

# **SUGGESTIONS ABOUT THE ROLE OF CARBON NANO-WHISKERS IN ELECTRICAL BREAKDOWN**

**Richard G. Forbes**

**Advanced Technology Institute &  
Dept. of Electrical and Electronic Engineering,  
University of Surrey**

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**Aim is to consider four questions:**

**B1. Is carbon relevant and what might be its role ?**

**B2. What do we know about FE from small carbon-based emitters ?**

**B3. How do carbon nanowhiskers/nanostructures grow ?**

**B4. How does growth initiate ?**

There are many indications in the literature that carbon and carbon-based molecules (CBMs) might be implicated in electrical breakdown, in particular in vacuum breakdown.

For example, the 1997 SLAC report [R2] used mass spectrometry to identify the presence (in RF accelerators, after some heating) of lines due to:

**C, CH, CH<sub>2</sub>, CH<sub>3</sub>, CH<sub>4</sub>, CO, CO<sub>2</sub> .**

Some particularly persuasive work has been carried out by a large French multi-institution collaborative group, in 2014-2016 [R3-R5]. This is a good starting point for discussion. What follows is my summary of their scientific argument.

The French work concerned "gas conditioning", in particular the influence of gas pressure on field electron emission (FE) current.

Both experimental studies and density functional theory (DFT) studies have been carried out.

The experimental work involved FE from a tungsten carbide (WC) substrate. Four gases (H<sub>2</sub>, He, N<sub>2</sub>, Ar) were used. A typical result is shown below.

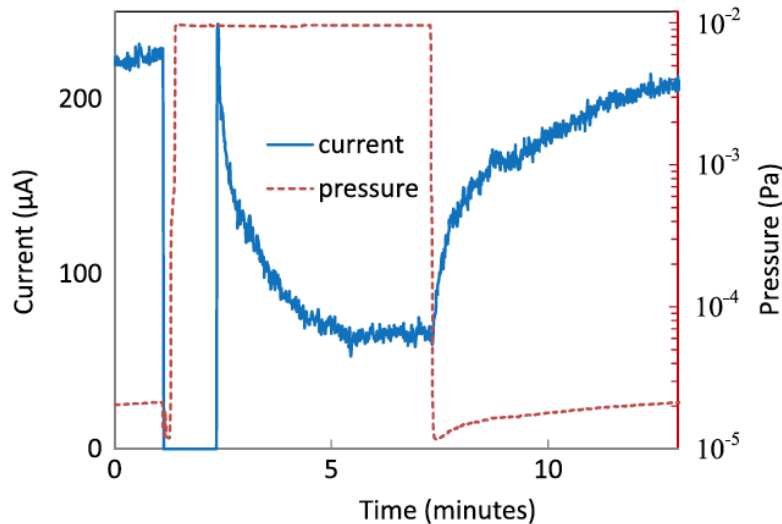


FIG. 3. Typical field emission current decrease and recovery caused by the injection and pumping down of helium: 2 cm gap distance, 30 kV applied voltage.

### Interpretation of results:

(a) The increased gas pressure removes an "emitting feature", probably as a result of ion bombardment.

(b) When the gas pressure is lowered again, the "emitting feature" is gradually restored.

Diagram courtesy: Almaksour et al. (2014) [R3], Fig. 3.

There are three obvious questions, and some obvious candidate answers.

(1) **What chemical species is primarily involved ?**

[W; or C; or something else from the "vacuum" environment ?]

(2) **What is the nature of the "emitting feature" ?**

[A field-enhancing nanostructure; or an adsorbed layer that modifies the work function; or an unexpected "something else" ?]

(3) **Where is the "primary species responsible" coming from ?**

[From the substrate; from the "vacuum"; by migration across the surface; or by some complicated multi-stage mechanism ?]

Taking questions (1) and (2) together yields the following primary options for the "current-recovery" process:

- (a) **Carbon build-up lowers the work function.**
- (b) **A metal (W) field-enhancing structure builds up.**
- (c) **A carbon field-enhancing structure builds up.**

**Using DFT methods, Márquez-Mijares, Lepetit and Lemoine (2016) [R4] explored the effect (on local work-function) of placing an adsorbed layer of carbon on a tungsten (100) surface.**

**They found that carbon adsorption increases the local work function, and thus would reduce the emission current.**

**This rules out option (a) on the previous slide, and leaves the two possibilities:**

- (b) A metal (W) field-enhancing structure builds up.**
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- (c) A carbon field-enhancing structure builds up.**

**The original experiments were on a tungsten carbide (WC) substrate. This is a very tough material, so it seems unlikely that tungsten atoms will be significantly mobile.**

**This leaves (c) as the most plausible hypothesis, particularly since it is also plausible that carbon or CBMs could be supplied from the "vacuum".**

**Further experiments by the French group, using SEM techniques, explored this. Two results seem particularly relevant ...**

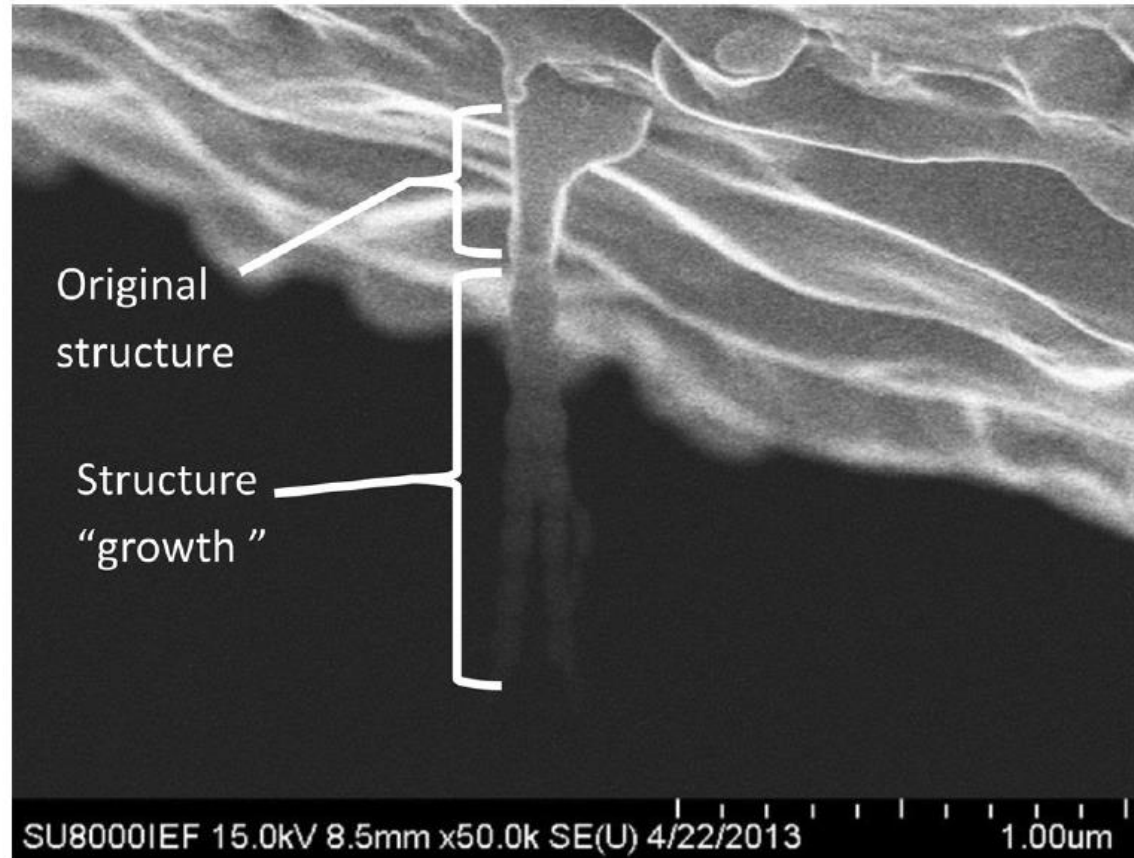


FIG. 3. SEM image of a structure grown on top of a pre-existing one. EDX analysis suggests that it consists mainly of carbon. The scale corresponding to  $1 \mu\text{m}$  is shown at the bottom right of the image.

Diagram courtesy: Márquez-Mijares et al. (2016) [R4], Fig. 3 .



