\left. +\frac{1}{8\pi}\left(\frac{1}{\varepsilon^\beta} - \frac{1}{\varepsilon^\alpha}\right)\frac{q^2}{R^4}\right\}[1 - 4\omega^2(1-15\alpha_2)^{-1}]^{-1}, \qquad (3.19)$$

$$C_1 = \left[\frac{3(1-3\alpha_1)E_\infty q}{4\pi R^2} - m\rho^\alpha wR\right] \Big/ \left[\frac{3}{2\pi}\alpha_1\left(\frac{1}{\varepsilon^\beta} - \frac{1}{\varepsilon^\alpha}\right)\frac{q^2}{R^4}\right],$$

and   (3.20)

$$C_2 = \epsilon^2/3, \quad C_n = 0 \quad (n > 2), \qquad (3.21)$$

where the following notations

$$\omega^2 = \frac{1}{16\pi\gamma}\left(\frac{1}{\varepsilon^\beta} - \frac{1}{\varepsilon^\alpha}\right)\frac{q^2}{R^3}(1-15\alpha_2),$$

$$\epsilon^2 = \epsilon_0^2/(1-\omega^2) \qquad (3.22)$$

were introduced.

Further, we will assume that $0 < \omega^2 < 1$. This inequality is secured by the small size of the condensation nucleus compared to the droplet size.

Expansion (3.14) for the f function is compatible with conditions (3.2), provided that equalities

$$C_0 = 0, \quad C_1 = 0 \qquad (3.23)$$

are fulfilled.

The first of equalities (3.23), with allowance for (3.19), determines the pressure drop $P_0^\alpha - P_0^\beta$ in the first approximation concerning the deviation from sphericity and, thereby, as we will see below, the chemical potential of a condensate molecule in the droplet, whereas the second of equalities (3.23), with allowance for (3.20), results in the relationship for the acceleration w of the noninertial coordinate system or for the droplet radius R in the inertial coordinate system where $w = g$:

$$w = \frac{3(1-3\alpha_1)E_\infty q}{4\pi R^3 m\rho^\alpha}. \qquad (3.24)$$

If it is assumed that $\alpha_1 = 0$ in (3.24) (i.e., that the liquid comprising the droplet is conductive), the charge will be distributed over the surface of the droplet, and from (3.24) we have the simple relationship $w = E_\infty q/M$, where M is the mass of the droplet.

Substituting (3.21) and (3.23) into (3.15) and (3.14), we find that

$$\delta\Phi_q^\alpha = -\left(\frac{1}{\varepsilon^\beta} - \frac{1}{\varepsilon^\alpha}\right)q\alpha_2\epsilon^2\frac{r^2}{R^3}P_2,$$

$$\delta\Phi_q^\beta = \frac{1}{3}\left(\frac{1}{\varepsilon^\beta} - \frac{1}{\varepsilon^\alpha}\right)q(1-3\alpha_2)\epsilon^2\frac{R^2}{r^3}P_2, \qquad (3.25)$$

$$f = \epsilon^2\frac{R}{3}P_2. \qquad (3.26)$$

Relationship (3.26) indicates that, in the approximation considered, the equation for the profile of the equilibrium surface of the droplet formed on the charged center in the external uniform field is identical to the equation for the spheroid elongated along the field with the center at the origin of the spherical coordinate system, the volume and the eccentricity of this spheroid being equal to $(4\pi/3)R^3$ and ϵ, respectively. Comparing (3.26) and (1.8), we have ascertained that ϵ is the small dimensionless parameter of a theory. It also follows from relationships (3.18) and (3.7) that Φ_{0E} has the order of ϵ; and according to (3.26) and (3.25), the values of f/R and $\delta\Phi_q$ have the order of ϵ^2, whereas it follows from inequality (3.10) and expressions (3.13) and (3.26) that $\delta\Phi_E$ has the order of ϵ^3. This justifies excluding the contributions of the f^2, $f\delta\Phi$, and $(\delta\Phi)^2$ orders containing coefficient $(\partial\Phi_0/\partial\theta)|_R$ from (2.11) and (2.12), as well as neglecting the summand proportional to $f(\partial\Phi_0^\beta/\partial\theta)^2|_R$ in the right-hand part of (3.1).

4. THE PROFILE OF THE DROPLET AND ELECTRIC POTENTIAL IN THE FIRST APPROXIMATION IN THE DEVIATION FROM SPHERICITY

Note now that an allowance has been made for the summands of the $f\Phi_{0E}$, $\Phi_{0E}\delta\Phi_q$, and $\delta\Phi_E$ orders in the right-hand part of equation (3.1) and in the boundary conditions (3.13), it is possible to find the contributions to f with an accuracy of the ϵ^3 order. In this approximation, the $\delta\Phi_E$ potentials differ from zero and, as is seen from the substitution of expressions (3.7) and (3.26) into equalities (3.13), satisfy the boundary conditions at the surface of the droplet:

$$(\delta\Phi_E^\alpha - \delta\Phi_E^\beta)\big|_R = -\frac{4}{15}\kappa\epsilon^3 R(2P_1 + 3P_3),$$

$$\frac{\partial}{\partial r}(\epsilon^\alpha\delta\Phi_E^\alpha - \epsilon^\beta\delta\Phi_E^\beta)\Big|_R = \frac{8}{15}\epsilon^\beta\kappa\epsilon^3(-P_1 + 6P_3), \quad (4.1)$$

where the introduced parameter

$$\kappa = [\pi\gamma(1 - \omega^2)/\epsilon^\beta R]^{1/2} \quad (4.2)$$

has the dimensionality of the electric field strength.

The solution of Laplace's equation for the $\delta\Phi_E$ function with the zeroth boundary conditions at the origin of the coordinate system and at infinity and conditions (4.1) at the surface of the droplet have the following form:

$$\delta\Phi_E^\alpha = -\frac{8}{5}\alpha_1\kappa\epsilon^3 rP_1,$$

$$\delta\Phi_E^\beta = (1 - 3\alpha_1)\frac{8}{15}\kappa\epsilon^3\frac{R^3}{r^2}P_1 + \frac{4}{5}\kappa\epsilon^3\frac{R^5}{r^4}P_3. \quad (4.3)$$

Now, in order to find $\delta\Phi_q$, let us write the function that sets the deviation of the droplet surface from the sphere with radius R as

$$f = R\left(\frac{\epsilon^2}{3}P_2 + \epsilon^3\sum_{n=0}^\infty A_nP_n\right), \quad (4.4)$$

where coefficients A_n will be determined below. The substitution of (3.6) and (4.4) into (3.12) yields

$$(\delta\Phi_q^\alpha - \delta\Phi_q^\beta)\big|_R = -\left(\frac{1}{\epsilon^\beta} - \frac{1}{\epsilon^\alpha}\right)\frac{q}{R}\left(\frac{\epsilon^2}{3}P_2 + \epsilon^3\sum_{n=0}^\infty A_nP_n\right),$$

$$\frac{\partial}{\partial r}(\epsilon^\alpha\delta\Phi_q^\alpha - \epsilon^\beta\delta\Phi_q^\beta)\Big|_R = 0. \quad (4.5)$$

