The mathematics of charged liquid drops

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1917- 2017: A centennial year

John Zeleny (1872–1951)

AIP Emilio Segrè Visual Archives

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THE

PHYSICAL REVIEW.

INSTABILITY OF ELECTRIFIED LIQUID SURFACES.

BY JOHN ZELENY.

IN a recent paper[1] a brief description was given of the appearance of a liquid surface undergoing disintegration owing to instability arising from an electric charge.

[1] Proc. Camb. Philos. Soc., 18, p. 71, 1915.

Instability of an electrified liquid surface

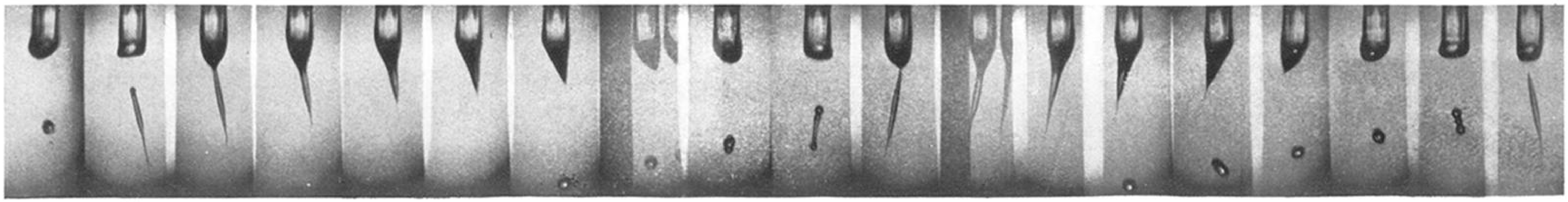

FIG. 1.

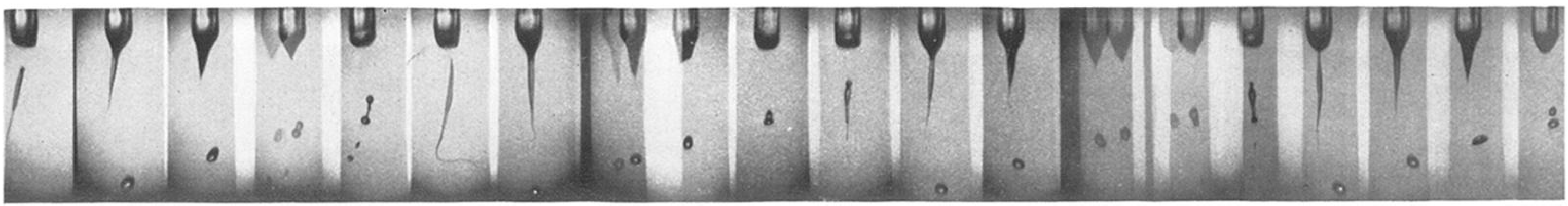

FIG. 2.

motivated by the analysis of Lord Rayleigh:
an isolated charged spherical drop
becomes **unstable**, when $Q > Q_R$:

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

Lord Rayleigh, *Phil. Mag.* **14**, 184-186 (1882)

FIG. 3.

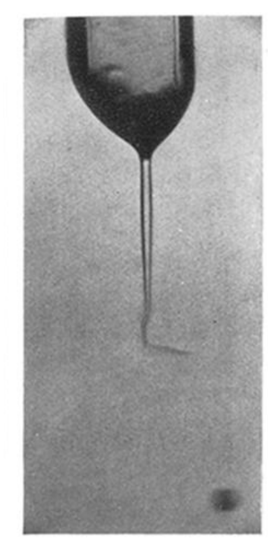

FIG. 4.

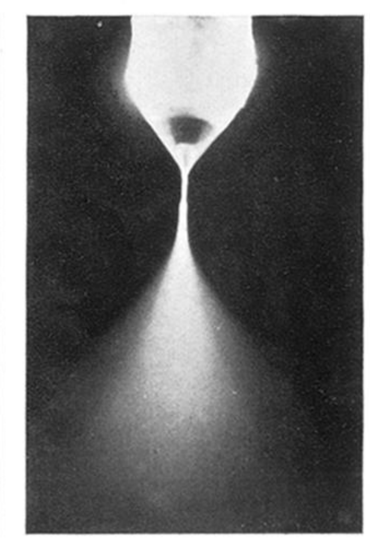

FIG. 5.

J. Zeleny, *Phys. Rev*. **10**, 1-6 (1917)

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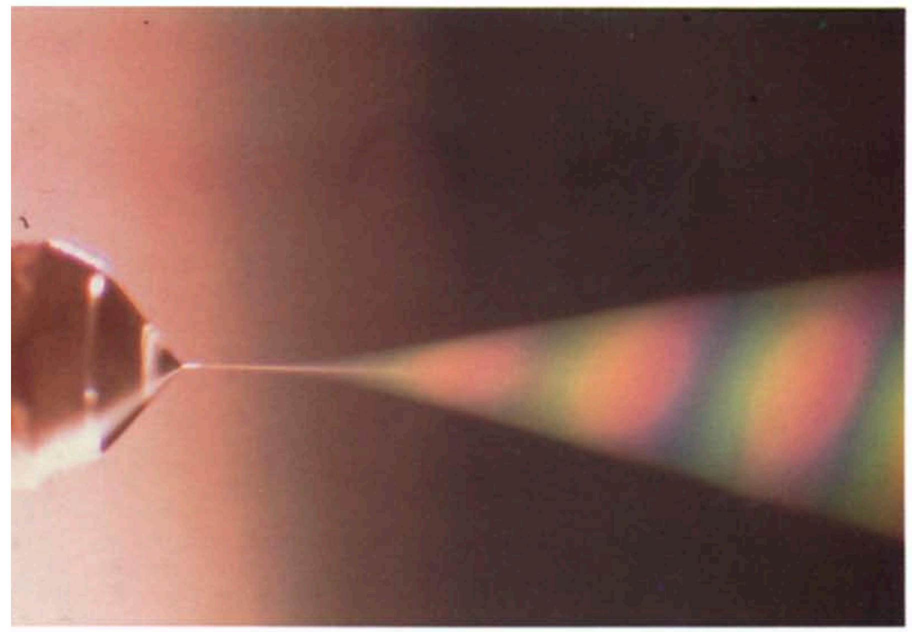
Electrospray

