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# Heterogeneous nucleation in multi-component vapor on a partially wettable charged conducting particle. I. Formulation of general equations: Electrical surface and line excess quantities

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Thermodynamics is applied to formulate general equations for internal energies and grand potential for a system consisting of 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. To take into account spontaneous polarization of surface layer molecules we introduce the electrical surface and line excess quantities. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4822046>]

## I. INTRODUCTION

Condensational growth, evaporation, and heterogeneous chemical processes are important phenomena in material science, fluid physics, aerosol physics and technology, atmospheric chemistry, and in cloud microphysics and cloud chemistry. A prerequisite for the start of condensation is homogeneous nucleation of new particles or the activation of pre-existing particles by heterogeneous nucleation. The latter can occur either on ions, soluble, or insoluble particles and is energetically easier than homogeneous nucleation.<sup>1</sup>

Several theories of heterogeneous nucleation have been developed that can be grouped by the kind of foreign nuclei they are dealing with. One component condensation on uncharged soluble nucleating centers consisting of various kind substances (hygroscopic, dissociating within a droplet, surface inactive and active) was considered in Refs. 2–12. An incomplete dissolution of nuclei, the formation of saturated solution layers around nuclei in the deliquescence process was treated in Refs. 13–22. The case of wettable and insoluble solid nucleus completely covered by thick liquid film was considered first by Krastanov.<sup>23</sup> Rusanov and Kuni<sup>24,25</sup> considered the role of surface forces in the formation of a liquid droplet as a thin single component film on a macroscopic wettable insoluble nucleus. The latter references also review early papers that consider the effect of surface forces. Djikaev and Donaldson<sup>26</sup> generalized the approach of Rusanov and Kuni to the wetting films on insoluble nuclei in binary vapor mixtures. The theory of the formation of separate droplet caps with a finite contact angle on the insoluble nucleus surface was developed by Fletcher,<sup>27</sup> and extended to binary systems by Lazaridis *et al.*<sup>28</sup> A mixed nucleus containing soluble

species and an insoluble partially wettable spherical core was considered in Refs. 29 and 30. The latter theory was generalized to multicomponent vapors in Refs. 31–33. Smorodin<sup>34,35</sup> considered the role of inhomogeneities of the nucleus surface in heterogeneous nucleation.

The experiments<sup>36–45</sup> have shown that electric charge of the seed lowers the vapor supersaturation needed for the formation of liquid drops, and that some substances prefer a certain sign of ions for nucleating. Volmer developed the first simple theory describing unary nucleation on ions<sup>47</sup> as an extension Thomson's description of the chemical potential of a charged droplet.<sup>46</sup> The theory adds a single electrostatic correction term to the classical formation free energy of a liquid drop. Such addition is proposed also in Refs. 48 and 49. Several attempts have been made to incorporate molecular characteristics within the framework of the capillarity theory.<sup>50–52</sup> Based on a thorough thermodynamical treatment Rusanov, Kuni, and Shchekin<sup>53–59</sup> derived the formation work and various relationships for the properties of an equilibrium droplet in multicomponent vapor. They considered the dependence on the magnitude and sign of charge of a seed particle at the center of the droplet. Sign effect follows from the assumed spontaneous polarization of interface surface molecules. Formulae that can be directly used in practical nucleation calculations, like extensions of Kelvin's and J. J. Thomson's equations, are, however, derived only for a unary system.

The classical ion induced nucleation theory was extended to binary vapor environment in Ref. 60. The size and the composition of a critical nucleus were found by finding the extremum of the classical reversible work of formation of a noncritical ion cluster. In finding the extremum the composition dependence of dielectric constant and the composition and size dependence of interfacial tension were taken into account. Such accounting suffers from thermodynamic

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inconsistency that was addressed in Ref. 61, where expressions, suitable for practical calculations of the size and composition of a critical nucleus, were derived. The above-mentioned papers on ion-induced nucleation dealt with systems of spherical symmetry. The effect of electric field on the nucleation of dielectric droplets in axially symmetric single component systems (droplets containing a core of negligible size with an electric dipole moment; droplet with or without a charged core of negligible size in homogeneous external electric field) was considered in Refs. 62–65. There are numerous studies dealing with the deformation of droplets in electric field motivated environmental and industrial interest like electrohydrodynamic atomization, the breakup of water drops in thunderstorms, the behavior of drops in ink-jet printers, the breakdown of insulators at electric power production and transmission.<sup>66</sup>

The critical supersaturation for the heterogeneous nucleation of single component vapor on charged particles of nanometer size has recently been measured.<sup>67–72</sup> Winkler *et al.*<sup>73</sup> condensed an organic vapor (*n*-propanol) on molecular ions, as well as on charged and uncharged inorganic nanoparticles. The process involves initial activation by heterogeneous nucleation. They found a smooth transition in activation behavior as a function of size. Furthermore, nucleation enhancement for charged particles and a substantial negative sign preference were quantitatively detected. The charge enhancement disappears for seed particles larger than 2 nm by radius. These experimental results were compared with the results of the classical theory of ion induced nucleation that assumes spherical symmetry. However, the seed particles generated in these experiments<sup>67,68,71</sup> were insoluble and only partially wettable (measured contact angle was larger than zero). Winkler *et al.* used among other seeds charged silver particles, and the activation of neutral silver seed particles is best described by the classical theory of heterogeneous nucleation with cap-shaped nucleus formation.<sup>74</sup> The current ion induced nucleation theory, although giving a rough picture of the observed behavior, fails to fully reproduce experiments, especially when the seed ions are very small. For the theoretical description of such systems with charged particles to be consistent the consideration of a cap-shaped nucleus configuration (see Fig. 1) is required. The spherical symmetry that is assumed in common ion induced theory, and greatly simplifies the model, is now lost.

In the classical theory of heterogeneous nucleation,<sup>27</sup> the reversible work of nucleus formation on spherical uncharged insoluble seed particle is related to the corresponding work of nucleus formation in a homogeneous vapor without any seed particles. There are several treatments of the classical theory of homogeneous nucleation of multicomponent vapors,<sup>61,75–79</sup> some of which are thermodynamically inconsistent. The consistent and inconsistent theories predict different sizes and compositions of the critical nucleus and yield different (by several orders of magnitude) nucleation rates at atmospheric conditions.<sup>80,81</sup> In this paper, we follow the consistent study of Nishioka and Kusaka<sup>78</sup> and Debenedetti and Reiss.<sup>79</sup> We study a cap-shaped, in general non-spherical, nucleus formed on a charged insoluble seed particles treated as a spherical conductor (see Fig. 1).

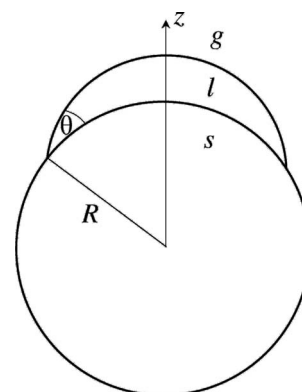


FIG. 1. Sketch of the cross section of a cap-shaped liquid nucleus  $l$  in the vapor phase  $g$  on a spherical conducting uncharged seed particle  $s$  of radius  $R$ . The liquid nucleus forms a contact angle  $\theta$  with the seed particle.

## II. FUNDAMENTAL THERMODYNAMICS

A critical liquid nucleus is a microscopic region of a new phase, which is in unstable equilibrium with the mother phase, in this case vapor. The reversible work of a critical nucleus formation represents the free energy barrier that a metastable system must surmount in passing from a local to a global minimum for the system free energy, and it is of primary interest in the field of nucleation. A rigorous and thermodynamically consistent expression for the reversible work of nucleus formation, from which the work of formation of the critical nucleus follows as an extremum condition, requires considering not only a critical nucleus but also non-critical nuclei, i.e., states that are not in equilibrium (stable or unstable) with the mother phase. To apply thermodynamic reasoning to such systems, it is necessary to introduce constraints that prevent the free exchange of matter between the nucleus and the mother phase. Constraints impose internal equilibrium throughout the inhomogeneous system consisting of a seed particle, the homogeneous interior of the nucleus, the interface zones and the surrounding mother phase.

### A. Basics laws of thermodynamics for each of the phases

We consider a system consisting of the homogeneous bulk phases of a spherical solid seed particle, a cap-shaped liquid nucleus, and surrounding vapor (consideration is valid also for a surrounding liquid phase immiscible with the nucleus), and interfaces between these bulk phases. The charge will be introduced later in Sec. III, where also the arguments for separate treatment of charging adopted here are presented.

All bulk phases and interfaces are constrained to be in equilibrium separately. The seed particle is assumed rigid, and thus the deformation work of it is ignored. System is isothermal. Let us divide the system into slices so that that every slice has the same amount of bulk phase volumes, surface areas, and three-phase contact line length, and consider one of these slices. Constraints avoid mass transfer between liquid, vapor, and surface phases, as well as the contact line phase, but there is mass transfer between liquid outside the slice and

the liquid part of the slice, vapor outside the slice and the vapor part of the slice. The same is valid for surface and contact line phases. A change in the internal energy of a slice is given according to the first and second laws of thermodynamics by

$$dU_l = TdS_l - p_l^0 dV_l + \sum_i \mu_{i,l} dN_{i,l}, \quad (1)$$

$$dU_g = TdS_g - p_g^0 dV_g + \sum_i \mu_{i,g} dN_{i,g}, \quad (2)$$

$$dU_a = TdS_a + \sigma_a dA_a + \sum_i \mu_{i,a} dN_{i,a}, \quad (3)$$

$$dU_L = TdS_L + \kappa dL + \sum_i \mu_{i,L} dN_{i,L}, \quad (4)$$

where Eq. (1) corresponds to the change of internal energy  $U_l$  of homogeneous bulk liquid part of the slice;  $T$  is the temperature;  $S_l$  is entropy of bulk liquid part of the slice;  $p_l^0$  is the pressure in bulk liquid around an uncharged seed particle;  $V_l$  is the volume of liquid part of the slice;  $\mu_{i,l}$  is the chemical potential of species  $i$  in the liquid part of the slice; and  $N_{i,l}$  is the number of molecules of species  $i$  in the liquid part of the slice. Analogous notations hold for Eqs. (2)–(4) describing internal energy changes in vapor (gas) phase, surface phases, and contact line, respectively. The distance to the outer boundary of the system in the gas phase part of the slice is taken very large but finite.  $p_g^0$  is the pressure in bulk vapor around uncharged seed particle or pressure far away from a charged seed particle that is considered later. Subscript  $a$  in Eq. (3) refers to different phase interfaces, and there is one equation (3) for each pair of phases ( $a = gl, ls, gs$ ;  $g$  – vapor,  $l$  – liquid,  $s$  – solid, see Fig. 1), where  $A_a$  is surface area and  $\sigma_a$  is the surface tension of surface  $a$ . Subscript  $L$  in Eq. (4) refers to the contact line and  $\kappa$  is the line tension of contact line.

## B. Interface zones and line tension

The real physical transition zone between neighboring bulk phases is not sharp. The properties of one phase change continuously to those of the neighboring phase. In Eq. (3) it is assumed that the surface is specified by the concept of the Gibbs dividing surface<sup>82</sup> and that the position of the dividing surface coincides with the surface of tension.<sup>82–85</sup>

When two interfaces are close to each other, as in case thin films between bulk phases or when interfaces approach one another in the region of three-phase contact line, the surface forces give rise to the disjoining pressure between interfaces. The measurements of disjoining pressure in planar films have shown that long-range dispersion and electrostatic force can have range more than 100 nm.<sup>86,87</sup> The width of interface zone, where the abrupt changes in density and/or composition occur, is of the order of 1 nm. This concerns also the interfaces of a film provided that the temperature is not too close to the critical temperature.<sup>88–90</sup> Thus, for droplets on solid substrate the intersurface forces cause only small changes in the density distribution across interfaces, and in the values of surface tension evoked by these density changes,

compared to the changes in the profile of liquid-vapor interface as it approaches substrate. Due to intersurface forces the microscopic profile of droplet surface near substrate is different from the macroscopic profile extrapolated into three-phase contact zone from the region outside the range of surface forces. Solomentsev and White<sup>91</sup> have shown that this difference in profiles gives rise to the line tension defined as the difference between free energies of the droplet per unit length of contact line when surface forces are turned on and off. There may or may not be a precursor film of condensed vapor on the substrate. In the former case precursor film contributes to the surface tension of substrate-vapor interphase and this is the only role that the film has in the determination of the microscopic drop shape. Still, the precursor film may be important for the beginning of heterogeneous nucleation. The concept of line tension is a macroscopic quantity, which may be added to the free energy balance and it yields the same macroscopic picture of the drop near the contact line as a full treatment of the microscopic drop shape. Solomentsev and White have used the Derjaguin approximation that reduces the interaction between curved surfaces to the interaction of planar surfaces. If we know the interaction law between planar surfaces their approach allows calculation of line tension for droplets having contact angles up to 20°. The treatment of line tension as a macroscopic concept is valid down to drop sizes of the order of the range of the interaction energy. In the Solomentsev and White<sup>91</sup> approach no explicit specification of the location of the dividing surfaces is made.

