ELECTROFORMATION PHENOMENA INDUCED BY THE ELECTRICAL GIBBS FUNCTION

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Introduction

1. **Introduction**

Talk topic is electroformation – also called thermal-field (TF) shaping. [Also forms part of electrohydrodynamics.]

Effect occurs both with liquids and solids.
Effect occurs both on macroscopic scale and at atomic level.

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Effect occurs both on macroscopic scale and at atomic level.

Examples are:

- Liquid metal ion source, electrospraying, mercury arc rectifier;
- Field-induced growth of whiskers and nanoprotrusions;
- Reconstruction effects, as observed by field electron microscopy (FEM) and by field ion microscopy (FIM);
- TF-migration of partial-ions on charged surfaces, as seen by FIM.

Introduction

Introduction (cont.)

My perception is that common physics underlies all these effects.

They are all driven by a thermodynamic potential I call the electrical Gibbs function (G^{el}) in which an electrical capacitance term plays a vital role.

A thermodynamic approach provides unifying theory, and could also be a source of interesting analogies.

At present, this topic does not normally appear in textbooks, and there are no review articles. Aim of this talk is to

- introduce relevant theoretical ideas
- discuss a phenomenon that occurs in cone-jet theory and seems to have wider implications

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Talk structure

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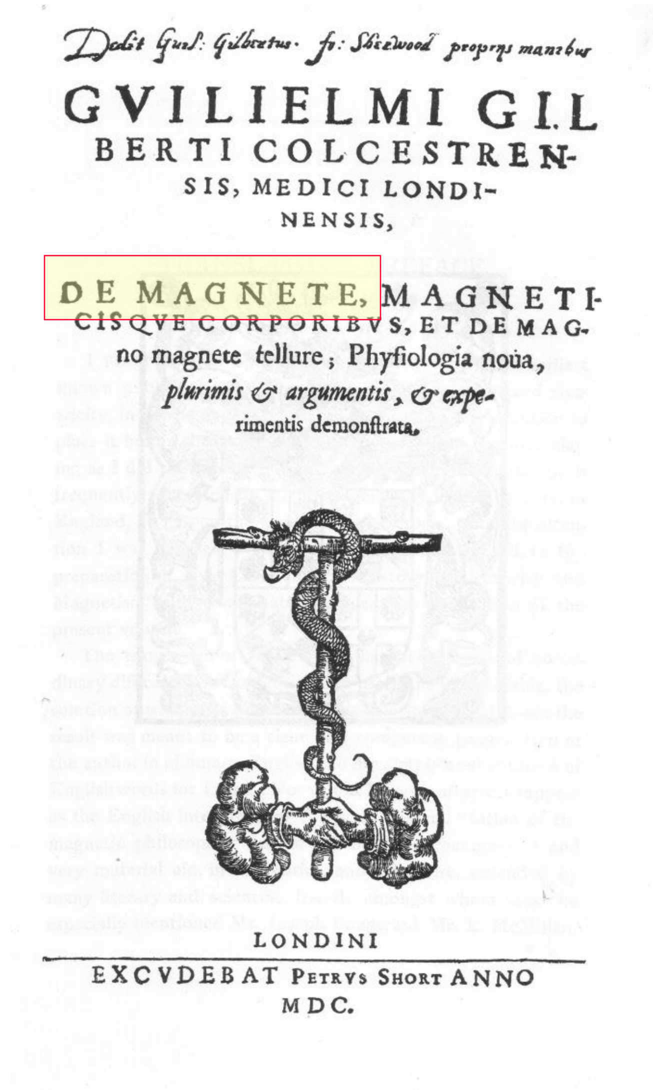
1. Introduction
2. Basic history of cone-jet phenomena
3. Definitions and some basic theoretical results
4. Cone-jet behaviour & its implications
5. Atomic-level effects
6. Some miscellaneous effects
7. Conclusions

Basic history of cone-jet phenomena

[Apologies if you have seen these slides before]

Effect of electric fields on conducting liquids

The first person to report relevant work was GILBERT in 1600 in his book *De Magnete*



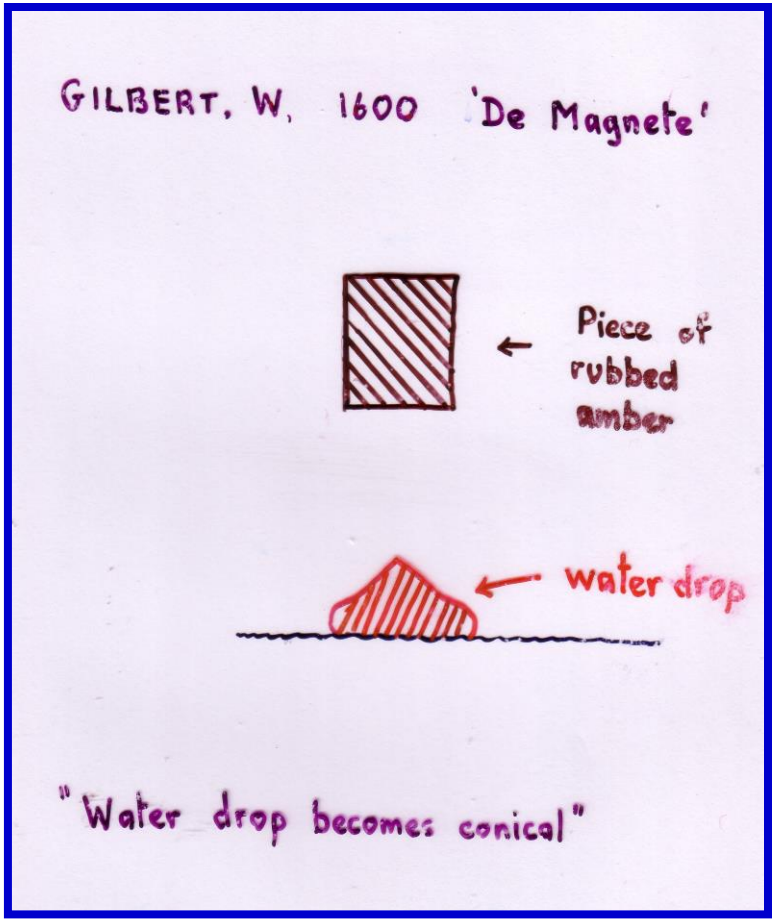
Dedit Gul: Gilbertus. fr: Sherwood proprijs manibus

GVILIELMI GIL
BERTI COLCESTREN-
SIS, MEDICI LONDI-
NENSIS,

DE MAGNETE, MAGNETI-
CISQVE CORPORIBVS, ET DE MAG-
no magnete tellure; Physiologia noua,
*plurimis & argumentis, & expe-
rimentis demonstrata.*

LONDINI
EXCVDEBAT PETRVS SHORT ANNO
MDC.

First known experiment (1600) on "Taylor" cones



Gilbert wrote (1600):

"..Hence it is probable that amber exhales something peculiar that attracts the bodies themselves, and not the air. It plainly attracts the body itself in the case of a spherical drop of water standing on a dry surface, for a piece of amber held at a suitable distance pulls towards itself the nearest particles and draws them up into a cone; were they drawn by the air the whole drop would come towards the amber..."

Stephen Gray's experiments (1732) – I

about an Inch or more. If it be a large Tube, there will firſt ariſe a little Mountain of Water from the Top of the Drop, of a conical Form, from the Vertex of which there proceeds a Light (very viſible when the Experiment is performed in a dark Room) and a ſnapping Noiſe, almoſt like that when the Fingers are held near the Tube, but not quite ſo loud, and of a more flat Sound: Upon this immediately the Mountain, if I may ſo call it, falls into the reſt of the Water, and puts it into a tremulous and waving Motion. I have now a few Days ſince repeated this Experiment in the Day-time, where the Sun ſhined: I perceived that there were ſmall Particles of Water thrown out of the Top of the Mount, and that ſometimes there would ariſe a very fine Stream of Water from the Vertex of the Cone, in the manner of a Fountain, from which there iſſued a fine Steam, or Vapour, whoſe Particles were ſo ſmall as not to be ſeen; yet it is certain that it muſt be ſo, ſince the under Side of the Tube was wet, as I found when I came to rub the Tube again;

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Stephen Gray's experiments (1732) – II

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ADDENDA Page 230.

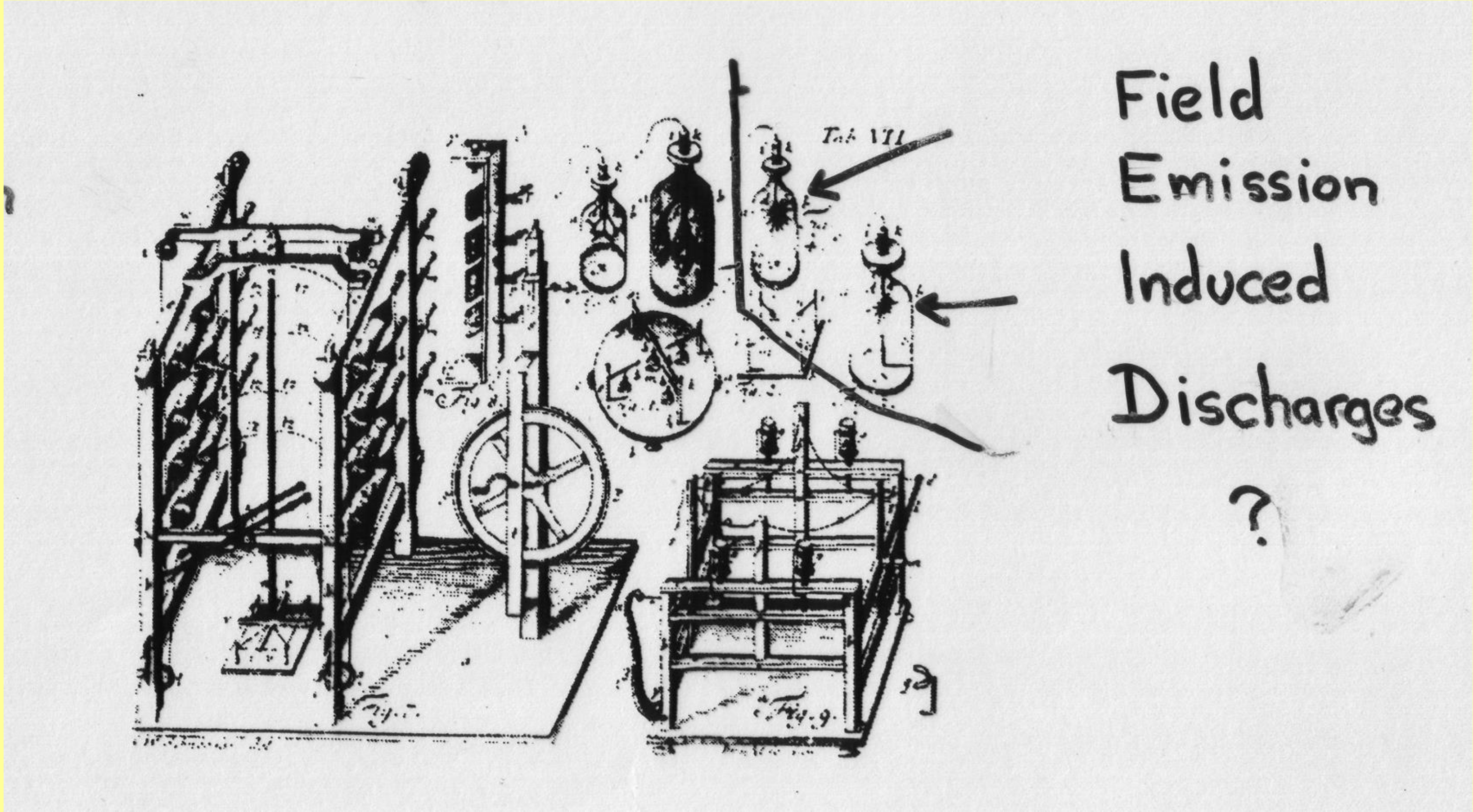
THE laſt Experiment was repeated with hot Water; when the Water was attracted much ſtronger, and at a much greater Diſtance: The Steam ariſing from the Vertex was in this Caſe viſible, and the Tube was ſprinkled with large Drops of Water. I tried the Experiment in the ſame Manner upon Quickſilver, which was likewiſe raiſed up; but by reaſon of its great Weight, not to ſo great an Height as the Water: The ſnapping Noiſe was louder, and laſted much longer than in the Water.