Corresponding solutions of Laplace's equation for the $\delta\Phi_q$ function are written as

$$\delta\Phi_q^\alpha = -\left(\frac{1}{\epsilon^\beta} - \frac{1}{\epsilon^\alpha}\right)$$

$$\times q\left[\epsilon^2\alpha_2\frac{r^2}{R^3}P_2 + \epsilon^3\sum_{n=0}^\infty(n+1)\alpha_nA_n\frac{r^n}{R^{n+1}}P_n\right], \quad (4.6)$$

and

$$\delta\Phi_q^\beta = \left(\frac{1}{\epsilon^\beta} - \frac{1}{\epsilon^\alpha}\right)q\left\{\epsilon^2\frac{(1-3\alpha_2)}{3}\frac{R^2}{r^3}P_2 \right.$$

$$\left. + \epsilon^3\sum_{n=0}^\infty[1-(n+1)\alpha_n]A_n\frac{R^n}{r^{n+1}}P_n\right\}. \quad (4.7)$$

As is apparent from (3.24), (3.22), (3.18), and (4.2), the acceleration w should be sought in the form of expansion

$$w = w^{(0)}\epsilon + w^{(1)}\epsilon^3 + \ldots, \quad (4.8)$$

where

$$w^{(0)} = \frac{\kappa q}{\pi m\rho^\alpha R^3}, \quad (4.9)$$

and $w^{(1)}$ is determined by the second condition of (3.2).

Substituting relationships (4.4), (3.5), and (3.11) with allowance for equalities (3.6), (3.7), (4.3), and (4.6)–(4.9) into the right-hand part of equation (3.1), we retain the contributions of the ϵ^3 order. From the solution of the resultant equation we find the coefficients A_n made with an allowance for (3.2)

$$A_n = 0 \quad (n \neq 3), \quad (4.10)$$

and

$$A_3 = \frac{1}{25}\frac{q}{R}\frac{\kappa}{\pi\gamma}\left(1 - \frac{25}{2}\alpha_2\right)\left(1 - \frac{4}{5}\omega^2\frac{1-14\alpha_3}{1-15\alpha_2}\right)^{-1}. \quad (4.11)$$

It follows from equation $A_1 = 0$ that

$$w^{(1)} = \frac{\kappa q}{\pi m\rho^\alpha R^3}\left(-\frac{6}{5}\alpha_1\right). \quad (4.12)$$

Substituting (4.10) and (4.11) into (4.6), (4.7), (4.4), and (1.5), we obtain

$$\delta\Phi_q^\alpha = -\left(\frac{1}{\epsilon^\beta} - \frac{1}{\epsilon^\alpha}\right)$$

$$\times q\left(\epsilon^2\alpha_2\frac{r^2}{R^3}P_2 + 4\epsilon^3\alpha_3A_3\frac{r^3}{R^4}P_3\right), \quad (4.13)$$

$$\delta\Phi_q^\beta = \left(\frac{1}{\epsilon^\beta} - \frac{1}{\epsilon^\alpha}\right)$$

$$\times q\left[\epsilon^2\frac{(1-3\alpha_2)}{3}\frac{R^2}{r^3}P_2 + \epsilon^3(1-4\alpha_3)A_3\frac{R^3}{r^4}P_3\right], \quad (4.14)$$

and

$$r(\theta) = R\left(1 + \frac{\epsilon^2}{3}P_2 + \epsilon^3 A_3 P_3\right).$$ (4.15)

Let us compare dependence (4.15) with the equation for a spheroid elongated along the z axis with the center at the origin of the spherical coordinate system, the volume and the eccentricity of this spheroid being equal to $(4\pi/3)R^3$ and ϵ, respectively, i.e., with equation

$$r(\theta) = R\frac{(1 - \epsilon^2)^{1/6}}{(1 - \epsilon^2\cos^2\theta)^{1/2}}.$$ (4.16)

The series expansion of (4.16) in powers of ϵ^2 (at $\epsilon^2 \ll 1$) with an accuracy up to the summands of the ϵ^4 order yields

$$r(\theta) = R\left[1 + \frac{\epsilon^2}{3}P_2 + \epsilon^4\left(-\frac{1}{45} + \frac{10}{63}P_2 + \frac{3}{35}P_4\right)\right].$$ (4.17)

As is seen, equation (4.15) for the profile of the equilibrium surface of the droplet differs beginning with the terms of the ϵ^3 order from the equation for a prolate spheroid. Since, at $4\epsilon^\alpha > 19\epsilon^\beta$, $A_3 > 0$ (which is essentially fulfilled for the majority of dielectrics), the $\epsilon^3 A_3 P_3$ summand in (4.15) indicates that the droplet with the charged center has an egglike shape; i.e., it is prolate in the field direction and oblate at the opposing end.

5. THE PROFILE OF THE DROPLET AND ELECTRIC POTENTIAL IN THE SECOND APPROXIMATION IN THE DEVIATION FROM SPHERICITY

As will be demonstrated below, in order to determine the contributions to the chemical potential of the droplet in terms of its deviation from the spherical shape, it is necessary to take into account at least the terms of the ϵ^4 order. This necessitates a consideration of the next (second) approximation according to the deviation from the sphericity. Let us now write the equation resulting from Laplace's equation with an accuracy of the $(f/R)^2$ order. To this end, we substitute expressions (1.4) at $z = (R + f)\cos\theta$, (2.11), and (2.12) into the right-hand part of equation (2.2). As a result, we obtain

$$\frac{2\gamma}{R} - \frac{\gamma}{R^2}\left\{2f + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial f}{\partial\theta}\right)\right\}$$

$$+ \frac{2\gamma}{R^3}\left\{f^2 + \frac{f}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial f}{\partial\theta}\right)\right\} = P_0^\alpha - P_0^\beta$$

$$+ \frac{(\epsilon^\alpha - \epsilon^\beta)}{8\pi}\left\{\frac{1}{R^2}\left(\frac{\partial\Phi_0^\beta}{\partial\theta}\right)^2 + \frac{\epsilon^\beta}{\epsilon^\alpha}\left(\frac{\partial\Phi_0^\beta}{\partial r}\right)^2\right\}\bigg|_R$$

$$+ \frac{1}{8\pi}\left\{\frac{2}{R^2}\frac{\partial\Phi_0^\beta}{\partial\theta}\frac{\partial}{\partial\theta}[\epsilon^\alpha\delta\Phi^\alpha - \epsilon^\beta\delta\Phi^\beta]\right.$$

