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The work of droplet formation on a charged condensation nucleus exposed to an external electric field

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Abstract

The analytical formulas for the work of droplet formation and the chemical potential in the droplet formed out of supersaturated vapor around the charged nucleus exposed to the external electric field have been derived. As an effect of combined electric fields, the formulas obtained take into account the acceleration as a whole of the droplet with the charged nucleus by the field, the displacement of the nucleus out of the center of the droplet mass and the resulting deformation of the droplet shape.
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1. Introduction

By now various aspects of droplet formation in the central field of a charged condensation nucleus, especially ion-induced nucleation, brought up since famous works of Wilson [1], have been elaborated by many investigators [2–6] both experimentally and theoretically. A related problem of the influence of the external electric field on thermodynamics of nucleation has also been actively considered in literature [7–13]. However, the combined effects of two, external and internal, electric fields have received little attention, although the joint appearance of both fields is rather typical in experiments on ion-induced nucleation [5,6]. External electric field is used in these experiments to separate positive and negative ions and to transport them into the nucleation zone in the experimental chamber. These combined effects are not just a sum of separate effects of internal and external fields since they cause the displacement of the condensation nucleus inside the forming droplet, acceleration of the droplet as whole, and distortion of the equilibrium droplet shape out of sphere. Breaking the spherical symmetry of the nucleating droplet and arising of additional inertia forces considerably complicate the standard thermodynamic approach to finding the thermodynamic characteristics of nu-

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cleation. The scheme of the improved approach which allows one to describe the effects of the combined fields in the thermodynamics of nucleation by means of solving the equation for the droplet profile was given in [14,15]. However, the paper [14] considered the specific situation with the condensation nucleus located at the mass center of the droplet formed, while the most typical is the situation with the nucleus shifted out of the center. The formalism has been modified in [15] to describe numerically the nonlinear effects of the external electric field with account for nuclear shift in the droplet. Here we present an analytical approach to general situation of condensation on an accelerated charged nucleus exposed to the external uniform electric field which is based on finding the expression for the work of droplet formation within the principles of thermodynamics of heterogeneous nucleation.

2. Basic expression for the work of droplet formation

Let a microscopic conducting nucleus of condensation with the mass m and the electric charge q is immersed in a gaseous surroundings (phase β with the dielectric permittivity ε^β) consisting of the supersaturated vapor and passive gas-carrier in external electric field with the intensity E_∞. We consider formation of a rather small incompressible dielectric droplet with the volume V (the nuclear volume is negligible as against V) and the number v of condensing molecules of the liquid (phase α with the dielectric permittivity ε^α). Taking into account the small size of the condensing droplet, we will assume that the external electric field is practically uniform and does not produce any hydrodynamic fluxes inside the droplet during its formation.

Let us write the minimal work W of droplet formation as:

$$W = -(\mu^\beta - \mu_\infty)v + W_s + W_{el} + W_{add} \qquad (2.1)$$

where μ^β and μ_∞ are the chemical potentials of molecules in the present vapor and in the equilibrium system liquid–vapor with flat interface (here and below the upper indices α and β show

that corresponding quantity refers to the liquid or gaseous phase, respectively), W_s is the work of formation of the droplet surface, W_{el} is the work of electrostatic forces at transferring the charged nucleus out the gaseous medium into the considered droplet, W_{add} is the work of some additional forces arising under joint influence of the electric fields and associated with the inertia forces. Because the nucleus is much smaller than the droplet, we omit in (2.1) the term related to the work of short-range wetting. Nevertheless the work of long-range wetting due to the charge of the nucleus is here taken into account by term W_{el}. The expression (2.1) agrees with the principles of thermodynamics of heterogeneous nucleation.

To continue we need to consider an appropriate coordinate system. It is convenient to choose the spherical coordinate system with the center located inside the droplet and the polar axis of the system directed along the symmetry axis of the droplet in the electric field (parallel to the intensity vector of the external uniform electric field). Let the system be centered on the nucleus in the initial state before the droplet formation. After the formation process the origin of the coordinate system may be chosen in the final state as well on the nucleus as at the center of the droplet mass. We will see that the results for the work of droplet formation and the chemical potential of the molecule in the droplet are independent of that choice for the final state. The term W_s for a non-spherical droplet surface in the formation work W can be represented in the coordinate system chosen as:

$$W_s = 2\pi\gamma \int_{-1}^{1} a\sqrt{a^2 + (1 - x^2)a_x^2}dx. \qquad (2.2)$$

Here we use the variable $x \equiv \cos\theta$ instead of the asymuth angle θ, γ is the surface tension for the liquid–vapor interface (considering the droplet as large enough, we assume that γ is a scalar quantity independent of electric field), $a(x)$ is the droplet profile, a_x is the derivative of the droplet profile with respect to variable x.