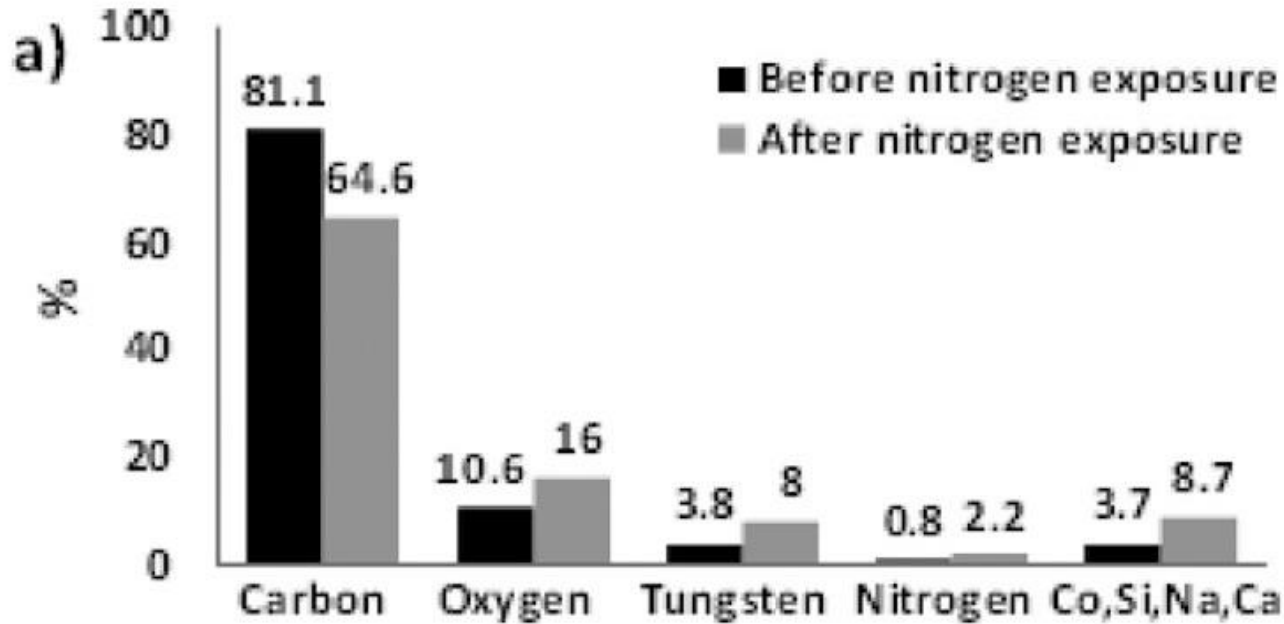


Diagram courtesy: Márquez-Mijares et al. (2016) [R4], Fig. 4(a).

**The French group argue:**

- (1) There is always more carbon at surface than any other species.
- (2) There is more carbon present than would be expected from the stoichiometry of WC – the rest must have come from the "vacuum".
- (3) After gas (N<sub>2</sub>) exposure (and the resulting ion bombardment), there is less carbon present – which is consistent with bombardment-induced removal of a carbon-based field-enhancing structure.

The full discussion in the French papers is more comprehensive than the outline given here, and is appropriately tentative. Overall, a brief summary is:

In respect of the gas conditioning experiments, the most plausible model hypothesis is:

- the partial destruction (by ion bombardment), and subsequent rebuilding of, carbon field-enhancing structures.

**The full discussion in the French papers is more comprehensive than the outline given here, and is appropriately tentative. Overall, a brief summary is:**

**In respect of the gas conditioning experiments, the most plausible model hypothesis is:**

- the partial destruction (by ion bombardment), and subsequent rebuilding of, carbon field-enhancing structures.**

**There is also an issue of the mechanism(s) involved in building protruding carbon nanostructures.**

**The French group argue that probably part of this lies in chemical effects induced by ion bombardment of carbon-based-molecules on the surface near the emitting structure: the bombardment induces changes that make the molecules "more reactive".**

Conditions may be somewhat different in other "breakdown situations".  
However, my view is that we should always seriously investigate the hypothesis that: **"sometimes, breakdown may be induced by carbon field-enhancing nanostructures"**.

Now look briefly at some of the things we know about field electron emission (FE) from small carbon-based emitters.

**What do we know about field electron emission  
from small carbon-based emitters ?**

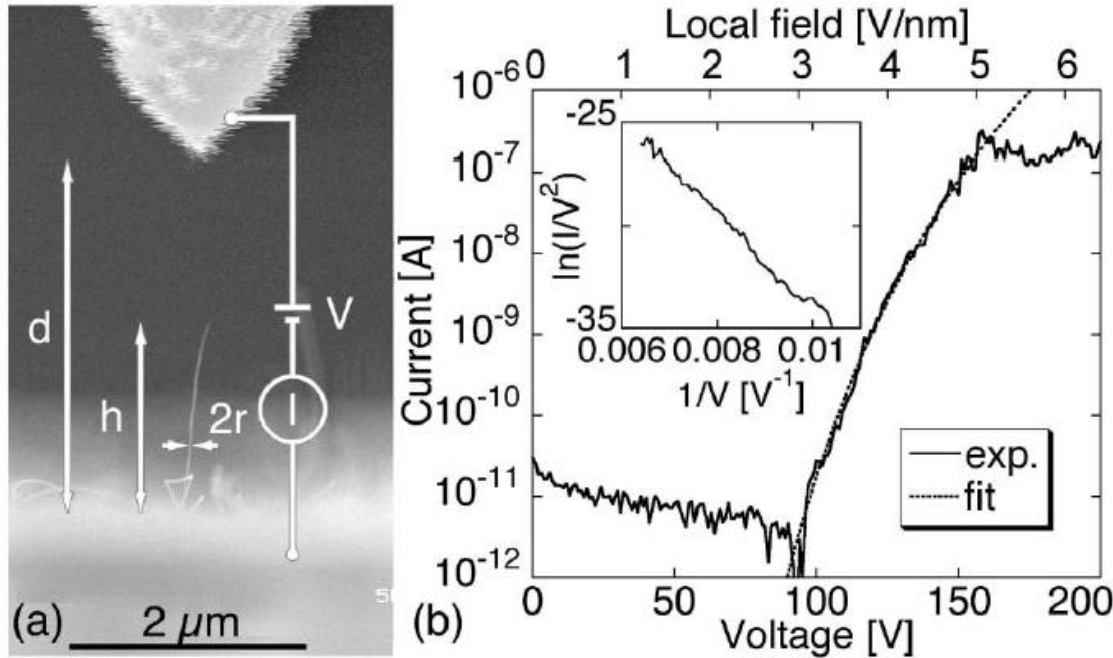
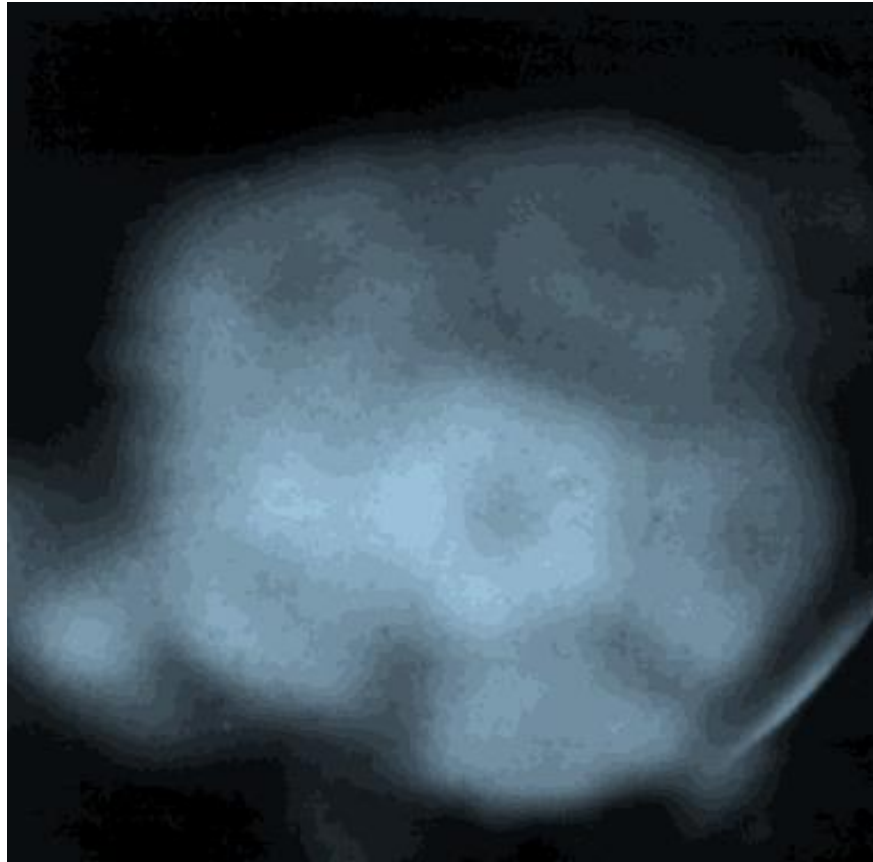


FIG. 2. (a) SEM micrograph of a nanotube of length  $h = 1.4 \mu\text{m}$  and radius  $r = 7.5 \text{ nm}$  with the sharp anode positioned at a distance  $d = 2.65 \mu\text{m}$ . (b) Corresponding  $I$ - $V$  curve with the best fit to the FN law ( $\gamma = 90 \pm 15$ ;  $A = 5 \times 10^{-16} \text{ m}^2$ ) in the dotted line. The FN plot is given in the inset.