John Fenn (1917–2010)

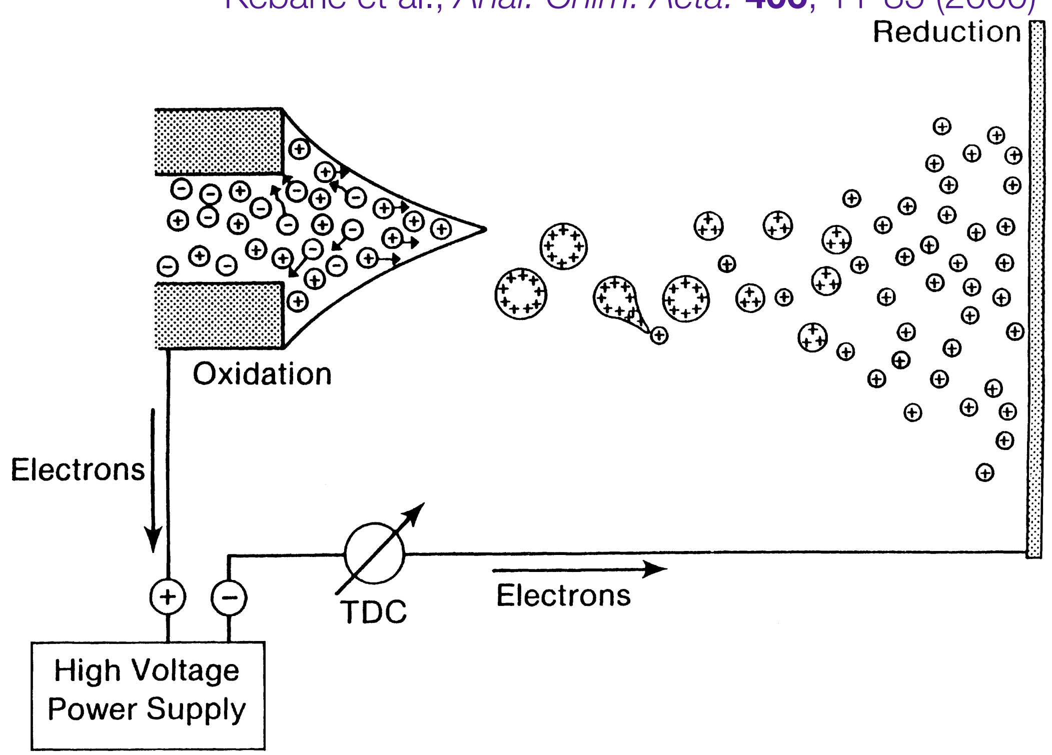
Nobel Prize
Chemistry, 2002

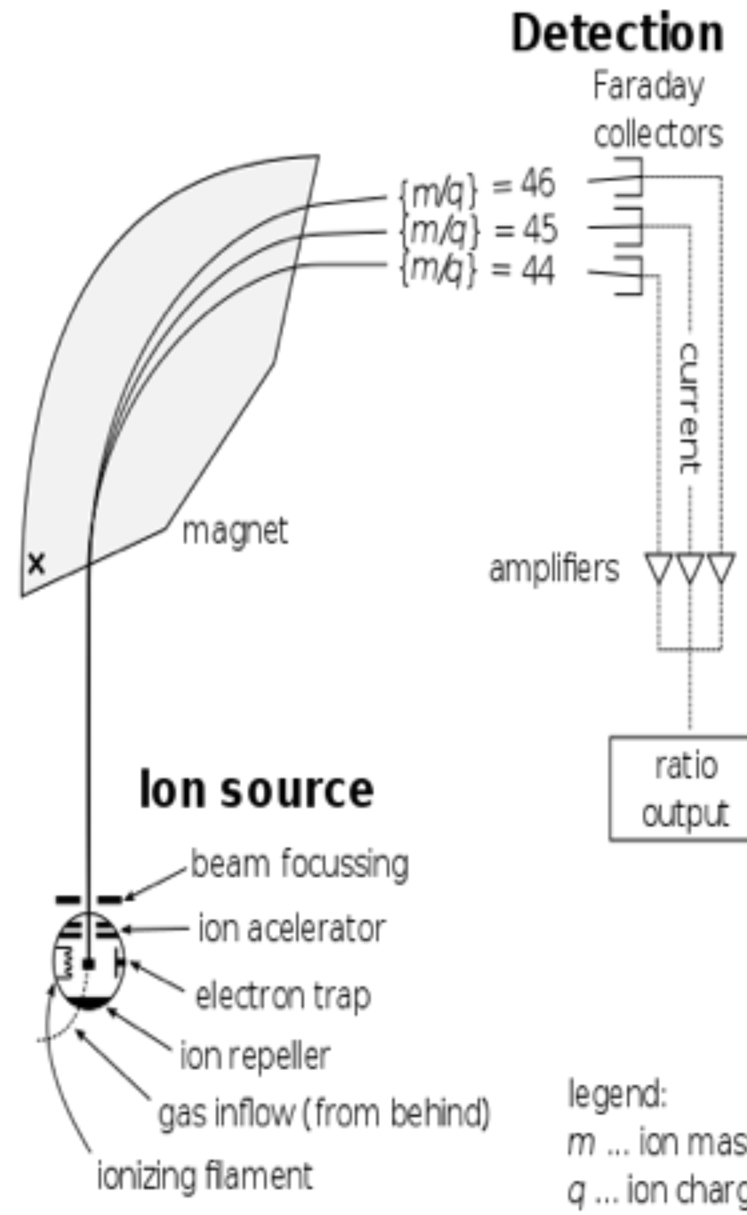
development of methods for identification and structure analyses of biological macromolecules