The work of electrostatic forces W_{el} depends on the charge q of the condensation nucleus and on the external electric field intensity E_∞. We may suppose (as it was shown in detail in [9]) that the external electric field is produced by a system of

charges, which are distributed with density:

$$\sigma(x) = (3\varepsilon^\beta / 4\pi) E_\infty x \qquad (2.3)$$

over the large enough sphere with radius R_σ around the center of the coordinate system. In this case the work W_{el} can be written as:

$$W_{el} = \frac{1}{2} q(\Phi_2^\alpha - \Phi_1^\beta)|_{S_n} - \pi R_\sigma^2 \int_{-1}^{1} dx \sigma(x)$$

$$\times (\Phi_2^\beta(R_\sigma, x) - \Phi_1^\beta(R_\sigma, x)) \qquad (2.4)$$

where Φ^α and Φ^β are the electric potentials taken at the location of the charges on the nucleus (at the conducting sphere S_n with radius R_n) and on the sphere with radius R_σ, indices 1 and 2 refer to the initial state (without the droplet) and to the final state (with the droplet), correspondingly.

If the droplet moves with the acceleration w in the direction of the applied external field then the droplet and the nucleus in the final state are exposed to the inertia force. In this case, the work W_{add} equals the work of the inertia force to shift the condensation nucleus and the center of the liquid mass away from the center of the coordinate system. Because the nuclear volume is considered negligible as against the droplet volume, the nuclear radius R_n is much smaller than $a(x)$, and we can write:

$$W_{add} = mwh + \frac{1}{2} \pi \rho^\alpha w \int_{-1}^{1} xa^4(x) dx \qquad (2.5)$$

where ρ^α is the mass density of the liquid phase and h is the displacement of the nucleus along the polar axis. The term W_{add} equals zero in the case of the coordinate system located at the center of mass of the whole droplet.

If the gravity force and the gas-resistance force are negligible against as the force from the external electric field with intensity E_∞ acting through the charged nucleus on the droplet, the resulting acceleration w of the droplet can be written as:

$$w = qE_\infty / (M + m) \qquad (2.6)$$

where $M = \rho^\alpha V$ is the mass of the liquid in the droplet.

3. The formulas for the electric potentials

The electric potentials Φ_1^β and Φ_2^β in the initial and the final state of the system can be written at the arbitrary point on the external sphere of radius R_σ in the form:

$$\Phi_1^\beta(R_\sigma, x) = q/\varepsilon^\beta R_\sigma - E_\infty R_\sigma x, \qquad (3.1)$$

$$\Phi_2^\beta(R_\sigma, x) = q/\varepsilon^\beta R_\sigma - E_\infty R_\sigma x + \mathscr{P}x/\varepsilon^\beta R_\sigma^2 \qquad (3.2)$$

where $\mathscr{P}$ is the resulting dipole moment of the whole droplet (we omit the terms with highest multipoles in (3.2) as $R_\sigma \to \infty$). In view of (3.1), (3.2), and (2.3), the formula (2.4) for the contribution W_{el} can be simplified as:

$$W_{el} = \frac{1}{2} q(\Phi_2^\alpha - \Phi_1^\beta)|_{S_n} - \frac{1}{2} E_\infty \mathscr{P}. \qquad (3.3)$$

Whereas the potential $\Phi_1^\beta|_{S_n}$ in the initial state can be easily determined as:

$$\Phi_1^\beta|_{S_n} = \frac{q}{\varepsilon^\beta R_n}, \qquad (3.4)$$

in order to find the potential $\Phi_2^\alpha(r, x)$ and the resulting dipole moment $\mathscr{P}$ in (3.3) one needs to solve the Laplace equation for the electric potential with the boundary conditions at the droplet surface;

$$\Delta \Phi_2^{\alpha,\beta} = 0, \qquad (3.5)$$

$$\Phi_2^\alpha|_S = \Phi_2^\beta|_S,$$
$$\varepsilon^\alpha (\nabla \Phi_2^\alpha, \vec{n})|_S = \varepsilon^\beta (\nabla \Phi_2^\beta, \vec{n})|_S \qquad (3.6)$$

where index S refers to the location at the droplet surface, $\vec{n}$ is the unity vector of external normal to the droplet surface. In the coordinate system adopted the conditions (3.6) have the form;

$$\Phi_2^\alpha(a(x), x) - \Phi_2^\beta(a(x), x) = 0, \qquad (3.7)$$

$$[\varepsilon^\alpha(a^2\Phi_{2r}^\alpha - (1-x^2)a_x\Phi_{2x}^\alpha)$$
$$- \varepsilon^\beta(a^2\Phi_{2r}^\beta - (1-x^2)a_x\Phi_{2x}^\beta)]|_{r=a(x)}$$
$$= 0 \qquad (3.8)$$

where the lower indices x and r denote the derivatives of the corresponding quantities with respect to variables x and r.