In the following we will not consider explicitly the disjoining pressure as its effect is covered by the introduction of line tension. We also ignore the possibility that at small contact angles the top of the cap-shaped droplet can remain in the range of surface forces and, therefore, the droplet shape can differ from the macroscopic case. The effect of possible precursor film is incorporated into the solid-vapor surface tension. We assume that the range of the intersurface forces diminishes with the size of seed particle so that we can use the concept of line tension down to seed particle and droplet sizes of the order of 1 nm. The energy of long-range dispersion interaction between planar surfaces is proportional  $\sim r^{-2}$ , but between molecules  $\sim r^{-6}$ , where  $r$  is the distances between surfaces or molecules. The nonretarded van der Waals energy for spherical single layer system depends on the ratio of the layer thickness to seed particle radius decaying drastically with the increase of this ratio.<sup>92,93</sup> Thus, at a given layer thickness the range of van der Waals interaction diminishes with the decrease of seed particle size.

Equations (3) and (4) imply that the chemical potential values of interface and contact line species, generally, do not coincide with the values of constrained bulk phases; consistent treatment of such an interface zone requires extra care. In this paper, we assume that for every surface of our constrained system there exists an equilibrium (stable or unstable) system of bulk phases with an interface between them. Chemical potentials of species are homogeneous throughout of this system. Bulk parts of this system are in states that generally do not coincide with the states of bulk phases in our constrained system. The application of Gibbs dividing surface method to this system gives us thermodynamic relation (3) that also

characterizes the surface phase in our constrained system, i.e., our constrained surface phase are represented by this interface of an equilibrium system. Analogical reasoning holds also for the contact line. Our constrained system is thus put together from equilibrium phases, but different phases of our system are not necessarily in equilibrium with one another.

### C. Fundamental equations

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.

Using Euler's theorem (slices have identical volumes, surface areas, and lengths of contact lines, we also assume an isotropy of interfaces) or integrating Eqs. (1)–(4) over extensive quantities while keeping the values of the intensive variables constant, we get the fundamental equations,

$$U_l = TS_l - p_l^0 V_l + \sum_i \mu_{i,l} N_{i,l}, \quad (5)$$

$$U_g = TS_g - p_g^0 V_g + \sum_i \mu_{i,g} N_{i,g}, \quad (6)$$

$$U_a = TS_a + \sigma_a A_a + \sum_i \mu_{i,a} N_{i,a}, \quad (7)$$

$$U_L = TS_L + \kappa L + \sum_i \mu_{i,L} N_{i,L}. \quad (8)$$

### D. Gibbs–Duhem and Gibbs adsorption equations

Taking the differential of fundamental equations (5)–(8) and comparing the result with Eqs. (1)–(4), we get the Gibbs–Duhem relations:

$$S_l dT - V_l dp_l^0 + \sum_i N_{i,l} d\mu_{i,l} = 0, \quad (9)$$

$$S_g dT - V_g dp_g^0 + \sum_i N_{i,g} d\mu_{i,g} = 0, \quad (10)$$

$$S_a dT + A_a d\sigma_a + \sum_i N_{i,a} d\mu_{i,a} = 0, \quad (11)$$

$$S_L dT + L d\kappa + \sum_i N_{i,L} d\mu_{i,L} = 0. \quad (12)$$

Gibbs–Duhem relations for surfaces, Eq. (11), are called Gibbs adsorption equations.

## III. THERMODYNAMICS OF CHARGING

Let a seed particle to be conducting and let the liquid nucleus and the surrounding vapor be homogeneous and isotropic dielectrics. We calculate the work that is needed to carry a charge  $q$  from infinity to a seed particle with a nucleus. If we will do charging in a way that corresponds more to a real experiment where a nucleus is free to adopt its size and shape according to the charge accumulated on seed particle, then the

work of charging includes also energy spent for the change of the volume and surface area of nucleus, i.e., the work of non-electrical forces evoked by electrical ones. The need to account these surface area and volume changes significantly complicates the calculation of the outcome of charging. To avoid these problems we introduce constraints. Constraints increase the number of thermodynamic variables that are separately controllable and that uniquely determine the state of a system. The space of states of constrained systems contains also the states of an original unconstrained system. The properties of the thermodynamic state of an original system that we are interested in should not depend on a thermodynamic path through which it is approached if thermodynamic calculations are made correctly. Two thought processes can replace the above-mentioned charging process. We can, first, without charging change the shape and volume of nucleus so that they correspond to the final state and then charge the nucleus without changing its shape and volume. Very strong electric field can change density profile in the nucleus bulk and surface regions, which, in principle, should be also taken into account. Also the polarization of liquid can exhibit saturation when permanent dipoles of molecules are aligned along the lines of very strong electric field. In this paper we limit ourselves to a linear relationship between dielectric displacement  $D$  and electric field  $E$  strength, first in the simplest form  $D = \varepsilon \varepsilon_0 E$ , where  $\varepsilon$  is the dielectric constant and  $\varepsilon_0$  is the permittivity of vacuum, extended in the Sec. IV B 1 to a more general form, where the dielectric constant  $\varepsilon$  is replaced by a dielectric tensor with two independent components and in the Sec. IV C still to a more general form (30). The latter equation enables to take into account possible spontaneous permanent polarization of surface layer molecules. Taking into account density changes due to strong electric field is outside the validity range of these relationships as the density change caused by the field is proportional to  $E^2$ .<sup>94</sup> This concerns also changes in surface tension values evoked through these density changes.

Constraints keep the shape and volume of a nucleus unchanged during the charging. The total system that contains the vapor and nucleus is thermally isolated, but the heat transfer between various parts of a system is allowed and temperature is constant throughout the whole system. We assume that gas phase is large enough to act as a heat and particle bath, so that the chemical potentials of each species in the vapor are constant. Charging is thus carried out isothermally and adiabatically for the total system. Carrying a small portion of charge  $\delta q$  from infinity to a seed particle we make a work against the electric field created by the charge  $q$  already at the seed particle. This charging work can be expressed as follows:

$$\delta W_q = \int_V \mathbf{E} \cdot \delta \mathbf{D} dV = \int_R^\infty E_\rho d\rho \delta q = \varphi \delta q, \quad (13)$$

where  $\varphi$  is the electrical potential of a seed particle having charge  $q$ ,  $E_\rho$  is the component of electric field strength along distance vector  $\rho$  from the center of seed particle to a given point,  $\delta \mathbf{D}$  is the variation of the vector of the dielectric displacement caused by variation of charge  $\delta q$ ,  $V$  is the volume of the system. The equality of the second and third forms

of Eq. (13) is shown, e.g., in Landau and Lifshitz.<sup>95</sup> We now select the narrow force tube of the dielectric displacement vector  $\mathbf{D}$  that connects a given point to the surface of the seed particle. The force tube begins just inside the seed particle, where the field is zero. The intersection area of the tube and some surface (e.g., interface surface) at a given point is  $dA$ . Using Gauss's law for a segment of the tube that extends from seed particle to a given point gives  $\int_A \mathbf{D} \cdot d\mathbf{A} = D_n dA = dq$ , where the integration is performed over the boundaries of the segment. Thus, the flux of dielectric displacement vector through the intersection area of the tube of force at given point gives the charge  $D_n dA = dq$  that the tube of force separates from the total surface charge of the seed particle. In the following we consider also hypothetical systems where the thicknesses of interface zones between bulk phases are zero. For such systems we can take a segment of infinitesimal stretch beginning just inside the seed particle, where the field is zero, and ending in the gas (or liquid) phase just outside the seed surface. Thus, the normal component of dielectric displacement at the seed surface equals the surface charge density  $D_n = dq/dA \equiv \eta_e$ .

We obtain the total work of charging by integrating Eq. (13) from charge 0 to  $q$ :

$$W_q = \int_0^q \varphi \delta q = \int_V \left( \int_0^{\mathbf{D}(q)} \mathbf{E} \cdot \delta \mathbf{D} \right) dV. \quad (14)$$

As constraints keep the shape and volume of a nucleus unchanged there are no changes in surface areas and volumes of the different phases during charging. Also the numbers of surface, liquid, and vapor molecules do not change. During charging emission or absorption of heat can occur in various parts of the system, which leads to heat transfer in the system at constant temperature (all processes are considered quasi-static) and, therefore, to the change of entropies of various phases although the total entropy of the whole system remains constant.

If we ignore spontaneous polarization of molecules in transition zone of interface (discussed later in Sec. IV C) and use the linear relationship  $D = \varepsilon \varepsilon_0 E$ , Eq. (14) can be expressed as

$$W_q = \frac{1}{2} \varphi q = \frac{1}{2} \int_{V_l + V_g} \mathbf{E} \cdot \mathbf{D} dV = \int_{V_l} \frac{D^2}{2\varepsilon \varepsilon_0} dV + \int_{V_g} \frac{D^2}{2\varepsilon \varepsilon_0} dV. \quad (15)$$

For potential  $\varphi$  we use the relation  $\varphi = q/C_l$ , where  $C_l$  is the electric capacitance of the whole system consisting of the seed particle with nucleus on its surface and the surrounding vapor. Due to the fixed shape and volume of the nucleus, and the linear relationship  $D = \varepsilon \varepsilon_0 E$ , the electric capacitance  $C_l$  does not depend on charge. The division of total volume of system into liquid and vapor volume parts is done along surfaces of tension of uncharged system. No excess quantities have been introduced for electrical entities. Dielectric constants in Eq. (15) are functions of position.

## IV. ELECTRICAL EXCESS QUANTITIES

### A. Work of charging for liquid-vapor interface

To calculate work of charging and introduce surface excess quantities we consider a small portion of an interfacial transition zone that is cut out by a narrow tube of force at some point (see Fig. 2). We use liquid-vapor interface as an example. The expressions for the solid-liquid or solid-vapor interface can be derived analogously.

Let us denote the central line of this tube of force with  $L_D$  and element vector along it with  $d\mathbf{L}_D$ . The central line serves as curvilinear coordinate whose origin is on the seed particle surface. We use the notation  $L_D$  also to indicate the coordinate of a point on this line.

We divide the tubular portion of the transition zone into layers by dividing surfaces perpendicular to the density gradient lines. Along these surfaces density and, therefore also dielectrical permittivity (since we ignore non-linear effects) are constants. In general, these layers are not orthogonal with the tube of force and line  $L_D$ . Locally, at a every given point of the transition zone, we can introduce an orthogonal coordinate system, where  $n$ -axis is directed along density gradient line, normal to dividing surface. Let  $t$ -axis be tangential to the dividing surface and in the plane that is determined by the directions of dielectric displacement  $\mathbf{D}$  and  $n$ -axis. The third axis,  $y$ -axis, is a tangent of the dividing surface orthogonal to the  $(\mathbf{D}, n)$ -plane. We can always to choose a volume element  $\Delta n \Delta t \Delta y$  with  $\Delta n \ll \Delta t$  and  $\Delta n \ll \Delta y$ . Applying Gauss's law ( $\nabla \cdot \mathbf{D} = 0$ ) and ignoring fluxes through the negligible surface areas  $\Delta n \Delta t$  and  $\Delta n \Delta y$  of the side walls, we conclude that the component of dielectric displacement vector,  $D_n$ , that enters the volume element is approximately equal to the component that exits the volume element. Applying Stoke's law to the electric field  $\mathbf{E}$  ( $\nabla \times \mathbf{D}^h = 0$ ) integrated over a loop formed by elements  $\Delta n$ ,  $\Delta t$ , the same can be said for the component  $E_t$ . Thus, components  $D_n$  and  $E_t$  change slowly compared with components  $D_t$  and  $E_n$  when we move through the transition zone. Following the Gibbs dividing surface method we consider a hypothetical system, where all properties of bulk

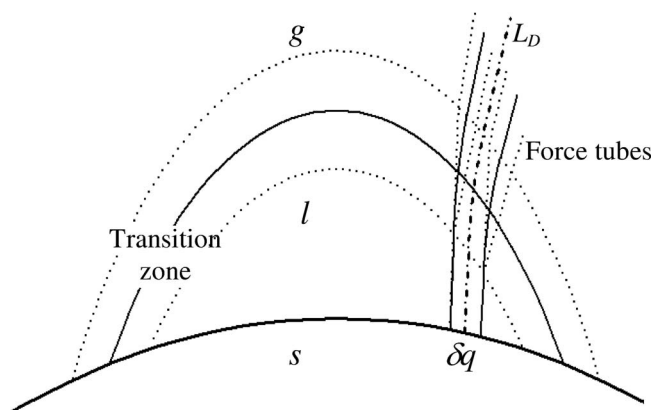


FIG. 2. Force tubes of dielectric displacement vectors in real and hypothetical systems. Only the surface transition zone of liquid-vapor interface is indicated. The dotted lines correspond to the tubes of forces in two hypothetical systems where the dividing surface is placed on inner and outer boundary of transition zone, respectively. Lines of hypothetical systems change abruptly their directions at corresponding dividing surfaces.

phases stay constant up to dividing surfaces. The above considerations show that the components  $D_n$  and  $E_t$  are continuous, i.e.,  $E_t^l = E_t^g$ ,  $D_n^l = D_n^g$  at the dividing surface of a hypothetical system whereas the field lines of  $\mathbf{D}$  and  $\mathbf{E}$  change abruptly their direction as the components  $D_t$  and  $E_n$  are discontinuous. As can be seen from Fig. 2, where for the clarity only the liquid-gas interface transition zone is indicated, the field lines of a hypothetical system deviate from the lines of the real system. This deviation depends on the location of dividing surface in the transition zone. Moving dividing surface from liquid bulk side into gas-phase bulk side so that in every new location it coincides with an isodensity surface, the tubes of force of successive hypothetical systems form a curvilinear cylinder that incorporates the real tube of force. As the field lines of hypothetical systems change abruptly their direction at a dividing surface they can not coincide with field lines of a real system in the transition zone even if they coincide in bulk phases. The field lines of the real system are smooth, although rapidly changing their direction in case the lines do not follow density gradient lines when passing through the transition zone.

