On well-posedness of variational models of charged drops

Cyrill B. Muratov* Matteo Novaga†

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Abstract

Electrified liquids are well known to be prone to a variety of interfacial instabilities that result in the onset of apparent interfacial singularities and liquid fragmentation. In the case of electrically conducting liquids, one of the basic models describing the equilibrium interfacial configurations and the onset of instability assumes the liquid to be equipotential and interprets those configurations as local minimizers of the energy consisting of the sum of the surface energy and the electrostatic energy. Here we show that, surprisingly, this classical geometric variational model is mathematically ill-posed irrespectively of the degree to which the liquid is electrified. Specifically, we demonstrate that an isolated spherical droplet is never a local minimizer, no matter how small is the total charge on the droplet, since the energy can always be lowered by a smooth, arbitrarily small distortion of the droplet's surface. This is in sharp contrast with the experimental observations that a critical amount of charge is needed in order to destabilize a spherical droplet. We discuss several possible regularization mechanisms for the considered free boundary problem and argue that well-posedness can be restored by the inclusion of the entropic effects resulting in finite screening of free charges.

Keywords: Coulomb fission, geometric variational problem, free boundary, ill-posedness, screening

1 Introduction

Electrospray is a technique commonly used to ionize large molecules in aqueous solution for the purposes of mass spectrometry [1]. Since the late 1980's, it has had a profound effect on the analytical chemistry of large biological molecules and won the 2002 Nobel Prize in Chemistry to J. B. Fenn [2]. The electrospray technique relies on the formation of a thin

*Department of Mathematical Sciences and Center for Applied Mathematics and Statistics, New Jersey Institute of Technology, Newark, NJ 07102

†Dipartimento di Matematica, Università di Pisa, Largo B. Pontecorvo 5, Pisa 56127, Italy

steady jet of an electrically conducting liquid upon application of a sufficiently high voltage to a capillary tip, as first observed by Zeleny [3]. As the voltage at the tip is increased, the liquid meniscus progressively distorts towards a conical shape, until at a critical voltage a "Taylor cone" is formed, emitting a thin liquid jet that quickly breaks into a fine mist of charged liquid droplets [4–6]. As the resulting droplets move through the ambient gas, the solvent slowly evaporates, pushing the droplets towards the so-called Rayleigh limit, corresponding to an instability of a conducting spherical drop with respect to arbitrarily small elongations [7]. Upon losing stability, the droplets undergo "Coulomb fission" by forming transient jets emitting tiny droplets that carry a small fraction of the parent droplet's mass, but a substantial fraction of its total charge [8–11]. This process repeats until the solvent in the daughter droplets is completely evaporated, and the remaining ions enter into the gas phase. Under certain conditions, direct evaporation of charged ionic species from the droplet is also possible [5, 6].

The onset of the phenomena described above has long been interpreted with the help of the basic variational model that treats the electrified liquid as a perfect conductor [4, 6, 7, 12, 13]. To describe the equilibrium configurations of a charged liquid droplet, one seeks local minimizers of the following geometric energy functional:

$$E(\Omega) = \sigma P(\Omega) + \frac{Q^2}{2C(\Omega)}, \qquad |\Omega| = V. \tag{1}$$

Here, $\Omega \subset \mathbb{R}^3$ is the spatial domain occupied by the liquid, $|\Omega|$ denotes the volume of Ω fixed to the value V, σ is the surface tension coefficient, Q is the total electric charge on the liquid droplet, $P(\Omega)$ is the perimeter of the set Ω understood in the sense of De Giorgi:

$$P(\Omega) = \sup\left\{ \int_\Omega \nabla \cdot \phi(y)\, dy : \ \phi \in C_c^1(\mathbb{R}^3; \mathbb{R}^3),\ |\phi| \le 1 \right\}, \tag{2}$$

which coincides with the surface area for regular sets [14], and $C(\Omega)$ is the electrical capacitance of Ω, which is defined as (using the SI units)

$$C^{-1}(\Omega) = \inf_{\mu(\Omega)=1} \int_\Omega \int_\Omega \frac{1}{4\pi\varepsilon_0 |x-y|}\, d\mu(x)\, d\mu(y), \tag{3}$$

where the infimum is taken over all non-negative Borel mesures ("charge densities") supported on Ω, and ε_0 is the permittivity of vacuum (assuming the ambient fluid has negligible dielectric response). Note that the infimum in (3) is attained whenever Ω is compact, with the minimizing measure concentrating on $\partial\Omega$ [15]. Also, $C(\Omega)$ can be equivalently expressed as [16]

$$C(\Omega) = \varepsilon_0 \inf_{\substack{u \in D^1(\mathbb{R}^3) \cap C(\mathbb{R}^3) \\ u \ge 1 \text{ in } \Omega}} \int_{\mathbb{R}^3} |\nabla u|^2 dx, \tag{4}$$

and the infimum is attained when Ω is a compact set with a sufficiently regular boundary.

