

The Equilibrium Shape, Chemical Potential, and Work of Formation for a Dielectric Drop in the Electric Field Induced by the Dipole of a Condensation Center

A. K. Shchekin and V. B. Varshavskii

Physics Research Institute, St. Petersburg State University, ul. Ul'yanovskaya 1, Petrodvorets, 198904 Russia

Received March 4, 1996

Abstract—An iterative procedure was formulated for finding the equilibrium surface profile of a drop that is formed in the axisymmetrical electric field induced by the dipole of the condensation center. By simultaneous consideration of the Laplacian hydrostatic formula (which makes allowance for the curvature of the drop surface and for the electric field of the central dipole) and Laplace's electrostatic equation, the correction for the non-sphericity of the surface, the chemical potential, and the work of the drop formation were calculated. The dependence of these parameters on the number of condensate molecules in the drop and on the dipole moment of the condensation center was determined in analytical form.

INTRODUCTION

When nucleation at charged particles or ions is studied, the drop formed around a condensation center is usually assumed to have a spherical surface. This assumption is clearly wrong for nucleation at centers that have nonzero electric dipole moments, because the drop is deformed by the axisymmetrical electric field (the field of a dipole). The non-sphericity of the drop must affect, for the given number of condensate molecules in the drop, the chemical potential of the condensate in this drop and the work of the drop formation; therefore, this deviation from sphericity should be taken into account in the theory of heterogeneous condensation. The non-sphericity corrections to the chemical potential of the condensate and to the work of the drop formation may have the same order of magnitude as the corrections for the polarization of the drop in the field of the condensation center, which are usually considered in the theory of ion-induced nucleation [1–3].

The polarization contribution to the work of the drop formation was studied in [4] for a drop in the electric field of a condensation center that has both an electric charge and a dipole moment. However, the approximations used in [4] for determining the electric field of the central dipole acting on the condensate molecules were too rough, the use of the Clausius–Mossotti equation for calculating the permittivity of a polar liquid that condenses around the foreign particle was not justified, and the activation energy of nucleation was found incorrectly. Moreover, the drop was regarded as spherical; as a result of this assumption, the corrections for the deformation of the drop in the electric field were

excluded from consideration in calculations of the drop formation work in [4].

In this communication, we develop an iterative method for simultaneous solution of the equation describing the equilibrium profile of the drop surface (obtained from Laplace's hydrostatic formula, which represents mechanical equilibrium for the curved surface of a dielectric drop in the axisymmetrical field induced by the dipole of the condensation center) and the Laplacian electrostatic equation for the foreign particle–drop–vapor system. Using this method, we find the equilibrium shape of the drop, the chemical potential of the condensate in it, and the work of its formation. At the limit of a conducting drop, the approach to the solution of the boundary problem for the Laplacian electrostatic equation in the case of a slightly non-spherical drop surface is similar to the method formulated in [5].

INITIAL EQUATIONS

Let us consider a drop with a solid insoluble foreign particle at its center; the size of the particle is negligible compared to that of the drop. The total electric charge of the particle is zero, but its dipole moment is not equal to zero. The drop contains v molecules of an incompressible liquid (the α phase) that has condensed from the surrounding vapor (the β phase). Hereafter, the α and β indices denote the values that refer to the liquid and vapor phases, respectively. Both phases are single-component; the effect of the gravitational field on the drop is assumed to be negligible.

The equilibrium shape of the drop in the field of the dipole is determined by the balance of pressures at any point of its surface [6]:

$$P_{NN}^{\alpha} - P_{NN}^{\beta} = P_{\gamma}, \quad (1)$$

where P_{γ} is the capillary pressure under the curved surface of the drop, and P_{NN}^{α} and P_{NN}^{β} , the normal components of the pressure tensor at a selected point of the drop surface (referring to the liquid and vapor pressures, respectively), are equal to

$$P_{NN}^{\alpha, \beta} = P_0^{\alpha, \beta} + P_E^{\alpha, \beta}. \quad (2)$$

Here, P_0 is the pressure in the phase in the absence of the dipole-induced electric field but under the condition that the chemical potential of the drop (the chemical potential of a liquid molecule in the drop) is equal to the potential in the presence of the field; P_E is the normal component of Maxwell's stress tensor at the surface of the drop on the side of the corresponding phase, such that [6]

$$P_E^{\alpha, \beta} = \frac{\varepsilon^{\alpha, \beta} (\mathbf{E}^{\alpha, \beta})^2}{8\pi} - \frac{\varepsilon^{\alpha, \beta} (E_N^{\alpha, \beta})^2}{4\pi}, \quad (3)$$

where ε is the permittivity, and \mathbf{E} and E_N are the vector of the electric field intensity and its component that is normal to the surface of the drop, respectively. The difference between equation (3) and the formula given in [6] is that the latter equation refers to the situation when the density of the phase in the absence of the field remains the same as in its presence.

In the electric field of the dipole, the equation for the equilibrium surface of the drop may be written as

$$r(\theta) = R + f(\theta), \quad (4)$$

where R is the radius of a sphere that has the same volume as the drop, and the $f(\theta)$ function makes allowance for the deviation of the drop surface from the spherical shape. Denoting the volume of the drop by V_v , we may write

$$V_v = (4\pi/3)R^3. \quad (5)$$

The volume V_v of a drop that contains v molecules of an incompressible liquid is equal to

$$V_v = v^{\alpha}v, \quad (6)$$

where v^{α} is the molecular volume of a liquid.

