

Heterogeneous nucleation in multi-component vapor on a partially wettable charged conducting particle. II. The generalized Laplace, Gibbs-Kelvin, and Young equations and application to nucleation

M. Noppel, H. Vehkamäki, P. M. Winkler, M. Kulmala, and P. E. Wagner

Citation: *J. Chem. Phys.* **139**, 134108 (2013); doi: 10.1063/1.4822047

View online: <http://dx.doi.org/10.1063/1.4822047>

View Table of Contents: <http://jcp.aip.org/resource/1/JCPSA6/v139/i13>

Published by the AIP Publishing LLC.

Additional information on J. Chem. Phys.

Journal Homepage: <http://jcp.aip.org/>

Journal Information: http://jcp.aip.org/about/about_the_journal

Top downloads: http://jcp.aip.org/features/most_downloaded

Information for Authors: <http://jcp.aip.org/authors>



Goodfellow

metals • ceramics • polymers
composites • compounds • glasses

Save 5% • Buy online
70,000 products • Fast shipping

Heterogeneous nucleation in multi-component vapor on a partially wettable charged conducting particle. II. The generalized Laplace, Gibbs-Kelvin, and Young equations and application to nucleation

M. Noppel,^{1,a)} H. Vehkamäki,² P. M. Winkler,³ M. Kulmala,² and P. E. Wagner³

¹*Institute of Physics, University of Tartu, 18 Ülikooli St., 50090 Tartu, Estonia*

²*Department of Physics, P.O. Box 64, 00014 University of Helsinki, Finland*

³*Fakultät für Physik, Universität Wien, Boltzmanngasse 5, A-1090 Wien, Austria*

(Received 5 June 2013; accepted 10 September 2013; published online 2 October 2013)

Based on the results of a previous paper [M. Noppel, H. Vehkamäki, P. M. Winkler, M. Kulmala, and P. E. Wagner, *J. Chem. Phys.* **139**, 134107 (2013)], we derive a thermodynamically consistent expression for reversible or minimal work needed to form a dielectric liquid nucleus of a new phase on a charged insoluble conducting sphere within a uniform macroscopic one- or multicomponent mother phase. The currently available model for ion-induced nucleation assumes complete spherical symmetry of the system, implying that the seed ion is immediately surrounded by the condensing liquid from all sides. We take a step further and treat more realistic geometries, where a cap-shaped liquid cluster forms on the surface of the seed particle. We derive the equilibrium conditions for such a cluster. The equalities of chemical potentials of each species between the nucleus and the vapor represent the conditions of chemical equilibrium. The generalized Young equation that relates contact angle with surface tensions, surface excess polarizations, and line tension, also containing the electrical contribution from triple line excess polarization, expresses the condition of thermodynamic equilibrium at three-phase contact line. The generalized Laplace equation gives the condition of mechanical equilibrium at vapor-liquid dividing surface: it relates generalized pressures in neighboring bulk phases at an interface with surface tension, excess surface polarization, and dielectric displacements in neighboring phases with two principal radii of surface curvature and curvatures of equipotential surfaces in neighboring phases at that point. We also re-express the generalized Laplace equation as a partial differential equation, which, along with electrostatic Laplace equations for bulk phases, determines the shape of a nucleus. We derive expressions that are suitable for calculations of the size and composition of a critical nucleus (generalized version of the classical Kelvin-Thomson equation). © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4822047>]

I. INTRODUCTION

In the preceding paper,¹ hereafter referred to as Paper I, we formulated general thermodynamic equations of internal energies and grand potential for a system consisting of a non-critical dielectric liquid nucleus of a new phase on a partially wettable charged conducting particle within a uniform macroscopic multicomponent mother phase. We studied a general cap-shaped nucleus (see Fig. 1), not necessarily having spherical form or axial symmetry, but we assumed that deviations from the spherical form are such that we can ignore the changes in surface and line tensions values invoked by these deviations. We introduced electrical surface and line excess quantities to take into account the contributions of interfacial and three phase contact zones to the electric field energy of a system. Spontaneous polarization of surface layer molecules was taken as a major contributor to the electrical excess quantities. The purpose of Paper I¹ was to lay the foundation for obtaining a rigorous and thermodynamically consistent expression for the reversible work of nucleus formation, and proper conditions for the critical nucleus which

are derived in this paper. We follow the consistent study of Nishioka and Kusaka² and Debenedetti and Reiss.³

In Sec. II, we derive the thermodynamically consistent expression of the reversible work of nucleus formation. Section III presents the conditions for a critical nucleus, where in Subsection III A, we first consider the change of electric field energy caused by infinitesimal deformation of an embryo at constant seed particle charge. The study of this change is required for the establishing thermodynamic equilibrium conditions at interface surfaces. Subsections III B and III C describe thermodynamic equilibrium at vapor-liquid dividing surface and at three phase contact line, respectively. In Subsection III D, we derive expressions for composition and size of a critical nucleus. Subsection III E considers how the generalized Laplace equation can be presented and used as a differential equation for the shape of a nucleus. Section IV makes conclusions.

II. THE WORK OF FORMATION

A constrained nucleus of any size is formed from vapor phase on a seed particle. Vapor acts as the bath of heat, pressure, and particles. The entire system is large, but closed.

^{a)}E-mail: madis.noppel@ut.ee. Tel.: +372-7-375857. Fax: +372-7-375556.

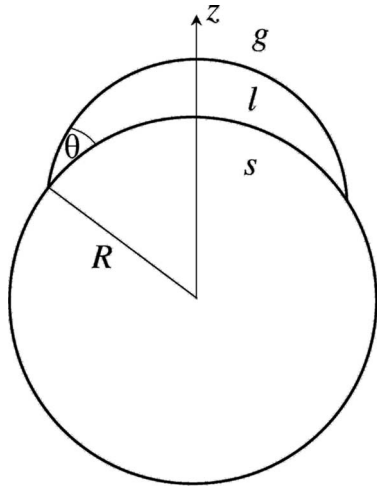


FIG. 1. Sketch of the cross section of a cap-shaped liquid nucleus l of radius r in the vapor phase g on a spherical conducting uncharged seed particle s of radius R . The liquid nucleus forms a contact angle θ with the seed particle.

The difference in the grand potentials between a case with a bare seed particle (Paper I,¹ Eq. (53)) and a seed particle with a liquid nucleus on it (Paper I,¹ Eq. (55)), in both cases immersed in the vapor phase, gives us the reversible work to form a general-size nucleus on a charged seed particle. Actually, the potential Eq. (55) in Paper I¹ is a hybrid potential for a constrained nucleus on a seed particle that acts as a grand potential with respect variables $\mu_{i,g}$ – the chemical potential of species i in vapor, and as Helmholtz free energy with respect to variables $N_{i,a}$, $N_{i,L}$ and $N_{i,l}$ – the numbers of i -type molecules of surface a ($a = gl, ls$), contact line and bulk liquid, respectively (see Eq. (56) in Paper I¹). The reversible work is

$$\begin{aligned}
 \Delta\Omega &= \Omega - \Omega^0 \\
 &= (p_g^0 - p_l^0)V_l + \sigma_{gl}A_{gl} + (\sigma_{ls} - \sigma_{gs})A_{ls} + \kappa L \\
 &\quad + \sum_a \sum_i (\mu_{i,a} - \mu_{i,g})N_{i,a} \\
 &\quad + \sum_i (\mu_{i,l} - \mu_{i,g})N_{i,l} + \sum_i (\mu_{i,L} - \mu_{i,g})N_{i,L} \\
 &\quad - \int_{A_{sl}} \frac{\overline{P_0^{sl}}}{\varepsilon_0} (\mathbf{D} - \mathbf{D}_0) \cdot d\mathbf{A}_{sl} \\
 &\quad - \int_{A_{sg}} \frac{\overline{P_0^{sg}}}{\varepsilon_0} (\mathbf{D} - \mathbf{D}_0) \cdot d\mathbf{A}_{sg} - \int_{A_{lg}} \frac{\overline{P_0^{lg}}}{\varepsilon_0} (\mathbf{D} - \mathbf{D}_0) \cdot d\mathbf{A}_{lg} \\
 &\quad + \frac{1}{2} \int_{V_l+V_g} (ED - E_0D_0)dV - q \int_L \frac{\kappa_P}{\varepsilon_0} dL \\
 &\quad + \frac{\overline{P_0^{sg}}}{\varepsilon_0} q - \frac{q^2}{8\pi\varepsilon_g\varepsilon_0 R}, \tag{1}
 \end{aligned}$$

where p_l^0 and p_g^0 are the pressures in bulk liquid and gas phases around an uncharged seed particle, respectively; V_l and V_g are the volumes of the embryo and vapor phase around the embryo, respectively; σ_a is the surface tension and A_a is

surface area of surface a ($a = gl, ls, gs$); κ is the line tension of contact line; L is the length of contact line; $\overline{P_0^a}$ is the surface excess polarization of surface a ($a = gl, ls, gs$); \mathbf{D} is the vector of the dielectric displacement around a charged seed particle; \mathbf{D}_0 is the vector of the dielectric displacement around an uncharged seed particle; E and E_0 are electric field strengths around a charged and an uncharged seed particle, respectively; R is the radius of a seed particle; $\kappa_P q$ is the excess quantity due to spontaneous polarization in contact line zone, where q is the seed particle charge and κ_P is the charge independent factor; $\kappa_P q/\varepsilon_0$ is the electrical line tension due to spontaneous polarization. The relations $V = V_l + V_g$ and $A_{gs}^0 = A_{ls} + A_{gs}$ have been used in Eq. (1), where V is the total volume of the system (excluding the volume of the seed particle) and A_{gs}^0 is surface area of a bare seed particle in vapor. Here, we have ignored the fact that the location of dividing surfaces for the liquid-solid A_{ls} and gas(vapor)-solid A_{gs} interfaces of a seed particle with a liquid nucleus on it can be different. The system boundary radius is set to infinity $\rho_{\text{lim}} = \infty$.

If electric line and surface excess quantities that are scalars are constant along three phase contact line and dividing surfaces of phases, respectively, that is, κ_P is constant and $\overline{P_0^a}$ is constant for each of the surfaces $a = lg, sl, sg$, Eq. (1) can be simplified to

$$\begin{aligned}
 \Delta\Omega &= \Omega - \Omega^0 \\
 &= (p_g^0 - p_l^0)V_l + \sigma_{gl}A_{gl} + (\sigma_{ls} - \sigma_{gs})A_{ls} \\
 &\quad + \left(\kappa - \frac{\kappa_P q}{\varepsilon_0}\right)L \\
 &\quad + \sum_a \sum_i (\mu_{i,a} - \mu_{i,g})N_{i,a} + \sum_i (\mu_{i,l} - \mu_{i,g})N_{i,l} \\
 &\quad + \sum_i (\mu_{i,L} - \mu_{i,g})N_{i,L} \\
 &\quad - \left(\frac{\overline{P_0^{sl}} + \overline{P_0^{lg}}}{\varepsilon_0}\right)q_{sl} - \frac{\overline{P_0^{sg}}}{\varepsilon_0}q_{sg} \\
 &\quad + \frac{1}{2} \int_{V_l+V_g} (ED - E_0D_0)dV - \frac{q^2}{8\pi\varepsilon_g\varepsilon_0 R} + \frac{\overline{P_0^{sg}}}{\varepsilon_0}q, \tag{2}
 \end{aligned}$$

where we have used Gauss's law $\int_{A_a} \mathbf{D} \cdot d\mathbf{A} = q$ and q_{sl} is the electric charge on the portion of seed particle surface covered by the liquid nucleus and q_{sg} is the electric charge on the portion of seed particle surface facing the gas phase. Conduction electrons are free to move all around the entire seed particle. Electrons are in thermal agitation. There is no fixed position for them on the seed surface. Therefore, the quantities q_{sl} and q_{sg} as average quantities can also have values that are only a fraction of the elementary charge. Of course, in the latter case the sum of q_{sl} and q_{sg} should be equal to the elementary charge carried onto the seed. Surface and line excess quantities due to spontaneous polarization introduce a clear dependence of the nucleus formation energy on the sign of the seed particle charge.

