

The effects of external electric field in thermodynamics of formation of dielectric droplet

V.B. Warshavsky, A.K. Shchekin *

Department of Statistical Physics, Research Institute of Physics, St Petersburg State University, Ulyanovskaya 1, Petrodvoretz 198904, Russia

Received 13 May 1998; accepted 9 September 1998

Abstract

The methods of deriving the relations describing the influence of the external electric field on thermodynamic characteristics and shape of a dielectric liquid droplet are considered. It is shown that the uniform external electric field enhances nucleation for a fixed vapor chemical potential due to decreasing the chemical potential per molecule in droplet and the work of droplet formation. The results are obtained by taking into account the axisymmetric prolongation of the droplet in the direction of the external electric field. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Nucleation; Droplet; Electric field; Shape

1. Introduction

There are several approaches to finding the effects of the external electric field on thermodynamics and shape of a dielectric droplet and characteristics of nucleation process in supersaturated vapors [1–4]. Below we present a systematic procedure that allows us to derive analytically all the formulas for thermodynamic quantities of a droplet and nucleation and for the droplet shape in the case of the uniform external electric field. This approach, based on macroscopic electrostatic and thermodynamic equations, can be easily extended to the case of arbitrary nonuniform exter-

nal electric field with axial symmetry, but it is not directly applicable for droplets condensing from very dense or near critical gases. We will discuss also the controversy in results for the formation free energy of a spherical droplet under the uniform electric field obtained earlier by Kashchiev [3] and Isard [4].

2. Basic equations

Let us consider a droplet formed out of the vapor-gas environment (phase β) in the external electric field. Let the droplet consists of ν molecules of an incompressible liquid dielectric (phase α). Hereafter, the indices α and β denote the quantities referred, correspondingly, to the

* Corresponding author. Fax: +7-812-428-7240; e-mail: alexander.shchekin@pobox.spbu.ru.

liquid and the vapor phase. Only one component in these phases is condensable. The effect of the gravity on the droplet is assumed to be negligible.

The equilibrium shape of the droplet in the external electric field is determined by the hydrostatic Laplace formula [5,6]:

$$P_0^\alpha - P_0^\beta - (\sigma_N^\alpha - \sigma_N^\beta) = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right), \quad (1)$$

where the left-hand side represents the difference of normal components of pressure tensor in the liquid and the vapor phases at the droplet surface in presence of the electric field, P_0 is the pressure in the phase in absence of the electric field but under condition that the chemical potential of the system (the droplet and the vapor phase) is equal to the chemical potential of the system in presence of the electric field, γ the surface tension of the condensing liquid, R_1 and R_2 are the principal radii of the surface curvature defined for a given point of the droplet surface. The quantities $\sigma_N^{\alpha,\beta}$ (defined for a given chemical potential of the system) are the normal components of Maxwell's stress tensor on the surface of the droplet from the side of corresponding phase [6]:

$$\sigma_N^{\alpha,\beta} = \frac{\varepsilon^{\alpha,\beta} (E_N^{\alpha,\beta})^2}{4\pi} - \frac{\varepsilon^{\alpha,\beta} (\vec{E}^{\alpha,\beta})^2}{8\pi}. \quad (2)$$

Here ε is the dielectric permittivity, \vec{E} and E_N are the vector of the electric field intensity and its component, which is normal to the droplet surface, respectively.

Equation for the equilibrium shape of the droplet in the external electric field can be written in the spherical coordinate system with the origin at the center of the droplet center of mass as

$$r(\theta) = R + f(\theta), \quad |f(\theta)|/R \ll 1, \quad (3)$$

where θ is the polar angle measured from the direction of the vector of external electric field intensity, $r(\theta)$ the distance from the origin of the coordinate system to a point on the droplet surface, R the radius of the sphere which has the same volume as the droplet, $f(\theta)$ stands for deviation of the droplet surface from spherical shape. We assume that the external field intensity is limited in magnitude and is able to cause only relatively small deviations of the droplet shape

from spherical one (which is consistent with the inequality in Eq. (3)). The volume V_v of the droplet containing v molecules of incompressible liquid equals $V_v = v^\alpha v$ where v^α is the molecular volume of liquid. Thus, evidently, we have