We can create a hypothetical transition zone by removing dielectric matter from the real transition zone on one side of dividing surface and adding it to the real transition zone at the other side of the dividing surface. This addition and removal is as if we added/removed dielectric matter into/from electric field of a charged seed particle. The addition and removal affects the electric field strength in the whole space (except seed particle interior), not only in the locations of removal and addition. Next we will show that the change in the electric field energy due to this addition and removal at fixed charge of seed particle can be expressed by an integral extended over the addition-removal zone volume alone

$$\begin{aligned} \Delta W &= \frac{1}{2} \int_V (\mathbf{E} \cdot \mathbf{D}) dV - \frac{1}{2} \int_V (\mathbf{E}^h \cdot \mathbf{D}^h) dV \\ &= \frac{1}{2} \int_{V_{tz}} (\mathbf{E} \cdot \mathbf{D}^h - \mathbf{E}^h \cdot \mathbf{D}) dV, \end{aligned} \quad (16)$$

where superscript  $h$  refers to a hypothetical system with step-wise change in properties at dividing surface;  $V_{tz}$  is the volume of transition zone where imaginary removal and addition procedure is performed. We can also consider not only the whole transition zone but also a small piece of it.

Before proving the validity of Eq. (16) let us first consider the interface zone related to the seed particle surface. Due to spill out of electrons a metal surface, the surface has an electrical double layer structure.<sup>96</sup> This double layer gives rise to electric field in the transition zone even when the seed particle is uncharged. Certainly, the mechanism of redistribution of charges and the formation of electrical double layer at metal surface is more complicated when surface is covered with liquid, but the double layer still exists. Thus, carrying charges from infinity to a seed particle we make a work not only against the electric field of the charges transported there earlier but also against the electric field of the double layer. The latter can be expressed as  $\delta q \Delta \varphi$ , where  $\Delta \varphi$  is the effective potential difference between a point just outside the double layer away from a seed particle and some reference point

inside double layer, and  $\delta q$  is the charge that is carried into the double layer. In general,  $\Delta \varphi$  depends on the position at seed particle surface, whether the position is taken at the liquid-solid or vapor-solid interface. Molecules adsorbed to the seed particle surface from gas or liquid side can form a layer that is spontaneously polarized. The potential difference due to this polarized layer gives contribution to the total potential difference  $\Delta \varphi$ . We are interested in the energy difference between states of seed particle with and without an embryo. If in both of these states the potential difference  $\Delta \varphi$  caused by the surface polarization is the same, the contribution of the double layer to the work of charging cancels out from the free energy of embryo formation. In the following proof of Eq. (16) we first consider such a case and ignore the presence of double layers at interfaces, leaving their treatment for later sections.

To prove Eq. (16) we follow Stratton<sup>97</sup> and represent the first form of it in the equivalent fashion

$$\begin{aligned} \Delta W &= \frac{1}{2} \int_V (\mathbf{E} \cdot \mathbf{D}) dV - \frac{1}{2} \int_V (\mathbf{E}^h \cdot \mathbf{D}^h) dV \\ &= \frac{1}{2} \int_{V_{tz}+V_2} (\mathbf{E} \cdot (\mathbf{D} - \mathbf{D}^h) + (\mathbf{E} - \mathbf{E}^h) \cdot \mathbf{D}^h) dV, \end{aligned} \quad (17)$$

where  $V = V_2 + V_{tz}$  is the volume of the system,  $V_2$  is the volume of the part of the system that remained intact by the imaginary removal and addition of dielectric matter, and  $V_{tz}$  is the volume of transition zone where such removal and addition is made. By expressing the electric field in terms of the potential,  $\mathbf{E} = -\nabla \cdot \varphi$ , we can write

$$\begin{aligned} \mathbf{E} \cdot (\mathbf{D} - \mathbf{D}^h) &= -\nabla \varphi \cdot (\mathbf{D} - \mathbf{D}^h) = -\nabla \cdot [\varphi(\mathbf{D} - \mathbf{D}^h)] \\ &\quad + \varphi \nabla \cdot (\mathbf{D} - \mathbf{D}^h) \end{aligned} \quad (18)$$

and apply the divergence theorem to the three distinct regions: gas, liquid, and seed particle, separated by surfaces of tension. We chose the direction of the surface normals away from the center of the seed particle as positive and express the sign of surface integrals accordingly. Thus, the integral  $\frac{1}{2} \int_{V_{tz}+V_2} \mathbf{E} \cdot (\mathbf{D} - \mathbf{D}^h) dV$  can be written as

$$\begin{aligned} &-\frac{1}{2} \int_{V_{tz}+V_2} \nabla \varphi \cdot (\mathbf{D} - \mathbf{D}^h) dV \\ &= +\frac{1}{2} \int_{A_{sg}+A_{lg}} \varphi(\mathbf{D} - \mathbf{D}^h)^g \cdot d\mathbf{A} + \frac{1}{2} \int_{V_g} \varphi \nabla \cdot (\mathbf{D} - \mathbf{D}^h) dV \\ &\quad + \frac{1}{2} \int_{A_{sl}} \varphi(\mathbf{D} - \mathbf{D}^h)^l \cdot d\mathbf{A} - \frac{1}{2} \int_{A_{lg}} \varphi(\mathbf{D} - \mathbf{D}^h)^l \cdot d\mathbf{A} \\ &\quad + \frac{1}{2} \int_{V_l} \varphi \nabla \cdot (\mathbf{D} - \mathbf{D}^h) dV \\ &\quad - \frac{1}{2} \int_{A_{sl}+A_{sg}} \varphi(\mathbf{D} - \mathbf{D}^h)^s \cdot d\mathbf{A} + \frac{1}{2} \int_{V_s} \varphi \nabla \cdot (\mathbf{D} - \mathbf{D}^h) dV \\ &= -\frac{1}{2} \int_{A_{ls}} \varphi \mathbf{D}^{h,l} \cdot d\mathbf{A} - \frac{1}{2} \int_{A_{sg}} \varphi \mathbf{D}^{h,g} \cdot d\mathbf{A} + \frac{1}{2} \int_{V_{tz,s}} \varphi \nabla \cdot \mathbf{D} dV = 0, \end{aligned} \quad (19)$$

where  $V_s$  is the volume of seed particle and  $V_{tz,s}$  is the volume of transition zone at seed particle surface, where the charge  $q$  carried to seed particle is distributed. Here only the integrals over the interface surfaces between the seed particle, the liquid embryo, and the gas phase are written down. The reasons are that the integral over an infinitely remote outer surface of the gas phase vanishes, since  $\mathbf{D}$  and  $\varphi$  diminish at least as fast as  $\rho^{-2}$  and  $\rho^{-1}$ , respectively, when distance from the seed particle (denoted  $\rho$ ) goes to infinity. The dielectric displacement  $\mathbf{D}$  and potential  $\varphi$  of the real system are continuous at interfaces. As shown before, boundary condition  $D_n^{h,g} = D_n^{h,l}$  holds at the surface of hypothetical system, and also surface integrals over liquid-vapor interface cancel out. We take into account that in hypothetical system the charge is located at the dividing surface of the seed particle as a surface charge and, therefore,  $\nabla \cdot \mathbf{D}^h = 0$  in all three bulk phases (*s, l, g*), Eq. (19) is obtained by applying divergence theorem to three bulk phases. Thus surface integrals in Eq. (19) represent integrals over surfaces that closely follow dividing surfaces, but still are taken inside bulk phases. Therefore, as field is zero inside the conductive seed,  $\mathbf{D}^{h,s} = 0$ , but this is not so on the liquid and gas side of the seed particle surface, where, as seen before,  $D_n^{h,l/g} = D_n^{h,l/g}$  (the vector  $\mathbf{D}^h$  is perpendicular to conductive seed particle surface) represent surface charge. Finally, for the real system the charge carried to the seed particle is distributed in the narrow transition zone of seed particle surface, and thus we reach the third form of Eq. (19).

The surface of tension of a seed particle is located in the transition zone. We assume that this surface coincides with the equipotential surface with potential value  $\varphi_{\text{equipot}} \approx \int_{V_{tz,s}} \varphi \nabla \cdot \mathbf{D} dV / q$ . This assumption is valid with a relative uncertainty of the order of the ratio of the width of transition zone to seed radius, with the effect of double layer on the potential distribution in transition zone ignored. The capacitance of a conducting sphere is proportional to its radius  $C \sim R$ , and difference in sphere radii equal to the width of transition zone  $\lambda$  leads to relative difference of electrical potentials of spheres equal to  $\lambda/R$ . The last term of the last line of Eq. (19) can thus be expressed as  $q\varphi_{\text{equipot}}$ , where  $q$  is the charge that is carried onto the seed particle, having the same value for both real and hypothetical systems. When moving along the equipotential surface, the potential in two first terms of the last line of Eq. (19),  $\varphi$  is constant taken out of the integrals. As shown before,  $D_n^{h,l}$  and  $D_n^{h,g}$  are equal to the surface charge densities, and the integrals together yield the total charge. Thus, also the third form of Eq. (19) reduces to zero.

Thus, the difference in the electric field energies between the real and the hypothetical system takes the form

$$\Delta W = \frac{1}{2} \int_{V_{tz}+V_2} (\mathbf{E} - \mathbf{E}^h) \cdot \mathbf{D}^h dV = \frac{1}{2} \int_{V_{tz}} (\mathbf{E} - \mathbf{E}^h) \cdot \mathbf{D}^h dV + \frac{1}{2} \int_{V_2} (\mathbf{E} - \mathbf{E}^h) \cdot \mathbf{D}^h dV. \quad (20)$$

Since in the volume  $V_2$  the dielectric constants of hypothetical and real system coincide and linear relation  $\mathbf{D} = \varepsilon \varepsilon_0 \mathbf{E}$

holds, the second integral of Eq. (20) is equivalent to

$$\frac{1}{2} \int_{V_2} (\mathbf{E} - \mathbf{E}^h) \cdot \mathbf{D}^h dV = \frac{1}{2} \int_{V_2} (\mathbf{D} - \mathbf{D}^h) \cdot \mathbf{E}^h dV. \quad (21)$$

Analogously with Eq. (19), expressing the electric field in the hypothetical system in terms of the potential of the hypothetical system,  $\mathbf{E}^h = -\nabla \cdot \varphi^h$ , we can derive result

$$\begin{aligned} \frac{1}{2} \int_{V_{tz}+V_2} (\mathbf{D} - \mathbf{D}^h) \cdot \mathbf{E}^h dV \\ = \frac{1}{2} \int_{V_{tz}} (\mathbf{D} - \mathbf{D}^h) \cdot \mathbf{E}^h dV + \frac{1}{2} \int_{V_2} (\mathbf{D} - \mathbf{D}^h) \cdot \mathbf{E}^h dV = 0, \end{aligned} \quad (22)$$

and hence the last term of Eq. (20) can be expressed as

$$\begin{aligned} \frac{1}{2} \int_{V_2} (\mathbf{E} - \mathbf{E}^h) \cdot \mathbf{D}^h dV = \frac{1}{2} \int_{V_2} (\mathbf{D} - \mathbf{D}^h) \cdot \mathbf{E}^h dV \\ = -\frac{1}{2} \int_{V_{tz}} (\mathbf{D} - \mathbf{D}^h) \cdot \mathbf{E}^h dV. \end{aligned} \quad (23)$$

Upon introducing Eq. (23) into Eq. (20), we obtain Eq. (16).