$$+ 2\epsilon^\beta\frac{\partial\Phi_0^\beta}{\partial r}\left[\frac{\partial\delta\Phi^\beta}{\partial r} - \frac{\partial\delta\Phi^\alpha}{\partial r}\right] - 2f\epsilon^\beta\frac{\partial\Phi_0^\beta}{\partial r}\left[\frac{\partial^2\Phi_0^\alpha}{\partial r^2} - \frac{\partial^2\Phi_0^\beta}{\partial r^2}\right]$$

$$- \frac{2(\epsilon^\alpha - \epsilon^\beta)}{R^3}f\left(\frac{\partial\Phi_0^\beta}{\partial\theta}\right)^2\bigg|_R - m\rho^\alpha w(R + f)\cos\theta$$

$$+ \left\{f^2\left[\epsilon^\beta\left(\frac{\partial^2\Phi_0^\beta}{\partial r^2}\right)^2 - \epsilon^\alpha\left(\frac{\partial^2\Phi_0^\alpha}{\partial r^2}\right)^2\right]\right.$$

$$+ f^2\epsilon^\beta\frac{\partial\Phi_0^\beta}{\partial r}\left[\frac{\partial^3\Phi_0^\beta}{\partial r^3} - \frac{\partial^3\Phi_0^\alpha}{\partial r^3}\right]$$

$$- \frac{2(\epsilon^\alpha - \epsilon^\beta)}{R^2}\left(\frac{\partial f}{\partial\theta}\right)^2\frac{\epsilon^\beta}{\epsilon^\alpha}\left(\frac{\partial\Phi_0^\beta}{\partial r}\right)^2$$

$$+ 2f\epsilon^\beta\frac{\partial\Phi_0^\beta}{\partial r}\left[\frac{\partial^2\delta\Phi^\beta}{\partial r^2} - \frac{\partial^2\delta\Phi^\alpha}{\partial r^2}\right]$$

$$+ 2f\left[\epsilon^\beta\frac{\partial^2\Phi_0^\beta}{\partial r^2}\frac{\partial\delta\Phi^\beta}{\partial r} - \epsilon^\alpha\frac{\partial^2\Phi_0^\alpha}{\partial r^2}\frac{\partial\delta\Phi^\alpha}{\partial r}\right]$$

$$+ \frac{4}{R^2}\epsilon^\beta\frac{\partial\Phi_0^\beta}{\partial r}\frac{\partial f}{\partial\theta}\left[\frac{\partial\delta\Phi^\beta}{\partial\theta} - \frac{\partial\delta\Phi^\alpha}{\partial\theta}\right]$$

$$+ \left[\epsilon^\beta\left(\frac{\partial\delta\Phi^\beta}{\partial r}\right)^2 - \epsilon^\alpha\left(\frac{\partial\delta\Phi^\alpha}{\partial r}\right)^2\right]$$

$$+ \frac{1}{R^2}\left[\epsilon^\alpha\left(\frac{\partial\delta\Phi^\alpha}{\partial\theta}\right)^2 - \epsilon^\beta\left(\frac{\partial\delta\Phi^\beta}{\partial\theta}\right)^2\right]\right\}\bigg|_R.$$ (5.1)

Additional constraints on the solution of differential equation (5.1) are still set by equalities (1.10) and (1.11), whereas the expression for $\delta\Phi$ entering into the right-hand part of equation (5.1) satisfies Laplace's equation with the boundary conditions (2.13), (2.14), and (2.15).

Let us find the expression for the $\delta\Phi$ potential in an explicit form as a function of spherical coordinates r and θ with an accuracy up to summand of the ϵ^4 order. To this end, we will search for $\delta\Phi$ in the form of (3.11). Hence, in order to derive the equation for the droplet surface in the second approximation according to the deviation from the non-sphericity, it is necessary to determine $\delta\Phi_E$ and $\delta\Phi_q$ with an accuracy of the ϵ^4 order.

According to (2.14) and (2.15), the boundary conditions at the surface of the droplet for Laplace's equation

for the $\delta\Phi_q$ function, with allowance for expressions (3.6) for the Φ_{0q}^{α} and Φ_{0q}^{β} potentials, may be written as

$$(\delta\Phi_q^{\alpha} - \delta\Phi_q^{\beta})|_R = \left(1 - \frac{\varepsilon^{\beta}}{\varepsilon^{\alpha}}\right)f\frac{\partial\Phi_{0q}^{\beta}}{\partial r}\Big|_R$$

$$+ f\frac{\partial}{\partial r}(\delta\Phi_q^{\beta} - \delta\Phi_q^{\alpha})|_R + \frac{f^2}{2}\frac{\partial^2}{\partial r^2}(\Phi_{0q}^{\beta} - \Phi_{0q}^{\alpha})\Big|_R,$$

(5.2)

and

$$\frac{\partial}{\partial r}(\varepsilon^{\alpha}\delta\Phi_q^{\alpha} - \varepsilon^{\beta}\delta\Phi_q^{\beta})\Big|_R = f\frac{\partial^2}{\partial r^2}(\varepsilon^{\beta}\delta\Phi_q^{\beta} - \varepsilon^{\alpha}\delta\Phi_q^{\alpha})|_R$$

$$+ \frac{1}{R^2}f_{\theta}\frac{\partial}{\partial\theta}(\varepsilon^{\alpha}\delta\Phi_q^{\alpha} - \varepsilon^{\beta}\delta\Phi_q^{\beta})\Big|_R.$$

(5.3)

The deviation of the droplet surface from the spheroidal shape described by equation (4.17) will be sought in the following form:

$$f(\theta) = R\left[\frac{\varepsilon^2}{3}P_2 + \varepsilon^3 A_3 P_3\right.$$

$$\left. + \varepsilon^4\left(-\frac{1}{45} + \frac{10}{63}P_2 + \frac{3}{35}P_4\right) + \varepsilon^4\sum_{n=0}^{\infty}B_n P_n\right],$$

(5.4)

where coefficient A_3 is set by relationship (4.11) and coefficients B_n are to be determined below.