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

Substituting principal curvatures $1/R_1$ and $1/R_2$ expressed in terms of the spherical coordinates with the accuracy up to terms $(f/R)^2$ on the right-hand side of Eq. (1) and substituting Eq. (2) on the left-hand side of Eq. (1), we obtain the following equation for the correction function $f(\theta)$:

$$\begin{aligned} & \frac{2\gamma}{R} - \frac{\gamma}{R^2} \left\{ 2f + \frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{df}{d\theta} \right) \right\} \\ & + \frac{2\gamma}{R^3} \left\{ f^2 + \frac{f}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{df}{d\theta} \right) \right\} \\ & = P_0^\alpha - P_0^\beta + \frac{\varepsilon^\alpha (\vec{E}^\alpha)^2}{8\pi} - \frac{\varepsilon^\beta (\vec{E}^\beta)^2}{8\pi} + \frac{\varepsilon^\beta (E_N^\beta)^2}{4\pi} \\ & - \frac{\varepsilon^\alpha (E_N^\alpha)^2}{4\pi}, \end{aligned} \quad (5)$$

where $(\vec{E}^{\alpha,\beta})^2$ and $(E_N^{\alpha,\beta})^2$ are determined at the point of the droplet surface described by Eq. (3). This equation can be complemented with the boundary conditions for a free droplet:

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

To specify the right-hand side of Eq. (5), we must solve the electrostatic Laplace equation for the electric potential Φ in the droplet-vapor system under the external field applied, with the boundary conditions at the droplet center of mass and at infinity:

$$|\Phi^\alpha|_{r \rightarrow 0} \leq 0, \quad \Phi^\beta \xrightarrow{r \rightarrow \infty} -Er \cos \theta, \quad (6)$$

where r is the radius of the observation point, E the absolute magnitude of the external electric field intensity as $r \rightarrow \infty$. The boundary conditions at the droplet surface are

$$\begin{aligned} \Phi^\alpha|_{r=r(\theta)} &= \Phi^\beta|_{r=r(\theta)} = \varepsilon^\alpha (\vec{n}, \nabla \Phi^\alpha)|_{r=r(\theta)} \\ &= \varepsilon^\beta (\vec{n}, \nabla \Phi^\beta)|_{r=r(\theta)}, \end{aligned} \quad (7)$$

where \vec{n} is the normal vector to the droplet surface.

The approximation of small deviations of the equilibrium droplet shape from sphere allows us to apply an iterative method of simultaneous solution of the Laplace electrostatic equation (with boundary conditions given by Eqs. (6) and (7)) and Eq. (5) for the droplet shape. This approximation is not in fact very restrictive and can be justified by the final result with taking into account the G.I. Taylor instability limit [7].

We will seek the solution of the Laplace electrostatic equation in the form

$$\Phi = \Phi_0 + \delta\Phi, \quad |\delta\Phi| \ll |\Phi_0|, \quad (8)$$

where potential Φ_0 satisfies the electrostatic Laplace equation for the droplet-vapor system with a spherical interface at $r = R$. Potential $\delta\Phi$ owes to non-sphericity of the droplet surface and satisfies the electrostatic Laplace equation with zero boundary conditions at the center and infinity. To obtain the boundary conditions for $\delta\Phi$ at the droplet surface, we need to substitute Eq. (8) into Eq. (7), take into account the Taylor expansion for potential in vicinity of $r = R$ and use the expression for \vec{n} as function of $r(\theta)$. This procedure gives in linear approximation in f and $\delta\Phi$ the following boundary conditions for $\delta\Phi$ at the droplet surface:

$$(\delta\Phi^\alpha - \delta\Phi^\beta)|_R = (1 - \varepsilon^\beta/\varepsilon^\alpha)f(\partial\Phi_0^\beta/\partial r)|_R, \quad (9)$$