III. THE CONDITION FOR A CRITICAL NUCLEUS

So far, we have constrained molecular numbers $N_{i,l}$, $N_{i,a}$, and $N_{i,L}$, as well as nucleus volume V_l , surface areas A_a , and triple line length L to have fixed values. The variation of these parameters around values of stable or unstable equilibrium nuclei should give minimal or maximal values, respectively, for the reversible work of nucleus formation. To obtain the extremity condition, we first calculate the differential of Eq. (1). The differentials of terms corresponding to a seed particle in the gas phase are zero as we vary the quantities describing the size and the shape of the liquid embryo and keep the gas phase properties constant. The differential of the reversible work of cluster formation is

$$\begin{aligned} d\Delta\Omega = & (p_g^0 - p_l^0)dV_l + \sigma_{gl}dA_{gl} + (\sigma_{ls} - \sigma_{gs})dA_{ls} + \kappa dL \\ & + \sum_a \sum_i (\mu_{i,a} - \mu_{i,g})dN_{i,a} \\ & + \sum_i (\mu_{i,l} - \mu_{i,g})dN_{i,l} + \sum_i (\mu_{i,L} - \mu_{i,g})dN_{i,L} \\ & + d\Omega_0 + d\Omega_{\delta q_1} + d\Omega_{\delta q_2} + d\Omega_{\delta\rho} \end{aligned}$$

$$\begin{aligned} = & (p_g^0 - p_l^0)dV_l + \sigma_{gl}dA_{gl} + (\sigma_{ls} - \sigma_{gs})dA_{ls} \\ & + \kappa dL + \sum_a \sum_i (\mu_{i,a} - \mu_{i,g})dN_{i,a} \\ & + \sum_i (\mu_{i,l} - \mu_{i,g})dN_{i,l} \\ & + \sum_i (\mu_{i,L} - \mu_{i,g})dN_{i,L} + d\Omega_{\delta\rho}, \end{aligned} \quad (3)$$

where we have used notations $d\Omega_0$, $d\Omega_{\delta q_1}$, $d\Omega_{\delta q_2}$, $d\Omega_{\delta\rho}$ to indicate the following terms:

$$\begin{aligned} d\Omega_0 = & \left\{ -V_l dp_l^0 + \sum_i N_{i,l} d\mu_{i,l} \right\} \\ & + \left\{ \sum_{a=sl,lg} \left(A_a d\sigma_a + \sum_i N_{i,a} d\mu_{i,a} \right) \right\} \\ & - A_{ls} d\sigma_{gs} + \left\{ L d\kappa + \sum_i N_{i,L} d\mu_{i,L} \right\}, \end{aligned} \quad (4)$$

$$d\Omega_{\delta q_1} = \left[\frac{1}{2} \int_{V_l+V_g} \mathbf{E} \cdot \delta \mathbf{D} dV - \sum_a \left(\int_{A_a} \frac{\overline{P_0^a}}{\varepsilon_0} \delta \mathbf{D} \cdot d\mathbf{A}_a \right) - \delta q \int_L \frac{\kappa_P}{\varepsilon_0} dL \right]_{\delta V=0, \delta A=0}, \quad (5)$$

$$d\Omega_{\delta q_2} = \left[\frac{1}{2} \int_{V_l+V_g} \mathbf{D} \cdot \delta \mathbf{E} dV - \frac{1}{2} \delta \int_{V_l+V_g} D_0 E_0 dV - \sum_a \left(\int_{A_a} \left[\frac{\delta \overline{P_0^a}}{\varepsilon_0} \mathbf{D} - \delta \left(\frac{\overline{P_0^a}}{\varepsilon_0} \mathbf{D}_0 \right) \right] \cdot d\mathbf{A}_a \right) - q \int_L \frac{\delta \kappa_P}{\varepsilon_0} dL \right]_{\delta V=0, \delta A=0}, \quad (6)$$

$$d\Omega_{\delta\rho} = \delta \left[- \int_{A_{sl}} \frac{\overline{P_0^{sl}}}{\varepsilon_0} (\mathbf{D} - \mathbf{D}_0) \cdot d\mathbf{A}_{sl} + \int_{V_l} \left(\frac{ED}{2} - \frac{E_0 D_0}{2} \right) dV - \int_{A_{lg}} \frac{\overline{P_0^{lg}}}{\varepsilon_0} (\mathbf{D} - \mathbf{D}_0) \cdot d\mathbf{A}_{lg} - \int_{A_{sg}} \frac{\overline{P_0^{sg}}}{\varepsilon_0} (\mathbf{D} - \mathbf{D}_0) \cdot d\mathbf{A}_{sg} + \int_{V_g} \left(\frac{ED}{2} - \frac{E_0 D_0}{2} \right) dV - q \int_L \frac{\kappa_P}{\varepsilon_0} dL \right]_{q, \delta V \neq 0, \delta A \neq 0}. \quad (7)$$

In Eq. (3), terms denoted by $d\Omega_0$ vanish due to the Gibbs–Duhem Eqs. (9), (12) and the Gibbs adsorption Eq. (11) given in Paper I.¹ It follows from Eq. (11) of Paper I¹ that $d\sigma_{gs} = 0$, as the state of the vapor is kept constant (T , $\{\mu_{i,g}\}$ are constant) and the interface between vapor and seed particle is open for mass transfer ensuring the equality of chemical potentials. The term $d\Omega_{\delta q_1}$ corresponds to the charging of seed particle (see Eqs. (40) and (46) in Paper I¹) at constant volume and shape of an embryo. As charge q is kept constant, this term is zero. The term $d\Omega_{\delta q_2}$ is zero due to

the Gibbs–Duhem Eqs. (44) and (48) in Paper I.¹ The term $d\Omega_{\delta\rho}$ describes the change of electrostatic energy at constant charge of seed particle when the volume and shape of an embryo are varied. These variations evoke changes in electrostatic energy not only in the location where the variations occur but all over the system. This term will be considered in Sec. III A.

It follows from Eq. (3) that the derivative of Eq. (1) with respect to $N_{i,l}$ at constant $\{N_{j \neq i,l}\}$, $\{N_{i,a}\}$, $\{N_{i,L}\}$, and constant volume V_l and shape of nucleus, i.e., at constrained embryo,

is zero when

$$\mu_{i,l} = \mu_{i,g}. \quad (8)$$

The derivative with respect to $N_{i,a}$ at constant $\{N_{j \neq i,a}\}$, $\{N_{i,l}\}$, $\{N_{i,L}\}$, and constant V_l and shape gives

$$\mu_{i,a} = \mu_{i,g}. \quad (9)$$

The derivative with respect to $N_{i,L}$ at constant $\{N_{j \neq i,L}\}$, $\{N_{i,l}\}$, $\{N_{i,a}\}$, and constant V_l and shape gives

$$\mu_{i,L} = \mu_{i,g}. \quad (10)$$

Equations (8)–(10) also hold for a critical embryo as it is one of the possible constrained embryos. In what follows, we use the condition that the values of chemical potentials are equal throughout the system.

A. The change of electric field energy due to an infinitesimal deformation of the embryo at constant charge

The estimation of thermodynamic equilibrium condition of an embryo requires the knowledge of the change of electric field energy that an infinitesimal deformation of the embryo shape causes at constant charge of seed particle, i.e., we must estimate the variation $d\Omega_{\delta\rho}$ given by Eq. (7).

The formation energy of an embryo given by Eq. (1) is expressed in terms of the properties of the hypothetical system and also includes the surface excess polarizations \overline{P}_0^{lg} (electric double layer, $a = lg, sl, sg$). An infinitesimal movement of the boundary of the embryo in the hypothetical system can also be considered as addition or removal of dielectric body and electric double layer into or from the electric field of seed particle. In deriving Eq. (16) of Paper I,¹ we ignored the surface excess polarization. Therefore, we must now reformulate Eq. (16) of Paper I.¹ Note that this reformulation is valid only for hypothetical systems. We consider two types of infinitesimal deformations of the embryo. The initial state of an embryo on seed particle is depicted in Fig. 1. First, we increase the volume of the embryo by choosing a portion of liquid-vapor interface that is not in contact with seed particle surface and move it infinitesimally outward (see Fig. 2, the embryo volume is increased by $dx dy \delta z$). Second, we move infinitesimally outward a portion of the gas-liquid interface that is in touch with seed particle surface (see Fig. 3). The movement of this portion is accompanied with the change of three phase contact line length. For the latter case, we will present only the result of surface element displacement, as the derivation is essentially similar with the first case.

1. Liquid-vapor surface element not adjacent to the three phase contact line

A surface element $dA_{lg} = dx dy$ is displaced by δz and its area increases to $dA_{lg,2} = (dx + \delta dx)(dy + \delta dy)$. The system

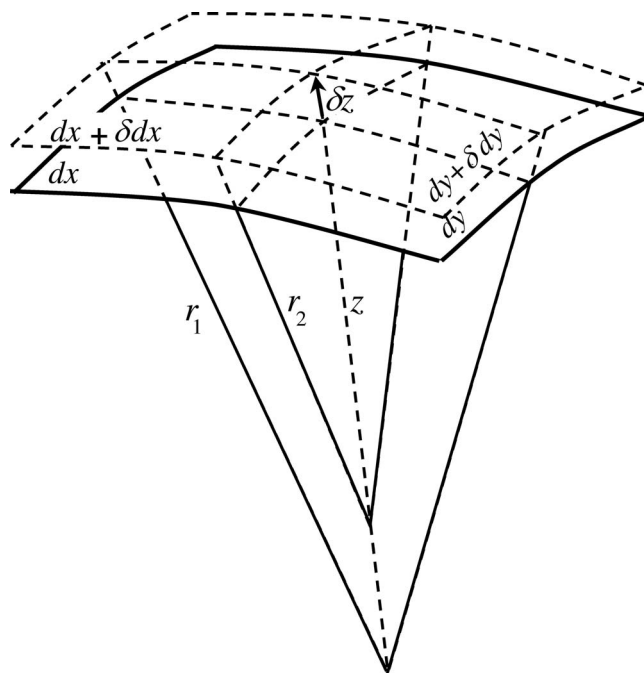


FIG. 2. The variation of surface area and volume due to an infinitesimal displacement δz of the surface of phase separation. The directions of x - and y -axes are chosen to correspond to the directions where surface has minimum and maximum curvatures with radii of curvature r_1 and r_2 .

with original surface element is characterized with surface areas A_a ($a = sl, sg, lg$) and volumes V_s, V_l, V_g . The system with a displaced surface element is characterized with surface areas $A_{lg,2} = A_{lg} - dA_{lg} + dA_{lg,2}$, $A_{sg,2} \equiv A_{sg}$, $A_{sl,2} \equiv A_{sl}$ and volumes $V_{s,2} \equiv V_s$, $V_{l,2} \equiv V_l + dV$, $V_{g,2} \equiv V_g - dV$, where $dV = dx dy \delta z$ (see Fig. 2). If we consider the original surface, the bottom and the deformed surface top of a “box,” the walls of the “box” have a surface area $2(dx\delta z + dy\delta z)$ which is an infinitesimally small quantity compared to the areas dA_{lg} and $dA_{lg,2}$ and, thus, we can ignore their contribution. The three phase contact line remains unchanged. The last form of Eq. (41), together with the correction Eq. (47) of Paper I¹ arising from the line excess energy, can be used to describe the electrostatic energy of the initial and final systems. Thus, the

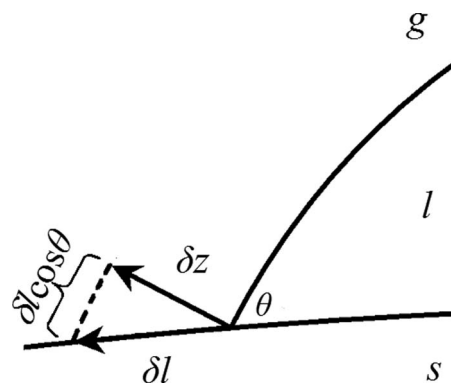


FIG. 3. The variation of surface areas and volume due to an infinitesimal displacement δz of the surface of vapor-liquid separation at three phase contact line. The liquid nucleus is denoted by l , the vapor phase by g , and the solid seed particle by s . The contact angle is θ and the displacement of the contact line δl .

change in the system energy due to the deformation is

$$\begin{aligned}
 d\Omega_q &= \Omega_{q,2} - \Omega_q \\
 &= - \int_{A_{sl}} \frac{\overline{P_0^{sl}}}{\varepsilon_0} (\mathbf{D}_2 - \mathbf{D}) \cdot d\mathbf{A} + \int_{V_l} \frac{\mathbf{E}_2 \cdot \mathbf{D}_2 - \mathbf{E} \cdot \mathbf{D}}{2} dV \\
 &\quad + \int_{dV} \frac{\mathbf{E}_2 \cdot \mathbf{D}_2 - \mathbf{E} \cdot \mathbf{D}}{2} dV \\
 &\quad - \int_{A_{lg}-dA_{lg}} \frac{\overline{P_0^{lg}}}{\varepsilon_0} (\mathbf{D}_2 - \mathbf{D}) \cdot d\mathbf{A} + \int_{dA_{lg}} \frac{\overline{P_0^{lg}}}{\varepsilon_0} (\mathbf{D} - \mathbf{D}_0) \cdot d\mathbf{A} \\
 &\quad - \int_{dA_{lg,2}} \frac{\overline{P_{0,2}^{lg}}}{\varepsilon_0} (\mathbf{D}_2 - \mathbf{D}_{0,2}) \cdot d\mathbf{A} \\
 &\quad - \int_{A_{sg}} \frac{\overline{P_0^{sg}}}{\varepsilon_0} (\mathbf{D}_2 - \mathbf{D}) \cdot d\mathbf{A} + \int_{V_{g,2} \equiv V_g - dV} \frac{\mathbf{E}_2 \cdot \mathbf{D}_2 - \mathbf{E} \cdot \mathbf{D}}{2} dV \\
 &\quad - q \int_{L_2} \frac{\kappa_{P,2}}{\varepsilon_0} dL + q \int_L \frac{\kappa_P}{\varepsilon_0} dL, \quad (11)
 \end{aligned}$$

where in the last form we have dropped terms involving only the field and polarization quantities of uncharged system, as energetic contribution of such quantities is already incorporated in the terms of Eq. (1) related to the uncharged system. We have also taken into account that the surface excess polarization remains unchanged at nondisplaced surfaces, that is, $\overline{P_{0,2}^{ij}} \equiv \overline{P_0^{ij}}$ for $a = sl, sg$. We can represent integrals over volume regions $V_l, V_{g,2}, dV$ in the last form of Eq. (11) in a form equivalent to Eq. (17) of Paper I¹

$$\begin{aligned}
 &\frac{1}{2} \int_V (\mathbf{E}_2 \cdot \mathbf{D}_2 - \mathbf{E} \cdot \mathbf{D}) dV \\
 &= \frac{1}{2} \int_V (\mathbf{E}_2 \cdot (\mathbf{D}_2 - \mathbf{D}) + (\mathbf{E}_2 - \mathbf{E}) \cdot \mathbf{D}) dV. \quad (12)
 \end{aligned}$$

Next, we can use Eq. (18) of Paper I¹ to represent the term $\mathbf{E}_2 \cdot (\mathbf{D}_2 - \mathbf{D})$ in the form

$$\begin{aligned}
 \mathbf{E}_2 \cdot (\mathbf{D}_2 - \mathbf{D}) &= -\nabla \varphi_2 \cdot (\mathbf{D}_2 - \mathbf{D}) \\
 &= -\nabla \cdot [\varphi_2 (\mathbf{D}_2 - \mathbf{D})] + \varphi_2 \nabla \cdot (\mathbf{D}_2 - \mathbf{D}).
 \end{aligned}$$

