Singularities in neutral and charged droplets in an electric field

Marco Fontelos (Mathematics Institute- CSIC)

S. Betelú (North Texas)
U. Kindelán (UPM)
O. Vantzos (CSIC)

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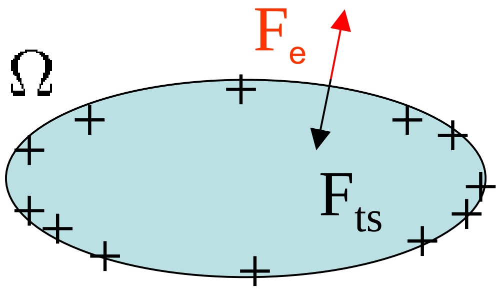
1. INTRODUCTION



$$\sigma = \varepsilon_0 E_n$$

Electrostatic Repulsion

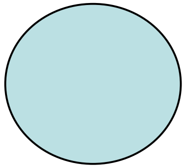
$$F_e = \frac{1}{2}\sigma E_n = \frac{1}{2}\varepsilon_0 E_n^2 = \frac{1}{2}\varepsilon_0 \left(\frac{\partial V}{\partial \vec{n}}\right)^2$$

Surface Tension

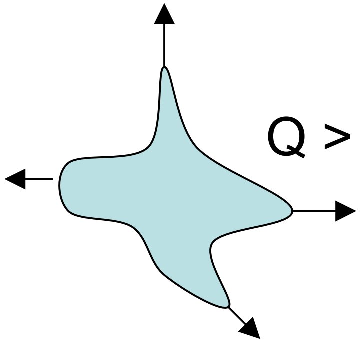
$$F_{ts} = \gamma\kappa\ ,\ \ (\kappa = \text{mean curvature})$$

Lord Rayleigh,1882:

$$Q_c = \sqrt{64\gamma\pi^2\epsilon_0 R^3}$$



$Q < Q_c$



$Q > Q_c$

Rayleigh's argument was variational:

Stationary configurations make the energy

$$E = \gamma A - \frac{1}{2}\varepsilon_0 \int |\mathbf{E}|^2$$

extremal.

$$\mathbf{E} = -\nabla V$$

$$\boxed{\begin{aligned} \Delta V &= 0 \text{ in } \mathbb{R}^3 \backslash \Omega, \\ V &= C \text{on } \partial\Omega, \\ V(\mathbf{r}) &\to 0 \text{as } |\mathbf{r}| \to \infty, \end{aligned}}$$

C is chosen such that $Q = -\varepsilon_0 \int_{\partial\Omega} \frac{\partial V}{\partial n}$

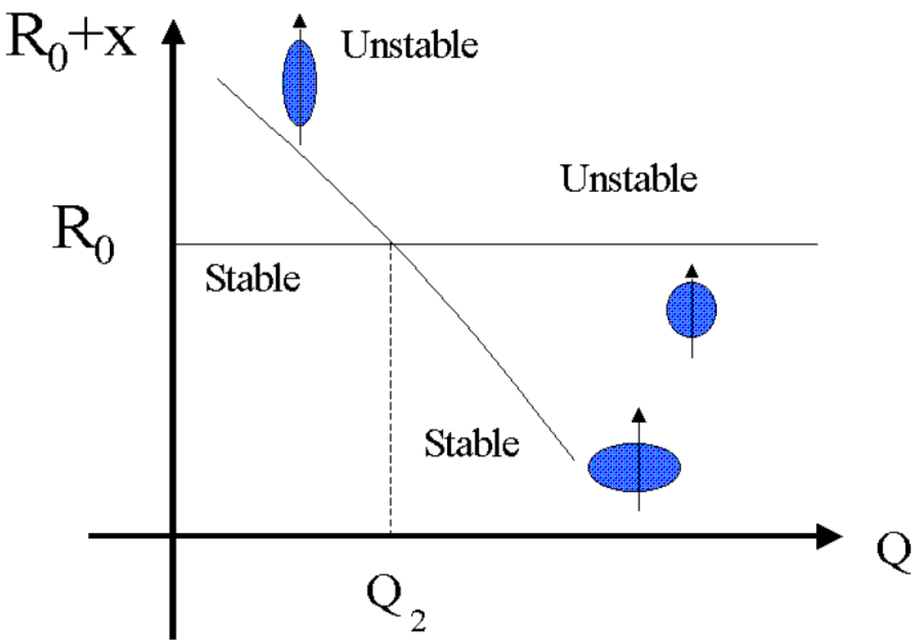
First variation:

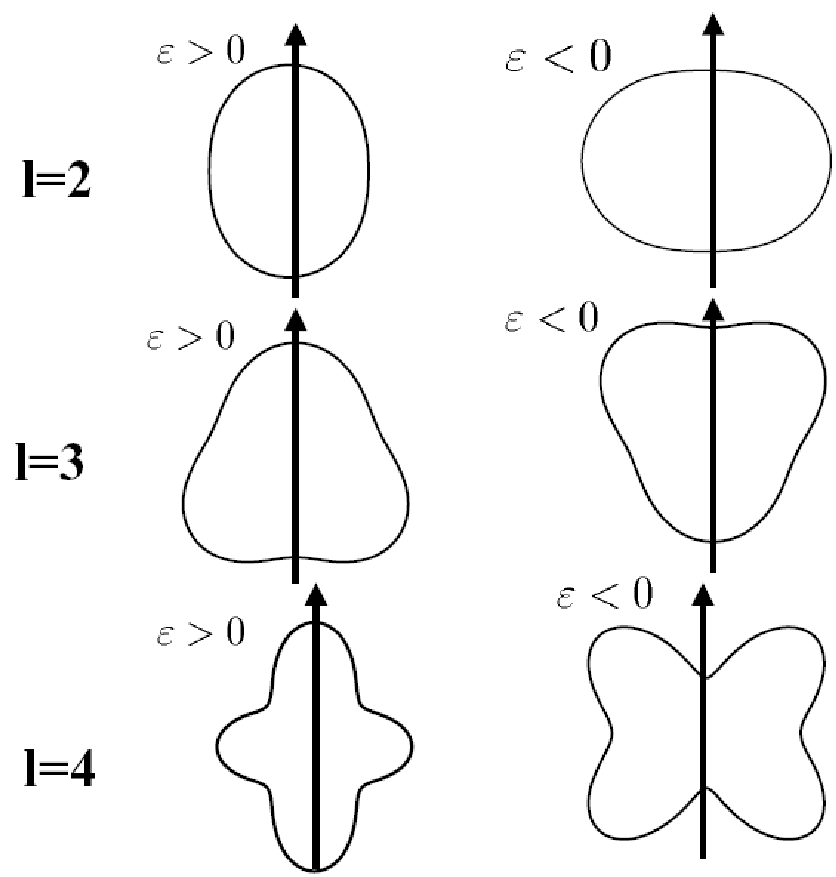
$$p = \gamma\kappa - \frac{\varepsilon_0}{2}\left(\frac{\partial V}{\partial n}\right)^2 \text{ on } \partial\Omega$$

Nonlinear
Nonlocal
elliptic PDE

In general, the drop is unstable under perturbations with the $Y_{l,m}(\theta, \varphi)$ Spherical harmonic if the charge is above

$$Q_{c,l} = \sqrt{16(l+2)\gamma\pi^2\varepsilon_0 R^3}$$

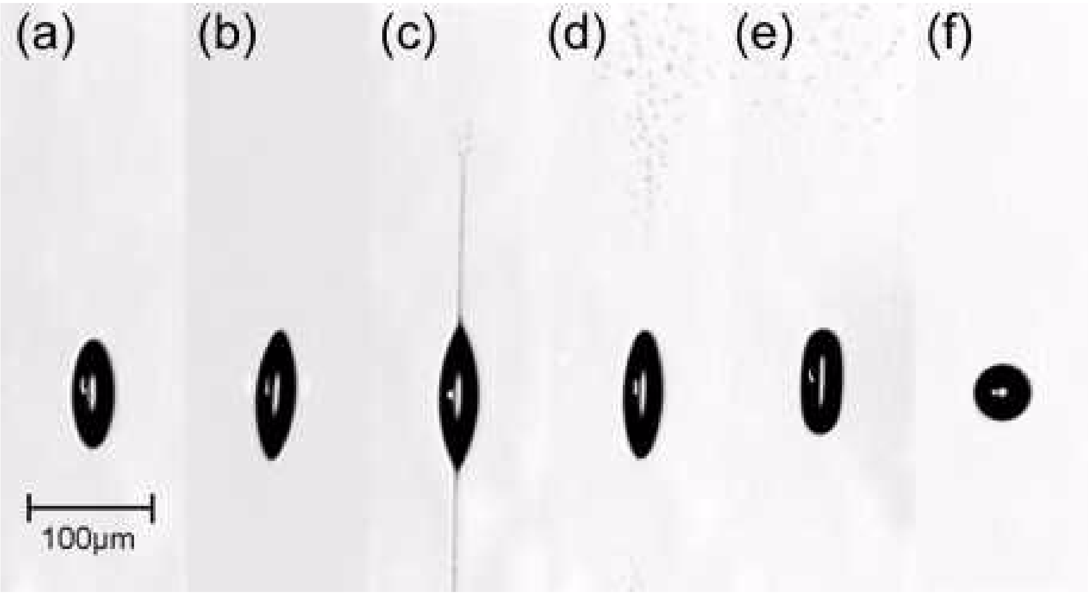


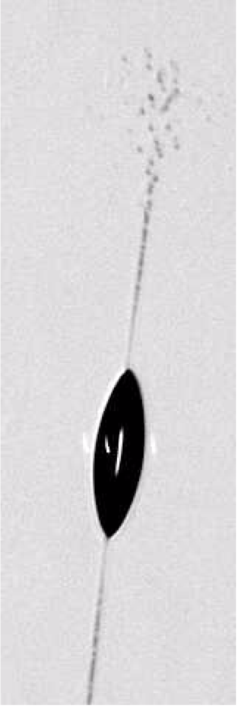


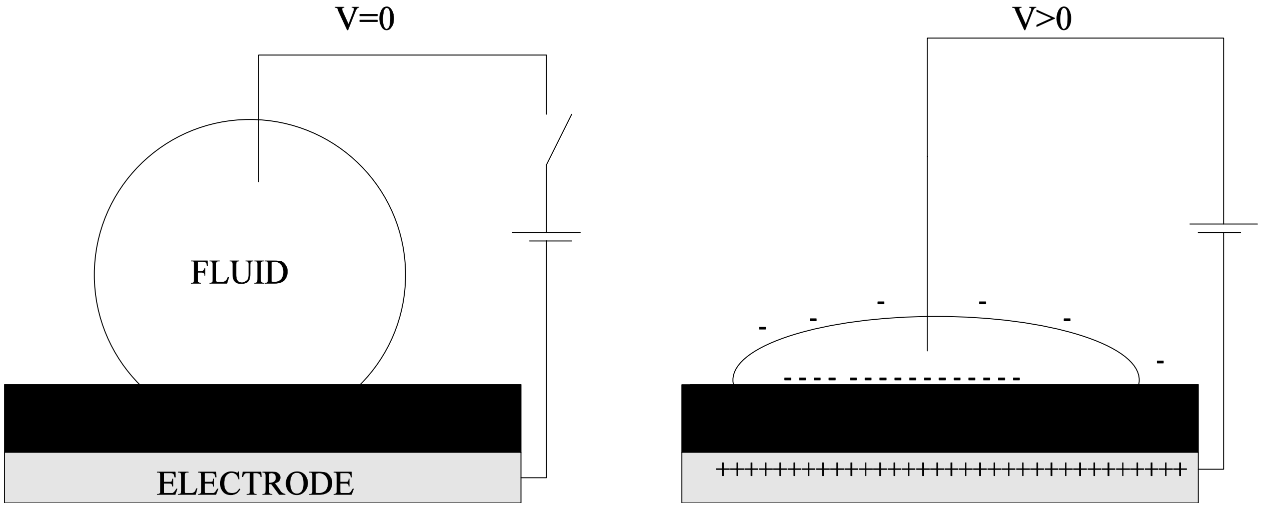
Symmetry-breaking bifurcations of charged drops.
(MAF, A. Frideman, Arch. Rat. Mech. Anal. 2004)

EXPERIMENTAL RESULTS

D. Duft et al., Rayleigh jets from levitated microdroplets,
Nature, vol. 421, 9 January 2003, pg. 128.

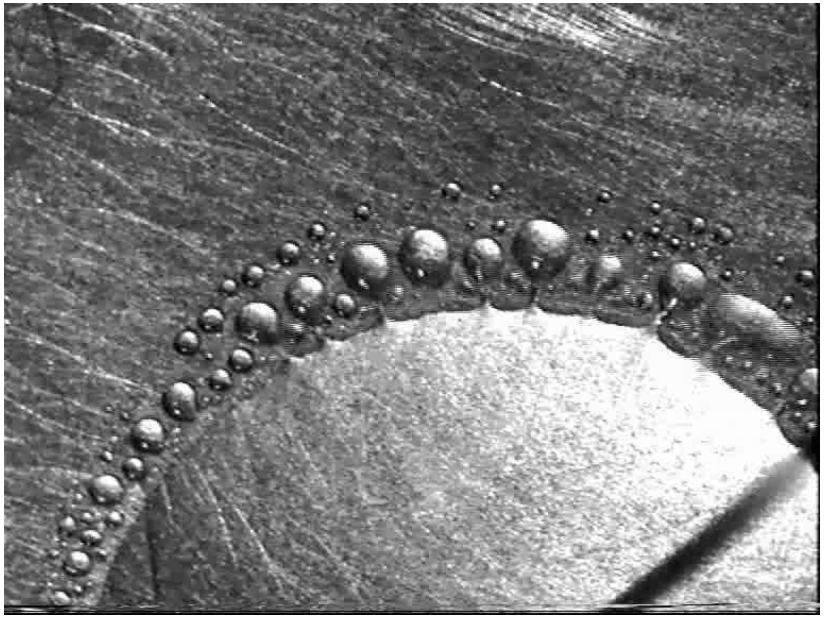






Lippmann effect (1875)

Electrowetting applications



(Movie from F. Mugele)

PHYSICAL RELEVANCE

- Electropainting-droplet spreading on solids.
- Electrospraying.
- Microencapsulation.
- Onset of rain affected by charge in drops.
- Microfluidics

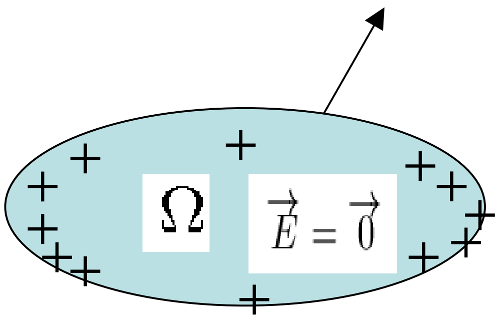
Fdez. de la Mora, Leisner, Barrero, Gañán-Calvo, Beauchamp,.....