$$\begin{aligned} & \left. \frac{\partial}{\partial r}(\varepsilon^\alpha\delta\Phi^\alpha - \varepsilon^\beta\delta\Phi^\beta) \right|_R \\ &= f \left. \frac{\partial^2}{\partial r^2}(\varepsilon^\beta\Phi_0^\beta - \varepsilon^\alpha\Phi_0^\alpha) \right|_R + \frac{\varepsilon^\alpha - \varepsilon^\beta}{R^2} \left. \frac{\partial f}{\partial \theta} \frac{\partial \Phi_0^\beta}{\partial \theta} \right|_R. \end{aligned} \quad (10)$$

Using the relations

$$(\vec{E}^{\alpha,\beta})^2|_{R+f} = (\nabla\Phi^{\alpha,\beta})^2|_{R+f}$$

and

$$(E_N^{\alpha,\beta})^2|_{R+f} = (\nabla\Phi^{\alpha,\beta}, \vec{n})^2|_{R+f}$$

in the right-hand side of Eq. (5), performing the Taylor expansion in the vicinity of $r = R$ and keeping only the terms of order up to $(f/R)^2$, we find

$$\begin{aligned} & \frac{2\gamma}{R} - \frac{\gamma}{R^2} \left\{ 2f + \frac{1}{\sin\theta} \frac{d}{d\theta} \left(\sin\theta \frac{df}{d\theta} \right) \right\} \\ & + \frac{2\gamma}{R^3} \left\{ f^2 + \frac{f}{\sin\theta} \frac{d}{d\theta} \left(\sin\theta \frac{df}{d\theta} \right) \right\} = P_0^\alpha - P_0^\beta \\ & + \frac{(\varepsilon^\alpha - \varepsilon^\beta)}{8\pi} \left\{ \frac{1}{R^2} \left(\frac{\partial\Phi_0^\beta}{\partial\theta} \right)^2 + \frac{\varepsilon^\beta}{\varepsilon^\alpha} \left(\frac{\partial\Phi_0^\beta}{\partial r} \right)^2 \right\} \Big|_R \\ & + \frac{1}{8\pi} \left\{ \frac{2}{R^2} \frac{\partial\Phi_0^\beta}{\partial\theta} \frac{\partial}{\partial\theta} [\varepsilon^\alpha\delta\Phi^\alpha - \varepsilon^\beta\delta\Phi^\beta] \right. \\ & - 2\varepsilon^\beta \frac{\partial\Phi_0^\beta}{\partial r} \left[\frac{\partial\delta\Phi^\alpha}{\partial r} - \frac{\partial\delta\Phi^\beta}{\partial r} \right] \\ & - 2f\varepsilon^\beta \frac{\partial\Phi_0^\beta}{\partial r} \left[\frac{\partial^2\Phi_0^\alpha}{\partial r^2} - \frac{\partial^2\Phi_0^\beta}{\partial r^2} \right] \\ & \left. - \frac{2(\varepsilon^\alpha - \varepsilon^\beta)}{R^3} f \left(\frac{\partial\Phi_0^\beta}{\partial\theta} \right)^2 \right\} \Big|_R. \end{aligned} \quad (11)$$

This is the equation for the droplet shape in its final form. As we will see below, the solution of this equation allows us also to find all the thermodynamic characteristics of the droplet.

3. Expressions for the equilibrium shape of droplet and for the electrostatic potential

One-component vapor-droplet system in an external electric field requires three independent thermodynamic variables for description. Let us choose in the capacity of them the temperature T , the electric field intensity E as $r \rightarrow \infty$, and the number ν of molecules in the droplet (or the droplet radius R). All other thermodynamic characteristics of the droplet will be considered as functions of this set of variables.