Potential Φ_2^α can be represented in the form

$$\Phi_2^\alpha(r,\ x) \equiv \Phi_{2q}^\alpha(r,\ x) + \Phi_{2R}^\alpha(r,\ x), \tag{3.9}$$

where Φ_{2q}^α the Coulomb potential for the charge q and $\Phi_{2R}^\alpha(r,\ x)$ is the reaction potential. At $r > h$ the potential Φ_{2q}^α can be written as the decomposition in Legendre's polynomials $P_k(x)$,

$$\Phi_{2q}^\alpha = \frac{q}{\varepsilon^\alpha} \sum_{k \geq 0} \frac{h^k}{r^{k+1}}\ P_k(x). \tag{3.10}$$

At the location of the nucleus we assume (with the same accuracy as in (3.4));

$$\Phi_{2q}^\alpha|_{S_n} = \frac{q}{\varepsilon^\alpha R_n}. \tag{3.11}$$

The droplet without the external field is a sphere and the condensation nucleus is located at the center of this sphere. If the intensity E_∞ of the external field is not high or the size of the droplet is small, then droplet deformation from the spherical shape as well as the displacement h of the condensation nucleus along the polar axis within the droplet will be relatively small. In consequence, quantities $a(x)$, $\Phi_2^\alpha(r,\ x)$ and $\Phi_2^\beta(r,\ x)$ can be represented as decomposition in E_∞ (in fact, it is a decomposition in a small parameter associated with E_∞, but for the sake of simplicity we will call the orders of the decomposition as orders in E_∞) where the coefficients themselves are the series in Legendre's polynomials $P_k(x)$. Bearing this in mind, we can write as $R_\sigma \to \infty$:

$$a(x) = \sum_{i \geq 0} E_\infty^i \sum_{k=0}^{i} d_k^{(i)} P_k(x), \tag{3.12}$$

$$\Phi_{2R}^\alpha(r,\ x) = \sum_{i \geq 0} E_\infty^i \sum_{k=0}^{i} c_k^{(i)} r^k P_k(x), \tag{3.13}$$

$$\Phi_2^\beta(r,\ x) = q/\varepsilon^\beta r - E_\infty r x + \sum_{i=1}^{\infty} E_\infty^i \sum_{k=0}^{i}$$
$$\times \frac{b_k^{(i)}}{r^{k+1}}\ P_k(x). \tag{3.14}$$

The decomposition coefficients $\{d_k^{(i)}\}$, $\{c_k^{(i)}\}$, and $\{b_k^{(i)}\}$ $(i = 0, 1, \ldots; k = 0, \ldots, i)$ in (3.12)–(3.14) can be determined with the help of an perturbative procedure which will be considered in Sections 5

and 6. In particular, comparing (3.14) with (3.2) allows us to provide a relationship for $\mathscr{P}$ in the form:

$$\mathscr{P} = \varepsilon^\beta \sum_{i=1}^{\infty} b_1^{(i)} E_\infty^i. \tag{3.15}$$

4. The generating properties of the work of droplet formation

Let us consider the generating properties of the work W of the droplet formation as a function of the number of molecules in the droplet, the charge q of the condensation nucleus, the external electric field intensity E_∞, and the displacement h of the condensation nucleus within the droplet. These properties are related to the thermodynamic meaning of quantity W. Because quantity W is the minimal work under specific conditions of droplet formation and thus may be expressed through the thermodynamic potentials which are appropriate for these conditions, the generating properties of the work W are the consequences of that for the thermodynamic potentials.

It is convenient to determine the radius R of the sphere which is equivalent in volume to the droplet, so that:

$$V = 4\pi R^3/3. \tag{4.1}$$

Assuming the liquid in the droplet to be incompressible, one obtains an additional condition on the droplet profile $a(x)$,

$$\int_{-1}^{1} (a^3(x) - R^3) dx = 0. \tag{4.2}$$

In view of (4.1) the number v of molecules in the droplet is related to the effective radius R as:

$$v = 4\pi R^3/3v^\alpha \tag{4.3}$$

where v^α is the volume per molecule in the liquid phase.