Further, we will consider only such dipole moments of the foreign particles and dimensions of the resultant drops for which

$$|f(\theta)|/R \ll 1, \quad (7)$$

accordingly, the $f(\theta)$ function will be referred to as the correction for the non-sphericity of the drop. In this case, equation (4) yields

$$\begin{aligned} V_v &= \frac{2\pi}{3} \int_0^{\pi} r^3(\theta) \sin\theta d\theta \\ &= \frac{2\pi R^3}{3} \int_0^{\pi} \left(1 + 3\frac{f}{R} + 3\left(\frac{f}{R}\right)^2\right) \sin\theta d\theta \end{aligned} \quad (8)$$

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

Considering (8) and making allowance for (5), we obtain a relationship for the non-sphericity correction f , which is important for further analysis:

$$\int_0^{\pi} (Rf + f^2) \sin\theta d\theta = 0. \quad (9)$$

A SET OF DIFFERENTIAL EQUATIONS DESCRIBING THE CORRECTION FOR THE NON-SPHERICITY OF THE DROP

The capillary pressure P_{γ} under a curved surface of a drop is determined as $P_{\gamma} = \gamma(1/R_1 + 1/R_2)$, 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 the spherical coordinates with a degree of accuracy up to terms of the $(f/R)^2$ order, we find that the capillary pressure P_{γ} assumes the form

$$\begin{aligned} P_{\gamma} &= \frac{2\gamma}{R} - \frac{\gamma}{R^2} \left\{ 2f + \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial f}{\partial\theta} \right) \right\} \\ &+ \frac{2\gamma}{R^3} \left\{ f^2 + \frac{f}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial f}{\partial\theta} \right) \right\}. \end{aligned} \quad (10)$$

Substituting (2) and (3) into the left-hand part of equation (1) and (10) into its right-hand part, we arrive at a differential equation with respect to the correction f for non-sphericity:

$$\begin{aligned} \frac{2\gamma}{R} - \frac{\gamma}{R^2} \left\{ 2f + \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial f}{\partial\theta} \right) \right\} \\ + \frac{2\gamma}{R^3} \left\{ f^2 + \frac{f}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial f}{\partial\theta} \right) \right\} = P_0^{\alpha} - P_0^{\beta} \quad (11) \\ + \frac{\varepsilon^{\alpha} (\mathbf{E}^{\alpha})^2}{8\pi} - \frac{\varepsilon^{\beta} (\mathbf{E}^{\beta})^2}{8\pi} + \frac{\varepsilon^{\beta} (E_N^{\beta})^2}{4\pi} - \frac{\varepsilon^{\alpha} (E_N^{\alpha})^2}{4\pi}, \end{aligned}$$

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 drop surface described by

equation (4). The boundary conditions for the f function in the case of a freely suspended drop are written in the form

$$(\partial f / \partial \theta)|_{\theta=0} = (\partial f / \partial \theta)|_{\theta=\pi} = 0. \quad (12)$$

To specify the right-hand part of (11) in an explicit form, we should solve Laplace's electrostatic equation for the potential Φ in the drop-vapor two-phase system placed in the field of the central dipole:

$$\Delta \Phi = 0 \quad (13)$$

with the boundary conditions

$$\Phi^\alpha|_{r=r(\theta)} = \Phi^\beta|_{r=r(\theta)}, \quad (14)$$

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

$$\Phi^\alpha \xrightarrow{r \rightarrow 0} \frac{p \cos \theta}{\varepsilon^\alpha r^2}, \quad \Phi^\beta \xrightarrow{r \rightarrow \infty} 0. \quad (15)$$

The boundary conditions (14) are set at the surface of the drop described by equation (4); the relationship determining the normal vector \mathbf{n} to this surface at each of its points is known from differential geometry:

$$\mathbf{n} = \left[1 + \frac{1}{r(\theta)^2} \left(\frac{\partial r(\theta)}{\partial \theta} \right)^2 \right]^{-1/2} \times \left(\mathbf{e}_r - \frac{1}{r(\theta)} \left(\frac{\partial r(\theta)}{\partial \theta} \right) \mathbf{e}_\theta \right), \quad (16)$$

where \mathbf{e}_r and \mathbf{e}_θ are the unit vectors in the radial and azimuthal directions at each point of the surface. The applicability of the first boundary condition in (15) is ensured by the above assumption that the size of the foreign particle is negligible compared to that of the drop.

Further, we will search for the solution of equation (13) with the boundary conditions (14) and (16) in the form

$$\Phi = \Phi_0 + \delta \Phi, \quad |\delta \Phi / \Phi_0| \ll 1, \quad (17)$$

where the Φ_0 potential satisfies Laplace's equation

$$\Delta \Phi_0 = 0 \quad (18)$$

in the drop-vapor system where the drop is a sphere with the radius R . In this case, the boundary conditions (14) at the surface of the drop are transformed for the Φ_0 potential into

$$\Phi_0^\alpha|_R = \Phi_0^\beta|_R, \quad \varepsilon^\alpha \frac{\partial \Phi_0^\alpha}{\partial r} \Big|_R = \varepsilon^\beta \frac{\partial \Phi_0^\beta}{\partial r} \Big|_R. \quad (19)$$

The conditions for Φ_0 at the origin of the coordinate system and at infinity are identical to the boundary conditions (15); therefore, the Φ_0 potential, exactly as Φ ,

contains a θ -dependent axisymmetrical contribution. The small addend $\delta \Phi$ to the Φ_0 potential in (17) is due to the assumed slight non-sphericity of the drop surface at $r = R$.