We will seek the simultaneous solution of the electrostatic Laplace equation for $\delta\Phi$ and Eq. (11) with the following iterative procedure. Taking into account that non-sphericity of the droplet surface is caused in the first order in small parameter f/R by θ -dependent part of potential Φ_0 , we can solve Eq. (11) in linear approximation neglecting the terms with $\delta\Phi$, f^2 and $f\Phi_0^2$. Substituting the result into the boundary conditions for $\delta\Phi$ given by Eqs. (9) and (10) and solving the electrostatic Laplace equation, we can find the expression for $\delta\Phi$. Finally, substituting the first approximation for f into the third term on the

left-hand side and terms on the right-hand side of Eq. (11), using the expressions for Φ_0 and $\delta\Phi$, we can find the second order correction to the droplet shape.

The requirement of fixed droplet volume for a given number v at ‘turning on’ and ‘turning off’ the external electric field imposes a condition on droplet shape in the form:

$$\int_0^\pi (Rf + f^2) \sin \theta \, d\theta = 0. \quad (12)$$

This condition gives a relationship to find the difference $P_0^\alpha - P_0^\beta$ as a function of the number v of condensate molecules in the droplet and the electric field intensity E . In view of the Gibbs–Duhem equation for the variation of the bulk phase pressure with variations of the chemical potential and temperature, all the thermodynamic characteristics of the droplet can be derived from the relationship for difference $P_0^\alpha - P_0^\beta$ [8].

The details of similar iteration method in finding the thermodynamic characteristics and shape of the droplet formed around the condensation nucleus with a large dipole moment were presented in [9].

As a result of the iteration procedure considered above, one can obtain the following expressions for the equilibrium droplet shape $r(\theta)$ and for the electric potentials Φ^α and Φ^β in the droplet and vapor-gas surroundings:

$$\begin{aligned} r(\theta) &= R \left[1 + \frac{\epsilon^2}{3} P_2 + \epsilon^4 \left(-\frac{1}{45} + \frac{10}{63} P_2 + \frac{3}{35} P_4 \right) \right] + R \\ &\quad \epsilon^4 \left[\left(\frac{29}{315} - \frac{4\epsilon^\beta}{5(\epsilon^\alpha + 2\epsilon^\beta)} \right) P_2 - \frac{1}{315} P_4 \right], \end{aligned} \quad (13)$$

$$\Phi^\alpha(r, \theta) = -\frac{3\epsilon^\beta E}{(\epsilon^\alpha + 2\epsilon^\beta)} \left[1 + \epsilon^2 \frac{2(\epsilon^\alpha - \epsilon^\beta)}{5(\epsilon^\alpha + 2\epsilon^\beta)} \right] r P_1, \quad (14)$$

$$\begin{aligned} \Phi^\beta(r, \theta) &= -Er \cos \theta \\ &\quad + \frac{(\epsilon^\alpha - \epsilon^\beta)ER^3}{(\epsilon^\alpha + 2\epsilon^\beta)} \left[1 + \epsilon^2 \frac{2(\epsilon^\alpha - \epsilon^\beta)}{5(\epsilon^\alpha + 2\epsilon^\beta)} \right] \frac{P_1}{r^2} + \\ &\quad \epsilon^2 \frac{3(\epsilon^\alpha - \epsilon^\beta)ER^5}{5(\epsilon^\alpha + 2\epsilon^\beta)} \frac{P_3}{r^4}, \end{aligned} \quad (15)$$

where

$$\epsilon^2 = \frac{9(\epsilon^\alpha - \epsilon^\beta)^2 \epsilon^\beta E^2 R}{16\pi\gamma(\epsilon^\alpha + 2\epsilon^\beta)^2} \quad (16)$$

is the small parameter of the iteration procedure, $P_i = P_i(\cos \theta)$ the Legendre polynomial of the i th order. The first term in parentheses in Eq. (13) corresponds to the contribution from prolate (along the direction of the external electric field) spheroid with the eccentricity ϵ . The second term in parentheses in Eq. (13) describes the deviation of the droplet shape from the prolate spheroid.

The expression for the shape of the dielectric and conducting droplets in the uniform external electric field was also obtained, correspondingly, in [2,10]. Nevertheless, because the left-hand side of Eqs. (5) and (11) was written in [2,10] only with a degree of accuracy up to terms of the first order in parameter f/R , the expression found in [2,10] is not correct for terms with factor ϵ^4 .