Pantano et al., *J. Aerosol Sci.* **25**, 1065-1077 (1994)



Kebarle et al., *Anal. Chim. Acta.* **406**, 11-35 (2000)





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Another kind of charged liquid: *nuclear matter*

nuclear matter: consists mostly of protons and neutrons

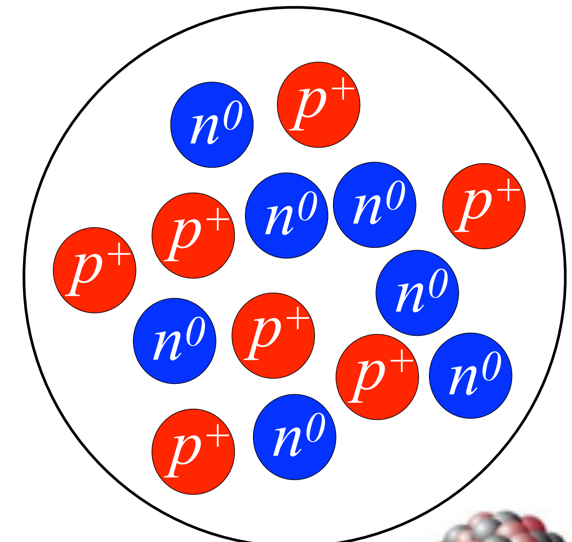
- nucleons (protons and neutrons) are attracted by strong forces and form a dense nuclear liquid

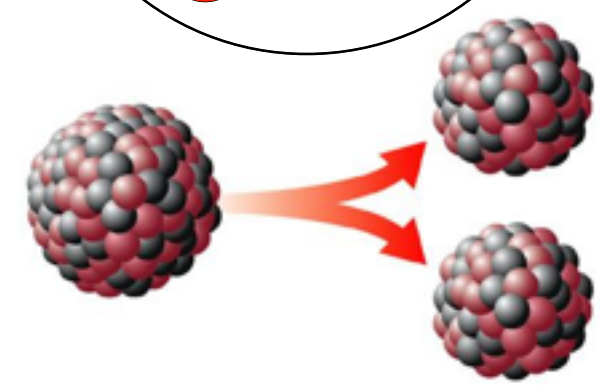
- near the nuclear liquid-vacuum interface nucleons experience reduction of the binding energy, resulting in surface tension

- protons move so fast that the charge is uniformly distributed throughout the nuclear liquid

- the competition of the attractive forces that tend to minimize the the surface area with Coulombic repulsion leads to *nuclear fission*

- the same processes govern dense stellar matter





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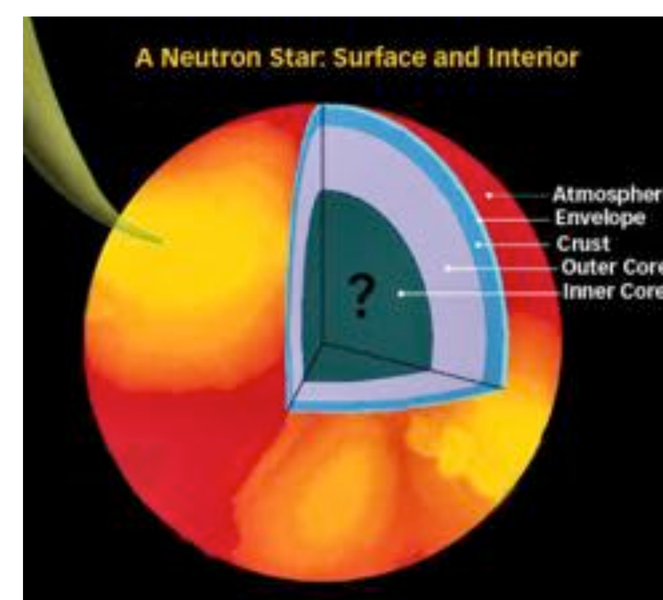

from sciencenews.org

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Gamow’s liquid drop model

George Gamow (1904–1968)

Portrait, 1932: courtesy of Elfriede and Igor Gamow

in December 1928, while visiting Niels Bohr in Copenhagen, George Gamow conceived of the liquid drop model of the atomic nucleus

the model treats nucleons as an incompressible, uniformly charged fluid with surface tension

<u>warning</u>: the original model is missing key physics (treats nuclear matter as a collection of alpha-particles)

the model was further refined and brought to agreement with experiments by Heisenberg and Von Weizsäcker, following the discovery of neutron

G. Gamow, *Proc. R. Soc. Lond. A.* **126**, 632-644 (1930);
W. Heisenberg, in: *Institut International de Physique Solvay* (Gauthier-Villars, Paris, 1934);
C. von Weizsäcker, *Z. Phys.* **96**, 431-458 (1935);

Gamow's liquid drop model

mathematically, the model gives rise to a geometric variational problem:

find $e(m) := \inf\{E(\Omega) : |\Omega| = m\},$ $E(\Omega) := \mathrm{Per}(\Omega) + \frac{1}{8\pi}\int_\Omega\int_\Omega \frac{1}{|x-y|}\,dx\,dy,$

here $\mathrm{Per}(\Omega)$ is the perimeter of the set Ω, a suitable generalization of surface area

in modern rendition, perimeter is defined in the sense of De Giorgi:

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

The purpose of the liquid drop model is to predict:

- the shape of nuclei
- non-existence of arbitrarily large nuclei
- existence of a nucleus with the largest binding energy

The ultimate triumph of the model was to explain the phenomenon of nuclear fission