### 1. An explicit form for estimating the work of charging for liquid–vapor interface

Now we derive an explicit formula for the differences in charging energies between real and hypothetical systems due to liquid–vapor interface. Still assuming there is no spontaneous polarization and thus using the simple relationship  $D = \varepsilon \varepsilon_0 E$ , Eq. (16) can then be written as

$$\begin{aligned} \Delta W = \frac{1}{2} \int_{V_{tz}} (\mathbf{E} \cdot \mathbf{D}^h - \mathbf{E}^h \cdot \mathbf{D}) dV = \frac{1}{2} \int_{V_{tz,l}} (\varepsilon_l - \varepsilon) \varepsilon_0 \mathbf{E}^{l,h} \\ \cdot \mathbf{E} dV + \frac{1}{2} \int_{V_{tz,g}} (\varepsilon_g - \varepsilon) \varepsilon_0 \mathbf{E}^{g,h} \cdot \mathbf{E} dV \\ \approx \frac{1}{2} \int_{V_{tz,l}} \left( (\varepsilon_l - \varepsilon) \varepsilon_0 E_t^2 + \left( \frac{1}{\varepsilon} - \frac{1}{\varepsilon_l} \right) \frac{D_n^2}{\varepsilon_0} \right) dV \\ + \frac{1}{2} \int_{V_{tz,g}} \left( (\varepsilon_g - \varepsilon) \varepsilon_0 E_t^2 + \left( \frac{1}{\varepsilon} - \frac{1}{\varepsilon_g} \right) \frac{D_n^2}{\varepsilon_0} \right) dV, \end{aligned} \quad (24)$$

where  $V_{tz,l}$  and  $V_{tz,g}$  are volumes of parts of transition zone contiguous with dividing surface in the neighboring phases, in present case liquid and gas phases, respectively;  $\varepsilon$  is the dielectric constant in transition zone,  $\varepsilon_l$  and  $\varepsilon_g$  are dielectric constants in bulk liquid and gas phases, respectively. In the last form of Eq. (24) it is taken into account that  $E_t \approx E_t^h$  and  $D_n \approx D_n^h$ , where subscripts *t* and *n* refers to the components that are parallel and normal to isodensity surfaces in the transition zone, respectively. It can be seen from the last form of Eq. (24) that the first term is positive and second term negative if dielectric constant  $\varepsilon$  monotonically changes from  $\varepsilon_l$  to  $\varepsilon_g$  in transition from liquid to gas phase. Even if dielectric constant  $\varepsilon$  does not behave monotonically due to composition of the surface region differing from bulk due to surface adsorption,



it is possible to choose the position of dividing surface so that  $\Delta W$  in Eq. (24) turns to be zero, as the non-monotonic behavior is limited to a narrow transition zone and by moving the dividing surface into either bulk liquid or bulk vapor phases one of the terms in the last form of Eq. (24) can be made to have large enough positive or negative value.

Moving dividing surface from the liquid bulk side into the gas-phase bulk side of transition zone, and taking difference of energies we find that the maximum difference in electric energies between real and hypothetical systems is of the order

$$\pm \frac{1}{2} \int_{V_{tz}} \left( (\varepsilon_l - \varepsilon_g) \varepsilon_0 E_t^2 + \left( \frac{1}{\varepsilon_g} - \frac{1}{\varepsilon_l} \right) \frac{D_n^2}{\varepsilon_0} \right) dV.$$

## B. Surface excess for liquid-vapor interface

Now we use the work of charging to derive an expression for the electric surface excess quantity at liquid-vapor interface. We consider a tube of force of hypothetical system in the transition zone. Similar analysis can be performed using the tube of force of the real system. The tube of force cuts a charge  $\delta q$  on the surface of the seed particle. Here we assume that the tube of force starts at a location outside the contact zone of three phases on seed particle. For the tube of force the term  $\mathbf{D}^h dV$  in Eq. (16) can be represented as  $\mathbf{D}^h dV = d\mathbf{L}_D^h D^h dA = d\mathbf{L}_D^h \delta q^h$ , with  $dA$  being the cross-section area of a hypothetical system tube of force.  $D^h dA = \delta q^h$  is constant along the tube of force. The tubes of force of real and hypothetical systems that cut out the same area  $dA$  of the dividing surface can cut out slightly different areas of the seed particle surface and, therefore, slightly different charges  $\delta q$  on seed particle surface. Next we use the relation  $\mathbf{E}^h \cdot d\mathbf{V} = (\mathbf{E}^h \cdot d\mathbf{L}_D^h)(\mathbf{D} \cdot d\mathbf{A}/\delta q^h)\delta q^h = (\mathbf{E}^h \cdot d\mathbf{L}_D^h)(\mathbf{D} \cdot \mathbf{D}^h/(D^h)^2)\delta q$ , where the term  $(\mathbf{D} \cdot d\mathbf{A}/\delta q^h) = (\mathbf{D} \cdot \mathbf{D}^h/(D^h)^2)$  describes the ratio of charges cut by real and hypothetical tubes of force that surround the surface element  $d\mathbf{A}$ . We have taken into account that  $dV = d\mathbf{L}_D^h \cdot d\mathbf{A}$ , and that vectors  $d\mathbf{L}_D^h$  and  $d\mathbf{A}$  point along the same direction while  $\mathbf{D}^h$  is parallel with them, and thus the scalar products of the vectors can be manipulated as shown above, for example,  $\mathbf{D} \cdot d\mathbf{A} = \mathbf{D} \cdot \mathbf{D}^h/D^h dA = \mathbf{D} \cdot \mathbf{D}^h/D^h \delta q^h/D^h$  where we have used also  $dA = \delta q^h/D^h$ . We can now cast Eq. (16) into the form

$$\Delta W = \frac{1}{2} \int_0^{q_{tz}} \overline{\Phi}^{lg} \delta q^h, \quad (25)$$

where  $q_{tz}$  is the total charge cut out on seed particle surface by force tubes penetrating the transition zone under consideration, and the charge element  $\delta q^h$  corresponds to a infinitely narrow tube of force. The integrand in Eq. (25)

$$\begin{aligned} \overline{\Phi}^{lg} = & \int_{L_{D,l}}^{L_{D,x}} \left( \mathbf{E} - \mathbf{E}^{l,h} \frac{\mathbf{D} \cdot \mathbf{D}^{l,h}}{(D^{l,h})^2} \right) d\mathbf{L}_D^h \\ & + \int_{L_{D,x}}^{L_{D,g}} \left( \mathbf{E} - \mathbf{E}^{g,h} \frac{\mathbf{D} \cdot \mathbf{D}^{g,h}}{(D^{g,h})^2} \right) d\mathbf{L}_D^h \end{aligned} \quad (26)$$

is the surface excess quantity of electric field equal to the potential jump through interface. Coordinate  $L_{D,x}$  indicates the location of dividing surface, in present case the surface of tension. Coordinates  $L_{D,l}$ ,  $L_{D,g}$  indicate locations in bulk liquid and gas phases, respectively, that are adjacent to two-phase

transition zone. Starting from these points the dielectric properties are changed so that they correspond the hypothetical system in the interface zone. The integration in Eq. (26) embraces only the transition zone. If systems have spherical symmetry, then dielectric displacement vectors of real and hypothetical systems have the same direction, force tubes cut out the same amount of charge on seed particle surface, and, therefore, the ratio  $\mathbf{D}\mathbf{D}^h/(D^h)^2$  cancel out from Eq. (26).

## 1. An explicit form for estimating the electrical surface excess at liquid-vapor interface

Now we want to estimate the magnitude of the electric surface excess (26). This excess arises from differences in dielectric properties of real and hypothetical systems, as the surface polarization is so far ignored. It is more comfortable to proceed by using the tubes of force of a real system, as then there is no need to change the division of the transition zone made by tubes of force when we go from one hypothetical system to another. Using the tubes of force of a real system Eq. (26) can be expressed as

$$\begin{aligned} \overline{\Phi}^{lg} = & \int_{L_{D,l}}^{L_{D,x}} \left( \mathbf{E} \frac{\mathbf{D}\mathbf{D}^{l,h}}{D^2} - \mathbf{E}^{l,h} \right) d\mathbf{L}_D \\ & + \int_{L_{D,x}}^{L_{D,g}} \left( \mathbf{E} \frac{\mathbf{D}\mathbf{D}^{g,h}}{D^2} - \mathbf{E}^{g,h} \right) d\mathbf{L}_D, \end{aligned} \quad (27)$$

where  $d\mathbf{L}_D$  is the element vector along electric field line in real system and spontaneous polarization is ignored.

As transition zone between phases is very narrow the tangential component of electrical field and normal component of electric displacement remain approximately constant in passing through the interface. Therefore, we can represent the field values of hypothetical system as  $E_t^h = E_t + \delta E_t^h$  and  $D_n^h = D_n + \delta D_n^h$ , respectively, where  $\delta E_t^h$  and  $\delta D_n^h$  are tiny corrections to the corresponding values of the real system. It follows from Eq. (24) that it is possible, for a given tube of force, to choose the location of the dividing surface so that  $\overline{\Phi}^{lg}(L_{D0}) = 0$ . Therefore, without spontaneous polarization and using the fact that Eqs. (24) and (25) give two different expressions for the same energy change evoked by the hypothetical change of dielectric properties in the part of transition zone intercepted by a given elementary tube of force of a real system, we can write

$$\begin{aligned} & [\overline{\Phi}^{lg}(L_{D,x}) - \overline{\Phi}^{lg}(L_{D0})] \delta q \\ & = \int_{\delta V_l(L_{D,x})} (\varepsilon_l - \varepsilon_t) \varepsilon_0 (E_t^{l,h} - E_t^{l,h0}) E_t dV \\ & \quad + \int_{\delta V_{lg}(L_{D,x}, L_{D0})} [(\varepsilon_g - \varepsilon_t) E_t^{g,h} - (\varepsilon_l - \varepsilon_t) E_t^{l,h0}] \varepsilon_0 E_t dV \\ & \quad + \int_{\delta V_g(L_{D0})} (\varepsilon_g - \varepsilon_t) \varepsilon_0 (E_t^{g,h} - E_t^{g,h0}) E_t dV \\ & \quad + \int_{\delta V_l(L_{D,x})} (\varepsilon_l - \varepsilon_n) \varepsilon_0 (E_n^{l,h} - E_n^{l,h0}) E_n dV \end{aligned}$$

$$\begin{aligned}
& + \int_{\delta V_{ig}(L_{Dx}, L_{D0})} [(\varepsilon_g - \varepsilon_n)E_n^{g,h} - (\varepsilon_l - \varepsilon_n)E_n^{l,h0}] \varepsilon_0 E_n dV \\
& + \int_{\delta V_g(L_{D0})} (\varepsilon_g - \varepsilon_n) \varepsilon_0 (E_n^{g,h} - E_n^{g,h0}) E_n dV \\
= & \int_{\delta V_l(L_{Dx})} \delta_{1,E} dV + \int_{\delta V_{ig}(L_{Dx}, L_{D0})} (\varepsilon_g - \varepsilon_l) \varepsilon_0 E_l^2 dV \\
& + \int_{\delta V_{ig}(L_{Dx}, L_{D0})} \delta_{2,E} dV + \int_{\delta V_g(L_{D0})} \delta_{3,E} dV \\
& + \int_{\delta V_l(L_{Dx})} \delta_{1,D} dV + \int_{\delta V_{ig}(L_{Dx}, L_{D0})} \left( \frac{1}{\varepsilon_l} - \frac{1}{\varepsilon_g} \right) \frac{D_n^2}{\varepsilon_0} dV \\
& + \int_{\delta V_{ig}(L_{Dx}, L_{D0})} \delta_{2,D} dV + \int_{\delta V_g(L_{D0})} \delta_{3,D} dV \\
\cong & \int_{\delta V_{ig}(L_{Dx}, L_{D0})} (\varepsilon_g - \varepsilon_l) \varepsilon_0 E_l^2 dV \\
& + \int_{\delta V_{ig}(L_{Dx}, L_{D0})} \left( \frac{1}{\varepsilon_l} - \frac{1}{\varepsilon_g} \right) \frac{D_n^2}{\varepsilon_0} dV, \quad (28)
\end{aligned}$$