4. The chemical potential and the work of droplet formation

Integrating the Gibbs–Duhem equation for an incompressible liquid droplet consisting of v molecules at fixed temperature, it can be easily found that the condensate chemical potential b_v , expressed in thermal energy units kT (k is the Boltzmann constant) and counted off the value of the chemical potential for the equilibrium of the bulk liquid with its vapor at flat interface, equals

$$b_v = (v^\alpha/kT)(P_0^\alpha - P_0^\beta). \quad (17)$$

Substituting the expression for the difference $P_0^\alpha - P_0^\beta$ into the right-hand side of Eq. (17) with the accuracy up to terms of order ϵ^4 , we find

$$b_v = \frac{2}{3}av^{-1/3} \left[1 - \frac{(\epsilon^\alpha + 2\epsilon^\beta)}{3(\epsilon^\alpha - \epsilon^\beta)} \epsilon^2 - \frac{4}{45} \epsilon^4 \right], \quad (18)$$

where a is the dimensionless surface tension: $a = (4\pi\gamma/kT)(3v^\alpha/4\pi)^{2/3}$. According to Eqs. (4) and (16), the terms with factors ϵ^2 and ϵ^4 , which are associated with the effects of the uniform external electric field, give additional contributions to the dependence of b_v on v . As we can see from Eq. (18), the effects of the uniform external electric

field decrease the chemical potential of condensate in droplet in comparison with that in absence of the electric field. The distortion of the droplet shape which is described in Eq. (18) by the last term in square parentheses makes the decreasing even stronger.

For a droplet consisting of ν molecules, the work of droplet formation F_ν , expressed in thermal energy units kT , can be calculated as

$$F_\nu = \int b_\nu d\nu - b\nu. \quad (19)$$

Here b is the dimensionless, expressed in thermal energy units kT and counted off the value of the chemical potential for the equilibrium of the bulk liquid with its vapor at flat interface, chemical potential of the supersaturated vapor. We can consider b as a fixed parameter of the theory. Thus the only quantity which depends on the intensity E in the right-hand side of Eq. (19) is b_ν .

Performing the integration in Eq. (19) over ν with taking into account Eqs. (4), (16) and (18), we find

$$F_\nu = -b\nu + a\nu^{2/3} \left[1 - \frac{2(\varepsilon^\alpha + 2\varepsilon^\beta)}{9(\varepsilon^\alpha - \varepsilon^\beta)} \varepsilon^2 - \frac{2}{45} \varepsilon^4 \right]. \quad (20)$$

Here we assume that the constant of integration is equal to zero. More precisely, it may be different from zero for very tiny droplets [11], but it is not affected by the presence of the external electric field because the effect of the field is associated with the dielectric matter of the droplet and should be dependent of ν .

5. The electric contribution to the work of droplet formation

Let us note now that the expression for the work of droplet formation in the external electric field can be written as

$$F_\nu = -b\nu + \gamma S/kT + W_{\text{el}}/kT \quad (21)$$

where S is the surface area of the droplet, W_{el} the electric contribution to the work of droplet formation. For a droplet with the shape described by Eq. (13), the droplet surface area can be written,

with the same degree of accuracy in small parameter ε^2 , as

$$S = 4\pi R^2 \left(1 + \frac{2}{45} \varepsilon^4 \right). \quad (22)$$

Thus we can derive from Eqs. (20)–(22) with the help of Eq. (4) and Eq. (16) the expression for W_{el}

$$W_{\text{el}} = -\frac{(\varepsilon^\alpha - \varepsilon^\beta)\varepsilon^\beta E^2 R^3}{2(\varepsilon^\alpha + 2\varepsilon^\beta)} \left[1 + \frac{2(\varepsilon^\alpha - \varepsilon^\beta)}{5(\varepsilon^\alpha + 2\varepsilon^\beta)} \varepsilon^2 \right]. \quad (23)$$

We can check this expression using other methods of finding the electric contribution to the work of droplet formation. It should be noted that all these approaches are applicable in the general case of the external electric field, not only in the case of uniform electric field intensity.