Meitner and Frisch, 1939; Bohr and Wheeler, 1939; Feenberg, 1939; Frenkel, 1939

A marriage of two older variational problems

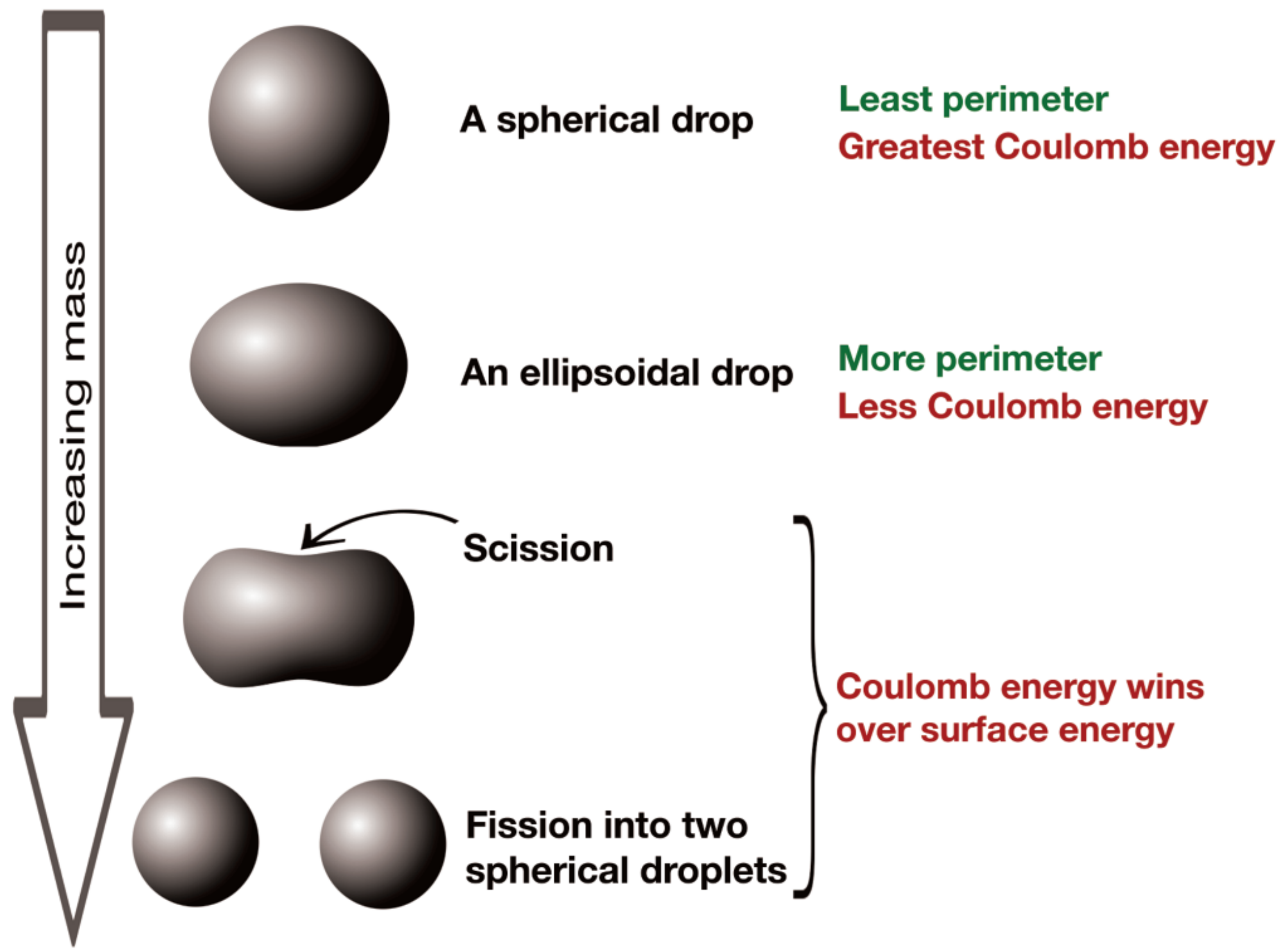
Gamow's model puts the two terms in the energy into a **direct opposition**:

- the perimeter is *minimized* by a ball
- the Coulombic energy is *maximized* by a ball

the relative strength of surface tension vs. Coulomb repulsion is measured by m

energy per unit mass under rescalings, $\lambda > 0$:

$$\lambda^{-3} E(\lambda\Omega) = \lambda^{-1} \operatorname{Per}(\Omega) + \frac{\lambda^2}{8\pi} \int_\Omega \int_\Omega \frac{1}{|x-y|} \, dx dy.$$



- for $m << 1$, surface tension dominates: expect minimizers to be balls
- for $m >> 1$, Coulomb energy dominates: expect minimizers not to exist

it is precisely the <u>competition</u> of these two terms that makes the problem highly non-trivial

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Review: R. Choksi, C. B. Muratov, I. Topaloglu, *Notices AMS* **64,** 1275-1283 (2017)

Gamow's model: current status

minimize

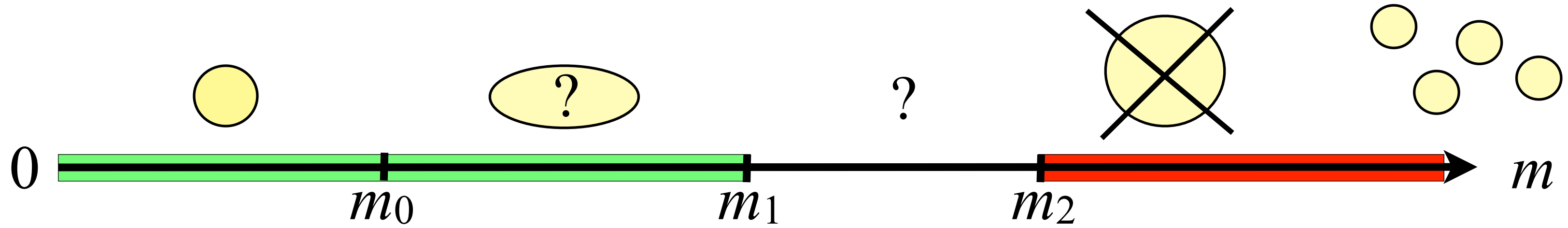
$$E(\Omega) := \mathrm{Per}(\Omega) + \frac{1}{8\pi} \int_\Omega \int_\Omega \frac{1}{|x-y|} \, dx \, dy,$$