Below we will assume that the relaxation of the droplet profile to an equilibrium one for a fixed number v of molecules in the droplet is faster than the rate of change of this number due to evapora-

tion and condensation processes. As a result, the work W of droplet formation can be considered as a function of the number v only (so-called one-path nucleation). Then one can find the chemical potential μ_v of the molecule in the droplet using the relation;

$$\left.\frac{\partial W}{\partial v}\right|_{\mu^\beta} = \mu_v - \mu^\beta. \tag{4.4}$$

Another relation, the condition of minimum of the work W with respect to h,

$$\left.\frac{\partial W}{\partial h}\right|_{E_\infty, q, R, \mu^\beta} = 0, \tag{4.5}$$

allows one to determine the displacement h.

As it was noted in [14], in addition to formulas (4.4) and (4.5), there are also the generating formulas for the electric potentials Φ_2^α, Φ_1^β on the nuclear surface, and the resulting dipole moment $\mathscr{P}$. In the case of accelerated droplets these formulas have the form:

$$\left.\left(\frac{\partial W}{\partial q} - \frac{\partial W_{add}}{\partial w}\frac{\partial w}{\partial q}\right)\right|_{E_\infty, R, \mu^\beta} = (\Phi_2^\alpha - \Phi_1^\beta)|_{S_n}, \tag{4.6}$$

$$\left.\left(\frac{\partial W}{\partial E_\infty} - \frac{\partial W_{add}}{\partial w}\frac{\partial w}{\partial E_\infty}\right)\right|_{q, R, \mu^\beta} = -\mathscr{P}. \tag{4.7}$$

5. The coordinate system centered on the nucleus

Let us first consider in the final state of the droplet formation the coordinate system centered on the nucleus. This is a natural choice of the coordinate system coinciding with the coordinate system in the initial state. In this system the nuclear displacement in the droplet equals zero and we will understand h as a distance between the condensation nucleus and the center of the liquid mass in the droplet. Assuming $h > 0$, we have:

$$\frac{1}{2}\pi\rho^\alpha \int_{-1}^{1} xa^4(x)dx = -Mh, \tag{5.1}$$

and, in view of (2.5), the contribution W_{add} equals:

$$W_{add} = -Mwh. \tag{5.2}$$

Substituting (3.12) into (4.2) and (5.1) and recognizing $M = \rho^\alpha 4\pi R^3/3$, one can find in first two orders in E_∞:

$$a(x) = R - hx - \frac{h^2}{3R} + d_2^{(2)}P_2(x)E_\infty^2 + O(E_\infty^3), \tag{5.3}$$

where the explicit form of coefficient $d_2^{(2)}$ in the decomposition of the droplet profile is not needed within the accuracy considered. Then, substituting (5.3) and (3.9), (3.10), (3.13), (3.14) in (3.7), (3.8) allows us to determine potentials Φ_{2R}^α and Φ_2^β with the same accuracy as:

$$\Phi_R^\alpha(r,\ x) = \frac{q(\varepsilon^\alpha - \varepsilon^\beta)}{\varepsilon^\alpha\varepsilon^\beta R} + \left(\frac{2q(\varepsilon^\alpha - \varepsilon^\beta)h}{\varepsilon^\alpha R^3} - 3\varepsilon^\beta E_\infty\right)$$

$$\times \frac{rx}{\varepsilon^\alpha + 2\varepsilon^\beta} +$$

$$+ \frac{(\varepsilon^\alpha - \varepsilon^\beta)(2qh + \varepsilon^\alpha R^3 E_\infty)h}{\varepsilon^\alpha(\varepsilon^\alpha + 2\varepsilon^\beta)R^3}$$

$$+ \frac{q(\varepsilon^\alpha - \varepsilon^\beta)(4h^2 - 3d_2^{(2)}RE_\infty^2)}{\varepsilon^\alpha(2\varepsilon^\alpha + 3\varepsilon^\beta)R^5}\ r^2 P_2(x) +$$

$$+ O(E_\infty^3), \tag{5.4}$$

$$\Phi_2^\beta(r,\ x) = -E_\infty rx + \frac{q}{\varepsilon^\beta r} + \frac{(\varepsilon^\alpha - \varepsilon^\beta)(\varepsilon^\beta R^3 E_\infty - qh)}{\varepsilon^\beta(2\varepsilon^\beta + \varepsilon^\alpha)}$$

$$\times \frac{x}{r^2} +$$

$$+ (\varepsilon^\alpha - \varepsilon^\beta)$$

$$\times \left(\frac{2q(2\varepsilon^\alpha + \varepsilon^\beta)h^2}{3\varepsilon^\beta(\varepsilon^\alpha + 2\varepsilon^\beta)(2\varepsilon^\alpha + 3\varepsilon^\beta)} - \frac{2R^3 hE_\infty}{\varepsilon^\alpha + 2\varepsilon^\beta}\right.$$

