Reversible work of the formation of a layer of a new phase on a spherical charged conductor within a uniform multicomponent macroscopic mother phase

M. Noppel
Institute of Environmental Physics, University of Tartu, 18 Ülikooli Str. 50090 Tartu, Estonia

H. Vehkamäki and M. Kulmala
Department of Physical Sciences, P.O. Box 64, FIN-00014 University of Helsinki, Finland

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A thermodynamically consistent formalism is applied to calculate the reversible work needed to form a small layer of a new phase (embryo) around a charged insoluble conducting sphere within a uniform macroscopic mother phase. To treat the embryos of arbitrary size which are not the critical nuclei (i.e., which are not fragments that are in unstable equilibrium with the mother phase), a constraint in the form of an external field is introduced. When a critical nucleus is of primary interest, the specification of this constraint is not required. The results that are obtained for a critical cluster do not depend on which path approaches a critical state. However, the properties of noncritical clusters depend on the external constraining field and this effect is discussed in detail. The obtained new expression for the work of embryo formation differs from the one commonly used in the nucleation literature. The conditions of its extrema yield the correct conditions of equilibrium between the critical nucleus and the mother phase. Expressions are derived that are suitable for practical calculations of the size and composition of a critical nucleus. © 2003 American Institute of Physics. [DOI: 10.1063/1.1620499]

I. INTRODUCTION

The reversible work of the formation of a small fragment of a new phase is of primary interest in the field of nucleation. A critical nucleus is a fragment of a new phase, which is in unstable equilibrium with the mother phase. The reversible work of a critical nucleus 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. In a fully molecular theory the initial stages of this process would involve the formation of some appropriate molecular cluster that later develops into a recognizable piece of the new phase. However, such molecular theories are not generally available for practically relevant systems, and one is forced to rely on quasiphenomenological theories in which the initial fragment is treated as though it were a piece of a stable phase with an appropriate allowance of surface effects, e.g., a droplet in vapor–liquid phase transition. To estimate the free energy change involved in the formation of a piece of the stable phase purely thermodynamic methods can be used.

Gibbs’ considered only a critical nucleus. Nishioka and Kusakà extended Gibbs’ interfacial thermodynamics to noncritical (arbitrarily sized) liquid clusters in the vapor of multicomponent systems. Their aim was to clarify the uncertainty over whether or not the size and composition dependence of interfacial tension must be taken into account in taking the extremity condition of the reversible work of a noncritical cluster formation, when deriving the size and the composition of a critical nucleus. The extension of interfacial thermodynamics was done under an additional constraint that maintained the number of molecules contained in a cluster. Debenedetti and Reiss also extended Gibbs’ interfacial thermodynamics to noncritical clusters of a general system, overstepping the limits of the system of a liquid cluster in a mother vapor phase. Their main interest was to get a thermodynamically consistent and rigorous expression for the reversible work of the formation of a noncritical cluster, from which the work of the formation of the critical nucleus follows as an extremum condition. In this context they focused on explicit consideration of the constraint that prevents the free transfer of matter between the embryo and the mother phase but did not pay attention to the effect that constraint exerts on the properties of a noncritical cluster. This effect was not essential for their task since on approaching a critical nucleus (the unstable equilibrium state for which a constraint is not required) the effect disappears. The difference between the thermodynamic potential values of the initial and final states of a thermodynamic system (the metastable and unstable equilibrium states in the present case) does not depend on a path connecting these states. Different paths defined by different constraints can be used to connect the initial and final states of a thermodynamic system. Both Nishioka and Kusakà and Debenedetti and Reiss obtained expressions for the reversible work of the formation of a noncritical cluster that differ from the one commonly used in the nucleation literature.

Djikaev et al. extended the method of using constraints by Debenedetti and Reiss to the case of the formation of multicomponent liquid droplets on solid, soluble or insoluble particles and obtained a rigorous and thermodynamically consistent expression for the reversible work of the forma-
tion of an arbitrary droplet (which may not be in equilibrium with the vapor phase). They indicate that considering a non-equilibrium droplet as an equilibrium one without imposing the necessary virtual constraints can lead to the dependence of the calculated free energy of embryo formation of the path of embryo formation. As an example, Djikaev et al.\(^4\) considered the condensation of a single-component vapor on a solid soluble particle (consisting of a single species). They used an integro-differential method within the framework of the common capillarity approximation (the presence of constraints is disregarded), and calculated the free energy of the formation of a droplet on two different paths in the plane of the two variables of the state of the droplet. The obtained values of free energy were different. In the present case, by our opinion, the example is not convincing, because the reason of divergence may not be the application of the common capillarity approximation, but the thermodynamic inconsistency of the modeling expression of the disjoining pressure used in the calculation. It is possible to connect the initial and final states, given as the critical droplets of different size, with two different paths consisting of the sequences of critical droplets of different size and composition. Integration along these paths that are close with the paths by Djikaev et al.\(^4\) should also give different values as this integration will lead to integrals over disjoining pressure that are similar to the corresponding integrals by Djikaev et al.\(^4\) and close to them by value, but in the present case the paths consist of the sequences of unstable equilibrium states (no constraints are needed). Like Debenedetti and Reiss,\(^3\) Djikaev et al.\(^4\) did not pay attention to effect the constraint exerts on the properties of a noncritical cluster.

In this paper we consider heterogeneous nucleation on a charged core or on ions of multicomponent systems.\(^5\)–\(^8\) We extend the approach by Rusanov and Kuni,\(^6\) who considered a critical nucleus formed on a charged conductive sphere, to the arbitrarily sized clusters with the aim of obtaining the expression for the reversible work of the formation of a noncritical cluster. Following Debenedetti and Reiss,\(^3\) we introduce explicitly a constraint as an external field that prevents the free transfer of matter between the noncritical cluster and the mother phase. Differently from Debenedetti and Reiss,\(^3\) who imposed an external field to act on the transition zone between the adjacent phases and a portion of the homogeneous interior of the droplet, we impose an external field to act in the environment of a cluster just outside of it and its transition zone. A constraint is not needed for a cluster of critical size. Enclosing of the cluster within an external field when the state of environment is changed keeps the state of the cluster and its transition zone unchanged. They remain in equilibrium and, therefore, there is no need for an external field to act on the whole transition zone. When a critical nucleus is of primary interest the specification of the particular constraint is not required, but this is not so for a noncritical nucleus provided that the thermodynamic quantities, which are the equilibrium concepts, can be applied with some accuracy also to a nonequilibrium system. For instance, if the evaporation rate of a noncritical cluster is estimated by considering “the equilibrium constants of evaporation–condensation reaction,” these constants are evaluated on the basis of the reversible work of a noncritical cluster. Therefore, the effect of a constraining field on the properties of a noncritical cluster is discussed in detail.

II. EQUATIONS FOR CONSTRAINED DROPLET IN VAPO

Consider a spherically symmetric multicomponent system in the center of which is a charged particle \(\gamma\) creating electric field (see Fig. 1). Suppose that this is a small conducting sphere with a charge distributed uniformly on its surface surrounded by dielectric fluids \(\alpha, \eta, \beta\). The phase \(\alpha\) is in equilibrium (unstable) with the phase \(\eta\). Preliminarily, the radius \(r^{a\eta}\) in Fig. 1 approximately indicates the position of the transition zone between the phases \(\alpha\) and \(\eta\). The radius \(r^{\eta\beta}\) in Fig. 1 indicates the location of an external field that prevents the free transfer of matter between the phases \(\eta\) and \(\beta\). The phase \(\eta\), which is in unstable equilibrium with a drop of the phase \(\alpha\), differs from the phase \(\beta\) only by the composition and pressure, not by the aggregate state. Following Rusanov and Kuni,\(^6\) the fundamental equations for such a system can be obtained if a conductor with its charged components is included into the system. The whole system may then be considered as without an external electric field, and ordinary thermodynamic equations may be applied. For a conical part of the system within the solid angle \(\omega\), it follows from the first and second laws of thermodynamics for an open system,

