Morphological instability of the dielectric Thomson nuclei

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The thermodynamic framework for the analysis of nucleation on charged ions was formulated by J. J. Thomson. It has proven itself a powerful tool for explaining the existing experimental data but it has never been tested in laboratory experiments. Our goal is to aid in potential experimental verification of Thomson's framework by considering the morphological stability of a more realistic nucleus—a dielectric. Thomson provided radial analysis and concluded stability. However, instability results when morphological variations are considered in the undersaturated conducting case. We extend Thomson's analysis and study the morphological stability of a dielectric nucleus. In the weakly supersaturated case, the larger of the two equilibrium spherical nuclei is radially unstable while the smaller one is radially and morphologically stable. In the undersaturated case, there exist spherical equilibrium nuclei that are radially stable (in agreement with Thomson's results) but morphologically unstable. This effect should yield itself to experimental verification.

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I. INTRODUCTION

The presence of electricity in heterogeneous systems gives rise to a plethora of fascinating effects such as various instabilities and formation of interfacial patterns. Many of these effects have been studied for well over a century. Theoretical efforts in this field resulted in a number of fundamental achievements, especially in the understanding of the energetic perspective on continuum systems with electromagnetic interaction.[1–4] The rapid discovery of new effects associated with electricity may be attributed to a number of factors including development of new materials and penetration of physics into the microscale and nanoscale levels.

Further technological progress requires new theoretical, experimental, and numerical methods. Transition to the nanoscale has lead to increased interest in many new problems including surface morphology of highly stressed thin solid films and formation of electric and magnetic domains. Similar questions arise in various applied problems such as growth of ordinary[5] and piezoelectric films and propagation of charged vacancies in crystals.[6] There is reason to believe that, with some adjustments, classical methods of thermodynamics will prove effective at the microscale and nanoscale. The problem of nucleation from vapor on charged nuclei is an important problem in colloidal chemistry and received a lot of attention in 1980s and 1990s. This class of problems has proven controversial from the modeling point view. Significant progress has been made recently (see Refs. 7 and 8 and references therein).

Problems of growth of piezoelectric and ferroelectric materials[9] raise new theoretical problems of thermodynamic equilibrium and stability in heterogeneous systems with phase transformations and electromagnetic interactions. Similar problems of equilibrium and stability appear in problems with solid phases.[10] Phase transformations under electromagnetic fields in systems with liquid phases were first explored by Thomson[11] and Leontovich.[12] Thomson's analysis found applications in numerous fields, including meteorology and the Wilson chamber.[13] Because of the growing number of applications, the classical results of Thomson need further attention. In one extension of Thomson's work,[14] his radial stability analysis of spherical conducting nuclei on ions was generalized to the question of overall morphological stability, with instability resulting in the undersaturated case.

Any significant advance in theoretical and numerical methods must be thoroughly verified experimentally since new predictions are often unexpected and counterintuitive. Further, new theoretical predictions are typically based on idealized models and their experimental verification may require close-to-ideal materials. Meanwhile, materials used in practical applications are complex multisystems. Phenomena that occur in those materials interact in complicated ways and may be impossible to study individually. While it may be productive to go down the path of more complicated and realistic models, it may be no less advantageous to pursue the same strategy in the experimental world: to start with the simplest and best understood materials and then gradually transition to those with more complicated structures. This approach would also require a partial revision and further advancement of the existing models which have been sufficient in explaining the results of the classical experiments. It is with this approach in mind that this work is undertaken, as we adopt as our starting point the classical experiments of J. J. Thomson and attempt to broaden his theory to include more complicated morphological effects.

This paper is concerned with the stability of a spherical liquid droplet formed on an electrically charged spherical inhomogeneity. The droplet, treated as a linear dielectric, carries zero net electric charge and is subject to evaporation. The droplet could be water (whose relative dielectric constant $\kappa \approx 80$), ink ($\kappa \approx 45$), or any other dielectric. The inhomogeneity could be a single ion whose net charge is equal to that of one or several electrons or a speck of dust whose charge density is roughly 10^{21} electrons/m^3.

J. J. Thomson was first to raise the question of stability. His analysis can be found in Ref. 11 and a textbook by Leontovich.[12] The variational method employed by Thomson can, in principle, be applied to the question of full three-dimensional stability. However, Thomson was only concerned with radial stability, a question to which he gave an

exhaustive answer. Had his radial analysis yielded instability, the question of *overall* instability would have been closed. This, for example, is the case for the larger of the two equilibrium nuclei in the weakly oversaturated case (relevant definitions to follow). However, Thomson concluded stability for the undersaturated droplet as well as for the smaller oversaturated droplet. Thus the essential question of overall three-dimensional stability remained unanswered. We generalize Thomson's analysis and address the question of morphological stability of the equilibrium nuclei.