$$\left. + \frac{2qd_2^{(2)}RE_\infty^2}{\varepsilon^\beta(2\varepsilon^\alpha + 3\varepsilon^\beta)}\right) \times$$

$$\times \frac{P_2(x)}{r^3} + O(E_\infty^3). \tag{5.5}$$

Reducing (5.4) to $\Phi_{2R}^\alpha|_{S_n}$ by assigning $r = 0$ and $x = 1$, taking as $\mathscr{P}$ the coefficient before $x/\varepsilon^\beta r^2$ in (5.5) as $\mathscr{P}$, we obtain:

$\Phi^{\alpha}_{2R}\big|_{r=0,x=1}$

$$= \left(\frac{1}{\varepsilon^{\beta}} - \frac{1}{\varepsilon^{\alpha}}\right)\frac{q}{R} + \frac{(\varepsilon^{\alpha} - \varepsilon^{\beta})hE_{\infty}}{\varepsilon^{\alpha} + 2\varepsilon^{\beta}} + \frac{2q(\varepsilon^{\alpha} - \varepsilon^{\beta})h^2}{\varepsilon^{\alpha}(\varepsilon^{\alpha} + 2\varepsilon^{\beta})R^3}$$

$$+ O(E^4_{\infty}), \tag{5.6}$$

$$\mathscr{P} = \frac{(\varepsilon^{\alpha} - \varepsilon^{\beta})(\varepsilon^{\beta}R^3E_{\infty} - qh)}{(\varepsilon^{\alpha} + 2\varepsilon^{\beta})}. \tag{5.7}$$

Let us find $\Phi^{\alpha}_2\big|_{S_n}$ with the help of (3.9), (3.11), and (5.6). Substituting the resulting relationship, (5.2) and (5.7) into (3.3), using (5.3) in (2.2) allows us to derive the final expression for the work of droplet formation. In view of (2.1) we have;

$$W = -(\mu^{\beta} - \mu_{\infty})v + 4\pi\gamma R^2 + \left(\frac{1}{\varepsilon^{\beta}} - \frac{1}{\varepsilon^{\alpha}}\right)\frac{q^2}{2}$$

$$\times \left(\frac{1}{R} - \frac{1}{R_n}\right) -$$

$$- \frac{\varepsilon^{\beta}(\varepsilon^{\alpha} - \varepsilon^{\beta})R^3E^2_{\infty}}{2(\varepsilon^{\alpha} + 2\varepsilon^{\beta})} + \frac{q(\varepsilon^{\alpha} - \varepsilon^{\beta})hE_{\infty}}{\varepsilon^{\alpha} + 2\varepsilon^{\beta}}$$

$$+ \frac{q(\varepsilon^{\alpha} - \varepsilon^{\beta})h^2}{\varepsilon^{\alpha}(\varepsilon^{\alpha} + 2\varepsilon^{\beta})R^3} -$$

$$- Mwh + O(E^4_{\infty}). \tag{5.8}$$

Solution of equation (4.5) in view of (5.8) and (2.6) with respect to h gives:

$$h = \left(3 - \frac{m(\varepsilon^{\alpha} - \varepsilon^{\beta})}{M\varepsilon^{\beta}}\right)\frac{M\varepsilon^{\alpha}\varepsilon^{\beta}R^3E_{\infty}}{2q(M + m)(\varepsilon^{\alpha} - \varepsilon^{\beta})}$$

$$+ O(E^3_{\infty}). \tag{5.9}$$

Now, substituting (5.9) back into (5.8) allows us to rewrite the formula for the work W of droplet formation in the final form:

$$W = -(\mu^{\beta} - \mu_{\infty})v + 4\pi\gamma R^2 + \left(\frac{1}{\varepsilon^{\beta}} - \frac{1}{\varepsilon^{\alpha}}\right)\frac{q^2}{2}$$

$$\times \left(\frac{1}{R} - \frac{1}{R_n}\right) -$$

$$- \frac{E^2_{\infty}R^3}{4}\frac{\left[(\varepsilon^{\alpha} - \varepsilon^{\beta})\dfrac{m}{M} - \varepsilon^{\beta}\right]^2 + 2\varepsilon^{\alpha}\varepsilon^{\beta}}{(\varepsilon^{\alpha} - \varepsilon^{\beta})\left(1 + \dfrac{m}{M}\right)^2} + O(E^4_{\infty}). \tag{5.10}$$