Diagram courtesy:  
J.M. Bonard et al.,  
Phys. Rev. Lettrs 89,  
197602 (2002), Fig. 2 .

**Long CNTs of relatively small radius can produce effectively linear FN plots, and thus seem to be good conductors.**



## **FEM image of clean closed carbon nanotube**

[Diagram courtesy:

Y. Saito, K. Hata & T. Murata, Japan J. Appl. Phys.39, L271 (2000), Fig. 2(a) .]

Kishimoto & Hata have reported observation of an adsorbed CO<sub>2</sub> molecule on a pentagonal ring.

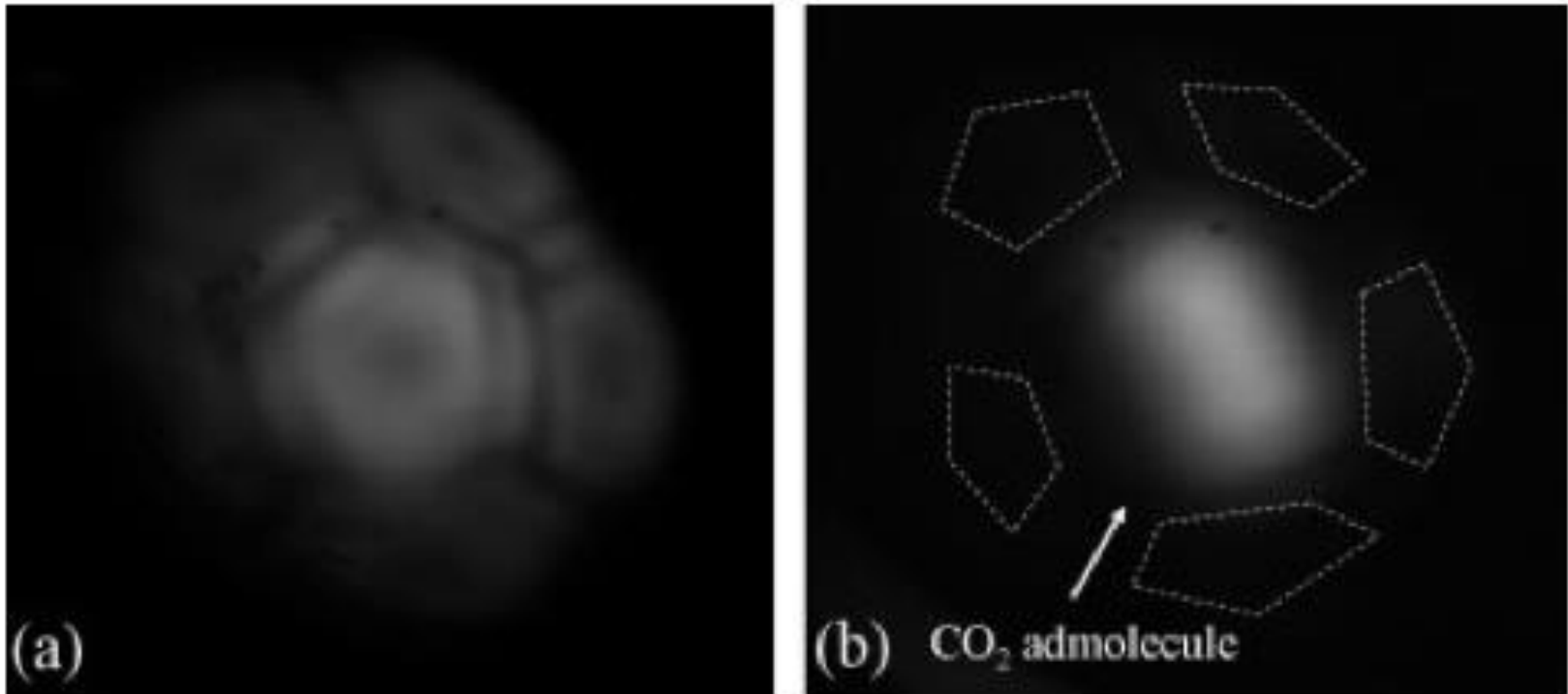
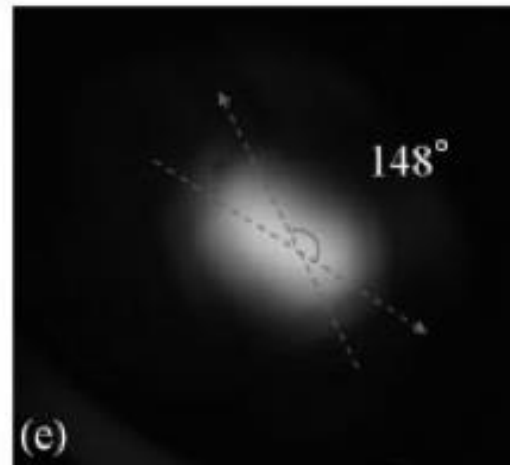
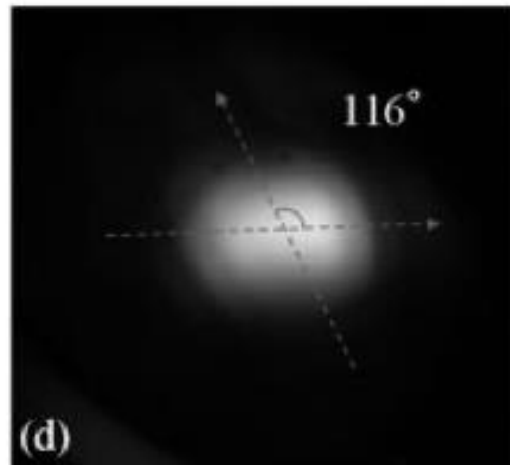
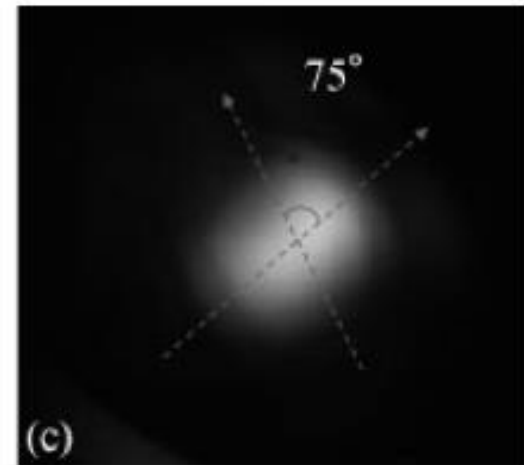
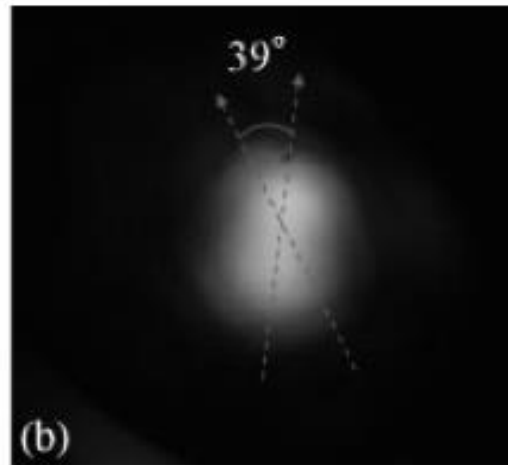
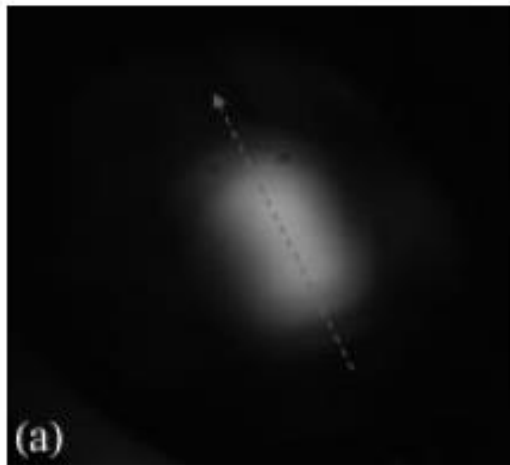


Diagram courtesy: Y. Kishimoto & K. Hata, Surf. Interface Anal. 40, 1669 (2008), Fig. 2 .