The energy in (1) is the sum of the surface energy associated with the liquid-gas interface and the electrostatic self-energy of a conducting body occupying Ω and carrying charge Q. It has been widely assumed that this energy is locally minimized by a ball of volume $V = \frac{4}{3}\pi R^3$, as long as the charge Q does not exceed the critical charge Q_R given by

$$Q_R = 8\pi\sqrt{\varepsilon_0 \sigma R^3}. \tag{5}$$

This result was obtained in the celebrated 1882 paper of Lord Rayleigh, who performed a *linear stability* analysis of the spherical droplet with respect to small non-spherical perturbations [7]. Similarly, the Taylor cone at the onset of jet formation has been interpreted as a self-similar equilibrium solution of the Euler-Lagrange equation associated with the energy in (1), leading to the prediction of a unique opening half-angle of about 49.3° [4]. Recent experiments to determine the instability threshold for levitating charged drops confirm the onset of instability at the Rayleigh limit charge $Q = Q_R$ [17] (for earlier studies, see [18–20]), although lower threshold values of Q have also been reported in the literature [8, 9, 21–23]. The latter could be attributed to the presence of an unstable prolate spheroid equilibrium state bifurcating from the ball at the Rayleigh limit, which may serve as a transition state for the spherical droplet agitated by the motion of the surrounding gas or thermal noise [4, 12, 13, 17]. The agreement between the predicted Taylor cone angle with those observed in experiments has been found to be less satisfactory [6].

2 Ill-posedness of the variational model of a perfectly conducting liquid drop

The overall consistency of the classical model describing the equilibrium charged droplet configurations presented in the introduction has recently been put into question by the work of Goldman, Novaga and Ruffini, in which it was noted that, surprisingly, the energy in (1) admits *neither global nor local minimizers* in the natural admissible classes of sets [24]. Specifically, the following result was established for minimizers of the energy in (1) (in what follows, all the physical and material constants are assumed to be fixed, leaving V and Q as the only free parameters).

Theorem 1 ([24], Theorems 1.1 and 1.3)**.** *For every $V > 0$ and $Q > 0$, the following statements are true:*

(i) There is no global minimizer of the energy E defined in (1) *among sets of finite perimeter.*

(ii) The ball of volume V is not a local minimizer of E defined in (1) *with respect to perturbations that are arbitrarily close to it in Hausdorff distance.*

Recall that the Hausdorff distance d_H bewteen sets A and B is defined as

$$d_H(A,B) = \max\left\{\sup_{x\in A}\inf_{y\in B}|x-y|, \sup_{y\in B}\inf_{x\in A}|x-y|\right\}, \tag{6}$$

where $|\cdot|$ is the Euclidian distance, and measures the closeness of their boundaries.

Non-existence of global minimizers in Theorem 1 has to do with the fact that one can construct a minimizing sequence for the energy in (1) that consists of one big ball carrying no charge and many tiny balls carrying all the charge Q off to infinity. Furthermore, confining the support of the minimizing sequence to a ball of slightly bigger radius than that of the original spherical droplet, one can still produce a sequence of competitor sets whose energy is strictly lower than that of a single ball. These sets again consist of a single large uncharged ball and a cloud of tiny, but highly charged balls within an arbitrarily small distance from the original spherical droplet's surface (for details, see [24]). These observations put into serious question the validity of the conducting drop model.

An objection to the above criticisms of the classical model is that all the competitor configurations considered in [24] consist of disconnected sets. Thus, in order for such a competitor to be realized in a physical system, highly charged tiny droplets need to be detached from the surface of the parent droplet, leading effectively to *charge evaporation*. The latter has been the subject of many works by the modeling community (see, e.g., [5] and references therein), and the basic finding has been that the thermal activation barriers typically appear to be too high for such a process to be significant. In particular, within the continuum model governed by (1), barrier heights have been estimated using an ansatz-based approach, predicting the prohibitively high values in the range of several eV [25].

Nevertheless, in what follows we demonstrate that an assumption of connectedness does not invalidate the conclusions of Theorem 1. Namely, we show that there exist competitor sets that are *homeomorphic* to a ball and are arbitrarily close to it in Hausdorff distance that have strictly lower energy than that of a single spherical droplet. Thus, we establish that the spherical droplet with volume V is *nonlinearly unstable* for all values of $0 < Q < Q_R$, contrary to the prediction of the linear theory [7], even for local perturbations that smoothly distort a small portion of the boundary of the spherical droplet along the normal. We note that it implies that within the classical theory (which also ignores discreteness of charges) there is no energy barrier to evaporate a small highly charged droplet. This result also implies that, surprisingly, the variational problem governed by the energy in (1) is *ill-posed*, and thus the classical model of conducting drops presents the picture that is physically incomplete. Some regularizing physical mechanisms are needed at short length scales to make it a physically valid model.