![FIG. 1. Thermodynamic system of a constrained noncritical layer of two phases \(\alpha\) and \(\eta\) around a charged conducting sphere \(\gamma\) surrounded by the phase \(\beta\). The interface between a conducting sphere \(\gamma\) and a layer of dielectric fluid \(\alpha\) is indicated by the radius of the surface of tension \(r^{\alpha\gamma}\). The spherical layers of dielectric fluids, \(\alpha\) and \(\eta\), are in equilibrium with each other. The radius of the surface of tension \(r^{\eta\beta}\) gives the position of their interface. The phases \(\alpha\) and \(\eta\) are constrained by an external field preventing mass transfer between the phases \(\beta\) and \(\eta\). The field operates in a narrow zone between the phases \(\eta\) and \(\beta\) at radius \(r^{\eta\beta}\). The field does not influence the transition zone between the phases \(\alpha\) and \(\eta\).](image-url)
\[ \delta U = T \delta S - \delta \omega \int_0^R \rho_T r^2 dr - p_N(R) \omega R^2 \delta R \]
\[ + \sum_i \mu_i \delta N_i^a \eta + \sum_j \mu_j \delta N_j^b + \sum \tilde{\mu}_j \delta \eta_j, \tag{1} \]

where \( U \) is the energy; \( T \) is the temperature; \( S \) is the entropy; \( \rho_T \) and \( p_N \) are the tangential and normal components of the pressure tensor, respectively; \( R \) is the radius of an infinitely distant boundary of the system (\( r \) is the radial coordinate); \( \mu_i^a \) is the chemical potential of the \( i \)-th component of the dielectric phases \( \alpha \) and \( \eta \); \( \mu_j^b \) is the chemical potential of the \( j \)-th component of the dielectric phase \( \beta \); \( \tilde{\mu}_j \) is the electrochemical potential of the \( j \)-th component of the spherical conductor \( \gamma \); \( N_i^a \eta \) is the total number of molecules of the \( i \)-th component of the dielectric phases \( \alpha \) and \( \eta \); \( N_j^b \) is the number of molecules of the \( j \)-th component of the dielectric phase \( \beta \), and \( N_j^\gamma \) is the number of molecules of the \( j \)-th component of the conductor. The first term on the right-hand side of Eq. (1) is connected to the transfer of heat between the system and its environment; the fourth, fifth, and sixth terms are connected with the transfer of mass. The second and third terms describe the work of deformation. Using Euler’s theorem and integrating Eq. (1) from \( \omega = 0 \) to a certain value \( \omega \), while keeping the values of the intensive variables constant, we get

\[ U = TS - \omega \int_0^R \rho_T r^2 dr + \sum_i \mu_i^a N_i^a \eta \]
\[ + \sum_j \mu_j^b N_j^b + \sum \tilde{\mu}_j N_j^\gamma. \tag{2} \]

Taking the differential of Eq. (2) and comparing the result with Eq. (1), we get the Gibbs–Duhem relation,

\[ S \delta T - \omega \delta \left( \int_0^R \rho_T r^2 dr \right) + p_N(R) \omega R^2 \delta R \]
\[ + \sum_i N_i^a \delta \mu_i^a + \sum_j N_j^b \delta \mu_j^b + \sum_j N_j^\gamma \delta \tilde{\mu}_j = 0. \tag{3} \]

For electrochemical potentials we use the standard expression

\[ \tilde{\mu}_j = \mu_j + e_j \varphi, \tag{4} \]

where \( e_j \) is the charge of ion \( j \), and \( \varphi \) is the electrical potential of the conductor. If the conductor contains also neutral components, their electrochemical potentials will be converted into chemical potentials automatically with Eq. (4) and, therefore, no separate terms need to be written for them in Eqs. (1)–(3). We use also the relationships

\[ \sum_j N_j^\gamma e_j = q = D 4 \pi r^2, \tag{5} \]
\[ \varphi = \int_0^R Edr, \tag{6} \]

where \( q \) is the charge of the conductor; \( D \) and \( E \) are the electric flux density and the electric field strength, respectively (directions from the center of the system are considered to be positive; \( D \) and \( E \) become zero inside the conductor).

Substitution of Eqs. (4)–(6) into Eqs. (1)–(3) leads to the following equations (we now set \( \omega = 4 \pi \) for a full sphere),

\[ \delta U = T \delta S - p_N(R) 4 \pi r^2 \delta R + \sum_i \mu_i^a \delta N_i^a \eta + \sum_j \mu_j^b \delta N_j^b \]
\[ + \sum \tilde{\mu}_j \delta N_j^\gamma + \int_0^R (\delta D 4 \pi r^2) Edr, \tag{7} \]
\[ U = TS - 4 \pi \int_0^R \rho_T r^2 dr + \sum_i \mu_i^a N_i^a \eta + \sum_j \mu_j^b N_j^b \]
\[ + \sum \tilde{\mu}_j N_j^\gamma + \int_0^R ED 4 \pi r^2 dr, \tag{8} \]
\[ S \delta T - 4 \pi (\int_0^r (\delta \rho_T) r^2 dr + p_N(R) 4 \pi r^2 \delta R + \sum_i N_i^a \delta \mu_i^a \]
\[ + \int_r^\infty (\delta E) D 4 \pi r^2 dr) = 0. \tag{9} \]

These equations refer to the whole conductor-dielectric system. However, since the quantities \( E \delta D \), \( E \delta D \) possess a local meaning, Eqs. (7)–(9) are applicable also to any spherical part of the system. By writing each equation for two values of \( R \left( r' \right. \) and \( r'' \) and subtracting one from the other, a corresponding equation for the bulk phase of the dielectric can be obtained. For a spherical layer of the bulk phase of the dielectric, we thus obtain equation

\[ S \delta T - 4 \pi \left( \int_{r'}^{r''} (\delta \rho_T) r^2 dr \right) + \sum_i N_i \delta \mu_i \]
\[ + \int_{r'}^{r''} (\delta E) D 4 \pi r^2 dr = 0, \tag{10} \]

where \( r' \) and \( r'' \) are kept fixed in the taking of variations. For a thin spherical layer we obtain

\[ \delta \rho_T = s_c dT + \sum_i \rho_i \delta \mu_i + D \delta E, \tag{11} \]

where \( s_c \) is the entropy density, and \( \rho_i \) is the number density of the component \( i \). The variation of \( R \) in Eq. (9) at a given physical state gives

\[ \rho_T - \rho_N = ED. \tag{12} \]

In the case of a homogeneous and isotropic dielectric we have a linear relationship \( D = \varepsilon \varepsilon_0 E \) and the integration of Eq. (11) at constant \( T \) and \( \mu_i \) gives

\[ \rho_T = p_0 + \frac{\varepsilon \varepsilon_0 E^2}{2} = p_0 + \frac{D^2}{2 \varepsilon \varepsilon_0}, \tag{13} \]

where \( p_0 \) is the pressure in the absence of electric field \( E = 0 \) at the same values of the temperature and chemical potentials; \( \varepsilon \) is the dielectric constant and \( \varepsilon_0 \) is the permittivity of vacuum. From Eqs. (12) and (13) it follows
\[ p_N - p_0 = \frac{\epsilon \epsilon_0 E^2}{2} - p_0 - \frac{D^2}{2 \epsilon \epsilon_0}. \quad (14) \]

### III. EXCESS QUANTITIES FOR AN INTERFACE

The system under consideration has four phases (the conductor \( \gamma \), the fluid phases \( \alpha \), \( \eta \), and \( \beta \)) and two interfaces. Between the phases \( \eta \) and \( \beta \), at the radius \( r'' \), an external field is applied that prevents free transfer between the phases. We use the Gibbs’ concept of a dividing surface for the interfaces and, also, for the region of an external field. The Gibbs dividing surface is a mathematical construct whose contour conforms to that of the physical transition zone within which the properties of one phase continuously change into those of the contiguous phase. The position of this dividing surface along the local normal to the physical contour can be chosen arbitrarily. Having made a choice, one treats the inhomogeneous system formally as though the various properties in the coexisting bulk phases remain the same as in the bulk phases up to the dividing surface. An accounting of the total amounts of the various extensive properties in the system, on this basis, will then be in error. For a given extensive quantity, the difference between the actual total amount and the “spurious” amount of the hypothetical system, where the bulk properties continue up to the dividing surface is defined as the surface excess. Properties of the bulk phases are chosen to coincide with the properties of the actual system off the transition zones of the interfaces. In our case, the temperature and the chemical potential values are well defined. Hence, even if the properties of the real system do not reach their bulk values off the transition zone, the properties of hypothetical bulk system are well defined.