Let us introduce the potential $(\Phi^\beta)_R$ of the reaction field which determines the difference of the electric potential in the vapor in presence of the droplet from that in absence of the droplet:

$$(\Phi^\beta)_R = \Phi^\beta + Er \cos \theta = \frac{\tilde{P} \cos \theta}{\varepsilon^\beta r^2} + \sum_{n=2}^{\infty} \frac{C_n}{r^{n+1}} P_n, \quad (24)$$

where \tilde{P} is the dipole moment of the droplet, C_n are the coefficients in decomposition of $(\Phi^\beta)_R$ in Legendre polynomials. As is well known, the electric contribution to the work of droplet formation in the external uniform field can be calculated as

$$W_{\text{el}} = -\frac{1}{2} \tilde{P} E. \quad (25)$$

As follows from Eq. (15) and Eq. (24), \tilde{P} equals

$$\tilde{P} = \frac{(\varepsilon^\alpha - \varepsilon^\beta)\varepsilon^\beta E^2 R^3}{(\varepsilon^\alpha + 2\varepsilon^\beta)} \left[1 + \frac{2(\varepsilon^\alpha - \varepsilon^\beta)}{5(\varepsilon^\alpha + 2\varepsilon^\beta)} \varepsilon^2 \right]. \quad (26)$$

Substitution of Eq. (26) into Eq. (25) yields the previous formula, Eq. (23).

Another formula for finding W_{el} is derived in [6] and can be written as

$$W_{\text{el}} = -\frac{1}{8\pi} \int_{V^\alpha} \vec{E}(\vec{D}^\alpha - \varepsilon^\beta \vec{E}^\alpha) dV, \quad (27)$$

where \vec{D}^α and \vec{E}^α are the electric displacement and the intensity of electric field inside the droplet, respectively, and integration is performed over the

volume of the droplet. It is easy to show the equivalency of Eqs. (25) and (27). We can use in Eq. (27) the direct expression for the electric field intensity \vec{E}^z inside the droplet. As follows from Eq. (14),

$$\vec{E}^z = \frac{3\varepsilon^\beta \vec{E}}{(\varepsilon^\alpha + 2\varepsilon^\beta)} \left[1 + \frac{2(\varepsilon^\alpha - \varepsilon^\beta)}{5(\varepsilon^\alpha + 2\varepsilon^\beta)} \varepsilon^2 \right]. \quad (28)$$

Taking into account the relationship $\vec{D}^z = \varepsilon^z \vec{E}^z$ and substituting Eq. (28) into Eq. (27), we again arrive at Eq. (23).

The Eq. (27) was used for calculation in [1] and gave a correct expression for W_{el} . Nevertheless, it should be noted that the shape of the droplet in [1] was assumed to be a prolate spheroid. This assumption does not allow one to find the corrections to the chemical potential of the droplet and to the work of droplet formation produced by deviation of the electric potential and droplet shape from that for prolate spheroid. There is no such restriction in our analysis.

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

$$b_v|_{v=v_c} = b. \quad (29)$$

If we solve this equation by perturbation technique with the use of Eqs. (4), (16) and (18), we find

$$v_c = v_{c0} \left\{ 1 - \frac{(\varepsilon^\alpha + 2\varepsilon^\beta)}{(\varepsilon^\alpha - \varepsilon^\beta)} \varepsilon_0^2 + \left[\frac{2(\varepsilon^\alpha + 2\varepsilon^\beta)^2}{3(\varepsilon^\alpha - \varepsilon^\beta)^2} - \frac{4}{15} \right] \varepsilon_0^4 \right\}, \quad (30)$$

where $v_{c0} = (2a/3b)^3$ is the critical size of the droplet in the absence of the external electric field, and $\varepsilon_0 \equiv \varepsilon|_{v=v_{c0}}$.