Five orientations of the adsorbed CO<sub>2</sub> molecule are observed.

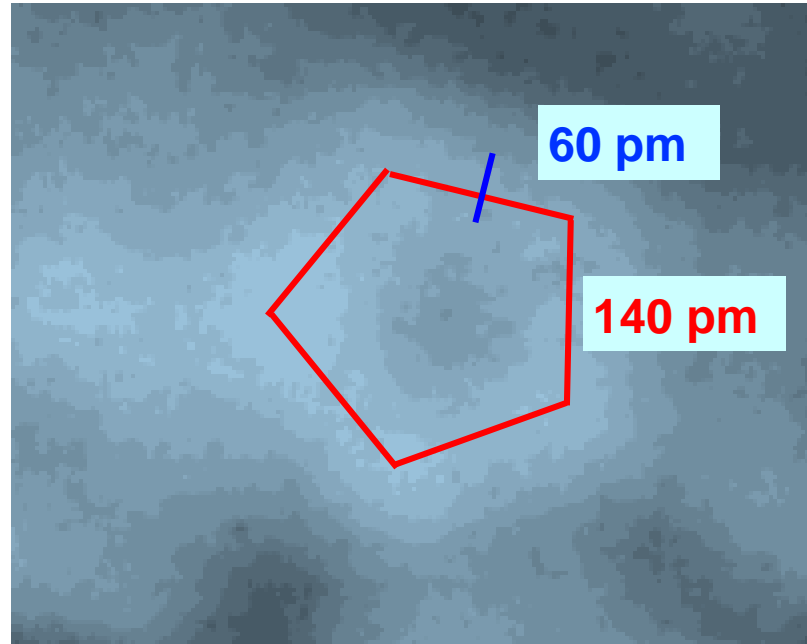
[Diagram courtesy: Y. Kishimoto & K. Hata, Surf. Interface Anal. 40, 1669 (2008), Fig. 3 .]



Hata interprets this as five orientations relative to the pentagonal ring.  
These micrographs suggest strongly that:

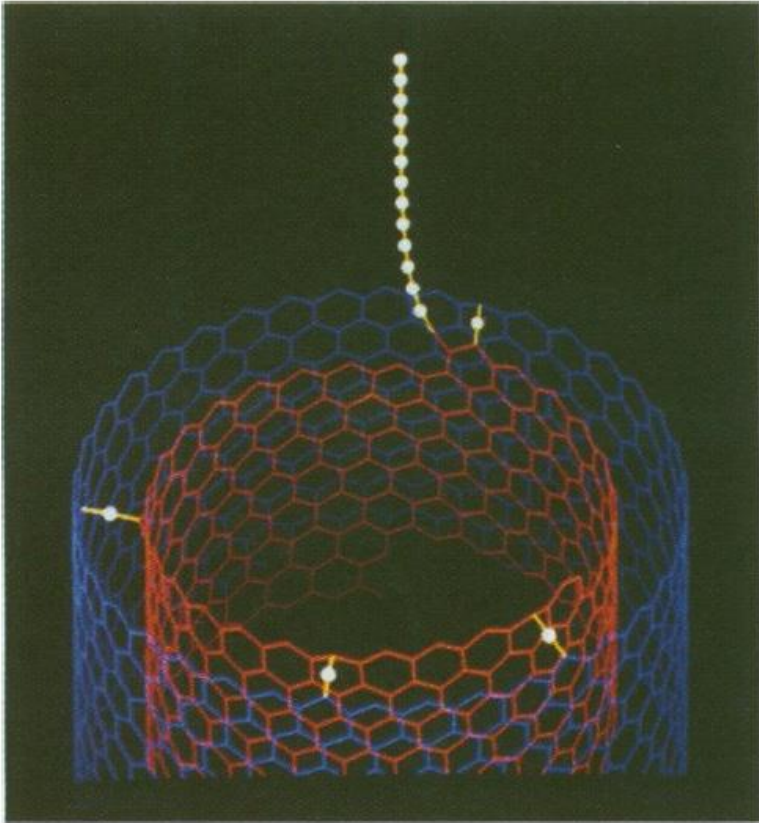
- (1) The pentagonal rings are rings of five carbon atoms.
- (2) Near-atomic-level imaging is possible in a field electron microscope if the underlying emitter radius is sufficiently small.
- (3) Emission can take place through an individual CO<sub>2</sub> molecule.

Inspection of images suggests that FEM resolution, assessed as a “object-side blurring-disc fall-off radius”, could be around 60 pm .



This is substantially less than textbook estimates, based on the Heisenberg uncertainty principle, which suggest values of 2000 pm or more.

[Presumably, either emission does not constitute a quantum-mechanical measurement, and/or existing resolution theory is significantly incomplete.]



**Fig. 4.** Model of the tip of a multiwalled nanotube showing a single  $C_n$  “atomic wire” extending out from the inner layer, held taut and straight by the electric field. The nanotubes used in this study

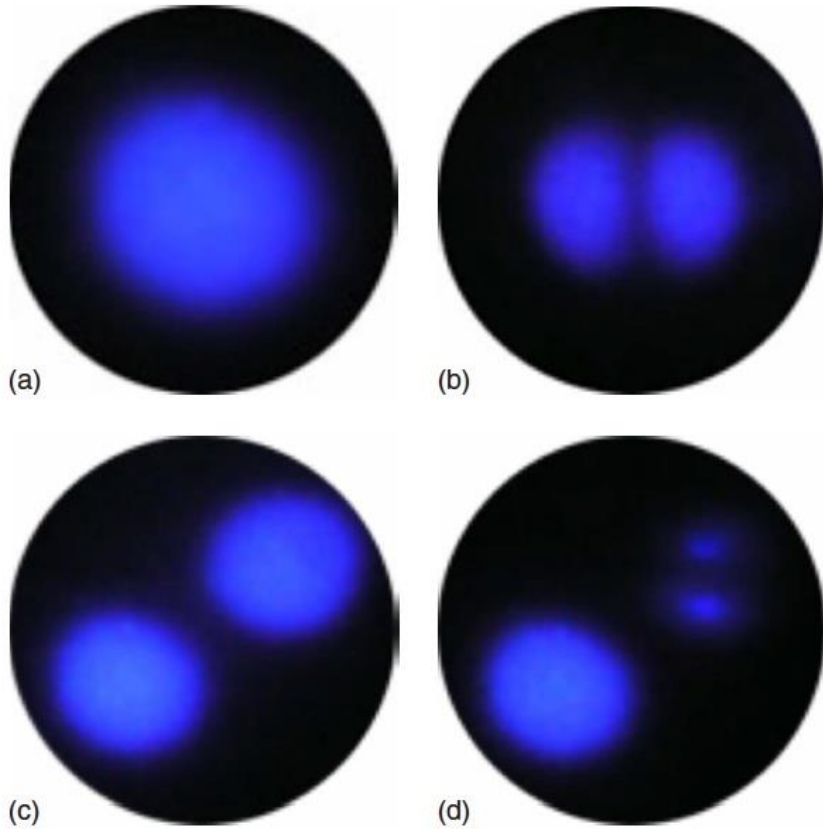
Many years ago (1995), Rinzler, Smalley & colleagues suggested that:

- (a) CNTs could unravel, to form “atomic wires”.
- (b) Atomic wires could carry significant current.
- (c) Observed “luminous flashes” were very probably due to atomic wires “burning up”.

Diagram courtesy:

A.G. Rinzler et al.. Science 269, 1550 (1995).

PHYSICAL REVIEW B 80, 165404 (2009)



More recently, Mikhailovsky et al. (2009) have claimed to observe FEM images of the end of "atomic chains".

FIG. 2. (Color online) FEEM images of the end atoms of carbon chains. (a) Singlet and (b), doublet of bright spots were acquired with a voltage 425 V. The singlet patterns represent the most stable configuration. (c) *s*-like images of two atoms at the end of chains. (d) Spontaneous *s*→*p* transformation of the FEEM pattern at constant voltage of one of atoms shown in c.