#### A. Surface of tension and surface tension

Let us consider a quantity \( \int p_T dV \), where \( dV \) is the volume of a portion of a system that is under the tangential component \( p_T \) of the pressure tensor and integration extends over the whole volume of the system. Due to the electric field, the pressure is not uniform even in the bulk parts of the system. The quantity \( d \omega \int p_T dV \) is the work of deformation, when the size of a conical system (see Fig. 1) is increased by a solid angle \( d \omega \). Consider a layer containing the contiguous phases \( \alpha \) and \( \eta \) and the interface between them. Suppose that one spherical boundary of the radius \( r' \) of the layer lies in the phase \( \alpha \) and another boundary of the radius \( r'' \) lies in the phase \( \eta \), where these phases have bulk properties, i.e., the properties of bulk matter at the same temperature and chemical potentials of the components as the actual system has. The Gibbs dividing surface of the radius \( r_s \) is chosen to lie in the interface region. The surface excess for the quantity \( \int_{r''}^{r'} p_T \pi r^2 dr \) is prescribed by

\[
\int_{r''}^{r'} p_T \pi r^2 dr - \int_{r'}^{r_s} p_T^\alpha \pi r^2 dr - \int_{r_s}^{r''} p_T^\eta \pi r^2 dr = -4 \pi r_s^2 \gamma_s. \quad (15)
\]

Practically, the integration in Eq. (15) is made over the interfacial zone, where \( p_T \) substantially differs from the tangential components of the pressure tensor of the bulk phases, \( p_T^\alpha \) and \( p_T^\eta \). Equation (15) gives the one-to-one relationship between the radius of the dividing surface \( r_s \) and the quantity \( \gamma_s \), which is also called a surface tension. Following Rusanov, the form of this relationship can be obtained by differentiating Eq. (15) with respect to \( r_s \) and keeping the physical state of the system unchanged (this constancy is denoted by `).

\[
\left( \frac{d \gamma_s}{dr_s} \right)^* = -\frac{2 \gamma_s}{r_s} + p_T^\alpha(r_s) - p_T^\eta(r_s). \quad (16)
\]

According to Eqs. (5) and (13),

\[
p_T^\alpha(r_s) - p_T^\eta(r_s) = p_0^\alpha - p_0^\eta + \frac{q^2}{32 \pi^2 \epsilon_0 r_s^4} \left( \frac{1}{\epsilon^a} - \frac{1}{\epsilon^\eta} \right). \quad (17)
\]

Substitution of this equation into Eq. (16) and the solution of the resulting differential equation gives

\[
\gamma_s = \frac{K}{r_s^2} + \frac{1}{3} (p_0^\alpha - p_0^\eta) r_s - \frac{q^2}{32 \pi^2 \epsilon_0 r_s^4} \left( \frac{1}{\epsilon^a} - \frac{1}{\epsilon^\eta} \right), \quad (18)
\]

where \( K \) is the integration constant. The value of \( K \) is determined by the behavior of the tangential component of the pressure tensor \( p_T(r) \) in the transition zone. For a system consisting of two bulk fluid phases \( \alpha \) and \( \eta \) separated by a spherical membrane of the radius \( r_s \) with the uniform tension \( \gamma \) and zero thickness, the condition of mechanical equilibrium leads to the formula:

\[
p_0^\alpha - p_0^\eta = \frac{2 \gamma}{r_s}. \quad (19)
\]

Due to electric field, the pressures \( p_0^\alpha \) and \( p_0^\eta \) depend on the radius \( r \). Equations (18) and (19) determine uniquely the values of the radius \( r_s \) and the surface tension \( \gamma \). By a mechanical effect (by acting forces) the interfacial zone can be modeled as a membrane of the tension \( \gamma \) located at the radius \( r_s \). By Gibbs, the dividing surface with this radius \( r_s \) that satisfies Eq. (19) is called the surface of tension. The following relations connect the pressure difference \( p_0^\alpha - p_0^\eta \) and the integration constant \( K \) with the parameters of the surface of tension,

\[
p_0^\alpha - p_0^\eta = \frac{2 \gamma}{r_s} + \frac{q^2}{32 \pi^2 \epsilon_0 r_s^4} \left( \frac{1}{\epsilon^a} - \frac{1}{\epsilon^\eta} \right), \quad (20)
\]

\[
K = \frac{1}{3} \pi r_s^2 + \frac{q^2}{48 \pi^2 \epsilon_0 r_s^4} \left( \frac{1}{\epsilon^a} - \frac{1}{\epsilon^\eta} \right). \quad (21)
\]

In the absence of electric field the derivative with respect to the radius \( r_s \) at the left-hand side of Eq. (16) is zero at the surface of tension, i.e., the surface of tension and the respective surface tension correspond to the minimum point of the function \( \gamma_s(r_s) \) of Eq. (18). This is not the case for a charged droplet. Using Eq. (14), the Laplace equation (19) may be presented as
In the following, the surfaces of tension are chosen as the dividing surfaces for the interfaces between the phases of $\gamma$ and $\alpha$, and $\alpha$ and $\eta$. Rusanov and Kuni have presented a more detailed discussion of interface properties, also considering the dependencies of these properties on the size and charge of the critical nucleus. This discussion is also applicable to the interfaces between the phases of $\gamma$ and $\alpha$, and $\alpha$ and $\eta$. Between the phases $\eta$ and $\beta$, at the radius $r^{\eta\beta}$, an external field is applied that prevents free transfer of molecules between the phases. The external field acts the inward of the dividing surface of the radius $r^{\eta\beta}$ but, differently from Debenedetti and Reiss, does not reach the transition zone between the phases $\alpha$ and $\eta$. As the external field is supposed to prevent free transfer of molecules between the phases ($\gamma$ and $\beta$, $\eta$ is in equilibrium with $\alpha$), there should exist a region next to the radius $r^{\eta\beta}$ that the molecules cannot reach, i.e., where an energy barrier exists with energy values not attainable for molecules. By such an effect, this part of the field can be taken as “a rigid partition” standing at the radius $r^{\eta\beta}$. The volume of this region is considered negligible. If an external field acts only as “a rigid partition” with respect for gas phase, dielectric permittivity is close to unity.

Let us consider, for the purpose of illustration, the effect of external field more detailed, when the phases $\eta$ and $\beta$ behave as an ideal gas. It follows from the mechanical equilibrium that

$$\nabla \cdot \mathbf{P} = - \sum_i \rho_i \nabla \psi_i(r),$$

where $\mathbf{P}$ is the pressure tensor and $\psi_i(r)$ is the potential of an external field acting on a molecule of the $i$th component [Debenedetti and Reiss used the notation $\psi_i(f(r))$. In case of spherical symmetry Eq. (23) reduces to

$$\frac{dp_i}{dr} + \frac{2}{r} (p_i - p_T) = - \rho_i \frac{d}{dr} \psi_i(r).$$

We suppose that the phase $\eta$ remains gaseous in the region of an external field. Substituting Eqs. (13) and (14) (these equations remain valid also in the presence of an external field) into Eq. (24) we obtain

$$\sum_i \frac{dp_{0i}}{dr} + \frac{q^2}{2 \varepsilon_0 \varepsilon_r \varepsilon} \sum_i \frac{d\varepsilon}{dp_{0i}} \frac{dp_{0i}}{dr} = - \sum_i \rho_0 \frac{d}{dr} \psi_i(r),$$

where $p_{0i}$ is the partial pressure of the $i$th component in the absence of electric field at the same values of the temperature and chemical potentials. A change in the density of the phase $\eta$ due to electric field is proportional to the square of electric field strength and, therefore, should not be taken into account in the differentials of Eq. (25) as this will depart from the validity range of the used linear relationship $D = \varepsilon_0 \varepsilon_r \varepsilon E$. The densities in Eq. (25) are the densities that correspond to the absence of electric field. According to the Debye equation,

$$\frac{d\varepsilon}{dp_{0i}} = \alpha_i + \frac{p_{ci}^2}{3 \varepsilon_0 k_b T},$$

where $\alpha_i$ and $p_{ci}$ are the polarizability and the permanent dipole moment of the molecules of the $i$th component, respectively, and $k_b$ is the Boltzmann constant. Taking into account that for gas phase, dielectric permittivity is close to one, $\varepsilon = 1$, applying Eq. (25) separately for each component, and using the ideal gas law we obtain
\[ p_0(r) = p_{0yi} \exp \left( - \int_{r'}^r \frac{1}{k_B T} \frac{q^2}{2 \epsilon_0 \epsilon \rho^2} \left[ \alpha_i + \frac{p_i^2}{3 \epsilon_0 k_B T} \right] \right) \times \frac{d \psi_i(r)}{dr} dr, \]  