2. EQUATIONS

2.1 ELECTRIC FIELD EQUATIONS

$$
\begin{aligned}
\Delta V &= 0 \text{ in } \mathbb{R}^3 \backslash \Omega \,, \\
V &= C \text{ on } \partial\Omega \,, \\
V(\mathbf{r}) &\to 0 \text{ when } |\mathbf{r}| \to \infty \,, \\
\vec{E} &= \vec{0} \text{ in } \Omega \left(\vec{E} = \nabla V \right)
\end{aligned}
$$

Conductor: $V = C$



Dielectric: $\Delta V = 0$

2.2 FLUID FLOW EQUATIONS

Small droplets (1-100μm) ,
inertial effects negligible (Re<<1) ⇨ Stokes Flux

$$\left.\begin{aligned} -\nabla p + \mu_1 \Delta \vec{u} &= \vec{0} \\ -\nabla \cdot \vec{u} &= 0 \end{aligned}\right\} \text{ in } \Omega(t)$$

Equilibrium of Forces on $\partial\Omega(t)$

$$(T^{(2)} - T^{(1)})\vec{n} = \left(\gamma\kappa - \frac{\sigma^2}{2\varepsilon_0}\right)\vec{n} \text{ on } \partial\Omega(t)$$

$$T_{ij}^{(k)} = -p\delta_{ij} + \mu_k\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right), \quad k = 1, 2$$

3. BOUNDARY INTEGRAL FORMULATION

Solution for the Potential

$$V(\mathbf{r}_0) = \frac{1}{4\pi}\int_{\partial\Omega(t)} \frac{\partial V}{\partial \overrightarrow{n}}(\mathbf{r})\frac{1}{|\mathbf{r}-\mathbf{r_0}|} - \cancel{V(\mathbf{r})\frac{\partial(1/|\mathbf{r}-\mathbf{r_0}|)}{\partial \overrightarrow{n}}}\, dS(\mathbf{r}).$$

With the constraint

$$Q = \varepsilon_0 \int_{\partial\Omega(t)} \frac{\partial V}{\partial \overrightarrow{n}}(\mathbf{r})dS(\mathbf{r}).$$

The solution of the Stokes system can be represented in terms of the integrals involving the boundary values of the velocity and its derivatives:

$$\begin{aligned} u_j(\mathbf{r}_0) &= -\frac{1}{4\pi}\frac{1}{\mu_1+\mu_2}\int_{\partial\Omega(t)} f_i(\mathbf{r})G_{ij}(\mathbf{r},\mathbf{r}_0)dS(\mathbf{r}) \\ &\quad -\frac{1}{4\pi}\frac{\mu_2-\mu_1}{\mu_2+\mu_1}\int_{\partial\Omega(t)} u_i(\mathbf{r})L_{ijk}(\mathbf{r},\mathbf{r}_0)n_k(\mathbf{r})dS(\mathbf{r}) \; . \end{aligned}$$

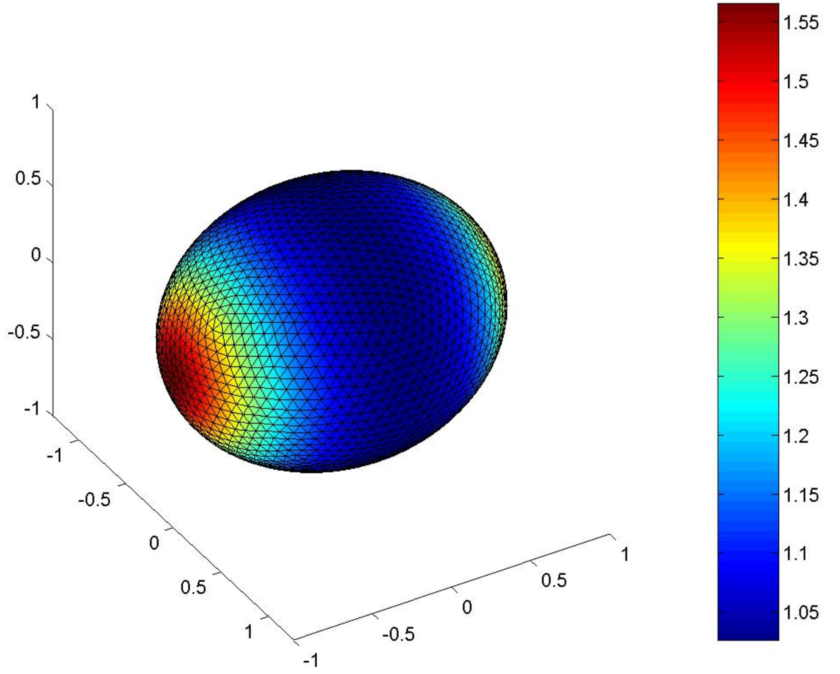
Where

$$\begin{aligned} G_{ij}(\mathbf{r},\mathbf{r}_0) &= \frac{\delta_{ij}}{|\mathbf{r}-\mathbf{r}_0|} + \frac{(r_i-r_{0,i})(r_j-r_{0,j})}{|\mathbf{r}-\mathbf{r}_0|^3} \\ L_{ijk}(\mathbf{r},\mathbf{r}_0) &= -6\frac{(r_i-r_{0,i})(r_j-r_{0,j})(r_k-r_{0,k})}{|\mathbf{r}-\mathbf{r}_0|^5} \\ f_i(\mathbf{r}) &= \left[\gamma\kappa(\mathbf{r}) - \frac{\varepsilon_0}{2}\left(\frac{\partial V}{\partial \vec{n}}\right)^2(\mathbf{r})\right] n_i(\mathbf{r}). \end{aligned}$$

Time discretization: explicit scheme

$$\mathbf{r}_0^k = \mathbf{r}_0^{k-1} + \vec{u}^{\,k-1}\triangle t$$

Triangularization of the initial surface

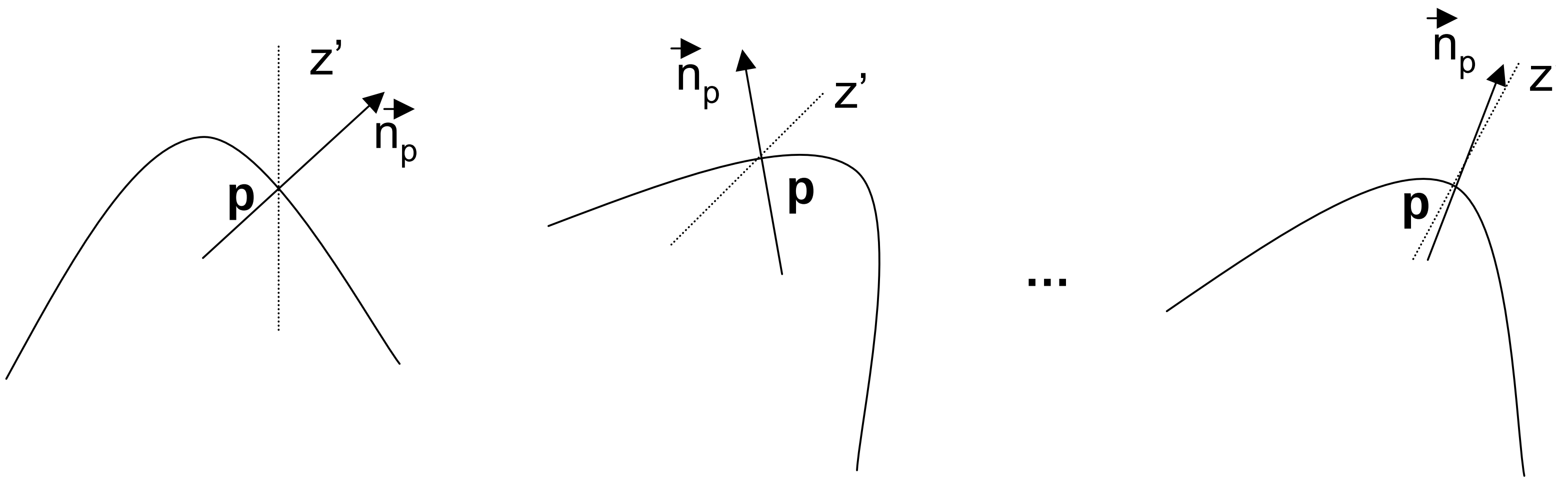


CURVATURE

Zinchenko et al. (1998)

- (p,x’,y’,z’) Local cartesian coordinates with origin in p.

- If the z’ axis has the same direction than $\vec{n}_p$ (normal to the surface in p) then a paraboloid containing p with its axis parallel to z’ will be a good local approximation of the surface.



CHARGE DENSITY

Considering the electric potential solution and taking into account that it is constant on the surface

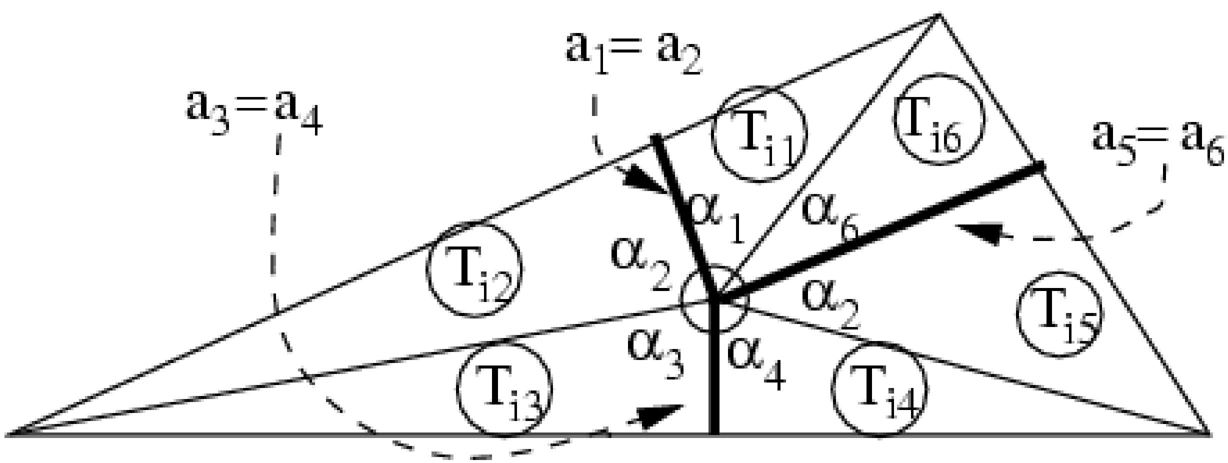
$$4\pi\varepsilon_0 V(\mathbf{r}_i) = C_1 = \int_{\partial\Omega(t)} \sigma(\mathbf{r}) \frac{1}{|\mathbf{r}-\mathbf{r}_i|} ds(\mathbf{r}) \qquad i = 1, \ldots, N_e,$$

$$\int_{\partial\Omega(t)} \sigma(\mathbf{r}) \frac{1}{|\mathbf{r}-\mathbf{r}_i|} ds(\mathbf{r}) \approx \sum_{j=1}^{N_e} \lambda_{ij}\sigma_j, \quad \text{with } \lambda_{ij} = \int_{T_j} \frac{1}{|\mathbf{r}-\mathbf{r}_i|} ds(\mathbf{r}) \text{ and } \sigma_j = \sigma(\mathbf{r}_j)$$

λ_{ij} calculation (two types of elements): $\Rightarrow$

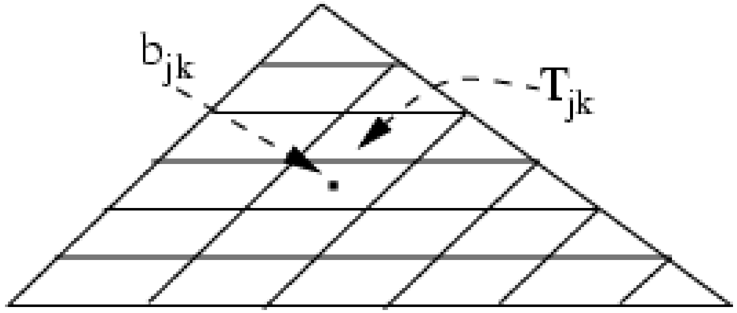
1) i=j (potential created by one element onto itself)

$$\lambda_{ii} = \int_{T_i} \frac{ds(\mathbf{r})}{|\mathbf{r} - \mathbf{r}_i|} = \int\int_{T_i} \frac{1}{\rho} \rho d\rho d\theta = \sum_{k=1}^{6} \int\int_{T_{ik}} d\rho d\sigma = \sum_{k=1}^{6} a_k \ln(\sec(\alpha_k) + \tan(\alpha_k)).$$



2) i≠j (potential created by element j onto element i)

$$\lambda_{ij} = \sum_{k=1}^{N_s} \lambda_{ij,k}, \qquad \lambda_{ij,k} = \frac{A_{T_{jk}}}{|\mathbf{b}_i - \mathbf{b}_{jk}|},$$



Once we know λ_{ij} we solve the following system:

$$\sum_{j=1}^{N_e} \lambda_{ij}\overline{\sigma}_j = C_1 \qquad i = 1, \ldots, N_e,$$

$\overline{\sigma}_i$ = fictitious charge density. Rescale to obtain the actual density:

$$\sigma_i = \frac{Q}{\overline{Q}}\overline{\sigma}_i \qquad i = 1, \ldots, N_e.$$

With:

$$\overline{Q} = \varepsilon_0 \sum_{i=1}^{N_e} \overline{\sigma}_i A_i$$

VELOCITY

Curvature and Charge Density already known

$$4\pi(\mu_2+\mu_1)u_j(\mathbf{r}_c) + (\mu_2-\mu_1)\int_{\partial\Omega}(u_i(\mathbf{r})-u_i(\mathbf{r}_c))L_{ijk}(\mathbf{r},\mathbf{r}_c)\mathbf{n}_k(\mathbf{r}dS(\mathbf{r}) =$$

$$+4\pi\left(\mu_1+\mu_2\right)\delta_{ij}u_i(\mathbf{r}_c)+\int_{\partial\Omega(t)}(f(\mathbf{r})-f(\mathbf{r}_c))n_i(\mathbf{r})G_{ij}(\mathbf{r},\mathbf{r}_c)dS(\mathbf{r})$$

Singularity removal:

$$\int_{\partial\Omega(t)} f(\mathbf{r})n_i(\mathbf{r})G_{ij}(\mathbf{r},\mathbf{r}_c)dS(\mathbf{r}) =$$

$$\int_{\partial\Omega(t)}(f(\mathbf{r})-f(\mathbf{r}_c))n_i(\mathbf{r})G_{ij}(\mathbf{r},\mathbf{r}_c)dS(\mathbf{r}) + \overbrace{\int_{\partial\Omega(t)} f(\mathbf{r}_c)n_i(\mathbf{r})G_{ij}(\mathbf{r},\mathbf{r}_c)dS(\mathbf{r})}^{\substack{0\\ ||}} =$$

$$\int_{\partial\Omega(t)}(f(\mathbf{r})-f(\mathbf{r}_c))n_i(\mathbf{r})G_{ij}(\mathbf{r},\mathbf{r}_c)dS(\mathbf{r})$$

$$\int_{\partial\Omega(t)} (f_i(\mathbf{r}) - f_i(\mathbf{r}_c))G_{ij}(\mathbf{r},\mathbf{r}_c)dS(\mathbf{r}) = \sum_{\substack{k=1\\k\neq c}}^{nod} (f_i(\mathbf{r}_k) - f_i(\mathbf{r}_c))G_{ij}(\mathbf{r}_k,\mathbf{r}_c)A_k$$