The term $\nabla \cdot (\mathbf{D}_2 - \mathbf{D})$ is zero, as there are no charges neither inside the “box” between the original and deformed surfaces nor in liquid and vapor phases. The application of the divergence theorem to the above expression leads to the result

$$\frac{1}{2} \int_V \mathbf{E}_2 \cdot (\mathbf{D}_2 - \mathbf{D}) dV = -\frac{1}{2} \int_A \varphi_2 (\mathbf{D}_2 - \mathbf{D}) \cdot d\mathbf{A}, \quad (13)$$

where A represents surface area of volume V and φ_2 is the electrostatic potential inside volume V in the immediate vicin-

ity of surface A . As before, we take the positive direction of surface elements of $d\mathbf{A}$ to be away from the seed particle and away from the liquid phase, and determine the signs of the surface integrals accordingly. Upon summing the first terms of the right hand side of Eq. (12) for volumes $V_l, V_{g,2}$, and dV , that is, the $\mathbf{E}_2 \cdot (\mathbf{D}_2 - \mathbf{D})$ integrals over $V_l, V_{g,2}$, and dV , we obtain

$$\begin{aligned}
 &\frac{1}{2} \int_{V_l} \mathbf{E}_2 \cdot (\mathbf{D}_2 - \mathbf{D}) dV + \frac{1}{2} \int_{V_{g,2}} \mathbf{E}_2 \cdot (\mathbf{D}_2 - \mathbf{D}) dV \\
 &\quad + \frac{1}{2} \int_{dV} \mathbf{E}_2 \cdot (\mathbf{D}_2 - \mathbf{D}) dV \\
 &= \frac{1}{2} \int_{A_{sl}} \frac{\overline{P_0^{sl}}}{\varepsilon_0} (\mathbf{D}_2 - \mathbf{D}) \cdot d\mathbf{A} + \frac{1}{2} \int_{A_{lg}-dA_{lg}} \frac{\overline{P_0^{lg}}}{\varepsilon_0} (\mathbf{D}_2 - \mathbf{D}) \cdot d\mathbf{A} \\
 &\quad + \frac{1}{2} \int_{dA_{lg,2}} \frac{\overline{P_{0,2}^{lg}}}{\varepsilon_0} (\mathbf{D}_2 - \mathbf{D}) \cdot d\mathbf{A} + \frac{1}{2} \int_{A_{sg}} \frac{\overline{P_0^{sg}}}{\varepsilon_0} (\mathbf{D}_2 - \mathbf{D}) \cdot d\mathbf{A}. \quad (14)
 \end{aligned}$$

Here, for making the general line of derivations more easier to follow in this section, we skip intermediate steps of the derivation leading to the last form of Eq. (14). They are given in Appendix A.

To calculate the sum of the second terms of Eq. (12) for volumes $V_l, V_{g,2}$, and dV , that is, the $(\mathbf{E}_2 - \mathbf{E}) \cdot \mathbf{D}$ integrals over $V_l, V_{g,2}$, and dV , we note that inside the gas and liquid phase volumes $V_l, V_{g,2}$ relation $(\mathbf{E}_2 - \mathbf{E}) \cdot \mathbf{D} = (\mathbf{D}_2 - \mathbf{D}) \cdot \mathbf{E}$ holds due to assumed linear relationship $\mathbf{D} = \varepsilon \mathbf{E}$. Thus, the integral of $(\mathbf{E}_2 - \mathbf{E}) \cdot \mathbf{D}$ over all volumes $V_l, V_{g,2}, dV$ can be represented, analogously with Eq. (14), as

$$\begin{aligned}
 &\frac{1}{2} \int_{V_l} \mathbf{E} \cdot (\mathbf{D}_2 - \mathbf{D}) dV + \frac{1}{2} \int_{V_{g,2}} \mathbf{E} \cdot (\mathbf{D}_2 - \mathbf{D}) dV \\
 &\quad + \frac{1}{2} \int_{dV} \mathbf{E} \cdot (\mathbf{D}_2 - \mathbf{D}) dV \\
 &= +\frac{1}{2} \int_{A_{sl}} \frac{\overline{P_0^{sl}}}{\varepsilon_0} (\mathbf{D}_2 - \mathbf{D}) \cdot d\mathbf{A} + \frac{1}{2} \int_{A_{lg}-dA_{lg}} \frac{\overline{P_0^{lg}}}{\varepsilon_0} (\mathbf{D}_2 - \mathbf{D}) \cdot d\mathbf{A} \\
 &\quad + \frac{1}{2} \int_{dA_{lg}} \frac{\overline{P_0^{lg}}}{\varepsilon_0} (\mathbf{D}_2 - \mathbf{D}) \cdot d\mathbf{A} + \frac{1}{2} \int_{A_{sg}} \frac{\overline{P_0^{sg}}}{\varepsilon_0} (\mathbf{D}_2 - \mathbf{D}) \cdot d\mathbf{A}. \quad (15)
 \end{aligned}$$

Transferring the integral over dV from the left hand side of the equation to the right hand side of it to get a more convenient form for reference in the following derivations, we obtain

$$\begin{aligned}
& \frac{1}{2} \int_{V_l+V_{g,2}} (\mathbf{E}_2 - \mathbf{E}) \cdot \mathbf{D} dV \\
&= \frac{1}{2} \int_{V_l} \mathbf{E} \cdot (\mathbf{D}_2 - \mathbf{D}) dV + \frac{1}{2} \int_{V_{g,2}} \mathbf{E} \cdot (\mathbf{D}_2 - \mathbf{D}) dV \\
&= -\frac{1}{2} \int_{dV} \mathbf{E} \cdot (\mathbf{D}_2 - \mathbf{D}) dV + \frac{1}{2} \int_{A_{sl}} \frac{\overline{P_0^{sl}}}{\epsilon_0} (\mathbf{D}_2 - \mathbf{D}) \cdot d\mathbf{A} \\
&\quad + \frac{1}{2} \int_{A_{lg}-dA_{lg}} \frac{\overline{P_0^{lg}}}{\epsilon_0} (\mathbf{D}_2 - \mathbf{D}) \cdot d\mathbf{A} \\
&\quad + \frac{1}{2} \int_{dA_{lg}} \frac{\overline{P_0^{lg}}}{\epsilon_0} (\mathbf{D}_2 - \mathbf{D}) \cdot d\mathbf{A} + \frac{1}{2} \int_{A_{sg}} \frac{\overline{P_0^{sg}}}{\epsilon_0} (\mathbf{D}_2 - \mathbf{D}) \cdot d\mathbf{A}.
\end{aligned} \tag{15'}$$

We can express the integral of both the terms on the right hand side of Eq. (12) over volume $V = V_l + V_{g,2} + dV$ as

$$\begin{aligned}
& \frac{1}{2} \int_V (\mathbf{E}_2 \cdot \mathbf{D}_2 - \mathbf{E} \cdot \mathbf{D}) dV \\
&= \frac{1}{2} \int_V \mathbf{E}_2 \cdot (\mathbf{D}_2 - \mathbf{D}) dV + \frac{1}{2} \int_V (\mathbf{E}_2 - \mathbf{E}) \cdot \mathbf{D} dV \\
&= \frac{1}{2} \int_V \mathbf{E}_2 (\mathbf{D}_2 - \mathbf{D}) dV + \frac{1}{2} \int_{V_l+V_{g,2}} (\mathbf{E}_2 - \mathbf{E}) \mathbf{D} dV \\
&\quad + \frac{1}{2} \int_{dV} (\mathbf{E}_2 - \mathbf{E}) \mathbf{D} dV \\
&= \frac{1}{2} \int_{dV} (\mathbf{E}_2 \cdot \mathbf{D} - \mathbf{E} \cdot \mathbf{D}_2) dV + \int_{A_{sl}} \frac{\overline{P_0^{sl}}}{\epsilon_0} (\mathbf{D}_2 - \mathbf{D}) \cdot d\mathbf{A} \\
&\quad + \int_{A_{lg}-dA_{lg}} \frac{\overline{P_0^{lg}}}{\epsilon_0} (\mathbf{D}_2 - \mathbf{D}) \cdot d\mathbf{A} \\
&\quad + \frac{1}{2} \int_{dA_{lg,2}} \frac{\overline{P_0^{lg}}}{\epsilon_0} (\mathbf{D}_2 - \mathbf{D}) \cdot d\mathbf{A} + \frac{1}{2} \int_{dA_{lg}} \frac{\overline{P_0^{lg}}}{\epsilon_0} (\mathbf{D}_2 - \mathbf{D}) \cdot d\mathbf{A} \\
&\quad + \int_{A_{sg}} \frac{\overline{P_0^{sg}}}{\epsilon_0} (\mathbf{D}_2 - \mathbf{D}) \cdot d\mathbf{A},
\end{aligned} \tag{16}$$

where the integral of $\mathbf{E}_2 \cdot (\mathbf{D}_2 - \mathbf{D})$ over volume $V_l + V_{g,2} + dV$ and the integral of $(\mathbf{E}_2 - \mathbf{E}) \cdot \mathbf{D}$ over $V_l + V_{g,2}$ in the third form of Eq. (16) are expressed using Eqs. (14) and (15'), respectively, to obtain the final form of Eq. (16). Upon introducing Eq. (16) into Eq. (11), we obtain the following relation for the change in the formation work due to the deformation:

$$\begin{aligned}
d\Omega_q &= \Omega_{q,2} - \Omega_q \\
&= \frac{1}{2} (\mathbf{E}_2 \cdot \mathbf{D} - \mathbf{E} \cdot \mathbf{D}_2) dV - \frac{\overline{P_0^{lg}}}{\epsilon_0} \left(\frac{\mathbf{D}_2 + \mathbf{D}}{2} - \mathbf{D}_{0,2} \right) \cdot d\mathbf{A}_{lg,2} \\
&\quad + \frac{\overline{P_0^{lg}}}{\epsilon_0} \left(\frac{\mathbf{D}_2 + \mathbf{D}}{2} - \mathbf{D}_0 \right) \cdot d\mathbf{A}_{lg}
\end{aligned}$$

$$\begin{aligned}
&= \frac{1}{2} (\mathbf{E}^l \cdot \mathbf{D}^g - \mathbf{E}^g \cdot \mathbf{D}^l) dV \\
&\quad - \frac{\overline{P_0^{lg}}}{\epsilon_0} \left(\frac{D_{n,f}^l + D_{n,f}^g}{2} - D_{0,n,f} \right) dA_{lg,2} \\
&\quad + \frac{\overline{P_0^{lg}}}{\epsilon_0} \left(\frac{D_{n,i}^l + D_{n,i}^g}{2} - D_{0,n,i} \right) dA_{lg}.
\end{aligned} \tag{17}$$

The last form of Eq. (17) takes into account that before the infinitesimal shift of the surface element dA_{lg} the volume dV contained gas phase, but after the shift it contains liquid phase. Subscript n refers to the component of dielectric displacement that is normal to the surface element, and subscripts i, f to the initial and final position of shifted boundary, respectively. Denoting changes in the gas-liquid interface polarization $\delta \overline{P_0^{lg}} = \overline{P_0^{lg}} - \overline{P_0^{lg}}$ surface area, $\delta dA_{lg} = dA_{lg,2} - dA_{lg}$, and dielectric displacement $\delta D_n^j = (D_{n,f}^j - D_{0,n,f}) - (D_{n,i}^j - D_{0,n,i})$, ($j = l, g$) and confining to the first order terms with respect to δ -denoted quantities, the last form of Eq. (17) can be approximated as

$$\begin{aligned}
d\Omega_q &= \frac{1}{2} (\mathbf{E}^l \cdot \mathbf{D}^g - \mathbf{E}^g \cdot \mathbf{D}^l) dV - \frac{\overline{P_0^{lg}}}{\epsilon_0} \frac{\delta D_n^l + \delta D_n^g}{2} dA_{lg} \\
&\quad - \frac{\overline{P_0^{lg}}}{\epsilon_0} \left(\frac{D_{n,i}^l + D_{n,i}^g}{2} - D_{0,n,i} \right) \delta dA_{lg} \\
&\quad - \frac{\delta \overline{P_0^{lg}}}{\epsilon_0} \left(\frac{D_{n,i}^l + D_{n,i}^g}{2} - D_{0,n,i} \right) dA_{lg}.
\end{aligned} \tag{18}$$

2. Liquid-vapor surface element adjacent to the three phase contact line

The location of the three phase contact line and the value of the corresponding line tension depend on how we choose the Gibbs dividing surface for all three interfaces. Here, it is assumed that the position of dividing surfaces coincides with the surface of tension. But, in general, the interception line of surfaces of tensions of interfaces does not coincide with the location of line of tension, and the curvature dependence of the line tension should be taken into account.⁴

An infinitesimal movement of a portion of liquid-vapor interface that is in touch with seed particle surface (see Fig. 3) evokes a change in the three phase contact line length. Let the length of three phase contact line element that will be displaced to be dL and the entire length of the three phase contact line L . In the new location, the line element will have a length dL_2 and system triple line length will be $L_2 = L - dL + dL_2$. We denote the coefficient of spontaneous line excess polarization (see Eq. (39) of Paper I¹) in new position as $\kappa_{p,2}$. Then the change of line energy is

$$\begin{aligned}
d\Omega_L &= \Omega_{L,2} - \Omega_L = -q \left(\int_{L_2} \frac{\kappa_{p,2}}{\epsilon_0} dL - \int_L \frac{\kappa_p}{\epsilon_0} dL \right) \\
&= -q \left(\frac{\kappa_p}{\epsilon_0} \delta dL + \frac{\delta \kappa_p}{\epsilon_0} dL \right),
\end{aligned} \tag{19}$$

where $\delta\kappa_p = \kappa_{p,2} - \kappa_p$ and $\delta dL = dL_2 - dL$ and only the same order infinitesimal quantities are retained in the last form of Eq. (19). Repeating the derivation of Eq. (17) for surface and volume elements of infinitesimal outward shift of a portion of the liquid-vapor interface depicted in Fig. 3, we obtain

$$\begin{aligned}
 d\Omega_q &= \Omega_{q,2} - \Omega_q \\
 &= \frac{1}{2}(\mathbf{E}_2 \cdot \mathbf{D} - \mathbf{E} \cdot \mathbf{D}_2) dV - \frac{\overline{P}_{0,2}^{lg}}{\varepsilon_0}(\mathbf{D}_2 - \mathbf{D}_{0,2}) \cdot \delta\mathbf{A}_{lg} \\
 &\quad - \frac{\overline{P}_0^{sl}}{\varepsilon_0}(\mathbf{D}_2 - \mathbf{D}_{0,2}) \cdot \delta\mathbf{A}_{sl} \\
 &\quad + \frac{\overline{P}_0^{sg}}{\varepsilon_0} \left(\frac{\mathbf{D}_2 + \mathbf{D}}{2} - \mathbf{D}_0 \right) \cdot \delta\mathbf{A}_{sl} - q \left(\frac{\kappa_P}{\varepsilon_0} \delta dL + \frac{\delta\kappa_P}{\varepsilon_0} dL \right) \\
 &= \frac{1}{2}(\mathbf{E}^l \cdot \mathbf{D}^g - \mathbf{E}^g \cdot \mathbf{D}^l) dV - \frac{\overline{P}_{0,2}^{lg}}{\varepsilon_0} (D_{2,n}^l - D_{0,2,n}^{lg}) \delta A_{lg} \\
 &\quad - \frac{\overline{P}_0^{sl}}{\varepsilon_0} (D_{2,n}^{sl} - D_{0,2,n}^{sl}) \delta A_{sl} \\
 &\quad + \frac{\overline{P}_0^{sg}}{\varepsilon_0} \left(\frac{D_{2,n}^{sl} + D_n^{sg}}{2} - D_{0,n}^{sg} \right) \delta A_{sl} \\
 &\quad - q \left(\frac{\kappa_P}{\varepsilon_0} \delta dL + \frac{\delta\kappa_P}{\varepsilon_0} dL \right), \quad (20)
 \end{aligned}$$

where in the last form we have introduced supplementary superscripts *s* and *g* at dielectric displacements for a clearer indication of the interface involved in each case.