(27)

where \( p_{0yi} \) is the partial pressure of the \( i \)th component in the inner part of the phase \( \eta \) at the radius \( r' \) where the potential \( \psi_i(r') \) has a constant value, which is taken zero. For molecules with a permanent dipole moment, the Debye equation is valid for the interaction energies of electric field and a dipole smaller than thermal energy \( k_B T \). Accordingly, Eq. (27) is valid only at such radius values for which this condition is fulfilled. At these radius values, the term with the polarization \( \alpha \) and the permanent dipole moment \( p_{ei} \) can be omitted in the exponent of Eq. (27) compared with \( k_B T \), and Eq. (27) reduces to the barometric formula

\[ p_{0yi} \exp \left( - \psi_i(r)/k_B T \right) \]

The chemical potential of the \( i \)th component is given by the equation \( \mu_i = \mu_i^{\text{int}} + \psi_i(r) \) (Debenedetti and Reiss), where \( \mu_i^{\text{int}} \) is the intrinsic chemical potential in the region of an external field. Substituting Eq. (13), where the pressure \( p_0 = \Sigma \mu_{0i} \), into Eq. (15) gives an expression for the calculation of the excess quantity \( \gamma \) at the radius \( r_s = \tau^{\gamma \beta} \). Thus, various values for surface tension as an excess quantity of the dividing surface of the radius \( r^{\gamma \beta} \) can be obtained depending on an external field \( \psi_i(r) \) applied to constrain a noncritical cluster.

C. Surface polarization and the surface excess number of molecules

The excess surface polarization is related to the excess strength of an electric field. Consider the last term in Eq. (7). According to Eqs. (1), (4), and (6) this term was originally \( \varphi \delta q \). Its excess quantity, with taking Eq. (6) into account, is

\[ \delta q \int_{r'}^r (E - E^0) dr + \delta q \int_{r'}^r (E - E^0) dr, \]

(28)

where the integration is carried out over the whole thickness of the surface layer between the phases \( \alpha \) and \( \eta \). Applying the formulas of electrostatics \( D = \epsilon_0 E + P \) and \( D = D^\eta \), Eq. (28) can be represented as \( - \delta q \bar{P}/\epsilon_0 \), where

\[ \bar{P} = \int_{r'}^r (P - P^0) dr + \int_{r'}^r (P - P^0) dr. \]

(29)

The state of polarization depends on an external electric field. There is a possibility that a spontaneous polarization exists in the surface layer, which should be taken into account. Thus in the absence of electric field \( D^\alpha = D^\gamma = 0 \), \( P^\alpha = P^\gamma = 0 \), Eq. (29) reduces to

\[ \bar{P}_0 = \int_{r'}^r P_0 dr, \]

(30)

where \( P_0 \) is the spontaneous polarization. \( \bar{P}_0/\epsilon_0 \) is the electrical potential difference between adjacent phases across the interface [see Eqs. (28) and (29)]. Surface excess number of molecules is defined as

\[ \int_{r'}^r (\rho_i - \rho_i^0) 4 \pi r^2 dr + \int_{r'}^r (\rho_i - \rho_i^0) 4 \pi r^2 dr = \bar{N}_i^{\alpha \eta}, \]

(31)

where \( \rho \) and \( n \) denote the phases \( (m = \gamma, \alpha \) and \( n = \alpha, \eta) \). The total number of the \( i \)th component molecules in the phases \( \gamma \) and \( \beta \), \( N_i^{\alpha \eta} \) and \( N_i^{\alpha \gamma} \), respectively, are the known values. The number of molecules, \( \bar{N}_i^{\alpha \eta} \), in a hypothetical system where the bulk properties remain the same up to the dividing surfaces, can be calculated when the radiuses of the dividing surfaces are given. Taking this into account we rewrite the surface excess numbers \( \bar{N}_i^{\alpha \eta} \) for the interfaces between the phases \( \alpha \) and \( \gamma \), and between the phases \( \eta \) and \( \beta \), in another way

\[ \bar{N}_i^{\alpha \eta} = (\bar{N}_i^{\alpha \eta} - (N_i^{\alpha \eta} - N_i^{\alpha \gamma})) + (N_i^{\alpha \eta} - N_i^{\alpha \gamma}) = \bar{N}_i^{\alpha \eta} + \bar{N}_i^{\alpha \gamma}, \]

(32)

where two symbols on the right-hand side of Eq. (32) are introduced to denote the parenthesized terms in the middle of Eq. (32), respectively. For the interface between the phases \( \alpha \) and \( \eta \) such partition is not unique and not requisite.

D. Fundamental equations for a spherical interface

Introducing the excess quantities in the above way, we obtain from Eqs. (7) to (9) the fundamental equations for a spherical interface in the field of a central charge,

\[ \delta U^{\alpha \eta} = T \delta S^{\alpha \eta} + \gamma^{\alpha \eta} \delta A^{\alpha \eta}, \]

\[ \delta U^{\alpha \eta} = T \delta S^{\alpha \eta} + \gamma^{\alpha \eta} \delta A^{\alpha \eta} + \sum_i \mu_i^{\alpha \eta} \delta N_i^{\alpha \eta} - \frac{q \delta P}{\epsilon_0}, \]

(33)

\[ \delta S^{\alpha \eta} = \delta T + \delta A^{\alpha \eta} \delta \gamma^{\alpha \eta} + \sum_i \delta N_i^{\alpha \eta} \delta \mu_i^{\alpha \eta} + \sum_i \delta N_i^{\alpha \eta} \delta \mu_i^{\alpha \eta} - \frac{q \delta P}{\epsilon_0} = 0. \]

(35)

It is assumed that chemical potentials for all the species of the conductor are uniform throughout, i.e., the value of a chemical potential does not depend on the position of a molecule in the conductor. In case of the interface between the phases \( \alpha \) and \( \eta \) the term \( \delta N_i^{\alpha \eta} (\mu_i^{\alpha} = \mu_i^{\eta}) \) must be taken, as indicated by Eq. (32), as \( N_i^{\alpha \eta} \).

When the thickness of the layer of the phase \( \alpha \) is so small that the properties of the phase \( \alpha \) do not reach their bulk values, then the excess quantities for the two boundary surfaces of the phase \( \alpha \) cannot be uniquely separated and they should be considered as forming one united excess quantity.

IV. THE WORK OF FORMATION

Using the excess quantities introduced above, we can rewrite Eq. (8) for the internal energy of a noncritical cluster around a spherical charged conductor. We do this in portions. For the second term we obtain
where \( V^{mn} \) is the volume inside the surface of tension of \( r^{mn} (mn = \{ \gamma \alpha, \alpha \eta; n \beta \}) \), and \( V \) is the volume of the system.

