

Morphological Instability of Liquid Metallic Nuclei Condensing on Charged Inhomogeneities

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We analyze the heterogeneous nucleation of liquid metallic phase from vapor on an electrically charged inhomogeneity. It is demonstrated theoretically that, regardless of magnitudes of surface tension of the phase interface and electric charge carried by the inhomogeneity, all spherical nuclei are necessarily unstable at all external pressures for which the system is undersaturated. In other words, small perturbations to the shape of the interface will cause it to move away from the equilibrium configuration. Our treatment of the problem is based on the continuum thermodynamic approach pioneered by Gibbs and Thomson.

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Rayleigh first predicted [1] that the shape of an isolated charged conducting drop is morphologically unstable if the electric charge is sufficiently great. The intuitive explanation for this effect is straightforward. The surface charges repel and are able to get farther away from each other by deforming the drop. To put it another way, the electrostatic energy of the system can be lowered by letting the drop deviate from spherical shape. Such deformation, however, is opposed by surface tension since the minimum surface energy is attained when the shape is spherical. The overall instability criterion reflects the balance between these forces. If R is the radius of the drop, Q is the net electric charge, and σ is the surface energy density of the boundary interface, then Rayleigh's criterion for morphological instability is

$$\frac{Q^2}{4\pi\sigma R^3} > 4.$$

For example, a drop of water of 1 mm in radius is unstable if it is charged to several volts.

Rayleigh's original study was picked up by many researchers including Tonks, Frenkel', Taylor, Melcher, Rosensweig, and others (see extensive lists of relevant references in [2] and [3]). Their research showed in general that, as in Rayleigh's original work, the presence of sufficiently large electrostatic or magnetostatic fields leads to the morphological destabilization of plane interfaces. This class of instabilities plays a role in the physics of vacuum discharges and in the operation of liquid metallic emitters of charged particles. These phenomena continue to be in a state of active research. One of the primary questions of interest is that of the equilibrium shape of destabilized interfaces [4]. From the mathematical point of view, such problems of equilibrium are challenging, deeply nonlinear problems with unknown boundaries, reminiscent of the classical problem of the equilibrium shape of a crystal [5].

In this Letter, we consider nucleation of a conducting liquid condensate on a charged inhomogeneity under

a given pressure. Although surface tension and electric charge play much the same role as in the problem considered by Rayleigh, we consider an additional phenomenon. Namely, we allow phase transformations to occur. Therefore, the total mass of the condensate is no longer fixed and Rayleigh's analysis is no longer applicable. Therefore, the problem needs to be reanalyzed.

The class of problems that simultaneously involve electric fields and phase transformations is a common one. For instance, morphological destabilization of a melting phase interface in ^3He under the action of a magnetostatic force is currently being researched (see [6,7], and references therein). Another problem of this sort, that of water vapor condensation on ions, is of importance in meteorology. This class of effects has been studied since the pioneering work by Thomson [8].

For the purpose of establishing a clear context for our study we present some classical results from the theory of heterogeneous nucleation, including those due to Thomson. Consider a heterogeneous liquid-vapor system at fixed absolute temperature T^* and let p^* be the equilibrium pressure for the two-phase configuration in the absence of surface tension and electric fields. In other words, p^* is the unique pressure at which the chemical potentials of both phases are equal. We say that the system that is under external pressure p^o is supersaturated (undersaturated) if $p^o > p^*$ ($p^o < p^*$). Now, taking the interface energy into account (but still leaving out the electric fields), the classical theory predicts that in the undersaturated case there exists no equilibrium two-phase configuration. In contrast, in the supersaturated case there exists an equilibrium spherical configuration of a certain radius R^* . R^* is known as the critical radius. This equilibrium configuration is always radially unstable. A nucleus of subcritical radius $R < R^*$ will evaporate, while a nucleus of supercritical radius $R > R^*$ will grow until all matter is transformed into liquid phase.