S. Gray, *Phil. Trans. (1683-1775) R. Soc. Lond.* 37, 227-230 & 260 (1732/33).

[available on line via JSTOR]

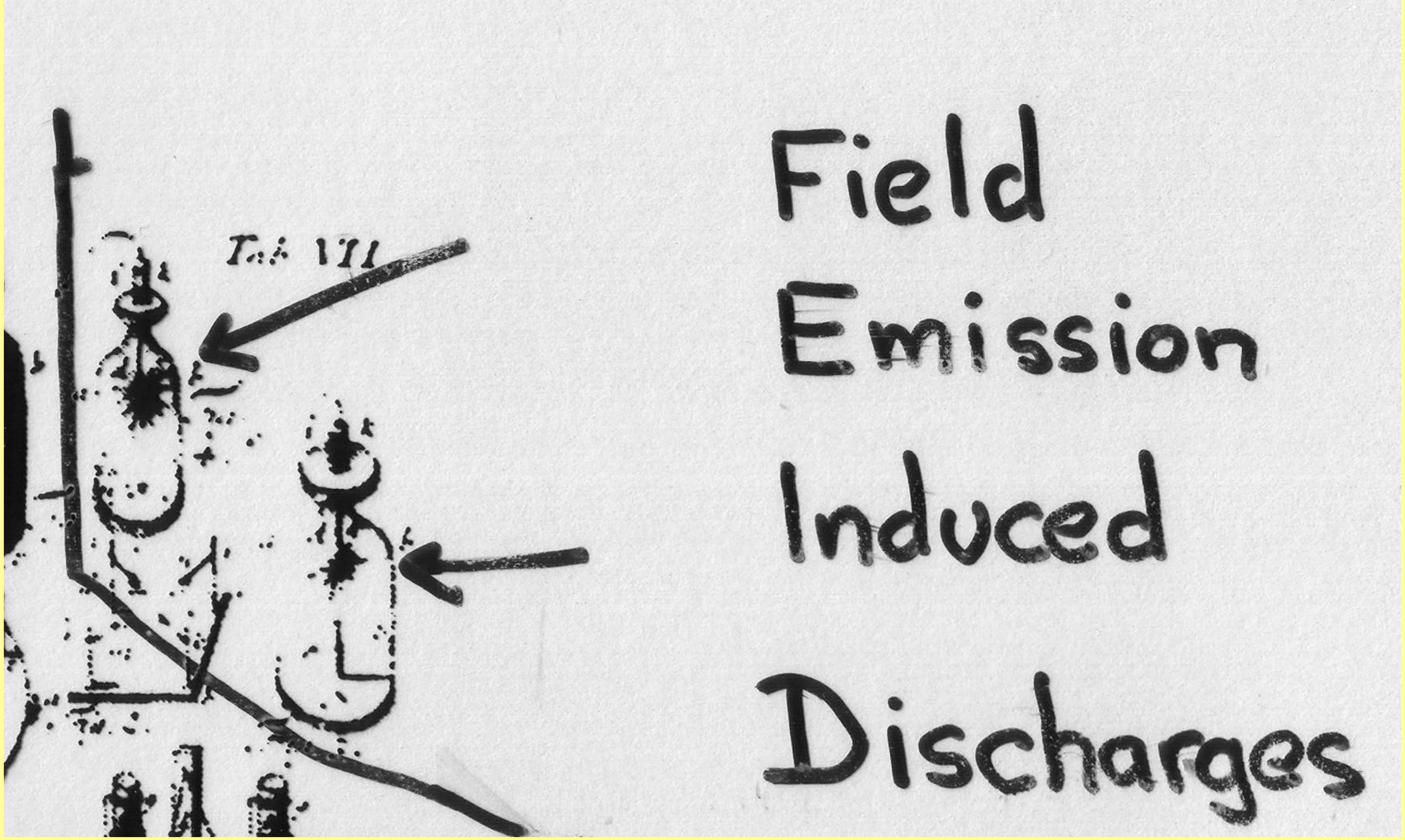
Vacuum breakdown - early report (1744)

A gas discharge (apparently induced by field electron emission) was first reported by Winkler, in 1744-5.



Vacuum breakdown - early report (1744)

The glass bottles contain pointed needles attached to a source of electricity



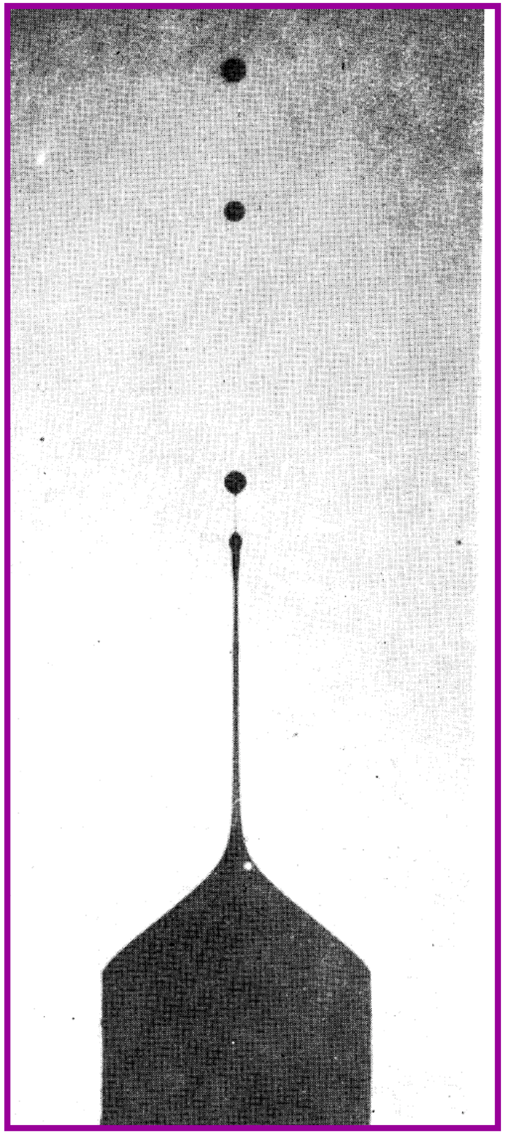
1730 to 1880

Five events worth noticing for present purposes:

- **Priestley (and several other European authors) wrote textbooks on electricity.**
- **"Electric fountains" became features in public scientific lectures.**

  ["They were popular, especially with children, because they sprayed water and glowed in the dark."]
- **Someone noticed that raindrops developed conical ends when subject to electric fields.**
- **Laplace developed a force-based theory of surface tension (1806), that yielded the formula $\Delta p = 2T/r$.**
- **Gibbs created thermodynamics (1875), which included a “thermodynamic” proof of the surface tension formula.**

Experimentally observed cone-jets



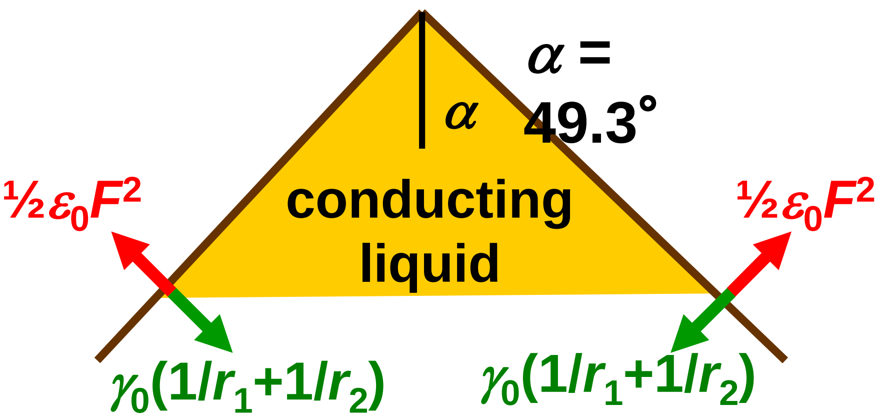
Field-induced water jet
Courtesy Taylor 1969

The mathematical Taylor cone

$$\tfrac{1}{2}\,\varepsilon_0 F^2 \;=\; \gamma^0\,(1/r_1 + 1/r_2)$$

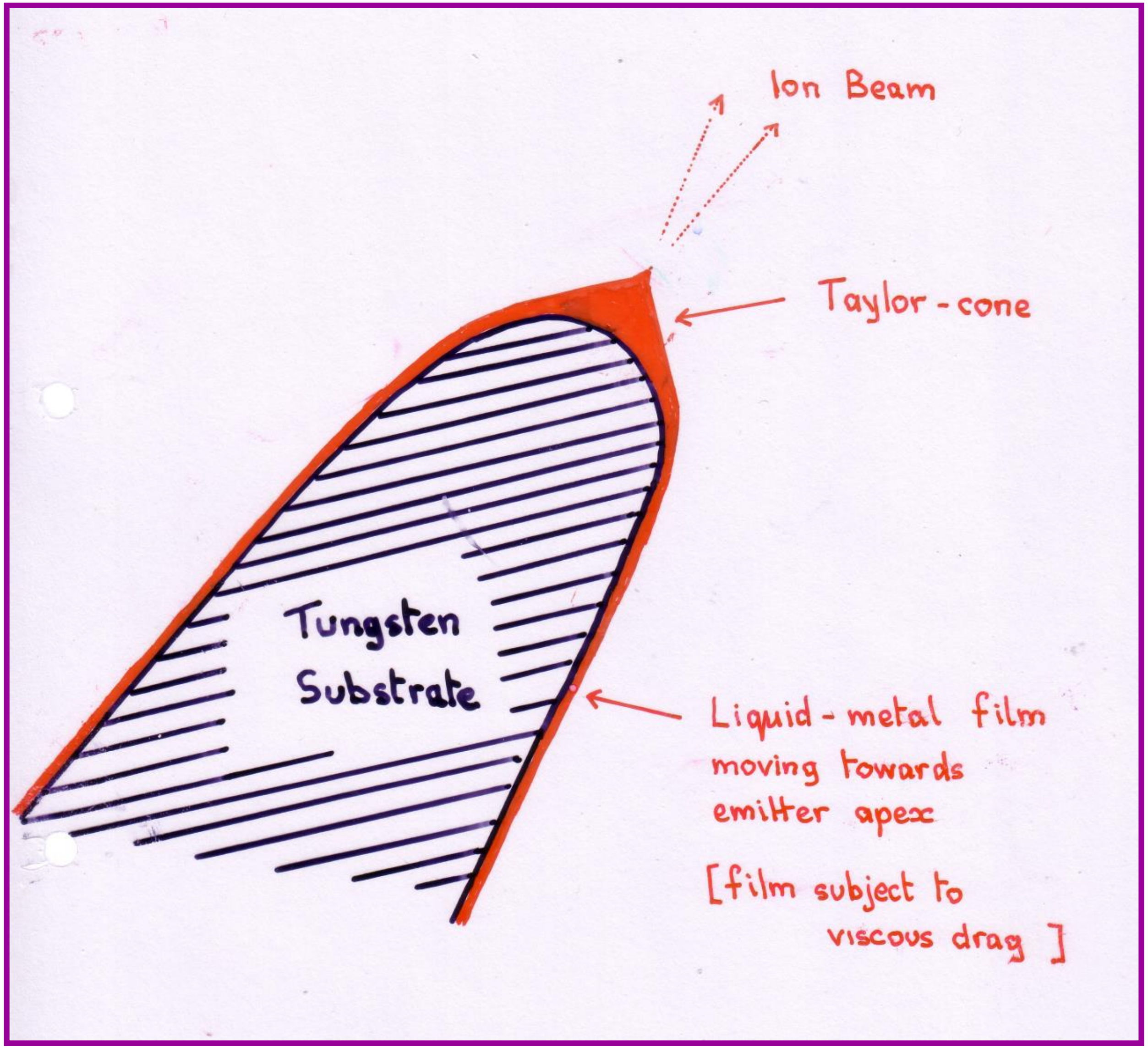
This equation must be true at every point on the surface.