B. The condition for mechanical equilibrium at gas-liquid dividing surface

In a mechanical equilibrium, an infinitesimal displacement of the dividing surface for gas-liquid interface should result in zero value for the change in the reversible work of nucleus formation given by Eq. (3). In other words, the sum of various forces performing work that act on the surface should be zero at every point of the surface. In general, the magnitude of these forces is different at different locations. In the following, we use the condition that the values of chemical potentials are equal throughout the system. We apply Eq. (3) to the deformation of a gas-liquid surface element studied in Sec. III A 1, and using Eq. (18) for $d\Delta\Omega$, we obtain

$$\begin{aligned}
 d\Delta\Omega_{\delta\rho} &= (p_g^0 - p_l^0) \delta V_l + \sigma_{lg} \delta dA_{lg} + \frac{1}{2} (\mathbf{E}^l \cdot \mathbf{D}^g - \mathbf{E}^g \cdot \mathbf{D}^l) dV_l \\
 &\quad - \frac{\overline{P}_0^{lg}}{\varepsilon_0} \frac{\delta D_n^l + \delta D_n^g}{2} dA_{lg}
 \end{aligned}$$

Thus, the third term on the right hand side of Eq. (21) can be written as

$$\begin{aligned}
 &\frac{1}{2} (\mathbf{E}^l \cdot \mathbf{D}^g - \mathbf{E}^g \cdot \mathbf{D}^l) dV_l \\
 &= \frac{1}{2} (\mathbf{E}_t^l \cdot \mathbf{D}_t^g + \mathbf{E}_n^l \cdot \mathbf{D}_n^g - \mathbf{E}_t^g \cdot \mathbf{D}_t^l - \mathbf{E}_n^g \cdot \mathbf{D}_n^l) dV_l \\
 &= \frac{1}{2} \left(\left(\mathbf{E}_t^g + \nabla_2 \frac{\overline{P}_0^{lg}}{\varepsilon_0} \right) \cdot \mathbf{D}_t^g + \mathbf{E}_n^l \cdot \mathbf{D}_n^l - \left(\mathbf{E}_t^l - \nabla_2 \frac{\overline{P}_0^{lg}}{\varepsilon_0} \right) \cdot \mathbf{D}_t^l - \mathbf{E}_n^g \cdot \mathbf{D}_n^g \right) dV_l
 \end{aligned}$$

$$\begin{aligned}
 &-\frac{\overline{P}_0^{lg}}{\varepsilon_0} \left(\frac{D_{n,i}^l + D_{n,i}^g}{2} - D_{0,n,i} \right) \delta dA_{lg} \\
 &-\frac{\delta \overline{P}_0^{lg}}{\varepsilon_0} \left(\frac{D_{n,i}^l + D_{n,i}^g}{2} - D_{0,n,i} \right) dA_{lg}, \quad (21)
 \end{aligned}$$

where we have added subscript $\delta\rho$ to indicate that the change, $d\Delta\Omega$, is due to the deformation of a gas-liquid surface element at constant charge.

Next, we will follow the approach applied by Landau and Lifshitz,⁵ and Gaydos *et al.*⁶ and consider an infinitesimal displacement of the dividing surface for gas-liquid interface away from three phase contact line.

Let the vapor-liquid dividing surface undergo an infinitesimal displacement. At each point of the original surface, we draw the normal (see Fig. 2). The length of the segment of the normal lying between the points where it intersects the displaced and original surfaces is denoted by δz . Let δz be positive if the displacement of the surface is towards the gas phase. Then a volume element between the two surfaces is $\delta V = \delta z dA = \delta V_l = -\delta V_g$, where $dA = dx dy$ is the area of the surface element. The local displacement of vapor-liquid dividing surface brings about the change of electric field energy $d\Omega_{\delta\rho}$ (see Eq. (17) or its approximate form Eq. (18)).

Let us divide the electric field in the bulk phases next to the surface into two components: one component, \mathbf{E}_n , perpendicular to the surface and another, \mathbf{E}_t , parallel to the surface, and recall from Paper I¹ that the normal component of dielectric displacement is continuous through the interface. Tangential component of electric field is continuous through interface if electrical double layer is independent of position on surface, i.e., if the surface gradient vanishes, $\nabla_2 \overline{P}_0^{lg} = 0$. The surface gradient (denoted by ∇_2) of a scalar function \overline{P}_0^{lg} at any point on a surface is a vector, tangential to the surface at that point, whose direction which gives the maximum arcuate of increase of \overline{P}_0^{lg} along the surface, and its magnitude is this maximum rate of increase of \overline{P}_0^{lg} . If the surface gradient is non-zero, there is the abrupt change in \mathbf{E}_t through the electrical double of interface, i.e.,

$$\mathbf{E}_t^g - \mathbf{E}_t^l = -\nabla_2 \frac{\overline{P}_0^{lg}}{\varepsilon_0}. \quad (22)$$

We should keep in mind that the excess polarization $\overline{P}_0^{lg} / \varepsilon_0$ is the potential difference between the two sides of the surface.

$$\begin{aligned}
&= \left[\frac{1}{2} (E_n^l D_n^l - E_t^l D_t^l) - \frac{1}{2} (E_n^g D_n^g - E_t^g D_t^g) + \left(\nabla_2 \frac{\overline{P_0^{lg}}}{\varepsilon_0} \right) \cdot \frac{\mathbf{D}^l + \mathbf{D}^g}{2} \right] dV_l \\
&= \left[(E_n^l D_n^l - \frac{1}{2} \mathbf{E}^l \cdot \mathbf{D}^l) - (E_n^g D_n^g - \frac{1}{2} \mathbf{E}^g \cdot \mathbf{D}^g) + \left(\nabla_2 \frac{\overline{P_0^{lg}}}{\varepsilon_0} \right) \cdot \frac{\mathbf{D}^l + \mathbf{D}^g}{2} \right] dV_l, \tag{23}
\end{aligned}$$

where we have also used the identity $1/2(E_n D_n - E_t D_t) = E_n D_n - 1/2 \mathbf{E} \cdot \mathbf{D}$.

The total work $d\Omega_{\delta\rho}$ done in displacing the surface is obtained by inserting result (23) to Eq. (21)

$$\begin{aligned}
d\Delta\Omega_{\delta\rho} &= \{p_g^0 - p_l^0 + [E_n^l D_n^l - \frac{1}{2} \mathbf{E}^l \cdot \mathbf{D}^l] - [E_n^g D_n^g - \frac{1}{2} \mathbf{E}^g \cdot \mathbf{D}^g]\} \delta z dA_{lg} \\
&+ \left(\nabla_2 \frac{\overline{P_0^{lg}}}{\varepsilon_0} \right) \cdot \left(\frac{\mathbf{D}^l + \mathbf{D}^g}{2} \right) \delta z dA_{lg} + \sigma_{lg} \delta dA_{lg} - \frac{\delta \overline{P_0^{lg}}}{\varepsilon_0} \left(\frac{D_{n,i}^l + D_{n,i}^g}{2} - D_{0,n} \right) dA_{lg} \\
&- \frac{\overline{P_0^{lg}}}{\varepsilon_0} \left(\frac{D_{n,i}^l + D_{n,i}^g}{2} - D_{0,n} \right) \delta dA_{lg} - \frac{\overline{P_0^{lg}}}{\varepsilon_0} \frac{\delta D_n^l + \delta D_n^g}{2} dA_{lg} \\
&= [p_g^0 - p_l^0 + (E_n^l D_n^l - \frac{1}{2} \mathbf{E}^l \cdot \mathbf{D}^l) - (E_n^g D_n^g - \frac{1}{2} \mathbf{E}^g \cdot \mathbf{D}^g)] \delta z dA_{lg} \\
&+ \left(\nabla_2 \frac{\overline{P_0^{lg}}}{\varepsilon_0} \right) \cdot \left(\frac{\mathbf{D}^l + \mathbf{D}^g}{2} \right) \delta z dA_{lg} + \sigma_{lg} \delta dA_{lg} - \frac{\delta \overline{P_0^{lg}}}{2\varepsilon_0} ((D_{n,i}^l - D_{0,n}^l) + (D_{n,i}^g - D_{0,n}^g)) dA_{lg} \\
&+ \frac{\overline{P_0^{lg}}}{\varepsilon_0} \{ [(D_{n,i}^l - D_{0,n}^l) \delta dA_{lg} + \delta D_n^l dA_{lg}] + [(D_{n,i}^g - D_{0,n}^g) \delta dA_{lg} + \delta D_n^g dA_{lg}] \} \\
&= [p_g^0 - p_l^0 + (E_n^l D_n^l - \frac{1}{2} \mathbf{E}^l \cdot \mathbf{D}^l) - (E_n^g D_n^g - \frac{1}{2} \mathbf{E}^g \cdot \mathbf{D}^g)] \delta z dA_{lg} \\
&+ \left(\nabla_2 \frac{\overline{P_0^{lg}}}{\varepsilon_0} \right) \cdot \left(\frac{\mathbf{D}^l + \mathbf{D}^g}{2} \right) \delta z dA_{lg} + \sigma_{lg} \delta dA_{lg} - \frac{\delta \overline{P_0^{lg}}}{2\varepsilon_0} [(\mathbf{D}^l - \mathbf{D}_0^l) + (\mathbf{D}^g - \mathbf{D}_0^g)] \cdot d\mathbf{A}_{lg} \\
&+ \frac{\overline{P_0^{lg}}}{\varepsilon_0} \{ \delta [(\mathbf{D}^l - \mathbf{D}_0^l) d\mathbf{A}_{lg}] + \delta [(\mathbf{D}^g - \mathbf{D}_0^g) d\mathbf{A}_{lg}] \}. \tag{24}
\end{aligned}$$

To obtain the last, more compact form, we have used the fact that the normal component of the dielectric displacement is continuous at the liquid-gas interface $D_{0,n}^g = D_{0,n}^l \equiv D_{0,n}$, written the term proportional to $\overline{P_0^{lg}} / \varepsilon_0$ in terms of differences between D and D_0 , collected together all the liquid and gas-related terms proportional to $\overline{P_0^{lg}} / \varepsilon_0$, and finally moved from the notation analogous to the line of Eq. (17) to the vector notation analogous to the previous line of that equation, also identifying the variations of products $(\mathbf{D}^i - \mathbf{D}_0^i) \cdot d\mathbf{A}_{lg}$, where $i = l, g$. The condition of thermodynamic equilibrium is, of course, $d\Omega_{\delta\rho} = 0$.

In addition to the surface area, A , there are the so-called principal radii r_1 and r_2 that characterize the curvature of a nonplanar surface at each point. They represent the directions where the surface has maximum and minimum curvatures and these directions are orthogonal. The variation of the area of

the dividing surface element δdA_{lg} caused by the displacement δz may be written as (see Fig. 2)

$$\delta dA = (dx + \delta dx)(dy + \delta dy) - dx dy = dx \delta dy + dy \delta dx, \tag{25}$$

where x is in the direction where curvature radius is r_1 and y is in the direction where curvature radius is r_2 . To find δdx and δdy , the following equality can be obtained using the geometric similarity of triangles shown in Fig. 2:

$$\frac{dx}{r_1} = \frac{dx + \delta dx}{r_1 + \delta z}, \tag{26}$$

which can be written as

$$\delta dx = \frac{dx}{r_1} \delta z. \tag{27}$$

Similarly, δdy can be found as

$$\delta dy = \frac{dy}{r_2} \delta z. \quad (28)$$

Substitution of Eqs. (27) and (28) into Eq. (25) results in

$$\delta dA = \left(\frac{1}{r_1} + \frac{1}{r_2} \right) dA \delta z. \quad (29)$$