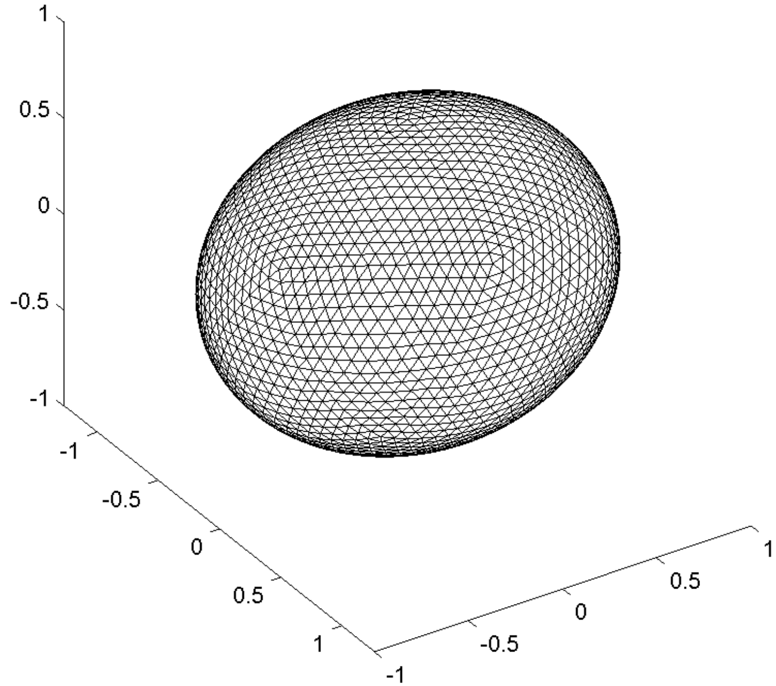
$$\int_{\partial\Omega(t)} (u_i(\mathbf{r})-u_i(\mathbf{r}_c))L_{ijk}(\mathbf{r},\mathbf{r}_c)n_k(\mathbf{r})dS(\mathbf{r}) = \sum_{\substack{m=1\\m\neq c}}^{nod} (u_i(\mathbf{r}_m)-u_i(\mathbf{r}_c))L_{ijk}(\mathbf{r}_m,\mathbf{r}_c)n_k(\mathbf{r}_m)A_k$$

$$A_k = \frac{1}{3}\sum_{j=1}^{ne(k)} A_j$$

Or we can use a quadrature scheme by interpolating to values inside the triangles.

4. NUMERICAL RESULTS

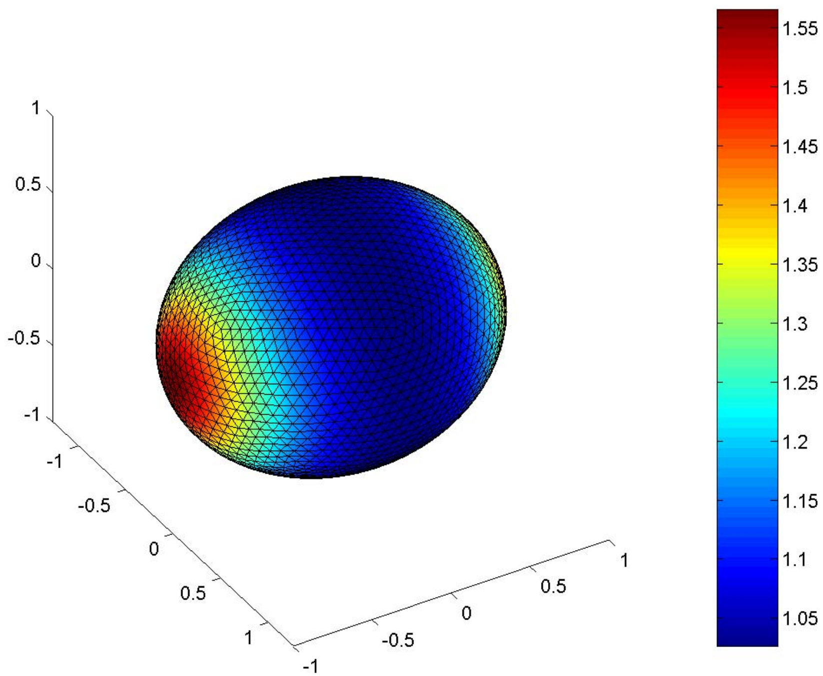
Prolate Spheroid: a=c=0.8, b=1
Mesh r2: elements=5120, mesh diameter=0.06

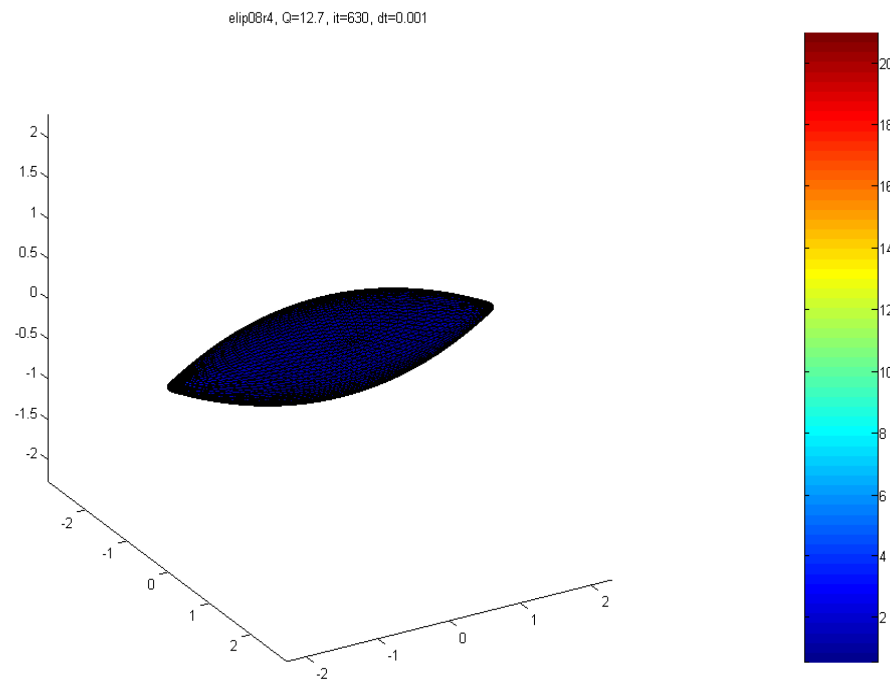


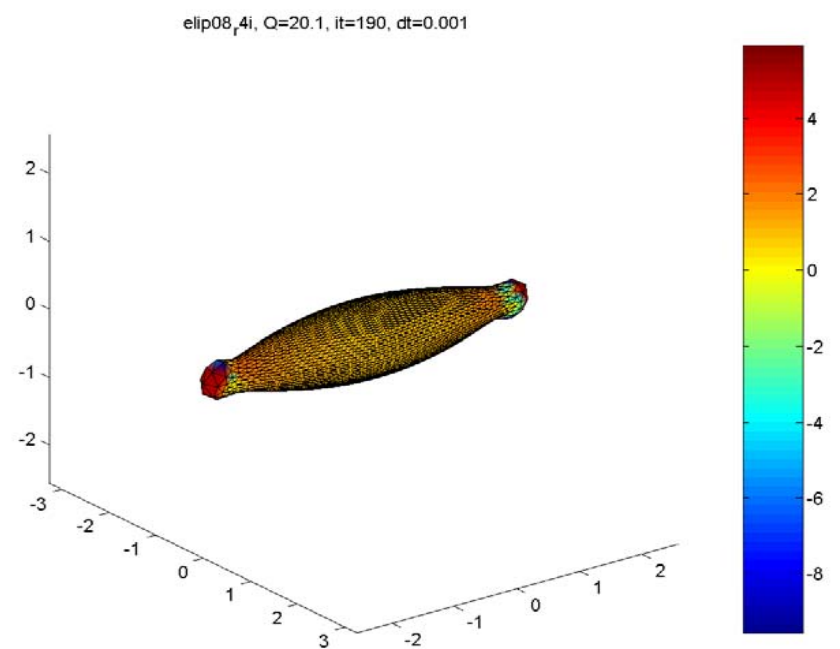
Two tests:

1. $Q=1.2Q_c$
2. $Q=2Q_c$

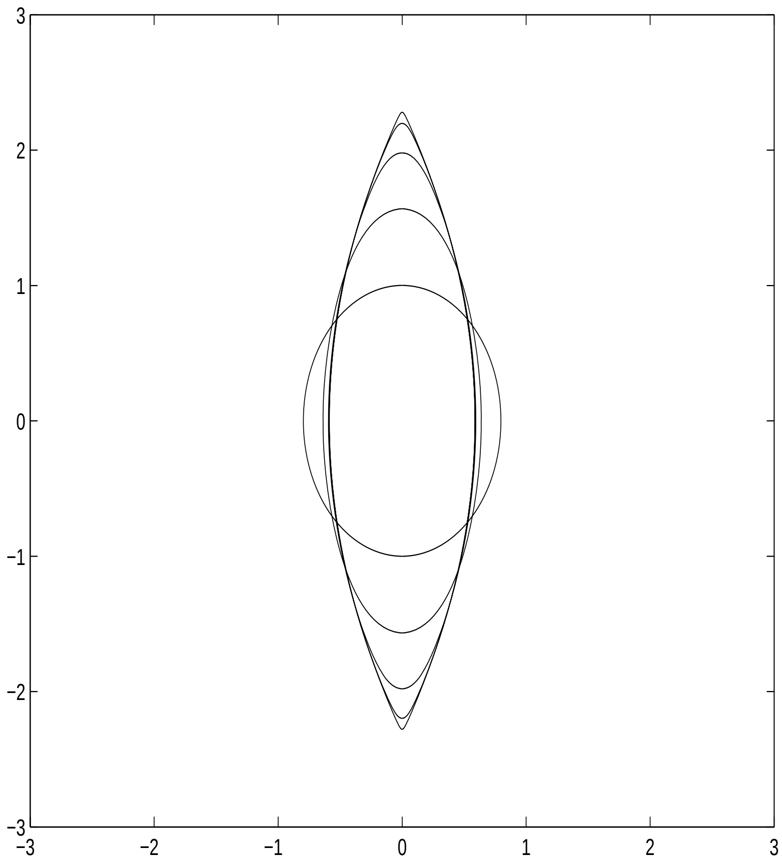
NUMERICAL RESULTS (cont.)