**There seems no doubt that whisker-like carbon nanostructures can grow at surfaces, and can field emit.**

**[Though, in my view, it is not yet convincingly confirmed that ideas about atomic wires and chains are valid.]**

**How do carbon nanowhiskers/nanostructures grow ?**

**Options seem to be one or both of:**

**(a) Grow at base, presumably by one or both of:**

**(i) catalytic effects (as per CNT growth);**

**(ii) surface chemistry induced by ion bombardment.**

**This presumably needs supply of carbon-based molecules across the surface.**



Options seem to be one or both of:

(a) **Grow at base, presumably by one or both of:**

(i) **catalytic effects (as per CNT growth);**

(ii) **surface chemistry induced by ion bombardment.**

**This presumably needs supply of carbon-based molecules across the surface.**

(b) **Grow at top, possibly by means of field-assisted chemistry and/or possibly with the help of ion bombardment.**

**This needs supply of carbon-based molecules to the emitter apex, by one or both of:**

(i) **supply through the vacuum;**

(ii) **supply "up the nanostructure" (most likely up surface).**

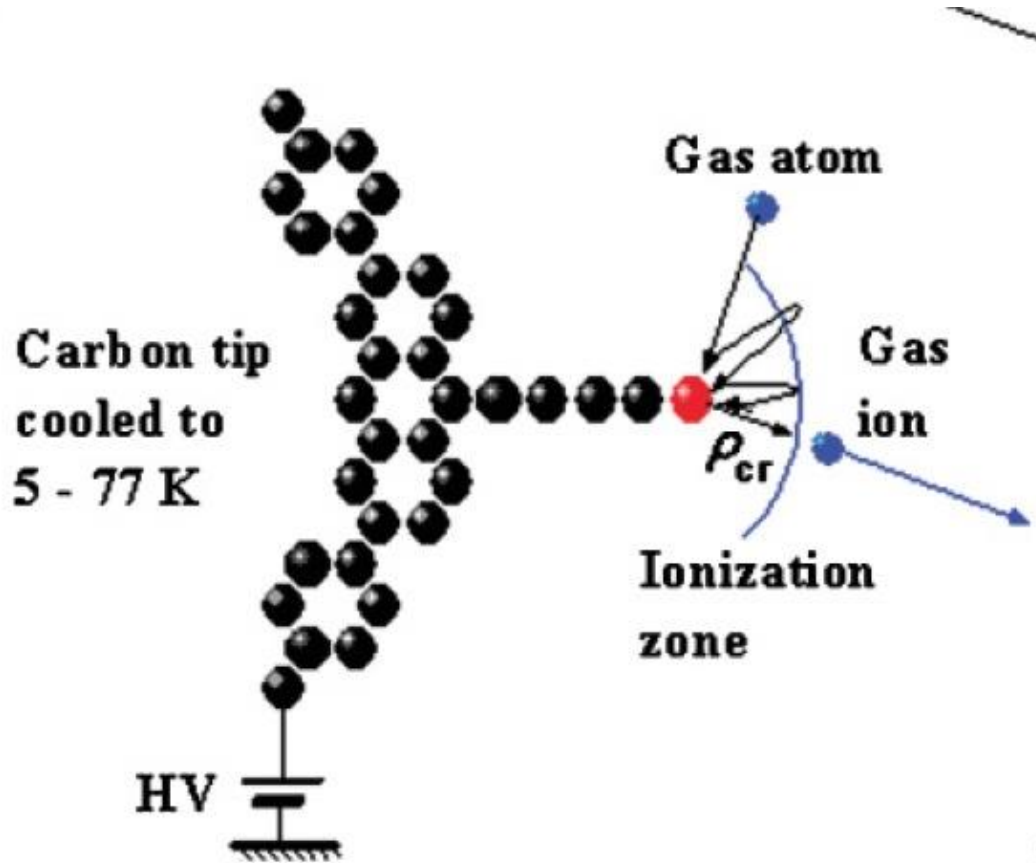


Diagram courtesy:  
E.V. Sadanov et al.,  
Phys. Rev. B 84, 035429 (2011),  
adapted from Fig. 5 .

Above shows attraction of imaging-gas atoms to tip of a field ion emitter. Attraction of polarized objects to a field electron emitter would be broadly similar [but without the ionization].

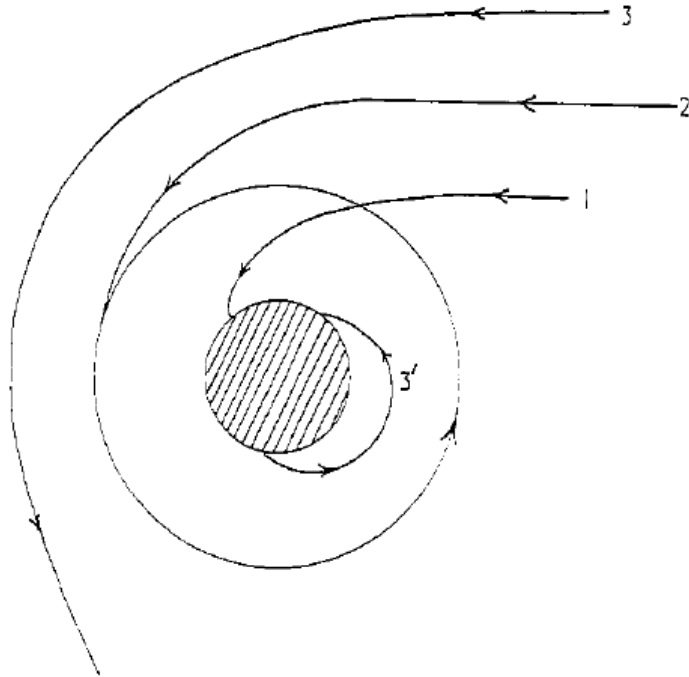


Figure 3. Typical trajectories of polarized gas atoms near a charged conducting sphere.

Diagram courtesy:

D.G. Brandon, Brit. J. Appl. Phys, 14, 474 (1963), Fig. 3 .

**In field ion microscopy, polarized imaging-gas atoms are attracted to a field ion emitter, and slower-moving atoms are captured by the emitter.**

**The same effects would attract polarized carbon atoms, polarized carbon-based molecules, and “polarized linear fragments”, towards the tip of a field electron emitter.**

[For gas-supply theory, see: Forbes (2009) [R6], and Sujiyama et al. (2010) [R7]. ]

**This effect might give some enhancement over the supply expected in zero field, due to standard gas kinetic effects.**

**The effect might be small for individual "gas-phase" carbon atoms\*\*, but larger for conducting carbon-based objects that (in the "gas phase") can develop a significantly higher electric dipole moment.**

\*\*As confirmed by Andreas Kyritsakis, during the workshop.

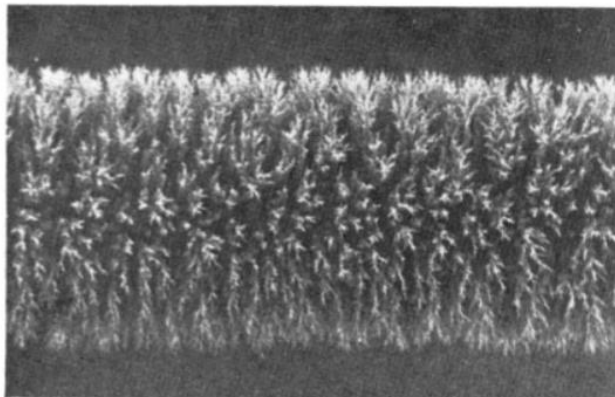
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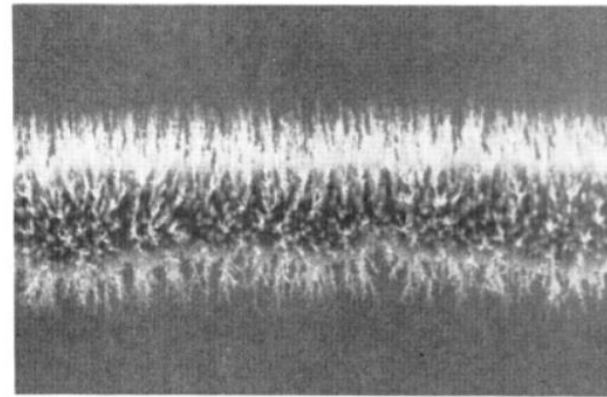
On arrival at the growing tip of the carbon nanostructure, it seems entirely plausible that the arriving entity could attach itself by means of some chemical reaction.