Analysis of morphological stability is always quite challenging from the analytical point of view. It inevitably displays the highly nonlinear characteristics typical of problems with an unknown interface. The reader is referred to the famous lectures by Nozières[15] in which he considers one of the most elementary problems of this kind—equilibrium shape of a rigid crystal.

The analysis of the physical problem considered here has been a long-standing goal of ours. However, our prior attempts have fallen short. Our best attempt so far is summarized in Ref. 14 where a simplified version of this problem was analyzed. Namely, it contains a theoretical study of a *conducting* condensate and reaches the following conclusions: In the weakly supersaturated case, there are two equilibrium spherical nuclei. The larger one is radially unstable while the smaller one is radially and morphologically stable. In the strongly supersaturated case, there are no equilibrium spherical nuclei. In the undersaturated case, there is a single equilibrium spherical nucleus that is radially stable but *morphologically unstable*. The fact of morphological instability in the undersaturated case predicted in Ref. 14 leads us to believe that instability is also possible in the dielectric case.

From the analytical point of view, a dielectric medium is *fundamentally different* from a conductor. Electric polarization is a primary vector field while electrostatic potential is a field driven by the distribution of free charge. Furthermore, the dielectric case is of far greater practical importance than the conductor. Most substances in nature are more accurately described as dielectrics. It is often said that all materials, including conductors, display dielectric features. Therefore, the effects predicted here can be more readily observed in nature or demonstrated in experiments.

Thomson's original analysis was motivated by practical needs in meteorology and in the experimental search for the electron. Subsequently, Thomson's work found applications in registration of elementary particles, colloidal and physical chemistry, and other areas. The original analysis was essentially based on macroscopic thermodynamic ideas but was later applied to nanoscale objects and even elementary particles. It is well known that the problem of correct formula of ponderomotive forces in polarized media still remains one of the most debatable problems in leading theoretical and applied physics journals. Thus, the validity of Thomson's thermodynamic analysis should be tested, first and foremost, on macroscopic systems.

Maximizing the possibility of experimental verification is the overarching goal of this paper. That is the main reason why an analysis of a dielectric substance was undertaken. Any experiment designed to verify the results presented here would also be a test of Thomson's overall thermodynamic framework which is yet to be challenged in a laboratory setting. The morphological instability discussed in this paper may prove to be an ideal candidate for a macroscopic experiment. (Some nanoscale experiments, relying on mass spectrometry, have been carried out in the past.[16]) An experiment that successfully confirms the existence of this instability would put the overall theoretical framework on more solid ground. Then the question of specific practical applications would become truly interesting.

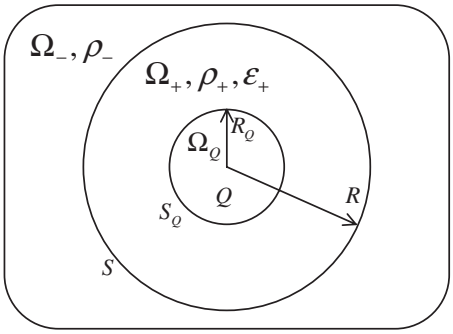

FIG. 1. Physical configuration and notation. Ω_Q is the charged particle, Ω_+ is the dielectric liquid phase of density ρ_+ and dielectric constant ε_+, and Ω_- is the electrically inert vapor phase of density ρ_-. The surface S is the phase interface and is at the center of our investigation.

Looking ahead, the results presented here are consistent with Thomson's radial analysis. However, it is shown in the undersaturated case that morphological instability is observed in a variety of scenarios. Further, a few interesting asymptotic modes are considered, including the conducting limit $\kappa \gg 1$. Finally, a system of equations for quasistatic evolution of the interface is presented. This system is useful for a variety of purposes, including discovering nonspherical stable equilibrium nuclei.

II. MODEL

Our full thermodynamic treatment of liquid-vapor equilibrium is based on the Gibbs variational approach. The thermodynamic theory of electricity is incorporated into the model. The reader is referred to the state-of-the-art references on the variational formulation of the laws of electricity.[1–4] We choose a model that can be found in Ref. 12 generalized to dielectrics. Figure 1 contains a diagram of the physical system. It is maintained at a fixed temperature that allows a heterogeneous equilibrium coexistence of two phases. The condensate is treated as a linear isotropic dielectric with the relative dielectric constant of κ, $\kappa > 1$. The gaseous phase and the vessel are electrically inert. The quantities $\rho_\pm$, $e_\pm$, and $V_\pm$ are mass densities, Helmholtz free-energy densities per unit mass, and total volumes of the two phases. Both phases are incompressible. We assume that the system is kept under fixed external pressure p^o.