For field *F*, Taylor (1964) used a conical solution of Laplace's equation. He found that a solution to the above equation existed when the cone half-angle $\alpha = 49.3^\circ$.

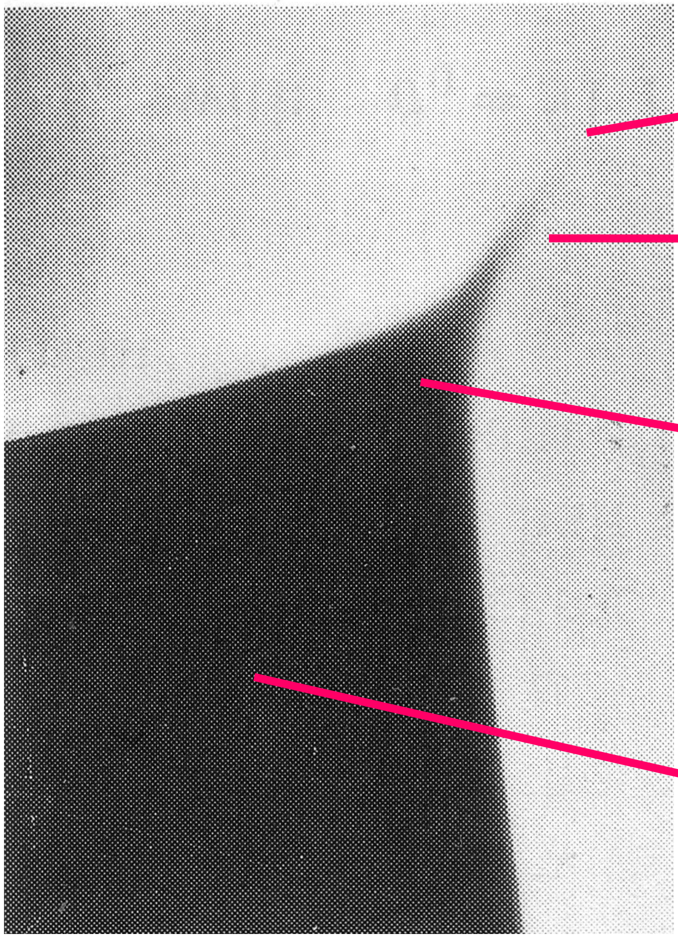


This is the well known (mathematical) Taylor cone.

Liquid metal ion source



Electron micrograph of emitting LMIS (at very high emission current)



Apex (radius ~ 1.5 nm)

Jet

Cusp or

Vena contracta

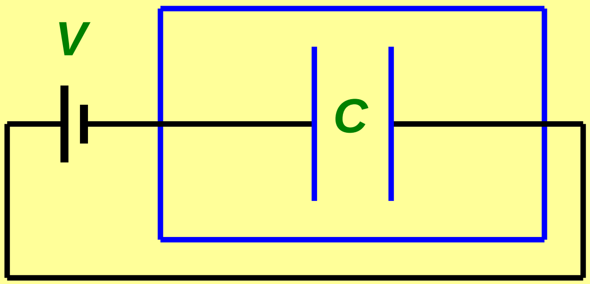
Taylor cone

Courtesy: Benassayag

Definitions and some basic theoretical results

The electrical Gibbs function

Consider a complex system that has internal capacitance *C*, and suppose that an ideal external battery (or ideal high-voltage generator) that supplies a voltage *V* is attached to the system.



If a change happens within the system that causes the capacitance to increase by an amount δC then the external voltage source will "charge" the increased capacitance, by passing charge $\delta q = V\delta C$ around the electrical circuit. The external source thus does electrical work w^{el} on the system, with $w^{el} = V^2\delta C$.

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The electrical Gibbs function

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Normally, as in the applications of interest to us, the change in capacitance is caused by a change in electrode shape.

Normally, the work done on the system in such a change is purely electrical: no external mechanical work is done.

To describe the thermodynamics of such changes, it is necessary to introduce electrical terms into Helmholtz free energies, and to introduce the electrical Gibbs function.

The electrical Gibbs function

A general definition of a Gibbs function G is

$$G = \mathscr{F} - w\ ,$$

where $\mathscr{F}$ is Helmholtz free energy, and w is the work done ON the system by an external agency.

The usual mechanical / chemical Gibbs function G^{mech} is

$$G^{\mathrm{mech}} = \mathscr{F} + pv\ .$$

The electrical Gibbs function G^{el} is

$$G^{\mathrm{el}} = \mathscr{F} - Vq\ ,$$

Since the voltage applied by a battery can be taken as constant:

$$\mathrm{d}G^{\mathrm{el}} = \mathrm{d}\mathscr{F} - V\mathrm{d}q\ .$$

The basic equation of electroformation

Let γ^0 denote the (zero-field) Helmholtz surface free energy per unit area. If variations in γ^0 with crystallographic orientation are disregarded, then $\mathscr{F}_{\text{surface}}$ can be written

$$\mathscr{F}_{\text{surface}} = \gamma^0 A \,,$$

where A is the relevant surface area

$\mathscr{F}_{\text{capacitance}}$ can be written in the alterative forms

$$\mathscr{F}_{\text{capacitance}} = \tfrac{1}{2} CV^2 = \tfrac{1}{2}\varepsilon_0 \int F^2 \mathrm{d}v \,,$$

where ε_0 is the electric constant, F is electric field, and the integral is taken over all relevant space.

Combining these expressions with the Gibbs function formula given earlier (taking q=CV) yields

$$G^{\text{el}} = \mathscr{F}_{\text{bulk}} + \gamma^0 A - \tfrac{1}{2} CV^2$$

This is the basic equation of electroformation.

Basic predictions

$$G^{el} = \mathscr{F}_{bulk} + \gamma^0 A - \frac{1}{2} C V^2$$

A general rule of thermodynamics is that a system tends to change in such a direction that its Gibbs function becomes more negative.

Basic predictions

$$G^{el} = \mathscr{F}_{bulk} + \gamma^0 A - \tfrac{1}{2} CV^2$$

A general rule of thermodynamics is that a system tends to change in such a direction that its Gibbs function becomes more negative.

When applied to the above equation, this rule predicts the following basic physical principle of electroformation:

1) When the applied voltage is very small, then the system-shape changes in such a way as to minimize the surface area.

2) When the applied voltage is sufficiently large, then the system-shape changes is such a way as to maximize the capacitance between the "active" (i.e. shape-changing) electrode and the counter-electrode.

3) There is a change-over condition, as voltage increases, from surface-area-driven behaviour to capacitance-driven behaviour.

Basic predictions

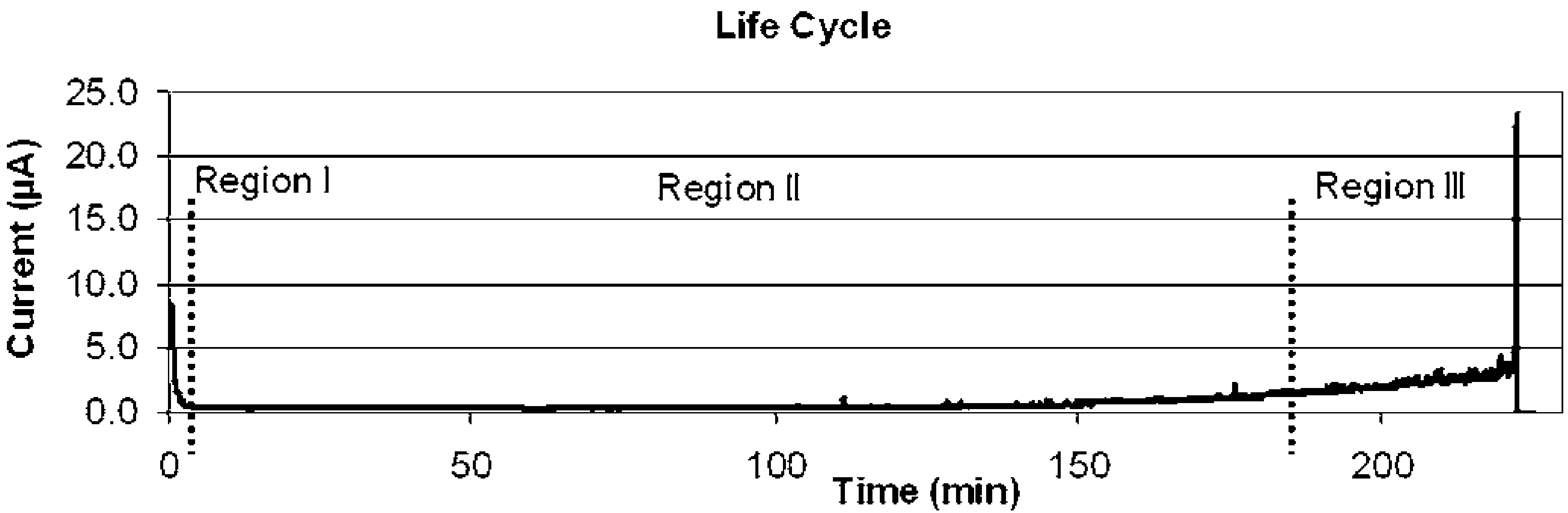
This basic principle is usually interpreted as implying in practice that:

1) **When the applied voltage is very small, the system blunts and tends to "ball up"). [But, for solids, the situation is more complicated because crystallographic dependence in g^0 can cause faceting to occur.]**