Now we proceed expressing the last three terms on the right hand side of Eq. (24) in terms of the principal radii. The force tube of dielectric displacement that surrounds the surface element dA cuts out on seed particle surface a charge dq that is different from the charge $dq + \delta dq$ cut out by the force tube surrounding displaced surface element $dA + \delta dA$. Gauss's law relates the difference in the scalar product of the dielectric displacement with the surface element to the difference in the surface charge as $\delta[(\mathbf{D} - \mathbf{D}_0)d\mathbf{A}] = \delta dq$. In general, the direction of the interface normal and the direction of the dielectric displacement vector $\mathbf{D} - \mathbf{D}_0$ at surface element $d\mathbf{A}$ do not coincide. If we denote the angle between these vectors by Greek letter ϑ , then $d\mathbf{A} \cdot \delta(\mathbf{D} - \mathbf{D}_0) = dA \delta(D_n - D_{0,n}) = dA \delta(|\mathbf{D} - \mathbf{D}_0| \cos \vartheta) = dA \delta(|\mathbf{D} - \mathbf{D}_0|) \cos \vartheta + |\mathbf{D} - \mathbf{D}_0| (\delta \cos \vartheta) dA$. Let us consider the dielectric displacement at the liquid side of the interface. The interface normal is directed into the gas phase. Then the area of the cross section of the force tube that encircles surface element dA is $dA_D = \cos \vartheta dA$ and $dq = (\mathbf{D} - \mathbf{D}_0) \cdot d\mathbf{A} = |\mathbf{D} - \mathbf{D}_0| \cos \vartheta dA$. Note that the cross section area $\cos \vartheta dA$ is considered negative, when vector $\mathbf{D} - \mathbf{D}_0$ points towards the seed particle. For a given force tube, the flux $|\mathbf{D} - \mathbf{D}_0| \cos \vartheta dA = dq$ is the same along tube of force. We now consider equipotential surface

at surface element dA of the undisplaced surface. In analogy with surface element dA , we can introduce principal radii r_3 and r_4 that characterize the curvature of equipotential surface (see Fig. 2, which should be interpreted now as taken along the force tube of dielectric displacement $\mathbf{D} - \mathbf{D}_0$). Then area of the cross section of the force tube at the displaced surface is

$$dA_D + \delta dA_D = dA_D + \left(\frac{1}{r_3} + \frac{1}{r_4} \right) dA_D \delta z_D, \quad (30)$$

where $\delta z_D = \delta z / \cos \vartheta$ is the distance between the displaced and undisplaced equipotential surfaces and $dA_D = \cos \vartheta dA$. Taking into account that $|\mathbf{D} - \mathbf{D}_0| dA_D = |\mathbf{D} - \mathbf{D}_0| (dA_D + \delta dA_D)$ or $|\mathbf{D} - \mathbf{D}_0| = |\mathbf{D} - \mathbf{D}_0| [1 / (1 + \delta dA_D / dA_D)] = |\mathbf{D} - \mathbf{D}_0| (1 - \delta dA_D / dA_D)$, where $(\mathbf{D} - \mathbf{D}_0)'$ is the dielectric displacement vector at displaced surface, we obtain

$$\begin{aligned} \delta dq &= |(\mathbf{D} - \mathbf{D}_0)'| (dA + \delta dA) (\cos \vartheta + \delta \cos \vartheta) \\ &\quad - |\mathbf{D} - \mathbf{D}_0| dA \cos \vartheta \\ &= |\mathbf{D} - \mathbf{D}_0| \left[\left(\frac{1}{r_1} + \frac{1}{r_2} \right) \cos \vartheta \right. \\ &\quad \left. - \left(\frac{1}{r_3} + \frac{1}{r_4} \right) + \frac{\partial \cos \vartheta}{\partial z} \right] dA \delta z. \end{aligned} \quad (31)$$

The above consideration is also valid for the dielectric displacement at vapor side of interface. Now we introduce subscripts l and g to differentiate between liquid and gas phase quantities.

Substitution of Eqs. (29) and (31) into $d\Delta\Omega_{\delta\rho} = 0$ with $d\Delta\Omega_{\delta\rho}$ given by Eq. (24) (and dividing the resulting equation by $\delta z dA$), yields the generalized Laplace equation

$$\begin{aligned} p_l^0 - p_g^0 - [E_n^l D_n^l - \frac{1}{2} \mathbf{E}^l \cdot \mathbf{D}^l] + [E_n^g D_n^g - \frac{1}{2} \mathbf{E}^g \cdot \mathbf{D}^g] - \left(\nabla_2^2 \frac{P_0^{lg}}{\varepsilon_0} \right) \cdot \left(\frac{\mathbf{D}^l + \mathbf{D}^g}{2} \right) \\ = \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \sigma_{gl} + \frac{\partial P_0^{lg}}{\partial c} \frac{1}{2} \left(\frac{1}{r_1^2} + \frac{1}{r_2^2} \right) \left(\frac{|\mathbf{D}^l - \mathbf{D}_0^l| \cos \vartheta^l + |\mathbf{D}^g - \mathbf{D}_0^g| \cos \vartheta^g}{2\varepsilon_0} \right) \\ - \frac{P_0^{lg}}{2\varepsilon_0} |\mathbf{D}^l - \mathbf{D}_0^l| \left[\left(\frac{1}{r_1} + \frac{1}{r_2} \right) \cos \vartheta^l - \left(\frac{1}{r_{3,l}} + \frac{1}{r_{4,l}} \right) - \frac{\partial \cos \vartheta^l}{\partial c} \frac{1}{2} \left(\frac{1}{r_1^2} + \frac{1}{r_2^2} \right) \right] \\ - \frac{P_0^{lg}}{2\varepsilon_0} |\mathbf{D}^g - \mathbf{D}_0^g| \left[\left(\frac{1}{r_1} + \frac{1}{r_2} \right) \cos \vartheta^g - \left(\frac{1}{r_{3,g}} + \frac{1}{r_{4,g}} \right) - \frac{\partial \cos \vartheta^g}{\partial c} \frac{1}{2} \left(\frac{1}{r_1^2} + \frac{1}{r_2^2} \right) \right], \end{aligned} \quad (32)$$

where $c = (1/r_1 + 1/r_2)/2$ is the average curvature of the surface, and the dependences of spontaneous polarization $\overline{P_0^{lg}}$ and angles ϑ^l , ϑ^g on the displacement $\delta z = -2(r_1^{-2} + r_2^{-2})^{-1} \delta c$ are transformed into the physically more relevant dependences on the average curvature. The terms $d \cos \vartheta^j / dc$ ($j = l, g$) describe the change of the angle between normals of the interface and the equipotential surfaces along the interface. These terms can be ignored at small cur-

atures. The last two terms in Eq. (32) are zero when the dividing surface is equipotential surface and remains an equipotential surface during the displacement.

Taking into account boundary conditions $D_n^l = D_n^g$ and $D_{n,0}^l = D_{n,0}^g$ at the liquid-vapor interface and that Eq. (22) is valid for both charged and uncharged system, and, therefore, $D_n^l - D_{n,0}^l = D_n^g - D_{n,0}^g$ and $\mathbf{E}_t^l - \mathbf{E}_{t,0}^l = \mathbf{E}_t^g - \mathbf{E}_{t,0}^g$ the relation between angles ϑ^l and ϑ^g can be presented in the

following form:

$$\tan \vartheta^g = \frac{|\mathbf{E}_t^g - \mathbf{E}_{t,0}^g|}{|\mathbf{E}_n^g - \mathbf{E}_{n,0}^g|} = \frac{\varepsilon_g}{\varepsilon_l} \tan \vartheta^l. \quad (33)$$

1. Connection to generalized pressure

We can combine the first term of Eq. (21), namely, $(p_g^0 - p_l^0)dV_l$, and the above Eq. (23), and by introducing a generalized pressure

$$\begin{aligned} p_j &= p_j^0 + \left(\nabla_2 \frac{\overline{P_0^{lg}}}{\varepsilon_0} \right) \cdot \frac{\mathbf{D}^j}{2} + \frac{1}{2} (E_t^j D_t^j - E_n^j D_n^j) \\ &= p_j^0 + \left(\nabla_2 \frac{\overline{P_0^{lg}}}{\varepsilon_0} \right) \cdot \frac{\mathbf{D}^j}{2} + \left(\frac{1}{2} \varepsilon_j \varepsilon_0 (E_t^j)^2 - \frac{1}{2} \varepsilon_j \varepsilon_0 (E_n^j)^2 \right) \\ &= p_j^0 + \left(\nabla_2 \frac{\overline{P_0^{lg}}}{\varepsilon_0} \right) \cdot \frac{\mathbf{D}^j}{2} - (\varepsilon_j \varepsilon_0 (E_n^j)^2 - \frac{1}{2} \varepsilon_j \varepsilon_0 \mathbf{E}_j^2), \end{aligned} \quad (34)$$

where $j = g, l$. In the last part of Eq. (34), a zero value sum $(\frac{1}{2} \varepsilon_j \varepsilon_0 E_n^2 - \frac{1}{2} \varepsilon_j \varepsilon_0 E_n^2)$ is added to the term in brackets. The last term of the last form of Eq. (34) coincides with the normal components of Maxwell's stress tensor applied by Warshavsky and Shchekin⁷ to the surface of the droplet from the side of phase j . They used this tensor to estimate the effect of external homogeneous electric field on the formation of dielectric droplet.

In comparison with Warshavsky and Shchekin,⁷ the additional term $(\nabla_2 \frac{\overline{P_0^{lg}}}{\varepsilon_0}) \cdot \frac{\mathbf{D}^j}{2}$ of Eq. (34) should be omitted, as these authors did not consider surface polarization. In Appendix B, the Maxwell's stress tensor at constant densities and constant chemical potentials of dielectrics, and the generalized pressure obtained above (with $\overline{P_0^{lg}}$ ignored) is also derived by considering a dielectric body between the conducting plates of a parallel-plate capacitor.

The work necessary to cause the change in the volume $\delta V = \delta z \delta A$ is

$$(p_g - p_l) \delta z \delta A = \left\{ \begin{aligned} & p_g^0 - p_l^0 + [(E_n D_n)_l - \frac{1}{2} (\mathbf{E} \mathbf{D})_l] - [(E_n D_n)_g - \frac{1}{2} (\mathbf{E} \mathbf{D})_g] \\ & + \left(\nabla_2 \frac{\overline{P_0^{lg}}}{\varepsilon_0} \right) \cdot \frac{\mathbf{D}^l + \mathbf{D}^g}{2} \end{aligned} \right\} \delta z \delta A. \quad (35)$$

C. Thermodynamic equilibrium at the three phase contact line

Next, we consider an equilibrium condition at the three phase contact line. Let the surface of vapor-liquid separation undergo an infinitesimal displacement δz that results in an infinitesimal displacement δl of contact line along seed particle surface perpendicular to contact line (see Fig. 3). Then a surface element on seed particle between the displaced and undisplaced contact lines is $\delta A = \delta l dL = \delta A_{sl} = -\delta A_{sg}$, where dL is a contact line element (the element is perpendicular to the plane of Fig. 3). The increase of the area of vapor-liquid separation surface, caused by the fact that the displacements δz and δl are not parallel, is $\delta A_{lg} = dL \cdot \delta l \cos \theta$. The length element $dL \cos \theta$ connects the tips of displacement vectors, where θ is the contact angle (see Fig. 3). The volume change that results from an infinitesimal displacement δz is in the order $\sim \delta z dL \delta l \cos \theta$. Therefore, we can ignore volume work compared with surface formation work which depends on the second order of the infinitesimal quantities, $\sim \delta l dL$. Besides the surface work, there is a work connected with the change δdL of line element dL , if the curvature of the projection of the contact line curve onto the tangent plane drawn at a given point to the seed particle is not zero. Let us denote the radius of this projection, so called geodesic curvature, with r_g . Then the change δdL of line element dL is (derivation is performed

analogously with Eqs. (26) and (27))

$$\delta dL = \frac{dL}{r_g} \delta l. \quad (36)$$

We apply Eq. (3) to the displacement under study, and use Eq. (20) for $d\Omega_{\delta\rho}$ to get the work connected with the displacement δz

$$\begin{aligned} & d\Omega_{\delta\rho} \\ &= \sigma_{gl} dL \delta l \cos \theta + (\sigma_{sl} - \sigma_{sg}) \delta l dL \\ & - \frac{\overline{P_0^{lg}}}{\varepsilon_0} (D_n^{lg} - D_{0,n}^{lg}) dL \delta l \cos \theta \\ & - \left(\frac{\overline{P_0^{sl}}}{\varepsilon_0} (D_n^{sl} - D_{0,n}^{sl}) - \frac{\overline{P_0^{sg}}}{\varepsilon_0} \left(\frac{D_n^{sl} + D_n^{sg}}{2} - D_{0,n}^{sg} \right) \right) \delta l dL \\ & + \left(\kappa - \frac{q\kappa_P}{\varepsilon_0} \right) \frac{dL}{r_g} \delta l - q \frac{\delta \kappa_P}{\varepsilon_0} dL, \end{aligned} \quad (37)$$

where we have ignored infinitesimal differences between values of excess polarization and dielectric displacement in systems of displaced and undisplaced surface elements. Dielectric displacement is considered to be perpendicular with conducting seed particle surface.

From the requirement $d\Omega_{\delta\rho} = 0$, we obtain the generalized Young equation

$$\begin{aligned} & \sigma_{gl} \cos \theta + (\sigma_{sl} - \sigma_{sg}) - \frac{\overline{P_0^{lg}}}{\varepsilon_0} (D_n^{lg} - D_{0,n}^{lg}) \cos \theta \\ & - \left(\frac{\overline{P_0^{sl}}}{\varepsilon_0} (D_n^{sl} - D_{0,n}^{sl}) - \frac{\overline{P_0^{sg}}}{\varepsilon_0} \left(\frac{D_n^{sl} + D_n^{sg}}{2} - D_{0,n}^{sg} \right) \right) \\ & + \left(\kappa - \frac{q\kappa_P}{\varepsilon_0} \right) \frac{1}{r_g} - \frac{q}{\varepsilon_0} \frac{\partial \kappa_P}{\partial r_g} = 0, \end{aligned} \quad (38)$$

where the identity $\delta r_g \equiv \delta l$ is used in deriving the last term, which describes the curvature dependence of the coefficient κ_P .

D. The condition of composition and size of a critical nucleus: Generalized Kelvin-Thomson equation

In deriving the generalized Laplace equation (32), we used the fact that our system is at chemical equilibrium. Therefore, pressures p_g^0 and p_l^0 correspond to the pressures in bulk phases in the absence of electric field and these phases are at chemical equilibrium with our system. Hence, these pressures as reference pressures are the same for all points of bulk phases of our system (see also discussion in Appendix B).