Theorem 2. *For any $V > 0$ and $Q > 0$ there exists a smooth map $\phi_\delta : \mathbb{S}^2 \to (-\delta, \delta)$ such that if*

$$\Omega_{R,\delta} = \{x \in \mathbb{R}^3 \ : \ |x| \le R + \phi_\delta(x/|x|)\}, \tag{7}$$

then $|\Omega_{R,\delta}| = V$ *and* $E(\Omega_{R,\delta}) < E(B_R)$*, where* $R > 0$ *is such that* $V = \frac{4}{3}\pi R^3$*, for all* $\delta > 0$ *sufficiently small. Moreover, one can choose* $\operatorname{supp}\phi_\delta \subset B_{\delta/R}(\nu_0)$ *for some* $\nu_0 \in \mathbb{S}^2$*.*

Here B_R denotes the ball of radius R centered at the origin in $\mathbb{R}^3$ and $B_\delta(\nu_0)$ denotes a ball of radius δ centered at ν_0 on $\mathbb{S}^2$. The set $\Omega_{R,\delta}$ is the subgraph of the function $r = R + \phi_\delta(\nu)$ in spherical coordinates. The perturbation ϕ_δ is illustrated in Fig. 1(a) and has the form of a slender axially-symmetric protrusion from the sphere, with a small indentation around to conserve volume.

Proof. Let $\eta \in C^\infty(\mathbb{R})$ be a cutoff function such that $\eta'(t) \le 0$ for all $t \in \mathbb{R}$, $\eta(t) = 1$ for $t \le 1$ and $\eta(t) = 0$ for $t \ge 2$. We introduce

$$r = \delta e^{-R/\delta}, \qquad r' = (rR\delta^2)^{1/4}, \tag{8}$$

and note that $r \ll r' \ll \delta$ for $\delta \ll R$. We then define the function ϕ_δ in (7) as follows:

$$\phi_\delta(\nu) = \delta\eta\left(\frac{R|\nu-\nu_0|}{r}\right) - h\eta\left(\frac{2R|\nu-\nu_0|}{r'}\right)\left\{1 - \eta\left(\frac{2R|\nu-\nu_0|}{r'}\right)\right\}, \tag{9}$$

where ν_0 is some fixed point on $\mathbb{S}^2$ and $h \sim r^2\delta/r'^2$ is chosen so that $|\Omega_{R,\delta}| = V$ (here and in the rest of the proof the symbol "$\sim$" indicates asymptotic equivalence as $\delta \to 0$ up to a universal positive constant, term-wise for sums). The latter is always possible when $\delta \ll R$, and under this assumption we also have $h \ll r'$.

We next estimate from above the energy difference $\Delta E = E(\Omega_{R,\delta}) - E(B_R)$. In doing so, we can choose a suitable measure μ in the right-hand of (3). We take

$$d\mu = \frac{1}{4\pi R^2}\chi_{\partial B_R \setminus B_{r'}(R\nu_0)}dS + \frac{q}{Q|C_{r,\delta}|}\chi_{C_{r,\delta}}dx, \tag{10}$$

where χ_A denotes the characteristic function of the set A, dS stands for the surface measure concentrated on ∂B_R, $q = Qr'^2/(4R^2) \ll Q$ is the charge in the spherical cap of radius r' and $C_{r,\delta} = \{x \in \mathbb{R}^3 : R < |x| < R + \delta,\ x/|x| \in B_{r/R}(\nu_0)\} \subset \Omega_{R,\delta}$ is a truncated cone. Namely, we transfer the charge q contained in the spherical cap of radius r' and spread it uniformly into a set which for $\delta \ll R$ is essentially a straight cylinder of radius r and height δ above ∂B_R and below $\partial\Omega_{R,\delta}$. It is not difficult to see that with this configuration we have $\Delta E \le \Delta E_0$, where

$$\Delta E_0 \sim \sigma(r\delta + h^2) + \frac{q^2}{\varepsilon_0\delta}\ln\left(\frac{\delta}{r}\right) - \frac{qQ}{\varepsilon_0 R^2}\,\delta. \tag{11}$$

With our choices of r and r', (11) and (5) yield

$$\Delta E_0 \sim \frac{Q^2}{\varepsilon_0 R}\left\{\left(\frac{\delta Q_R^2}{RQ^2} + 1\right)\left(\frac{\delta}{R}\right)e^{-R/\delta} - \left(\frac{\delta}{R}\right)^{5/2} e^{-R/(2\delta)}\right\}. \tag{12}$$