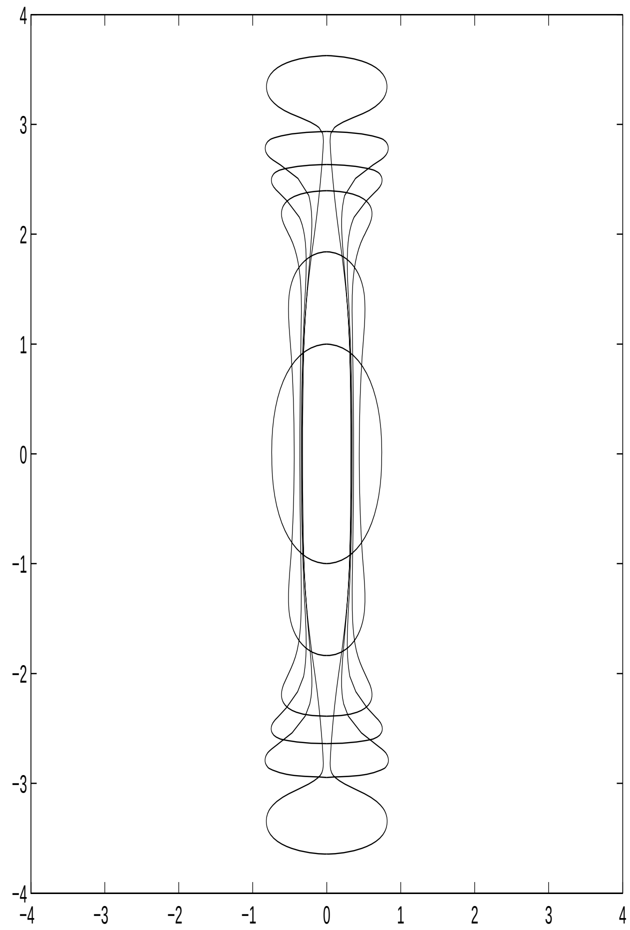




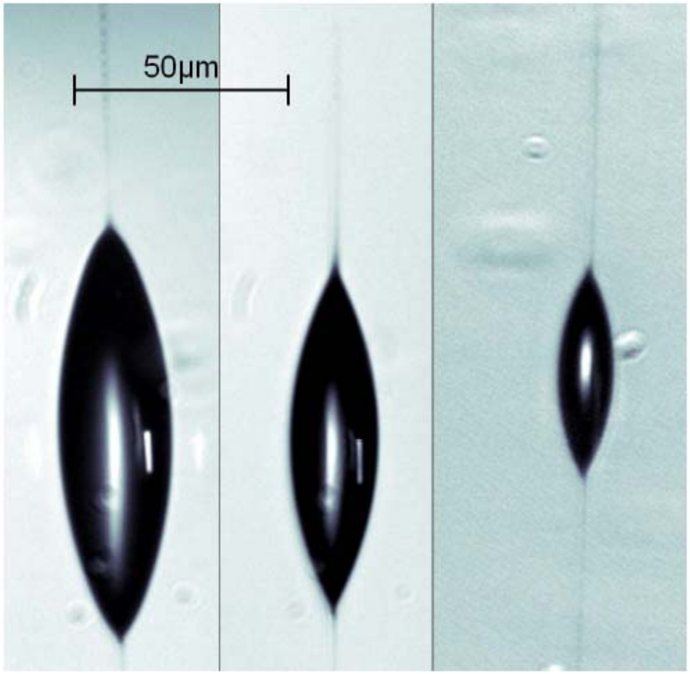


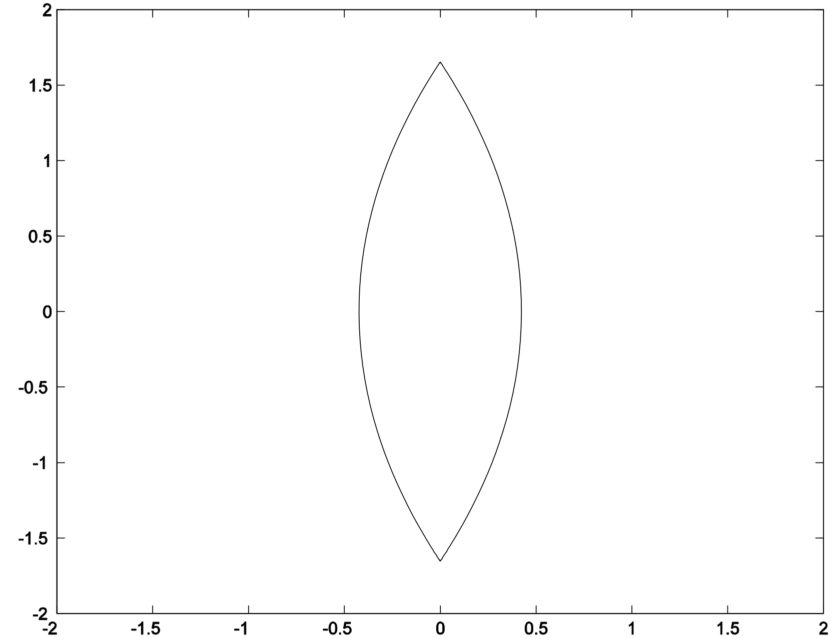
AXISYMMETRIC CALCULATION

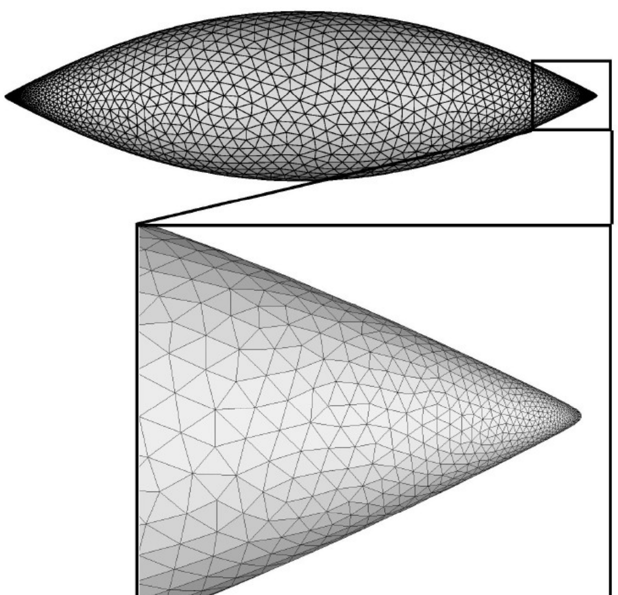


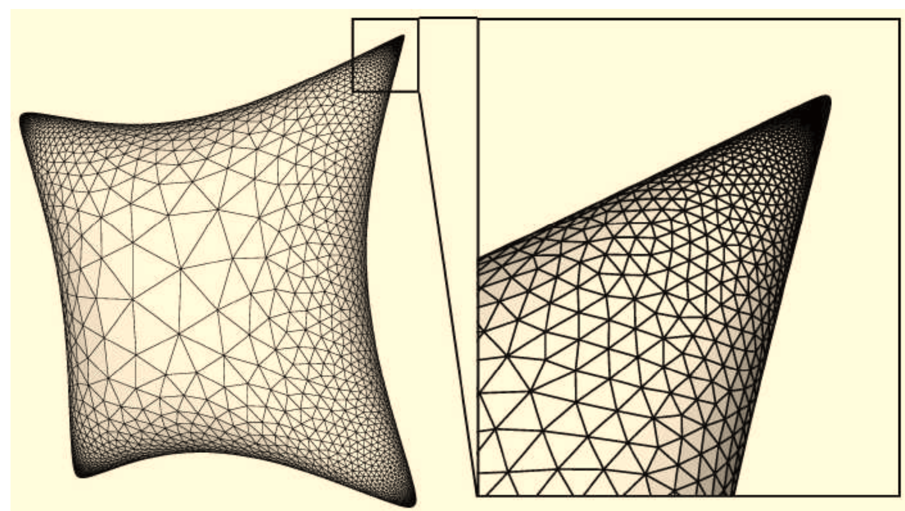


NUMERICAL RESULTS (cont.)

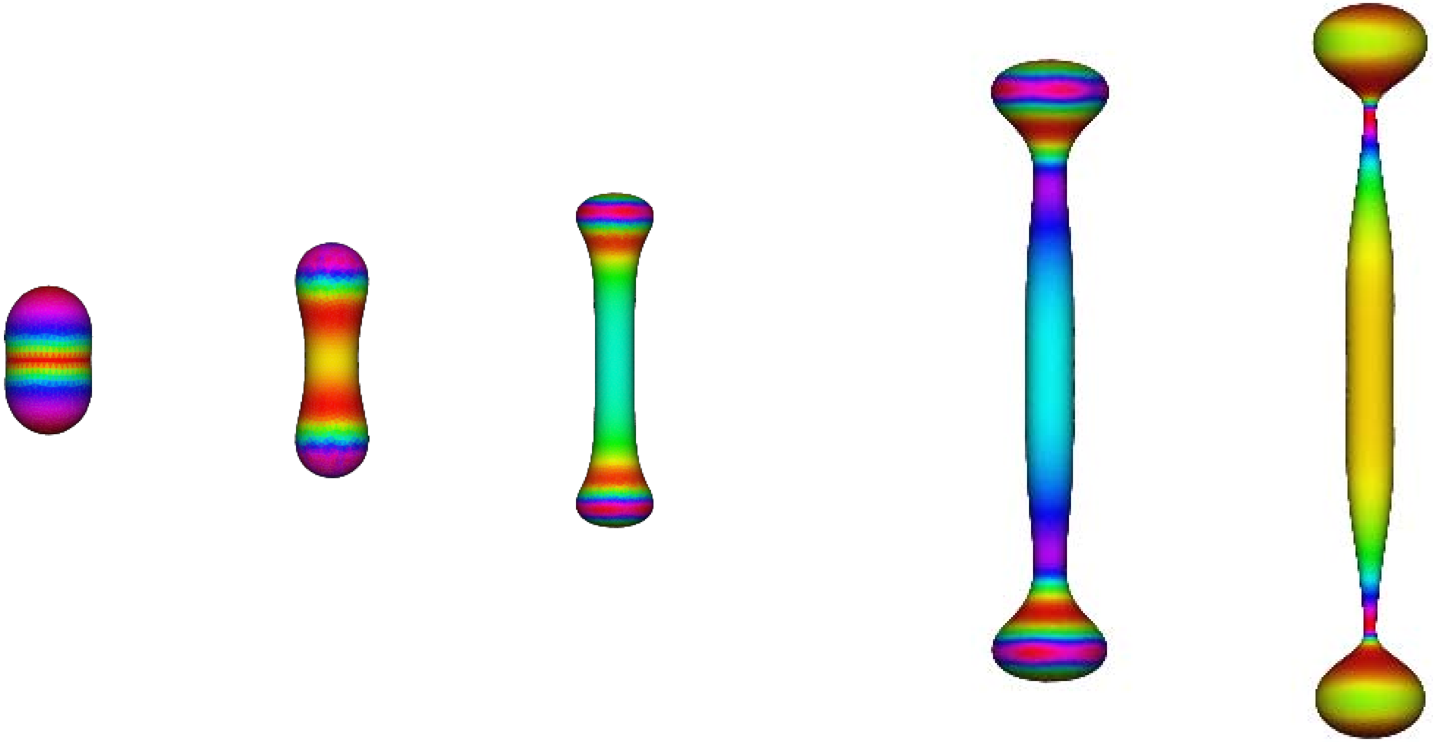






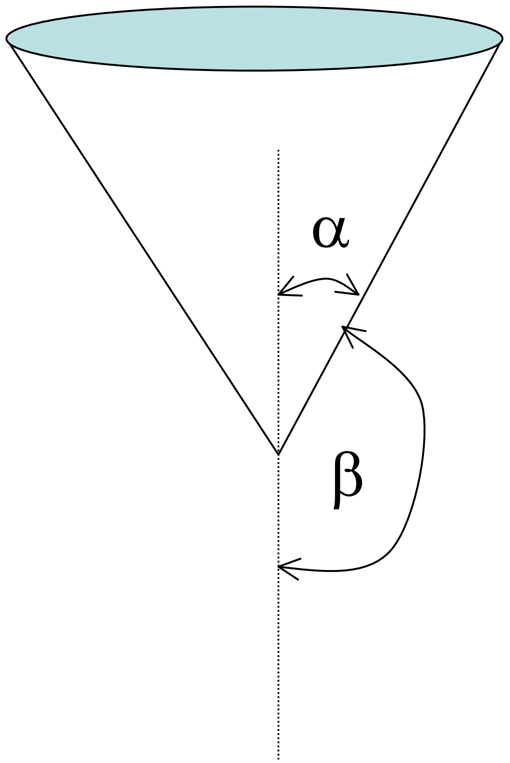


NUMERICAL RESULTS (cont.)



5. Dynamic Taylor cones

Stationary solutions



Potential

$$V = A r^{\nu} P_{\nu}(\cos\theta),$$

Electric field

$$E_t = -\nu A r^{\nu-1} P_{\nu}(\cos\beta),$$

$$E_n = A r^{\nu-1} \sin\theta P'_{\nu}(\cos\beta).$$

No tang. component $\quad P_{\nu}(\cos\beta)=0.$

Balance of forces $\quad -\dfrac{\gamma}{r\ \tan\beta} = \dfrac{\epsilon_0}{2} E_n^2,$

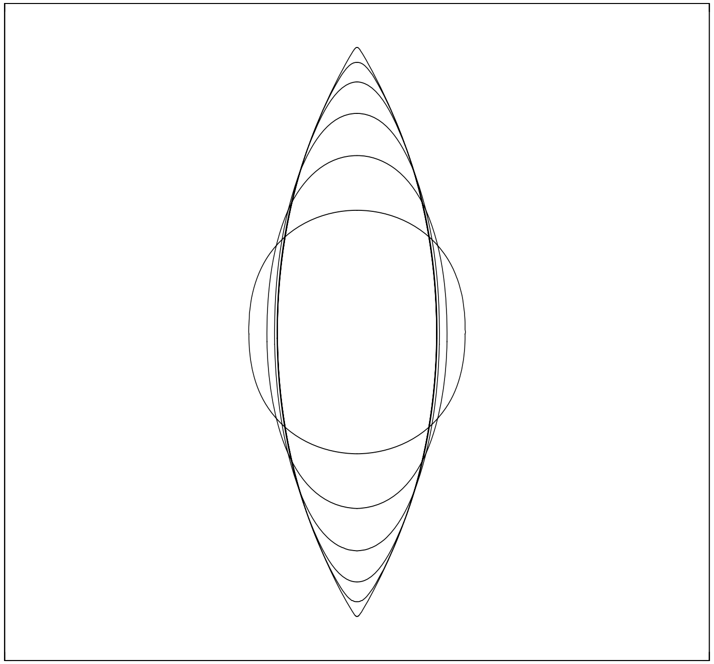
Solution: $\quad \nu = 1/2$

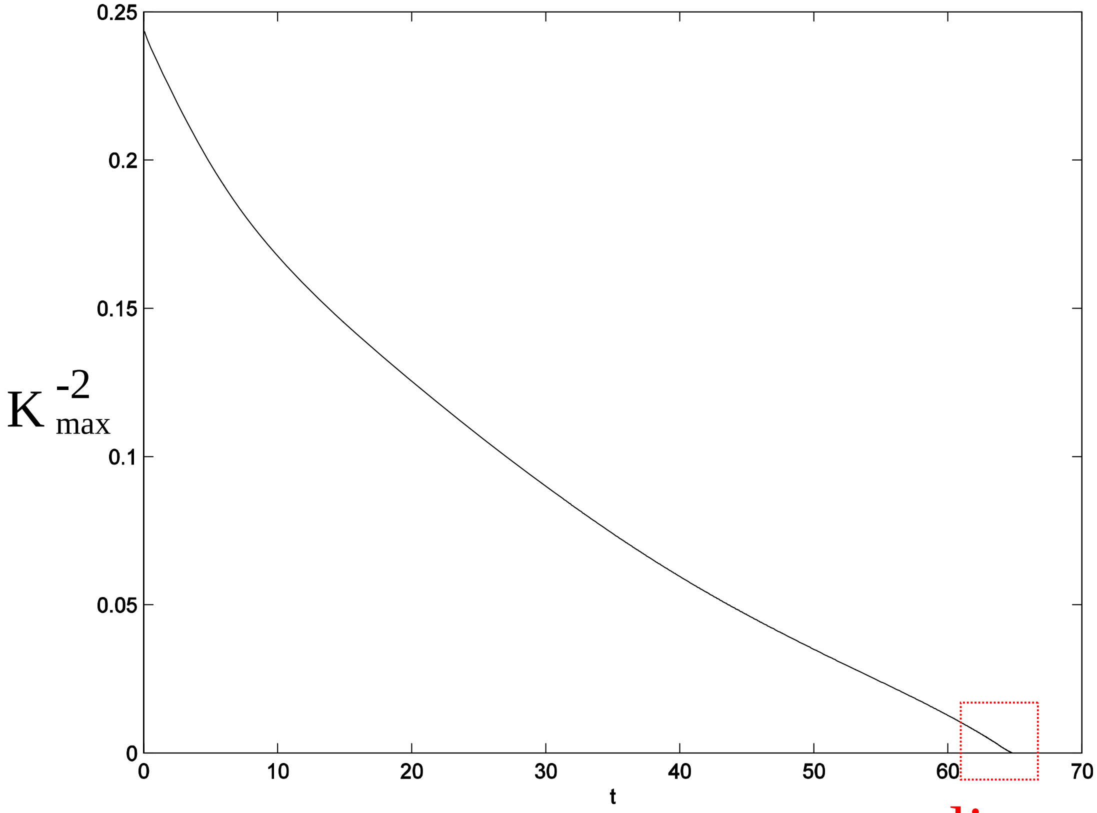
$\beta = 130.71^{\circ}$

G. I. Taylor 1964 $\quad \boxed{\alpha = 49.3^{o}}$

Contradiction with experiments!!

Axisymmetric profiles





This suggests the following similarity variables:

$$\rho = \frac{r}{(t_0 - t)^{\frac{1}{2}}} \; , \; \xi \equiv \frac{z}{(t_0 - t)^{\frac{1}{2}}}$$

and looking for sim. sols.:

$$\begin{aligned} h &= (t_0 - t)^{\frac{1}{2}} f(\rho) \; , \\ p &= \frac{1}{(t_0 - t)} P(\xi, \rho) \; , \\ \vec{u} &= \frac{1}{(t_0 - t)^{\frac{1}{2}}} \vec{U}(\xi, \rho) \; . \end{aligned}$$

$$V = \Phi(\xi, \rho)$$

Similarity Equations

The functions $(\mathbf{U}, P)$ satisfy Stokes system

$$-\nabla_\xi P + \mu_k \Delta_\xi \mathbf{U} = 0, \ \nabla_\xi \cdot \mathbf{U} = 0$$

together with the condition

$$(T^{(2)} - T^{(1)})\mathbf{n}_\xi = -\frac{\Sigma^2}{2\varepsilon_0}\mathbf{n}_\xi \ ,$$

Surf. Tension
Subdominant!