Substituting Eq. (30) into Eq. (20) and using Eqs. (4) and (16), we find the work of formation of a critical-sized droplet:

$$(F)_{v_c} = (F_0)_{v_{c0}} \left\{ 1 - \frac{2(\varepsilon^\alpha + 2\varepsilon^\beta)}{3(\varepsilon^\alpha - \varepsilon^\beta)} \varepsilon_0^2 + \left[\frac{(\varepsilon^\alpha + 2\varepsilon^\beta)^2}{3(\varepsilon^\alpha - \varepsilon^\beta)^2} - \frac{2}{15} \right] \varepsilon_0^4 \right\}, \quad (31)$$

where $(F_0)_{v_{c0}} = av_{c0}^{2/3}/3$ is the work of formation of a critical-sized droplet in the case of homogeneous nucleation.

As follows from Eqs. (30) and (31), the main contributions of the order of ε_0^2 to the right-hand side of Eqs. (30) and (31), obtained for spherical droplet, are negative, while the resulting spheroidal corrections of the order of ε_0^4 are positive. In spite of the fact that both corrections to the work of the droplet formation, Eq. (20), and to the chemical potential, Eq. (18), associated with the external electric field, reduce the corresponding quantities, we see from Eqs. (30) and (31) that the resulting spheroidal corrections of the order of ε_0^4 slightly increase v_c and $(F)_{v_c}$.

The above results were obtained for the case when the vapor chemical potential was the same in presence and absence of the uniform external electric field. As follows from the main contribution to Eq. (31), in this case the presence of the external uniform electric field enhance nucleation in the supersaturated vapor.

In the case where the vapor supersaturation is the same in the presence and absence of the uniform external electric field, the situation may be different [12]. One should take into account that the shift of the vapor chemical potential for molecules with large permanent electric dipole moment in the uniform field (for a fixed vapor supersaturation) may be larger than that of the chemical potential of condensate in droplet given by Eq. (18). In this case the external uniform electric field increases the work of formation of a critical-sized droplet and impedes nucleation.

6. The results for W_{el} obtained by Kashchiev and Isard

There is a controversy in the results for W_{el} obtained earlier by Kashchiev [3] and Isard [4] in the case of uniform external electric field intensity under assumption that the droplet is spherical. The spherical case corresponds to neglecting the correction term in parentheses in Eq. (23). The result of Kashchiev is different from that in Eq. (23) by sign and by factor 1/3 whereas the result of Isard coincides with Eq. (23) in the approxima-

tion considered. Below we would like to present some additional arguments to the consideration of the controversy of Kashchiev's result (the first consideration was given earlier in [4]).

Let us suppose that the sources of the electric field, which is external for the vapor system, are the charges distributed over a sphere with radius R_σ enclosing the part of the vapor system. We assume that the radius R_σ is large to compare with the size of a droplet, which can be formed at the center. If the charge density is

$$\sigma(\theta) = -(3/4\pi)\varepsilon^\beta E \cos \theta, \quad (32)$$

then the electric field inside the sphere is uniform with the intensity E . Outside the sphere the electric field intensity is nonuniform, and the electric potential decreases as $\Phi_1(r, \theta) = -ER_\sigma^3 \cos \theta / r^2$.

Let us now consider the formation of a liquid droplet out of vapor inside the sphere. The vapor system is materially open, thus the chemical potential of the system is fixed and equals the vapor chemical potential outside the sphere on an infinite distance from the sources of the field. We can set it the same as the vapor chemical potential in the absence of the external electric field. Note, that similar situation with the vapor chemical potential is in the case of ion-induced nucleation.