The presence of electric fields changes the picture considerably [8]. Thomson studied the equilibrium and radial

stability of the dielectric liquid drop condensing on ions and based his approach on varying the overall size of the spherical nuclei. This allowed him to calculate the radius of an equilibrium nucleus and its stability with respect to purely radial perturbations. This analysis yielded the following results: In the undersaturated case, an equilibrium radius always exists regardless of the values of other relevant parameters and, further, the equilibrium nucleus is radially stable. In the *weakly* oversaturated case, there are two equilibrium spherical configurations, one radially stable and one radially unstable. In the *strongly* oversaturated case no two-phase equilibrium configuration is possible. These results are not entirely surprising from the formal standpoint. In the context of Rayleigh's problem, in trying to come up with an unstable combination we can independently vary the size of the drop and the induced charge. Therefore, we can always find an unstable configuration by shrinking the drop while keeping the net charge constant. In contrast, in Thomson's problem the equilibrium radius is uniquely determined by the total present charge and whether or not some instability criterion analogous to Rayleigh's is satisfied is not at all clear.

It is of great interest, then, to consider a conducting liquid condensing on a charged particle. We consider the conditions necessary for the equilibrium of the system and, not surprisingly, obtain conclusions close to those due to Thomson regarding radial stability. We then consider the stability of equilibrium spherical configurations with respect to arbitrary perturbations of the equilibrium shape of the surface. We conclude that some of the equilibrium nuclei that are radially stable are, in fact, morphologically unstable.

The full thermodynamical treatment of the problem of equilibrium and stability of heterogeneous systems should be based on the Gibbs variational principles (see, for instance, [9]). We choose a simple model inspired by Leontovitch [10]. According to this model the system is maintained at a fixed temperature that allows a heterogeneous equilibrium coexistence of two phases. The liquid condensate is assumed to be a perfect conductor while the gaseous phase and the vessel are assumed to be insulating with dielectric constant 1. We use the notation (please refer to Fig. 1) ρ_{\pm} , e_{\pm} , and V_{\pm} to denote the mass densities, the free energy densities per unit mass, and the total volumes of the phases. Both phases are assumed incompressible. We assume that the system is kept under fixed external pressure p^o and that σ , the surface energy density of the liquid-vapor interface, is independent of the surface charge density.

The thermodynamic approach permits us to relax many of these assumptions. For instance, we can assume the gas to be dielectric. However, it is worth noting that for mercury (a prime candidate for the experimental verification of the effects announced here) the dielectric constant deviates from unity by less than 10^{-3} and so the assumption of zero polarization seems to be a safe one. Further, we

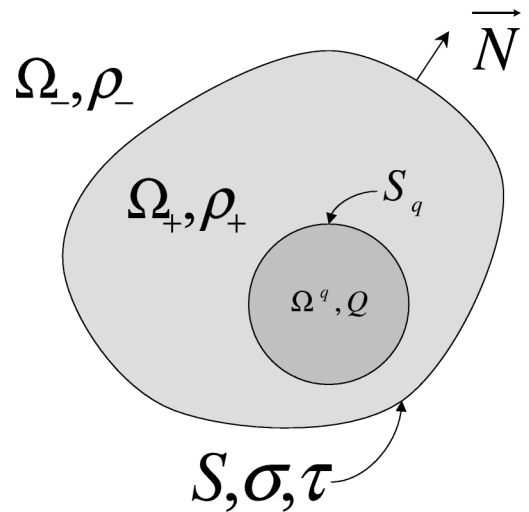


FIG. 1. Geometry of the problem. Ω_q , Ω_+ , and Ω_- are the domains occupied by the charged particle, the liquid phase, and the vapor phase, respectively. S_q and S are the charge-liquid and liquid-vapor interfaces. Q is the total charge carried by the particle and τ is the surface charge density distribution on S . ρ_+ and ρ_- are the densities of the liquid and the vapor phases. \vec{N} is the outward normal to the interfaces.

can assume that the surface energy density is a function of the surface charge density. Other assumptions, such as incompressibility, can be relaxed as well. Our thermodynamic approach will remain robust under the weaker assumptions. On the other hand, the obtained results will be more cumbersome and the claim of instability will lose some of its generality. We, therefore, leave out the treatment of the problem under relaxed assumption in order to make our main statement as clear as possible.