The last term of Eq. (8) can be rewritten as

\[
\int_0^R \varepsilon_0^* \left( -\frac{q}{\varepsilon_0^*} - \frac{q^2}{8 \pi \varepsilon_0^*} \right) \left( \frac{1}{r^{\gamma \alpha}} - \frac{1}{r^{\alpha \eta}} \right) \frac{dE}{vd},
\]

\[
- \frac{q^2}{8 \pi \varepsilon_0^*} \left( \frac{1}{r^{\gamma \alpha}} - \frac{1}{r^{\alpha \eta}} \right)\left( \frac{1}{r^{\eta \beta}} - \frac{1}{R} \right).
\]

(38)

For a spherical charged conductor surrounded with the phase \( \beta \) of dielectric fluid Eq. (8) can be rewritten as

\[
U^\beta = TS^\beta - V^{\gamma \beta} p^{\gamma \beta} + \gamma^{\beta \gamma} a^{\gamma \beta} - p^0(\gamma V^{\gamma \beta})
\]

\[
+ \frac{q^2}{8 \pi \varepsilon_0^*} \left( \frac{1}{r^{\gamma \beta}} - \frac{1}{R} \right) - \sum_i \mu_i^{\beta \gamma} \frac{q^2}{8 \pi \varepsilon_0^*} \left( \frac{1}{r^{\gamma \beta}} - \frac{1}{R} \right).
\]

(39)

Let us derive the formula for the reversible work to form a noncritical cluster constrained to contain \( \{ N^{\alpha \eta}, i = 1,2,\ldots,n \} \) molecules. We consider a multicomponent system of radius \( R \) in which \( T \) and \( \{ \mu_i^{\beta \gamma}, i = 1,2,\ldots,n \} \) (hereafter the simplified notation \( \{ \mu_i^{\beta \gamma} \} \) is used) are kept constant. The temperature is uniform throughout the system. For this open boundary system (the system is closed with respect to the components of the conducting sphere), reversible work (we apply here the approach used by Nishioka and Kasaka, but the derivation by Debenedetti and Reiss can be applied as well) is given by a change of the following thermodynamic potential,

\[
\Lambda = U - TS - \sum_i \mu_i^{\beta \gamma} N_i.
\]

(40)

where \( V^{\gamma \alpha} \) is the volume of the conductor inside the surface of tension of \( r^{\gamma \alpha} \), \( p^{\gamma \alpha} \) is the isotropic pressure in the volume of the conductor, and \( A^{mn} = 4 \pi (r^{mn})^2 (mn = \{ \gamma \alpha, \alpha \eta; n \beta \}) \). Integration by parts, where Eqs. (11) and (13) and \( r^2 dr = d(r^3) \) are used, allows Eq. (36) to be expressed as

\[
-4 \pi \int_0^R \frac{p r^2 dr}{4 \pi r^2} = -V^{\gamma \alpha} p^{\gamma \alpha} + \gamma^{\gamma \alpha} A^{\gamma \alpha} - 4 \pi \int_r^{\gamma \alpha} p^a r^2 dr
\]

\[
+ \gamma^{\gamma \alpha} A^{\gamma \alpha} - 4 \pi \int_r^{\gamma \alpha} p^a r^2 dr
\]

\[
+ \gamma^{\gamma \alpha} A^{\gamma \alpha} - 4 \pi \int_r^{\gamma \alpha} p^a r^2 dr,
\]

(36)

where \( U, S, \{ N_i \} \) represent the values for the entire system (numbers \( \{ N_i \} \) do not contain values for the species of the conducting sphere).

Indicating values for the state of a homogeneous phase \( \beta \) containing a conducting charged sphere with superscript \( \beta \) we obtain from the above equation, where Eq. (39) is substituted that

\[
\Lambda^\beta = U^\beta - TS^\beta - \sum_i \mu_i^{\beta \gamma} N_i
\]

\[
= V^{\gamma \beta} p^{\gamma \beta} + \gamma^{\beta \gamma} a^{\beta \gamma} - p^0(\gamma V^{\gamma \beta})
\]

\[
+ \frac{q^2}{8 \pi \varepsilon_0^*} \left( \frac{1}{r^{\gamma \beta}} - \frac{1}{R} \right)
\]

\[
= \sum_j \mu_j^{\gamma \beta} N^\beta_j - \frac{q^2}{8 \pi \varepsilon_0^*} \left( \frac{1}{r^{\gamma \beta}} - \frac{1}{R} \right).
\]

(41)

For the state of the system, where a conducting sphere, covered with a two-phase layer of \( \{ N^{\alpha \eta}_i \} \) molecules (phases \( \alpha \) and \( \eta \) are in equilibrium), exists together with the phase \( \beta \), \( \Lambda \) can be obtained by substituting Eqs. (8), (37), and (38) into Eq. (40), resulting in

\[
\Lambda = \Gamma + \bar{A} + \bar{A} + \bar{A} + \bar{A} + \bar{A} + \bar{A} = \sum_i \mu_i^{\gamma \beta} N_i^{\alpha \eta}.
\]

(42)

where

\[
\Gamma = -V^{\gamma \alpha} p^{\gamma \alpha} + \sum_j \mu_j^{\gamma \alpha} N^\gamma_j
\]

(42a)

\[
\bar{\Gamma} = \gamma^{\gamma \alpha} A^{\gamma \alpha} + \sum_j \mu_j^{\gamma \alpha} N^\gamma_j + \sum_i \mu_i^{\gamma \alpha} N^\gamma_i + \frac{q^2}{8 \pi \varepsilon_0^*} \left( \frac{1}{r^{\gamma \alpha}} - \frac{1}{R} \right).
\]

(42b)
\[ A = -4\pi \int_{r_{\alpha}}^{r_{\beta}} \rho_{\alpha} r^2 dr + \sum_i \mu_i^{\alpha} N_i^{\alpha} + 4\pi \int_{r_{\alpha}}^{r_{\beta}} D E N r^2 dr \]
\[ = -p_0^{\alpha}(V_{\alpha}^\eta - V_{\gamma}^\eta) + \frac{q^2}{8\pi\varepsilon_0\varepsilon_\eta} \left( \frac{1}{r_{\alpha}} - \frac{1}{r_{\beta}} \right) + \sum_i \mu_i^{\alpha} N_i^{\alpha} \] (42c)
\[ \bar{A} = \gamma_0^{\alpha} A^{\alpha} + \sum_i \mu_i^{\alpha} N_i^{\alpha} - \frac{q \bar{P}^\eta}{\varepsilon_0}, \] (42d)
\[ H = -4\pi \int_{r_{\alpha}}^{r_{\beta}} p_{\alpha} r^2 dr + \sum_i \mu_i^{\alpha} N_i^{\alpha} + 4\pi \int_{r_{\alpha}}^{r_{\beta}} D E N r^2 dr \]
\[ = -p_0^{\eta}(V_{\beta}^\eta - V_{\alpha}^\eta) + \frac{q^2}{8\pi\varepsilon_0\varepsilon_\eta} \left( \frac{1}{r_{\alpha}} - \frac{1}{r_{\beta}} \right) + \sum_i \mu_i^{\beta} N_i^{\beta}. \] (42e)
\[ \bar{H} = \gamma_0^{\beta} A^{\beta} + \sum_i \mu_i^{\beta} N_i^{\beta} - \frac{q \bar{P}^\eta}{\varepsilon_0}, \] (42f)
\[ B = -4\pi \int_{r_{\alpha}}^{R} p_{\beta} r^2 dr + 4\pi \int_{r_{\alpha}}^{R} D E N r^2 dr \]
\[ = -p_0^{\eta}(V - V_{\beta}^\eta) + \frac{q^2}{8\pi\varepsilon_0\varepsilon_\eta} \left( \frac{1}{r_{\alpha}} - \frac{1}{R} \right), \] (42g)
\[ N_i^{\eta} = N_i^{\alpha} + N_i^{\beta} + \bar{N}_i^{\eta} + N_i^{\eta} + \bar{N}_i^{\eta}. \] (42h)

In Eqs. (42) capital letters indicate the bulk phases \( \gamma, \alpha, \eta, \) and \( \beta, \) respectively, and capital letters with bars indicate the interfaces between them.