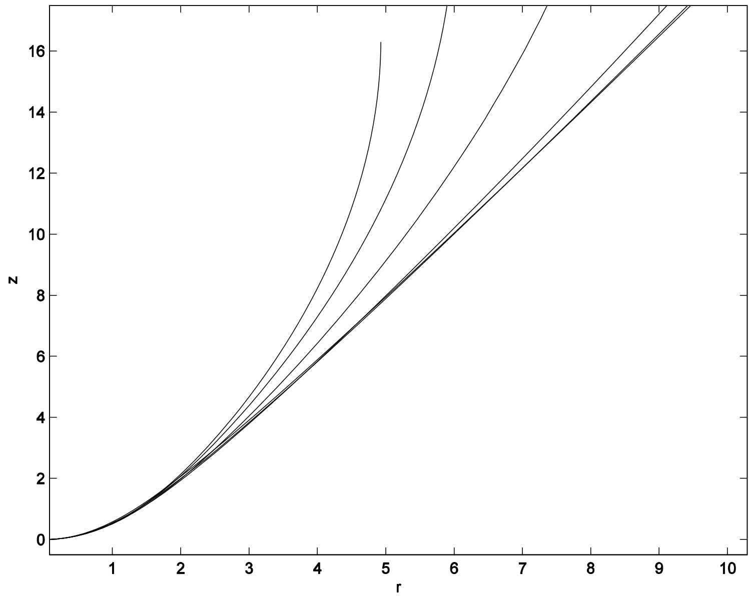
where

$$T^{(k)} = -PI + \mu_k \left(\nabla_\xi U + \nabla_\xi U^t\right) \ , \ k = 1, 2 \ .$$

and

$$\Sigma\left(\xi_1\right) = \left(\nabla_\xi \Phi \cdot \mathbf{n}_\xi\right)\left(\xi_1, f\left(\xi_1\right)\right)$$

Rescaled profiles

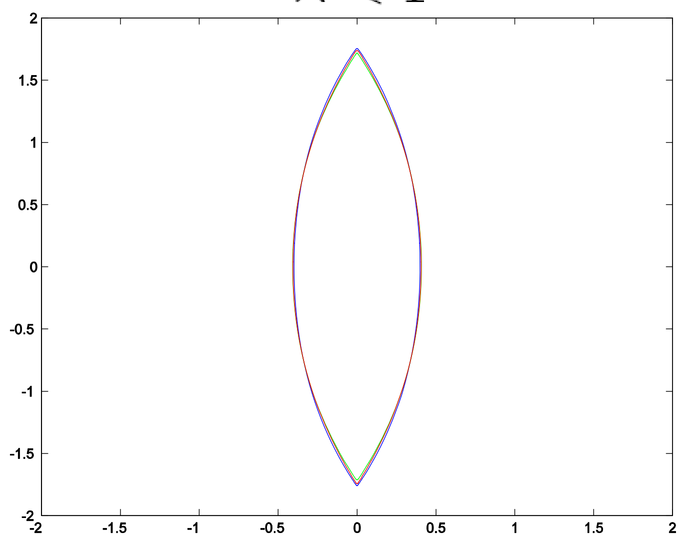


Cone semiangle approx. 30º

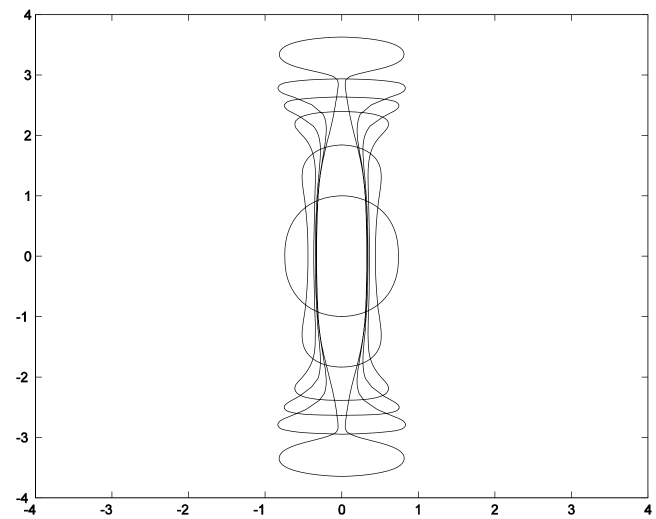
Taylor: 49.3º

$$\lambda \equiv \frac{\mu_2}{\mu_1} = 1$$

$\lambda < 1$



$\lambda > 1$



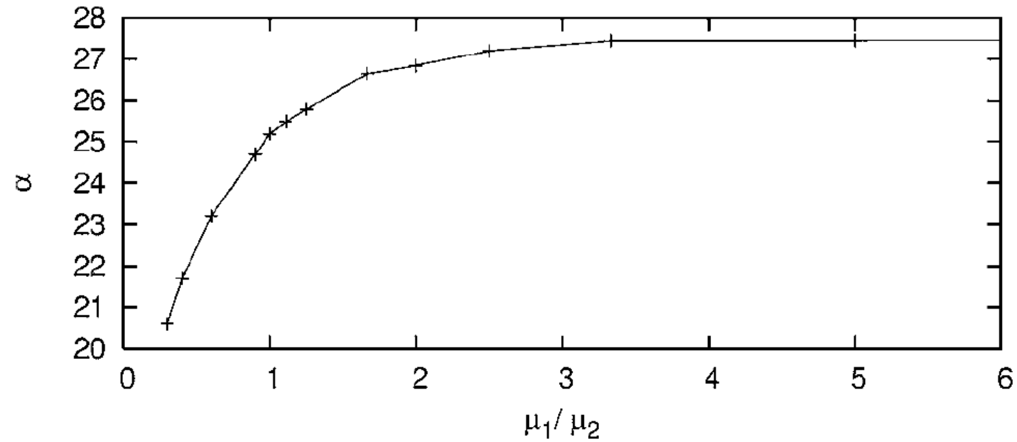


FIG. 4. Semiangle of the conical tips, as a function of the ratio of viscosities μ_1/μ_2.

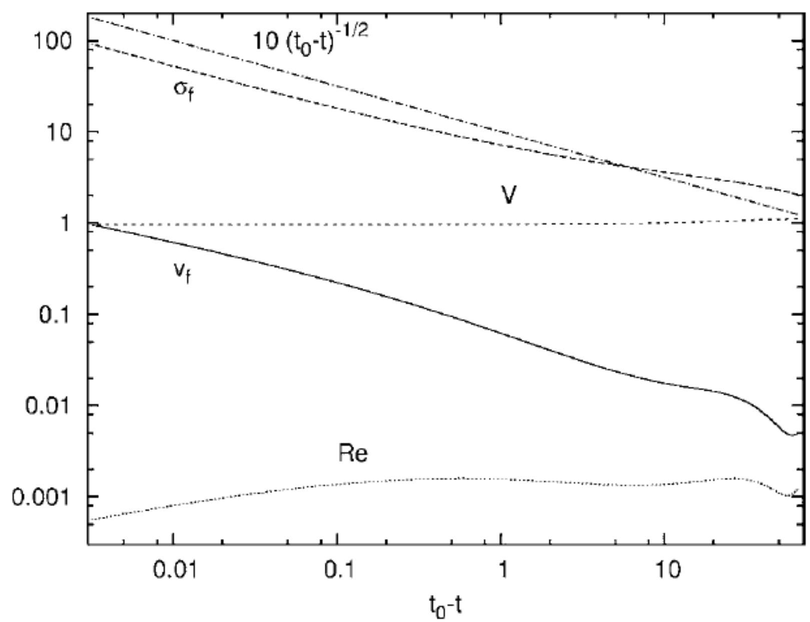
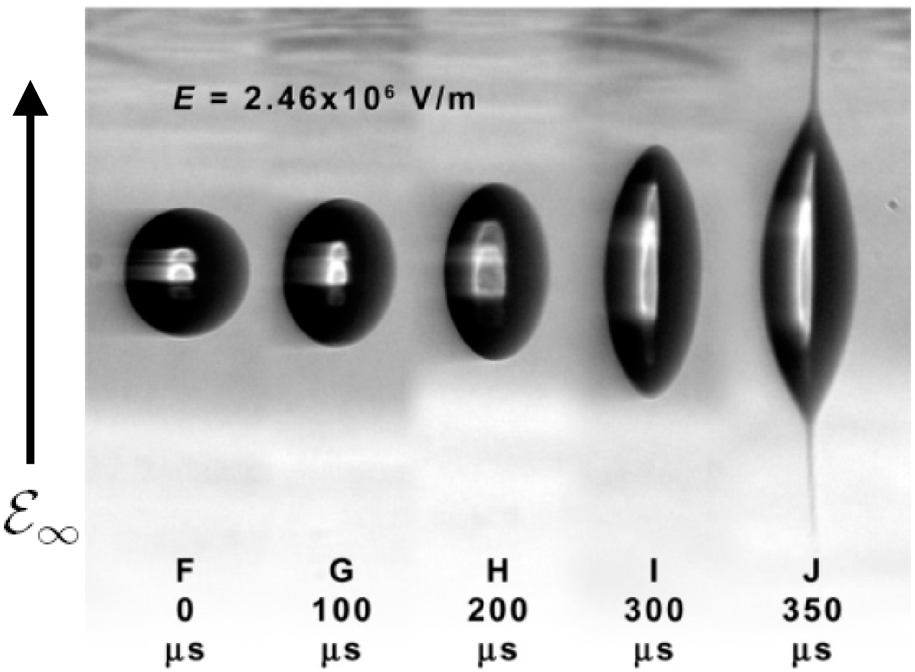


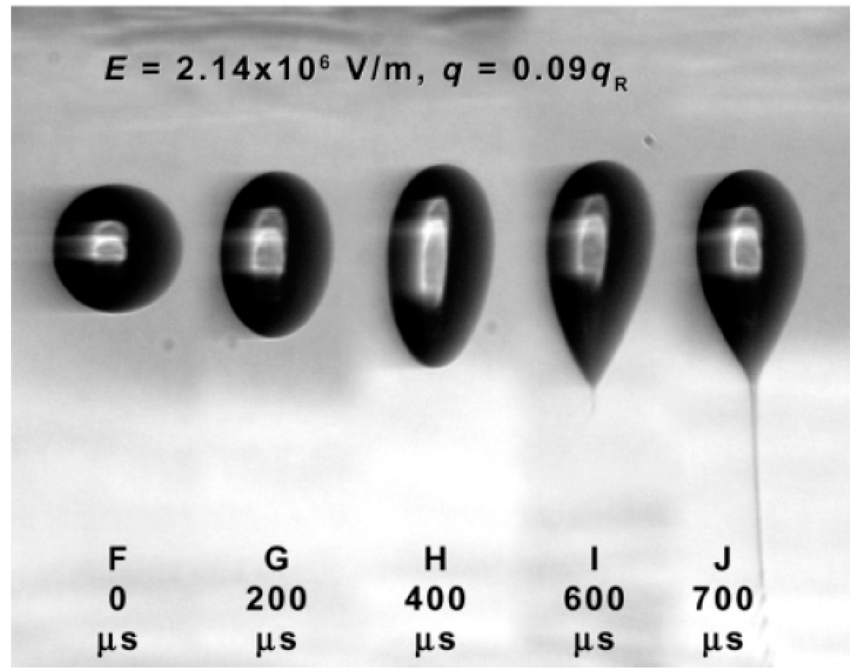
FIG. 3. Maximum charge density at the tip of the drop σ_f and fluid velocity at the tip v_f of droplets with critical charge, with ratios of viscosities μ_1/μ_2=1. The line on the top is a power law with exponent −1/2. The potential V and the Reynolds number Re are bounded during the evolution.

6. Drops in an electric field

Uncharged drop



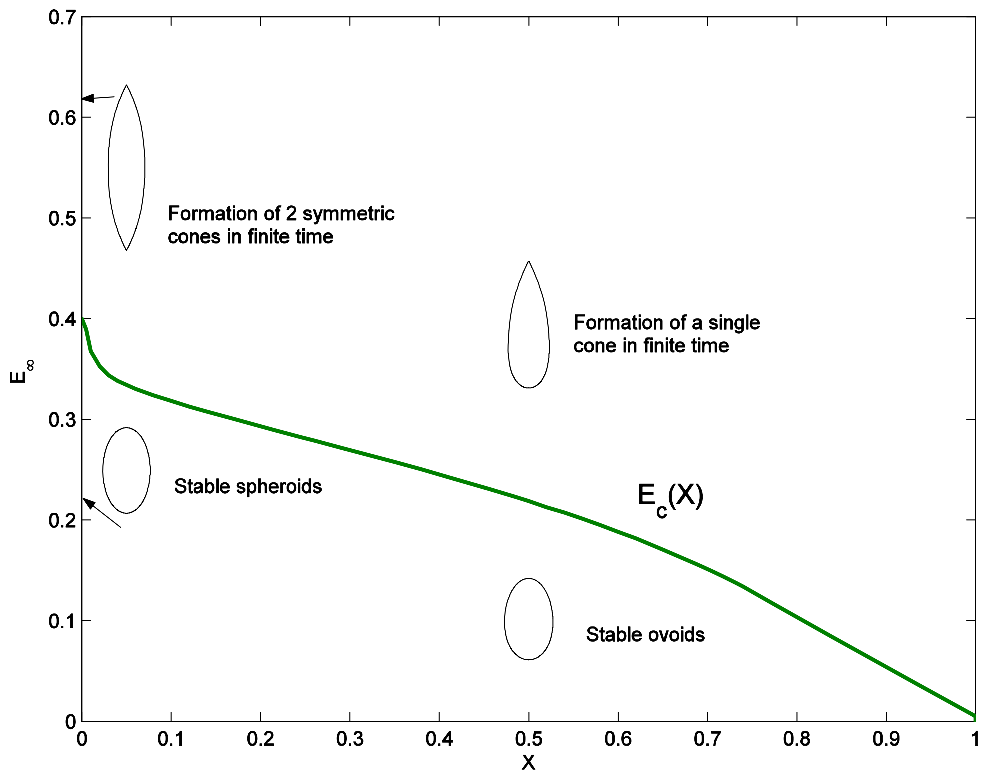
Charged drop



Grimm and Beauchamp, J. Phys. Chem. B **2005,** *109*, 8244-8250

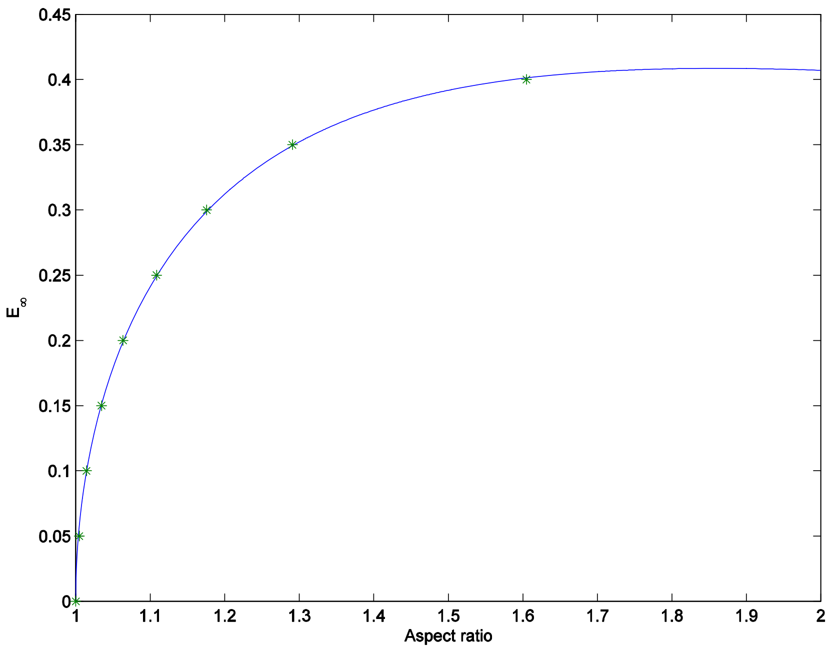
$$\boxed{X = \frac{Q^2}{24\gamma\pi\varepsilon_0 Vol.}} \quad \boxed{E_\infty = \sqrt{\frac{\varepsilon_0 Vol^{\frac{1}{3}}}{\gamma}}\mathcal{E}_\infty}$$