The domain Ω_Q with boundary S_Q is occupied by a spherical charged particle of radius R_Q. The particle carries a uniformly distributed charge Q. The domain Ω_+ is occupied by the condensate and Ω_- is occupied by the gaseous phase.

The two phases are separated by the interface S.

Suppose that $\mathbf{P}$ is the polarization field inside the dielectric, $\varphi(z)$ is the potential field, $\mathbf{G}=-\nabla\varphi$ is the electric field, and $\mathbf{D}=\varepsilon_0 G+\mathbf{P}$ is the electric displacement, where ε_0 is the permittivity of free space. The electrostatic fields are governed by the following system: (i) within the phases

$$\nabla \cdot \mathbf{D} = 0, \tag{1a}$$

(ii) across the interfaces S and S_Q,

$$[\varphi] = [\mathbf{D}] \cdot \mathbf{N} = 0, \tag{1b}$$

where $[X]=X_+-X_-$ is the jump in the enclosed quantity across the interface and $\mathbf{N}$ is the outward normal.

Our approach is based on the minimization of energy. Let ε be the permittivity of the dielectric substance $(\kappa=\varepsilon/\varepsilon_0)$. The Gibbs free energy G of the system is the sum of the terms associated with each phenomenon—internal energy, pressure, electricity, and surface tension.

$$G = V_+\rho_+ e_+ + V_-\rho_- e_- + (V_+ + V_-)p^o + \int_{Space} \frac{\varepsilon G^2}{2} d\Omega + \sigma \int_S dS, \tag{2}$$

where σ is surface tension. Using the constant mass equation

$$\rho_- V_- + \rho_+ V_+ = M = \text{const}, \tag{3}$$

we can rewrite Eq. (2), dropping an immaterial constant,

$$G = V_+\rho_+(p^o - p^*)[\rho^{-1}] + \int_{Space} \frac{\varepsilon G^2}{2} d\Omega + \sigma \int_S dS, \tag{4}$$

where

$$p^* = -\frac{[e]}{[\rho^{-1}]} \tag{5}$$

is the saturation pressure in the absence of electricity.

In order to explore equilibrium configurations and their stability, we must calculate the first and second variations in the energy [Eq. (4)]. This general approach will allow us to explore the equilibrium of both spherical and nonspherical equilibrium nuclei and their stability with respect to arbitrary infinitesimal perturbations of the interface.

We treat the location of the interface S as an independent variation. Using the techniques of the calculus of moving surfaces,[17] it is straightforward to show that the first variation dG of the energy [Eq. (4)] is given by the surface integral

$$dG = -\int_S C\left\{N_i N_j [T^{ij}] + \sigma B^\alpha_\alpha + \frac{[\rho](p^o - p^*)}{\rho_-}\right\} dS, \tag{6}$$

where N_i are the covariant components of the outward normal $\mathbf{N}$, the quantity

$$T^{ij} = \frac{1}{2}\delta^{ij} E_k D^k - E^i D^j \tag{7}$$

is the Maxwell tensor of electrostatic stresses[1] and B^α_α (the trace of the curvature tensor B^α_β) is the mean curvature. Since we are free to choose arbitrary infinitesimal normal displacements C of the interface S, we conclude that equilibrium occurs when

$$N_i N_j [T^{ij}] + \sigma B^\alpha_\alpha + \frac{[\rho](p^o - p^*)}{\rho_-} = 0. \tag{8}$$

Equation (8), combined with Eqs. (1a) and (1b), governs the equilibrium of the system. In order to test whether a given configuration satisfies the equilibrium equations, the electrostatic system [Eqs. (1a) and (1b)] is solved first and then condition (8) is tested. The presented system has a nonlinearity caused by the presence of an unknown boundary. It is unclear whether the presented system can be solved analytically. It can, however, be solved numerically. Below we suggest an approach that can be employed in computing general equilibrium configurations. In order for the suggested method to work, such equilibrium configurations must be stable in the physical sense.