Thus $\Delta E_0 < 0$ for all sufficiently small δ. □

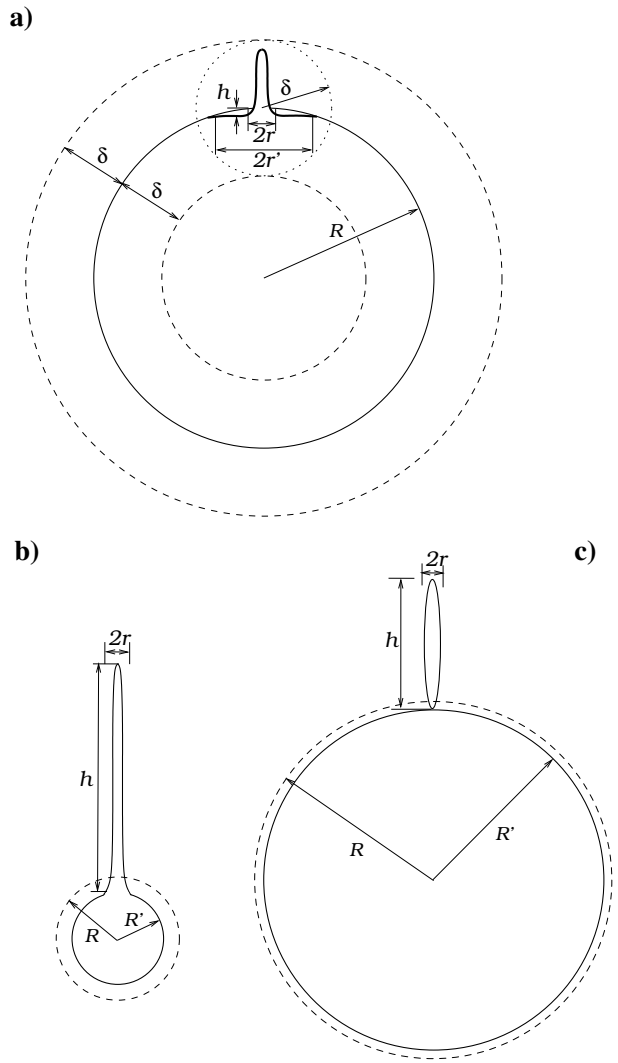

Figure 1: Different choices of perturbations of B_R that may lower the energy in (1): (a) a small smooth localized distortion of the interface; (b) a long tentacle; and (c) a prolate spheroid joined to a shrunk ball.

We also note that choosing a configuration $\Omega_{h,r}$ shown in Fig. 1(b), which consists of a smooth approximation to the union of a ball of radius R' and a long cylindrical "tentacle" of radius $r \ll R$ and height $h \gg R$, provided that $\frac{4}{3}\pi R'^3 = \frac{4}{3}\pi R^3 - \pi r^2 h$, one can see that by spreading the charge Q over the surface of the tentacle the energy of such a configuration can be made arbitrarily close to that of an uncharged ball. Indeed, for $r \ll h$ one can write

$$E(\Omega_{h,r}) \leq 4\pi\sigma R^2 + 2\pi\sigma r h + \frac{Q^2}{4\pi\varepsilon_0 h}\left\{\ln\left(\frac{2h}{r}\right) - 1\right\} + o(1), \tag{13}$$

where we used an asymptotic formula for the capacitance of a slender cylinder [26]. Therefore, optimizing this expression in r for fixed h, we get $r(h) = 8Q^2R^3/(Q_R^2 h^2)$ and

$$E(\Omega_{h,r(h)}) \leq E(B_R) - \frac{Q^2}{4\pi\varepsilon_0 h}\left\{\frac{h}{2R} - \ln\left(\frac{h^3 Q_R^2}{4R^3 Q^2}\right)\right\} + o(1). \tag{14}$$

One sees from these computations that for $Q < Q_R$ and $h \gtrsim R\ln(Q_R/Q)$ we once again have $E(\Omega_{h,r(h)}) < E(B_R)$ and, moreover, $\lim_{h\to\infty} E(\Omega_{h,r(h)}) = 4\pi\sigma R^2$. In particular, this implies that global minimizers of the energy in (1) do not exist among connected sets for any $Q > 0$.

Remark 1. *The proof of Theorem 2 can be easily extended to any compact set Ω with smooth boundary that is a critical point of the energy E.*

In other words, the ill-posedness of the variational problem associated with E is not related with the specific assumption of a spherical drop as the equilibrium configuration in Theorem 2. We note that well-posedness may be restored if one seeks minimizers in the class of sets with sufficiently smooth boundary (say, of class $C^{1,1}$). In particular, the ball is a local minimizer in the class of sets that satisfy the δ-ball condition (see [24, Definition 2.18]) for all $0 < Q < Q_c$, with Q_c depending on $\delta > 0$ [24, Theorem 1.4]. This is consistent with the linear stability result of Rayleigh [7]. Moreover, possibly decreasing the value of Q_c, one sees that the ball is also the unique global minimizer of E in this class [24, Theorem 1.7]. Still, the restriction on the regularity of the admissible sets appears to be rather artificial. In fact, as can be seen from Theorem 2, the value of Q_c in the above results must go to zero as $\delta \to 0$, which is the limit in which the regularity assumption on the admissible sets disappears.

Alternatively, existence of minimizers for E is restored in the class of *convex* sets [27]. Therefore, failure of existence must necessarily be associated with the competitor sets Ω that are concave somewhere. This is consistent with the behavior of the Taylor cone, as the liquid typically assumes a convex configuration prior to the formation of the cone [4,6], while convexity is broken by the formation of the liquid jet.