Thus the reversible work \( W_{\text{rev}}^{\eta} \) to form a general-size cluster is given by
\[ W_{\text{rev}}^{\eta} = A - \Lambda^{\beta} \]
\[ = W_n - (p_0^{\alpha} - p_0^{\beta})(V_{\alpha}^\eta + \frac{1}{2}(\mu_i^{\alpha} - \mu_i^{\beta}))N_i^{\alpha} \]
\[ + \gamma_0^{\alpha} A^{\alpha} - \frac{q^2}{8\pi\varepsilon_0\varepsilon_\eta} \left( \frac{1}{r_{\alpha}} - \frac{1}{r_{\beta}} \right) \bar{P}^\eta \]
\[ - \frac{q \bar{P}^\eta}{\varepsilon_0} + (p_0^{\alpha} - p_0^{\beta})(V_{\beta}^\eta - V_{\alpha}^\eta) + \gamma_0^{\beta} A^{\beta} \]
\[ - \frac{q^2}{8\pi\varepsilon_0\varepsilon_\eta} \left( \frac{1}{r_{\alpha}} - \frac{1}{r_{\beta}} \right) \bar{P}^\beta \]
\[ - \frac{q \bar{P}^\beta}{\varepsilon_0} \] (43)

where we have used the notation,
\[ W_n = -V_{\gamma}^\eta p_{\gamma}^\eta + V_{\gamma}^\beta p_{\gamma}^\beta + \sum_j (\mu_j^{\gamma} - \mu_j^{\beta})N_j^\gamma \]
\[ + \gamma_0^{\gamma} A^{\gamma} - \gamma_0^{\gamma} A^{\gamma} - (p_0^{\gamma} V_{\gamma}^\eta - p_0^{\beta} V_{\gamma}^\eta) \]
\[ + \frac{q^2}{8\pi\varepsilon_0\varepsilon_\eta} \left( \frac{1}{r_{\gamma}^\eta} - \frac{1}{r_{\beta}^\gamma} \right) \bar{P}^\gamma \]
\[ - \frac{q \bar{P}^\gamma}{\varepsilon_0} + q \bar{P}^\beta \] (44)

Equations (5), (13), (14), and (19) have been used to transform the left-hand side of Eq. (44) into the right-hand side. Quantity \( W_n \) is the total work of the transfer of a charged particle from the phase \( \beta \) into the phase \( \alpha \) at the given temperature and chemical potentials in the phases \( \alpha \) and \( \beta. \) For example, if the particle is a single ion, the phase \( \alpha \) is a liquid, and the phase \( \beta \) is a gas, then \( W_n \) is the solvation work. The quantity is not associated with the nucleus of a new phase and can be measured in an independent experiment.

If the volume of the phase \( \alpha \) is remarkably larger than the volume of the interface, \( V_{\gamma}^\eta - V_{\gamma}^\alpha \gg V_{\gamma}^\beta - V_{\gamma}^\eta, \) and, therefore, we can take \( r_{\beta}^\gamma \approx r_{\gamma}^\beta, \) or say that the phase \( \alpha \) is a liquid phase and the phases \( \eta \) and \( \beta \) are the vapor phases [the difference in the number densities of molecules in the liquid and vapor phases is typically 3–4 orders of magnitude that allows to neglect the seventh and ninth terms on the right-hand side of Eq. (43)], then the above equation can be simplified,
\[ W_{\text{rev}}^{\eta} = W_n - (p_0^{\alpha} - p_0^{\beta})(V_{\gamma}^\eta - V_{\gamma}^\alpha) + \sum_i (\mu_i^{\alpha} - \mu_i^{\beta})N_i^{\alpha} \]
\[ + \gamma_0^{\alpha} A^{\alpha} + \frac{q^2}{8\pi\varepsilon_0\varepsilon_\eta} \left( \frac{1}{r_{\gamma}^\alpha} - \frac{1}{r_{\beta}^\gamma} \right) \bar{P}^\gamma \]
\[ - \frac{q \bar{P}^\gamma}{\varepsilon_0} - \frac{q \bar{P}^\beta}{\varepsilon_0} \] (45)

In the absence of a charged conductor \( (q = 0, W_n = 0) \) this equation reduces, as it should, to the equation by Nishioka and Kusaka\(^2\) and Debenedetti and Reiss.\(^3\) The result of Nishioka and Kusaka\(^2\) is obtained if a constraining external field acts as a rigid partition positioned in the homogeneous vapor phase just outside the cluster, and a liquid cluster in vapor is considered. In this case the term \( (p_0^{\gamma} - p_0^{\beta})(V_{\gamma}^\eta - V_{\gamma}^\alpha) \) in Eq. (43) is numerically negligible compared with other terms and \( \gamma_{\gamma}^{\eta} = 0. \) As long as \( \gamma_{\gamma}^{\eta} \gg \gamma_{\gamma}^{\beta}, \) \( P_{\gamma}^{\alpha} \gg \bar{P}^{\gamma} \) and the excess number of molecules for the diving surface of the radius \( r_{\gamma}^\alpha, \) \( |\bar{N}_i^{\eta}| \gg |\bar{N}_i^{\gamma}| + (p_0^{\gamma} - p_0^{\beta})(V_{\gamma}^\beta - V_{\gamma}^\eta), \) the effect of constraint on the properties of a noncritical cluster is not essential.

If the bulk phase \( \alpha \) is incompressible, then the integration of Eq. (11) at \( E = 0, \) the temperature, \( T, \) and the composition of the phase are kept invariant and thereafter the multiplication with \( V_{\gamma}^\eta - V_{\gamma}^\alpha \) gives
\[ (p_0^{\alpha} - p_0^{\beta})(V_{\gamma}^\eta - V_{\gamma}^\alpha) = \sum_i (\mu_i^{\alpha}(p_0^\alpha) - \mu_i^{\alpha}(p_0^\beta)), \] (46)
where \( N_i^{\alpha b} = (V_{\gamma}^\eta - V_{\gamma}^\alpha) \rho_i \) and \( \mu_i^{\alpha}(p_0^{\alpha} - p_0^{\beta}) \) is the chemical potential of the component \( i \) in the phase \( \alpha \) at the pressure \( p_0^{\alpha} \) in the absence of electric field, respectively. Substitution of this equation into Eq. (45) yields
where it is assumed that for a given constraint $\gamma^{\beta\eta}=0$ and $\bar{p}^{\beta\eta}=0$. This equation, if we ignore the second and, frequently also, the last term, is usually applied in papers on ion-induced nucleation in gas phase (Yue and Chan,5 Raes and Janssens,7 White and Kassner,15 to mention some).

V. THE CONDITION OF A CRITICAL NUCLEUS

The condition that a cluster formed be a critical nucleus is given by the extremity condition of Eq. (43) under constant values for $T$, $\{\mu^\beta_i\}$ and $V$. We keep fixed also the radius $r^{\eta\beta}$, denoting the position of the external field. Taking the differential of Eq. (43), it follows that

$$dW_{\text{rev.s}} = dG + d\Gamma + dA + d\bar{A} + dH + d\bar{H} - \sum_i \mu^\beta_i dN_i^{\eta\alpha} = 0.$$  

The differential $dH=0$ as the state of the phase $\beta$ is kept constant. We consider in detail the terms $dA$ and $d\bar{A}$. Other terms can be dealt with analogically. For the term $dA$ we obtain

$$dA = d\left[-4\pi \int_{r^{\gamma\alpha}} p_i^{\alpha} r^2 dr + \sum_i \mu^\alpha_i N_i^{\eta\alpha} + 4\pi \int_{r^{\gamma\alpha}} D E^\alpha r^2 dr\right]$$

$$= [-p_i^{\alpha}(r^{\gamma\alpha}) + qE^\alpha(r^{\gamma\alpha}) A^{\alpha\gamma} d r^{\alpha\gamma} + \mu^\alpha_i N_i^{\eta\alpha} + 4\pi \int_{r^{\gamma\alpha}} D (dE^\alpha) r^2 dr + \sum_i N_i^{\eta\alpha} d\mu_i^\alpha + 4\pi \int_{r^{\gamma\alpha}} D (dE^\alpha) r^2 dr].$$  