among all measurable sets $\Omega \subset \mathbb{R}^3$, with $|\Omega| = m$

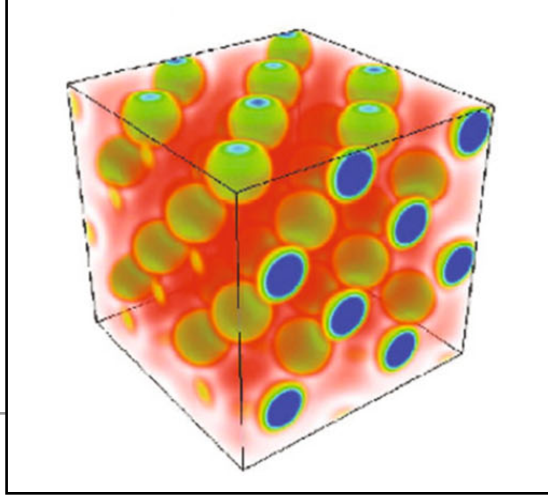
Theorem 1. *There exist constants $0 < m_0 \leq m_1 \leq m_2$ such that:*

(1) *If $m \leq m_1$, then there* **exists** *a minimizer.*
(2) *If $m \leq m_0$, then the* **unique** *minimizer is a* **ball**.
(3) *If $m > m_2$, then there is* **no minimizer**.

the result of this theorem, in this form, was obtained in Knüpfer and M, 2014
some earlier existence results can be found in Choksi and Peletier, 2010
an independent proof of radial symmetry is in Julin, 2014
an independent proof of non-existence can be found in Lu and Otto, 2014



Generalized minimizers



from Okamoto et al., 2013

what happens when minimizers fail to exist? Knüpfer, M, Novaga, 2016

define *generalized minimizers*: finite collections of minimizers “infinitely far apart”

$$m = \sum_{i=1}^{N} m_i \quad \text{and} \quad e(m) = \sum_{i=1}^{N} e(m_i).$$

Theorem 2 (Existence of generalized minimizers)**.** *For any $m \in (0, \infty)$ there exists a generalized minimizer $(\Omega_1, \ldots, \Omega_N)$ of E with total mass m. Moreover, after a possible modification on a set of Lebesgue measure zero, the support of each component Ω_i is bounded, connected and has analytic boundary.*

$$\mathcal{I} = \{m > 0 : e(m) \text{ is attained}\} \qquad f(m) := \frac{e(m)}{m} \qquad f^* := \inf_{m \in \mathcal{I}} f(m)$$

from compactness of generalized minimizers and Lipschitz continuity of $e(m)$, we obtain that $\mathcal{I}$ is compact ⇒ together with universal estimates on the components, this yields:

$$f(m) \geq f^* \textit{ for all } m > 0 \qquad \mathcal{I}^* := \left\{ m^* \in \mathcal{I} \ : \ f(m^*) = \inf_{m \in \mathcal{I}} f(m) \right\} \neq \varnothing.$$

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independently obtained by Frank and Lieb, 2015

Perfectly conducting liquid drops

first treated by Lord Rayleigh, 1882, assuming the liquid is a perfect conductor

stable equilibrium shapes are local minimizers of the following energy:

$$E(\Omega) = \sigma P(\Omega) + \frac{Q^2}{2C(\Omega)}, \quad |\Omega| = V, \quad \Omega \subset \mathbb{R}^3$$

= surface energy + capacitary energy, where, equivalently:

$$C^{-1}(\Omega) = \inf_{\mu(\Omega)=1} \int_\Omega \int_\Omega \frac{1}{4\pi\varepsilon_0 |x-y|} \, \mathrm{d}\mu(x) \, \mathrm{d}\mu(y) \quad \text{or} \quad C(\Omega) = \varepsilon_0 \inf_{\substack{u \in D^1(\mathbb{R}^3) \cap C(\mathbb{R}^3) \\ u \geq 1 \text{ in } \Omega}} \int_{\mathbb{R}^3} |\nabla u|^2 \, \mathrm{d}x$$

C the electrical capacitance of the liquid drop

Note: the energy coincides with that of Gamow's model, if μ is a multiple of the Lebesgue measure

a ball is always a critical point of the energy

EL equation: $2\sigma H = \frac{\varepsilon_0}{2} |\nabla \phi|^2 + \lambda$

Lord Rayleigh, 1882, computed the second variation of the energy and found that the ball is a local minimizer of the energy iff $0 < Q < Q_R$, where