2) **When the applied voltage is sufficiently large, the system sharpens and/or grows nanoprotrusions).**

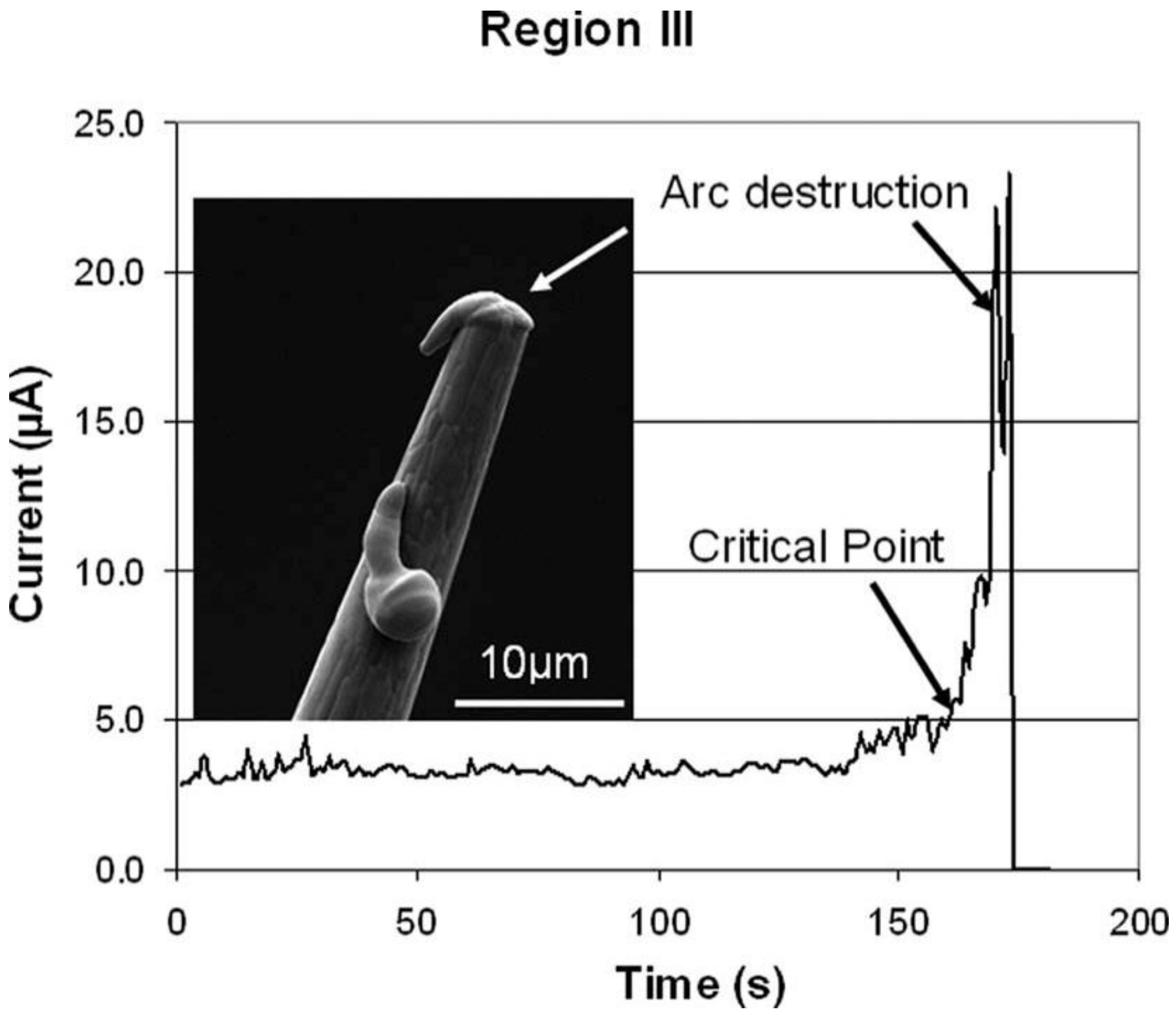
[However, as we shall see, the implications may be more complex.]

Life cycle of cold W field electron emitter



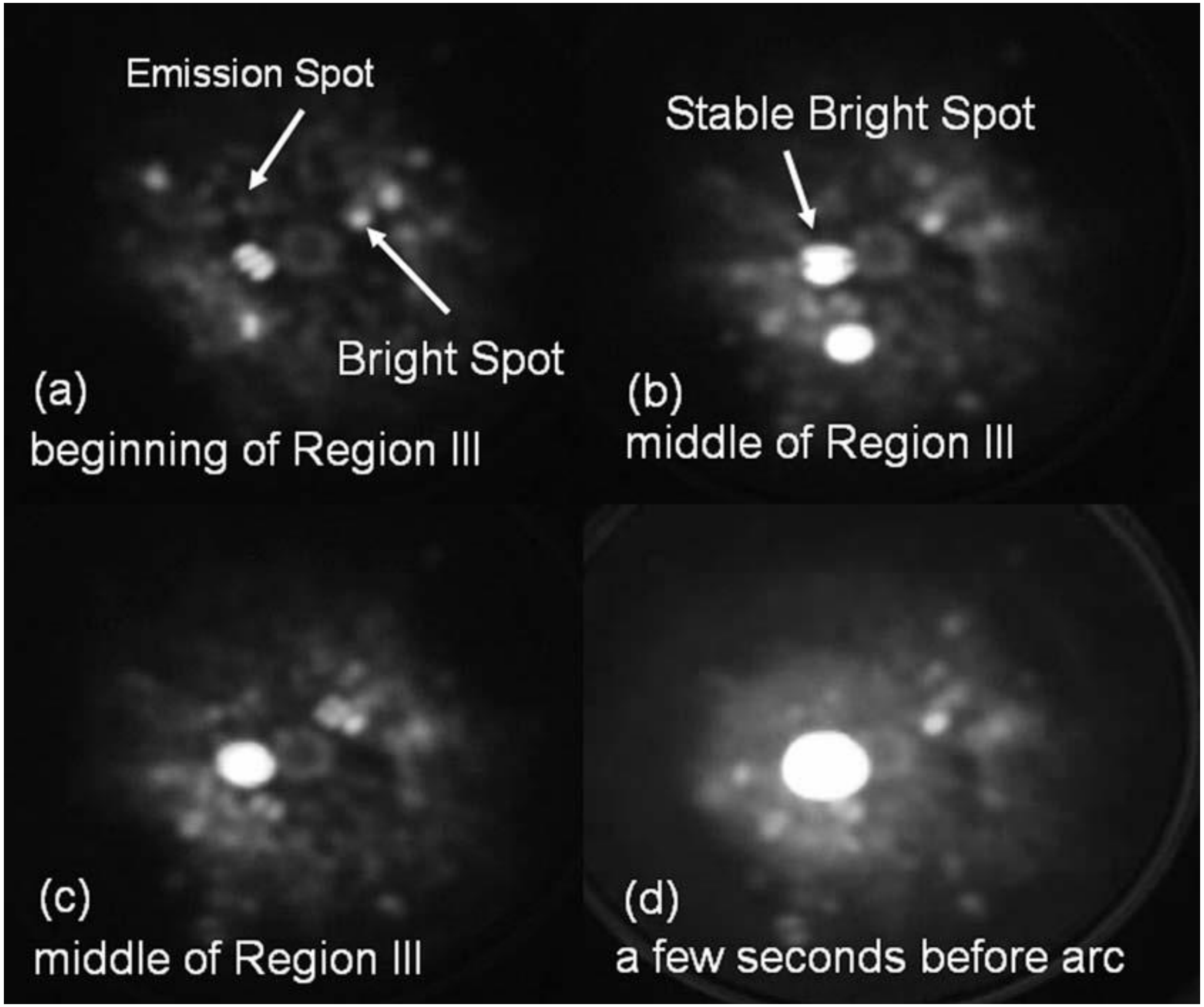
Courtesy: Yeong & Thong, J. Appl. Phys, 99, 104903 (2006)

Life cycle of cold W field electron emitter



Courtesy: Yeong & Thong, J. Appl. Phys, 99, 104903 (2006)

Life cycle of cold W field electron emitter



This sequence shows unambiguously that, with cold metal field electron emitters, arc initiation is preceded by nanoprotrusion growth on top of the field electron emitter.

Courtesy: Yeong & Thong, J. Appl. Phys, 99, 104903 (2006)

Basic voltage-based change-over condition

The physics of change-over is of particular interest, but discussions appear tricky to implement.

In basic discussions, it is assumed that changes in $\mathscr{F}_{\text{bulk}}$ may be disregarded.

In the special ideal case where γ^0 is assumed uniform and the system comprises a sphere of radius r, surrounded by a spherical counter-electrode of very large radius, we may assume that: $A = 4\pi r^2$, $C \approx 4\pi\varepsilon_0 r$. The basic equation of electroformation then becomes

$$G^{\text{el}} = F_{\text{bulk}} + 4\pi\gamma^0 r^2 - 2\pi\varepsilon_0 V^2 r .$$

It is assumed that change-over corresponds to the mathematical condition $\partial G^{\text{el}}/\partial r = 0$. This leads to the voltage-based change-over condition that the change-over voltage V_{co} is given by

$$(V_{\text{co}})^2 = (4/\varepsilon_0)\, \gamma^0 r .$$

Stress-based change-over condition

$$(V_{co})^2 = (4/\varepsilon_0)\,\gamma^0 r \,.$$

If, in the ideal spherical case under discussion, we put $V_{co} = rF_{co}$, where F_{co} is the change-over field, then this gives the stress-based change-over condition:

$$\tfrac{1}{2}\varepsilon_0 (F_{co})^2 = 2\gamma^0/r \,.$$

This may be read as:

"Maxwell-stress outwards equals surface-tension stress inwards" .

Stress-based change-over condition

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This formula is not in itself new – the voltage-based condition appears in Maxwell's 1873 textbook – but it has sometimes previously been derived as an ansatz. This time a route has been found to derive it (as an approximation) from thermodynamics.

The formula has found significant use in field emitter development, by assuming that it can be applied as a local condition, with $1/r$ taken as the sum of local principal radii of curvature.