The formation of a dielectric droplet of radius R inside the charged sphere will change the potential at the sphere with fixed charge density $\sigma(\theta)$, or the charge density will be changed if we fix potential at the sphere. If the formation occurs at fixed charge density $\sigma(\theta)$ (it means according to Eq. (32) that the intensity E is fixed at the sphere), then the electric potential inside and outside the sphere is

$$\begin{aligned} \Phi_2^z(r, \theta) &= -\frac{3\varepsilon^\beta E}{\varepsilon^\alpha + 2\varepsilon^\beta} r \cos \theta, \quad (r \leq R) \\ \Phi_2^\beta(r, \theta) &= -Er \cos \theta + \frac{\varepsilon^\alpha - \varepsilon^\beta}{\varepsilon^\alpha + 2\varepsilon^\beta} ER^3 \frac{\cos \theta}{r^2}, \\ (R \leq r \leq R_\sigma) \\ \Phi_2^\beta(r, \theta) &= -ER_\sigma^3 \frac{\cos \theta}{r^2} + \frac{\varepsilon^\alpha - \varepsilon^\beta}{\varepsilon^\alpha + 2\varepsilon^\beta} ER^3 \frac{\cos \theta}{r^2}, \\ (R_\sigma \leq r). \end{aligned} \quad (33)$$

The electric contribution to the work of droplet formation can be written in the form:

$$W_{el} = \frac{1}{2} \oint_A \sigma(\theta)(\Phi_2 - \Phi_1) dA, \quad (34)$$

where the difference $\Phi_2 - \Phi_1$ determines the change of the electrical potential (as a result of droplet formation) at the sphere with the surface area A . The Eq. (34) can be converted to the fundamental formula

$$W_{el} = \frac{1}{8\pi} \int_V (\vec{E}_2 \vec{D}_2 - \vec{E}_1 \vec{D}_1) dV, \quad (35)$$

with the integration performed over the volume V of the whole vapor system including the part outside the charged sphere (subscripts 1 and 2 indicate the initial and the final state of the system), which was used by Kashchiev [3]. However, Kashchiev incorrectly used for \vec{E}_1 , \vec{E}_2 , \vec{D}_1 , and \vec{D}_2 only the expressions inside the sphere and supposed the radius R_σ of the sphere to be infinitely large. If one substitutes the difference $\Phi_2 - \Phi_1$ into Eq. (34) (or expressions for \vec{E}_1 , \vec{E}_2 , \vec{D}_1 , and \vec{D}_2 into Eq. (35)) that follows from Eq. (33), he will obtain exactly the spherical approximation for Eq. (23).

Acknowledgements

Alexander Shchekin thanks the Russian Foundation for Basic Research (grant no. 96-02-18959) for the financial support of this work.

References

- [1] K.J. Cheng, Phys. Lett. 106A (1984) 403.
- [2] A.I. Grigoriev, E.I. Mukhina, in: Nauchnoe priborostroyeniye. Formirovaniye puchkov zariazhennykh chactitz, Leningrad, 1990, p.21 (in Russian).
- [3] D. Kashchiev, Phil. Mag. 25 (1972) 459.
- [4] J.O. Isard, Phil. Mag. 35 (1977) 817.
- [5] L.D. Landau, E.M. Lifshitz, Fluid Mechanics, Pergamon, Oxford, 1987.
- [6] L.D. Landau, E.M. Lifshitz, Electrodynamics of Continuum Media, Pergamon, Oxford, 1984.
- [7] G.I. Taylor, Proc. Roy. Soc. Lond. 280A (1964) 383.
- [8] V.B. Warshavsky, A.K. Shchekin, in: Fizika aerodispersnykh sistem (Physics of aerodispersed systems), no. 36

- (special issue devoted to Proceedings of XVII Conference Dispersed systems of CIS) 1996, p. 61 (in Russian).
- [9] A.K. Shchekin, V.B. Varshavskii, *Colloid J. Eng. Tr.* 58 (4) (1996) 538.
- [10] A.I. Grigoriev, S.O. Shiryaeva, *Zh. Tech. Phys.* 57 (1987) 1706.
- [11] A.I. Rusanov, F.M. Kuni, A.K. Shchekin, *Colloid J. R* 49 (2) (1987) 266.
- [12] K.J. Oh, G.T. Gao, X.C. Zeng, *J. Chem. Phys.* 1998 (submitted).