THE SURFACE OF THE DROP IN THE FIRST APPROXIMATION BY NON-SPHERICITY

The set of equations (11) and (13) with allowance made for (4), (7), and (17) may be solved by the following iterative procedure. The non-sphericity of the drop surface is determined (with a degree of accuracy up to the first order of the small value f/R) by the θ -dependent axisymmetrical contribution to the Φ_0 potential, which is easily found from (18) and (19). To find the deviation from the spherical shape of the surface with an accuracy up to the second order of the same small value f/R , we must also know the $\delta \Phi$ potential, which, in turn, depends on the first-order correction to the radius of the spherical drop at $r = R$.

For a spherical drop, we may write

$$E^2|_R = \left(\frac{\partial \Phi_0}{\partial r} \Big|_R \right)^2 + \frac{1}{R^2} \left(\frac{\partial \Phi_0}{\partial \theta} \Big|_R \right)^2, \quad (20)$$

$$E_N^2|_R = \left(\frac{\partial \Phi_0}{\partial r} \Big|_R \right)^2.$$

Using equation (11), retaining only infinitesimal terms of the first order by the f/R parameter in its left-hand part, and substituting (20) with allowance made for (19) into its right-hand part, we obtain a linear differential equation of the second order with respect to f :

$$\frac{2\gamma}{R} - \frac{\gamma}{R^2} \left\{ 2f + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial f}{\partial \theta} \right) \right\} = (P_0^\alpha - P_0^\beta) + \frac{(\varepsilon^\alpha - \varepsilon^\beta)}{8\pi} \times \left\{ \frac{1}{R^2} \left(\frac{\partial \Phi_0^\beta}{\partial \theta} \right)^2 + \frac{\varepsilon^\beta}{\varepsilon^\alpha} \left(\frac{\partial \Phi_0^\beta}{\partial r} \right)^2 \right\}. \quad (21)$$

By solving of this equation, we may find the correction for non-sphericity in the first approximation. An additional constraint on the solution of (21) may be obtained from (9) if we leave only the contribution of the order of f/R in the integrand of (9):

$$\int_0^\pi f \sin \theta d\theta = 0. \quad (22)$$

As is apparent from (4), (7), (17), (21), and the strong inequality $|\delta \Phi| \ll |\Phi_0|$, if $\varepsilon^2 \ll 1$ is a small dimensionless parameter of the theory, which characterizes the deviation from sphericity and will be found by further calculations, then the orders of the Φ_0 , $|f|/R$, and $\delta \Phi$ values are ε , ε^2 , and ε^3 , respectively.

The solution of equation (18) with the boundary conditions (19) and (15) has the standard form:

$$\begin{aligned}\Phi_0^\alpha &= \frac{2(\varepsilon^\alpha - \varepsilon^\beta)p}{(\varepsilon^\alpha + 2\varepsilon^\beta)\varepsilon^\alpha R^3} r \cos\theta + \frac{p \cos\theta}{\varepsilon^\alpha r^2} \quad (r < R), \\ \Phi_0^\beta &= \frac{3p \cos\theta}{(\varepsilon^\alpha + 2\varepsilon^\beta) r^2} \quad (r > R).\end{aligned}\quad (23)$$

Substituting expressions (23) into the right-hand part of (21) and taking (19) into consideration, we obtain

$$\begin{aligned}2f + \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial f}{\partial\theta} \right) &= \frac{R^2}{\gamma} \\ \times \left\{ \frac{2\gamma}{R} - (P_0^\alpha - P_0^\beta) - \varepsilon^2 \frac{4(\varepsilon^\alpha + 2\varepsilon^\beta)\gamma}{3(\varepsilon^\alpha - \varepsilon^\beta)R} \right\} &+ \varepsilon^2 \frac{4}{3} R P_2,\end{aligned}\quad (24)$$

where

$$\varepsilon^2 \equiv \frac{9(\varepsilon^\alpha - \varepsilon^\beta)(\varepsilon^\alpha - 4\varepsilon^\beta)p^2}{16\pi\gamma(\varepsilon^\alpha + 2\varepsilon^\beta)^2 \varepsilon^\alpha R^5}, \quad (25)$$

and $P_2 = P_2(\cos\theta)$ is the Legendre polynomial of the second degree. Hereafter, we consider only such parameters of the problem (the dipole moment of the foreign particle p , the permittivity ε^α , the surface tension γ , and the size of the drops R) at which the ε^2 parameter is small: $\varepsilon^2 \ll 1$.

Equation (24) is satisfied by the function

$$\begin{aligned}f &= \frac{R^2}{2\gamma} \\ \times \left\{ \frac{2\gamma}{R} - (P_0^\alpha - P_0^\beta) - \varepsilon^2 \frac{4(\varepsilon^\alpha + 2\varepsilon^\beta)\gamma}{3(\varepsilon^\alpha - \varepsilon^\beta)R} \right\} &- \varepsilon^2 \frac{R}{3} P_2.\end{aligned}\quad (26)$$

This function is compatible with condition (22) if the relationships

$$f = -\varepsilon^2 \frac{R}{3} P_2, \quad (27)$$

and

$$P_0^\alpha - P_0^\beta = \frac{2\gamma}{R} \left(1 - \varepsilon^2 \frac{2(\varepsilon^\alpha + 2\varepsilon^\beta)}{3(\varepsilon^\alpha - \varepsilon^\beta)} \right) \quad (28)$$

are true.