In order to write the right-hand parts of the boundary conditions (5.2) and (5.3) in an explicit form, let us substitute (3.6), (4.13), (4.14), and (5.4) into the right-hand parts of equations (5.2) and (5.3), and, retaining the contributions of the ε^4 order, we obtain the following equalities:

$$(\delta\Phi_q^{\alpha} - \delta\Phi_q^{\beta})|_R = \left(\frac{1}{\varepsilon^{\beta}} - \frac{1}{\varepsilon^{\alpha}}\right)\frac{q}{R}\left\{-\frac{\varepsilon^2}{3}P_2 - \varepsilon^3 A_3 P_3\right.$$

$$+ \varepsilon^4\left[\left(-\frac{1}{45} + \frac{\alpha_2}{3}\right) + \left(-\frac{2}{9} + \frac{10}{21}\alpha_2\right)P_2\right.$$

(5.5)

$$\left.\left. + \left(-\frac{1}{5} + \frac{6}{7}\alpha_2\right)P_4 - \sum_{n=0}^{\infty}B_n P_n\right]\right\},$$

and

$$\frac{\partial}{\partial r}(\varepsilon^{\alpha}\delta\Phi_q^{\alpha} - \varepsilon^{\beta}\delta\Phi_q^{\beta})\Big|_R = \left(1 - \frac{\varepsilon^{\beta}}{\varepsilon^{\alpha}}\right)\frac{q}{R^2}$$

(5.6)

$$\times \varepsilon^4\left[\left(\frac{5}{21} - \frac{5}{7}\alpha_2\right)P_2 + \left(\frac{10}{7} - \frac{30}{7}\alpha_2\right)P_4\right].$$

The solution of Laplace's equation for the $\delta\Phi_q$ function with the zeroth boundary conditions at $r \longrightarrow 0$ and $r \longrightarrow \infty$ and conditions (5.5) and (5.6) at the surface of the droplet is expressed as

$$\delta\Phi_q^{\alpha} = \left(\frac{1}{\varepsilon^{\beta}} - \frac{1}{\varepsilon^{\alpha}}\right)q\left\{-\varepsilon^2\alpha_2\frac{r^2}{R^3}P_2 - 4\varepsilon^3\alpha_3 A_3\frac{r^3}{R^4}P_3\right.$$

$$+ \varepsilon^4\left[\left(-\frac{1}{45} + \frac{\alpha_2}{3}\right)\frac{1}{R} + \left(-\frac{3}{7}\alpha_2 + \frac{5}{7}\alpha_2^2\right)\frac{r^2}{R^3}P_2\right.$$

(5.7)

$$\left.\left. + \frac{3}{7}\alpha_4\frac{r^4}{R^5}P_4 - \sum_{n=0}^{\infty}(n+1)\alpha_n B_n\frac{r^n}{R^{n+1}}P_n\right]\right\},$$

and

$$\delta\Phi_q^{\beta} = \left(\frac{1}{\varepsilon^{\beta}} - \frac{1}{\varepsilon^{\alpha}}\right)q\left\{\varepsilon^2\frac{(1 - 3\alpha_2)}{3}\frac{R^2}{r^3}P_2\right.$$

$$+ \varepsilon^3(1 - 4\alpha_3)A_3\frac{R^3}{r^4}P_3 + \varepsilon^4\left[\left(\frac{2}{9} - \frac{19}{21}\alpha_2 + \frac{5}{7}\alpha_2^2\right)\frac{R^2}{r^3}P_2\right.$$

$$+ \left(\frac{1}{5} - \frac{6}{7}\alpha_2 + \frac{3}{7}\alpha_4\right)\frac{R^4}{r^5}P_4$$

(5.8)

$$\left.\left. + \sum_{n=0}^{\infty}[1 - (n+1)\alpha_n]B_n\frac{R^n}{r^{n+1}}P_n\right]\right\}.$$

The boundary conditions for Laplace's equation for the $\delta\Phi_E$ function at the surface of the droplet are still set by the relationships (3.13). In order to write them in an explicit form, let us substitute expressions (3.7) and (5.4) into the right-hand parts of (3.13). As a result, we obtain

$$(\delta\Phi_E^{\alpha} - \delta\Phi_E^{\beta})|_R = \kappa R\left[\varepsilon^3\left(-\frac{8}{15}P_1 - \frac{4}{5}P_3\right)\right.$$

(5.9)

$$\left. + \varepsilon^4 A_3\left(-\frac{12}{7}P_2 - \frac{16}{7}P_4\right)\right],$$

$$\frac{\partial}{\partial r}(\varepsilon^{\alpha}\delta\Phi_E^{\alpha} - \varepsilon^{\beta}\delta\Phi_E^{\beta})\Big|_R = \kappa\varepsilon^{\beta}\left[\varepsilon^3\left(-\frac{8}{15}P_1 + \frac{16}{5}P_3\right)\right.$$

(5.10)

$$\left. + \varepsilon^4 A_3\left(-\frac{24}{7}P_2 + \frac{80}{7}P_4\right)\right].$$

The solutions of Laplace's equation for the $\delta\Phi_E$ function with the zeroth boundary conditions at $r \longrightarrow 0$ and $r \longrightarrow \infty$ and conditions (5.9) and (5.10) at the surface of the droplet are written as

$$\delta\Phi_E^{\alpha} = \kappa\left(-\varepsilon^3\frac{8}{5}\alpha_1 r P_1 - \varepsilon^4\frac{60}{7}\alpha_2 A_3\frac{r^2}{R}P_2\right),$$

(5.11)

and

$$\delta\Phi_E^{\beta} = \kappa\left\{\varepsilon^3\left[\frac{8}{15}(1 - 3\alpha_1)\frac{R^3}{r^2}P_1 + \frac{4}{5}\frac{R^5}{r^4}P_3\right]\right.$$

(5.12)

$$\left. + \varepsilon^4\left[\frac{12}{7}(1 - 5\alpha_2)A_3\frac{R^4}{r^3}P_2 + \frac{16}{7}A_3\frac{R^6}{r^5}P_4\right]\right\}.$$

Let us now substitute relationships (5.4), (3.6), (3.7), (5.7), (5.8), (5.11), and (5.12) into equation (5.1). After rather complicated calculations we obtain, with allowance for conditions (1.10) and (1.11), that coefficients B_n in (5.4) are equal to:

$$B_2 = \frac{1}{(1-\omega^2)}\left\{\frac{29}{315} - \frac{4}{5}\alpha_1 + \omega^2\left[-\frac{1}{35} + \frac{4}{5}\alpha_1\right.\right.$$
$$\left.\left. - \frac{5}{14}\alpha_2 - \frac{1}{63(1-15\alpha_2)} + \Lambda\frac{12(2-25\alpha_2)}{175(1-15\alpha_2)}\right]\right\},$$

(5.13)

$$B_4 = \left\{-\frac{1}{315} + \omega^2\left[\frac{2}{189} - \frac{10}{63}\alpha_2 - \frac{2(1-81\alpha_4)}{189(1-15\alpha_2)}\right.\right.$$
$$\left.\left. + \Lambda\frac{32(4-49\alpha_3)}{1575(1-15\alpha_2)}\right]\right\}\left[1 - \frac{2(1-15\alpha_4)}{3(1-15\alpha_2)}\omega^2\right]^{-1},$$

(5.14)

$$B_n = 0 \quad (n \neq 2, 4),$$

(5.15)

where

$$\Lambda = \frac{\varepsilon^\alpha}{(\varepsilon^\alpha - \varepsilon^\beta)}(1-\omega^2)$$
$$\times\left(1 - \frac{25}{2}\alpha_2\right)\left(1 - \frac{4}{5}\omega^2\frac{1-14\alpha_3}{1-15\alpha_2}\right)^{-1}.$$