Change-over fields

$$\tfrac{1}{2}\varepsilon_0(F_{co})^2 \;=\; 2\gamma^0/r\,.$$

This formula can be re-arranged into the form

$$r^{1/2}F_{co} \;=\; (4\gamma^0/\varepsilon_0)^{1/2} \;=\; c_{TF}\,.$$

Some selected vales of c_{TF} are:

	γ0 eV/nm2	cTF V nm^−1/2		γ0 eV/nm2	cTF V nm^−1/2
Al	5.7	20.3	Ag	6.0	20.9
Si	5.4	19.8	Ta	13.4	31.2
Ti	10.3	27.3	W	15.6	33.6
Fe	11.7	29.1	Pt	11.2	28.5
Cu	8.1	24.3	Au	7.3	23.0
Nb	11.9	29.3	Hg	3.1	15.0
Mo	14.0	31.9			

For example, for tungsten:

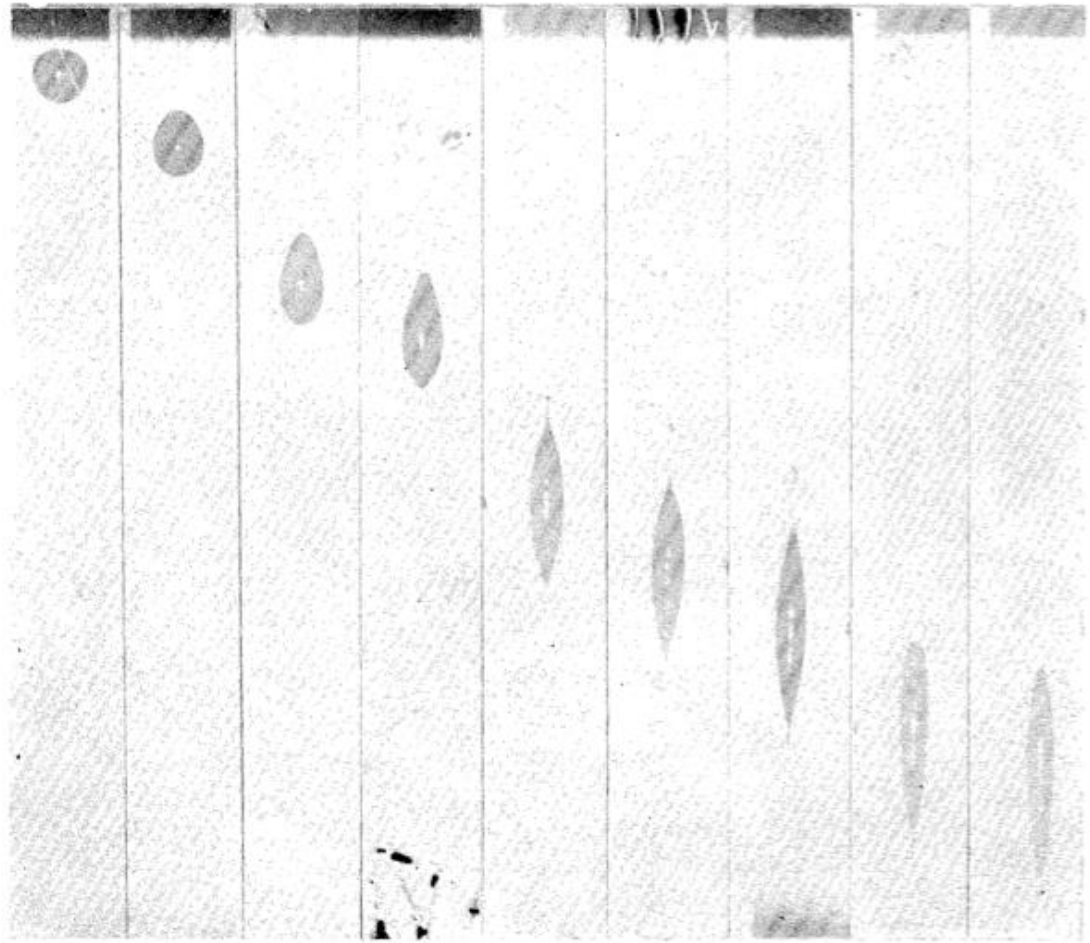
a 1 nm radius tip has $F_{co} \approx 34$ V/nm ;

a 100 nm radius tip has $F_{co} \approx 3.4$ V/nm .

Cone-jet behaviour

(aka “pointed raindrops”)

"Pointed water droplets"



Droplet falling in electric field: Courtesy: Macky, 1931.

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"Pointed water droplets"

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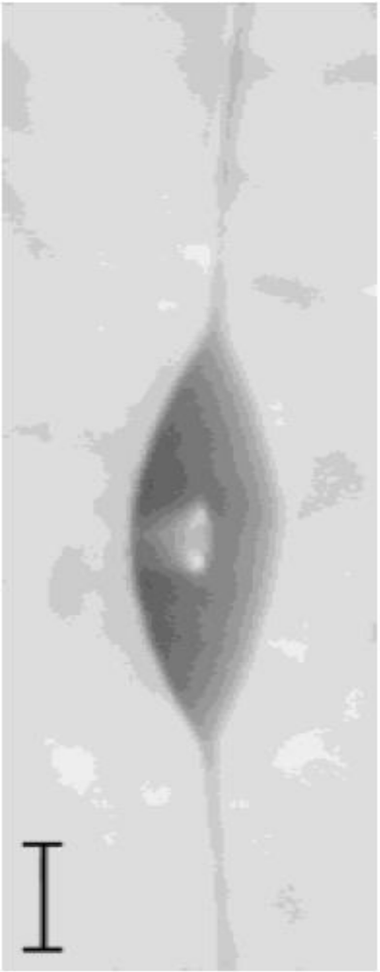
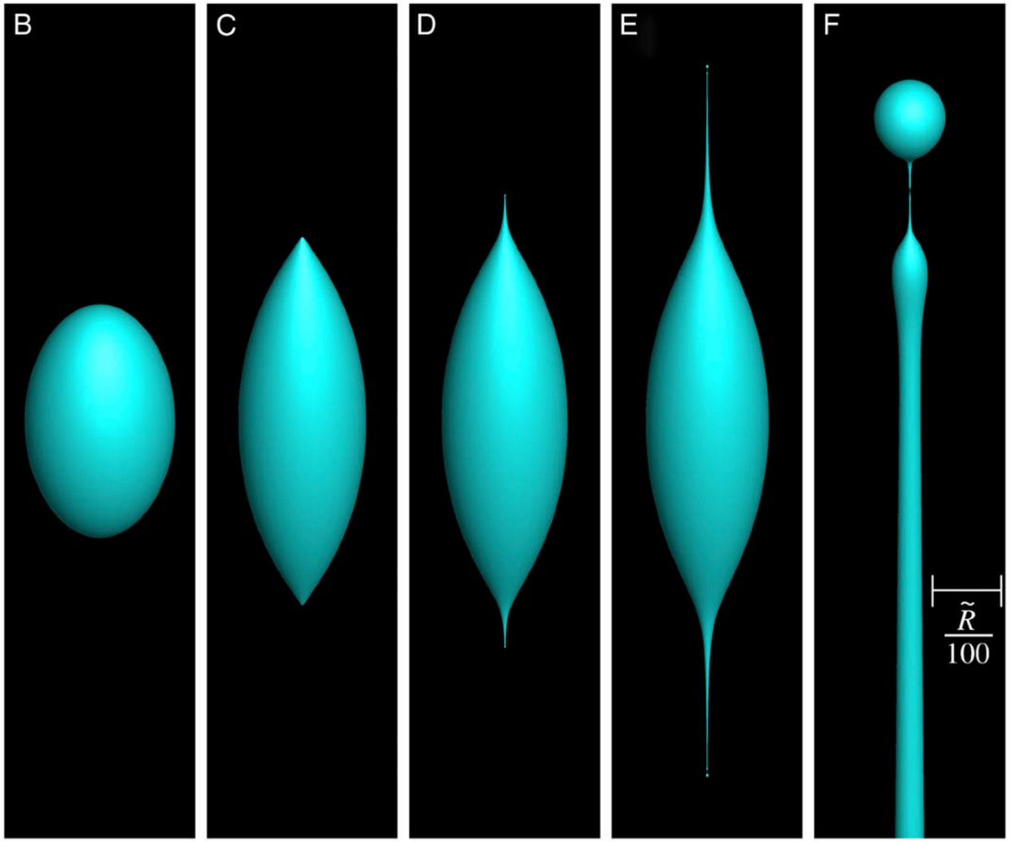


Courtesy:

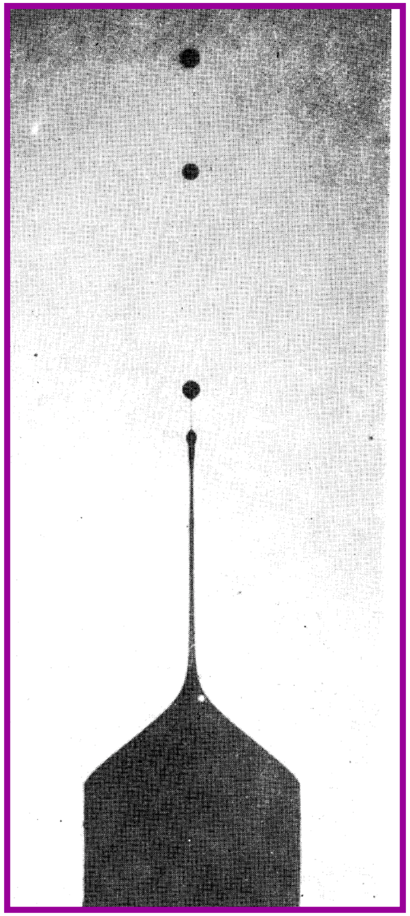
Grimm and Beauchamp, 2003:

1730 to 1870



Simulation of water droplet in electric field: Courtesy: Collins et al., 2013

Experimentally observed large droplets

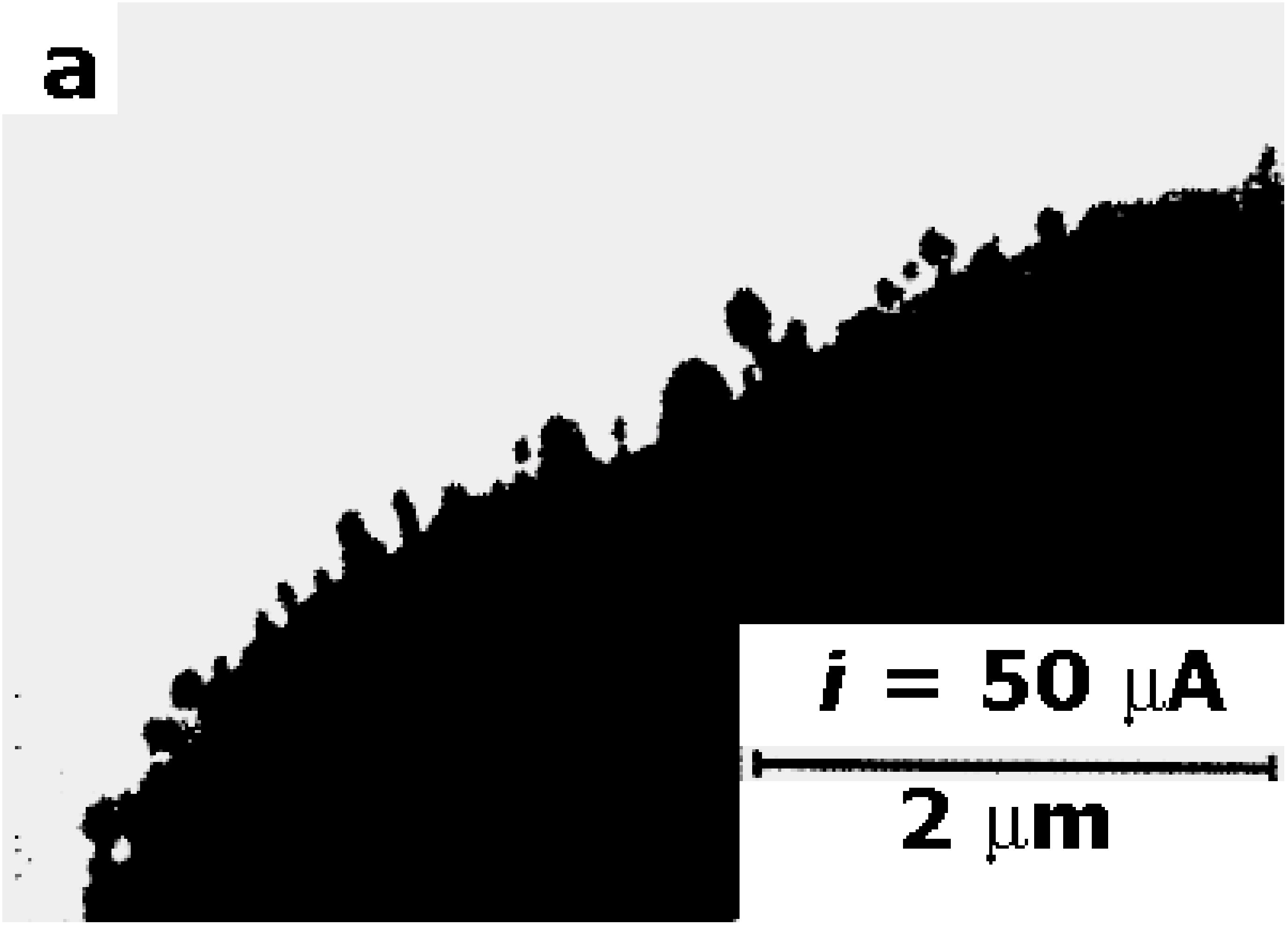


Field-induced water jet
Courtesy Taylor 1969

It seems clear that negative hydrostatic pressure inside the drop is drawing liquid into it