With allowance made for (27), equation (4) for the equilibrium surface of the drop is written as

$$r(\theta) = R \left(1 - \frac{\varepsilon^2}{3} P_2 \right). \quad (29)$$

Let us compare (29) with the equation of an oblate spheroid, whose center is situated at the origin of the spherical coordinate system and whose volume and eccentricity are equal to $(4\pi/3)R^3$ and ε , respectively, that is, with the equation

$$r(\theta) = R \frac{(1 - \varepsilon^2)^{1/3}}{(1 - \varepsilon^2 \sin^2\theta)^{1/2}}. \quad (30)$$

Expansion of (30) in a power series of ε^2 (at $\varepsilon^2 \ll 1$) yields

$$r(\theta) = R \left(1 - \frac{\varepsilon^2}{3} P_2 + \varepsilon^4 \left[-\frac{1}{45} - \frac{11}{63} P_2 + \frac{3}{35} P_4 \right] \right), \quad (31)$$

where $P_4 = P_4(\cos\theta)$ is the Legendre polynomial of the fourth degree. As is apparent from comparison of (29) and (31), the equation for the equilibrium surface of a drop containing an electric dipole at its center is identical (in the first approximation by non-sphericity) to the equation of an oblate spheroid with a degree of accuracy up to terms of the order of ε^2 , and the small parameter ε^2 has a geometrical meaning: the squared eccentricity of the spheroid.

Evidently, the small value of the ε^2 parameter means that the drop-size-dependent electric contribution to the work of the drop formation is small compared to the work of the drop surface formation. Let us express the ε^2 parameter in terms of the ratio between these two values. The potential of the electric field inside the drop may be written as

$$\Phi^\alpha = \frac{p \cos\theta}{\varepsilon^\alpha r^2} + \Phi_R, \quad (32)$$

where Φ_R is the potential of the reaction field acting on the dipole; this field determines the difference between the electric field in a drop with the radius R and the field of the dipole in an infinite liquid. The drop-size-dependent electric contribution to the work of the drop formation is determined in terms of the reaction field potential by the relationships [8]

$$W_{el} = -\frac{1}{2} \mathbf{p} \mathbf{E}_R, \quad \mathbf{E}_R = -\nabla \Phi_R|_{r=0}. \quad (33)$$

Comparing (32) and (33), let us find the Φ_R potential and substitute it into (33). As a result, we obtain

$$W_{el} = \frac{(\varepsilon^\alpha - \varepsilon^\beta)p^2}{(\varepsilon^\alpha + 2\varepsilon^\beta)\varepsilon^\alpha R^3}. \quad (34)$$

Further, let us make allowance for the fact that the work W_{sur} of the surface formation in the currently considered first approximation by the small parameter ε^2 is equal to

$$W_{sur} = 4\pi\gamma R^2. \quad (35)$$

Table

Compound	$\gamma, 10^{-3} \text{ N m}^{-2}$	ϵ^α	$T, ^\circ\text{C}$	ϵ^2
Acetone	23.7	20.8	20	0.048
Methyl ethyl ketone	24.6	18.5	20	0.049
Ethanol	22.0	25.6	20	0.046
Methyl acetate	23.8	6.7	25	0.047
Chlorobenzene	32.6	5.6	25	0.026

Now, returning to definition (25) for the ϵ^2 parameter and using (34) and (35), we find

$$\epsilon^2 = \frac{9(\epsilon^\alpha - 4\epsilon^\beta) W_{el}}{4(\epsilon^\alpha + 2\epsilon^\beta) W_{sur}}. \quad (36)$$

The table shows the squared eccentricities for drops of different substances formed around a KCl molecule with the dipole moment $p_{KCl} = 8D$.

The γ and ϵ^α values in the table are obtained from [9]. The squared eccentricities are found for drops with the equivalent radius $R = 5 \times 10^{-10}$ m. For other inorganic dipoles and condensing substances, as well as for greater R values, the ϵ^2 parameter is even smaller. Thus, ϵ^2 is indeed a small parameter of the problem. For drops with greater squared eccentricities than those given in the table (for example, drops that nucleate at organic molecules, whose dipole moments may exceed P_{KCl} , or at macroscopic particles with large dipole moments), the expressions for the surface shape and for the difference between the pressures in the phases must include at least one more term of the expansion (of the order of ϵ^4). As a result, the next (second) approximation by non-sphericity should be considered.