(5.16)

Substituting (5.4) into (5.1) and using (5.13)–(5.15), we find

$$r(\theta) = R\left[1 + \frac{\varepsilon^2}{3}P_2 + \varepsilon^3 A_3 P_3\right.$$
$$\left. + \varepsilon^4\left(-\frac{1}{45} + \frac{10}{63}P_2 + \frac{3}{35}P_4\right) + \varepsilon^4(B_2 P_2 + B_4 P_4)\right],$$

(5.17)

Another important result obtained from the solution of equation (5.1) with allowance for conditions (1.10) and (1.11), respectively, is represented by the expressions for the difference $P_0^\alpha - P_0^\beta$ and the acceleration w. For the difference $P_0^\alpha - P_0^\beta$, we find

$$P_0^\alpha - P_0^\beta = \frac{2\gamma}{R} - \frac{1}{8\pi}\left(\frac{1}{\varepsilon^\beta} - \frac{1}{\varepsilon^\alpha}\right)\frac{q^2}{R^4}$$
$$ - \frac{3(1-3\alpha_1)\varepsilon^\beta E_\infty^2}{8\pi} - \frac{8}{45}\frac{\gamma}{R}\varepsilon^4 + \frac{14}{45}\frac{\gamma}{R}\omega^2\varepsilon^4.$$

(5.18)

The acceleration w in the considered approximation is determined by relationships (4.8), (4.9), and (4.12).

6. THE CHEMICAL POTENTIALS OF CONDENSATE MOLECULE IN THE DROPLET AND THE VAPOR

Let us now determine thermodynamic parameters that are required to describe heterogeneous nucleation. We begin this consideration with the chemical potential of the condensate molecule in the droplet.

It follows from the Gibbs–Duhem equation that the chemical potential b_V of a droplet composed of v molecules of incompressible liquid, expressed in kT units and calculated with reference to the chemical potential of the bulk liquid in equilibrium with its vapor at a flat interface, is equal to

$$b_V = (P_0^\alpha - P_0^\beta)/kT\rho^\alpha.$$

(6.1)

Substituting (5.18) into (6.1), passing from the R variable to v in the resultant expression with the help of (1.7), and using definitions (3.18) and (3.22), we find

$$b_V = \frac{2}{3}av^{-1/3}\left[1 - \frac{1}{3(1-3\alpha_1)}\epsilon^2 - \frac{4}{45}\epsilon^4\right]$$
$$ - \frac{1}{3}a_q v^{-4/3}\left[1 - \frac{(1-15\alpha_2)}{3(1-3\alpha_1)}\epsilon^2 - \frac{7}{45}(1-15\alpha_2)\epsilon^4\right],$$

(6.2)

where the following notations,

$$a = \frac{4\pi\gamma}{kT}\left(\frac{3}{4\pi\rho^\alpha}\right)^{2/3},$$

$$a_q = \frac{q^2}{2kT}\left(\frac{1}{\varepsilon^\beta} - \frac{1}{\varepsilon^\alpha}\right)\left(\frac{4\pi\rho^\alpha}{3}\right)^{1/3}$$

(6.3)

are introduced.

As follows from definitions (3.18) and (3.22) with allowance for (1.7), the ϵ^2 value is a function of v. Using (6.3), we obtain

$$\epsilon^2 = \frac{9(1-3\alpha_1)a_E v^{1/3}}{2a - a_q(1-15\alpha_2)v^{-1}},$$

(6.4)

where the new dimensionless value a_E is defined by the relationship

$$a_E \equiv \frac{3(1-3\alpha_1)\varepsilon^\beta E_\infty^2}{8\pi\rho^\alpha kT}.$$

(6.5)

The meaning of the dimensionless value a_E becomes understandable if we neglect in (6.2) the summands of the order of ϵ^4. In this case, substituting (6.4) into (6.2), we find

$$b_V = \frac{2}{3}av^{-1/3} - \frac{1}{3}a_q v^{-4/3} - a_E.$$

(6.6)

As is seen, in the approximation considered, the a_E value is responsible for a decrease in the chemical potential of the condensate in a droplet due to the presence of the external uniform electric field. This

decrease appears to be identical for droplets of all sizes (for which $\epsilon^2 > 0$). However, it follows from the more general formula (6.2) that allowances made for summands of the order of ϵ^4 leads to a v-dependent addend to the chemical potential:

$$b_v = \frac{2}{3}av^{-1/3} - \frac{1}{3}a_qv^{-4/3} - a_E$$

$$-\frac{3}{5}(1 - 3\alpha_1)^2 a_E^2 \frac{8a - 7a_q(1 - 15\alpha_2)v^{-1}}{[2a - a_q(1 - 15\alpha_2)v^{-1}]^2}v^{1/3}. \qquad (6.7)$$

As follows from (3.19) and (3.23), in the first approximation with respect to small parameter ϵ^2 the variation in the droplet shape does not affect the chemical potential (it is determined by the sum of the Φ_{0q} and Φ_{0E} electric potentials). The deviation of the droplet from the spherical shape starts to affect the chemical potential only in the second approximation in the deviation from sphericity [the fourth summand in the right-hand part of equation (6.7)].

Note now that if it is assumed that, in (6.6) $a_q = 0$ [i.e., if it is assumed that, as follows from (6.3), $q = 0$], the a_E value will be responsible for a decrease in the chemical potential for the homogeneous droplet in the external field. However, with the allowance made for the summands of ϵ^4 order in (6.2), the correction to the chemical potential seems to be different at $q = 0$ and $q \neq 0$ (the corresponding formula at $q = 0$ was derived earlier in [13, 14]). Hence, it is the allowance made for the summands of the ϵ^4 order that permits us to describe the joint effects of the central field of the charged nucleus of the droplet and the external uniform electric field in the thermodynamics of heterogeneous nucleation.

Let us now find how the chemical potential of the condensate molecule in vapor changes in the presence of the electric field at a given vapor supersaturation. It follows from the Gibbs–Duhem relationship that the chemical potential b of the condensate molecule in vapor, expressed in kT units and calculated with reference to the chemical potential corresponding to the equilibrium between vapor and liquid at the flat interface, may be written as

$$b = b_0(\rho^\beta(\mathbf{r})) - \frac{1}{8\pi}\frac{(E^\beta(\mathbf{r}))^2}{kT}\frac{\partial\epsilon^\beta}{\partial\rho^\beta(\mathbf{r})}, \qquad (6.8)$$

where $b_0(\rho^\beta(\mathbf{r})) = \ln[\rho^\beta(\mathbf{r})/\rho_s^\beta]$ in the approximation of the perfect gas. Here, $\rho^\beta(\mathbf{r})$ is the density of the number of vapor molecules at a point with the coordinate $\mathbf{r}$, $E^\beta(\mathbf{r})$ is the strength of the electric field at the same point, and ρ_s^β is the density of the number of molecules in vapor in equilibrium with the liquid at a flat interface at the same temperature, but in the absence of the electric field. In the bulk vapor, at a sufficient distance from the droplet, we have $E^\beta(\mathbf{r}) \longrightarrow E_\infty$, and $\rho^\beta(\mathbf{r}) \longrightarrow \rho_\infty^\beta$.