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

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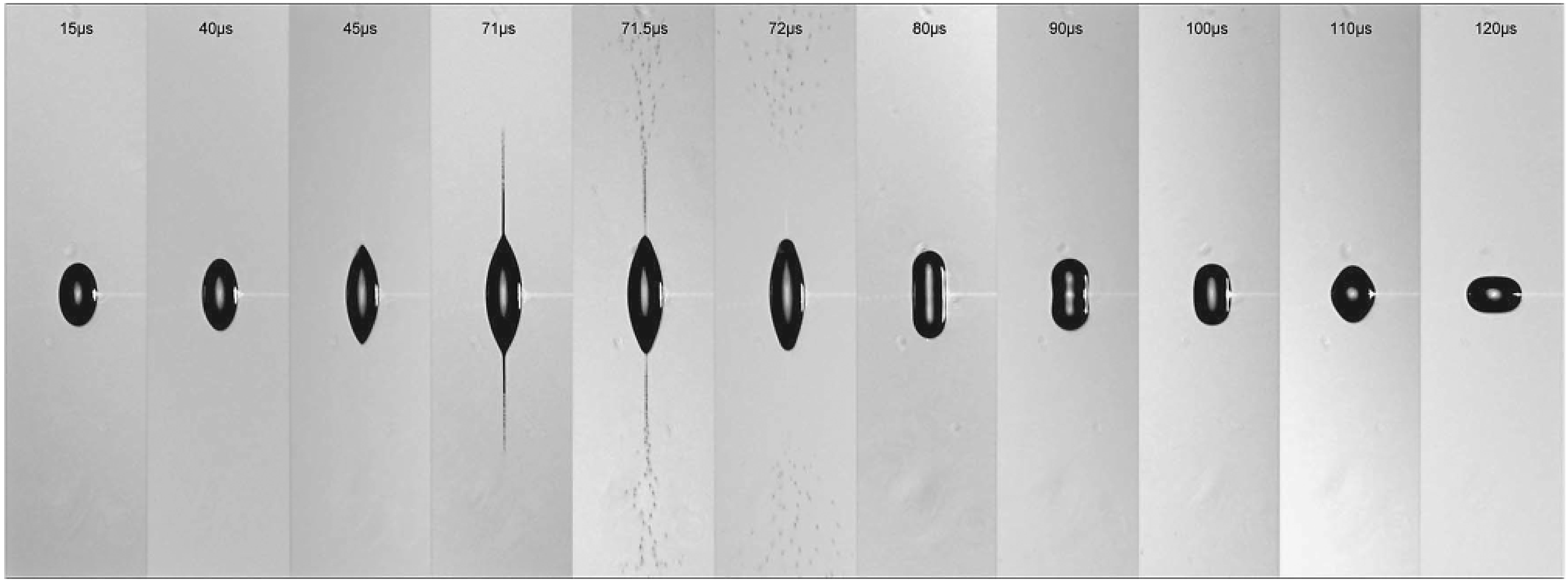
Instability of a charged conducting drop



from Giglio et al., *Phys Rev. E* **77**, 036319 (2008)

- as the solvent evaporates, the instability threshold is reached at a critical value of R
- the droplet elongates until a cone-like singularity appears at the top and the bottom
- immediately after the appearance of sharp tips a thin liquid jet issues from the tips
- the jet carries away a significant portion of the charge, but very small portion of mass

- the drop then returns to the equilibrium spherical shape

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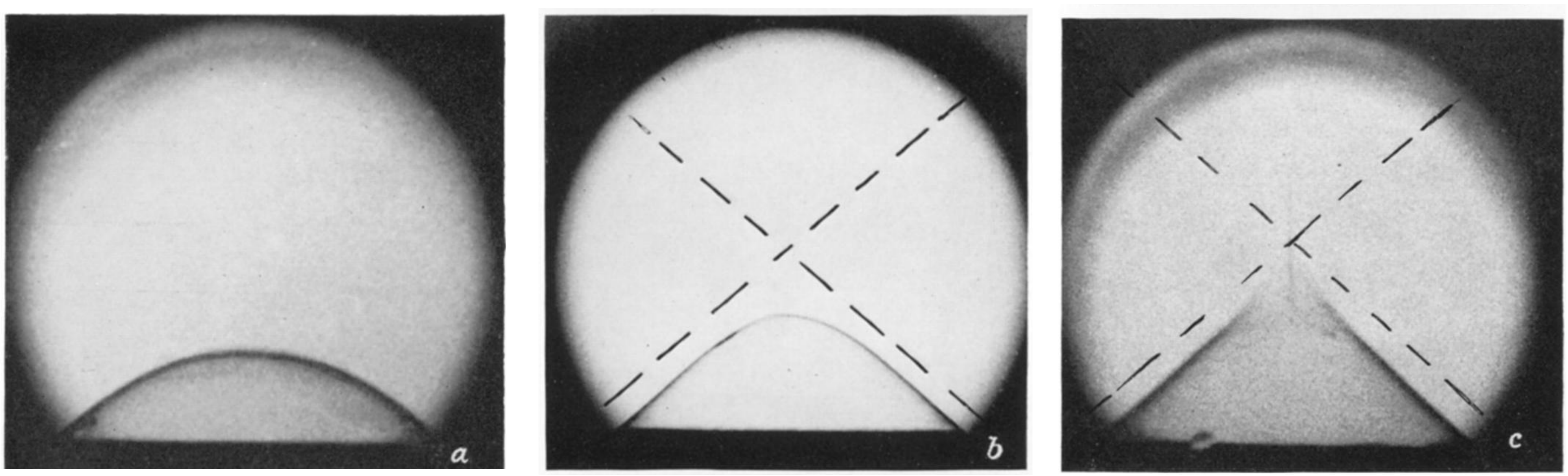
Taylor cone

the appearance of a cone-like singularity can also be seen in the equilibrium meniscus



G. I. Taylor, *Proc. R. Soc. Lond. A* **280**, 383-397 (1964)

Taylor, 1964, constructed a self-similar solution of the EL equation in the form of a cone

the mechanical equilibrium between the capillary and Coulomb forces dictates the cone half-angle of ~49.3 degrees

below the critical voltage the interface attains a convex equilibrium shape

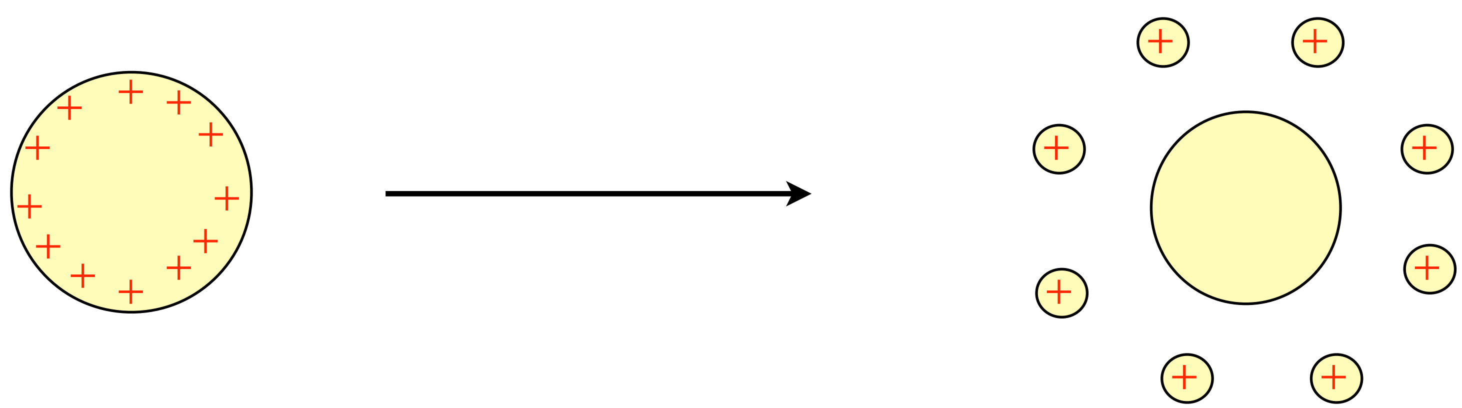
Are equilibrium drops minimizers of the energy?