3 Well-posedness of the variational model with finite screening

It is appropriate to compare the results just obtained with those for another version of the energy in (1), namely, the *liquid drop model* of the atomic nucleus [28–30]. From the variational standpoint, this model is defined by the energy

$$E_0(\Omega) = \sigma P(\Omega) + \frac{Q^2}{8\pi\varepsilon_0 V^2} \int_\Omega \int_\Omega \frac{1}{|x-y|}\, dx\, dy, \qquad |\Omega| = V, \tag{15}$$

and can be obtained from (1) by fixing the measure μ in (3) to be the uniform probability measure over Ω (uniform charge distribution). For this model (upon rescaling), Knüpfer and Muratov [31] recently proved that minimizers of E_0 among sets of finite perimeter exist for all $0 < Q < Q_1$, while no minimizers exist for all $Q > Q_2 \geq Q_1$ (for non-existence, see also [32]). Moreover, global minimizers of E_0 are balls for all $0 < Q < Q_0$ for some $Q_0 \leq Q_1$, and it has been further conjectured that $Q_0 = Q_1 = Q_2$ [33]. Regardless of the validity of this conjecture, a ball of volume V is a local minimizer of the energy if and only if $0 < Q < Q_{c2}$, where Q_{c2} is the critical charge for the onset of fission [30, 34, 35].

Non-existence of minimizers for the energy in (15) has to do with the tendency of the minimizing sequences to become disconnected for large enough charge densities, with the connected components moving off to infinity away from each other to minimize their mutual Coulombic repulsion [36]. Existence of minimizers is restored for all $Q > 0$ when the set Ω is confined to a ball of sufficiently large radius [37]. In this sense the variational model associated with the energy in (15) is well-posed for all charges, in sharp contrast with the one in (1). Furthermore, minimizers of E_0 are regular, in the sense that the boundary of a minimizing set consists of at most finitely many smooth two-dimensional manifolds [31, 35, 37].

The difficulty with the variational problem associated with the energy in (1) has to do with the freedom in the choice of the measure μ (charge distribution) that likes to concentrate on the singularities of the boundary of Ω. In some sense, the measures allowed by boundedness of the Coulombic energy can be more singular than the measure associated with the essential boundary of a set of finite perimeter, leading to a kind of incompatibility between the two. In reality, several mechanisms may limit the ability of charges to concentrate on the liquid interface. In the following, we show that one such mechanism is provided by the finite screening length in the conducting liquid.

To proceed, we need to incorporate the entropic effects associated with the presence of free ions in the liquid. We start with the free energy of a dilute strong electrolyte

containing, for simplicity, only two monovalent ionic species [38, 39]:

$$F(\Omega, n_+, n_-) = \sigma P(\Omega) + \frac{\varepsilon_0}{2}\int_{\mathbb{R}^3} a_\Omega(x)|\nabla v|^2 dx \\ + k_B T \int_\Omega \left(n_+ \ln \frac{n_+}{n_0} + n_- \ln \frac{n_-}{n_0} \right) dx. \tag{16}$$

Here $a_\Omega(x) = 1 + (\varepsilon - 1)\chi_\Omega(x)$, where $\varepsilon \geq 1$ is the dielectric constant of the liquid and χ_Ω is the characteristic function of Ω, $k_B T$ is temperature in the energy units, n_+ and n_- are the number densities of the positive and negative ions, respectively, $n_0 = \frac{1}{2V}\int_\Omega (n_+ + n_-)\, dx$ is the average free ion density per species, v is the electrostatic potential solving

$$-\varepsilon_0 \nabla \cdot (a_\Omega(x)\nabla v) = \rho \qquad \text{in } \mathcal{D}'(\mathbb{R}^3), \tag{17}$$

where the charge density $\rho = e(n_+ - n_-)$ in Ω and zero outside Ω, and e is the elementary charge. We next assume that $|\rho| \ll e n_0$, i.e., that the deviations from the mean for each ionic component are small, and expand the entropy term in ρ, with $n_\pm \simeq n_0 \pm \frac{\rho}{2e}$. This yields a Debye-Hückel-type free energy

$$\mathcal{F}(\Omega, v) = \sigma P(\Omega) + \frac{\varepsilon_0}{2}\int_{\mathbb{R}^3} a_\Omega(x)|\nabla v|^2 dx + \frac{k_B T}{4e^2 n_0}\int_\Omega \rho^2\, dx, \tag{18}$$

where now ρ is assumed to be defined by v via (17).

Since we are interested in the local well-posedness of the variational problem governed by $\mathcal{F}$, we are further going to assume that the set Ω is confined to a spherical container B_R such that $|B_R| > V$, so that the possibility of connected components of Ω escaping to infinity is precluded. Under this assumption, we show that minimizers of the energy $\mathcal{F}$ exist for all values of $Q > 0$. More precisely, let us define an admissible class

$$\mathcal{A} = \left\{ (\Omega, v) :\ \Omega \subset B_R,\ |\Omega| = V,\ \int_\Omega \rho\, dx = Q,\ \rho = 0 \text{ in } \mathbb{R}^3 \backslash \Omega \right\}, \tag{19}$$

where $\Omega \subset \mathbb{R}^3$ is a set of finite perimeter and $v \in D^1(\mathbb{R}^3)$ is such that ρ defined by (17) belongs to $L^2(\mathbb{R}^3)$. Then we have the following result.