Then, using the Clausius–Mosotti formula $(\epsilon^\beta - 1)/(\epsilon^\beta + 2) = 4\pi\rho_\infty^\beta\chi^\beta/3$, where χ^β is the polarizability of vapor molecule, equation (6.8) may be rewritten at $\epsilon^\beta \approx 1$ as

$$b = b_0(\rho_\infty^\beta) - b_E, \qquad (6.9)$$

where

$$b_0(\rho_\infty^\beta) = \ln(1 + \zeta), \qquad (6.10)$$

$$b_E \equiv \frac{\chi^\beta E_\infty^2}{2kT}, \qquad (6.11)$$

and $\zeta = (\rho_\infty^\beta - \rho_s^\beta)/\rho_s^\beta$ is the vapor supersaturation.

The threshold value ζ_{th} of vapor supersaturation, beginning with which the generation of droplets on nuclei becomes barrierless, is an important thermodynamic characteristic of heterogeneous nucleation. Denoting the threshold value of the chemical potential of vapor by b_{th}, we obtain from (6.9) and (6.10)

$$\zeta_{th} = \exp(b_{th} + b_E) - 1. \qquad (6.12)$$

Given that $b_{th} = \max b_v$, where $\max b_v$ is the maximal chemical potential of the condensate in a droplet and the fact that in the absence of the external field the coordinate of the point of maximum b_v at the v axis is equal to $v_0 = 2a_q/a$, we find from (6.7) and (6.12) that

$$\zeta_{th} + 1 \approx \exp\left[\frac{1}{2}a\left(\frac{a}{2a_q}\right)^{1/3}\right]\left\{1 + \left(\frac{b_E}{a_E} - 1\right)\frac{2a_E}{a}\left(\frac{2a_q}{a}\right)^{1/3}\right. \qquad (6.13)$$

$$\left. + \left[\frac{1}{2}\left(\frac{b_E}{a_E} - 1\right)^2 - \frac{(1 - 3\alpha_1)^2(3 + 35\alpha_2)}{5(1 + 5\alpha_2)^2}\right]\left[\frac{2a_E}{a}\left(\frac{2a_q}{a}\right)^{1/3}\right]^2\right\},$$

where it is taken into account that expansion (6.7) is applicable in the vicinity of the point of maximal chemical potential, when the strong inequality

$$2(a_E/a)(2a_q/a)^{1/3} \ll 1 \qquad (6.14)$$

is fulfilled.

Inequality (6.14) plays an important controlling role in the theory of heterogeneous nucleation, because it allows us to make estimations of the influence of the external field that are independent of the size of nucleating droplets. For example, for the nucleation of water vapors we have $a = 10$ and $a_q = 160$ at $T = 300$ K. For the fulfillment of inequality (6.14), it is necessary for the inequality $a_E \ll 1.6$ to be fulfilled. As follows from (6.5), this inequality limits the highest permissible values of the strength of external field E_∞: $E_\infty \ll 4 \times 10^9$ V/m. It is evident that condition (6.14) is virtually always fulfilled.

Let us find the b_E/a_E ratio. Using (6.5) and (6.11) and taking into account that the polarizability of vapor molecule χ^β is determined by the electronic χ_e^β and ori-

entational $p^2/3kT$ contributions (p is the value of the dipole moment of a vapor molecule), we have

$$\frac{b_E}{a_E} = \frac{4\pi(\varepsilon^\alpha + 2\varepsilon^\beta)\rho^\alpha}{3\ (\varepsilon^\alpha - \varepsilon^\beta)\varepsilon^\beta}\left(\chi_e^\beta + \frac{p^2}{3kT}\right). \qquad (6.15)$$

As is seen from (6.15), the b_E/a_E ratio is positive and independent of the strength of the external electric field and the droplet size. For vapors of polar liquids, this ratio cannot be larger than unity. For example, for water vapor at $T = 300$ K, $\varepsilon^\alpha = 81$, $\chi_e^\beta = 1.44 \times 10^{-30}$ m^3, $p = 1.84$ D, and $\rho^\alpha = 3 \times 10^{28}$ m^{-3}; correspondingly, $b_E/a_E = 4$. The fact that the b_E/a_E ratio can be larger than unity implies that the critical and threshold values of supersaturation for the corresponding vapor increase in the presence of the external uniform electric field.

7. THE WORK OF DROPLET FORMATION

Let us now consider the work of droplet formation. The work F_ν of formation of the droplet composed of ν condensate molecules is equal to the difference of the free energies of the resultant nucleus–droplet–vapor system and the initial nucleus–vapor system. Expressed in kT units, this work is determined by the relationship

$$F_\nu = -b\nu + W_s/kT + W_{el}/kT + F_n. \qquad (7.1)$$

Here, W_s is the work of the droplet surface formation; W_{el} is the work of field sources at a given chemical potential b of vapor; and F_n is a constant that is independent of the number of condensate molecules in the droplet and secures the tendency of the work of droplet formation F_ν to vanish at $\nu \longrightarrow 0$. In the general case, this constant has the meaning of the work of wetting of the condensate nucleus by the bulk condensate. This work is expressed in kT units and includes both the electric contribution and the contribution related to the intermolecular forces at the nucleus–liquid interface. When the size of the nucleus compared to droplet sizes [see the first of boundary conditions (2.5)] and the contribution of intermolecular forces at the nucleus–liquid interface can are neglected, we have $F_n = -(1/\varepsilon^\beta - 1/\varepsilon^\alpha)(q^2/2kTR_n)$, where R_n is the radius of the condensation nucleus.