Let z be the spatial coordinates in the Eulerian description of continuum medium. We associate “+” with the liquid phase and “-” with the gaseous phase. Let Ω_+ (Ω_-) be the domain occupied by the liquid (vapor) phase and let S be the interface between the two phases. We assume that the unit normal \mathbf{N} is external to Ω_q at S_q and external to Ω_+ at S . Let the total charge Q be distributed over the surface S with nonuniform density τ . Let $\varphi(z)$ and $\mathbf{E}(z) = -\nabla\varphi(z)$ be the potential and the electric fields. They are governed by the following system:

(i) within the phases

$$\nabla \cdot \mathbf{E} = 0; \quad (1)$$

(ii) across the interface S

$$[\varphi]_{\pm}^{\pm} = 0, \quad (2)$$

$$[\mathbf{E}]_{\pm}^{\pm} \cdot \mathbf{N} = -4\pi\tau, \quad (3)$$

where $[a]_{\pm}^{\pm}$ denotes the jump in the enclosed quantity across the interface.

We base our approach on the minimization of the total energy as in [10]

$$\mathcal{E} = \left\{ \begin{array}{l} V_+ \rho_+ e_+ + V_- \rho_- e_- \\ + \int_{\text{space}} d\Omega \frac{1}{8\pi} E^2 + \sigma \int_S dS \\ + p^o (V_+ + V_-) \end{array} \right\}. \quad (4)$$

Introducing the equilibrium pressure $p^* = -(e_+ - e_-)/(\rho_+^{-1} - \rho_-^{-1})$ we can rewrite Eq. (4) to within an immaterial additive constant as

$$\mathcal{E} = \left\{ \begin{array}{l} V_+ \rho_+ (p^o - p^*) (\rho_+^{-1} - \rho_-^{-1}) \\ + \int_{\text{space}} d\Omega \frac{1}{8\pi} E^2 + \sigma \int_S dS \end{array} \right\}. \quad (5)$$

The stable equilibrium configuration corresponds to the minimum of the energy \mathcal{E} with respect to arbitrary variations of the interface S .

In order to explore equilibrium configuration of the system in question and its stability we have to calculate the first and the second variations of the total energy (5). Such a general approach allows us to explore both spherical and nonspherical equilibrium nuclei and their stability with respect to arbitrary infinitesimal perturbations of the interface. For the spherical nuclei the search for the equilibrium shape reduces to the calculation of the equilibrium radius R . Equating to zero the first variation of the total energy leads to the following equation for the equilibrium radius:

$$\frac{1}{R} - \frac{1}{16\pi} \frac{Q^2}{\sigma R^4} = \frac{(p^o - p^*)(\rho_+ - \rho_-)}{2\sigma\rho_-}. \quad (6)$$

Introduce the following quantities:

$$R' = \sqrt[3]{\frac{Q^2}{4\pi\sigma}}; \quad R^* = \frac{2\sigma\rho_-}{(p^o - p^*)(\rho_+ - \rho_-)}; \quad (7)$$

$$h \equiv R'/R; \quad b = R'/R^*.$$

Here, R' has the dimensions of length and characterizes the physical properties of the substances, while R^* is the aforementioned equilibrium radius of the critical nucleus in the absence of electric fields. In the oversaturated case ($p^o > p^*$), R^* is positive and is, therefore, endowed with the discussed physical meaning. In the undersaturated case ($p^o < p^*$), R^* is negative and, while deprived of physical meaning, is nevertheless useful below. The sign of the nondimensional parameter b indicates whether the system is oversaturated ($b > 0$) or undersaturated ($b < 0$). Finally, h is yet another dimensionless parameter characterizing the equilibrium radius of the nucleus. Using these parameters the equilibrium equation can be conveniently nondimensionalized as follows:

$$h^4 - 4h + 4b = 0. \quad (8)$$

It is easily observed that in the undersaturated case ($b < 0$) the positive root of the equation is greater than $\sqrt[3]{4}$.