**Growth mechanisms of this general kind were used by Beckey and colleagues** [H.B. Linden, E. Hilt & H.D. Beckey, J. Phys. E: Sci. Instrum. 11, 1033 (1978)] **to grow carbon-based emitters for field ion mass spectrometry of organic molecules ...**

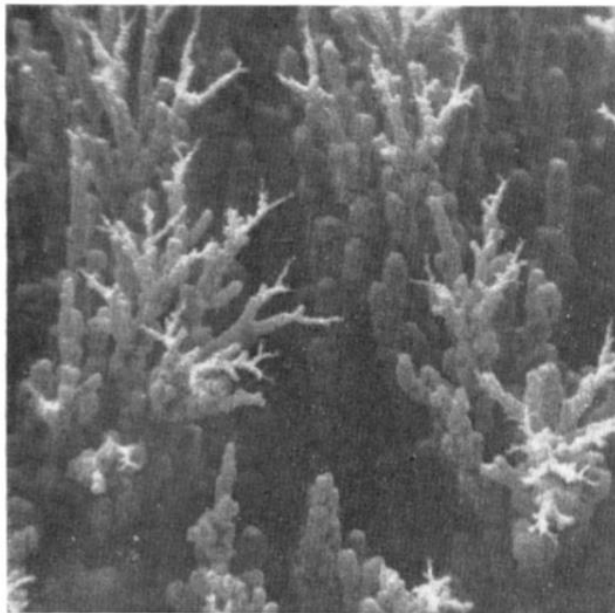
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(a)

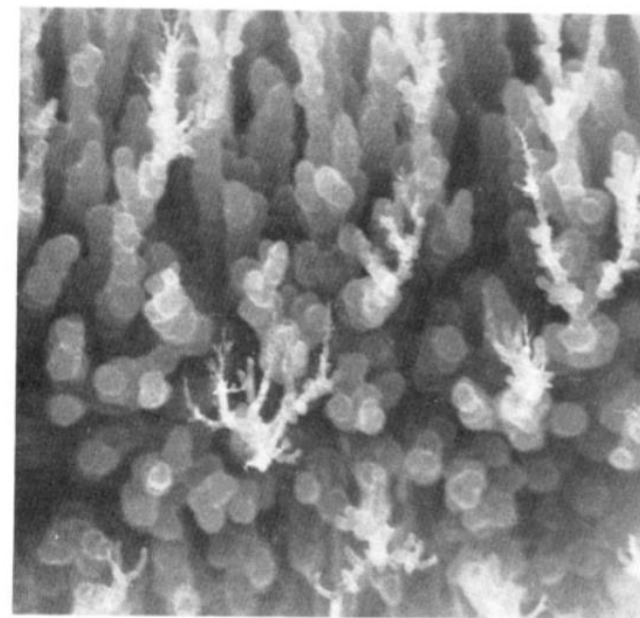


(b)

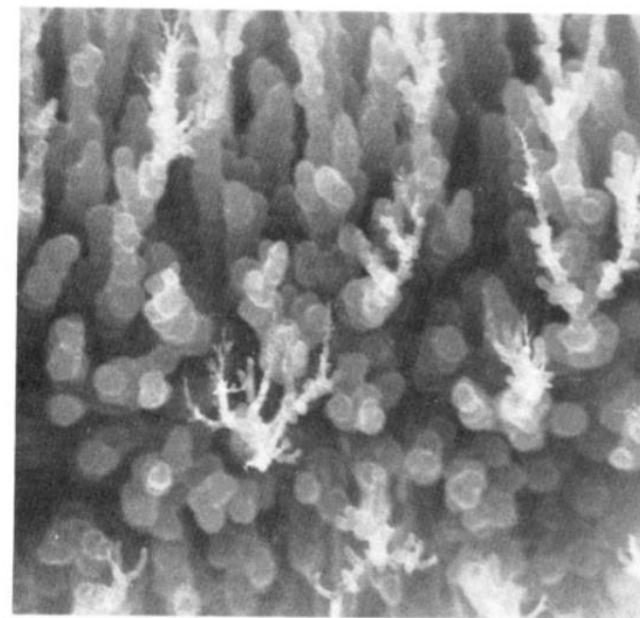


(c)

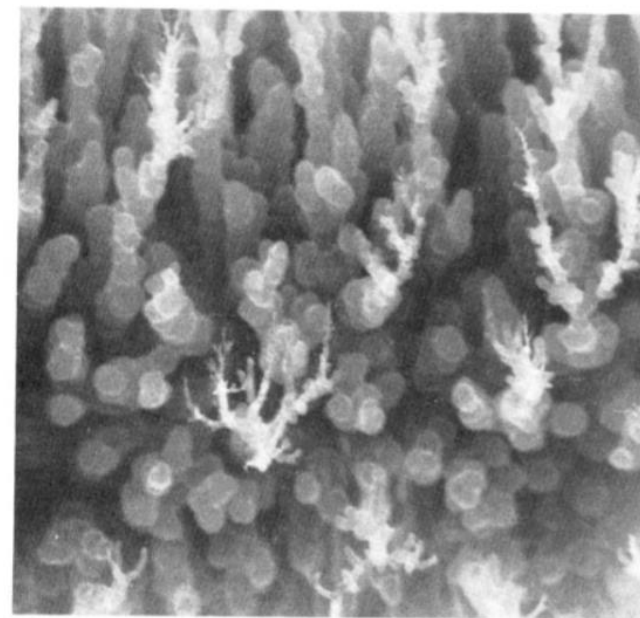
**Figure 2** Scanning electron micrographs of an HR emitter covered with carbon needles at magnifications of (a)  $30\times$ , (b)  $390\times$ , (c)  $2500\times$ .



(a)

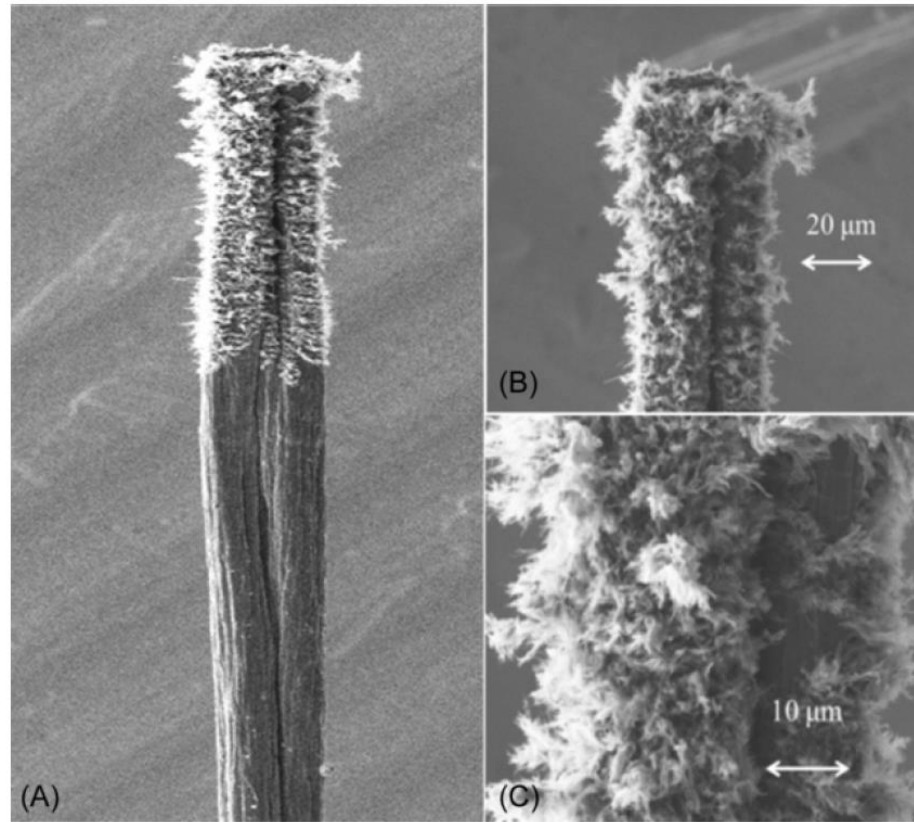


(b)



(c)

**Figure 3** HT emitter covered with carbon needles at magnifications of (a)  $34\times$ , (b)  $340\times$ , (c)  $2500\times$ .



**FIG. 5**

SEM images of a Cambridge fiber after FE measurements during which FE was observed from the sidewall of the fiber. (A) Evidence of damage on the tip and on the sidewall near the tip of the fiber. (B) and (C) Higher-resolution SEM images of the sidewalls near the tip of the fiber showing the CNTs in that region have been ripped apart during FE.