where  $\delta V(L_{Dx})$  is the volume of the part of a given force tube of a real system that reaches from the transition zone boundary at liquid side to the coordinate (both hypothetical systems are in liquid phase in this region)  $L_{Dx}$ ,  $\delta V(L_{Dx}, L_{D0})$  is the volume of the force tube part located between coordinates  $L_{Dx}$  and  $L_{D0}$  (system  $h$  with dividing surface at  $L_{Dx}$  is gas, system  $h0$  with dividing surface at  $L_{D0}$  is liquid),  $\delta V(L_{D0})$  is the volume of the force tube part located between coordinate  $L_{D0}$  and the gas phase boundary of transition zone (both hypothetical systems are in gas phase in this region). Here we have introduced a more general model for describing dielectric properties of anisotropic transition zone – a dielectric tensor that has only two independent components – the component  $\varepsilon_n$  for the normal to the surface layer direction and  $\varepsilon_t$  for directions along the surface layer (see also Sec. IV C). We have defined  $\delta_{1,E} = (\varepsilon_l - \varepsilon_t) \varepsilon_0 E_t (\delta E_t^{l,h} - \delta E_t^{l,h0})$ ,  $\delta_{2,E} = \varepsilon_0 E_t [(\varepsilon_g - \varepsilon_t) \delta E_t^{g,h} - (\varepsilon_l - \varepsilon_t) \delta E_t^{l,h0}]$ ,  $\delta_{3,E} = (\varepsilon_g - \varepsilon_t) \varepsilon_0 E_t (\delta E_t^{g,h} - \delta E_t^{g,h0})$ ,  $\delta_{1,D} = (1/\varepsilon_n - 1/\varepsilon_l) (\delta D_n^{l,h} - \delta D_n^{l,h0}) D_n / \varepsilon_0$ ,  $\delta_{2,D} = ((\frac{1}{\varepsilon_n} - \frac{1}{\varepsilon_g}) \delta D_n^{g,h} - (\frac{1}{\varepsilon_n} - \frac{1}{\varepsilon_l}) \delta D_n^{l,h0}) D_n / \varepsilon_0$ , and  $\delta_{3,D} = (1/\varepsilon_n - 1/\varepsilon_g) (\delta D_n^{g,h} - \delta D_n^{g,h0}) D_n / \varepsilon_0$ . The last form of Eq. (28) gives the principal part of electrical field surface excess quantity at a given location of the dividing surface. The terms containing integrands  $\delta_{i,E}$  and  $\delta_{i,D}$  ( $i = 1, 2, 3$ ) are dropped in the last form as insignificant corrections, and they are proportional to quantities  $E_t \delta E_t$  or  $D_n \delta D_n$ , whereas the leading terms are proportional to  $E_t^2$  and  $D_n^2$ . We see that the electrical surface excess consists of two parts. One part is connected with component of electric field tangential to the surface and another with the component of dielectric displacement normal to it. In a system with spherical symmetry the first part is absent.

We have considered excess quantity at liquid-vapor interface. For other interfaces the same principle can be used. As the seed particle is assumed to be spherical and conductive we can choose the tubes of force of real and hypothetical systems to have the same directions at seed particle surface. In a real system charges are distributed not only along the surface but also along the depth of interfacial zone. There is an electrical double layer at surface of seed particle affected by adsorption of molecules from vapor or liquid and, therefore, also a potential jump across interface.<sup>96,99</sup> Thus, in case of seed particle surface the electrical surface excess introduced above incorporates both the double layer peculiarities in metal side of surface and spontaneous polarization of adsorbed molecules. It should be noted that if we enclose a seed particle both with and without an embryo in an electrical double layer of constant strength (e.g., if an isotropic embryo forms on top of a precursor film so that its formation does not affect the electrical double layer of the film-covered seed particle; this also means that the effect of overlapping of the surface layers at solid-liquid and liquid-vapor interfaces on double layer in contact line zone can be ignored), the formation energy of an embryo as a difference of these two states does not change. The location of the dividing surface, chosen so that the electrical potential (electrical capacitance) of seed particle in hypothetical system coincides with potential in real system, does not necessarily coincide with surface of tension, and a relation analogous to Eqs (27) and (28) are valid.

### C. Surface polarization

A dielectric medium of the surface layer is anisotropic and there is a possibility that surface molecules are spontaneously polarized. In this case the most general form that represents the linear relation between the components of the electric displacement and the electric field is<sup>98</sup>

$$D_i = \varepsilon_{ik} \varepsilon_0 E_k + D_{0i}, \quad (29)$$

where  $\mathbf{D}_0$  is a constant vector, and quantities  $\varepsilon_{ik}$  form the dielectric tensor. We assume here that the vector  $\mathbf{D}_0$  is normal to the interface surface and the dielectric tensor has only two independent components – the component  $\varepsilon_n$  for the normal to the surface layer direction and  $\varepsilon_t$  for directions along the surface layer. Thus, next we consider a relationship more general than  $D = \varepsilon \varepsilon_0 E$

$$\begin{aligned}
D_n &= \varepsilon_n \varepsilon_0 E_n + D_{0n}, \\
D_t &= \varepsilon_t \varepsilon_0 E_t.
\end{aligned} \quad (30)$$

Using Eq. (30) we can express Eq. (26) in the form

$$\begin{aligned}
\overline{\Phi}^{lg} &= \int_{L_{D,l}}^{L_{D,x}} \left( \frac{D_n}{\varepsilon_n \varepsilon_0} - \frac{D_n^{l,h} \mathbf{D} \cdot \mathbf{D}^{l,h}}{\varepsilon_l \varepsilon_0 (D^{l,h})^2} \right) \mathbf{n} \cdot d\mathbf{L}_D^h \\
&+ \int_{L_{D,x}}^{L_{D,g}} \left( \frac{D_n}{\varepsilon_n \varepsilon_0} - \frac{D_n^{g,h} \mathbf{D} \cdot \mathbf{D}^{g,h}}{\varepsilon_g \varepsilon_0 (D^{g,h})^2} \right) \mathbf{n} \cdot d\mathbf{L}_D^h \\
&- \int_{L_{D,l}}^{L_{D,g}} \frac{\mathbf{P}_0}{\varepsilon_0} \cdot d\mathbf{L}_D^h + \int_{L_{D,l}}^{L_{D,x}} \left( E_t - E_t^{l,h} \frac{\mathbf{D} \cdot \mathbf{D}^{l,h}}{(D^{l,h})^2} \right) \mathbf{t} \cdot d\mathbf{L}_D^h \\
&+ \int_{L_{D,x}}^{L_{D,g}} \left( E_t - E_t^{g,h} \frac{\mathbf{D} \cdot \mathbf{D}^{g,h}}{(D^{g,h})^2} \right) \mathbf{t} \cdot d\mathbf{L}_D^h, \quad (31)
\end{aligned}$$

where  $\mathbf{n}$  is the unit vector normal to the surface layers and  $\mathbf{t}$  is the unit vector tangential to the surface layers and laying in the plane determined by vectors  $\mathbf{D}^h$  and  $\mathbf{n}$ ,  $\mathbf{P}_0 = \mathbf{D}_0/\varepsilon_n$  describes the spontaneous polarization of surface layer. In case of spherical symmetry there are no terms containing field components tangential to interface surface in Eq. (31). Also the ratio  $\mathbf{D}\mathbf{D}^h/(D^h)^2$  cancel out.

The surface excess polarization

$$\overline{P_0^{lg}} = \int_{L_{D,l}}^{L_{D,s}} \mathbf{P}_0 \cdot d\mathbf{L}_D^h \quad (32)$$

can be considered as the dipole moment per unit area, i.e., spontaneous polarization of molecules in interfacial zone is reduced to the dipole moment of unit area of dividing surface. There is electric double layer charge distribution along the dividing surface. The potential jump across the double layer can be expressed as

$$\varphi_g - \varphi_l = \frac{\overline{P_0^{lg}}}{\varepsilon_0}. \quad (33)$$

In deriving Eqs. (26) and (31) we used a hypothetical system consisting of pieces of bulk phases with dividing boundary surfaces at which the bulk dielectric constant of one phase changes stepwise into dielectric constant of another phase. In case there are spontaneously polarized surface molecules in a real system our hypothetical system requires upgrading. The layers of spontaneously polarized molecules are sources of electric field and these sources should also be taken into account in a hypothetical system. The easiest way to do this is to introduce an electrical double layer of zero thickness with the strength given by Eqs. (32) and (33) at dividing surfaces of hypothetical system. It should be kept in mind that the electric field created by spontaneous polarization around a seed particle in real and hypothetical systems is present even in case of uncharged seed particle. The energy of this field is incorporated into surface energies of the neutral real system and should not be accounted as the charging energy. Still, the energy of the charging process that is related to carrying the charge through spontaneous double layers of real or hypothetical systems must be taken into account. This double layer crossing energy is described by the potential difference given by Eq. (33), which is the same both for real and hypothetical systems, multiplied by a amount of charge that is carried from infinity to the seed particle through a force tube that crosses double layer at a given location. A force tube under consideration can belong to a hypothetical system as in Eq. (31) or to a real system as in Eq. (27). We assume that spontaneous polarization in real system is only weakly dependent on the position along surface layer and, therefore, we can ignore a possible small difference in the values of excess polarization  $\overline{P_0^{lg}}$ , which could be evoked by the use of different force tubes, i.e., real or hypothetical tubes, in defining the value of excess polarization.

In case of systems of complete spherical symmetry the effect of a double layer on the charging energy of either the real or the hypothetical system is independent on the location of double layer with respect to the seed particle surface as long as the potential jump across the double layer is the

same, and all charges are completely carried through the double layer. Thus, we then can neglect the field of double layers (the difference of field values between real and hypothetical double layers, which exists only inside the transition zone) in Eq. (31) (or in Eq. (27)) and consider, based on superposition principle, that the values of field in Eq. (31) are only due to charges that are transported onto seed particle and the difference in field values of real and hypothetical systems is only due to the difference in dielectric properties of these systems. In a spherically symmetric case the spontaneous polarization term should thus be omitted in Eqs. (28) and (31) remains valid.

The seed particle is assumed rigid and conductive. Thus, we expect that with good approximation the transition zone at the seed particle surface can be considered as a set of two subsystems that are conical interceptions of spherical layers adjacent to liquid and vapor phases, respectively. The three phase contact zone is ignored. A shift of hypothetical double layer due to spontaneous polarization (not changing the location of the net charge, which must stay inside the double layer) inside the transition zone does not change the charging energy. A shift in the location of the double layer in liquid-vapor transition zone does change the charging energy. This is because moving the double layer changes the amount of charge that the hypothetical layer embraces at seed particle surface (see Fig. 2 and consider depicted boundaries of transition zone as two different positions of hypothetical double layer). We can estimate the order of magnitude of the difference between charging energies of hypothetical and real systems due to polarization by calculating the difference of charging energies between two hypothetical systems where hypothetical double layers are placed at outer and inner boundaries of liquid-vapor transition zone keeping the location of the dividing surface related to the stepwise change of the dielectric constant. If we ignore the change in surface charge distribution of the seed caused by the difference in location of double layers, we can express the difference in charging energies as  $\pm(P_0^{sl} + P_0^{lg} - P_0^{sg})q_{tz,s} / \varepsilon_0$ , where  $q_{tz,s}$  is the charge on the contact area of the seed with liquid-vapor transition zone (See Fig. 2). We have neglected here the possible dependence of surface excess polarizations on the location. We assume that seed particle charge  $q \gg q_{tz,s}$  and ignore, therefore, the difference in interface polarizations between real and hypothetical non-spherical systems, i.e., Eq. (28) remains valid.

#### D. Electrical line excess

The distribution of dielectric properties of matter in the contact region of three phases differs from the distributions in bulk regions and in regions of two-phase interfaces. The electric surface excess quantity as given by Eq. (31) cannot be uniquely separated into parts for different dividing surfaces crossed by a tube of force on its way from the interior of the seed particle through liquid phase in the contact zone, where the properties are different from bulk, to the interior of the bulk gas phase. Even if the tube crosses only one dividing surface in the contact zone, the surface excess quantity will still be rapidly changing function of the distance of the crossing

point from the contact line of three dividing surfaces. The dielectric properties of three phase contact zone change rapidly both in the direction normal to the dividing surface and in the direction along to the dividing surface but perpendicular to the three phase contact line. The excess quantity as defined for a two-phase interface is not well suited for three phase contact line.