THE EQUATION FOR THE SURFACE OF THE DROP IN THE SECOND APPROXIMATION BY ITS DEVIATION FROM THE SPHERICAL SHAPE

Let us also make allowance for the non-sphericity of the drop while we determine the potential of the electric field in the drop and vapor. In the linear approximation by the f and $\delta\Phi$ deviations, the $\Phi^{\alpha,\beta}$ potential and its gradient at some point at the surface of the drop are expressed as

$$\Phi^{\alpha,\beta}|_{R+f} = \Phi_0^{\alpha,\beta}|_R + \delta\Phi^{\alpha,\beta}|_R + f \frac{\partial \Phi_0^{\alpha,\beta}}{\partial r} \Big|_R, \quad (37)$$

$$\nabla \Phi^{\alpha,\beta}|_{R+f} = \nabla \Phi_0^{\alpha,\beta}|_R + \nabla \delta\Phi^{\alpha,\beta}|_R + f \frac{\partial (\nabla \Phi_0^{\alpha,\beta})}{\partial r} \Big|_R.$$

In the same approximation, if we make allowance for (16) and (17), the $(\mathbf{E}^{\alpha,\beta})^2|_{R+f} = (\nabla \Phi^{\alpha,\beta})^2|_{R+f}$,

and $(E_N^{\alpha,\beta})^2|_{R+f} = (\nabla \Phi^{\alpha,\beta}, \mathbf{n})^2|_{R+f}$ values are determined by the formulas

$$\begin{aligned} (\mathbf{E}^{\alpha,\beta})^2|_{R+f} = & \left\{ \left(\frac{\partial \Phi_0^{\alpha,\beta}}{\partial r} \right)^2 + \frac{1}{R^2} \left(\frac{\partial \Phi_0^{\alpha,\beta}}{\partial \theta} \right)^2 \right. \\ & + 2 \frac{\partial \Phi_0^{\alpha,\beta}}{\partial r} \frac{\partial \delta\Phi^{\alpha,\beta}}{\partial r} + \frac{2}{R^2} \frac{\partial \Phi_0^{\alpha,\beta}}{\partial \theta} \frac{\partial \delta\Phi^{\alpha,\beta}}{\partial \theta} \\ & \left. + f \frac{\partial}{\partial r} \left(\frac{\partial \Phi_0^{\alpha,\beta}}{\partial r} \right)^2 + f \frac{\partial}{\partial r} \left(\frac{1}{2} \frac{\partial \Phi_0^{\alpha,\beta}}{\partial \theta} \right)^2 \right\} \Big|_R, \end{aligned} \quad (38)$$

and

$$\begin{aligned} (E_N^{\alpha,\beta})^2|_{R+f} = & \left\{ \left(\frac{\partial \Phi_0^{\alpha,\beta}}{\partial r} \right)^2 + 2 \frac{\partial \Phi_0^{\alpha,\beta}}{\partial r} \frac{\partial \delta\Phi^{\alpha,\beta}}{\partial r} \right. \\ & \left. + f \frac{\partial}{\partial r} \left(\frac{\partial \Phi_0^{\alpha,\beta}}{\partial r} \right)^2 - \frac{2f_\theta}{R^2} \frac{\partial \Phi_0^{\alpha,\beta}}{\partial r} \frac{\partial \Phi_0^{\alpha,\beta}}{\partial \theta} \right\} \Big|_R. \end{aligned} \quad (39)$$

As follows from (13), (17), and (18), the small addend $\delta\Phi$ to the potential in the right-hand parts of (37)–(39) satisfies the equation

$$\Delta \delta\Phi = 0. \quad (40)$$

Considering (15) and taking (17) into account, we arrive at the boundary conditions for equation (40) at the points of zero and infinity:

$$\delta\Phi^\alpha \xrightarrow{r \rightarrow 0} 0, \quad \delta\Phi^\beta \xrightarrow{r \rightarrow \infty} 0. \quad (41)$$

To formulate the boundary conditions for equation (40) at the surface of the drop, let us substitute (37) into (14). Using (16) in the linear approximation by f and considering (19), we obtain

$$(\delta\Phi^\alpha - \delta\Phi^\beta)|_R = \left(1 - \frac{\epsilon^\beta}{\epsilon^\alpha} \right) f \frac{\partial \Phi_0^\beta}{\partial r} \Big|_R, \quad (42)$$

$$\begin{aligned} \frac{\partial}{\partial r} (\epsilon^\alpha \delta\Phi^\alpha - \epsilon^\beta \delta\Phi^\beta) \Big|_R = & f \frac{\partial^2}{\partial r^2} (\epsilon^\beta \Phi_0^\beta - \epsilon^\alpha \Phi_0^\alpha) \Big|_R \\ & + \frac{(\epsilon^\alpha - \epsilon^\beta)}{R^2} f_\theta \frac{\partial \Phi_0^\beta}{\partial \theta} \Big|_R. \end{aligned} \quad (43)$$

The boundary conditions (42) and (43) complete the formulation of the $\delta\Phi$ determination problem.

As a result, substituting (38) and (39) into the right-hand part of equation (11) and taking (19) into consid-

eration, we obtain an equation for f with an accuracy up to terms of the order of ϵ^4 inclusive:

$$\begin{aligned} & \left. \frac{2\gamma}{R} - \frac{\gamma}{R^2} \left\{ 2f + \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial f}{\partial\theta} \right) \right\} \right|_R \\ & + \frac{2\gamma}{R^3} \left\{ f^2 + \frac{f}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial f}{\partial\theta} \right) \right\} \\ & = P_0^\alpha - P_0^\beta + \frac{(\epsilon^\alpha - \epsilon^\beta)}{8\pi} \left\{ \frac{1}{R^2} \left(\frac{\partial\Phi_0^\beta}{\partial\theta} \right)^2 + \frac{\epsilon^\beta}{\epsilon^\alpha} \left(\frac{\partial\Phi_0^\beta}{\partial r} \right)^2 \right\} \Bigg|_R \\ & + \frac{1}{8\pi} \left\{ \frac{2}{R^2} \left(\frac{\partial\Phi_0^\beta}{\partial\theta} \right) \frac{\partial}{\partial\theta} [\epsilon^\alpha \delta\Phi^\alpha - \epsilon^\beta \delta\Phi^\beta] \right. \\ & - 2\epsilon^\beta \left(\frac{\partial\Phi_0^\beta}{\partial r} \right) \left[\frac{\partial\delta\Phi^\alpha}{\partial r} - \frac{\partial\delta\Phi^\beta}{\partial r} \right] - 2f\epsilon^\beta \left(\frac{\partial\Phi_0^\beta}{\partial r} \right) \\ & \left. \times \left[\frac{\partial^2\Phi_0^\alpha}{\partial r^2} - \frac{\partial^2\Phi_0^\beta}{\partial r^2} \right] - \frac{2(\epsilon^\alpha - \epsilon^\beta)}{R^3} f \left(\frac{\partial\Phi_0^\beta}{\partial\theta} \right)^2 \right\} \Bigg|_R. \end{aligned} \quad (44)$$

The additional condition for the solution of the differential equation (44) is specified by (9), exactly as above.

Let us find an explicit expression for the $\delta\Phi$ correction to the potential as a function of the spherical coordinates r and θ . After substitution of the expressions from (27) and (23), the boundary conditions (42) and (43) for equation (40) assume the form

$$\begin{aligned} (\delta\Phi^\alpha - \delta\Phi^\beta) \Big|_R &= \frac{2p(\epsilon^\alpha - \epsilon^\beta)\epsilon^2}{5(\epsilon^\alpha + 2\epsilon^\beta)\epsilon^\alpha R^2} (3P_3 + 2P_1), \\ \frac{\partial}{\partial r} (\epsilon^\alpha \delta\Phi^\alpha - \epsilon^\beta \delta\Phi^\beta) \Big|_R &= \frac{2p(\epsilon^\alpha - \epsilon^\beta)\epsilon^2}{5(\epsilon^\alpha + 2\epsilon^\beta)R^3} (6P_3 - P_1). \end{aligned} \quad (45)$$

The solution of equation (40) with the boundary conditions (41) and (45) is

$$\begin{aligned} \delta\Phi^\alpha &= \frac{2p(\epsilon^\alpha - \epsilon^\beta)(\epsilon^\alpha - 4\epsilon^\beta)\epsilon^2}{5(\epsilon^\alpha + 2\epsilon^\beta)^2 \epsilon^\alpha R^3} rP_1 \\ &+ \frac{12p(\epsilon^\alpha - \epsilon^\beta)\epsilon^2}{5\epsilon^\alpha(3\epsilon^\alpha + 4\epsilon^\beta)R^5} r^3P_3, \\ \delta\Phi^\beta &= \frac{6p(\epsilon^\alpha - \epsilon^\beta)\epsilon^2}{5(\epsilon^\alpha + 2\epsilon^\beta)^2 r^2} P_1 - \frac{6p(\epsilon^\alpha - \epsilon^\beta)R^2\epsilon^2}{5\epsilon^\alpha(3\epsilon^\alpha + 4\epsilon^\beta)r^4} P_3. \end{aligned} \quad (46)$$

Substituting the expressions (23), (27), and (46) into the right-hand part of equation (44), we find the solu-

tion of this equation that satisfies the condition (9):

$$\begin{aligned} r(\theta) &= R \left(1 - \frac{\epsilon^2}{3} P_2 + \left[-\frac{1}{45} - \frac{11}{63} P_2 + \frac{3}{35} P_4 \right] \epsilon^4 \right) \\ &+ R\epsilon^4 (\alpha P_2 + \beta P_4), \end{aligned} \quad (47)$$

where the α and β coefficients are defined by the relationships

$$\begin{aligned} \alpha &= -\frac{139}{315} \\ &+ \frac{28}{5} \frac{(1 + 10\epsilon^\beta/7\epsilon^\alpha)}{(1 - 4\epsilon^\beta/\epsilon^\alpha)(1 + 2\epsilon^\beta/\epsilon^\alpha)(1 + 4\epsilon^\beta/3\epsilon^\alpha)}, \end{aligned} \quad (48)$$

and

$$\beta = -\frac{19}{105} - \frac{32}{5} \frac{\epsilon^\beta/\epsilon^\alpha}{(1 + 4\epsilon^\beta/3\epsilon^\alpha)(1 - 4\epsilon^\beta/\epsilon^\alpha)}. \quad (49)$$

The first parenthesized expression in the right-hand part of (47) defines the surface of the oblate spheroid (31); the second one specifies the difference of the equilibrium drop shape from the spheroid. An important conclusion based on the above analysis is the observation that the non-sphericity of the drop profile strongly depends on the ratio between the permittivities of the drop and vapor. As is also apparent from (47), the most significant contribution to the deviation of drop surface from the spheroidal shape is due to the summand with the α coefficient in the right-hand part of (47).

Another important result obtained by solution of (44) under the condition (9) is the formula

$$P_0^\alpha - P_0^\beta = \frac{2\gamma}{R} \left(1 - \frac{2(\epsilon^\alpha + 2\epsilon^\beta)}{3(\epsilon^\alpha - 4\epsilon^\beta)} \epsilon^2 + \frac{8}{45} \epsilon^4 \right), \quad (50)$$

which is a refined version of (28) with a degree of accuracy up to ϵ^4 .