The corresponding formula for the chemical potential μ_v of the molecule in the droplet is derived from (4.4) and (5.10) in view of $M = \rho^{\alpha}4\pi R^3/3$ and (4.3) as:

$$\mu_v = \mu_{\infty} + \frac{2\gamma v^{\alpha}}{R} - \left(\frac{1}{\varepsilon^{\beta}} - \frac{1}{\varepsilon^{\alpha}}\right)\frac{v^{\alpha}q^2}{8\pi R^4} - 3$$

$$\times \frac{(2\varepsilon^{\alpha} + \varepsilon^{\beta})\varepsilon^{\beta}\left(3\dfrac{m}{M} + 1\right)v^{\alpha}}{16\pi(\varepsilon^{\alpha} - \varepsilon^{\beta})\left(1 + \dfrac{m}{M}\right)^3}E^2_{\infty} +$$

$$+ 3\frac{\left[\varepsilon^{\alpha} + 3\varepsilon^{\beta} - (\varepsilon^{\alpha} - \varepsilon^{\beta})\dfrac{m}{M}\right]\dfrac{m^2}{M^2}v^{\alpha}}{16\pi\left(1 + \dfrac{m}{M}\right)^3}E^2_{\infty} + O(E^4_{\infty}). \tag{5.11}$$

Finally with the help of (3.4), (3.9), (3.11), and (5.10) it can be easily checked that equations (5.6) and (5.7) satisfy formulas (4.6) and (4.7).

6. The results for the coordinate system of the droplet center of mass

Let now the origin of the coordinate system in the final state of the droplet formation coincide with the droplet center of mass (i.e. the center of droplet + nucleus mass). Evidently we have in this case $W_{add} = 0$ and the displacement h of the nucleus in this system is non-zero. Correspondingly equation (2.5) gives:

$$mh = -\frac{1}{2}\pi\rho^{\alpha}\int_{-1}^{1}xa^4(x)dx. \tag{6.1}$$

Substituting (3.12) into (4.2) and (6.1), one can find in two first orders in E_{∞}:

$$a(x) = R - \frac{mhx}{M} - \frac{m^2 h^2}{3RM^2} + d_2^{(2)} P_2(x) E_\infty^2$$
$$+ O(E_\infty^3), \tag{6.2}$$

where the explicit form of coefficient $d_2^{(2)}$ in the decomposition of the droplet profiles is not needed as in the previous case within the accuracy considered. Then, substituting (6.2) and (3.9), (3.10), (3.13), (3.14) in (3.7), (3.8) allows us to determine potentials Φ_{2R}^α and Φ_2^β with the same accuracy as:

$$\Phi_{2R}^\alpha(r,\ x) = \frac{(\varepsilon^\alpha - \varepsilon^\beta)q}{\varepsilon^\alpha \varepsilon^\beta R}$$
$$+ \left[\frac{2(\varepsilon^\alpha - \varepsilon^\beta)(M+m)qh}{\varepsilon^\alpha R^3 M} - 3\varepsilon^\beta E_\infty \right]$$
$$\times \frac{rx}{2\varepsilon^\beta + \varepsilon^\alpha} +$$
$$+ \frac{m(\varepsilon^\alpha - \varepsilon^\beta)h}{M(2\varepsilon^\beta + \varepsilon^\alpha)} \left[\frac{2(M+m)qh}{\varepsilon^\alpha R^3 M} + E_\infty \right]$$
$$+ \frac{(\varepsilon^\alpha - \varepsilon^\beta)q}{\varepsilon^\alpha (2\varepsilon^\alpha + 3\varepsilon^\beta) R^4} \times$$
$$\times \left[\frac{(3M^2 + 6mM + 4m^2)h^2}{RM^2} - 3d_2^{(2)} E_\infty^2 \right] r^2 P_2(x)$$
$$+ O(E_\infty^3), \tag{6.3}$$

$$\Phi_2^\beta(r,\ x) = -E_\infty rx + \frac{q}{\varepsilon^\beta r}$$
$$+ \left[\left(3 - \frac{m}{M} \frac{\varepsilon^\alpha - \varepsilon^\beta}{\varepsilon^\beta} \right) qh \right.$$
$$\left. + (\varepsilon^\alpha - \varepsilon^\beta) R^3 E_\infty \right] \times$$
$$\times \frac{x}{(2\varepsilon^\beta + \varepsilon^\alpha) r^2}$$
$$+ \left[\left\{ 5 - \frac{2m(\varepsilon^\alpha - \varepsilon^\beta)}{3M(2\varepsilon^\beta + \varepsilon^\alpha)} \left(3 - \frac{m(2\varepsilon^\alpha + \varepsilon^\beta)}{M\varepsilon^\beta} \right) \right\} \right]$$
$$\times \frac{qh^2}{2\varepsilon^\alpha + 3\varepsilon^\beta} -$$

$$- \frac{2mR^3(\varepsilon^\alpha - \varepsilon^\beta)hE_\infty}{M(2\varepsilon^\beta + \varepsilon^\alpha)} + \frac{2qR(\varepsilon^\alpha - \varepsilon^\beta)d_2^{(2)} E_\infty^2}{\varepsilon^\beta (2\varepsilon^\alpha + 3\varepsilon^\beta)} \right] \frac{P_2(x)}{r^3}$$
$$+ O(E_\infty^3). \tag{6.4}$$