We assume that liquid nucleus is incompressible and use Maxwell equation⁸

$$d\mu_{i,l} = v_{i,l} dp^0, \quad (39)$$

where $v_{i,l}$ is the partial molecular volume of species i . Integrating Eq. (39), the chemical potential of species i in the liquid interior of a nucleus can be presented as

$$\mu_{i,l}(p_l^0, x_{i,l}) = \mu_{i,l}(p_g^0, x_{i,l}) + v_{i,l}(p_l^0 - p_g^0), \quad (40)$$

where $x_{i,l}$ is the mole fraction of species i . Applying the conditions requiring equality of chemical potentials, Eqs. (8) and (9), we can express Eq. (40) as

$$\Delta\mu_i = -v_{i,l}(p_l^0 - p_g^0), \quad (41)$$

where $\Delta\mu_i \equiv \mu_{i,l}(p_g^0, x_{i,l}) - \mu_{i,g}(p_g^0, x_{i,g})$.

Considering the vapor as a mixture of ideal gases, the liquid solution to be incompressible, and using equilibrium conditions for species i in saturated vapor above a flat surface of liquid solution with given mole fractions $x_{i,l}$, the difference $\Delta\mu_i$ can be presented as⁹

$$\Delta\mu_i \cong -k_b T \ln \left(\frac{A_{i,g}}{A_{i,l}(x_{i,l})} \right), \quad (42)$$

where $A_{i,g} = p_{i,g}^0 / p_{i,sat}^{pure}$ is the gas-phase activity of species i , $p_{i,sat}^{pure}$ is the saturated vapor pressure of species i over flat surface of pure liquid, $p_{i,g}^0$ is the partial pressure of species i in the nucleating vapor, $A_{i,l}(T, x_{i,l}) = p_{i,sat}^0 / p_{i,sat}^{pure}$ is the liquid-phase activity, $p_{i,sat}^0$ is the partial pressure of free molecules of component i in the equilibrium vapor above a flat surface of a liquid solution which composition is given by mole fractions $x_{i,l}$, and k_b is the Boltzmann constant.

Substituting Eqs. (32) and (42) into Eq. (40), we obtain

$$\begin{aligned} k_b T \ln \left(\frac{A_{i,g}}{A_{i,l}(x_{i,l})} \right) &= v_i \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \sigma_{gl} + v_i [E_n^l D_n^l - \frac{1}{2} \mathbf{E}^l \cdot \mathbf{D}^l] + v_i [E_n^g D_n^g - \frac{1}{2} \mathbf{E}^g \cdot \mathbf{D}^g] \\ &+ v_i \left(\nabla_2 \frac{\overline{P_0^{lg}}}{\varepsilon_0} \right) \cdot \frac{\mathbf{D}^l + \mathbf{D}^g}{2} \\ &+ v_i \frac{\partial \overline{P_0^{lg}}}{\partial c} \frac{1}{2} \left(\frac{1}{r_1^2} + \frac{1}{r_2^2} \right) \left(\frac{|\mathbf{D}^l - \mathbf{D}_0^l| \cos \vartheta^l + |\mathbf{D}^g - \mathbf{D}_0^g| \cos \vartheta^g}{2\varepsilon_0} \right) \\ &- v_i \frac{\overline{P_0^{lg}}}{2\varepsilon_0} |\mathbf{D}^l - \mathbf{D}_0^l| \left[\left(\frac{1}{r_1} + \frac{1}{r_2} \right) \cos \vartheta^l - \left(\frac{1}{r_{3,l}} + \frac{1}{r_{4,l}} \right) \right. \\ &\quad \left. - \frac{\partial \cos \vartheta^l}{\partial c} \frac{1}{2} \left(\frac{1}{r_1^2} + \frac{1}{r_2^2} \right) \right] \\ &- v_i \frac{\overline{P_0^{lg}}}{2\varepsilon_0} |\mathbf{D}^g - \mathbf{D}_0^g| \left[\left(\frac{1}{r_1} + \frac{1}{r_2} \right) \cos \vartheta^g - \left(\frac{1}{r_{3,g}} + \frac{1}{r_{4,g}} \right) \right. \\ &\quad \left. - \frac{\partial \cos \vartheta^g}{\partial c} \frac{1}{2} \left(\frac{1}{r_1^2} + \frac{1}{r_2^2} \right) \right]. \end{aligned} \quad (43)$$

Equation (43) is valid for every point of critical nucleus surface, and left and right hand sides of this equation depend on

the composition of the embryo. Note that in case of spherical symmetry only the first line remains in Eq. (43), i.e., we

get well-known Kelvin-Thomson equation for spherical liquid layer around charged seed.

E. The generalized Laplace equation as a differential equation for the shape of a nucleus

Note that the derivations presented so far can also be conducted without the assumption of axial symmetry. In the following, this assumption is however necessary. In spherical coordinates, where the zenith angle ϕ ($0 \leq \phi \leq \Phi$) is taken from the positive z -axis that coincides with the symmetry axis of our system (see Fig. 4), the position of the gas-liquid surface can be presented with a function $r(\phi)$, where r denotes the radial distance from an origin taken at the center of seed particle. Well known formulae for mean curvature from differential geometry give

$$\frac{1}{r_1} + \frac{1}{r_2} = \frac{r^2 + 2(r')^2 - rr''}{(\sqrt{(r')^2 + r^2})^3} + \frac{r \sin \phi - r' \cos \phi}{r \sin \phi \sqrt{(r')^2 + r^2}}, \quad (44)$$

where r' and r'' are the first and second order derivatives of the curve $r(\phi)$ with respect to zenith angle ϕ , respectively. Thus, the generalized Laplace equation (32) is a second order differential equation for the curve $r(\phi)$. This equation can be complemented with the boundary conditions for a nucleus

$$\left. \begin{aligned} (dr/d\phi)|_{\phi=0} &= 0 \\ (dr/d\phi)|_{r=R} &= -R \tan \theta \end{aligned} \right\}, \quad (45)$$

where R is the seed particle radius and θ is the contact angle that can be determined from the generalized Young equation (38). The change of the zenith angle ϕ by $-d\phi$ starting from contact line on seed particle surface will change the position on the surface $r(\phi)$ along radial distance by $dr_{\parallel} = -r'(\phi)d\phi$ (see Fig. 4). The corresponding change along seed particle surface perpendicular to the radial direction is $dr_{\perp} = Rd\phi$.

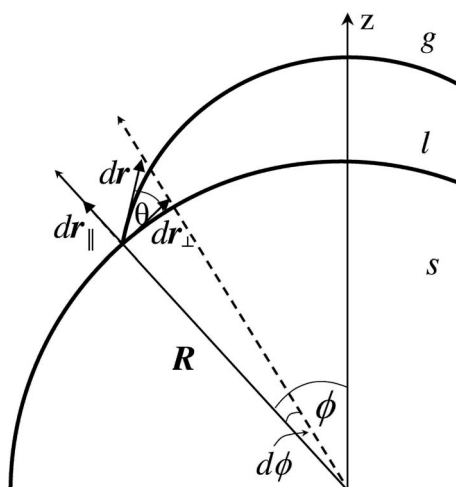


FIG. 4. The tangential change along the nucleus surface $r(\phi)$ with the change of the zenith angle ϕ by $-d\phi$ starting from contact line. This change is divided into two components: the component along radial distance dr_{\parallel} and the component along seed particle surface perpendicular to the radial direction dr_{\perp} , respectively. The liquid nucleus is denoted by l , the vapor phase by g , and the solid seed particle by s .

The slope of $r(\phi)$ at contact line is determined by the contact angle θ and, thus, is $\tan \theta = dr_{\parallel}/dr_{\perp} = -r'(\phi)d\phi/(Rd\phi)$.

If we present the location of liquid-vapor separation surface as a function $z = z(\rho_z)$, where ρ_z is distance to the z -axis, i.e., to the axis of rotational symmetry, then the mean curvature of the surface $r(\rho_z)$ is given by the following simpler equation:

$$\frac{1}{r_1} + \frac{1}{r_2} = \frac{z''}{(\sqrt{1 + (z')^2})^3} + \frac{z'}{\rho_z \sqrt{1 + (z')^2}}, \quad (46)$$

but the application of this equation can be more complicated than that of Eq. (44) as for larger nuclei covering more than half of seed particle surface or having contact angle larger than a right angle there are two values of coordinate z for the position of vapor-liquid separation surface corresponding to the same value of coordinate ρ_z .

To specify the dielectric displacement D and the electric field strength E values in the left-hand side of Eq. (32), we must solve the electrostatic Laplace equation $\Delta\varphi = 0$ for the electric potential φ around the seed particle inside the liquid nucleus and in the surrounding vapor with the boundary conditions at the seed particle and nucleus surfaces and at infinity

$$\left. \begin{aligned} \varphi|_{\rho=R} &= \text{Const.}, \\ \varphi|_{\rho \rightarrow \infty} &= 0, \\ \varphi_a|_{\rho=R} &= \varphi_s|_{\rho=R} + \frac{P_0^{sa}}{\varepsilon_0}, \\ a &= g \text{ either } l, \\ D_n^a|_{\rho=R} &= D_n^s|_{\rho=R}, \\ \mathbf{E}_t^s|_{\rho=R} &= 0, \\ \mathbf{E}_t^a|_{\rho=R} &= -\nabla_2 \frac{P_0^{sa}}{\varepsilon_0}, \\ \varphi_g|_{\rho=r} &= \varphi_l|_{\rho=r} + \frac{P_0^{lg}}{\varepsilon_0}, \\ D_n^g|_{\rho=r} &= D_n^l|_{\rho=r}, \\ \mathbf{E}_t^g|_{\rho=r} &= \mathbf{E}_t^l|_{\rho=r} - \nabla_2 \frac{P_0^{lg}}{\varepsilon_0}. \end{aligned} \right\} \quad (47)$$

The charge q of seed particle that corresponds to the constant electrical potential value in the first equation of the set of Eqs. (47) is given by the following equation:

$$\oint_{4\pi R^2} D_n^a dA_a = q, \quad (48)$$

where dA_a is a surface element of the seed particle, a is either gs or lg indicating that a surface element can separate either gas-solid or liquid-solid phases around seed particle.

Both the generalized Laplace equation (32) and the generalized Young equation (38) contain the value of dielectric displacement at surfaces of uncharged system. Therefore, the electrostatic Laplace equation $\Delta\varphi = 0$ have to be solved also for the uncharged seed ($q = 0$ in Eq. (48)) using boundary

conditions (47), or the calculations should be repeated for the seed having the same charge but in the absence of double layers. The difference of dielectric displacements of the latter calculations also represents dielectric displacement of uncharged system.

The mean curvature of an equipotential surface can be represented as¹⁰

$$\frac{\partial |\mathbf{E} - \mathbf{E}_0|}{\partial z} = -|\mathbf{E} - \mathbf{E}_0| \left(\frac{1}{r_3} + \frac{1}{r_4} \right), \quad (49)$$

or

$$\frac{\nabla |\nabla(\varphi - \varphi_0)| \cdot \nabla(\varphi - \varphi_0)}{(\nabla(\varphi - \varphi_0))^2} = \left(\frac{1}{r_3} + \frac{1}{r_4} \right), \quad (50)$$

where z is the normal direction to the equipotential surface at the point under consideration, directed along the electric field $\mathbf{E} - \mathbf{E}_0 = (\mathbf{D} - \mathbf{D}_0)/\varepsilon$.

The requirement of simultaneous consistent solution of electrostatic Laplace equation and Eq. (32) makes the exact determination of a function $r(\phi)$ rather complicated in practice. The adjustment of solution methods used in numerous studies¹¹ dealing with the deformation of droplets in electric field can be adopted for obtaining the shape of a nucleus of given volume from Eq. (32). It should be noted that the properties of a critical nucleus must in addition to generalized Laplace equation (32) also satisfy the generalized Kelvin-Thomson equations (43). Actually one of the equations (43) can be used instead of the Laplace equation (32) for determining the shape of the nucleus. For axially symmetrical systems, governing equations can be reduced to a system of algebraic equations using Legendre polynomial expansion. Such expansion is done and algebraic equations solved in Ref. 12, where the equilibrium parameters of a small dielectric one-component droplet are studied, by placing a droplet that contains charged condensation nucleus into a uniform external electric field.

IV. CONCLUSIONS

A thermodynamically consistent formalism is applied to calculate the reversible work needed to form a dielectric liquid nucleus of a new phase on a charged insoluble conducting seed particle within a uniform macroscopic mother phase. We

consider a general form of cap-shape nucleus not necessarily having spherical form or axial symmetry, but we assume that deviations from the spherical form are such that we can ignore the changes in surface and line tensions values invoked by these deviations. Electrical surface and line excess quantities due to spontaneous polarization of molecules in interfacial and triple line zones that were introduced in Paper I¹ are used to derive thermodynamic work of embryo formation. Our new expression for the work of nucleus formation agrees with the results of Nishioka and Kusaka² and Debenedetti and Reiss³ for homogenous nucleation if we ignore terms with the seed particle surface area and charge in our result. The conditions of its extrema yield the correct conditions of equilibrium between the critical nucleus and the mother phase. We derive a generalized Laplace equation expressing the condition of mechanical equilibrium at nucleus surface, and a generalized Young equation giving thermodynamic equilibrium at the three phase contact line. We also derive a generalized Kelvin-Thomson equation suitable for calculations of the size and composition of a critical nucleus. The generalized Laplace equation is also presented for axially symmetrical systems as differential equation describing the effect of the electric field of charged seed particle on the shape of a nucleus. This equation can be solved only with the simultaneous consistent solution of electrostatic Laplace equations for bulk phases.

ACKNOWLEDGMENTS

This work was supported by the Estonian Science Foundation (Grant No. 8806), the Estonian Research Council Targeted Financing Project (SF0180043s08), and Academy of Finland (Project No. 1127372, Center of Excellence Program Project No. 1118615, The Computational Science Research Programme of Academy of Finland Project No. 135054), European Research Council Starting Grant No. 257360-MOCAPAF.