Theorem 3. *For any $V > 0$, $Q > 0$ and $R > 0$ such that $|B_R| > V$ there exists a minimizer of $\mathcal{F}$ in $\mathcal{A}$.*

Proof. We follow the approach of [40,41] developed for purely dielectric problems and apply the direct method of calculus of variations. We consider a minimizing sequence (Ω_n, v_n) for $\mathcal{F}$ in $\mathcal{A}$. By the energy bound, up to extracting a subsequence, there exist (Ω, v) such that $\chi_{\Omega_n} \rightharpoonup \chi_\Omega$ in $BV(\mathbb{R}^3)$ and $v_n \rightharpoonup v$ in $D^1(\mathbb{R}^3)$. Up to extracting a further subsequence, we have that the functions ρ_n defined by (17) with v replaced by v_n converge weakly in $L^2(\mathbb{R}^3)$ to a function ρ which also solves (17) with the limit function v.

By the semicontinuity of the perimeter [14] and Ioffe semicontinuity result [42], we get that

$$\mathcal{F}(\Omega, v) \leq \liminf_{n\to\infty} \mathcal{F}(\Omega_n, v_n) = \inf_{\mathcal{A}} \mathcal{F}. \tag{20}$$

It remains to prove that $(\Omega, v) \in \mathcal{A}$. The fact that $\Omega \subset B_R$ and $|\Omega| = V$ follows from the convergence of χ_{Ω_n} to χ_Ω in $L^1(\mathbb{R}^3)$. The conditions $\int_\Omega \rho\, dx = \int_{\mathbb{R}^3} \rho\chi_\Omega\, dx = Q$ and $\rho = 0$ on $\mathbb{R}^3\backslash\Omega$, which can be written as $\int \rho(1-\chi_\Omega)\phi\, dx = 0$, for any $\phi \in \mathcal{D}(\mathbb{R}^3)$, follows from the strong convergence of χ_{Ω_n} to χ_Ω in $L^2(\mathbb{R}^3)$ and the weak convergence of ρ_n to ρ in $L^2(\mathbb{R}^3)$. We thus proved that $(\Omega, v) \in \mathcal{A}$ and hence is a minimizer of $\mathcal{F}$. □

This result is again in sharp contrast with the one in Theorem 1. Further results concerning the minimizers of $\mathcal{F}$ such as the regularity of their interfaces and the shape and connectedness of minimizers are expected to follow. In particular, in the special case of $\varepsilon = 1$, i.e., when the dielectric polarizability of the liquid could be neglected (or in the case of a dielectrically matched ambient fluid), one should be able to proceed along the lines of the arguments in [31, 43] to establish smoothness of the minimizers, as well as the fact that the minimizers are balls for all $0 < Q < Q_c$, for some $Q_c > 0$ (even in the absence of confinement). For $Q > Q_c$ and the confinement radius R sufficiently large one would expect the minimizers to develop into a number of connected components of size not exceeding much the Debye radius $r_D = \sqrt{\varepsilon_0 \varepsilon k_B T/(2n_0 e^2)}$ (for a similar phenomenon in the absence of screening, see [36]). The reason for the latter is because for spherical droplets whose size is much greater than r_D the energy in (1) is a good approximation for the one in (18), which then implies that one could decrease $\mathcal{F}$ by splitting the droplet into many small ones and redistributing the charge, just like in the case of the energy in (1).

4 Discussion

To summarize, the classical variational model of a charged liquid drop that treats the liquid as a perfect conductor is mathematically ill-posed. Neither global, nor local minimizers exist for this model, with or without the presence of confinement. This is related to the fact that the energy of a smooth charged equipotential droplet can always be decreased by growing small, sharp protrusions that are highly charged. Thus, any amount of spatially uncorrelated noise should be enough to trigger the nonlinear instability identified by us.

We note that this nonlinear instability can be related to another, *linear* instability that has recently been demonstrated for thin insulating membranes separating two different electrolytes in an applied electric field [44]. There it was shown that at large enough applied voltages depending on the characteristics of the electrolytes the membrane undergoes a long-wave instability, which can be interpreted as a consequence of the effective membrane surface tension coefficient turning *negative*. Naturally, negative surface tension is a sign of ill-posedness of the model considered in [44] in the macroscopic limit. In our case,

the problem is even more singular, in the sense that the energy in (1) exhibits a *nonlinear* instability even for arbitrarily small values of charge (within the continuum approximation).