Spherical nuclei are one particular family of equilibrium configurations. For a spherical nucleus, the equilibrium [Eq. (8)] reduces to a one-dimensional algebraic equation for the equilibrium radius. All the elements in Eq. (6) are readily calculated. The mean curvature B^α_α is given by[18]

$$B^\alpha_\alpha = -\frac{2}{R}. \tag{9}$$

Since the unperturbed electrostatic potential is radial

$$\varphi(r) = \frac{Q}{4\pi\varepsilon_0}\begin{cases} \dfrac{1}{\kappa r} + \dfrac{1}{R}\left(1 - \dfrac{1}{\kappa}\right), & R_Q < r < R \\ \dfrac{1}{r}, & R < r \end{cases} \tag{10a}$$

and its derivative is given by

$$\varphi'(r) = \frac{Q}{4\pi\varepsilon_0}\begin{cases} -\dfrac{1}{\kappa r^2}, & R_Q < r < R \\ -\dfrac{1}{r^2}, & R < r, \end{cases} \tag{10b}$$

the "normal" components $N_i N_j T^{ij}$ of the Maxwell tensor [Eq. (7)] at the phase interface are given by

$$N_i N_j T^{ij} = \left(\frac{Q}{4\pi\varepsilon_0}\right)^2 \frac{1}{R^4}\begin{cases} -\dfrac{\varepsilon_0^2}{2\varepsilon} & r \to R \\ -\dfrac{\varepsilon_0}{2} & R \leftarrow r. \end{cases} \tag{11}$$

Therefore, the normal jump in the Maxwell tensor is

$$N_i N_j [T^{ij}] = \frac{Q^2(\varepsilon - \varepsilon_0)}{32\pi^2 \varepsilon \varepsilon_0 R^4}. \tag{12}$$

Substitute Eqs. (9) and (12) in the general equilibrium, Eq. (8). The result is a polynomial equation for the equilibrium radius R,

$$\frac{1}{16\pi^2\sigma\varepsilon_0}\frac{Q^2}{R^4}\left(\frac{\varepsilon-\varepsilon_0}{\varepsilon}\right)-\frac{4}{R}+\frac{2(p^o-p^*)[\rho]}{\sigma\rho_-}=0. \quad (13)$$

Equation (13) is nondimensionalized by introducing two length scales, R^* and R',

$$R'=\left[\frac{Q^2(\varepsilon-\varepsilon_0)}{16\pi^2\sigma\varepsilon_0\varepsilon}\right]^{1/3}, \quad (14a)$$

$$R^*=\frac{2\sigma\rho_-}{(p^o-p^*)[\rho]}. \quad (14b)$$

The positive quantity R' is characteristic of the relative magnitudes of the electric and surface energies. The quantity R^*, which can be positive as well as negative, does not have a direct physical interpretation. It represents the equilibrium radius of the critical nucleus in the absence of electric fields. Importantly, when electric fields are absent, the equilibrium picture is not just different—it is almost completely reversed. In the *oversaturated* case $p^o>p^*$ and $R^*>0$, there is an equilibrium nucleus of radius R^*. In the *undersaturated* case $p^o<p^*$ and $R^*<0$, there are no equilibrium nuclei where the liquid phase is inside the vapor phase.

Introduce dimensionless quantities y, u, and a,

$$y^{-1}=\frac{R}{R_Q}, \quad (15a)$$

$$u^{-1}=\frac{R'}{R_Q}, \quad (15b)$$

$$a^{-1}=\frac{R^*}{R_Q}. \quad (15c)$$

The sign of a coincides with that of R^* and indicates whether the system is oversaturated ($a>0$) or undersaturated ($a<0$). In terms of y, u, and a, the equilibrium condition (13) reads

$$y^4-4u^3y+4u^3a=0. \quad (16)$$

III. EQUILIBRIUM SPHERICAL CONFIGURATIONS

A graph of $f_{u,a}(y)=y^4-4u^3y+4u^3a$ is presented in Fig. 2 for several values of the parameter a. The system is oversaturated for positive a and undersaturated for negative a. Each positive root of $f_{u,a}(y)$ corresponds to an equilibrium spherical configuration. The larger the root, the smaller the equilibrium radius. For the borderline case of $a=0$, the curve passes through the origin. Therefore, in that case, there is a single equilibrium configuration. When the system is *slightly supersaturated*, $a<3u/4$, there are two distinct equilibrium radii. In the *strongly saturated* case, $a>3u/4$, no equilibrium nuclei exist.

In the *undersaturated case*, $a<0$, there is a single equilibrium radius. The undersaturated case is our primary focus. One can see from Fig. 2 that the equilibrium radius diminishes as the level of undersaturation increases. However, for any undersaturated configuration, the positive root of $f(y)$ is greater than $\sqrt[3]{4}u$. This relationship will play an important role in the stability analysis of undersaturated equilibrium configurations.