APPENDIX A: DETAILED DERIVATION STEPS OF EQ. (14)

The detailed intermediate steps that lead from the first form of Eq. (14) to the last form of it are

$$\begin{aligned} & \frac{1}{2} \int_{V_l} \mathbf{E}_2 \cdot (\mathbf{D}_2 - \mathbf{D}) dV + \frac{1}{2} \int_{V_{g,2}} \mathbf{E}_2 \cdot (\mathbf{D}_2 - \mathbf{D}) dV + \frac{1}{2} \int_{dV} \mathbf{E}_2 \cdot (\mathbf{D}_2 - \mathbf{D}) dV \\ &= \frac{1}{2} \int_{A_{sl}} \varphi_{2,l} (\mathbf{D}_2 - \mathbf{D}) \cdot d\mathbf{A} - \frac{1}{2} \int_{A_{lg}} \varphi_{2,l} (\mathbf{D}_2 - \mathbf{D}) \cdot d\mathbf{A} + \frac{1}{2} \int_{A_{sg}} \varphi_{2,g} (\mathbf{D}_2 - \mathbf{D}) \cdot d\mathbf{A} \\ &+ \frac{1}{2} \int_{A_{lg} - dA_{lg} + dA_{lg,2}} \varphi_{2,g} (\mathbf{D}_2 - \mathbf{D}) \cdot d\mathbf{A} + \frac{1}{2} \int_{dA_{lg}} \varphi_{2,l} (\mathbf{D}_2 - \mathbf{D}) \cdot d\mathbf{A} - \frac{1}{2} \int_{dA_{lg,2}} \varphi_{2,l} (\mathbf{D}_2 - \mathbf{D}) \cdot d\mathbf{A} \\ &= \frac{1}{2} \int_{A_{sl}} \varphi_{2,l} (\mathbf{D}_2 - \mathbf{D}) \cdot d\mathbf{A} - \frac{1}{2} \int_{A_{lg} - dA_{lg} + dA_{lg,2}} (\varphi_{2,l} - \varphi_{2,g}) (\mathbf{D}_2 - \mathbf{D}) \cdot d\mathbf{A} + \frac{1}{2} \int_{A_{sg}} \varphi_{2,g} (\mathbf{D}_2 - \mathbf{D}) \cdot d\mathbf{A} \\ &= \frac{1}{2} \int_{A_{sl}} \varphi_{2,s} (\mathbf{D}_2 - \mathbf{D}) \cdot d\mathbf{A} + \frac{1}{2} \int_{A_{sl}} \frac{\overline{P}_0^{sl}}{\varepsilon_0} (\mathbf{D}_2 - \mathbf{D}) \cdot d\mathbf{A} + \frac{1}{2} \int_{A_{lg} - dA_{lg}} \frac{\overline{P}_0^{lg}}{\varepsilon_0} (\mathbf{D}_2 - \mathbf{D}) \cdot d\mathbf{A} \end{aligned}$$

$$\begin{aligned}
& + \frac{1}{2} \int_{dA_{lg,2}} \frac{\overline{P_{0,2}^{lg}}}{\epsilon_0} (\mathbf{D}_2 - \mathbf{D}) \cdot d\mathbf{A} + \frac{1}{2} \int_{A_{sg}} \varphi_{2,s} (\mathbf{D}_2 - \mathbf{D}) \cdot d\mathbf{A} + \frac{1}{2} \int_{A_{sg}} \frac{\overline{P_0^{sg}}}{\epsilon_0} (\mathbf{D}_2 - \mathbf{D}) \cdot d\mathbf{A} \\
& = \frac{1}{2} \int_{A_{sl}} \frac{\overline{P_0^{sl}}}{\epsilon_0} (\mathbf{D}_2 - \mathbf{D}) \cdot d\mathbf{A} + \frac{1}{2} \int_{A_{lg}-dA_{lg}} \frac{\overline{P_0^{lg}}}{\epsilon_0} (\mathbf{D}_2 - \mathbf{D}) \cdot d\mathbf{A} \\
& + \frac{1}{2} \int_{dA_{lg,2}} \frac{\overline{P_{0,2}^{lg}}}{\epsilon_0} (\mathbf{D}_2 - \mathbf{D}) \cdot d\mathbf{A} + \frac{1}{2} \int_{A_{sg}} \frac{\overline{P_0^{sg}}}{\epsilon_0} (\mathbf{D}_2 - \mathbf{D}) \cdot d\mathbf{A}, \tag{A1}
\end{aligned}$$

where potential jumps at surfaces in the fourth form of Eq. (A1) are replaced according to the generalizations of Eq. (33) of Paper I¹ with surface excess polarizations. This also concerns the replacement of potentials just outside of seed particle surface, $\varphi_{2,l}$, $\varphi_{2,g}$, with the potential of seed particle $\varphi_{2,s}$. It should be noted that the potential φ_2 is continuous at the surface element dA_{lg} , and therefore the sum of surface terms for this element cancel out. As potential $\varphi_{2,s}$ is constant everywhere in the interior of the seed particle, and the charge of seed particle is kept constant during surface displacement, the surface integrals containing $\varphi_{2,s}$ cancel out and are thus dropped in the last form of Eq. (A1).

APPENDIX B: PRESSURE IN ELECTRIC FIELD: MAXWELL STRESS TENSOR

Usually, to describe the effect of electric field on a bulk dielectric body, the expression of the Maxwell stress tensor^{13,14} is used. In deriving the Maxwell stress tensor for dielectric liquid, Landau and Lifshitz¹³ base their treatment on the principle that the forces acting on any finite volume in a body can be reduced to forces applied to the surface of that volume. This is a consequence of the law of conservation of momentum. The surface force density is subsequently taken as the stress tensor. Liu and Stierstadt¹⁴ point out that the electromagnetic field exchanges momentum with the material, so the total momentum of both (electromagnetic field and the material with macroscopic flow) remains conserved. Their derivation of the Maxwell stress tensor is broader in focus and validity than that by Landau and Lifshitz.¹³

We consider surface forces in dielectric fluid with no macroscopic flow of fluid. The flux of momentum due to molecules and photons through a surface element $d\mathbf{A} = \mathbf{n}dA$ from outside into a volume element is just the force $-\Pi_{ik}dA_k = -\Pi_{ik}n_k dA$ by which the environment acts on the volume. The minus sign above is taken because the normal vector \mathbf{n} to the surface element is outwards of the volume element. The force per unit surface area by which the matter in the volume element acts on its environment is $\Pi_{ik}n_k$. The quantity $\Pi_{i,k}$ is the component of a tensor that gives the force component in the direction of i th axis acting on unit surface area perpendicular to k th axis.

Any small part of the surface can be considered as a flat and the dielectrics and electric field next to it as homogeneous. It can be imagined that electric field in this layer is

created by conducting plates of parallel-plate capacitor surrounding the layer. We will follow the general method for determining surface forces. The work done in virtual displacement of the walls of a box containing this part of surface layer is equal to the corresponding change of an appropriate thermodynamic potential.

If we consider a small volume element, where the medium and electric field can be considered homogeneous, then the change of internal energy per volume unit, u , can be presented as (see Eq. (1) of Paper I,¹ where due to fixed volume $dV = 0$, and using the second form of Eq. (13) of Paper I¹)

$$du = Tds + \sum_i \mu_i d\tau_i + \mathbf{E}d\mathbf{D}, \tag{B1}$$

where s is the entropy density and τ_i is the number density of species i .

We have considered charging of the seed particle where the total system was thermally isolated and closed, but the gas phase was large enough to keep the temperature through the total system constant. Also species were free to move inside bulk phases of liquid and vapor. Therefore, if we consider a small volume inside a bulk gaseous phase, the chemical potentials and temperature are the thermodynamic parameters that are kept constant during charging. Although chemical potentials are also kept uniform in liquid nucleus of constant volume and shape, however, their values may not preserve during charging unless the mass exchange with gas phase is allowed. At constant temperature and chemical potentials, an appropriate thermodynamic potential to consider is the grand potential (per unit volume)

$$\varpi = u - Ts - \sum_i \mu_i \tau_i. \tag{B2}$$

Internal energy density u also includes here the electric field energy. Adding to the left hand side of Eq. (B1), a quantity $d(-Ts - \sum_i \mu_i \tau_i)$ and to the hand right side an equivalent quantity $-sdT - Tds - \sum_i \mu_i d\tau_i - \sum_i \tau_i d\mu_i$, we obtain

$$d\varpi = -sdT - \sum_i \tau_i d\mu_i + \mathbf{E}d\mathbf{D}. \tag{B3}$$

Equation (B3) shows that the value of thermodynamic potential ϖ is determined by the temperature, chemical potentials, and the dielectric displacement.

For comparison with frequently referred results for electrical forces in liquids at constant temperature and density (see, e.g., Landau and Lifshitz¹³), we also consider the following thermodynamic potential,¹⁵ although the expression of forces that follow from this potential does not apply to our thermodynamic system:

$$\tilde{f} = u - Ts - \mathbf{E}\mathbf{D}, \quad (\text{B4})$$

where analogously with Eq. (B3)

$$d\tilde{f} = -s_l dT + \sum_i \mu_i d\tau_i - \mathbf{D}d\mathbf{E}, \quad (\text{B5})$$

i.e., temperature, number densities τ_i , and electric field strength \mathbf{E} are the independent variables that determine the potential \tilde{f} . The potential \tilde{f} is appropriate for charging processes, where temperature and number densities are constant and varying potential difference of an imaginary capacitor changes field strength.

Let us denote with $\delta\Phi$ the change of a thermodynamic potential in the deformation of bulk dielectrics volume element V and let ϕ be the potential per unit volume. The choice for a thermodynamic potential depends on the specific thermodynamic path considered. When deformation is done at given temperature, mass, and electrical potentials of electrodes, the appropriate thermodynamic potential is the potential $\delta\Phi = \delta\tilde{F} = \delta \int_V \tilde{f} dV$.¹³ When deformation is done at given temperature, chemical potentials, and electric charge, the appropriate thermodynamic potential is given by $\delta\Phi = \delta\Omega = \delta \int_V \varpi_l dV$.

The potential change $\delta\Phi$ in deforming volume element V is

$$\delta\Phi \equiv \delta \int_V \phi dV = - \oint (\Pi_{i,k} \delta r_i) dA_k, \quad (\text{B6})$$

where δr_i is the infinitesimal (or virtual) displacement of the surface, and $dA_k = n_k dA$. The work done by the matter in the volume element against its environment leads to the decrease of potential Φ .

In simple geometries, if ϕ and $\Pi_{i,k} \delta r_i$ are uniform (electric field and pressure are location independent in our small volume element), Eq. (B6) reduces to

$$\delta\Phi = \delta(\phi V) = \phi \delta V + V \delta\phi = -A_k \Pi_{i,k} \delta r_i. \quad (\text{B7})$$

Since ϕ is known, we shall evaluate $A_k \Pi_{i,k} \delta r_i$ while taking both A_k and δr_i to point in all three orthogonal directions and hereby obtain all nine components of $\Pi_{i,k}$. We choose one of the axis of the coordinate system parallel to the electric field, thus the remaining two are perpendicular to the field.

Following Liu and Stierstadt,¹⁴ we consider a parallel-plate capacitor that is filled with a dielectric fluid. Denoting the three linear dimensions of the capacitor as x , y , z , with $x \ll y, z$, the three pairs of surfaces (see Fig. 5) have the areas $A_x = yz$, $A_y = xz$, $A_z = xy$, respectively; and the volume is $V = xyz$. Taking the two metal plates as shown in Fig. 5, the electric fields E, D are along the x -axis. (We neglect the small fringing fields at the edges or it is also possible to consider small portion of dielectric in the center of capacitor where electric field is uniform. Surfaces confining this small

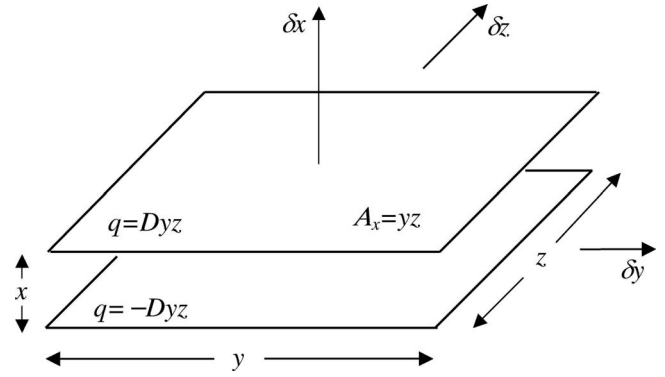


FIG. 5. Metal plates with constant charge, dielectric fluid sandwiched between them. Displacing upper plate δx or δz (or δy), respectively, decompresses and shears the fluid.

volume behave similar to surfaces of a capacitor in virtual displacements.)

We now successively displace the three surfaces with surface areas A_x, A_y, A_z , respectively, in all three directions, $\delta r_i = \delta x, \delta y, \delta z$ (which is why the capacitor has to be finite), while holding constant the following quantities: (a) temperature T , masses $\tau_i V$, and the electrical potentials of electrodes ($\Delta\phi = \phi_{upper} - \phi_{lower} = \text{const.}$) or (b) temperature T , chemical potentials μ_i , and electric charges $q = \pm DA_x$ (the dielectric displacement in parallel plate capacitor is proportional to the surface density of free charges on capacitor plates). Because of the simple geometry, Eq. (B7) holds and will be used.

First, we displace the upper surface (metal plate) with area $A_x = yz$. When the displacement is δx , we have for the case (a) ($\phi = \tilde{f}$)

$$\delta T = 0, \delta V = A_x \delta x, \delta E/E = -\delta x/x = \delta\tau_i/\tau_i. \quad (\text{B8})$$

Here, for a parallel plate capacitor $E = \Delta\phi/x$, and thus $\delta E = -\Delta\phi \delta x/x^2$, and the requirement for constant mass leads to $\delta(\tau_i V) = V \delta\tau_i + \tau_i \delta V = xyz \delta\tau_i + \tau_i yz \delta x = 0$. For the case (b) ($\phi = \varpi$), we have

$$\delta T = 0, \delta\mu_i = 0, \delta V = A_x \delta x, \delta D = 0. \quad (\text{B9})$$

If the displacement is δy or δz (implying a shear motion of upper metal plate), we have $\delta T, \delta V, \delta\tau_i, \delta E = 0$ or $\delta T, \delta V, \delta\mu_i, \delta D = 0$, respectively. Inserting changes corresponding to the three directions x, y , and z into Eq. (B7) and using Eqs. (B4) and (B5), or Eqs. (B2) and (B3), for ϕ and $d\phi$ we obtain for the case (a) ($\phi = \tilde{f}$)

$$\begin{aligned} \Pi_{x,x} \delta x &= \left(Ts + \sum_i \mu_i \tau_i - u \right) \delta x \\ &= - \left(\tilde{f} - \sum_i \tau_i \frac{\partial \tilde{f}}{\partial \tau_i} \Big|_{\mathbf{E}, T, \tau_{j \neq i}} + E_x D_x \right) \delta x, \\ \Pi_{z,x} &= \Pi_{y,x} = 0, \end{aligned} \quad (\text{B10})$$

where we have cancelled out the surface area A_x from both sides and used Eq. (B8).