We now attempt to reconcile the differences between the models governed by the energies in (1) and (18), as expressed by Theorems 1 and 3, in connection with the behavior of real charged drops. To this end, we obtain a quantitative upper bound for the energy E of the configurations in the form of spherical droplets with long slender protrusions. To get an analytical handle on the energy, we assume that the protrusion has the shape of a prolate spheroid of radius r and height h that touches a ball of radius $R' = R\sqrt[3]{1 - hr^2/(2R^3)}$, which is chosen so as to conserve the volume, starting from a spherical droplet of radius R. See Fig. 1(c) for an illustration. Note that we do not make any assumptions on the values of r and h, as long as R' is positive. The upper bound for the energy in (1) is then obtained by assuming the equilibrium charge density (as in the definition of the capacitance) with total charge q on the surface of the spheroid and the uniform charge density with total charge $Q - q$ on the surface of the ball.

Denoting the set above by $\Omega_{h,r}$, we have

$$E(\Omega_{h,r}) \leq E_{\text{surf}} + E_{\text{ball}} + E_{\text{ell}} + E_{\text{int}}, \tag{21}$$

where E_{surf}, E_{ball}, E_{ell} and E_{int}, are the total surface energy, the electrostatic self-energy of the ball, the electrostatic self-energy of the spheroid and the electrostatic interaction energy between the ball and the spheroid, respectively. Because of our assumptions on the shapes, all but the last quantity above have closed form expressions (for the capacitance of the spheroid, see, e.g., [15], the other expressions are elementary):

$$E_{\text{surf}} = \pi\sigma \left(4R'^2 + 2r^2 + \frac{rh^2 \arcsin\sqrt{1 - \frac{4r^2}{h^2}}}{\sqrt{h^2 - 4r^2}} \right), \tag{22}$$

$$E_{\text{ball}} = \frac{(Q-q)^2}{8\pi\varepsilon_0 R'}, \tag{23}$$

$$E_{\text{ell}} = \frac{q^2 \ln\left[h\left(\sqrt{h^2 - 4r^2} + h\right)/(2r^2) - 1 \right]}{8\pi\varepsilon_0\sqrt{h^2 - 4r^2}}. \tag{24}$$

Furthermore, the interaction energy is easily seen to be estimated above as follows:

$$E_{\text{int}} \leq \frac{q(Q-q)}{8\pi\varepsilon_0} \left(\frac{1}{R'} + \frac{1}{R' + h} \right). \tag{25}$$

Note that for $h \ll R$ this expression gives an asymptotically sharp value for the interaction energy.

Given the values of r and h, we can minimize in q the expression obtained by adding up the right-hand sides of (22)–(25). The resulting cumbersome expression may then be evaluated for any r and h such that $2r < h < 2R^3/r^2$. In reality, we are interested in the

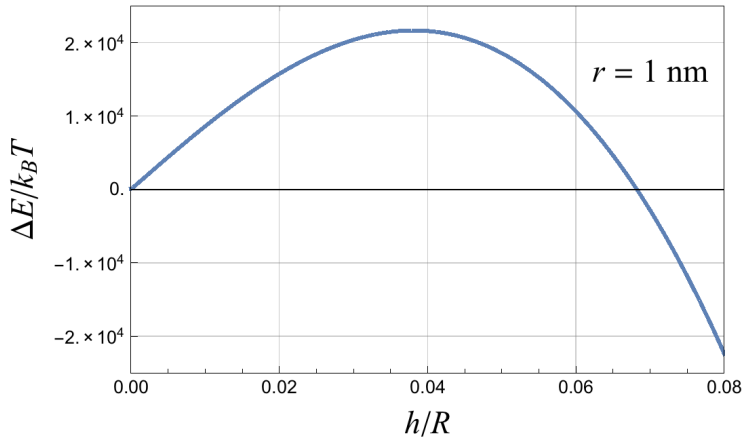

Figure 2: The dependence of $\Delta E(r,h)$ on h for $r = 1$ nm in the case of a spherical water drop at 20°C with radius $R = 10$ μm charged to $Q = \frac{1}{2}Q_R$.

regime when both r and h are much smaller than R. The difference between the obtained value and $E(B_R)$ is denoted as $\Delta E(r,h)$, with $\Delta E(r,h) > 0$ implying that the ball of radius R has lower energy and vice versa.

We computed $\Delta E(r,h)$ as a function of h for different choices of r in the case of water drops at 20°C of radius $R = 10$ μm (a typical value from the experiments) charged to 50% of the Rayleigh limit, i.e., for $\sigma = 0.073$ N/m and $Q = \frac{1}{2}Q_R$. We found that for r fixed and $r \lesssim h \lesssim R$, the value of $\Delta E(r,h)$ is initially an increasing function of h for small h, reaching a maximum at $h = h_{\max}$. After that, the value of $\Delta E(r,h)$ is a decreasing function of h and becomes negative at some $h = h_0 > h_{\max}$, indicating an instability. When the value of r is decreased, the value of $\Delta E(r, h_{\max})$ decreases as well. A natural short scale cutoff value for r is $r = r_D$, which indicates the length scale at which the assumption of the droplet being a perfect conductor is no longer justified. For large salt concentrations, the value of r_D goes down to $r_D \simeq 1$ nm, which is also comparable to interatomic distances. Substituting this value of r to the obtained expression, we obtain the dependence shown in Fig. 2.