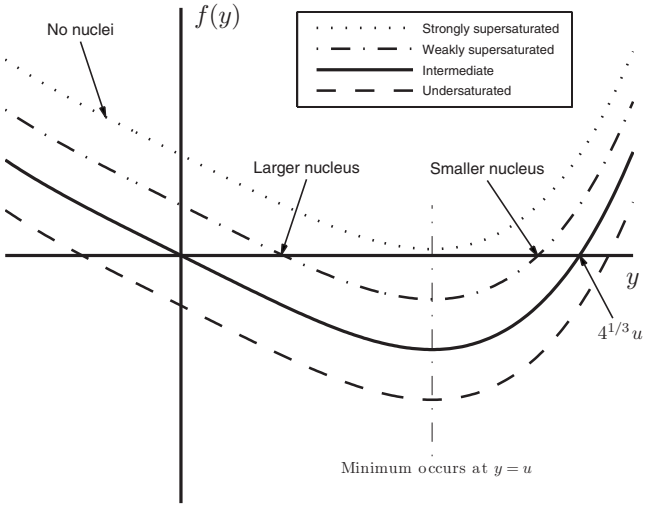

FIG. 2. Analysis of $f_{u,a}(y)=y^4-4u^3y+4u^3a$ as a function of y. The function $f_{u,a}(y)$ is the nondimensionalized first variation total energy and y is the nondimensionalized inverse radius. Therefore, a zero of $f_{u,a}(y)$ indicates an equilibrium configuration and a positive slope indicates radial stability.

IV. RADIAL STABILITY OF EQUILIBRIUM SPHERICAL CONFIGURATIONS

In the previous section we summarized all equilibrium spherical configurations. However, whether a particular equilibrium configuration can be observed in experiment is dictated by its stability properties. In this section we address the partial question of *radial* stability. The overall morphological stability is treated in the following section.

An equilibrium spherical configuration is radially stable when

$$\frac{d}{dy}f_{u,a}(y)>0. \quad (17)$$

Since $df_{u,a}(y)/dy=4y^3-4u^3$, this condition is equivalent to

$$y>u. \quad (18)$$

On the other hand, for undersaturated nuclei, $y>\sqrt[3]{4}u$, as derived in the previous section. Therefore, condition (18) always holds. Consequently, *all undersaturated equilibrium spherical nuclei are radially stable*.

For *slightly supersaturated* nuclei, the radial stability condition (18) holds for the larger root but not for the smaller root. Consequently, *in slightly supersaturated systems* ($a<3u/4$), the smaller equilibrium spherical nucleus is radially stable and the larger is radially unstable. (In the strongly supersaturated case, there are no equilibrium radial configurations.)

V. A NEED FOR FURTHER ANALYSIS

An equilibrium physical configuration is considered stable if it returns to its original state when subjected to an arbitrary

infinitesimal perturbation. Conversely, if there is even a single infinitesimal perturbation that results in the system moving away from its equilibrium, such configuration is considered unstable.

In our problem, the larger equilibrium nucleus in the slightly supersaturated case is radially unstable. It is, therefore, unstable in the overall sense. However, the smaller equilibrium nucleus in the slightly supersaturated case as well as the only equilibrium nucleus in the undersaturated case are radially stable. Therefore, the question of their overall stability remains open. We must investigate their stability with respect to general morphological perturbations of the interface S.

It is quite common for a physical system to be radially stable but morphologically unstable. In Ref. 14, a universal morphological *instability* was theoretically predicted in the undersaturated case, despite radial stability. In another spectacular example from low-temperature physics, an identical situation is observed for $2S$ and $3S$ electron bubbles.[19,20] These and numerous other examples show that the question of morphological stability is essential.

We would also like to note morphological stability is not necessarily the end of the story, either. The analysis presented in this paper is based on *smooth* variations. It is therefore possible that while an equilibrium configuration is stable with respect to smooth perturbations it is unstable with respect to perturbations with discontinuities either in the perturbation itself or higher derivatives.