surprisingly, Goldman, Novaga and Ruffini, 2015, showed that the minimum of

$$E(\Omega) = \sigma P(\Omega) + \frac{Q^2}{2C(\Omega)}, \quad |\Omega| = V, \quad \Omega \subset \mathbb{R}^3$$

is **not attained** for any $V > 0$ and $Q > 0$ - also in a container

explanation: it is better to evaporate many small droplets which carry away all the charge



choose N balls of radius $r_N = N^{-\beta}$ with $\beta \in (\frac{1}{2}, 1)$ far apart and distribute the charge uniformly between them. Then:

$$\sigma P(B_0) \leq E(\Omega) \leq \sigma P(B_0^N) + 4\sigma\pi r_N^2 N + \frac{Q^2}{8\pi\varepsilon_0 r_N N} \qquad |B_0^N| = V - \frac{4}{3}\pi r_N^3 N$$

$\Rightarrow$ the infimum of the energy is given by surface energy alone

However, minimizer **exists** for all $V > 0$ and $Q > 0$ among convex sets

Are equilibrium drops local minimizers?

again, surprisingly, balls are **never** local minimizers in any reasonable sense: M, Novaga, 2016

Theorem 3. *For any $V > 0$ and $Q > 0$ there exists a smooth map $\phi_\delta : \mathbb{S}^2 \to (-\delta, \delta)$ such that if*

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

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 supp $\phi_\delta \subset B_{\delta/R}(\nu_0)$ for some $\nu_0 \in \mathbb{S}^2$.

same conclusion holds for any smooth critical point of the energy

find a <u>small</u> smooth perturbation to lower energy: $\Delta E \leq \Delta E_0$,

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

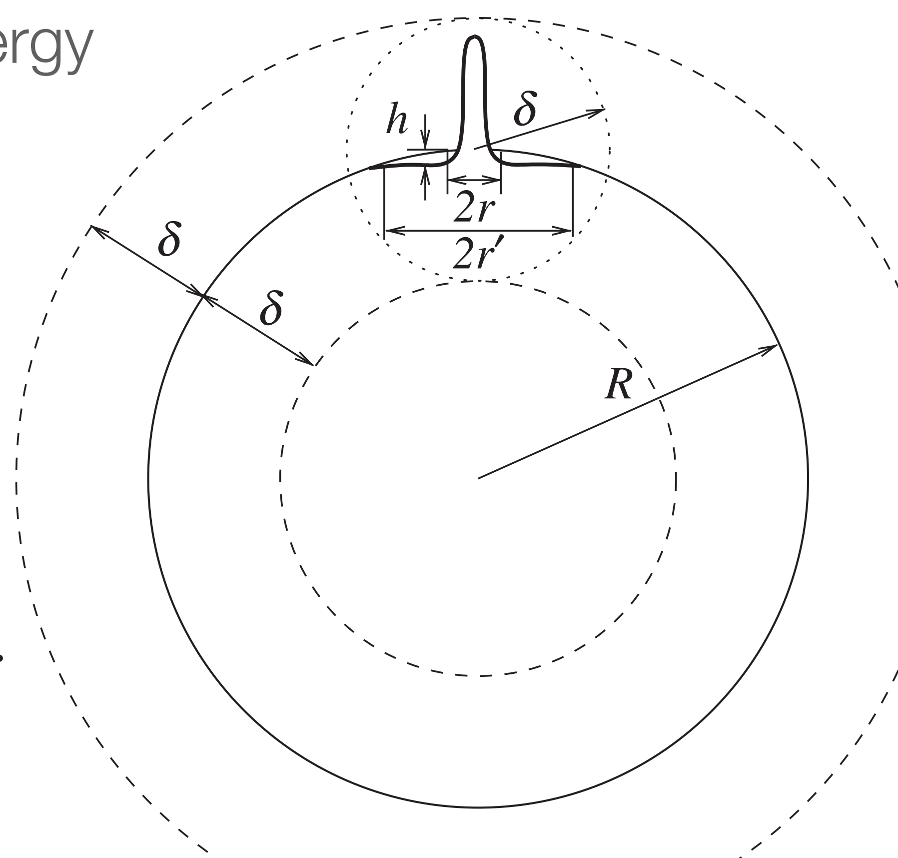
$$h \sim r^2 \delta / r'^2$$

$$q = Q r'^2 / (4R^2)$$

choosing $r = \delta e^{-R/\delta}$, $r' = (rR\delta^2)^{1/4}$, we get

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

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



The variational problem is *ill-posed*

$$E_{3d}^{Q}(K) = \sigma \mathcal{H}^2(\partial K) + \frac{Q^2}{2C(K)}$$

there is an intrinsic incompatibility between the perimeter and the capacitary energy:

- the perimeter functional does not see sets of zero Lebesgue measure
- the capacitary energy does not see sets of zero harmonic capacity

the charges may concentrate on sets of zero Lebesgue measure

a possible way out is to strengthen the definition of the surface measure

still does not work for 3-d electrostatic problems:

- the 2-d Hausdorff surface measure does not see sets of Hausdorff dimension $s < 2$
- the 3-d harmonic capacity is positive for sets of Hausdorff dimension $s > 1$

thus, there is a gap $1 < s < 2$ between the two

the classical variational model does not describe the physics of conducting charged drops

more **physics** needs to be incorporated to restore well-posedness (surface tension insufficient)

possible remedies: finite screening length, discreteness of charges, etc.