Let us first determine the W_{el} contribution. We introduce the Φ_R^α and Φ_R^β potentials of the response field acting on the droplet nucleus and of the sources of the external field in vapor, respectively. Let us represent Φ_R^α and Φ_R^β as

$$\Phi_R^\alpha = \Phi^\alpha - \frac{q}{\varepsilon^\alpha r}, \qquad (7.2)$$

and

$$\Phi_R^\beta = \Phi^\beta + E_\infty r\cos\theta = \frac{\mathcal{P}\cos\theta}{\varepsilon^\beta r^2} + \sum_{\substack{n=0 \\ n \neq 1}}^{\infty} c_n \frac{1}{r^{n+1}} P_n, \qquad (7.3)$$

where $\mathcal{P}$ is the value of the dipole moment in the expansion of the Φ_R^β potential in the Legendre polynomials. The droplet-size-dependent electric contribution to the work of droplet formation is determined by the formula [16]:

$$W_{el} = \frac{1}{2}q\Phi_R^\alpha\bigg|_{r=0} - \frac{1}{2}\mathcal{P}E_\infty. \qquad (7.4)$$

The Φ^α and Φ^β potentials are defined by relationships (3.8)–(3.10), which are opened in an explicit form using (3.6), (3.7), (5.7), and (5.8) [with allowance for (5.13)–(5.15), (5.11), and (5.12)]. Substituting the thus-obtained Φ^α and Φ^β values into (7.2) and (7.3) and taking into account definitions (3.22), (3.18), and (4.2) for the ε^2 and κ values, we obtain

$$\Phi_R^\alpha\bigg|_{r=0} = \left(\frac{1}{\varepsilon^\beta} - \frac{1}{\varepsilon^\alpha}\right)\frac{q}{R}\left(1 - \frac{1 - 15\alpha_2}{45}\varepsilon^4\right),$$

$$\mathcal{P} = (1 - 3\alpha_1)\varepsilon^\beta E_\infty R^3\left[1 + \frac{2}{5}(1 - 3\alpha_1)\varepsilon^2\right]. \qquad (7.5)$$

Substituting (7.5) into (7.4), we finally obtain the expression for W_{el}:

$$W_{el} = \left(\frac{1}{\varepsilon^\beta} - \frac{1}{\varepsilon^\alpha}\right)\frac{q^2}{2R}\left(1 - \frac{1 - 15\alpha_2}{45}\varepsilon^4\right)$$

$$- \frac{1}{2}(1 - 3\alpha_1)\varepsilon^\beta E_\infty^2 R^3\left[1 + \frac{2}{5}(1 - 3\alpha_1)\varepsilon^2\right]. \qquad (7.6)$$

The work of formation of the droplet surface is equal to

$$W_s = \gamma S, \qquad (7.7)$$

where S is the surface area of the droplet whose profile is set by relationship (5.17). Considering that in the considered second approximation according to the deviation from the sphericity

$$S = 2\pi R^2\int_0^\pi d\theta \sin\theta\left(1 + \frac{2f}{R} + \frac{f^2}{R^2} + \frac{1}{2}\frac{f_\theta^2}{R^2}\right), \qquad (7.8)$$

we find

$$W_s = 4\pi\gamma R^2\left(1 + \frac{2}{45}\varepsilon^4\right). \qquad (7.9)$$

Passing from the R variable in expressions (7.6) and (7.9) to ν with the help of formula (1.7), substituting the resultant expressions into the right-hand part of (7.1), and also using (3.16), (3.18), (3.22), and (6.3), we find

$$F_v = -bv + av^{2/3}\left[1 - \frac{2}{9(1 - 3\alpha_1)}\epsilon^2 - \frac{2}{45}\epsilon^4\right]$$

$$+ a_q v^{-1/3}\left[1 + \frac{1 - 15\alpha_2}{9(1 - 3\alpha_1)}\epsilon^2 + \frac{1}{45}(1 - 15\alpha_2)\epsilon^4\right] + F_n. \tag{7.10}$$

Considering (6.4), (6.9), and (6.10), we can represent expression (7.10) for F_v in the following form:

$$F_v = -\ln(1 + \zeta)v + av^{2/3} + a_q v^{-1/3} + (b_E - a_E)v$$

$$- \frac{9}{5}(1 - 3\alpha_1)^2 a_E^2 \frac{v^{4/3}}{(2a - a_q(1 - 15\alpha_2)v^{-1})} + F_n. \tag{7.11}$$

8. CRITICAL AND EQUILIBRIUM SIZES OF THE DROPLET AND THE ACTIVATION BARRIER OF NUCLEATION

Now let us write the expression for the activation barrier of nucleation, which is determined by the difference between the maximum and minimum of the work of droplet formation at a given value of the vapor supersaturation ζ.

The critical v_c and equilibrium (stable) v_e sizes of the droplet, whose works of formation F_v are characterized by the maximum and minimum, respectively, are determined by the roots of equations

$$b_v|_{v = v_c} = b, \quad b_v|_{v = v_e} = b \tag{8.1}$$

and conditions

$$(\partial^2 F_v / \partial v^2)|_{v = v_c} < 0, \quad (\partial^2 F_v / \partial v^2)|_{v = v_e} > 0. \tag{8.2}$$

Let us first discuss the problem of the applicability of the expressions for chemical potential b_v and the work of formation F_v, which are derived in previous sections, for determining critical and equilibrium droplet sizes. As follows from (1.8) and (3.26), expansions (6.7) and (7.11) for b_v and F_v are valid when the inequality $0 < \epsilon^2/3 \ll 1$ is fulfilled. In addition, the sizes of equilibrium and critical droplets should be sufficient to neglect the sizes of the charged condensation nucleus.

With allowance for (6.4), inequality $\epsilon^2/3 \ll 1$ can be rewritten as

$$3(1 - 3\alpha_1)a_E v^{1/3} \ll 2a - a_q(1 - 15\alpha_2)v^{-1}. \tag{8.3}$$

Inequality (8.3) reflects the correctional character of the effects of the external electric field, whereas the effects due to the central electric field, which are responsible for the very existence of an equilibrium droplet, are taken into account in the principal order in relationships (6.7) and (7.11) via the summands with the a_q coefficient. At the value of vapor supersaturation ζ_{th} corresponding to the threshold of barrierless nucleation, when the v_e and v_c sizes are identical, inequality (8.3) is transformed into inequality (6.14), setting a constraint on the maximum value of the strength E_∞ of the external field. It is easy to see that, at virtually the

same constraints on E_∞, inequality (8.3) will be fulfilled even at lower (than threshold) values of vapor supersaturation ζ that fit the $0 < \zeta < \zeta_{th}$ range, where v_e is not too small, whereas, in contrast, v_c is not too large compared to $v_0 = 2a_q/a$. The activation barrier of nucleation may still be overcome precisely at these values of supersaturation ζ; hence, the process of heterogeneous nucleation of the droplets in vapor may actually be observed in practice. In a typical case of water vapor nucleation on single-charged ions, the equilibrium droplets contain about 15–30 water molecules and noticeably surpass the ion size in the pre-threshold range of supersaturations, which is our main concern.