In order to investigate the morphological stability of the equilibrium configuration of the spherical nucleus we need an expression for the second energy variation with respect

to arbitrary infinitesimal perturbations of the interface. It is given by the formula

$$\delta^2 \mathcal{E} = \int dS C \left(\begin{array}{l} \frac{1}{8\pi} \mathbf{N}[\nabla(E^2)]_+^+ C - \frac{1}{4\pi} (\delta \mathbf{E} \cdot \mathbf{E})^- \\ - \tau \kappa (\delta \phi)^+ - \sigma (\Delta_S C + \frac{2}{R} C) \end{array} \right) + \int dS \delta \tau (\delta \phi)^+, \quad (9)$$

where C is the small displacement of the interface in the direction of the unit normal \mathbf{N} , Δ_S represents the surface Laplacian [distinct from the spatial Laplacian Δ in the electrostatic system (1)–(3)], κ is the mean curvature, and $(\cdot)^+$ and $(\cdot)^-$ represent the limit values of the enclosed quantities as one approaches the surface either from the liquid phase (+) or from the gaseous phase (−). Finally, $\delta\tau$, $\delta\phi$, and $\delta\mathbf{E}$ are the small corrections to the surface charge density and the electric and potential fields.

We expand the displacement of the interface C in terms of the spherical harmonics:

$$C = \sum_{l=0, |m| < l} c_{l,m} Y_{l,m}(\phi, \theta).$$

A routine calculation leads to the following expression for the second variation in terms of the $c_{l,m}$:

$$\frac{\delta^2 \mathcal{E}}{\frac{Q^2}{4\pi R}} = \sum_{l=0, |m| < l} c_{l,m}^2 \frac{(l+2)(l-1)}{2l+1} \times \frac{(h^3 - l - 2)(h^3 + l - 1)}{h^6}. \quad (10)$$

Radial variations correspond to $l = 0$ in which case we have

$$\delta^2 \mathcal{E}_{0,0} = \frac{Q^2}{2\pi R} (1 - h^{-3})(2h^{-3} + 1)c_{0,0}^2,$$

which is seen to be strictly positive in the undersaturated case since $h^3 > 4$. Therefore, our configuration is radially stable in the undersaturated case. In the supersaturated case one of the equilibrium radii is seen to be stable while the other one is unstable (as one of the roots of $h^4 - 4h + 4b = 0$ is less than 1 and the other one is greater than 1). Translational variation corresponds to $l = 1$ and Eq. (10) indicates neutral translational stability since for $l = 1$, $\delta^2 \mathcal{E}_{1,0} = 0$. For the second spherical harmonic ($l = 2$) the second energy variation is

$$\begin{aligned} \delta^2 \mathcal{E}_{2,0} &= \frac{Q^2}{5\pi R} (h^{-3} + 1) \frac{4 - h^3}{h^3} c_{2,0}^2 \\ &= \frac{4Q^2}{5\pi R} (h^{-3} + 1) \frac{b}{h^4} c_{2,0}^2. \end{aligned} \quad (11)$$

Formula (11) leads to our central statement. We remind our readers that $b < 0$ in the undersaturated case and $b > 0$ in the supersaturated case. We conclude that the system is morphologically unstable ($\delta^2 \mathcal{E}_{2,0} < 0$) in the undersaturated state. According to Eq. (10), for any

given higher harmonic $l \geq 2$ the general criterion for instability reads

$$h^3 > l + 2. \quad (12)$$

In the undersaturated case, for sufficiently large values of $-b$ the equilibrium value of h is equal to $\sqrt[4]{-4b}$. Hence, according to the criterion (12), in the undersaturated case each harmonic can become unstable if the inhomogeneity carries a sufficiently large charge Q . This criterion for higher values of l is not as universal as the criterion for $l = 2$ which is always satisfied under the assumptions made. For a fixed charge Q , all sufficiently large harmonics are stable due to the morphologically stabilizing influence of surface tension.

In conclusion, the results presented here are rather general as they are not sensitive to the specific properties of the substance or the magnitude of the electric charge. The predicted phenomenon should yield itself to experimental verification. Further, numerical experiments based on the quasistatic approach described in [11] will indicate whether there exist nonspherical stable configurations and give us a glimpse of the patterns formed by the developing interfaces.

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