The last three terms of Eq. (51) vanish due to the Gibbs–Duhem relation, Eq. (10). Terms in square brackets, which are the collections of differentials of $A$ with respect to $r^{\alpha\eta}$ and $r^{\gamma\alpha}$, respectively, are the normal components of the pressure tensor. It follows that

$$d\bar{A} = \frac{2\gamma^{\alpha\gamma}}{r^{\alpha\gamma}} A^{\alpha\gamma} d r^{\alpha\gamma} + \sum_i \mu^\alpha_i d\bar{N}_i^{\eta\alpha} + A^{\alpha\gamma} d\gamma^{\alpha\gamma}$$

$$+ \sum_i \bar{N}_i^{\eta\alpha} d\mu_i^\alpha - \frac{q\bar{p}^{\alpha\eta}}{e_0}. \tag{52}$$

where the last three terms vanish because of the Gibbs–Duhem relation for the interface, Eq. (35). The first term on the right-hand side of Eq. (51) (in square brackets) together with the corresponding term of $dH$ and the first term of Eq. (52) vanish due to the Laplace Eq. (19). The application of the Gibbs–Duhem relations, Eqs. (10) and (35), and the Laplace equation to all terms in Eq. (50) gives

$$dW_{\text{rev.s}} = \sum_i \mu^\alpha_i (d\bar{N}_i^{\eta\alpha} + dN_i^{\eta\alpha} + d\bar{N}_i^{\eta\alpha} + dN_i^{\eta\alpha} + d\bar{N}_i^{\eta\alpha})$$

$$- \sum_i \mu^\beta_i dN_i^{\eta\eta} = 0. \tag{53}$$

It follows from Eq. (53) that the condition for a critical nucleus is

$$\mu^\alpha_i = \mu^\beta_i, \quad i = 1, 2, ..., n. \tag{54}$$

In nucleation literature the extremity conditions are usually taken with respect to the number of molecules $N_i^{\eta\alpha}$ in a cluster. Therefore, let us consider molecule numbers $\{N_i^{\eta\alpha}\}$.
as independent variables and show that the extremity conditions with respect to these variables result in Eq. (54). Thus the state of the system of a noncritical cluster in the phase $\beta$ are determined by variables $(T, \{N_i^\alpha\}, \{\mu_i^\alpha\})$. The state of the system containing a critical cluster does not depend on a path by which it is approached. By applying the extremity condition for simplicity to Eq. (49) [in the case of incompressibility of the phase $\beta$ the following reasoning gives the same result also for Eq. (43)] under $T, \{\mu_i^\beta\}, r^\gamma$ kept invariant, we obtain

$$
\frac{dW^{rev}}{dN_i^\alpha} = \sum_k (\mu_k^\alpha(p_0^\theta) - \mu_k^\beta) \frac{dN_k^\alpha}{dN_i^\alpha} + \sum_i N_i^\alpha d\mu_i^\alpha(p_0^\theta) \frac{dN_i^\alpha}{dN_i^\alpha} + \sum_k (\mu_k^\alpha(p_0^\theta) - \mu_k^\beta) \frac{d(N_i^\alpha - N_i^\beta)}{dN_i^\alpha} + \gamma^\alpha \frac{dA^\alpha}{dN_i^\alpha}
$$

$$+
\sum_k \frac{d\mu_k^\alpha(p_0^\theta)}{dN_i^\alpha} (N_i^\alpha - N_i^\beta) + \frac{d\gamma^\alpha}{dA^\alpha} \frac{q}{\epsilon_0} \frac{dA^\alpha}{dN_i^\alpha} q \frac{d\gamma^\alpha}{dA^\alpha} \frac{q}{\epsilon_0} \frac{dA^\alpha}{dN_i^\alpha} \frac{q^2}{8\pi\epsilon_0} \left( \frac{1}{\epsilon^\beta} - \frac{1}{\epsilon^\alpha} \right) \frac{1}{(r^\alpha)^2} \frac{dr^\alpha}{dN_i^\alpha} = 0.
$$

In Eq. (55) the fifth, sixth, and seventh terms vanish due to the Gibbs–Duhem Eq. (35). It is assumed that $N_i^\alpha \equiv N_i^\alpha + \tilde{N}_i^\alpha$. The second term cancels because of the Gibbs–Duhem equation for the bulk phase [Eq. (10), where $D=0$ and $\partial T = \partial \mu_i^\beta = 0$]. Next, we transform the Gibbs–Duhem Eq. (10) and then apply it to cancel the last term in Eq. (55). Expressing the pressure $p_r$ in Eqs. (10)–(13) and, thereafter, replacing $\partial \mu_i^\beta$ with $\Sigma \rho_i \partial \mu_i^\beta(p_0^\theta, q=0)$ [the result of Eq. (11), where $D=0$ and $\partial T = 0$] in the obtained expression, we get

$$-
\sum_i N_i^\alpha \frac{d\mu_i^\alpha(p_0^\theta, q=0)}{dN_i^\alpha} \frac{d\mu_i^\alpha}{dN_i^\alpha} q = 0 - \frac{q^2}{8\pi\epsilon_0} \left( \frac{1}{\epsilon^\beta} - \frac{1}{\epsilon^\alpha} \right)
$$

$$\times \delta\epsilon\alpha + \sum_k N_i^\alpha \frac{d\mu_i^\alpha(p_0^\theta, q=0)}{dN_i^\alpha} = 0.
$$

Hence, if to take $\delta\mu_i^\alpha(p_0^\theta, q=0) = \delta\mu_i^\alpha(p_0^\theta, q) \equiv \epsilon$ (the variation of chemical potentials is carried out so that their changed values remain the same throughout the bulk phase $\alpha$), then $\delta\epsilon\alpha = 0$ and the last term of Eq. (55) vanishes. The first term of Eq. (55) can be transformed as follows:

$$
\sum_k (\mu_k^\alpha(p_0^\theta) - \mu_k^\beta) \frac{dN_k^\alpha}{dN_i^\alpha} \frac{dN_k^\alpha}{dN_i^\alpha} = \sum_k (\mu_k^\alpha(p_0^\theta) - \mu_k^\beta) \frac{dN_k^\alpha}{dN_i^\alpha} \frac{dN_k^\alpha}{dN_i^\alpha} - \sum_k (\mu_k^\alpha(p_0^\theta) - \mu_k^\alpha(p_0^\theta)) \frac{dN_k^\alpha}{dN_i^\alpha} \frac{dN_k^\alpha}{dN_i^\alpha}.
$$

The second term on the right-hand side of Eq. (57) can be converted, according to Eq. (46), into $-(p_0^\alpha - p_0^\gamma) d(V_i^\alpha - V_i^\beta) dN_i^\alpha$. It follows from geometrical relations that $d(V_i^\alpha - V_i^\beta) dN_i^\alpha = 4\pi (r_i^\alpha)^2 dr_i^\alpha dN_i^\alpha$ and $dA_i^\alpha dN_i^\alpha = 8\pi r_i^\alpha dr_i^\alpha dN_i^\alpha$. Substitution of the first of these relations into Eq. (57) and then Eq. (57) into Eq. (55), in which the second geometrical relation is used in the fourth term, result in Eq. (54) because of the Laplace equation (19) [in the notation of Eq. (19) $\eta$ should be replaced by $\beta$].

Let us now express the chemical potential $\mu_i^\alpha(p_0^\alpha)$ of the component $i$ in the phase $\alpha$ in the field of a central charge at the pressure $p_0^\alpha$ far away from the charge and at the electrical field $q/(4\pi\epsilon_0 r^\alpha)$ through the chemical potential $\mu_i^\alpha(p_0^\alpha)$ of the same phase, but at the far away pressure $p_0^\beta$ and at the electrical field $q/(4\pi\epsilon_0 r^\beta)$, i.e., at the pressure and electrical field strength values of the phase $\beta$. In both cases the phase $\alpha$ is in equilibrium and the chemical potentials, $\mu_i^\alpha(p_0^\alpha)$ and $\mu_i^\alpha(p_0^\beta)$, do not depend on the radius $r$ from central charge.