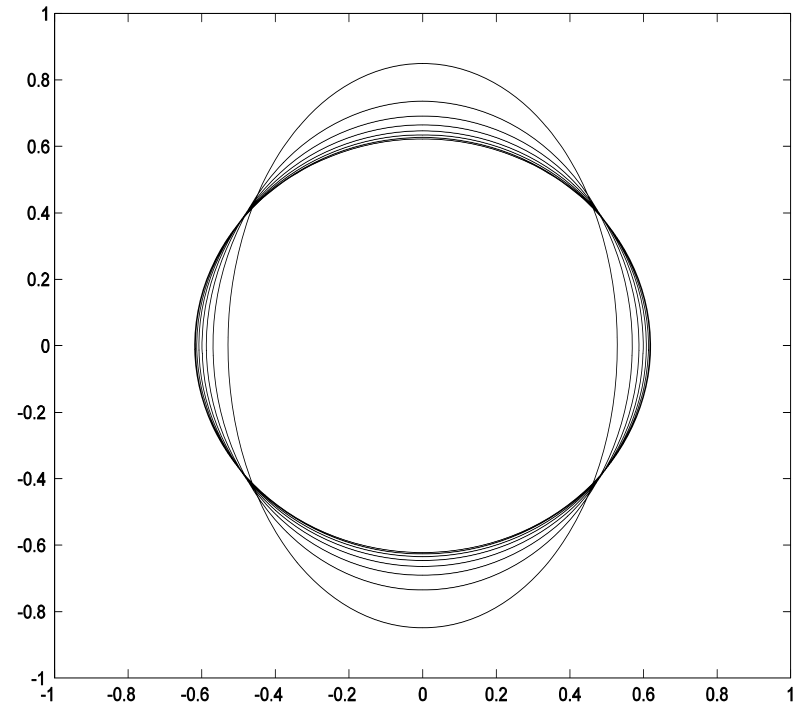
$$\mathcal{E}_\infty z_0 + V_0 = \frac{1}{4\pi\epsilon_0}\int_{\partial\Omega(t)} \frac{\sigma(\mathbf{r})}{|\mathbf{r} - \mathbf{r_0}|} dS(\mathbf{r})$$



Taylor 1964. Uncharged drops in an external electric field

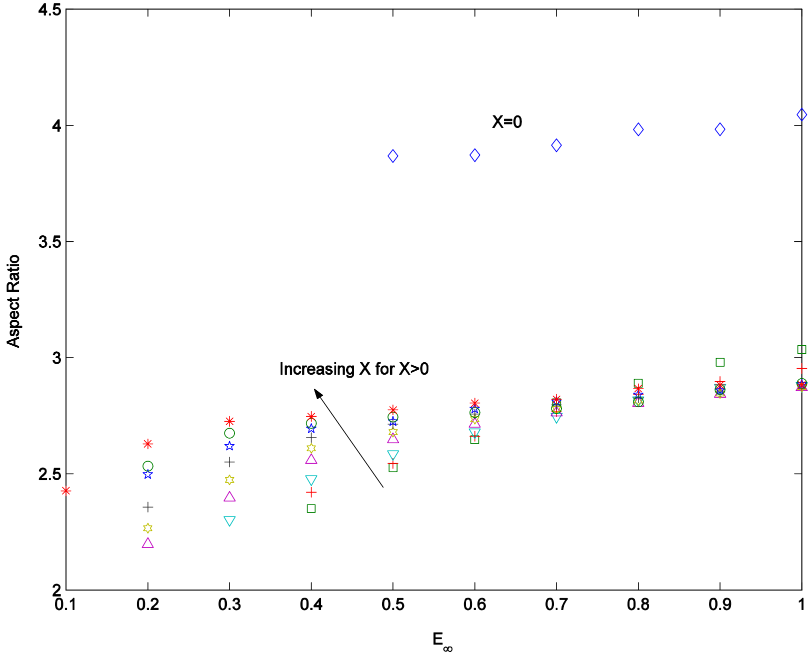
$$E_\infty(\gamma) = \left(\frac{4\pi}{3}\right)^{\frac{1}{6}} \gamma^{-\frac{4}{3}}(2-\gamma^{-3}-\gamma^{-1})^{\frac{1}{2}} \left[\frac{1}{2(1-\gamma^{-2})^{\frac{3}{2}}} \ln\left(\frac{1+(1-\gamma^{-2})^{\frac{1}{2}}}{1-(1-\gamma^{-2})^{\frac{1}{2}}}\right) - \frac{1}{1-\gamma^{-2}}\right]$$

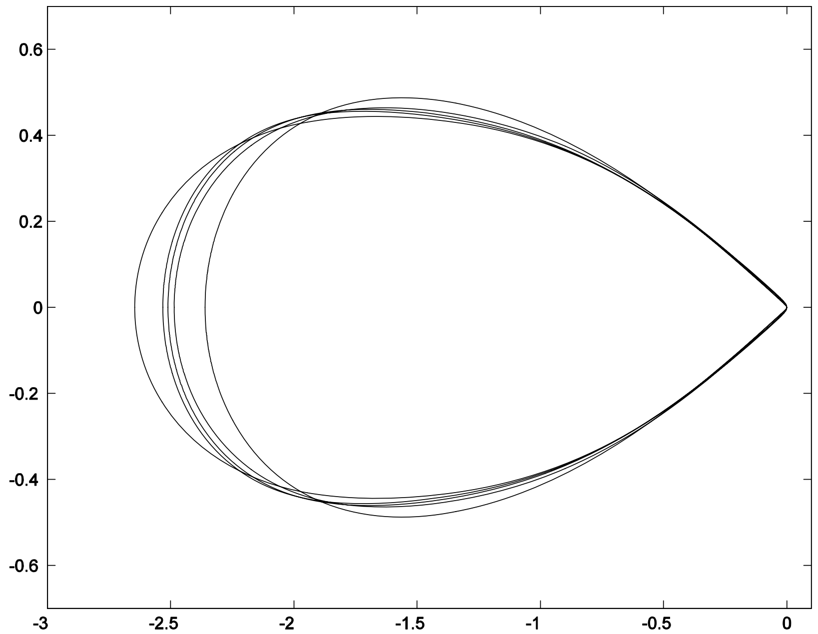




$$E_\infty < 0.409...$$

Unstable drops → Conical singularities





Aspect ratio

$$\lambda \equiv \frac{\mu_2}{\mu_1} = 2.5$$

$(X, E_\infty) = (0.2, 0.4), (0.3, 0.6), (0.7, 0.5), (0.9, 0.5), (0.1, 0.9)$

Semiangle 27.5º ± 1.1º

Flow and potential in cones

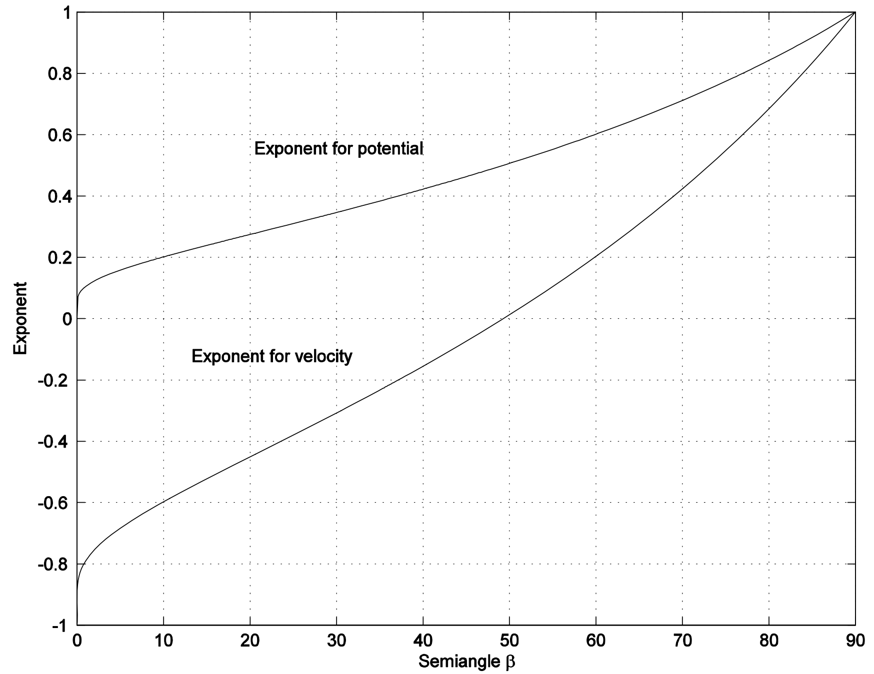
$$\mathbf{u} = a\nabla\Psi + b\left(\nabla(z\Lambda) - 2\Lambda\mathbf{e}_z\right)$$
$$p = 2b\frac{\partial\Lambda}{\partial z}\ ,$$

$\Rightarrow$

$$\Psi = r^{\lambda+1}P_{\lambda+1}(\cos\theta)$$
$$\Lambda = r^{\lambda}P_{\lambda}(\cos\theta)$$

Balance between normal stress and electrostatic forces $\Rightarrow$ $V = r^{\frac{\lambda+1}{2}}P_{\frac{\lambda+1}{2}}(\cos\theta)$

No tangential component of electric field $\Rightarrow$ $P_{\frac{\lambda+1}{2}}(\cos\alpha) = 0$



Zero shear Stress $\Rightarrow$

- Relationship between a and b

OR

- $\begin{pmatrix} u_r \\ u_\theta \end{pmatrix} = r^{-1} \begin{pmatrix} C\cos\theta \\ -\frac{C}{2}\sin\theta \end{pmatrix}$ with $p = C\frac{\cos\theta}{r^2}$

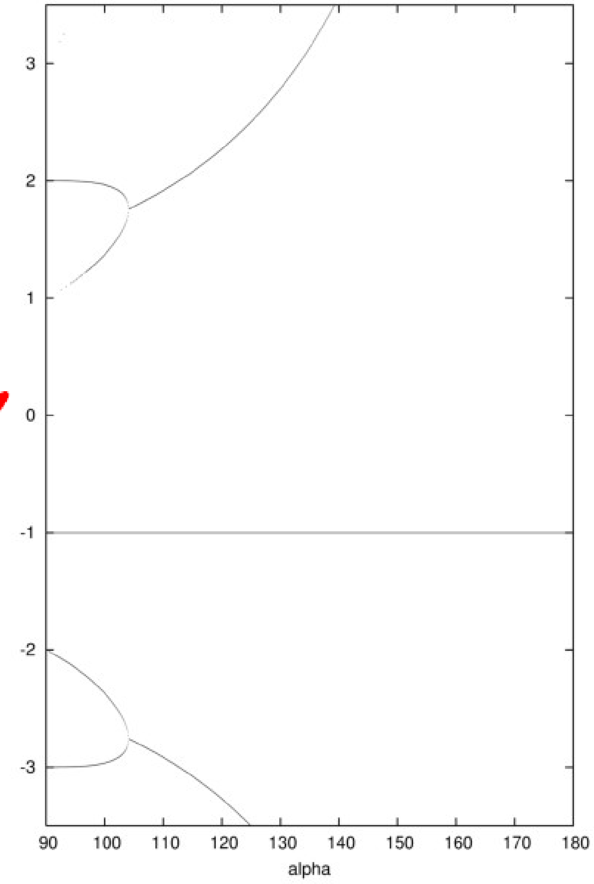
Solutions with zero stress

$$\vec{u} = r^{\nu}\vec{f}(\theta)$$

General solution:

$$\vec{u} = r^{\lambda}\vec{g}(\theta) + A(t)r^{-1}\vec{f}(\theta) + \ldots$$

ν



$$\boxed{\mathbf{r}_t = \mathbf{v} \sim C r^{\lambda} \quad \Rightarrow \quad r \sim \tau^{\alpha} \quad with \quad \tau = t_0 - t}$$

$$\alpha = \frac{1}{1-\lambda} \text{ or } \alpha = \frac{1}{2}$$

Two possible singular behaviours:

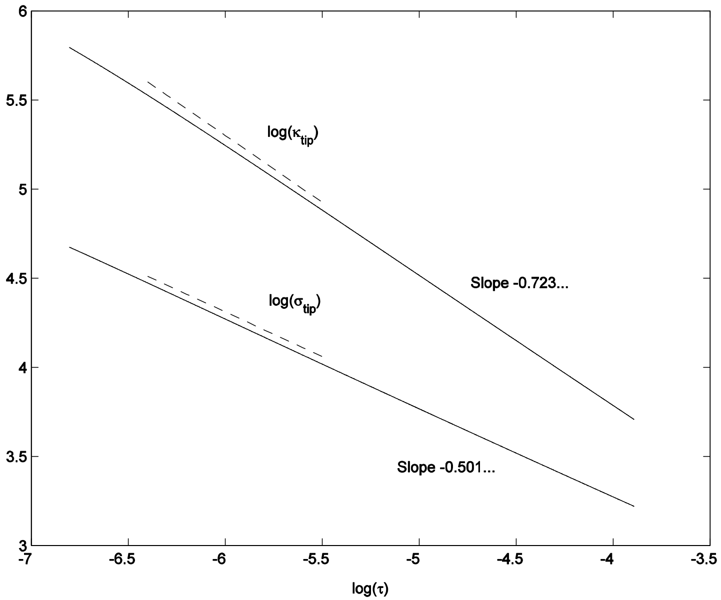
$$\kappa_{tip} = O(\tau^{-\alpha}) \ , \ \sigma_{tip} = O(\tau^{-\frac{1}{2}}) \ , \ v_{z,tip} = O(\tau^{\alpha-1})$$ Under external field

$$\kappa_{tip} = O(\tau^{-\frac{1}{2}}) \ , \ \sigma_{tip} = O(\tau^{-\frac{1}{2}}) \ , \ v_{z,tip} = O(\tau^{-\frac{1}{2}})$$ No external field

The 1/r solution for the velocity is only possible for drops that are symmetric wrt the equatorial plane so that the stress field behaves decays at infinity faster than $1/r^2$.