For the case (b) ($\phi = \varpi$),

$$\begin{aligned}\Pi_{x,x}\delta x &= \left(Ts + \sum_i \mu_i \tau_i - u\right) \delta x = -\varpi \delta x, \\ \Pi_{x,z} &= \Pi_{x,y} = 0,\end{aligned}\quad (\text{B11})$$

respectively. Here, we have used Eq. (B9). We present the second form of $\Pi_{x,x}$ in Eq. (B10) to show that our result coincides with the result by Landau and Lifshitz.¹⁶ This form follows from Eq. (B7) if we represent, applying Eqs. (B5) and (B8), the term $V\delta\tilde{f}$ in Eq. (B7) as follows:

$$\begin{aligned}V\delta\tilde{f} &= V\left(\sum_i \mu_i \delta\tau_i - \mathbf{D}\delta\mathbf{E}\right) \\ &= yz\left(\sum_i \frac{\partial\tilde{f}}{\partial\tau_i}\bigg|_{\mathbf{E},T,\tau_{j\neq i}} \delta\tau_i - D_x\delta E_x\right) \\ &= yzx\left(\sum_i \frac{\partial\tilde{f}}{\partial\tau_i}\bigg|_{\mathbf{E},T,\tau_{j\neq i}} \frac{-\tau_i\delta x}{x} - D_x\frac{-E_x\delta x}{x}\right).\end{aligned}\quad (\text{B12})$$

If the surface is the backward surface with area $A_z = xy$ and the displacement δz (see Fig. 5), we have for case (a) $\delta V = A_z\delta z$, $\delta\tau_i/\tau_i = -\delta z/z$, and δT , $\delta E = 0$. For case (b), we have δT , $\delta\mu_i = 0$, $\delta V = A_z\delta z$, and $\delta D/D = -\delta z/z$. If the displacement is δx or δy , we have (a) δV , $\delta\tau_i$, $\delta E = 0$ and (b) δV , $\delta D = 0$, respectively. Hence,

$$\begin{aligned}\Pi_{z,z}\delta z &= \left(Ts + \sum_i \mu_i \tau_i + E_x D_x - u\right) \delta z \\ &= -\left(\tilde{f} - \sum_i \tau_i \frac{\partial\tilde{f}}{\partial\tau_i}\bigg|_{\mathbf{E},T,\tau_{j\neq i}}\right) \delta z, \quad \Pi_{x,z} = \Pi_{y,z} = 0\end{aligned}\quad (\text{B13})$$

and

$$\begin{aligned}\Pi_{z,z}\delta z &= \left(Ts + \sum_i \mu_i \tau_i + E_x D_x - u\right) \delta z \\ &= (-\varpi + E_x D_x) \delta z, \quad \Pi_{x,z} = \Pi_{y,z} = 0,\end{aligned}\quad (\text{B14})$$

respectively. Again, the last form of $\Pi_{z,z}$ in Eq. (B13) are presented to show that our result agrees with the result by Landau and Lifshitz.¹⁶ Note, that the sign of our surface force tensor $\Pi_{i,j}$ is chosen opposite to the Maxwell stress tensor by Landau and Lifshitz.¹⁶ Note also that the second form of Eqs. (B10) coincides with the second form of Eq. (B11) and the second form of Eqs. (B13) coincides with the second form of Eq. (B14), i.e., when we start from the same thermodynamic state the surface force tensor is independent of the thermodynamic path. More detailed discussion is presented in Ref. 14.

As the directions along y - and z -axis are equivalent, we know without repeating the calculation that a displacement of lateral surface with area $A_y = xz$ yields $\Pi_{z,z} = \Pi_{y,y}$ and $\Pi_{z,y} = \Pi_{x,y} = 0$. (The term $E_x D_x$ in Eq. (B14) is a result of the

metal plates being squeezed or stretched, causing the change of surface charge density of plates and, thus, the dielectric displacement, $\delta D/D = -\delta z/z$. It can be imagined that every metal plate consists of two conducting surfaces with zero thickness that are in contact and can slide with respect to one another without friction, thus, making the change of plate areas possible.)

In Eqs. (B2) and (B4), and (B10)–(B14), there is no separation into zero-field and electromagnetic contributions. Integrating Eqs. (B3) and (B5) at constant temperature and chemical potentials μ_i or at constant temperature and densities τ_i from zero to a given field strength values, we obtain (here we assume that the relation $D = \varepsilon\varepsilon_0 E$ holds)

$$\varpi = \varpi(D=0) + \frac{1}{2}\mathbf{E}\mathbf{D} = -p^0 + \frac{\varepsilon\varepsilon_0 E^2}{2}, \quad (\text{B15})$$

$$\tilde{f} = \tilde{f}(E=0) - \frac{1}{2}\mathbf{E}\mathbf{D} = -p^0 + \sum_i \mu_i(E=0)\tau_i - \frac{\varepsilon\varepsilon_0 E^2}{2}, \quad (\text{B16})$$

respectively.

The surface force tensor is represented only by two non-zero values: the value of a component acting along electric field perpendicular to imaginary metal plates and the value of a component perpendicular to electric field direction and tangential to imaginary metal plates. We denote these components with subscripts N and T , respectively. We consider the tensor $\Pi_{i,j}$ as a generalized pressure tensor. Taking the last forms of $\Pi_{x,x}$ and $\Pi_{z,z}$ in Eqs. (B11) and (B14), respectively, and using the last form of Eq. (B15), we obtain

$$\Pi_N = p^0(T, \mu_i) - \frac{\varepsilon\varepsilon_0 E^2}{2} = p^0(T, \mu_i) - \frac{D^2}{2\varepsilon\varepsilon_0}, \quad (\text{B17})$$

and

$$\Pi_T = p^0(T, \mu_i) + \frac{\varepsilon\varepsilon_0 E^2}{2} = p^0(T, \mu_i) + \frac{D^2}{2\varepsilon\varepsilon_0}, \quad (\text{B18})$$

respectively. Rusanov and Kuni¹⁷ obtained these results for a system of spherical symmetry.

Taking the last forms of $\Pi_{x,x}$ and $\Pi_{z,z}$ in Eqs. (B10) and (B13), respectively, and using the last form of Eq. (B16), we obtain

$$\Pi_N = p^0(T, \tau_i) - \frac{\varepsilon_0 E^2}{2} \left(\varepsilon + \sum_i \tau_i \frac{\partial\varepsilon}{\partial\tau_i}\bigg|_{T,\tau_{j\neq i}}\right), \quad (\text{B19})$$

and

$$\Pi_T = p^0(T, \tau_i) + \frac{\varepsilon_0 E^2}{2} \left(\varepsilon - \sum_i \tau_i \frac{\partial\varepsilon}{\partial\tau_i}\bigg|_{T,\tau_{j\neq i}}\right), \quad (\text{B20})$$

respectively, in accordance with the result by Landau and Lifshitz.¹⁸ Note that zero field pressure in Eqs. (B17) and (B18) differs from that in Eqs. (B19) and (B20), and also the dielectric constants correspond to different states. In a state to which Eqs. (B17) and (B18) apply, the chemical potentials of species coincide with chemical potentials in the absence of electric field. In state referred by Eqs. (B19) and (B20), the

chemical potentials are¹⁹

$$\mu_i = \mu_i(E = 0) - \frac{\varepsilon_o E^2}{2} \frac{\partial \varepsilon}{\partial \tau_i} \Big|_{T, \tau_{j \neq i}}. \quad (\text{B21})$$

In the absence of electric field, the generalized pressure $\Pi_{i,k}$ reduces to the hydrostatic pressure p^0 . The generalized pressure is not zero in vacuum ($p^0 = 0$). The pressure is then caused by momentum carried by photons.

- ¹M. Noppel, H. Vehkamäki, P. M. Winkler, M. Kulmala, and P. E. Wagner, *J. Chem. Phys.* **139**, 134107 (2013).
²K. Nishioka and I. Kusaka, *J. Chem. Phys.* **96**, 5370 (1992).
³P. G. Debenedetti and H. Reiss, *J. Chem. Phys.* **108**, 5498 (1998).
⁴A. I. Rusanov, *Surf. Sci. Rep.* **58**, 111 (2005).
⁵L. D. Landau and E. M. Lifshitz, *Fluid Mechanics* (Pergamon, Oxford, 1987).
⁶J. Gaydos, Y. Rotenberg, L. Boruvka, P. Chen, and A. W. Neumann, "The generalized theory of capillarity," in *Applied Surface Thermodynamics*, Surface Science Series Vol. 63, edited by A. W. Neumann and J. K. Spelt (CRC Press, 1996).
⁷V. B. Varshavsky and A. K. Shchekin, *Colloids Surf., A* **148**, 283 (1999).
⁸H. Vehkamäki, *Classical Nucleation Theory in Multicomponent Systems* (Springer, Berlin, 2006), Sec. 3.1.
⁹Reference 8, Sec. 2.6.
¹⁰E. G. Bakhoun, *J. Electrostatics* **66**, 561 (2008).
¹¹C. T. O'Konski and H. C. Thacher, *J. Phys. Chem.* **57**, 955 (1953); G. I. Taylor, *Proc. R. Soc. London, Ser. A* **280**, 383 (1964); C. G. Garton and Z. Krasucki, *ibid.* **280**(1381), 211 (1964); J. Latham and I. W. Roxburgh, *ibid.* **295**, 84 (1966); A. K. Azad and J. Latham, *Atmos. Sci.* **25**, 66 (1968); P. R. Brazier-Smith and J. Latham, *Nature (London)* **220**, 689 (1968); *Proc. R. Soc. London, Ser. A* **312**, 277 (1969); M. A. Abbas and J. Latham, *Q. J. R. Meteorol. Soc.* **95**, 63 (1969); A. K. Azad and J. Latham, *J. Atmos. Terr. Phys.* **32**, 345 (1970); C. E. Rosenkilde, *Proc. R. Soc.*

- London, Ser. A* **312**, 473 (1969); P. R. Brazier-Smith, *Phys. Fluids* **14**, 1 (1971); S. Torza, R. G. Cox, and S. G. Mason, *Philos. Trans. R. Soc. London, Ser. A* **269**, 295 (1971); B. C. Srivastava and T. P. Pandya, *J. Colloid Interface Sci.* **83**, 35 (1981); M. J. Miksis, *Phys. Fluids* **24**, 1967 (1981); P. M. Adornato and R. A. Brown, *Proc. R. Soc. London, Ser. A* **389**, 101 (1983); D. Zrnić, R. Doviak, and P. Mahapatra, *Radio Sci.* **19**, 75, doi:10.1029/RS019i001p00075 (1984); N. Dodgson and C. Sozou, *ZAMP* **38**, 424 (1987); J. D. Sherwood, *J. Fluid Mech.* **188**, 133 (1988); K. V. Beard, J. Q. Feng, and C. Chuang, *J. Atmos. Sci.* **46**, 2404 (1989); C. C. Chuang and K. V. Beard, *ibid.* **47**, 1374 (1990); H. Li, T. C. Halsey, and A. Lobkovsky, *Europhys. Lett.* **27**, 575 (1994); O. A. Basaran and L. E. Scriven, *Phys. Fluids A* **1**, 795 (1989); **1**, 799 (1989); *J. Colloid Interface Sci.* **140**, 10 (1990); F. K. Wohlhuter and O. A. Basaran, *J. Fluid Mech.* **235**, 481 (1992); O. A. Basaran and F. K. Wohlhuter, *ibid.* **244**, 1 (1992); F. K. Wohlhuter and O. A. Basaran, *J. Magn. Magn. Mater.* **122**, 259 (1993); M. T. Harris and O. A. Basaran, *J. Colloid Interface Sci.* **170**, 308 (1995); K. Adamiak, *J. Electrostat.* **51–52**, 578 (2001); A. I. Grigor'ev, *Tech. Phys.* **47**, 834 (2002); E. K. Zholkovskij, J. H. Masliyah, and J. Czarnecki, *J. Fluid Mech.* **472**, 1 (2002); A. Bateni, S. S. Susnar, A. Amirfazli, and A. W. Neumann, *Langmuir* **20**, 7589 (2004); A. Bateni, A. Ababneh, J. A. W. Elliott, A. W. Neumann, and A. Amirfazli, *Adv. Space Res.* **36**, 64 (2005); D. Langemann, *Math. Comput. Simul.* **63**, 529 (2003); D. Langemann and M. Krüger, *Math. Comput. Simul.* **66**, 539 (2004); N. Dubash and A. J. Mestel, *J. Fluid Mech.* **581**, 469 (2007); *Phys. Fluids* **19**, 072101 (2007); J. Hua, L. K. Lim, and C.-H. Wang, *Phys. Fluids* **20**, 113302 (2008).
¹²K. Shchekin, M. S. Kshevetskii, and V. B. Varshavskii, *Colloid J.* **64**, 488 (2002).
¹³L. D. Landau and E. M. Lifshitz, *Electrodynamics of Continuum Media* (Pergamon, Oxford, 1984), Sec. 15.
¹⁴M. Liu and K. Stierstadt, e-print [arXiv:cond-mat/0010261v1](http://arxiv.org/abs/cond-mat/0010261v1) [cond-mat.soft] (2000).
¹⁵Reference 13, Sec. 10.
¹⁶Reference 13, Eq. (15.7).
¹⁷A. I. Rusanov and F. M. Kuni, *J. Colloid Interface Sci.* **100**, 264 (1984).
¹⁸Reference 13, Eq. (15.9).
¹⁹Reference 13, Eq. (10.19).