THE WORK OF DROP FORMATION

Now let us determine the thermodynamic parameters that are required for the description of heterogeneous nucleation. Firstly, let us consider the work of drop formation. To determine this value, we must find the expressions for the potential of the reaction field acting on the dipole and for the work of the drop surface formation (with a degree of accuracy up to ϵ^3 and ϵ^4 , respectively).

The potential of the reaction field acting on the dipole is determined according to formula (32) with allowance made for (17), (23), and (46):

$$\begin{aligned} \Phi_R &= \frac{2p(\epsilon^\alpha - \epsilon^\beta)}{\epsilon^\alpha(\epsilon^\alpha + 2\epsilon^\beta)R^3} \left[1 - \frac{(\epsilon^\alpha - 4\epsilon^\beta)\epsilon^2}{5(\epsilon^\alpha + 2\epsilon^\beta)} \right] rP_1 \\ &+ \frac{12p(\epsilon^\alpha - \epsilon^\beta)\epsilon^2}{5\epsilon^\alpha(3\epsilon^\alpha + 4\epsilon^\beta)R^5} r^3P_3. \end{aligned} \quad (51)$$

Substituting (51) into (33), we find the drop-size-dependent electric contribution to the work of the drop formation with an accuracy up to terms of the ϵ^4 order:

$$W_{el} = 4\pi\gamma R^2 \left[\frac{4(\epsilon^\alpha + 2\epsilon^\beta)}{9(\epsilon^\alpha - 4\epsilon^\beta)} \epsilon^2 - \frac{4}{45} \epsilon^4 \right]. \quad (52)$$

For a drop with the surface described by expressions (47)–(49), the work of the surface formation W_{sur} is equal to

$$W_{sur} = 4\pi\gamma R^2 \left(1 + \frac{2}{45} \epsilon^4 \right). \quad (53)$$

For a drop comprising v molecules, the work of formation F_v is equal to the difference between the free energies of the final (foreign particle–drop–vapor) and initial (particle–vapor) system and may be expressed (in kT units) by the formula

$$F_v = -bv + W_{sur}/kT + W_{el}/kT + C. \quad (54)$$

Here, b is the dimensionless (expressed in kT units) chemical potential of the supersaturated condensing vapor, calculated with reference to the chemical potential of vapor in equilibrium with the liquid at a flat interface, and the constant C (independent of the number of molecules) ensures that the work of the drop formation F_v tends to zero at $v \rightarrow 0$. In the general case, the physical meaning of this constant is the work (expressed in kT units) associated with the wetting of the foreign particle by the bulk phase of the condensate; this work includes both an electric contribution and a contribution that is due to intermolecular forces acting at the particle–liquid interface. If the condensation center is a molecular dipole with insignificant size (compared to that of the drop) for the formulation of the first boundary condition in (15), we neglect the contribution of intermolecular forces at the particle–liquid interface and obtain $C = -(1/\epsilon^\beta - 1/\epsilon^\alpha)(p^2/3kTR_n^3)$, where R_n is the radius of the foreign particle. For the sum of both contributions (dependent on the size of the drop and independent of it) that constitute the work of the dipole transfer from the vapor to the drop, the condition

$$\frac{W_{el}}{kT} + C \leq 0 \quad (55)$$

is true. The sign of equality in (55) represents the initial state of the system. As a nucleus appears and grows, W_{el} decreases, and the inequality (55) becomes strict. In the bulk of the liquid, W_{el} is equal to zero.

Passing from the R variable in (52) and (53) to v with the use of (5) and (6) and then substituting the resultant expressions into the right-hand part of (54), we obtain

$$F_v = F_0 + \left\{ av^{2/3} \left(\frac{4(\epsilon^\alpha + 2\epsilon^\beta)}{9(\epsilon^\alpha - 4\epsilon^\beta)} \epsilon^2 - \frac{2}{45} \epsilon^4 \right) + C \right\}, \quad (56)$$

where $F_0 = -bv + av^{2/3}$ is the work of formation for a homogeneously generated drop, and a is the dimensionless surface tension:

$$a = \frac{4\pi\gamma}{kT} \left(\frac{3v^\alpha}{4\pi} \right)^{2/3}. \quad (57)$$

The ϵ^2 parameter as a function of v , according to (25) and (57), is represented by the following expression:

$$\epsilon^2 \equiv \frac{3\pi(\epsilon^\alpha - \epsilon^\beta)(\epsilon^\alpha - 4\epsilon^\beta)}{(\epsilon^\alpha + 2\epsilon^\beta)^2 \epsilon^\alpha v^\alpha kT} p^2 a^{-1} v^{-5/3}. \quad (58)$$

THE CHEMICAL POTENTIAL

For an incompressible liquid comprising v molecules, the chemical potential b_v , expressed in kT units and calculated (exactly as b) with reference to the chemical potential of the bulk liquid in equilibrium with its vapor at a flat interface, is equal to

$$b_v = \frac{v^\alpha}{kT} (P_0^\alpha - P_0^\beta). \quad (59)$$

This relationship allows us to determine the chemical potential b_v of the drop with the use of (50). Substituting the expression kTb_v/v^α , which follows from (59), into the left-hand part of (50) instead of $P_0^\alpha - P_0^\beta$ and passing from the R variable to v with the help of (5) and (6), we take (57) into account and find

$$b_v = \frac{2}{3} av^{-1/3} \left(1 - \frac{2(\epsilon^\alpha + 2\epsilon^\beta)}{3(\epsilon^\alpha - 4\epsilon^\beta)} \epsilon^2 + \frac{8}{45} \epsilon^4 \right). \quad (60)$$

Note that the expression for the chemical potential of the drop b_v might have been obtained via the general thermodynamic relationship

$$\frac{dF_v}{dv} = b_v - b. \quad (61)$$

Indeed, if we substitute the expression (56) for F_v into the left-hand part of (61), differentiate it by v with allowance made for (58), and substitute formula (60) for b_v into the right-hand part of (61), we arrive at an identity.