From Fig. 2, one can see that the maximum value of $\Delta E(r_D,h)$ for $r_D = 1$ nm is of the order of $10^4 k_B T$ and is attained at $h = h_{\max} \simeq 0.4$ μm. The corresponding value of the charge in the protrusion is $q \simeq 130e$, so the continuum approximation is still reasonable. We interpret this value as the energy barrier that needs to be overcome in order for a long slender protrusion with radius of order r_D to be able to grow to decrease the energy of a spherical droplet. The value of ΔE found indicates that the barrier is prohibitively high, implying that thermal fluctuations would not be able to excite this mode of instability in a real system. In fact, even for methanol drops ($\sigma = 0.023$ N/m) or radius $R = 100$ nm we

find that the estimated barrier height ΔE is of the order of several hundred $k_B T$, making it prohibitively high even in this case. Thus, we believe that for finite screening length the nonlinear instability discovered by us requires the level of thermal activation that may not be readily available at room temperatures. Even if the estimate for the barrier height above only represents the upper bound for the actual barrier, we believe that the predicted order of magnitude for ΔE should adequately represent the actual barrier heights. Thus, our arguments suggest that in real systems the instability leading to the ill-posedness of the model governed by the energy in (1) is suppressed by the low levels of thermal noise. This might explain why the experimentally observed instability threshold for suspended charged drops typically coincides with the threshold of Rayleigh instability [8]. We note that a computation of the true energy barrier (within the continuum model considered) would require a detailed numerical study of the saddle points of the energy in (18) involving an optimization over the shape of the protrusion and is beyond the scope of the present study.

The conclusion above, however, needs to be taken with caution. What our estimates suggest is that the onset of the nonlinear instability of charged spherical drops is typically suppressed in a quiescent medium. At the same time, in reality the drops are agitated by the motion of the surrounding fluid and interactions with other drops, as well as interaction with charged electrodes. Surface agitation due to hydrodynamic effects may provide enhanced nonequilibrium fluctuations of the interface that under certain conditions could trigger our instability. Similarly, the presence of the external electric fields could modify the energy barrier to make the instability driven by thermal noise much more likely. Consider, for example, the case of a drop as in Fig. 2 placed in an external field with magnitude $|\mathbf{E}| = 3 \times 10^5$ V/m. Since this value is two orders of magnitude lower than the field generated by the drop itself, the drop shape and the charge distribution will be only slightly perturbed away from those for a perfect sphere. At the same time, the presence of the field lowers the value of the maximum of $\Delta E(r_D, h)$ by $\Delta E_{\text{ext}} \simeq -qR|\mathbf{E}|$ (to the leading order for small enough r_D and h). We find that for this magnitude of the external field the barrier height $\Delta E(r_D, h)$ decreases by a factor of 2. Further increase in the magnitude of $|\mathbf{E}|$ leads to a further decrease of the barrier (within the assumptions of our analysis), and the barrier height may decrease yet further in the presence of surface contaminants that are attracted to the region of charge concentration. Therefore, interactions with other drops, as well as interactions with charged electrodes, may be able to trigger our instability mechanism via thermal fluctuations at room temperature and, in particular, result in the onset of Coulombic fission below the Rayleigh limit [8,9,21–23]. This also strongly suggests a mechanism for the experimental observations in [45, 46], in which a long slender tentacle abruptly appeared as charged droplets passed a region with a strong electric field.

Before concluding, let us comment on several other possible mechanisms that could regularize the variational problem for the energy in (1). One natural candidate for such a mechanism is discreteness of charges. It provides a short-scale cutoff equal to the average distance between the individual ions. The importance of point charges for the process

of Coulombic fission during electrospray was pointed out in [47] and further quantified in [48]. We note that in the case of a very different electrified liquid, namely, liquid helium, charges are known to be able to form a Wigner crystal on the liquid-gas interface [49, 50]. Yet another possible mechanism may involve stabilization of the interfaces due to the effective bending rigidity supplied by the charged boundary layer, as discussed in [44].

Finally, we note that the ill-posedness of the variational problem associated with (1) raises some questions about the validity of various numerical studies of the onset of Rayleigh instability and the formation of Taylor cones that treat the electrified liquid as a conductor (see, e.g., [12, 51–54]). The numerical discretization naturally provides a short-scale cutoff, which is unrelated to the one in the actual physical system. Because of the underlying ill-posedness, however, one could expect failure of convergence when resolving interfacial singularities as the numerical grid is refined. Therefore, in view of our results the predictions of such numerical studies may need to be taken with caution.

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Ethics statement

This research does not contain human or animal subjects.

Data accessibility

This paper does not have any supporting data.

Competing interests

We have no competing interests.

Authors' contributions

Both authors contributed equally in formulating, carrying out and writing up the resutls of this research. The final version has been approved by both authors for publication.

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