We can divide total interfacial zone into two categories of zones – two-phase zones and three-phase zone to introduce excess corrections to the hypothetical system under consideration. We can attribute an electrical line excess quantity to the interception line of three dividing surfaces, but the division into two- and three-phase interface zones is not uniquely determined. The two-phase part covers the regions of dividing surfaces that are outside the three-phase contact zone. Therefore, it is more appropriate to extrapolate the values of electrical surface excess quantities into three-phase zone and define line excess accordingly to keep the balance of energy. Let us consider an element of three-phase contact zone with width  $dL$  along the line of contact of three dividing surfaces (see Fig. 3).

Next we will use Eq. (16) and for the modification of integrals, we will consider tubes of force of a hypothetical system. We represent the charge  $\delta q^h$  that is cut out by a tube of force of the hypothetical system from the dividing surface of the seed particle as  $\delta q^h = \eta_e^h dL dr$ , where  $\eta_e^h$  is the charge density on seed particle surface at a point crossed by the tube of force. The surface area element  $dL dr$  is represented by the product of the length element  $dL$  of three phase contact line with the length element  $dr$  taken along seed particle dividing surface perpendicular to the three phase contact line. Then, analogously with Eqs. (25) and (26), the integral over an element of three-phase contact zone can be written as

$$\begin{aligned} \kappa_{el} = & \frac{1}{2} \int_0^{\Delta r} \int_{L_{D,s}}^{L_{D,g}} \left( \mathbf{E} - \mathbf{E}^h \frac{\mathbf{D} \cdot \mathbf{D}^h}{(D^h)^2} \right) \cdot d\mathbf{L}_{\mathbf{D}}^h \eta_e^h dr \\ & - \int_0^{\lambda_{lg}} \frac{\overline{\Phi}^{lg} \eta_e^h(\lambda_{lg})}{d\lambda_{lg}} dr d\lambda_{lg} \\ & - \int_0^{\lambda_{sl}} \frac{\overline{\Phi}^{sl} \eta_e^h(\lambda_{sl})}{d\lambda_{sl}} dr d\lambda_{sl} \\ & - \int_0^{\lambda_{sg}} \frac{\overline{\Phi}^{sg} \eta_e^h(\lambda_{sg})}{d\lambda_{sg}} dr d\lambda_{sg}, \end{aligned} \quad (34)$$

where we have used the notation  $\kappa_{el}$  to indicate the electrical excess quantity per unit length of the three phase contact line,  $\lambda_a$  denotes distance from the three phase contact line along  $a$ -dividing surface ( $a = lg, sl, sg$ ). We have used the same notation for the upper bounds of the integrals to indicate the final coordinates of integration outside the three-phase contact zone. The notation  $dr/d\lambda_{lg}$  is the ratio of length elements  $dr$  and  $d\lambda_{lg}$  cut by the hypothetical tube of force from dividing surface of seed particle and dividing surface  $lg$ , respectively. For dividing surfaces  $a = sl$  and  $a = sg$ ,  $d\lambda_a = dr$ .  $\eta_e^h(\lambda_a)$  is the charge density of the seed particle surface at a point that is connected with the dividing surface point  $\lambda_a$  by a tube of force of the hypothetical system.  $\overline{\Phi}^a$  is the value of electrical surface excess quantity extrapolated into the re-

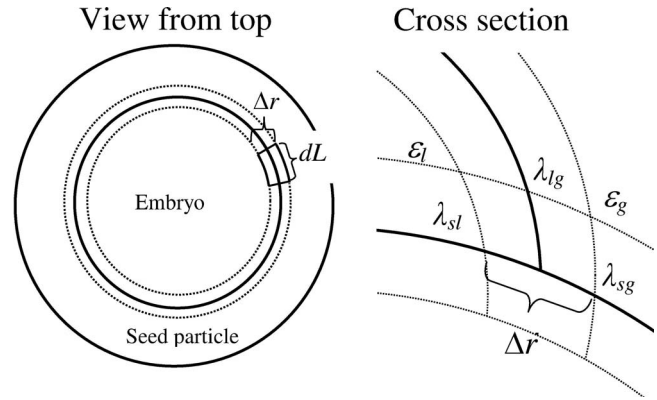


FIG. 3. Top and cross section views of the element of three-phase contact zone and line.

gion of three-phase contact line along dividing surface  $a$  ( $a = lg, sl, sg$ ). It should be noted that we obtain the charging energy of the real system by adding electrical excess energies of interface surfaces, Eqs. (25) and (26) (these equations are written for liquid-vapor interface, but equations for other interfaces are analogous) and electrical line excess energy (Eq. (34) that is integrated over the three phase contact line) to the charging energy of the hypothetical system. We assume that excess quantities for the interface surfaces of the hypothetical system are specified up to the three phase contact line by extrapolation. Then the addition of line excess energy results in cancelling out of extrapolated parts of surface and line excesses for the charging energy of the real system. For Eq. (34) only the first term preserves. This term can be expressed as

$$\begin{aligned} & \frac{1}{2} \int_0^{\Delta r} \int_{L_{D,s}}^{L_{D,g}} \left( \mathbf{E} - \mathbf{E}^h \frac{\mathbf{D} \cdot \mathbf{D}^h}{(D^h)^2} \right) \cdot d\mathbf{L}_{\mathbf{D}}^h \eta_e^h dr \\ & = \frac{1}{2} \int_0^{\Delta r} \int_{L_{D,s}}^{L_{D,g}} \left( \boldsymbol{\epsilon}^{-1} \mathbf{D} - \frac{\mathbf{D}^h \mathbf{D} \cdot \mathbf{D}^h}{\epsilon_{l,g} (D^h)^2} \right) \cdot d\mathbf{L}_{\mathbf{D}}^h \eta_e^h dr \\ & \quad - \int_0^{\Delta r} \int_{L_{D,s}}^{L_{D,g}} \left( \frac{\mathbf{P}_0^{tpc}}{\epsilon_0} \right) \cdot d\mathbf{L}_{\mathbf{D}}^h \eta_e^h dr, \end{aligned} \quad (35)$$

where  $\boldsymbol{\epsilon}^{-1} \mathbf{D}$  is the product of the inverse dielectric tensor (see Eq. (29)) with the vector of the dielectric displacement of the real system, the notation  $\epsilon_{l,g}$  indicates the value of dielectric constant that is equal to  $\epsilon_l$  when a tube of force of hypothetical system is crossing liquid phase and it is  $\epsilon_g$  when gas phase is passed. The term  $\mathbf{P}_0^{tpc} = \boldsymbol{\epsilon}^{-1} \mathbf{D}_0^{tpc}$  (see Eq. (29)) describes possible spontaneous polarization in the three phase contact line region.

It follows from Eq. (34) the electrical line excess  $\kappa_{el}$  turns to zero if the surface charge density on the seed particle at the location of three-phase contact zone is zero. It is known that electric field and surface charge density are zero at obtuse angles of charged conducting body,<sup>100</sup> e.g., at three phase contact line of Fig. 1, where the seed with a nucleus is considered as one uniform conducting body. Therefore, in case of a nucleus with large dielectric constant on conducting seed particle, the electrical line excess is negligible.

Collecting terms that describe spontaneous polarization separately we can write Eq. (34) as

$$\kappa_{el} = \kappa_E - \frac{\kappa_P q}{\varepsilon_0}, \quad (36)$$

$$\begin{aligned} \kappa_E = & \frac{1}{2} \int_0^{\Delta r} \int_{L_{D,S}}^{L_{D,g}} \left( \boldsymbol{\varepsilon}^{-1} \mathbf{D} - \frac{\mathbf{D}^h \cdot \mathbf{D}^h}{\varepsilon_{l,g} (D^h)^2} \right) \cdot d\mathbf{L}_D^h \eta_e^h dr \\ & - \int_0^{\lambda_{lg}} \overline{\Phi_E^{lg}} \eta_e^h(\lambda_{lg}) \frac{dr}{d\lambda_{lg}} d\lambda_{lg} \\ & - \int_0^{\lambda_{sl}} \overline{\Phi_E^{sl}} \eta_e^h(\lambda_{sl}) \frac{dr}{d\lambda_{sl}} d\lambda_{sl} \\ & - \int_0^{\lambda_{sg}} \overline{\Phi_E^{sg}} \eta_e^h(\lambda_{sg}) \frac{dr}{d\lambda_{sg}} d\lambda_{sg}, \end{aligned} \quad (37)$$

$$\begin{aligned} \kappa_P q = & \frac{1}{2} \int_0^{\Delta r} \int_{L_{D,S}}^{L_{D,g}} \mathbf{P}_0^{tpc} \cdot d\mathbf{L}_D^h \eta_e^h dr \\ & - \int_0^{\lambda_{lg}} \overline{P_0^{lg}} \eta_e^h(\lambda_{lg}) \frac{dr}{d\lambda_{lg}} d\lambda_{lg} \\ & - \int_0^{\lambda_{sl}} \overline{P_0^{sl}} \eta_e^h(\lambda_{sl}) \frac{dr}{d\lambda_{sl}} d\lambda_{sl} \\ & - \int_0^{\lambda_{sg}} \overline{P_0^{sg}} \eta_e^h(\lambda_{sg}) \frac{dr}{d\lambda_{sg}} d\lambda_{sg}, \end{aligned} \quad (38)$$

where symbols  $\overline{\Phi_E^a}$  ( $a = lg, sl, sg$ ) mark extrapolated values for electrical surface excess quantities in a case where spontaneous surface polarization is ignored (e.g., Eq. (31), with the term containing polarization  $\mathbf{P}_0$  is dropped out). We have denoted the excess quantity due to spontaneous polarization as a product  $\kappa_P q$ , where  $q$  is the charge and  $\kappa_P$  is charge independent factor. Next we will find an expression for the coefficient  $\kappa_P$  in Eq. (38). We adopt linear relationship between the dielectric displacement and the electric field,  $D = \varepsilon \varepsilon_0 E + \varepsilon P_0^{tpc}$  (Eq. (29) as the form given by Eq. (30) is not applicable to the three phase contact line zone), and charge a seed particle keeping the volume and shape of both nucleus and the seed constant. Therefore, the potential of seed particle and charge density on particle surface are proportional to the total charge of the seed  $q$ . The electrical capacitance of the seed,  $C$ , is constant. The seed particle capacitance can be considered to be a sum of capacitances connected in parallel. Each capacitance is related to a surface element  $dA$ . We can express the capacitance related to a surface element  $dA$  as  $dC = C_A dA$ , where  $C_A$  is the capacitance per unit area. Here the capacitance is defined as  $dC = dq/d\varphi$ , the ratio of added charge  $dq$  to the potential change  $d\varphi$  caused by charge addition. The capacitance  $C_A$  is location dependent when there is a nucleus on seed particle. We can now express the surface charge density as  $\eta_e = C_A(\varphi - \varphi_0) = C_A q/C$ , where  $\varphi - \varphi_0 = q/C$  is the electrical potential change of seed particle when charge  $q$  is carried onto the seed particle. The notation  $\varphi_0$  refers to the potential of uncharged seed particle. As discussed earlier, there is a double layer charge distribution on the surface of a conducting seed particle. This double layer causes a potential jump. Therefore, in general, even an uncharged seed particle has nonzero potential. The capacitances  $C$  and  $C_A$  do not depend

on charge. Thus (see Eq. (38)) also the coefficient,

$$\begin{aligned} \kappa_P = & \frac{1}{C^h} \int_0^{\Delta r} \int_{L_{D,S}}^{L_{D,g}} (\mathbf{P}_0^{tpc}) d\mathbf{L}_D^h C_A^h dr \\ & - \frac{1}{C^h} \int_0^{\lambda_{lg}} \overline{P_0^{lg}} C_A^h(\lambda_{lg}) \frac{dr}{d\lambda_{lg}} d\lambda_{lg} \\ & - \frac{1}{C^h} \int_0^{\lambda_{sl}} \overline{P_0^{sl}} C_A^h(\lambda_{sl}) \frac{dr}{d\lambda_{sl}} d\lambda_{sl} \\ & - \frac{1}{C^h} \int_0^{\lambda_{sg}} \overline{P_0^{sg}} C_A^h(\lambda_{sg}) \frac{dr}{d\lambda_{sg}} d\lambda_{sg}, \end{aligned} \quad (39)$$

does not depend on charge. Here superscript  $h$  indicates that we consider tubes of force and capacitances of the hypothetical system. The larger the seed particle the smaller is the coefficient  $\kappa_P$  as the integration in Eq. (39) covers only a narrow three phase contact line zone region on the seed particle surface.