Reducing (6.3) to $\Phi_{2R}^\alpha|_{S_n}$ by assigning $r = h$ and $x = 1$, taking the coefficient before $x/\varepsilon^\beta r^2$ in (6.4) as $\mathscr{P}$, we obtain:

$$\Phi_{2R}^\alpha|_{S_n} = \left(\frac{1}{\varepsilon^\beta} - \frac{1}{\varepsilon^\alpha} \right) \frac{q}{R} - \left[3 - \frac{m(\varepsilon^\alpha - \varepsilon^\beta)}{M\varepsilon^\beta} \right]$$
$$\times \frac{\varepsilon^\beta hE_\infty}{2\varepsilon^\beta + \varepsilon^\alpha} +$$
$$+ \frac{2(\varepsilon^\alpha - \varepsilon^\beta)(M+m)^2 qh^2}{R^3 M^2 \varepsilon^\alpha (2\varepsilon^\beta + \varepsilon^\alpha)} + O(E_\infty^4), \tag{6.5}$$
$$\mathscr{P} = \frac{\varepsilon^\beta (\varepsilon^\alpha - \varepsilon^\beta) R^3 E_\infty}{2\varepsilon^\beta + \varepsilon^\alpha} + \left[3 - \frac{m(\varepsilon^\alpha - \varepsilon^\beta)}{M\varepsilon^\beta} \right] \frac{\varepsilon^\beta qh}{2\varepsilon^\beta + \varepsilon^\alpha}$$
$$+ O(E_\infty^3). \tag{6.6}$$

The formula for $\Phi_2^\alpha|_{S_n}$ can be easily found with the help of (3.9), (3.11), and (6.5). Substituting the resulting relationship and (6.6) into (3.3) and using (6.2) in (2.2) allow us to derive the final expression for the work of droplet formation. Then in view of (2.1) together with (2.2) and (3.3) we have:

$$W = -(\mu^\beta - \mu_\infty)\nu + 4\pi\gamma R^2 + \left(\frac{1}{\varepsilon^\beta} - \frac{1}{\varepsilon^\alpha} \right) \frac{q^2}{2}$$
$$\times \left(\frac{1}{R} - \frac{1}{R_n} \right) -$$
$$- \frac{\varepsilon^\beta (\varepsilon^\alpha - \varepsilon^\beta) R^3 E_\infty^2}{2(2\varepsilon^\beta + \varepsilon^\alpha)} - \left[3 - \frac{m(\varepsilon^\alpha - \varepsilon^\beta)}{M\varepsilon^\beta} \right] \frac{\varepsilon^\beta qhE_\infty}{2\varepsilon^\beta + \varepsilon^\alpha} +$$
$$+ \frac{(\varepsilon^\alpha - \varepsilon^\beta)(M+m)^2 q^2 h^2}{R^3 M^2 \varepsilon^\alpha (2\varepsilon^\beta + \varepsilon^\alpha)} + O(E_\infty^4). \tag{6.7}$$

Substituting (6.7) in (4.5) and solving the resulting equation for h gives:

$$h = \left[3 - \frac{m(\varepsilon^\alpha - \varepsilon^\beta)}{M\varepsilon^\beta} \right] \frac{\varepsilon^\alpha \varepsilon^\beta M^2 R^3 E_\infty}{2q(\varepsilon^\alpha - \varepsilon^\beta)(M+m)^2}$$
$$+ O(E_\infty^3). \tag{6.8}$$

Now, substituting (6.8) back into (6.7) allows us to rewrite the formula for the work W of droplet formation again in the form of (5.10).

Thus the corresponding formula for the chemical potential μ_v of the molecule in the droplet which is derived from (4.4) and (5.10) in view of $M = \rho^\alpha 4\pi R^3/3$ and (4.3) is the same as in (5.11). This confirms what was said in Section 2 about the independence of the results for the work of droplet formation and the chemical potential of the molecule in the droplet on the choice for the origin of the coordinate system in the final state of droplet formation. Even though, evidently, the droplet profiles are different in the coordinate systems which have been considered here in Sections 5 and 6, the difference is not essential for thermodynamics of nucleation within the accuracy used to obtain these formulas.