VI. SECOND VARIATION

In order to investigate the morphological stability of the equilibrium configuration of the spherical nucleus we calculate the second energy variation with respect to arbitrary normal infinitesimal perturbations of the interface C. The second variation is derived by analyzing the first variation [Eq. (6)] using the techniques of the calculus of variations and moving surfaces. We first note several key identities from the calculus of moving surfaces. If F is three-dimensional field that its variation δF on the surface is related to its variation ∂F in space by the *chain rule*

$$\delta F = \partial F + CN^i \nabla_i F. \tag{19}$$

This relationship is used in the analysis of the electrical term in the first variation [Eq. (6)]. The variation δB^α_α of mean curvature is given by

$$\delta B^\alpha_\alpha = \Delta_S C + CB^\beta_\alpha B^\alpha_\beta, \tag{20}$$

where Δ_S is the surface Laplacian and $B^\beta_\alpha B^\alpha_\beta$ is known as the third ground form of a surface.[18]This relationship is required for the analysis of the surface-tension term in the first variation [Eq. (6)]. The variation $\delta \mathbf{N}$ of the normal vector is given by

$$\delta \mathbf{N} = -\nabla_S C, \tag{21}$$

where ∇_S is the surface gradient.

Let $\partial\varphi$ be the variation in the electrostatic potential φ induced by the infinitesimal normal deformation C of the boundary S. It requires a separate calculation outlined below. The second variation d^2G of the Gibbs free energy G in the vicinity of an equilibrium configuration is obtained by finding variations in each of the terms in the first variation [Eq. (6)]. The result is

$$d^2G = \int_S dSC \left\{ \begin{array}{c} 2N_i N^j [\varepsilon \nabla_j \partial\varphi \nabla^i \varphi] \\ + 2CN_i N^j N^k [\varepsilon \nabla^i \varphi \nabla_j \nabla_k \varphi] \\ - CN^k [\varepsilon \nabla_k \nabla_i \varphi \nabla^i \varphi] \\ - [\varepsilon \nabla_i \partial\varphi \nabla^i \varphi] \\ - \sigma(\Delta_S C + CB^\beta_\alpha B^\alpha_\beta) \end{array} \right\}. \tag{22}$$

This expression is valid for arbitrary equilibrium configurations. The discontinuity jump $[\varepsilon \nabla_i \partial\varphi \nabla^i \varphi]$ has the following interpretation:

$$[\varepsilon \nabla_i \partial\varphi \nabla^i \varphi] = \varepsilon (\nabla_i \partial\varphi \nabla^i \varphi)^+ - \varepsilon_0 (\nabla_i \partial\varphi \nabla^i \varphi)^-. \tag{23}$$

Decompose the displacement C of the interface in spherical harmonics $Y_{lm}(\theta,\alpha)$,

$$C = R_Q \sum_{l,m} C_{lm} Y_{lm}(\theta,\alpha). \tag{24}$$

The spherical harmonics are orthogonal and normalized to unity over the unit sphere,

$$\int_{|r|=1} |Y_{lm}(\theta,\alpha)|^2 dS = 1. \tag{25}$$

All of the ingredients in the integral [Eq. (22)] can be expressed in terms of C_{lm}. Recall that the trace of the third groundform is given by[18]

$$B^\beta_\alpha B^\alpha_\beta = \frac{2}{R^2}. \tag{26}$$

The spherical harmonics Y_{lm} are eigenfunctions of the surface Laplacian Δ_S, with corresponding eigenvalues $-l(l+1)$ on the unit sphere. Therefore, on the sphere of radius R, the eigenvalue is $-l(l+1)R^{-2}$ and the surface Laplacian of C is given by

$$\Delta_S C = -\frac{R_Q}{R^2} \sum_{l,m} l(l+1) C_{lm} Y_{lm}(\theta,\alpha). \tag{27}$$

The quantities $N_i N^j N^k [\varepsilon \nabla^i \varphi \nabla_j \nabla_k \varphi]$ and $N^k [\varepsilon \nabla_k \nabla_i \varphi \nabla^i \varphi]$ are obtained from the unperturbed potential φ,

$$N_i N^j N^k [\varepsilon \nabla^i \varphi \nabla_j \nabla_k \varphi] = \frac{y^5(1-\kappa)}{8\pi^2 \varepsilon_0} \frac{Q^2}{R_Q^5}, \tag{28a}$$

$$N^k [\varepsilon \nabla_k \nabla_i \varphi \nabla^i \varphi] = \frac{y^5(1-\kappa)}{8\pi^2 \varepsilon_0} \frac{Q^2}{R_Q^5}. \tag{28b}$$