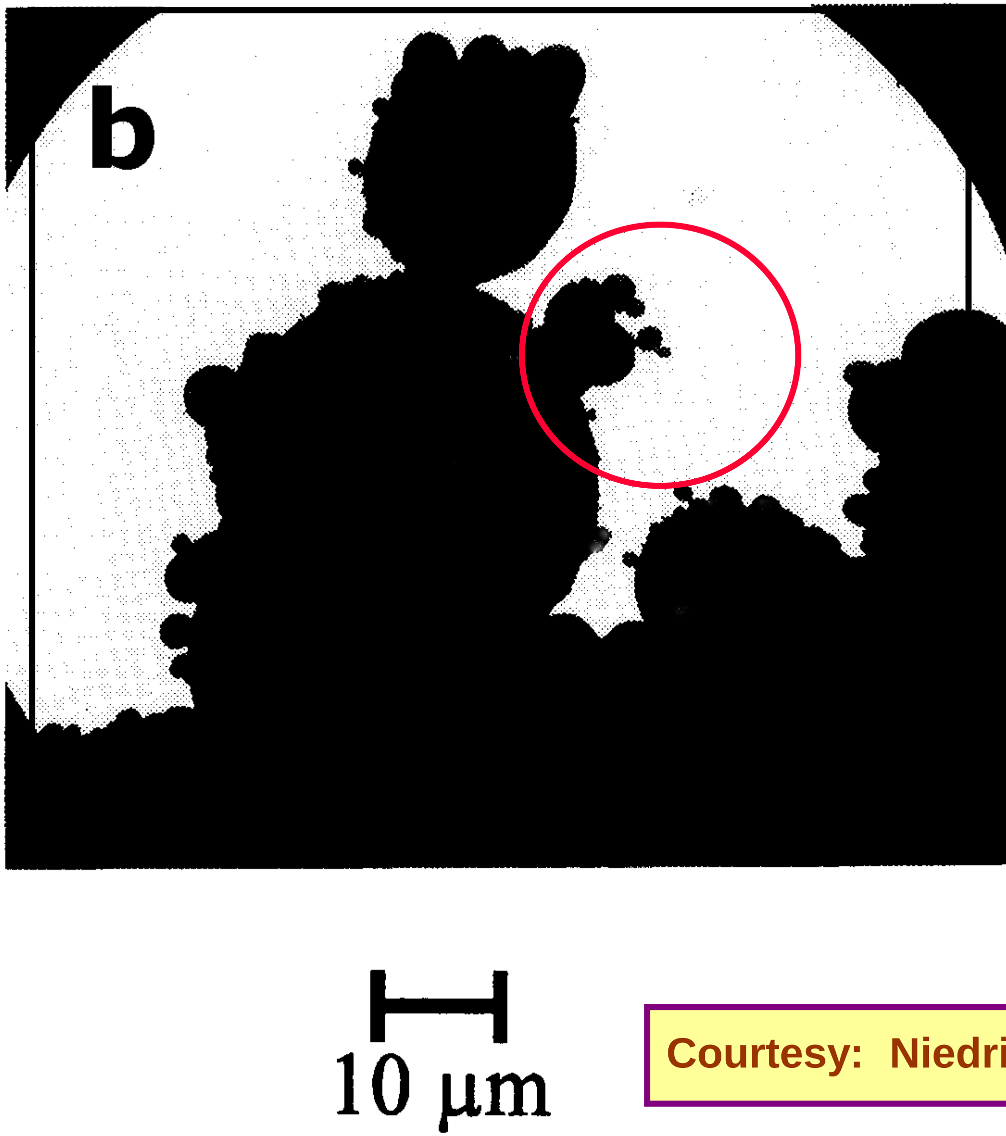
However, in terms of the system energetics, the full reasons behind this effect are not clear.

LMIS Dynamic effects



Courtesy: Niedrig, Driesel, Praprotnik

LMIS Dynamic effects

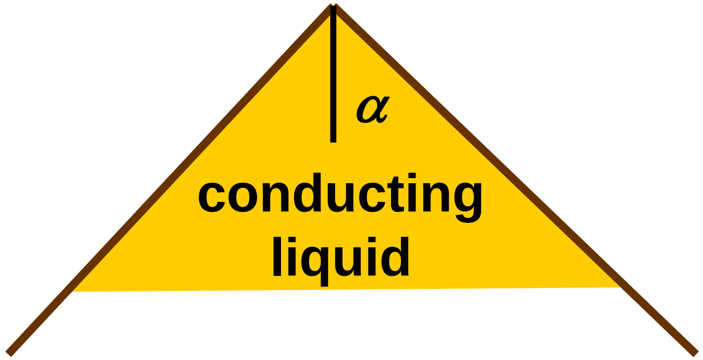


One logical explanation of the circled effect is that the thermodynamic drive changes several times as the protrusion is growing.

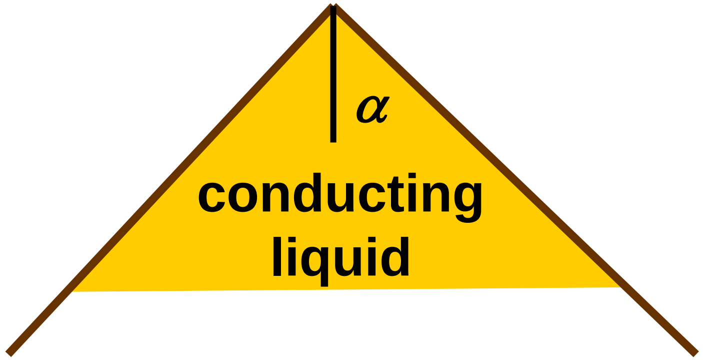
Perhaps a disruptive event of some kind causes a change in growth mode.