Finally with the help of equations (4.6), (4.7) and (5.10) we obtain:

$$\Phi^\alpha_{2R}\big|_{S_n} = \left(\frac{1}{\varepsilon^\beta} - \frac{1}{\varepsilon^\alpha}\right)\frac{q}{R}, \tag{6.9}$$

$$\mathscr{P} = \frac{\left[(\varepsilon^\alpha - \varepsilon^\beta)\dfrac{m}{M} - \varepsilon^\beta\right]^2 + 2\varepsilon^\alpha\varepsilon^\beta}{2(\varepsilon^\alpha - \varepsilon^\beta)\left(1 + \dfrac{m}{M}\right)^2} \; R^3 E_\infty. \tag{6.10}$$

It can be easily proved with the help of (3.4), (3.9), (3.11), and (6.8) that formulas (6.5) and (6.6) coincide with (6.9) and (6.10), respectively.

7. Discussion

The formulas (5.10) and (5.11) for the work of droplet formation W and the chemical potential of condensate μ_v present the main result of this note. If the ratio m/M of the nuclear mass to the droplet mass is very small then these formulas can be rewritten in the most simple form as:

$$W = -(\mu^\beta - \mu_\infty)v + 4\pi\gamma R^2 + \left(\frac{1}{\varepsilon^\beta} - \frac{1}{\varepsilon^\alpha}\right)\frac{q^2}{2}$$

$$\times \left(\frac{1}{R} - \frac{1}{R_n}\right) -$$

$$-\frac{\varepsilon^\beta(2\varepsilon^\alpha + \varepsilon^\beta)}{4(\varepsilon^\alpha - \varepsilon^\beta)} \; R^3 E_\infty^2 + O(E_\infty^4), \tag{7.1}$$

$$\mu_v = \mu_\infty + \frac{2\gamma v^\alpha}{R} - \left(\frac{1}{\varepsilon^\beta} - \frac{1}{\varepsilon^\alpha}\right)\frac{q^2 v^\alpha}{8\pi R^4}$$

$$-\frac{3\varepsilon^\beta(2\varepsilon^\alpha + \varepsilon^\beta)v^\alpha}{16\pi(\varepsilon^\alpha - \varepsilon^\beta)} \; E_\infty^2 + O(E_\infty^4). \tag{7.2}$$

The accuracy in these formulas is sufficient for an analysis of nucleation in external fields. In view of characteristic small size of condensing droplets the effects of an external field should be considerably smaller than the effects of the internal field of the charged condensation nucleus.

Formulas (5.10) and (5.11) allow one to pass directly to the situation of the central field by setting the intensity E_∞ of the external field to zero. However, there is no transition to the case of single external field by setting $q = 0$ in these formulas. According to formula (23), (18), and (16) in [9], the work of droplet formation and the chemical potential of condensate in homogeneous droplet under external field can be written in our notation as:

$$W = -(\mu^\beta - \mu_\infty)v + 4\pi\gamma R^2 - \frac{\varepsilon^\beta(\varepsilon^\alpha - \varepsilon^\beta)}{2(2\varepsilon^\alpha + \varepsilon^\beta)} \; R^3 E_\infty^2$$

$$+ O(E_\infty^4), \tag{7.3}$$

$$\mu_v = \mu_\infty + \frac{2\gamma v^\alpha}{R} - \frac{3\varepsilon^\beta(\varepsilon^\alpha - \varepsilon^\beta)v^\alpha}{8\pi(2\varepsilon^\alpha + \varepsilon^\beta)} \; E_\infty^2 + O(E_\infty^4).$$

$$\tag{7.4}$$

As one can see (7.3) and (7.4) do not coincide with the corresponding formulas obtained by setting $q = 0$ neither in (5.10) and (5.11) nor in (7.1) and (7.2). This is a consequence of the fact that the displacement h is inversely proportional to the nuclear charge q. Nevertheless the transition to the single external field is possible in (5.8) or (6.7), if one set here $h = 0$ simultaneously with $q = 0$.

These results show that the combined effects of the external uniform and the internal Coulomb field of a charged nucleus in heterogeneous formation of a droplet are not just a sum of effects of the separate fields. Mainly this is due to displacement of the nucleus out of the droplet

center. According to (5.9) and (6.8), this displacement depends on the mass ratio and the dielectric permittivities of the phases in the case of accelerated droplet and can be towards or backwards the vector of external electric field intensity.

Acknowledgements

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