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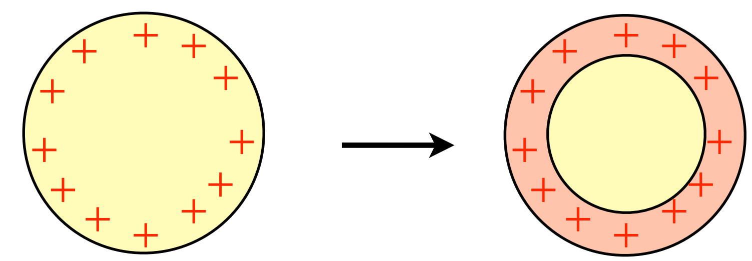
M, Novaga, 2016

The model with finite screening

in a perfect conductor the charges go to the boundary



in reality, thermal effects cause finite penetration length

the *free energy*:

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

where

$$-\varepsilon_0 \nabla\cdot(a_\Omega(x)\nabla v) = \rho \quad \text{in } \mathcal{D}'(\mathbb{R}^3), \qquad a_\Omega(x) = 1 + (\varepsilon - 1)\chi_\Omega(x), \qquad \rho = e(n_+ - n_-)$$

expand in the spirit of Debye-Hückel theory - Gamow's model for $\varepsilon = 1$, $R \ll r_D = \sqrt{\frac{\varepsilon_0 k_B T}{n_0 e^2}}$

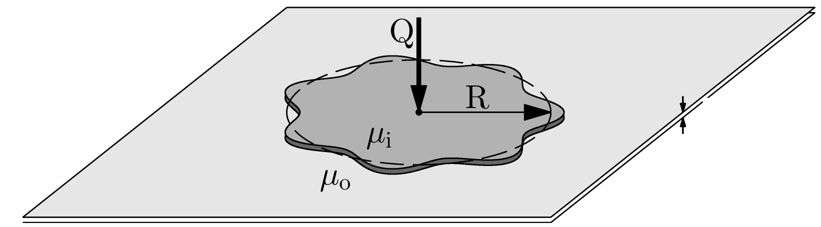
$$\mathcal{F}(\Omega, v) = \sigma P(\Omega) + \frac{\varepsilon_0}{2}\int_{\mathbb{R}^3} a_\Omega(x)|\nabla v|^2\,\mathrm{d}x + \frac{k_\mathrm{B}T}{4e^2 n_0}\int_\Omega \rho^2\,\mathrm{d}x$$

admissible class => existence of minimizers in a container

M, Novaga, 2016

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

Flat charged drops



from Gin and Daripa, *Phys. Fluids* **27**, 012101 (2015)

what about charged drops in a Hele-Shaw cell? borderline case

1-d interfacial energy vs. 1-Riesz capacity (=Newtonian capacity associated with 3-d space)

minimize for $\Omega \subset \mathbb{R}^2$

$$E_{2d}^{Q}(\Omega) := \sigma \ell \mathscr{H}^1(\partial\Omega) + \frac{Q^2}{8\pi\varepsilon\varepsilon_0}\mathscr{I}_1(\Omega), \qquad \mathscr{I}_\alpha(\Omega) := \inf\left\{ \int_\Omega \int_\Omega \frac{d\mu(x)\,d\mu(y)}{|x-y|^\alpha} \ : \ \mu(\Omega) = 1 \right\}$$

rescaling

$$\mathscr{E}_\lambda^Q(\Omega) := \frac{E_{2d}^Q(L\Omega)}{\sigma \ell L}, \qquad \lambda := \frac{Q^2}{8\pi\varepsilon\varepsilon_0 \sigma \ell L^2}, \qquad \mathscr{E}_\lambda^Q(\Omega) = \mathscr{H}^1(\partial\Omega) + \lambda \mathscr{I}_1(\Omega),$$

we get for $\mathscr{A}_m := \{\Omega \in \mathscr{A} \ : \ |\Omega| = m\}$ $\quad \mathscr{A} := \{\Omega \subset \mathbb{R}^2 \ : \ \Omega \text{ compact}, \ |\Omega| > 0, \ \mathscr{H}^1(\partial\Omega) < \infty\} / \sim .$

Theorem 4. *Let $\lambda > 0$, $m > 0$, let $R = \sqrt{m/\pi}$, and define $\lambda_0^Q := \frac{4m}{\pi}$. Then:*

(i) The closed ball $\overline{B}_R$ is the unique (up to translation) minimizer of $\mathcal{E}_\lambda^Q$ over $\mathcal{A}_m$, if $\lambda \le \lambda_0^Q$.

(ii) There is no minimizer of $\mathcal{E}_\lambda^Q$ over $\mathcal{A}_m$, if $\lambda > \lambda_0^Q$.

splitting at $\lambda_{c1}^Q := \dfrac{4m\sqrt{2}}{\pi}.$

$$A \sim B \text{ if } \mathscr{H}^1(A \setminus B) = \mathscr{H}^1(B \setminus A) = 0.$$

Conclusions and outlook

- competition of capillary forces with long-range repulsion produces a very rich set of behaviors
- these emergent behaviors depend quite delicately on the precise mathematical details of the models, despite similar physics
- for Gamow's and related models, the main challenge is in the global aspects: Is the solution always a ball? Can there be non-spherical minimizers?
- for capacitary problems, even the basic local properties are an issue due to lack of regularity
- for 3-d conducting charged drops, new physics needs to be incorporated into the models to resolve the issue of ill-posedness
- ill-posedness also needs to be addressed in the computational models of charged liquid drops

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