The first term on the right hand side of Eq. (36) can be reduced to zero by changing the location of the three phase contact line by moving the dividing surfaces. This follows from the arguments presented after Eq. (24) and in deriving Eq. (28). Actually, these arguments apply if we consider a hypothetical system with an excess line quantity whose value is given by Eq. (38) and ignore difference between field sources due to spontaneous polarization of real and hypothetical systems, i.e., we consider that field values in Eq. (37) are generated only by seed particle charges and differences in dielectric constants. The location of the three phase contact line where Eq. (37) reduces to zero, however, does not necessarily correspond to the location of dividing surfaces which sets corresponding terms in surface excess values to zero (see Eq. (28)).

## V. WORK OF CHARGING INCLUDING EXCESS QUANTITIES

In Eq. (13)  $\delta q$  represents the change of electric charge for the whole surface of seed particle, but it can be considered also locally as a change of charge of on some part of the seed particle surface that is cut out by a tube of force related to the dielectric displacement vector.

Keeping this in mind we replace the real system with a hypothetical system that includes surface and line excess polarizations with values given by Eqs. (32) and (38), respectively, and, for simplicity, assume that the locations of surfaces of tension yields zero values for electrical excess quantities apart from those connected with spontaneous polarization, i.e., corrections given by Eqs. (28) and (37) are zero. Let us consider a tube of force of infinitely narrow width. The entire space around seed particle can be divided into these elementary tubes of force. We use the central field line of an elementary tube of force as a coordinate line and denote coordinate along it, as before, with  $L_D$ . For each segment of the elementary tube of force in a bulk phase we use an integral given by second form of Eq. (13). In the spirit of the last form of Eq. (13), every intersection of the elementary tube of force with a dividing interfacial surface is associated with a potential jump  $\Delta\varphi_a$  given by equation (33), leading to a

contribution  $\delta W_q = -\Delta\varphi_a\delta dq = -(\overline{P_0^a}/\varepsilon_0)\delta dq$  in the work of charging the seed, where  $\delta dq$  is the variation of charge  $dq$  separated by elementary tube of force on seed particle surface. A minus sign in front of second and third forms here reflects the point that electric field and potential in the third and last forms of Eq. (13), respectively, are related by  $\mathbf{E} = -\nabla \cdot \varphi$ . We use the result  $\delta D_n = \delta dq/dA = \delta\eta_e$ , leading to  $\delta dq = \delta\eta_e dA_a$  where  $dA_a$  is cross-section area of an elementary tube of force with surface  $a$  ( $a = sl, sg$ ) and  $D_n$  is the component of the dielectric displacement vector normal to interface surface. Thus, for the total surface of seed particle the integration over elementary tubes of force gives the following form for Eq. (13):

$$\begin{aligned} \delta W_q &= \varphi \left( \int_{A_{sl}} \delta\eta_e dA + \int_{A_{sg}} \delta\eta_e dA \right) \\ &= \int_{V_l} \mathbf{E} \cdot \delta\mathbf{D} dV - \frac{\int_{A_{sl}} (\overline{P_0^{sl}} + \overline{P_0^{lg}}) \delta\eta_e dA_{sl}}{\varepsilon_0} \\ &\quad + \int_{V_g} \mathbf{E} \cdot \delta\mathbf{D} dV - \frac{\int_{A_{sg}} \overline{P_0^{sg}} \delta\eta_e dA_{sg}}{\varepsilon_0} \\ &= - \int_{A_{sl}} \frac{\overline{P_0^{sl}}}{\varepsilon_0} \delta D_n dA_{sl} + \int_{V_l} \mathbf{E} \cdot \delta\mathbf{D} dV - \int_{A_{lg}} \frac{\overline{P_0^{lg}}}{\varepsilon_0} \delta D_n dA_{lg} \\ &\quad - \int_{A_{sg}} \frac{\overline{P_0^{sg}}}{\varepsilon_0} \delta D_n dA_{sg} + \int_{V_g} \mathbf{E} \cdot \delta\mathbf{D} dV \\ &= - \int_{A_{sl}} \frac{\overline{P_0^{sl}}}{\varepsilon_0} \delta\mathbf{D} \cdot d\mathbf{A}_{sl} + \int_{V_l} \mathbf{E} \cdot \delta\mathbf{D} dV - \int_{A_{lg}} \frac{\overline{P_0^{lg}}}{\varepsilon_0} \delta\mathbf{D} \cdot d\mathbf{A}_{lg} \\ &\quad - \int_{A_{sg}} \frac{\overline{P_0^{sg}}}{\varepsilon_0} \delta\mathbf{D} \cdot d\mathbf{A}_{sg} + \int_{V_g} \mathbf{E} \cdot \delta\mathbf{D} dV. \end{aligned} \quad (40)$$

The second form follows from the last form of Eq. (13) as the sum of the integrals represent the total charge of the seed particle. The surface excess polarization  $\overline{P_0^{lg}}$  in the second term of third form of Eq. (40) is estimated at the point of interception of gas-liquid dividing surface with an elementary tube of force that starts from surface element  $dA_{sl}$ . As an elementary tube covering an area  $dA_{sl}$  at the seed surface covers an area  $dA_{lg}$  at the gas-liquid interface, and the tube encompasses surface charge  $\delta\eta_e dA_{sl}$ , we can write  $\delta\eta_e dA_{sl} = \delta D_n dA_{sl} = \delta D_n dA_{lg}$ , which result in the equality between the third and fourth forms of Eq. (40). While the second form of Eq. (40) represents the energy change for the whole system, the individual terms of the third, fourth and fifth forms of Eq. (40) have also a local meaning representing energy changes in bulk and surface phases. If spontaneous polarization terms  $\overline{P_0^{ij}}/\varepsilon_0$  in Eq. (40) do not depend on the position of the dividing surface, they can be taken out of the integrals.

We can get the total energy that is required to charge a seed particle up to a charge  $q$  if we integrate Eq. (40) over the charge. The energy of the nonzero electric field (with potential  $\varphi_0$ ) of an uncharged seed particle due to surface polarization is incorporated into the surface energy of the electrically neutral system and should not be accounted as the charging energy. We assume that the linear relationship  $\mathbf{D} = \varepsilon\varepsilon_0\mathbf{E}$  holds for bulk phases. During charging the shape and volume of a nucleus and seed particle are kept constant. Therefore, the electric capacitance  $C_l = q/(\varphi - \varphi_0)$  does not depend on charge,  $(\varphi - \varphi_0)$  being the potential change evoked by the charge  $q$ , and the potentials can be expressed as  $\varphi = \varphi_0 + q/C_l$ . The integration of the last form of Eq. (13) and third, fourth, and fifth forms of Eq. (40) gives alternative forms for the charging work

$$\begin{aligned} W_q &= \int \varphi \delta q = \frac{q^2}{2C_l} + \varphi_0 q = \frac{\varphi + \varphi_0}{2} q \\ &= \int_{V_l} \left( \frac{ED}{2} - \frac{E_0 D_0}{2} \right) dV - \frac{\int_{A_{sl}} (\overline{P_0^{sl}} + \overline{P_0^{lg}}) \eta_e dA_{sl}}{\varepsilon_0} \\ &\quad + \int_{V_g} \left( \frac{ED}{2} - \frac{E_0 D_0}{2} \right) dV - \frac{\int_{A_{sg}} \overline{P_0^{sg}} \eta_e dA_{sg}}{\varepsilon_0} \\ &= - \int_{A_{sl}} \frac{\overline{P_0^{sl}}}{\varepsilon_0} (D_n - D_{0,n}) dA_{sl} + \int_{V_l} \left( \frac{ED}{2} - \frac{E_0 D_0}{2} \right) dV \\ &\quad - \int_{A_{lg}} \frac{\overline{P_0^{lg}}}{\varepsilon_0} (D_n - D_{0,n}) dA_{lg} \\ &\quad - \int_{A_{sg}} \frac{\overline{P_0^{sg}}}{\varepsilon_0} (D_n - D_{0,n}) dA_{sg} + \int_{V_g} \left( \frac{ED}{2} - \frac{E_0 D_0}{2} \right) dV \\ &= - \int_{A_{sl}} \frac{\overline{P_0^{sl}}}{\varepsilon_0} (\mathbf{D} - \mathbf{D}_0) \cdot d\mathbf{A}_{sl} + \int_{V_l} \left( \frac{ED}{2} - \frac{E_0 D_0}{2} \right) dV \\ &\quad - \int_{A_{lg}} \frac{\overline{P_0^{lg}}}{\varepsilon_0} (\mathbf{D} - \mathbf{D}_0) \cdot d\mathbf{A}_{lg} \\ &\quad - \int_{A_{sg}} \frac{\overline{P_0^{sg}}}{\varepsilon_0} (\mathbf{D} - \mathbf{D}_0) \cdot d\mathbf{A}_{sg} + \int_{V_g} \left( \frac{ED}{2} - \frac{E_0 D_0}{2} \right) dV, \end{aligned} \quad (41)$$

where  $\eta_e$  is the surface density of charges carried on seed particle from infinity. When an embryo which has polarized interface surfaces as sources of field is formed on an uncharged seed particle it evokes redistribution of charges on the surface of the conducting seed if the spherical symmetry is broken. This density of charges is not included in surface density  $\eta_e$ .  $\mathbf{D}_0$  is the dielectric displacement vector around uncharged seed particle, and  $\mathbf{D} - \mathbf{D}_0$  is the change of dielectric displacement evoked by charges  $\eta_e$ . Note that the charging work

Eq. (41) obtained by integration of Eq. (40) depends on the shape of the embryo. If we ignore polarization effects Eq. (41) reduces formally to Eq. (15) (note however that in Eq. (15) we considered dielectric constant to depend on the position in interface zones).

If the surface excess polarizations  $\overline{P}_0^{ij}$  are independent of location, the three last forms of Eq. (41) can be expressed as

$$W_q = \int_{V_l} \frac{ED - E_0 D_0}{2} dV - \frac{(\overline{P}_0^{sl} + \overline{P}_0^{lg})q_{sl}}{\varepsilon_0} + \int_{V_g} \frac{ED - E_0 D_0}{2} dV - \frac{\overline{P}_0^{sg}q_{sg}}{\varepsilon_0}, \quad (42)$$

where  $q_{sl}$  and  $q_{sg}$  are charges on surface areas of the seed particle adjacent to liquid and gas phases, respectively.

Taking a variation of Eq. (41) (we will consider the fourth and fifth forms of it and use relation  $\varphi = \varphi_0 + q/C_l$  again) and assuming fixed shape and volume of the system we get

$$\begin{aligned} \delta W_q &= \frac{1}{2}(\varphi + \varphi_0)\delta q + \frac{1}{2}q\delta(\varphi + \varphi_0) \\ &= \frac{1}{2}(\varphi + \varphi_0)\delta q + \frac{1}{2}q\delta\left(\frac{q}{C_l} + 2\varphi_0\right) \\ &= \varphi\delta q + \frac{1}{2}q^2\delta\left(\frac{1}{C_l}\right) + q\delta\varphi_0 \\ &= \frac{1}{2} \int_{V_l+V_g} \mathbf{E} \cdot \delta \mathbf{D} dV + \frac{1}{2} \int_{V_l+V_g} \mathbf{D} \cdot \delta \mathbf{E} dV - \frac{1}{2} \delta \int_{V_l+V_g} D_0 E_0 dV \\ &\quad - \sum_a \left( \int_{A_a} \left[ \frac{\delta \overline{P}_0^a}{\varepsilon_0} \mathbf{D} + \frac{\overline{P}_0^a}{\varepsilon_0} \delta \mathbf{D} - \delta \left( \frac{\overline{P}_0^a}{\varepsilon_0} \mathbf{D}_0 \right) \right] \cdot d\mathbf{A}_a \right) \end{aligned} \quad (43)$$

and subtracting the second and last forms of Eq. (40) from the second line and last two lines of Eq. (43), respectively, we obtain

$$\begin{aligned} &\frac{q^2}{2} \delta \left( \frac{1}{C_l} \right) + q\delta\varphi_0 \\ &= + \frac{1}{2} \int_{V_l+V_g} \mathbf{D} \cdot \delta \mathbf{E} dV - \frac{1}{2} \delta \int_{V_l+V_g} D_0 E_0 dV \\ &\quad - \sum_a \left( \int_{A_a} \left[ \frac{\delta \overline{P}_0^a}{\varepsilon_0} \mathbf{D} - \delta \left( \frac{\overline{P}_0^a}{\varepsilon_0} \mathbf{D}_0 \right) \right] \cdot d\mathbf{A}_a \right) = 0, \end{aligned} \quad (44)$$

i.e., at given charging state the sum of variations presented above has to be zero.