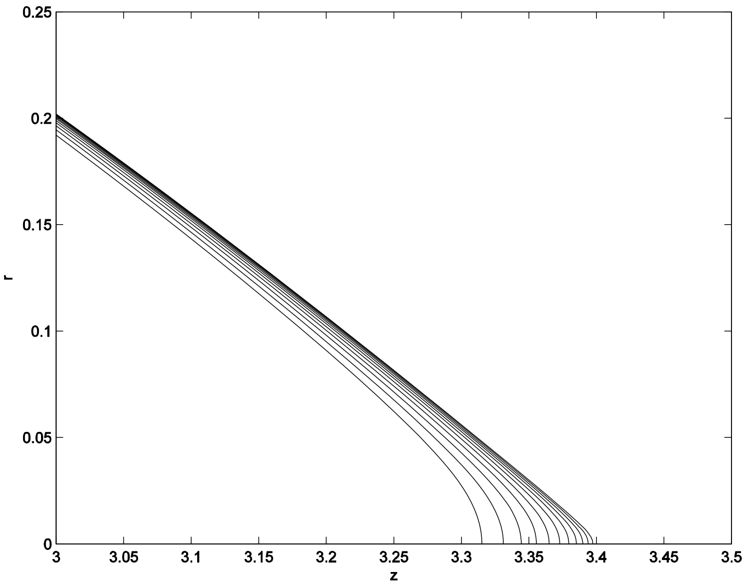
Selfsimilarity:

$$\mathbf{r} = \tau^{\alpha}\xi \qquad \mathbf{u}(\mathbf{r}, t) = \tau^{\alpha-1}\mathbf{U}(\xi) \qquad p = \tau^{-2}P(\xi) \qquad V(\mathbf{r}, t) = \tau^{\alpha-\frac{1}{2}}\Phi(\xi)$$

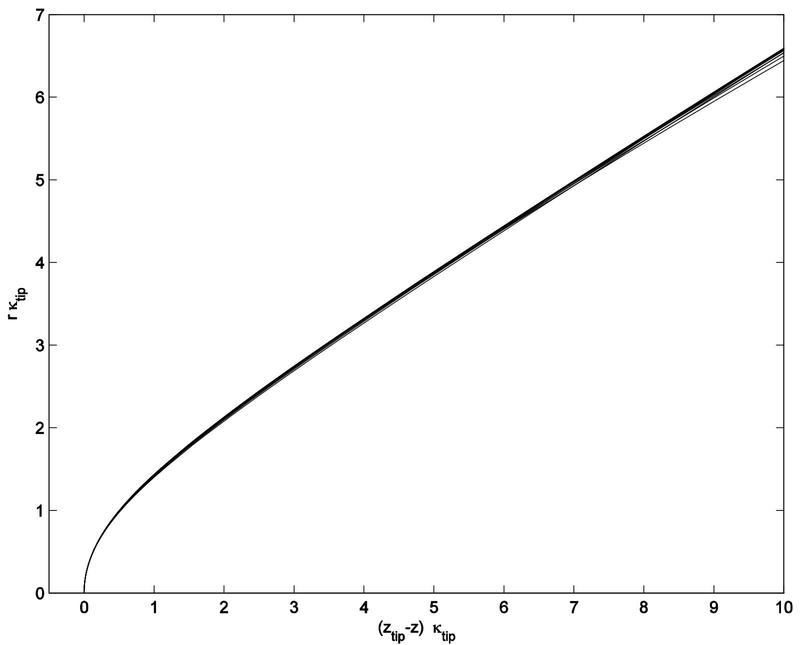


The theoretical slopes are -0.74 and -0.5

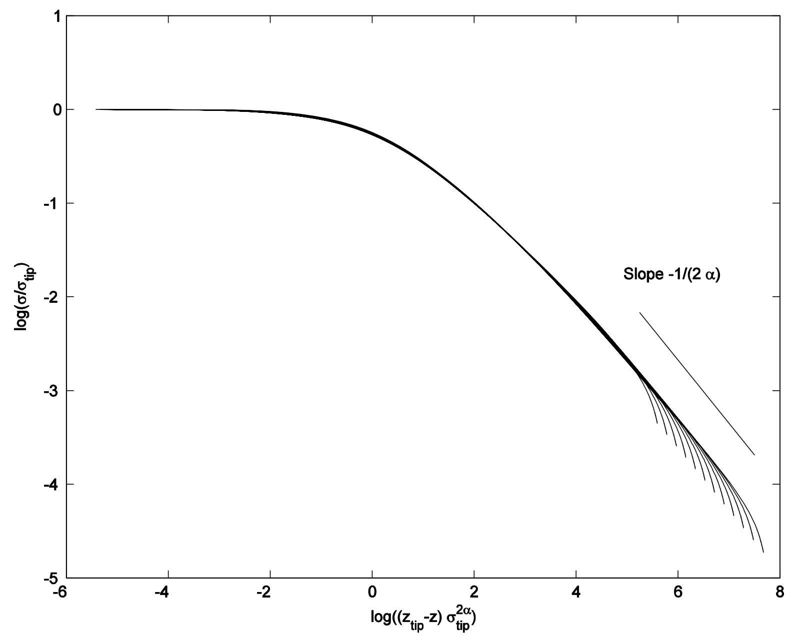
Drop's profiles near the tip



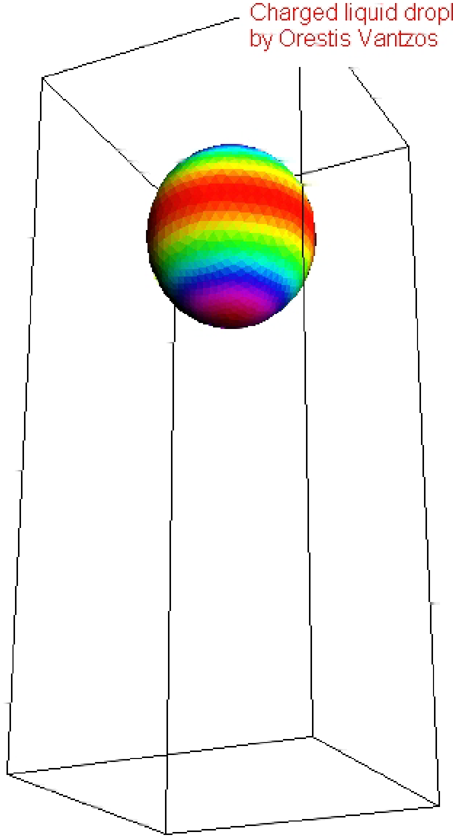
Rescaled drop's profiles near the tip



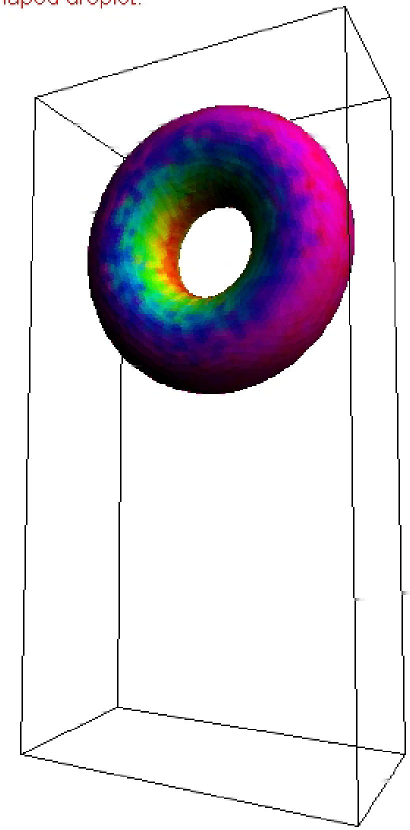
Rescaled surface charge profiles



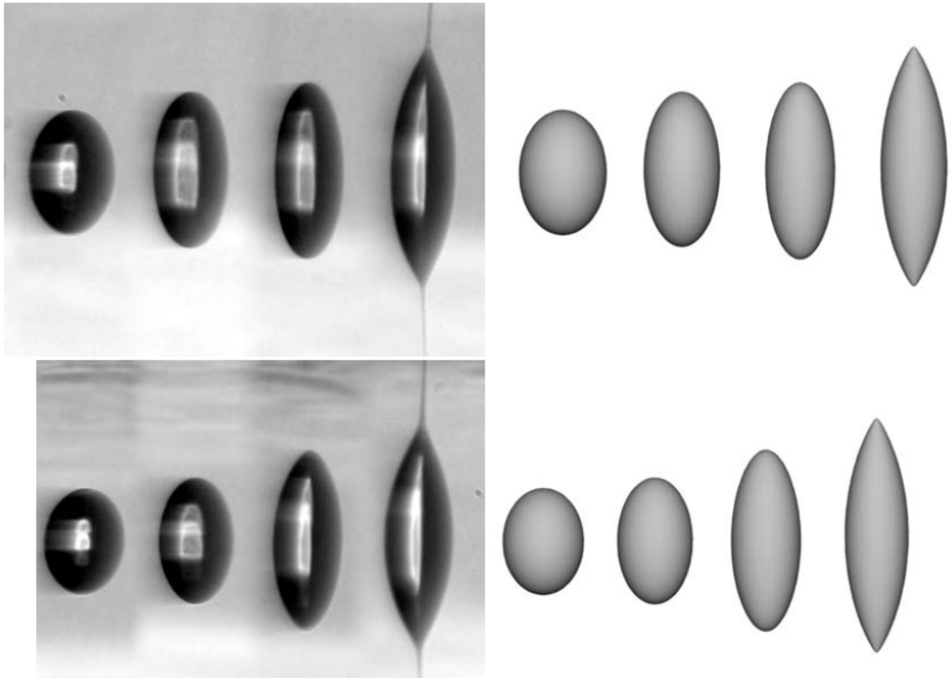
Charged liquid droplet forms a singularity
by Orestis Vantzos



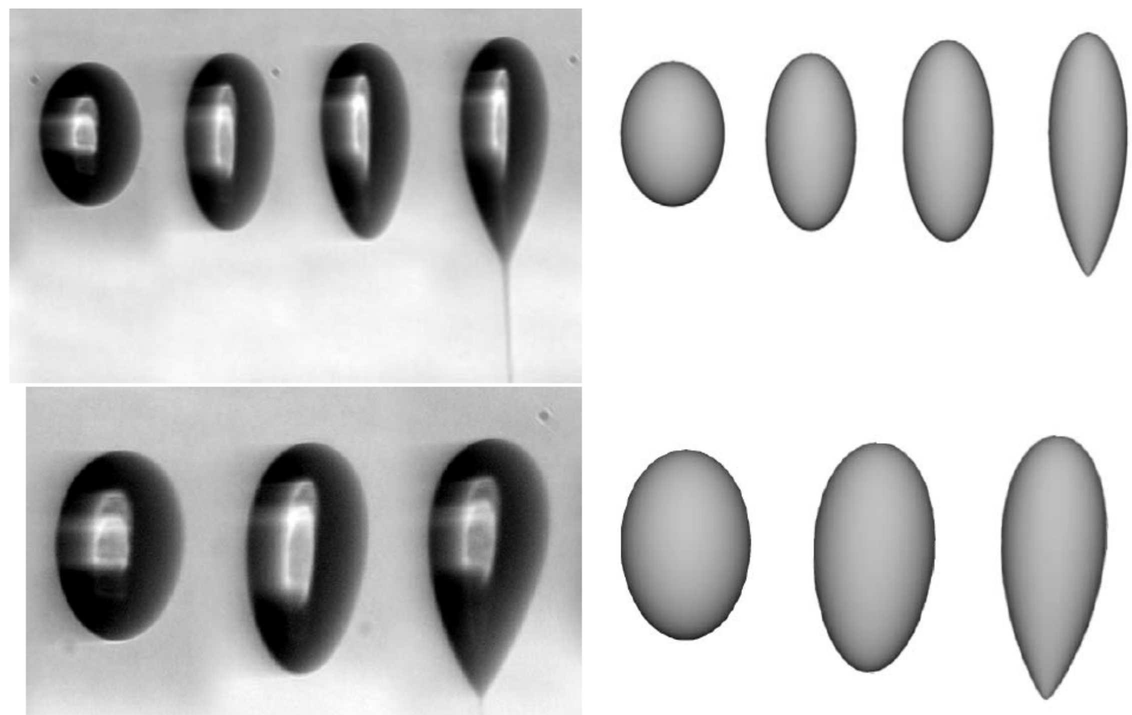
Evolution of a torus shaped droplet.
by Orestis Vantzos



Comparison with Grimm and Beauchamp's experiments

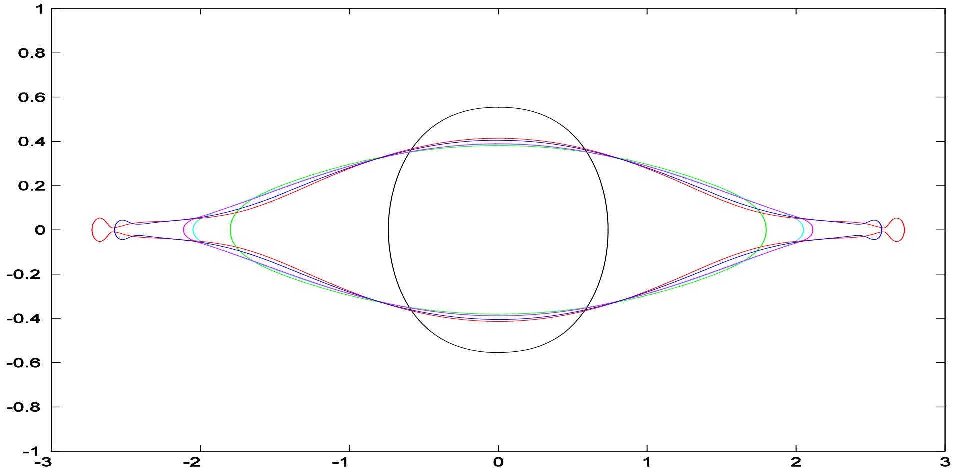


Uncharged



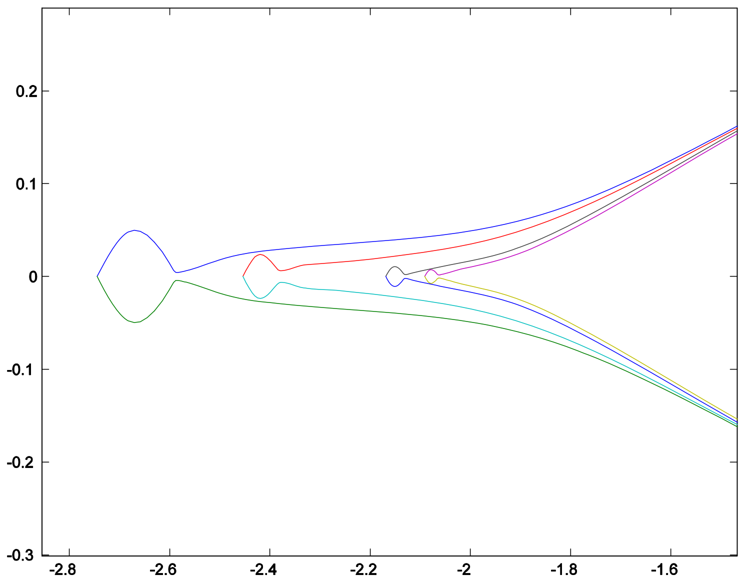
Charged

Model finite conductivity



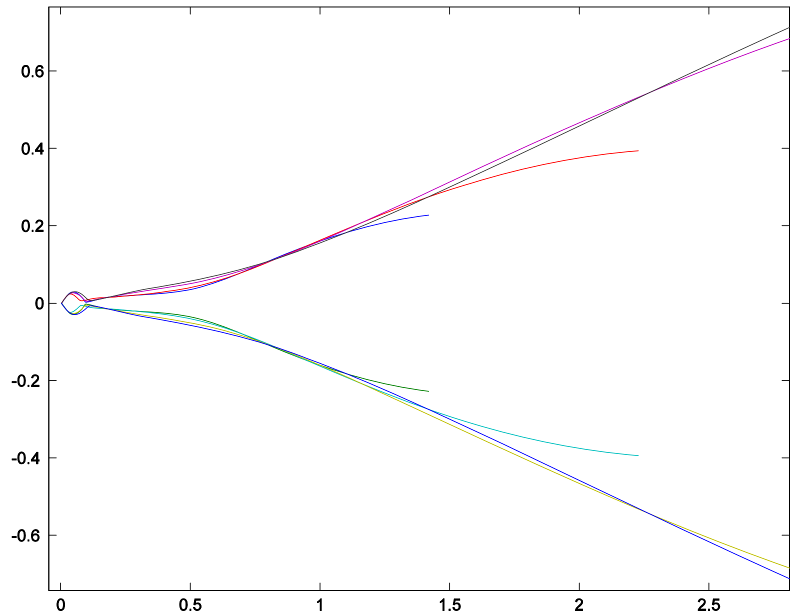
Conductivity restricted to the surface

$$\boxed{\frac{d\sigma}{dt} = \nabla_s \bullet \left(-K\nabla_s V + D\nabla_s \sigma\right)}$$