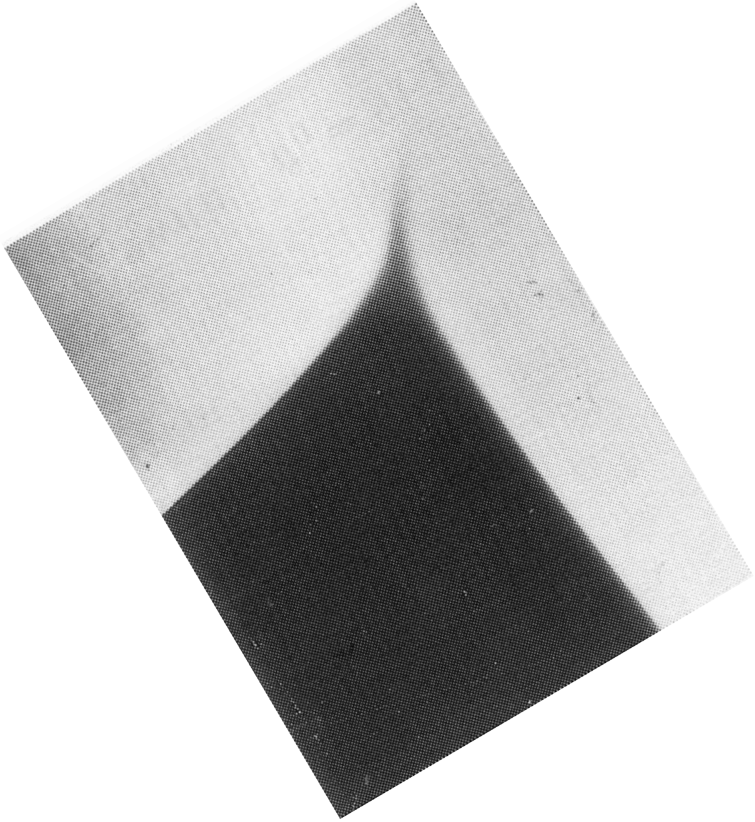
Courtesy: Niedrig, Driesel, Praprotnik

The inaccessible region



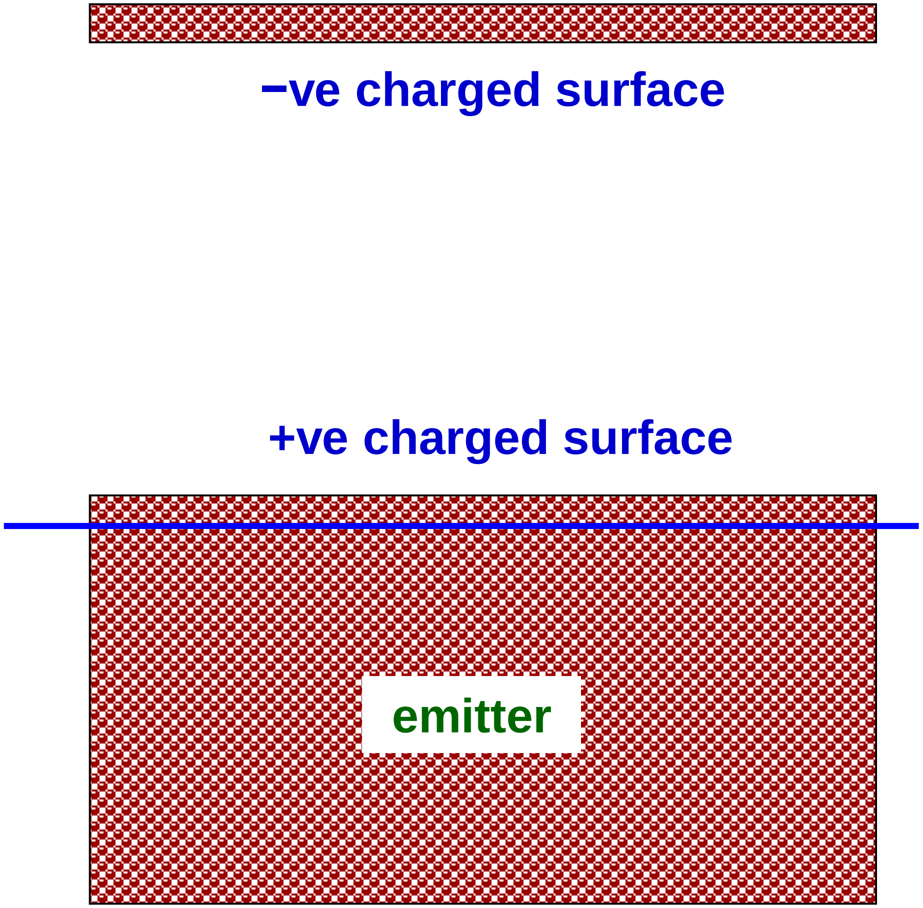
The inaccessible region





Atomic level effects

The field dependence of bonding energy



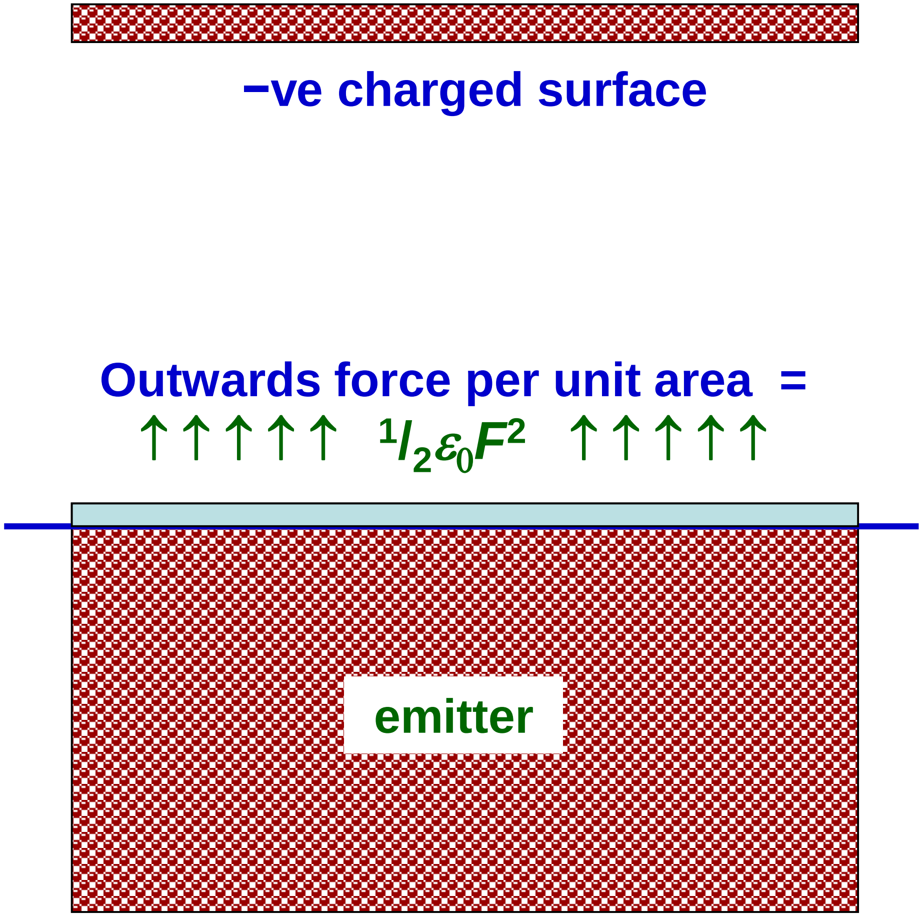
The next few slides show that the application of a high electric field changes the bonding energy of surface atoms, because the removal of EACH atom changes the capacitance of the sytem.

Model the emitter and its surroundings by a capacitor, as shown.

Plan is to determine the work per atom needed to remove top two atomic layers (above blue line).

Notice that this will leave the surface exactly the same as before.

The field dependence of bonding energy



Step 1:

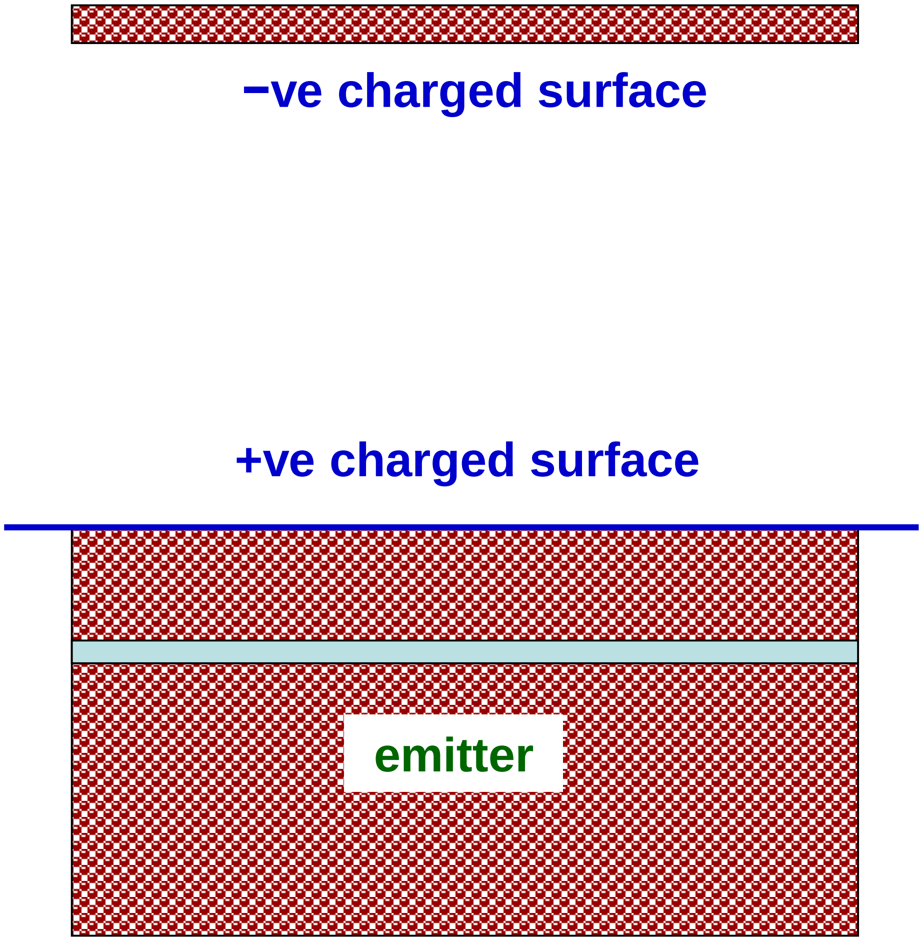
Pull whole emitter back by two atomic layers.

Work w_1 done per atom is:

$$w_1 = {}^{1}/_{2}\varepsilon_0 F^2 \Omega$$

where Ω is the atomic volume.

The field dependence of bonding energy



Step 2:

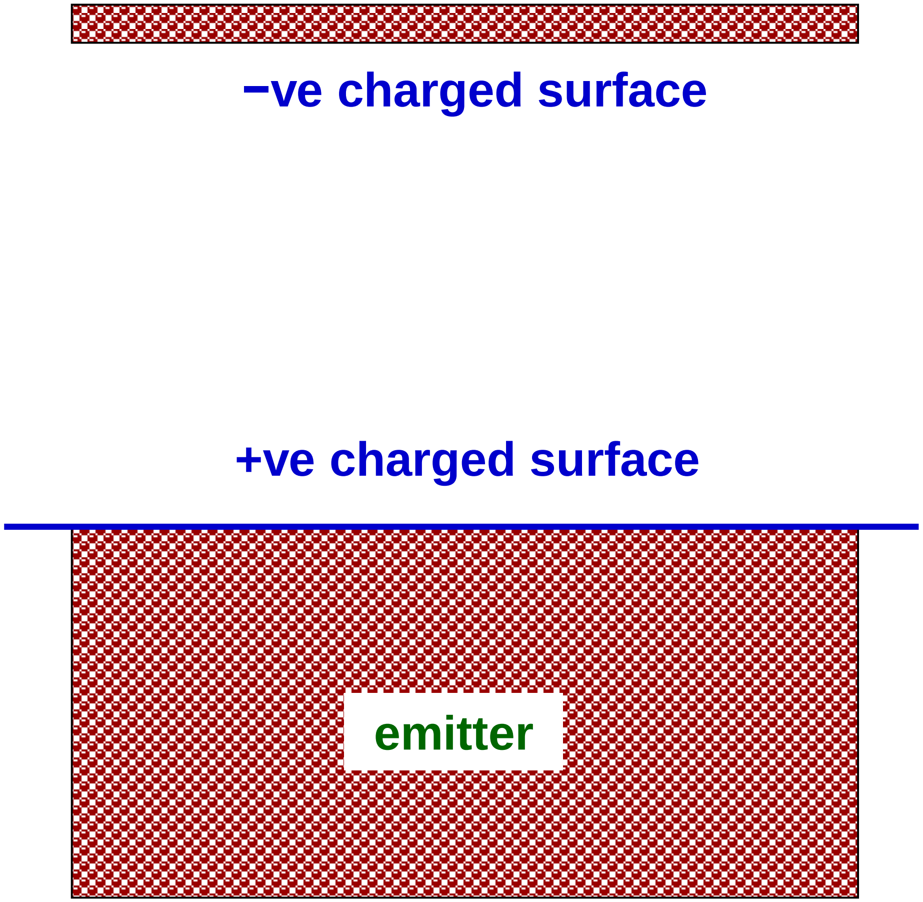
Remove two layers of atoms from deep inside the emitter, and then close up.

Work w_2 done per atom is:

$$w_2 = \Lambda^0$$

where Λ^0 is the zero-field bonding energy.