The expression for the first-order perturbation $\partial\varphi$ of the electric field φ is obtained by solving a perturbation of the electrostatic system [Eqs. (1a) and (1b)]. The following system is valid for spherical configurations:

$$\nabla_i \nabla^i \partial\varphi = 0, \tag{29a}$$

$$[\partial\varphi] = C\frac{Q(\varepsilon-\varepsilon_0)}{4\pi\varepsilon_0\varepsilon R^2}, \tag{29b}$$

$$N^i[\varepsilon\nabla_i\,\partial\,\varphi] = 0. \tag{29c}$$

The solution is given by the harmonic series,

$$\partial\varphi(r,\theta,\alpha) = \frac{1}{4\pi\varepsilon_0}\frac{Q}{R_Q}\sum_{l,m} Z_l(r)Y_{lm}(\theta,\alpha), \tag{30}$$

where

$$Z_l(r) = \begin{cases} A_+\dfrac{r^l}{R_Q^l} + B_+\dfrac{r^{-l-1}}{R_Q^{-l-1}}, & \text{for } R_Q < r < R \\ B_-\dfrac{r^{-l-1}}{R_Q^{-l-1}}, & \text{for } R < r < \infty \end{cases} \tag{31}$$

and

$$A_+ = -y^{-(l-1)}\frac{C_{lm}}{\kappa D}(l+1)(\kappa l+\kappa+l)(\kappa-1), \tag{32a}$$

$$B_+ = -y^{-(l-1)}\frac{C_{lm}}{\kappa D}l(\kappa-1)^2(l+1), \tag{32b}$$

$$B_- = y^{-(l-1)}\frac{C_{lm}}{\kappa D}l\kappa(\kappa-1)\times\begin{pmatrix} -(\kappa-1)(l+1) \\ +y^{-(2l+1)}(\kappa l+\kappa+l)\end{pmatrix}, \tag{32c}$$

$$D = y^{-(2l+1)}(\kappa l+\kappa+l)(\kappa l+l+1)\cdots - l(\kappa-1)^2(l+1). \tag{32d}$$

The remaining terms in Eq. (22) can be found by differentiating Eq. (30) with respect to r and evaluating the result at the boundary.

We now substitute these expressions in the second variation [Eq. (22)] and obtain an expansion of d^2G in terms of C_{lm}. The result is a diagonal quadratic form in C_{lm},

$$d^2G = \frac{Q^2}{16\pi^2\varepsilon_0 R_Q}\sum_{l,m} A_{lm}|C_{lm}|^2, \tag{33}$$

where

$$A_{lm} = \frac{(l-1)(l+1)l(\kappa-1)^2y^{2l+1} - (\kappa l+\kappa+l)[(l-1)l\kappa-(l+1)(l+2)]}{-l(l+1)(\kappa-1)^2y^{2l+1} + (\kappa l+\kappa+l)(\kappa l+l+1)}y^3 + u^3(l-1)(l+2). \tag{34}$$

This expression leads to the criteria of overall morphological stability. In order for the system to be stable, all A_{lm} must be positive,

$$A_{lm} > 0. \tag{35}$$

This general criterion for morphological stability includes radial variations ($l=0$) and translational variations ($l=1$). The simplest variations that result in a change in shape take place when $l=2$. Greater l correspond to higher harmonics and represent more complex morphological perturbations. When testing for morphological stability, each term A_{lm} is evaluated at the equilibrium value of y determined by Eq. (15a).

Radial perturbations, $l=0$. A_{00} is given by

$$A_{00} = 2(y^3-u^3) \tag{36}$$

and leads to conclusions entirely consistent with Thomson's results and the radial analysis presented above. In the undersaturated case, y is always greater than u. Consequently, the sole equilibrium nucleus is radially stable. In the supersaturated case, the smaller nucleus ($y>u$) is radially stable while the larger ($y<u$) is radially unstable.

Translational perturbations, $l=1$. A_{1m} is given by

$$A_{1m} = \frac{6(2\kappa+1)y^3}{(2\kappa+1)(\kappa+2)-2(\kappa-1)^2y^3}. \tag{37}$$

We find that $A_{1m}>0$ for all combinations of parameters. Therefore, the equilibrium spherical nucleus is stable with respect to translation of the phase interface as a rigid body.