Solving equations (8.1) with allowance for (6.7), (6.9), (6.10), and (7.11) according to the perturbation theory, we obtain

$$v_e = v_{e0}\left\{1 - \frac{9a_E}{2a}\left(\frac{b_E}{a_E} - 1\right)\frac{v_{e0}^{4/3}}{(v_0 - v_{e0})}\right.$$

$$+ \frac{27a_E^2}{20a^2}v_{e0}^{5/3}\left[\frac{(4 - 7\omega_{e0}^2)(1 - 3\alpha_1)^2}{(v_0 - v_{e0})}\frac{(1 - 3\alpha_1)^2}{(1 - \omega_{e0}^2)}\right. \tag{8.4}$$

$$\left.\left. - \frac{5}{2}v_{e0}\left(\frac{b_E}{a_E} - 1\right)^2\frac{(4v_{e0} - 7v_0)}{(v_0 - v_{e0})^3}\right]\right\},$$

and

$$v_c = v_{c0}\left\{1 + \frac{9a_E}{2a}\left(\frac{b_E}{a_E} - 1\right)\frac{v_{c0}^{4/3}}{(v_{c0} - v_0)}\right.$$

$$+ \frac{27a_E^2}{20a^2}v_{c0}^{5/3}\left[\frac{(-4 + 7\omega_{c0}^2)(1 - 3\alpha_1)^2}{(v_{c0} - v_0)}\frac{(1 - 3\alpha_1)^2}{(1 - \omega_{c0}^2)}\right. \tag{8.5}$$

$$\left.\left. + \frac{5}{2}v_{c0}\left(\frac{b_E}{a_E} - 1\right)^2\frac{(4v_{c0} - 7v_0)}{(v_{c0} - v_0)^3}\right]\right\},$$

where v_{e0} and v_{c0} are the sizes of equilibrium and critical nuclei in the theory of nucleation on charged nuclei at the same value of vapor supersaturation ζ, which are determined by relationships

$$\frac{2}{3}av_{c0}^{-1/3} - \frac{1}{3}a_q v_{c0}^{-4/3} = \ln(1 + \zeta),$$

$$\frac{2}{3}av_{e0}^{-1/3} - \frac{1}{3}a_q v_{e0}^{-4/3} = \ln(1 + \zeta); \tag{8.6}$$

$$(\partial^2 F_v^{(0)} / \partial v^2)|_{v = v_{c0}} < 0, \quad (\partial^2 F_v^{(0)} / \partial v^2)|_{v = v_{e0}} > 0$$

($F_v^{(0)}$ is the formation work of the droplet composed of v molecules and the charged condensation nucleus: $F_v^{(0)} = -\ln(1 + \zeta)v + av^{2/3} + a_q v^{-1/3} + F_n$). In the right-hand parts of relationships (8.4) and (8.5), we used also expression (3.22) for ω^2, which, after passing from the

R variable to v and using notations (6.3) and $v_0 = 2a_q/a$, acquires the form

$$\omega^2 = (v_0/4v)(1 - 15\alpha_2). \qquad (8.7)$$

It was also assumed that $\omega_{c0} \equiv \omega|_{v = v_{c0}}$ and $\omega_{e0} \equiv \omega|_{v = v_{e0}}$.

Substituting now the thus-derived expressions (8.4) and (8.5) into the condition determining the activation barrier of nucleation $\Delta F_v = F_v|_{v = v_c} - F_v|_{v = v_e}$ and using expression (7.11), we obtain

$$\Delta F_v = \Delta F_v^{(0)} + (b_E - a_E)(v_{c0} - v_{e0})$$

$$+ \frac{9a_E^2}{4a}\left\{ v_{c0}^{4/3}\left[\frac{(b_E/a_E - 1)^2 v_{c0}}{(v_{c0} - v_0)} - \frac{2(1 - 3\alpha_1)^2}{5(1 - \omega_{c0}^2)} \right] \right. \qquad (8.8)$$

$$\left. + v_{e0}^{4/3}\left[\frac{(b_E/a_E - 1)^2 v_{e0}}{(v_0 - v_{e0})} + \frac{2(1 - 3\alpha_1)^2}{5(1 - \omega_{e0}^2)} \right] \right\},$$

where $\Delta F_v^{(0)}$ is the activation barrier of nucleation on the charged nucleus at a given vapor supersaturation in the absence of the external uniform electric field:

$$\Delta F_v^{(0)} = -\ln(1 + \zeta)(v_{c0} - v_{e0})$$

$$+ a(v_{c0}^{2/3} - v_{e0}^{2/3}) + a_q(v_{c0}^{-1/3} - v_{e0}^{-1/3}). \qquad (8.9)$$

If we assume in previous relationships that $b_E = 0$ and substitute the chemical potential b of vapor instead of $\ln(1 + \zeta)$, we may obtain relationships for the sizes of equilibrium and critical nuclei and the activation barrier of nucleation in the presence and absence of the external field at a fixed chemical potential of the vapor. From (8.8) at $b_E/a_E > 1$, it is easy to establish that, at a given vapor supersaturation in the presence of the external field, the activation barrier becomes higher (as was first noticed in [12]), whereas, in contrast, at a given chemical potential it becomes lower.

Let us now specify four control relationships, which allow us to check the self-consistency of the thermodynamic characteristics of the nucleation on the charged nucleus in the external uniform electric field, which were derived in this communication.

Firstly, note that the expression for the chemical potential b_v of the droplet can be obtained using the common thermodynamic relationship

$$\left.\frac{dF_v}{dv}\right|_{T, q, E_\infty} = b_v - b. \qquad (8.10)$$

Secondly, relationships (7.6) and (7.9) are valid for any spheroid with a small eccentricity. The substitution (in an explicit form) of expression for F_v into the con-

ditions for the mechanical equilibrium of the spheroidal droplet

$$\partial F_v/\partial\epsilon^2|_{T, q, E_\infty, v} = 0, \quad \partial^2 F_v/\partial(\epsilon^2)^2|_{T, q, E_\infty, v} > 0 \qquad (8.11)$$

makes it possible to determine the second order eccentricity of a spheroid. Substituting (7.1) [with allowance made for (7.6) and (7.9)] into condition (8.11), we arrive as expected, at expression (3.22) for ϵ^2 and inequality $0 < \omega^2 < 1$.

Thirdly, the common thermodynamic relationship, which allows us to check the validity of the expressions obtained for the activation barrier of nucleation ΔF_v (8.8), the sizes of equilibrium v_e (8.4) and critical v_c (8.5) nuclei, is the equality

$$d\Delta F_v/db|_{T, q, E_\infty} = -(v_c - v_e). \qquad (8.12)$$

Fourthly, for the droplet-size-dependent part of the work of formation F_v, according to any procedure and accuracy of determination, the following general expressions

$$\left.\frac{\partial F_v}{\partial q}\right|_{T, v, E_\infty} = \frac{1}{kT}\Phi_R^\alpha\Big|_{r = 0},$$

$$\left.\frac{\partial F_v}{\partial E_\infty}\right|_{T, v, q} = -\frac{1}{kT}(\mathscr{P} - v\chi^\beta E_\infty), \qquad (8.13)$$

should be fulfilled, which are in agreement with (7.4).

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