The field dependence of bonding energy



Step 1 + Step 2:

So the total work per atom done to remove an atom in the presence of surface field *F* is

$$\Lambda^F = \Lambda^0 + {}^1/_2\,\varepsilon_0 \Omega F^2$$

The field dependence of activation energy for TF migration

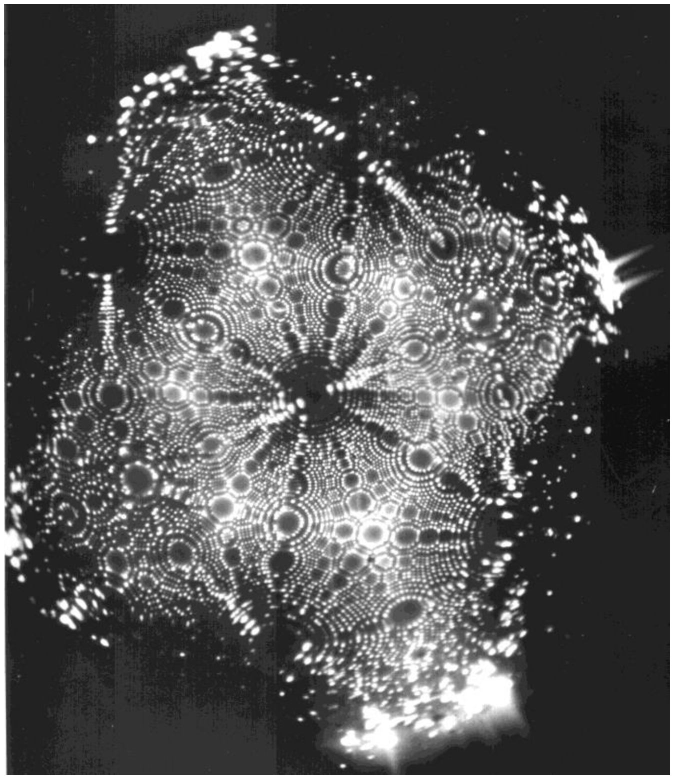
$$\Lambda^F = \Lambda^0 + {}^1/_2\varepsilon_0\Omega F^2$$

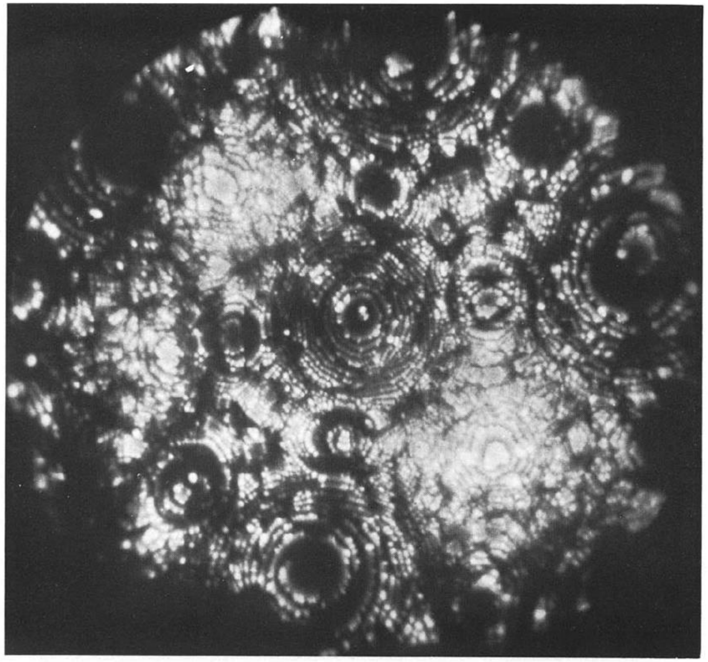
In high applied fields, when the entity migrating on a surface is a significantly charged atom (i.e., a partial ion), the field term reduces the activation energy for thermal-field migration.

This effect is presumably included in the Helsinki molecular dynamics calculations.

Some miscellaneous effects, and conclusions

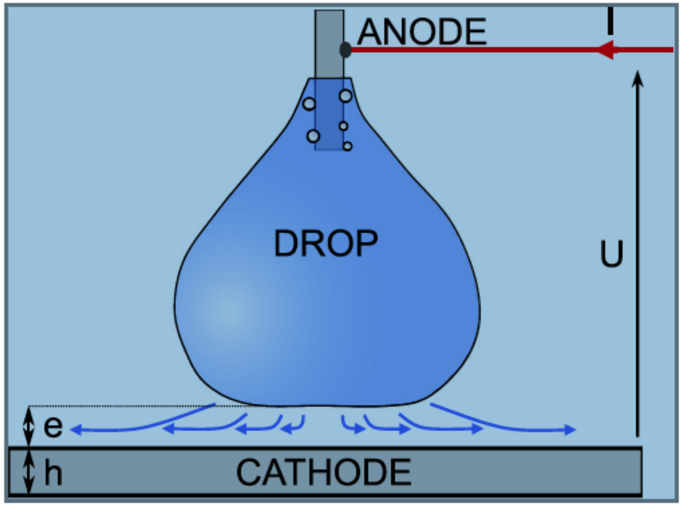
T-F effects on Tungsten

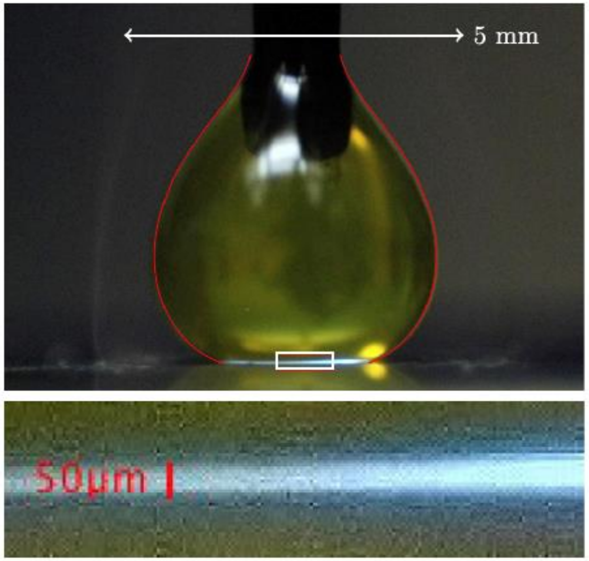




At high temperature, even a tungsten field ion emitters will "slip" under the influence of the field stresses due to high electric fields. Courtesy, Southworth et al.]

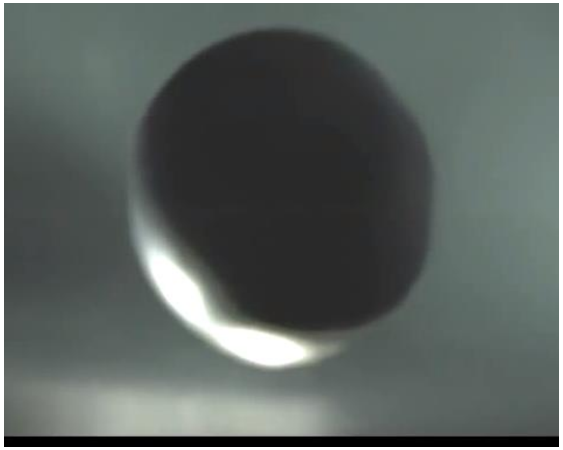
The "electrical Leidenfrost effect"





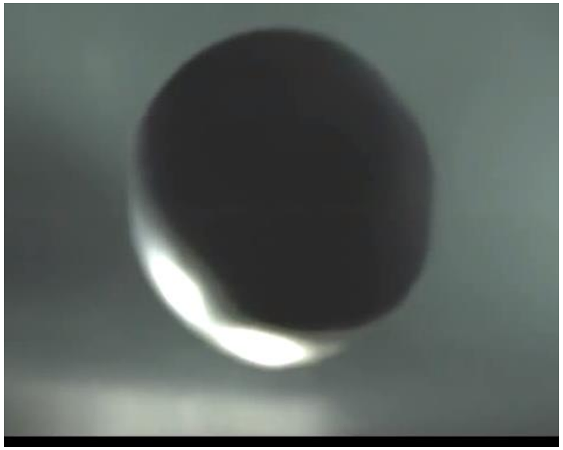
Courtesy: Poulain et al, 2015

Reaction of sodium with water



Courtesy: Mason et al., 2015

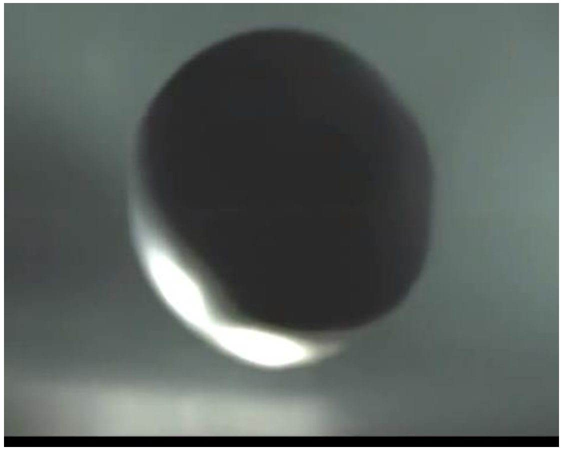
Reaction of sodium with water



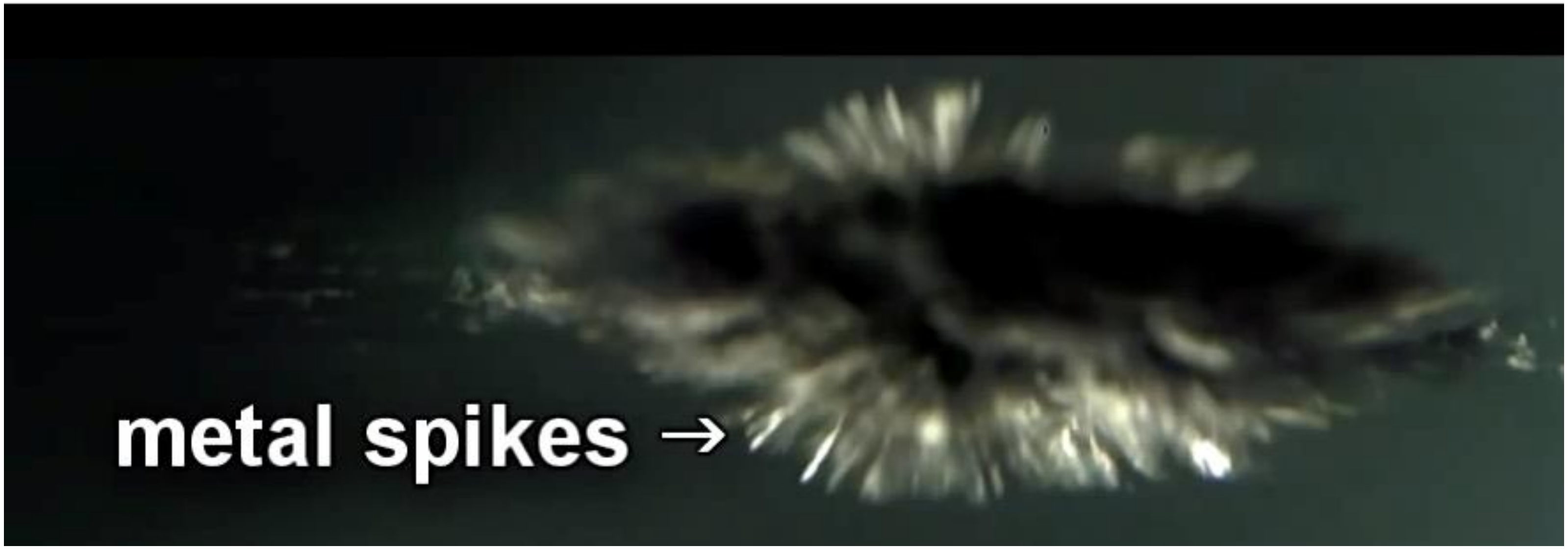
Hypothesis: initial heating drives off electrons, leaving positively charged body, and then we get:

Courtesy: Mason et al., 2015

Reaction of sodium with water



Hypothesis: initial heating drives off electrons, leaving positively charged body, and then we get:



Courtesy: Mason et al., 2015

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Summary & Conclusion

1. The pedagogy of electroformation has been tidied a little.
2. Our understanding of electrically driven jets is a bit better.
3. We still don’t totally understand the physics of what happens on the side of the cone of an operating LMIS.
4. It looks entirely plausible that growth of a nanoprotrusion could be triggered by an “external event” of some kind.
5. Although much more remains to be done, and the situations are not exactly similar, “macroscopic” electroformation effects might be an interesting source of ideas and hypotheses about what might happen on the nanoscale.

SEPARATOR

Thanks for your attention