Consider at first an incompressible bulk phase in a uniform electric field. Variation of Eq. (12) and substitution of it into Eq. (10), and then differentiation of Eq. (10) with respect to $N_i$, yield

$$
u_{i,e} \delta T - v_i \delta p_N + \delta \mu_i - v_i E \delta D = 0,
$$

where $v_i = (\partial V_{i,e}/\partial N_i)|_{T,D,p_N}$ is the partial volume per molecule of the component $i$, and $V$ is the volume of a system containing $\{N_i\}$ molecules. Let us consider a narrow spherical layer of the phase $\alpha$ at some radius $r$ from the central charge where the electric field can be considered uniform and integrate Eq. (58) with $\delta T = \delta D = 0$ from $p_0^\beta - q^2/(32\pi^2 e^\alpha \epsilon_0 r^\alpha)$ to $p_0^\alpha = q^2/(32\pi^2 e^\alpha \epsilon_0 r^\alpha)$ (normal components of pressure tensor). We obtain

$$\mu_i^\alpha(p_0^\alpha, D) - \mu_i^\alpha(p_0^\beta, D) = \mu_i^\alpha(p_0^\theta) - \mu_i^\alpha(p_0^\beta) q, r
$$

$$+ q^2/(32\pi^2 e^\alpha \epsilon_0 r^\alpha),
$$

where $q$ indicates the central electrical charge, $p_0^\alpha$ and $p_0^\beta$ are the pressure values far away from the charge $q$. While the value of the chemical potential $\mu_i^\alpha(p_0^\alpha)$ is the same for all
values of the radius from the charge (the phase \( \alpha \) around a charge at the far away pressure \( p_0^\beta \) is in the state of equilibrium), this is not so for the potential \( \mu_i^\gamma(p_0^\beta, q, r) \). The dependence of the latter on the radius is indicated in the list of parameters by symbol \( r \). If the values of the chemical potential \( \mu_i^\gamma(p_0^\beta, q, r) \) were the same everywhere then, according to Eq. (14), the value of the pressure component \( p_0^\beta \) at \( r \) should be \( p_0^\beta = q^2/(2\pi^2\varepsilon a_0 r^3) \) (if far away from the charge the pressure is \( p_0^\beta \)) but it is \( p_0^\beta = q^2/(2\pi^2\varepsilon a_0 r^3) \). The integration of Eq. (58) was done at \( D = \text{const} \). Therefore, in the phase \( \alpha \) at the pressure \( p_0^\beta \) the strength of electric field around a charged conductor differs from the strength of electric field around the conductor in the phase \( \beta \). To get the state of the phase \( \alpha \) where the pressure as well as the strength of electric field coincide with the corresponding quantities of the phase \( \beta \), and where the chemical potential values are the same everywhere in the phase \( \alpha \), we integrate Eq. (58) at constant pressure, temperature, and radius along electric charge from \( q \) to \( q \sqrt{\varepsilon /\varepsilon^0} \). The result is

\[
\mu_i^\alpha(p_0^\beta, q \sqrt{\varepsilon /\varepsilon^0}) - \mu_i^\gamma(p_0^\beta, q, r) = \frac{v_i q^2}{32\pi^2\varepsilon_0 r^4} \left( \frac{1}{\varepsilon^0} - \frac{1}{\varepsilon^a} \right). \tag{60}
\]

The value of the chemical potential \( \mu_i^\alpha(p_0^\beta, q \sqrt{\varepsilon /\varepsilon^0}) \) is the same for all values of the radius, and there is no need to indicate to the charge \( q \sqrt{\varepsilon /\varepsilon^0} \).

Using the Laplace equation (19) we can rewrite Eq. (59) for the radius \( \gamma^\alpha \eta \) in the form

\[
\mu_i^\alpha(p_0^\beta) - \mu_i^\alpha(p_0^\beta, q, r) = \frac{v_i q^2}{32\pi^2\varepsilon_0} \frac{1}{\gamma^\alpha \eta}. \tag{61}
\]

Subtracting Eq. (60) from Eq. (61), we obtain

\[
\mu_i^\alpha(p_0^\beta) - \mu_i^\gamma(p_0^\beta) = \frac{2v_i q^2}{32\pi^2\varepsilon_0} \gamma^\alpha \eta - \frac{q^2}{32\pi^2\varepsilon_0} \times \left( \frac{1}{\varepsilon^0} - \frac{1}{\varepsilon^a} \right) (\gamma^\alpha \eta)^4. \tag{62}
\]

where \( \mu_i^\alpha(p_0^\beta) \) are the chemical potentials with the same value for the whole phase \( \alpha \) with the pressure value \( p_0^\alpha \) at infinity (the indication of the central charge is not needed). Equation (62), where the potential \( \mu_i^\gamma(p_0^\beta) \) is taken equal to the potential in phase \( \beta \), \( \mu_i^\gamma(p_0^\beta) = \mu_i^\beta \), represents the set of equations that determine the composition and radius of a critical nucleus. For small values of \( \gamma^\alpha \eta \) and not very high suprasaturated vapor there are typically two values of the radius that satisfy the equation \( \mu_i^\gamma(p_0^\beta) = \mu_i^\beta \). The smaller value \( (r_1) \) corresponds to a metastable and the larger value \( (r_2) \) to an unstable (critical) cluster. Substitution of Eq. (62) into Eq. (49) yields the reversible work of a cluster, which is in (metastable or unstable) equilibrium with vapor,

\[
W_{\text{rev}} = \frac{\gamma^\alpha \eta a^\alpha \eta}{3} + \frac{q^2}{6\pi\varepsilon_0} \left( \frac{1}{\varepsilon^0} - \frac{1}{\varepsilon^a} \right) \frac{1}{r^\alpha \eta} - \frac{q^2 P^\alpha \eta}{8\pi\varepsilon_0} - \frac{q^2}{8\pi\varepsilon_0} \times \left( \frac{1}{\varepsilon^0} - \frac{1}{\varepsilon^a} \right) \left[ \frac{1}{r^\alpha \eta} + \frac{(\gamma^\alpha \eta)^3}{3(\gamma^\alpha \eta)^4} \right] + \frac{8\pi A}{3} \frac{(\gamma^\alpha \eta)^3}{\gamma^\alpha \eta}. \tag{63}
\]

The energy barrier for a nucleation process is given by \( AW = W_{\text{rev}}(r_2) - W_{\text{rev}}(r_1) \). The surface tension in Eqs. (62) and (63) depends on the electric charge of the nucleus. Rusanov and Kunh have discussed this dependence.

VI. CONCLUSIONS

A thermodynamically consistent formalism is applied to calculate the reversible work needed to form a small layer of a new phase (embryo) around a charged insoluble conducting sphere within a uniform macroscopic mother phase. To treat the embryos of an arbitrary size that are not the critical nuclei, a constraint in the form of an external field is introduced. The value of the work of the formation of a noncritical cluster depends on the constraint used. When a critical nucleus is of primary interest, the differences between the constrained clusters are not essential. All these constrained clusters give the same extremity conditions and the same value for the reversible work of a critical cluster. But the value of which constrained cluster should be applied, when we want, for instance, to estimate the evaporation rate of a noncritical cluster? In the classical nucleation theory the evaporation rate of various size clusters is estimated on the basis of equilibrium size distribution, which is proportional to \( \exp(-W_{\text{rev}}/k_B T) \). Applying the values of differently constrained clusters we obtain different values of evaporation rate for these clusters of the same size. The constraint states are not equivalent to each other and in this respect we agree with the conclusion of Kusaka that the resulting constrained equilibrium states for which the reversible work of formation are evaluated are relevant to nucleation if and only if the states approximate closely the ones that have actually been realized during nucleation.

For the vapor–liquid phase transition, taking into account the large density difference between vapor and liquid and the fact that the liquid properties are rather insensitive to the pressure, it is reasonable to assume that the evaporation rate of a noncritical cluster coincides with the evaporation rate of a critical cluster of the same size, i.e., it is reasonable to treat noncritical clusters as critical clusters of the same size. The latter case corresponds to a noncritical cluster constrained by an external field acting as a rigid partition positioned in the homogeneous vapor phase just outside the cluster and its interfacial transition zone. This external field does not influence the values of excess quantities. The term \( \Sigma_i(\mu_i^\alpha - \mu_i^\beta) N_i^\alpha/\eta \) in Eq. (45) can be interpreted as a reversible work that is needed to carry \( N_i^\alpha/\eta \) molecules of the gas phase \( \beta \) from a given state to a gas phase state, which is in equilibrium with a cluster of \( N_i^\beta/\eta \) molecules.

The new expression obtained in this paper for the work of embryo formation around a charged conducting sphere differs from the one commonly used in the nucleation litera-
ture; the expression reduces to the expression by Debenedetti and Reiss\cite{Debenedetti1998} and Nishioka and Kusaka\cite{Nishioka1992} for uncharged clusters. Its extrema conditions yield the correct conditions of equilibrium between the critical nucleus and the mother phase. The expressions, which are obtained in a thermodynamically consistent way, form a basis for practical calculations of the size and composition of a critical as well as a noncritical clusters on a charged core and their reversible work of formation.

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