Lowest order morphological perturbations, $l=2$. A_{2m} is given by

$$A_{2m} = -\frac{6(\kappa-1)^2y^5-(3\kappa+2)(2\kappa-12)}{6(\kappa-1)^2y^5-(3\kappa+2)(2\kappa+3)}y^3 + 4u^3. \tag{38}$$

This expression leads to the conclusion that all equilibrium weakly supersaturated nuclei are morphologically stable. Therefore, Thomson's conclusion regarding radial stability of the smaller equilibrium nucleus is also valid for morphological perturbations. However, in the undersaturated case, *both stability and instability are possible depending on the combination of parameters*. This phenomenon is not revealed by Thomson's analysis. On the other hand, the possibility of stability in the undersaturated case represents a qualitative difference between a dielectric substance and a conductor. For example, for water ($\kappa=80$) the equilibrium is morphologically stable if $y>0.86$. The general recipe for determining stability is to compute u and a from the physical parameters of the system according to Eqs. (15b) and (15c). Then the equilibrium radius R represented by y can be determined by solving Eq. (16). Finally, the system can be tested against

the instability criterion $A_{2m}<0$. Furthermore, this recipe can be "inverted" to determine the values of the parameters required to observe an instability.

Higher order morphological perturbations, $l>2$. The stabilizing influence of surface tension grows with l. As a result, $A_{lm}>0$ for all combinations of parameters for $l>2$. This represents a marked contrast to Rayleigh's instability of an isolated liquid droplet,[21] where an electrical charge that is large enough is capable of destabilizing any given harmonic. In this behavior we observe the stabilizing influence of phase transformations.

We now investigate two asymptotic limits. First consider the conducting limit, $\kappa \gg 1$. The instability criterion [Eq. (35)] becomes $y^3u^{-3}>4$. This is equivalent to $y>4^{1/3}u$ which is synonymous with undersaturation, as illustrated in Fig. 2. This conducting limit leads to conclusions consistent with the analysis of a conducting substance in Ref. 14. This is an example in which treating a conductor as a limiting case of a dielectric results in a regular limit. The next asymptotic that we consider will not have this property.

Consider the mode in which the condensate covers the inhomogeneity with a thin crown characterized by y being nearly 1. This takes place when $u^{-3}=4(1-a)$. The instability criterion [Eq. (35)] for $l=2$ reads

$$\frac{2\kappa+3}{5\kappa}+2u^3<0, \tag{39}$$

indicating stability in all cases. In this, our system possesses an intriguing feature. Namely, the limits $\kappa \gg 1$ and $y \approx 1$ are not interchangeable. In this limiting behavior, a dielectric is *unlike* a conductor, which is always unstable in the undersaturated case. This example also shows that calculations performed for a "thin layer" mode must be accomplished with utmost care.

VII. QUASISTATIC EVOLUTION

We present an evolution law by which nonspherical equilibrium configurations can be discovered. It is apparent that nonspherical equilibrium configurations exist on nonspherical charged inhomogeneities. Furthermore, the possibility has not been ruled out that on a spherical inhomogeneity an unstable spherical nucleus will deform to a stable nonspherical configuration.

The master system of quasistatic evolution consists of the electrostatic system [Eqs. (1a) and (1b)] combined with this equation for C,

$$\frac{C}{d\tau}=N_iN_j[T^{ij}]+\sigma B^{\alpha}_{\alpha}+\frac{[\rho](p^o-p^*)}{\rho_-}, \tag{40}$$

where T^{ij} is the Maxwell tensor defined in Eq. (7). According to Eq. (6), this choice of C guarantees monotonic decrease in the energy. Note, we write $C/d\tau$ because heretofore we interpreted C as infinitesimal normal displacements while the right-hand side of Eq. (40) is meant to express the desired *rate* of normal deformation.

It follows immediately from Eq. (6) that the energy [Eq. (4)] is monotonically diminished by Eq. (40). This technique reveals stable equilibrium shapes by starting with an arbitrary configuration. Given a current configuration of the interface, one must determine the electrostatic fields by solving Eqs. (1a) and (1b) and then advance the interface along the outward normal according to Eq. (40). By iterating this procedure one can arrive at stable equilibrium shapes—if such shapes exist. So far we have been unable to discover such configurations numerically but we are not yet prepared to conclude that no stable equilibrium shapes exist and continue to refine our numerical techniques.

VIII. CONCLUSION

J. J. Thomson's radial stability analysis left open the question of morphological stability of dielectric nuclei. In this work, Thomson's approach is generalized to address this question. We concluded that in the weakly oversaturated case the smaller equilibrium nucleus is morphologically stable. (The radial instability of the larger nucleus was discovered by Thomson.) However, in the undersaturated case, morphological instability is possible under a variety of scenarios, such as a large charge Q or a high relative dielectric constant κ. The fact that stability is also possible in the undersaturated case represents a qualitative difference between a dielectric substance and a conductor, the latter being universally unstable in the undersaturated case. On the other hand, the fact that dielectric substances can also display the instability greatly expands the number of experiments that could verify Thomson's thermodynamic model.

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