The minus sign at the principal term in (60), which represents the effect of the field induced by the dipole of the condensation center, indicates that heterogeneous nucleation (at high dipole moments of the foreign particle) is possible. Then, the dependence of the chemical potential of the drop b_v on v has a maximum, which determines the threshold chemical potential of vapor; above this threshold, heterogeneous nucleation is barrierless. When the chemical potential of vapor is lower than the threshold value, the first (closest to the origin of the drop size axis) extremum of the work of drop formation is a minimum, and the activation barrier of nucleation is determined by the difference between the maximal and minimal works of formation [10].

Note that the analytical theory developed in this communication (and based on the perturbation theory) does not let us correctly calculate the position of the minimum point for the work of the drop formation or the threshold chemical potential of vapor. However, our theory enables us to find corrections both to the critical size of the drop and to the work associated with the formation of the critical drop (corrections to the maximum of the drop formation work). These results are sufficient for describing the nucleation process in the case when the drop-size-dependent contribution to the electric energy of the drop W_{el} is relatively small. In this case, the maximal chemical potential of the drop and, even more so, the minimal work of formation correspond to a drop whose size is smaller than that of the foreign particle. Evidently, nucleation is homogeneous in this case (as follows, for example, from the table, this is the case of molecular condensation centers) [10].

The critical drop size v_c for the given chemical potential of vapor b is determined as the root of the equation

$$b_v|_{v=v_c} = b. \quad (62)$$

If we solve this equation according to the perturbation theory with the use of (60) and (58), we find

$$v_c = v_{c_0} \times \left\{ 1 - 2 \frac{\epsilon^\alpha + 2\epsilon^\beta}{\epsilon^\alpha - 4\epsilon^\beta} \epsilon_0^2 - \frac{8}{15} \left[10 \left(\frac{\epsilon^\alpha + 2\epsilon^\beta}{\epsilon^\alpha - 4\epsilon^\beta} \right)^2 - 1 \right] \epsilon_0^4 \right\}, \quad (63)$$

where $v_{c_0} = (2a/3b)^3$ is the critical size of the drop in the theory of homogeneous nucleation in the absence of a field induced by the condensation center, and $\epsilon_0 \equiv \epsilon|_{v=v_{c_0}}$. Apparently, if a drop contains a foreign particle with its electric field being that of a dipole, the presence of this particle reduces the critical size of the drop.

Substituting (63) into (56) and using (58), we find the work of formation for a critical-sized drop:

$$(F)_{v_c} = (F_0)_{v_{c_0}} + \left\{ a v_{c_0}^{2/3} \left[\frac{4(\epsilon^\alpha + 2\epsilon^\beta)}{9(\epsilon^\alpha - 4\epsilon^\beta)} \epsilon_0^2 - \frac{2}{45} \left(-10 \left(\frac{\epsilon^\alpha + 2\epsilon^\beta}{\epsilon^\alpha - 4\epsilon^\beta} \right)^2 + 1 \right) \epsilon_0^4 \right] + C \right\}, \quad (64)$$

where $(F_0)_{v_{c_0}} = a v_{c_0}^{2/3} / 3$ is the work of formation for a critical-sized drop in the case of homogeneous nucleation. As is apparent from (52), (55), and (57), the sum in braces in the right-hand part of (64) is negative.

Thus, the presence of a condensation center with its electric field being that of a dipole also reduces the work of formation for a critical-sized drop.

CONCLUSION

When studying the formation of a liquid-phase nucleus at a charged foreign particle with a much smaller size than that of critical nuclei, researchers usually neglect the contributions of the dipole and higher electric moments to the electric field of the particle in comparison with the predominant contribution of the monopole. For uncharged condensation centers, where the monopole contribution is absent but the electric dipole moment is significant, we should consider the contribution to the thermodynamic characteristics of nucleation that is due to the dipole of the particle.

Our analysis shows that the description of nucleation thermodynamics in the axisymmetrical field of the central dipole requires simultaneous solution of equations for the drop surface shape and for the electric potential. The drop-size-dependent electric contribution to the work of the drop formation was small compared to the work of the surface formation; this fact enabled us to use an iterative method for finding the equation of the equilibrium surface shape, the chemical potential, and the work of the drop formation in the form of expansions in powers of the small parameter ϵ^2 .

With a degree of accuracy up to terms of the ϵ^2 order, the surface of the drop in the field of the central dipole is an oblate spheroid, and ϵ plays the role of its eccentricity. The chemical potential and the work of the drop formation in this approximation remain the same as they would for a spherical drop in the field of the central dipole. If we make allowance for terms of the ϵ^4 order, the surface of the drop no longer remains a spheroid. The chemical potential and the work of the drop formation in this approximation depend on the nonsphericity of the drop.

ACKNOWLEDGMENTS

This work was partially supported by the International Science Foundation, project no. s953.

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