In the case of a seed particle surrounded by gas phase spherical symmetry allows us to write Eq. (41) also as

$$W_q = \frac{q^2}{8\pi\varepsilon_g\varepsilon_0} \frac{1}{R} - \frac{\overline{P}_0^{sg}}{\varepsilon_0} q, \quad (45)$$

where  $R$  is the radius of the spherical seed particle.

Equations (41) and (43), and (44) are written as integrals over elementary tubes of force that cover the whole sur-

face of the seed particle, but they can be written also for a tube of force that cuts out only a part of seed particle surface. Of course, only terms that are relevant for a force tube under consideration should be kept in Eqs. (41), (43), and (44). It should be noted that force tubes run along field vectors of dielectric displacement  $\mathbf{D} - \mathbf{D}_0$ . Displacement  $\mathbf{D} - \mathbf{D}_0$  is proportional to the charge  $q$  of seed particle, and as long as the shape and volume of nucleus and spontaneous polarization of surfaces are kept constant, and the relationship  $\mathbf{D} = \varepsilon\varepsilon_0\mathbf{E}$  holds for bulk phases, also the shape and position a tube of force in space are kept unchanged during charging due to linearity of governing equations of electrostatics.

So far we have considered the charging of hypothetical system that includes surface excess polarizations. For better agreement of our hypothetical system with a real system we should also consider the electrical line excess. As in case of surface excess quantities we ignore the line excess due to the difference of dielectric constant in three phase contact line zone from their constant values in bulk and surface phases described by Eq. (37), assuming that the location of three phase contact line assures its value is zero. In the following we only study the line excess due to surface polarization. The increase of line energy of spontaneously polarized three phase contact line at charging of seed particle by charge  $\delta q$  can be expressed as (see Eqs. (38) and (39))

$$\delta W_L = -\delta q \int_L \frac{\kappa_P}{\varepsilon_0} dL = -\delta q \frac{\kappa_P}{\varepsilon_0} L, \quad (46)$$

where  $L$  is the length of three phase contact line. The last form of Eq. (46) corresponds to the case where coefficient  $\kappa_P$  is independent of position on the three phase contact line. The integration of Eq. (46) gives (for charging at constant shape and volume of the nucleus)

$$W_L = -q \int_L \frac{\kappa_P}{\varepsilon_0} dL = -q \frac{\kappa_P}{\varepsilon_0} L. \quad (47)$$

Taking variation of Eq. (47) and subtracting Eq. (46) from the result we obtain

$$-q\delta \int_L \frac{\kappa_P}{\varepsilon_0} dL = 0, \quad (48)$$

i.e., at given charging conditions the integral under variation sign cannot change.

## VI. INTERNAL ENERGIES AND GRAND POTENTIAL

As discussed earlier before Eq. (13), with respect to the total system charging is done adiabatically, but subsystems are charged at constant temperature and volume. The gaseous phase is taken to be large, and heat transfer between subsystems is allowed. The amount of charging work in a reversible process at constant volume and temperature is equal to the change of Helmholtz free energy  $\Delta F = \Delta(U - TS)_{T,V}$ . The entropy change at charging is  $\Delta S^q = (\partial \Delta F / \partial T)_{V,q}$ , which gives, e.g., for any bulk phase  $\Delta S^q = \int_V \varepsilon_0 E^2 (\partial \varepsilon / \partial T)_V dV$ .<sup>101</sup>

The internal energy change of subsystem  $i$  is  $\Delta U_i = \Delta F_i + T\Delta S_i^q = W_q^i + T\Delta S_i^q$ , where  $W_q^i$  is the work of charging

of subsystem  $i$ . This work is given for the bulk phases and interfaces between them by the last form of Eq. (41), and for the three phase contact line by Eq. (47). Therefore, we obtain internal energies of bulk phases, surfaces, and three phase contact line for charged system by adding charging energies (see Eqs. (41) and (47)) to Eqs. (5)–(8) and accounting also for the change of entropies. Using  $D_{lg} = \varepsilon\varepsilon_0 E_{lg}$  the bulk, surface, and line energies become

$$U_l^q = T(S_l + \Delta S_l^q) - p_l^0 V_l + \sum_i \mu_{i,l} N_{i,l} + \int_{V_l} \frac{D^2 - D_0^2}{2\varepsilon_l \varepsilon_0} dV, \quad (49)$$

$$U_g^q = T(S_g + \Delta S_g^q) - p_g^0 V_g + \sum_i \mu_{i,g} N_{i,g} + \int_{V_g} \frac{D^2 - D_0^2}{2\varepsilon_g \varepsilon_0} dV, \quad (50)$$

$$U_a^q = T(S_a + \Delta S_a^q) + \sigma_a A_a + \sum_i \mu_{i,a} N_{i,a} - \int_{A_a} \frac{\overline{P}_0^a}{\varepsilon_0} (D_n - D_{0,n}) dA_a \quad (a = sl, sg, lg), \quad (51)$$

$$U_L^q = T(S_L + \Delta S_L^q) + \kappa L + \sum_i \mu_{i,L} N_{i,L} - q \int_L \frac{\kappa_P}{\varepsilon_0} dL. \quad (52)$$

We assumed that the gas phase is large enough to act as heat and particle bath, that is, to keep the temperature through the total system constant and preserve chemical potentials of each species in the vapor phase despite nucleus formation processes on the seed particle. Thus, we will use grand potential to find the equilibrium state of the system. For a system containing a charged seed particle in vapor, but no liquid nucleus yet, we obtain

$$\Omega_0 \equiv U_0 - T S_0 - \sum_i \mu_{i,g} N_i = \sigma_{gs} A_{gs}^0 - p_g^0 V + \int_V \frac{ED}{2} dV - \int_{A_{gs}^0} \frac{\overline{P}_0^{sg}}{\varepsilon_0} D_n dA_a = \sigma_{gs} A_{gs}^0 - p_g^0 V + \frac{q^2}{8\pi\varepsilon_g \varepsilon_0} \left( \frac{1}{R} - \frac{1}{\rho_{\text{lim}}} \right) - \frac{\overline{P}_0^{sg}}{\varepsilon_0} q, \quad (53)$$

where  $U_0 = U_g^q + U_{sg}^q$  is the internal energy of the system,  $S_0 = S_g + S_{sg}$  is the entropy of the system (the  $T\Delta S$  terms of Eqs. (49)–(52) cancel out as the entire system was charged adiabatically),  $V$  is the total volume of the system (seed particle volume is excluded),  $R$  is the radius of the spherical seed particle,  $\rho_{\text{lim}}$  is the radius of very distant boundary of the system,  $N_i$  is the total number of molecules of species  $i$  (surface excess plus gas phase numbers). The chemical potentials for surface and vapor phases for each component are equal. We have not constrained mass transfer.

Taking the differential of the defining form  $U_0 - T S_0 - \sum_i \mu_{i,g} N_i$  of Eq. (53) and using Eqs. (2) and (3), and (40) (in the latter the terms related to liquid should be omitted and spherical symmetry accounted for) we obtain the differential of the grand potential:

$$d\Omega_0 = -S_0 dT + \sigma_{sg} dA_{sg}^0 - p_g^0 dV - \sum_i N_i d\mu_{i,g} - \int_{A_{sg}^0} \frac{\overline{P}_0^{sg}}{\varepsilon_0} \delta \mathbf{D} \cdot d\mathbf{A}_{sg}^0 + \int_{V_g} \mathbf{E} \cdot \delta \mathbf{D} dV. \quad (54)$$

The grand potential for a seed particle in the vapor is a function of temperature, seed particle surface area, system volume, chemical potentials of all of the molecular species, and dielectric displacement vector.

For a system containing a charged seed particle with a liquid nucleus on its surface in a vapor, we obtain

$$\begin{aligned} \Omega &\equiv U - T S - \sum_i \mu_{i,g} N_i \\ &= -p_l^0 V_l - p_g^0 V_g + \sum_a \sigma_a A_a + \kappa L \\ &\quad + \sum_a \sum_i (\mu_{i,a} - \mu_{i,g}) N_{i,a} \\ &\quad + \sum_i (\mu_{i,l} - \mu_{i,g}) N_{i,l} + \sum_i (\mu_{i,L} - \mu_{i,g}) N_{i,L} \\ &\quad - \int_{A_{sl}} \frac{\overline{P}_0^{sl}}{\varepsilon_0} (\mathbf{D} - \mathbf{D}_0) \cdot d\mathbf{A}_{sl} \\ &\quad + \int_{V_l} \left( \frac{ED}{2} - \frac{E_0 D_0}{2} \right) dV - \int_{A_{lg}} \frac{\overline{P}_0^{lg}}{\varepsilon_0} (\mathbf{D} - \mathbf{D}_0) \cdot d\mathbf{A}_{lg} \\ &\quad - \int_{A_{sg}} \frac{\overline{P}_0^{sg}}{\varepsilon_0} (\mathbf{D} - \mathbf{D}_0) \cdot d\mathbf{A}_{sg} - q \int_L \frac{\kappa_P}{\varepsilon_0} dL \\ &\quad + \int_{V_g} \left( \frac{ED}{2} - \frac{E_0 D_0}{2} \right) dV, \end{aligned} \quad (55)$$

where  $U = U_l^q + \sum_a U_a^q + U_g^q + U_L^q$  is the total internal energy of the system,  $S = S_l + \sum_a S_a + S_g$  is the total entropy of the system (again, the  $T\Delta S$  terms of equations (49)–(52) cancel out as the entire system was charged adiabatically),  $N_i = N_{i,l} + N_{i,g} + \sum_a N_{i,a}$  is the total number of  $i$ -type molecules of the system,  $V = V_l + V_g$  is the total volume of the system (excluding again the volume of the seed particle).

Taking the differential of the defining form  $U_0 - T S_0 - \sum_i \mu_{i,g} N_i$  of Eq. (55) and using Eqs. (1)–(4) and (40) and



Eq. (46), we obtain the differential for the grand potential:

$$\begin{aligned}
 d\Omega = & -SdT - p_g^0 dV_g - p_l^0 dV_l + \sum_a \sigma_a dA_a \\
 & - \sum_i N_{i,g} d\mu_{i,g} + \sum_i (\mu_{i,l} - \mu_{i,g}) dN_{i,l} \\
 & + \sum_a \sum_i (\mu_{i,a} - \mu_{i,g}) dN_{i,a} + \sum_i (\mu_{i,L} - \mu_{i,g}) dN_{i,L} \\
 & + \left( \kappa - q \frac{\kappa_P}{\epsilon_0} \right) dL - \int_{A_{sl}} \frac{\overline{P_0^{sl}}}{\epsilon_0} \delta \mathbf{D} \cdot d\mathbf{A}_{sl} \\
 & + \int_{V_l} \mathbf{E} \cdot \delta \mathbf{D} dV - \int_{A_{lg}} \frac{\overline{P_0^{lg}}}{\epsilon_0} \delta \mathbf{D} \cdot d\mathbf{A}_{lg} - \int_{A_{sg}} \frac{\overline{P_0^{sg}}}{\epsilon_0} \delta \mathbf{D} \cdot d\mathbf{A}_{sg} \\
 & + \int_{V_g} \mathbf{E} \cdot \delta \mathbf{D} dV - \delta q \int_L \frac{\kappa_P}{\epsilon_0} dL. \quad (56)
 \end{aligned}$$

Eq. (56) shows independent parameters that determine the value of the grand potential for a constrained nucleus on a seed particle immersed in a vapor. We see that the potential Eq. (55) is actually a hybrid potential. It is a grand potential with respect to variables  $\mu_{i,g}$  – the chemical potential of species  $i$  in vapor and Helmholtz free energy with respect to variables  $N_{i,a}$  and  $N_{i,L}$  – the number of  $i$  – type molecules of surface  $a$  ( $a = gl, ls$ ) and the number of  $i$  – type molecules of contact line, respectively.

## VII. CONCLUSIONS

A thermodynamical formalism is applied to a system consisting of a dielectric liquid nucleus of a new phase on a charged insoluble conducting seed particle within a uniform multicomponent 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. We replace the real system with a hypothetical system, where properties, including dielectric constants, of bulk phases preserve their values up to a dividing surface. We introduce electrical surface and line excess quantities to take into account the difference between real and hypothetical system. We also consider electrical surface and line excess quantities due to spontaneous polarization of molecules on surfaces between the phases and at the three phase contact line. Potential jumps at phase interfaces caused by surface polarization together with line tension are used to derive internal energies and grand potential for the system. The reversible work needed to form a nucleus of a new phase on a seed particle, and the conditions of equilibrium between the critical nucleus and the mother phase are considered in Paper II.<sup>102</sup>

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