Cahay and colleagues have investigated FE from carbon fibres.

After some period of operation, it was found that the carbon fibres had "split apart".

[Or did they grow mini-needles, as a result of re-adsorption of thermally evaporated carbon ?]

[Diagram provided by: M. Cahay (Elsevier Handbook, in press, 2019).

**It is well known that very high fields can affect surface chemistry.**

**Extreme examples are:**

**formation of tungsten helides;**

**field-induced etching of tungsten by nitrogen.**

**It seems not implausible that somewhat lower fields have an influence on carbon chemistry.**

**Alternatively, relatively ordinary chemical mechanisms may operate, or ion bombardment might be playing a role.**



**How does growth initiate ?**

**Current thinking is that very small surface structures (with low field enhancement factors) usually tend to collapse.**

**Thus, the most plausible initiation mechanisms seem to be:**

- (a) Growth on top of an existing substrate feature.**
- (b) Formation of a linear carbon-based molecule “flat” on the surface, which subsequently gets “pulled upright” by Maxwell stress.**

**As regards (b), there seems evidence that “structure forming reactions” might take place at surfaces, either naturally, and/or by some surface catalytic effect, and/or with assistance from ion bombardment.**

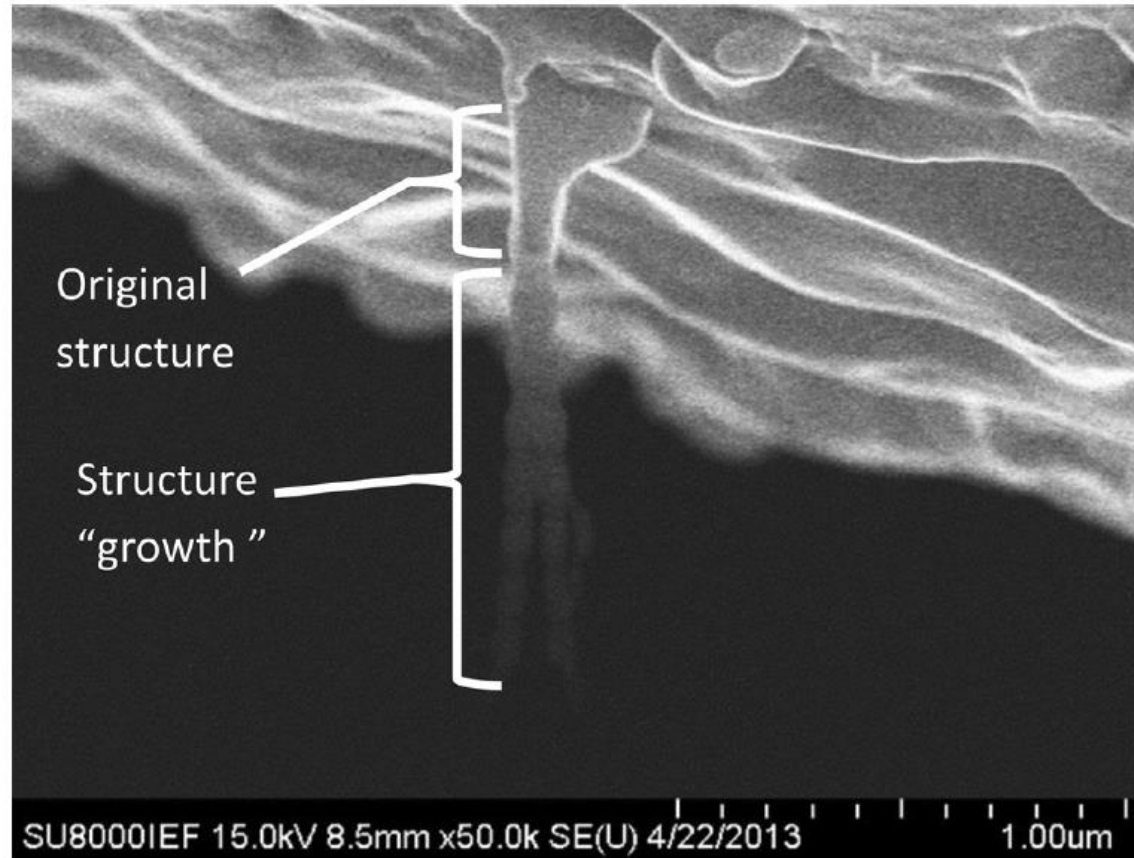


FIG. 3. SEM image of a structure grown on top of a pre-existing one. EDX analysis suggests that it consists mainly of carbon. The scale corresponding to  $1 \mu\text{m}$  is shown at the bottom right of the image.

Diagram courtesy: Márquez-Mijares et al. (2016) [R4], Fig. 3 .

# Resonance-stabilized hydrocarbon-radical chain reactions may explain soot inception and growth

K. O. Johansson<sup>1\*</sup>, M. P. Head-Gordon<sup>2,3</sup>, P. E. Schrader<sup>1</sup>,  
K. R. Wilson<sup>3</sup>, H. A. Michelsen<sup>1\*</sup>

Mystery surrounds the transition from gas-phase hydrocarbon precursors to terrestrial soot and interstellar dust, which are carbonaceous particles formed under similar conditions. Although polycyclic aromatic hydrocarbons (PAHs) are known precursors to high-temperature carbonaceous-particle formation, the molecular pathways that initiate particle formation are unknown. We present experimental and theoretical evidence for rapid molecular clustering–reaction pathways involving radicals with extended conjugation. These radicals react with other hydrocarbon species to form covalently bound complexes that promote further growth and clustering by regenerating resonance-stabilized radicals through low-barrier hydrogen-abstraction and hydrogen-ejection reactions. Such radical–chain reaction pathways may lead to covalently bound clusters of PAHs and other hydrocarbons that would otherwise be too small to condense at high temperatures, thus providing the key mechanistic steps for rapid particle formation and surface growth by hydrocarbon chemisorption.

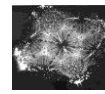
Abstract taken from: Science 361, 997 (2018).

**Part of what has been presented is speculative, but it seems that we ought to take seriously the possibility that (in appropriate circumstances) carbon nanostructures might form at surfaces, and contribute to electrical breakdown events.**

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**It is NOT being suggested that the cause of breakdown is ALWAYS a carbon field-enhancing structure. Perhaps ....**

- **in some contexts, metal structures may be the cause.**
- **in some contexts, carbon structures may be the cause.**
- **in some contexts, both metal and carbon structures may cause breakdown.**



**Thanks for your attention**

**Aim is to cover two topics:**

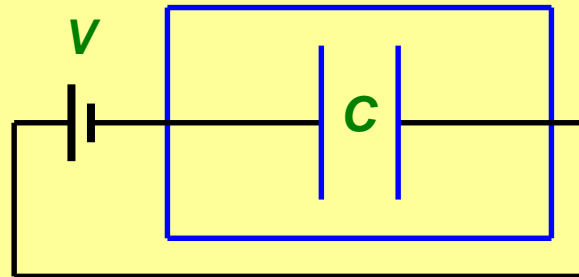
- A: Aspects of electrical thermodynamics and applications**
- B: The possible role of carbon in electrical breakdown**



- 1. Elements of electrical thermodynamics theory**
- 2. Illustrations of the limiting regimes**
- 3. Particular arguments about equilibrium shapes**
- 4. Atomic level theoretical terms**

# Elements of electrical thermodynamics theory

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  $\delta C$  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  **$w^{el} = V^2 \delta C$** .

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.

A general definition of a Gibbs function  $G$  is

$$G = \psi - w,$$

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

The electrical Gibbs function  $G^{\text{el}}$  is

$$G^{\text{el}} = \psi - Vq,$$

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

$$\delta G^{\text{el}} = \delta \psi - V\delta q.$$

The Helmholtz free-energy  $\mathcal{G}$  has to contain:

- a bulk term;
- a zero-field surface-energy term, which involves the (zero-field) surface free energy per unit area  $\gamma^0$  (also called “surface tension”);
- field-dependent surface terms;
- a classical electrostatic-capacitance ( $C$ ) term, which can alternatively be interpreted as a field-stress term or as an electrostatic vacuum-field-energy term.