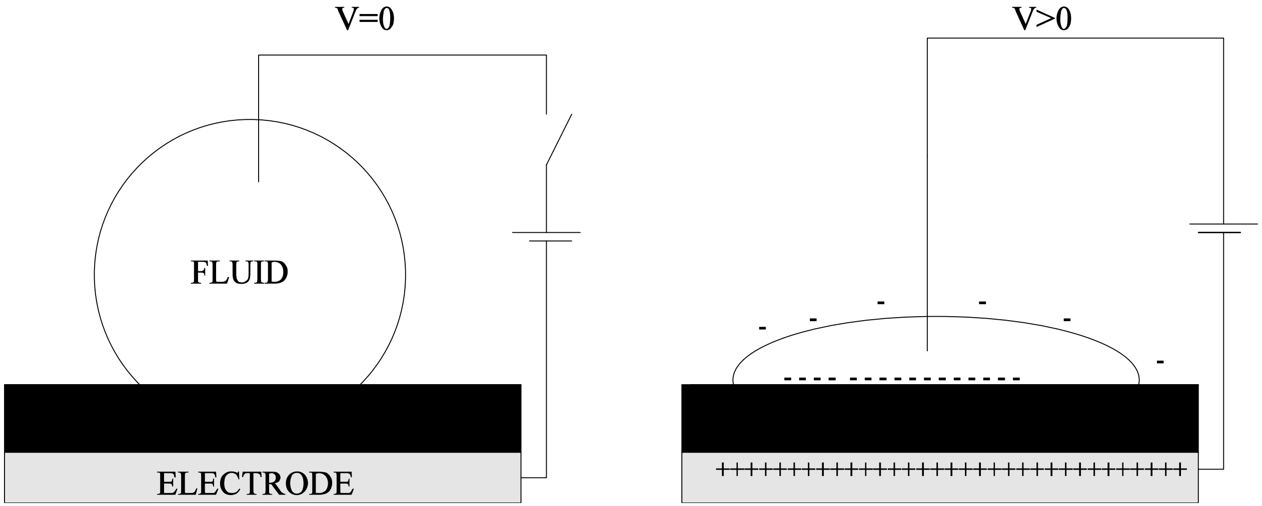


Profiles for several different “surface” conductivities

Rescales profiles

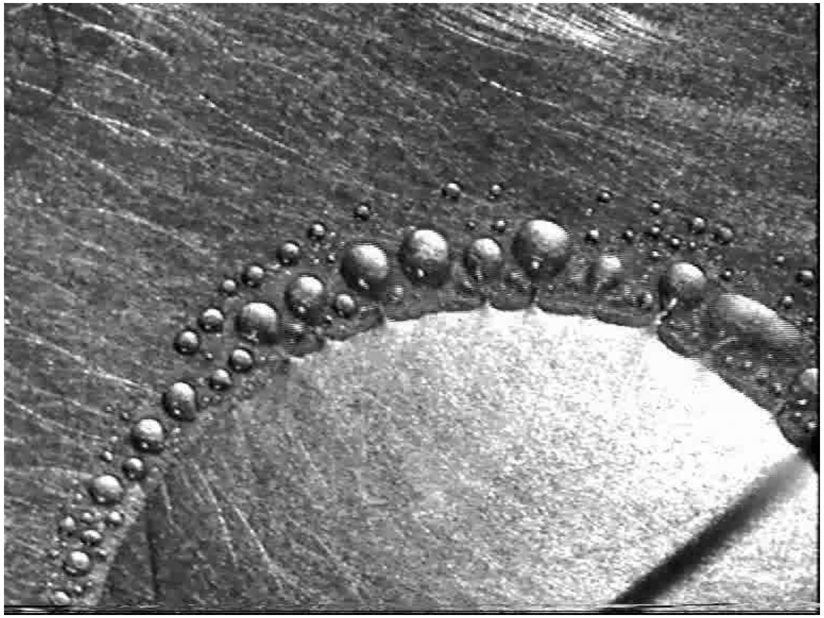


6. Drops on a solid



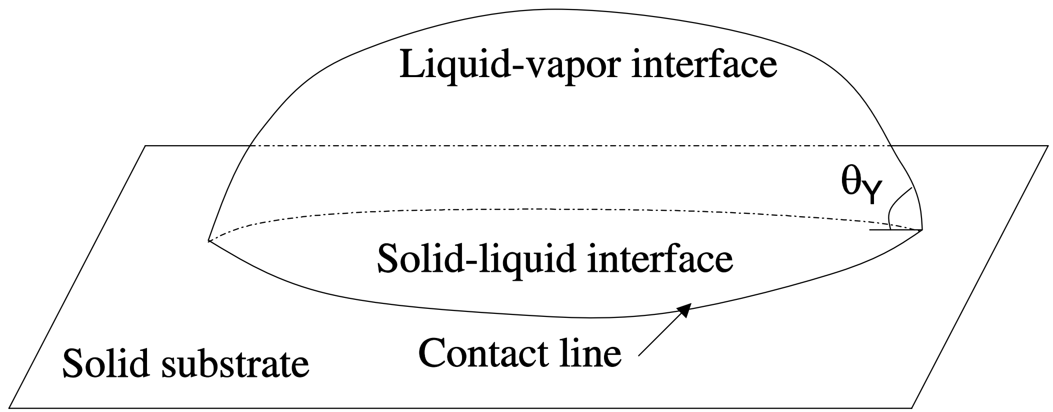
Lippmann effect (1875)

Electrowetting applications



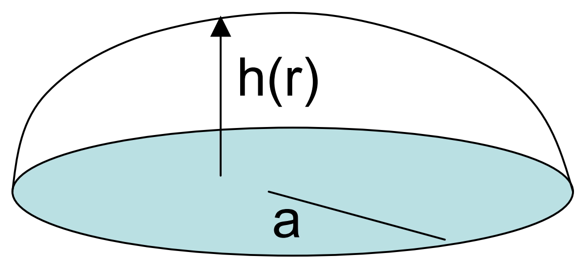
(Movie from F. Mugele)

$$E = [A_{lv} - (\cos\theta_Y)A_{sl}] - \frac{1}{2}CV_0^2$$



$$C = \int_{\mathbb{R}^3 \setminus \Omega_0} |\nabla V|^2 \, d\mathbf{x} \ .$$ with V=1 at the surface

While the area of a body can be easily evaluated, capacity is not easy to compute or even estimate in general.

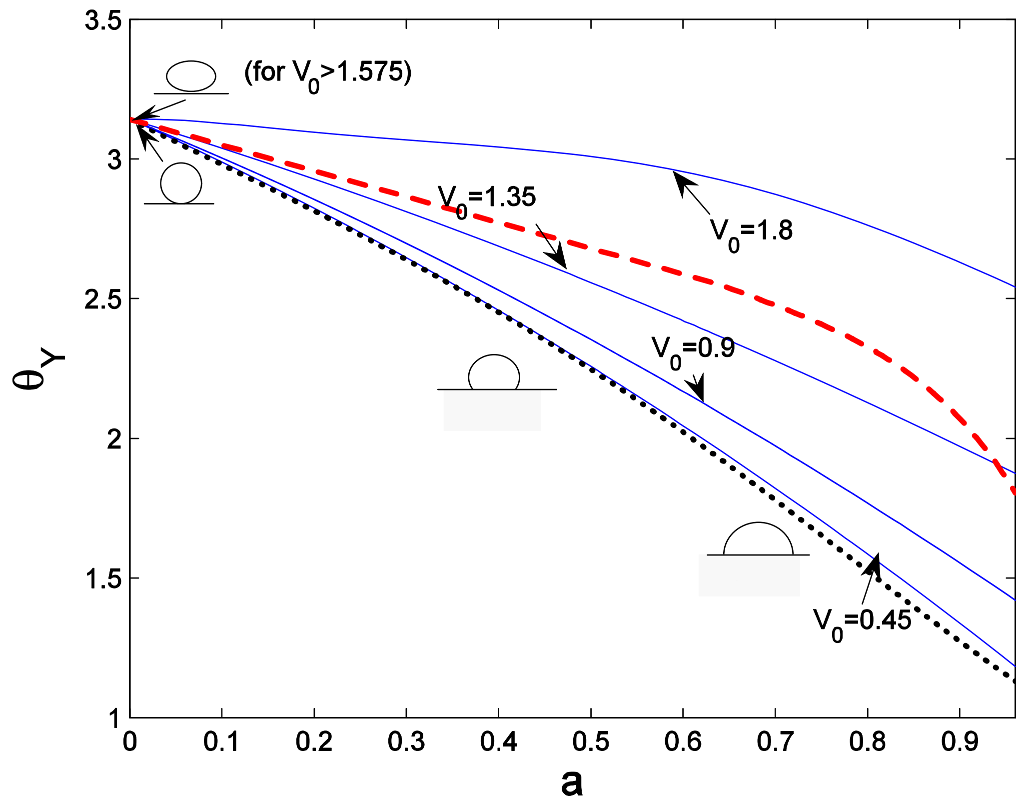


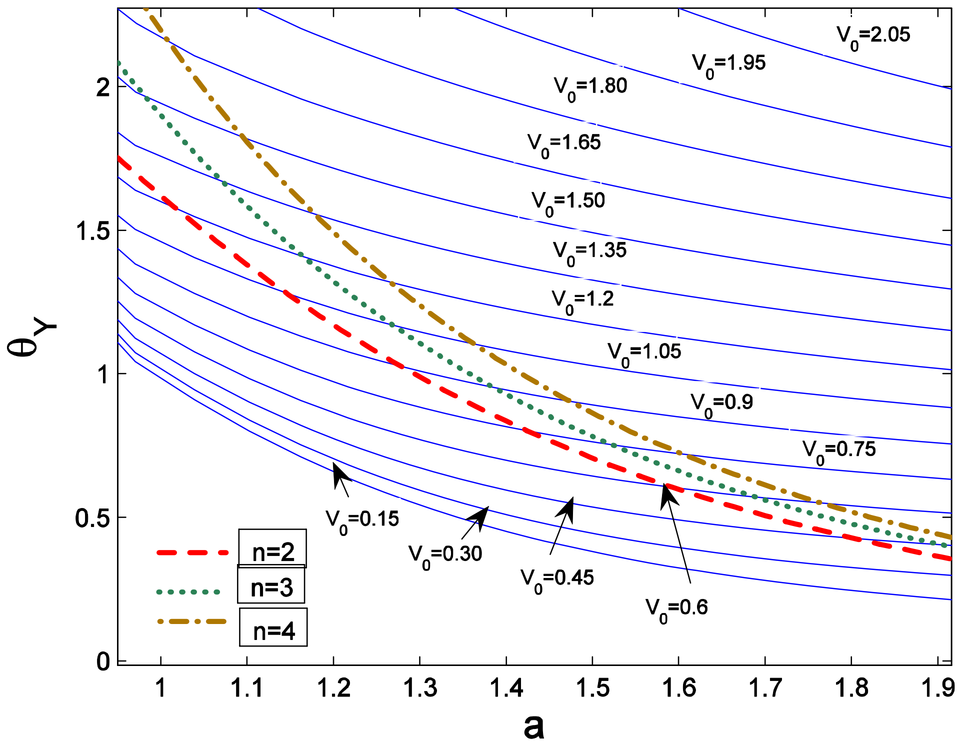
Nonlocal

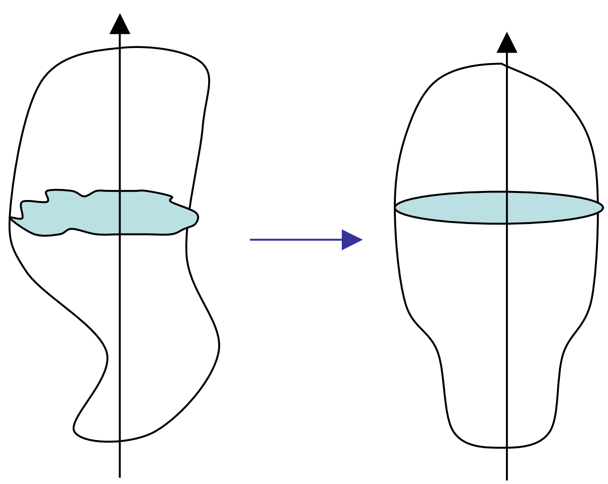
$$\gamma\kappa - \frac{\sigma^2}{2\varepsilon_0} = -p$$

Second order in h

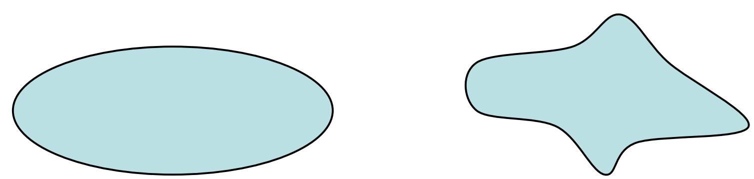
h(a)=0, h'(a)=-tan(θ_Y)







Schwarz symmetrization decreases capacity.



$C_0 \quad < \quad C_n$

Solutions non-axially symmetric are preferred if the body is suf. flat

CONCLUSIONS

• There is evidence of finite time singularities on electrically charged drops which are different to the classical Taylor's cone singularity.

• In the 3D simulation the global shape near the singularity is still axially symmetrical at the time of singularity formation.

• The formation of singularities does not appear to be restricted to circularly symmetric flows. We found that they can also appear in asymmetric configurations. In all cases they have the same shape pointing to selfsimilarity and universality. These features are still correct under the efect of a constant external electric field.

• Sufficiently flat axisymmetric drops on a solid are not stable and the instability may lead to non-axisymmetric configurations or to singularities.