If you use the simplest possible theory, you reach the formula

$$\delta G^{\text{el}} = \gamma^0 \delta A - \frac{1}{2} V^2 \delta C$$

where  $\delta A$  is change in surface area  $A$ .

$$\delta G^{el} = \gamma^0 \delta A - \frac{1}{2} V^2 \delta C$$

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

**This rule predicts**

- 1) When the applied voltage is very small, then the system-shape changes in such a way as to minimize the surface area, that is the system tends to “ball up”.**

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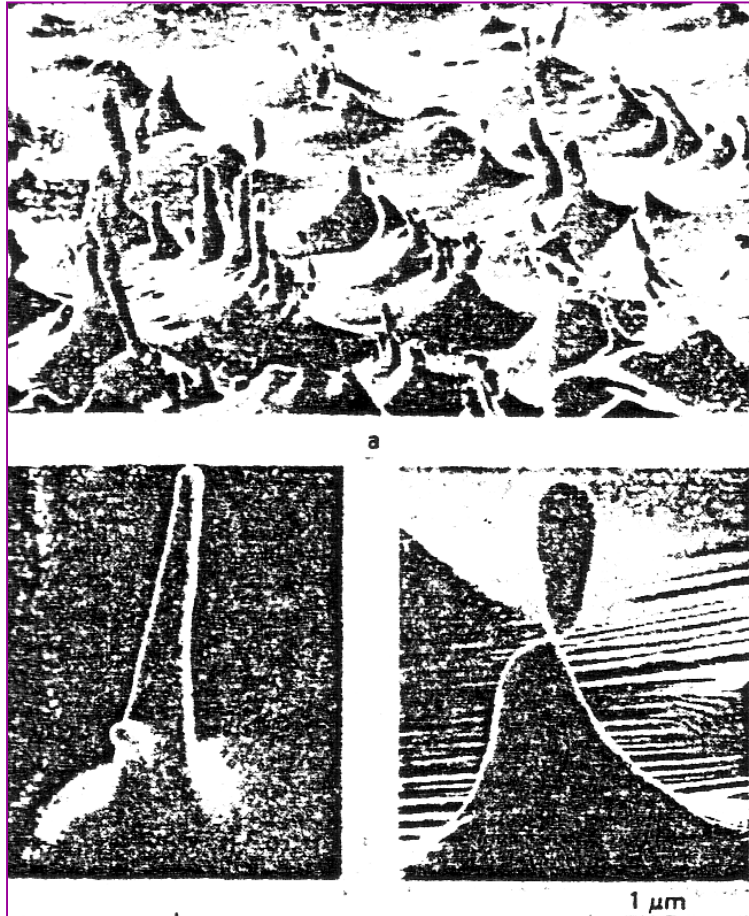
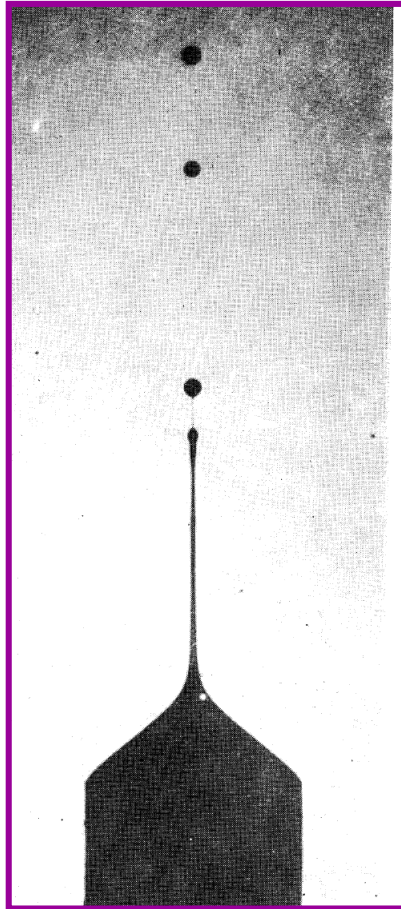
**A general rule of thermodynamics is that a system tends to change in such a direction that its Gibbs function becomes more negative.**

**This rule predicts**

- 1) When the applied voltage is very small, then the system-shape changes in such a way as to minimize the surface area, that is the system tends to “ball up”.**
- 2) When the applied voltage is sufficiently large, then the system-shape changes in such a way as to maximize the capacitance between the "active" (i.e. shape-changing) electrode and the counter-electrode, that is the system tends to “grow spikes”.**
- 3) There is a change-over condition, as voltage increases, from surface-area-driven behaviour to capacitance-driven behaviour.**



## Illustrations of the limiting regimes



**Tellis oil cone-jet.**  
Diagram courtesy: G.I.  
Taylor,  
Proc. R. Soc. Lond. A 313,  
435-475 (1969), Fig. 8b.

**Frozen field-induced metal cone-jets**  
Diagram courtesy: M.D. Gabovich,  
Sov. Phys. Uspekhi 26, 447 (1983), Fig. 8.

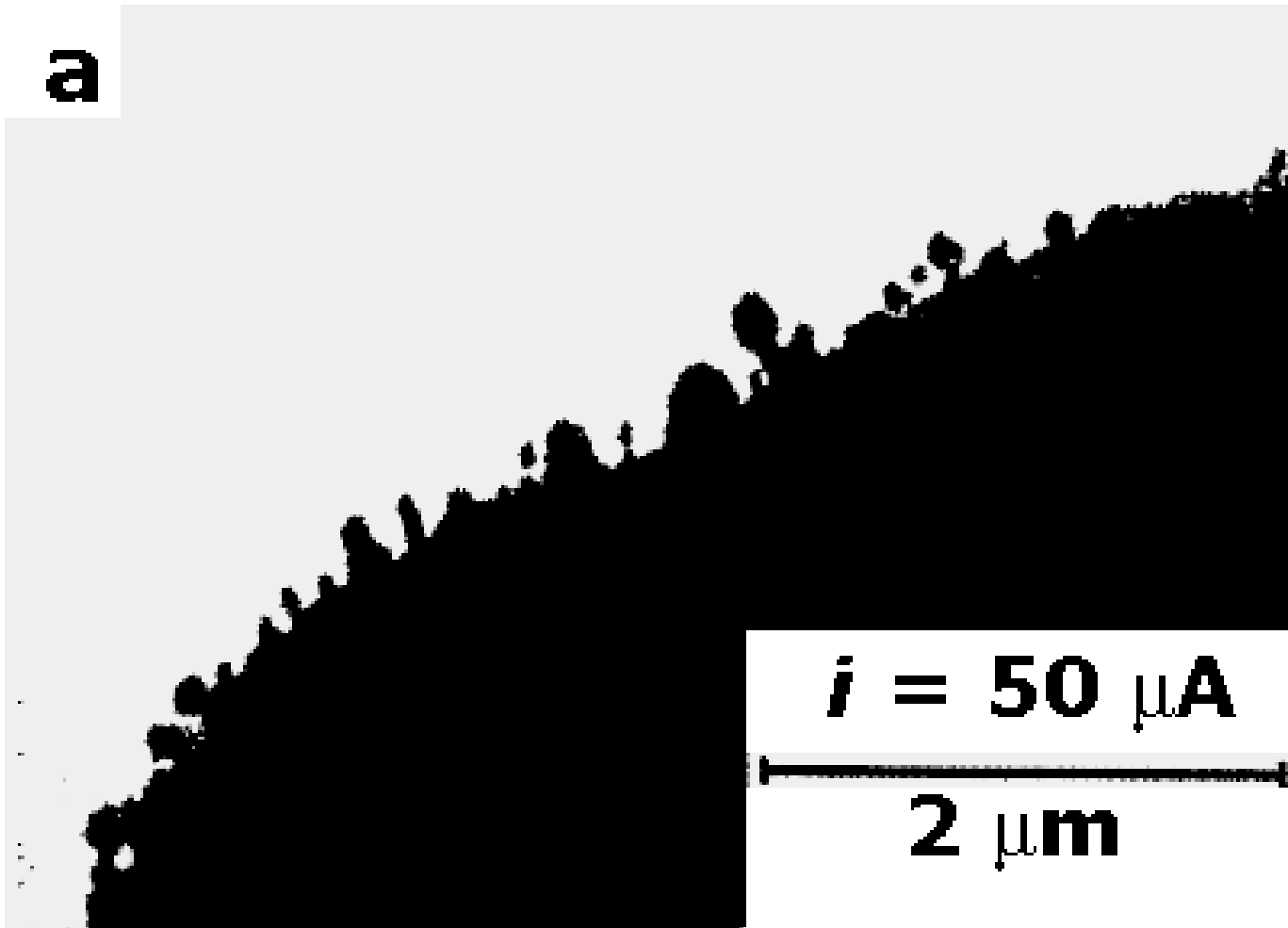
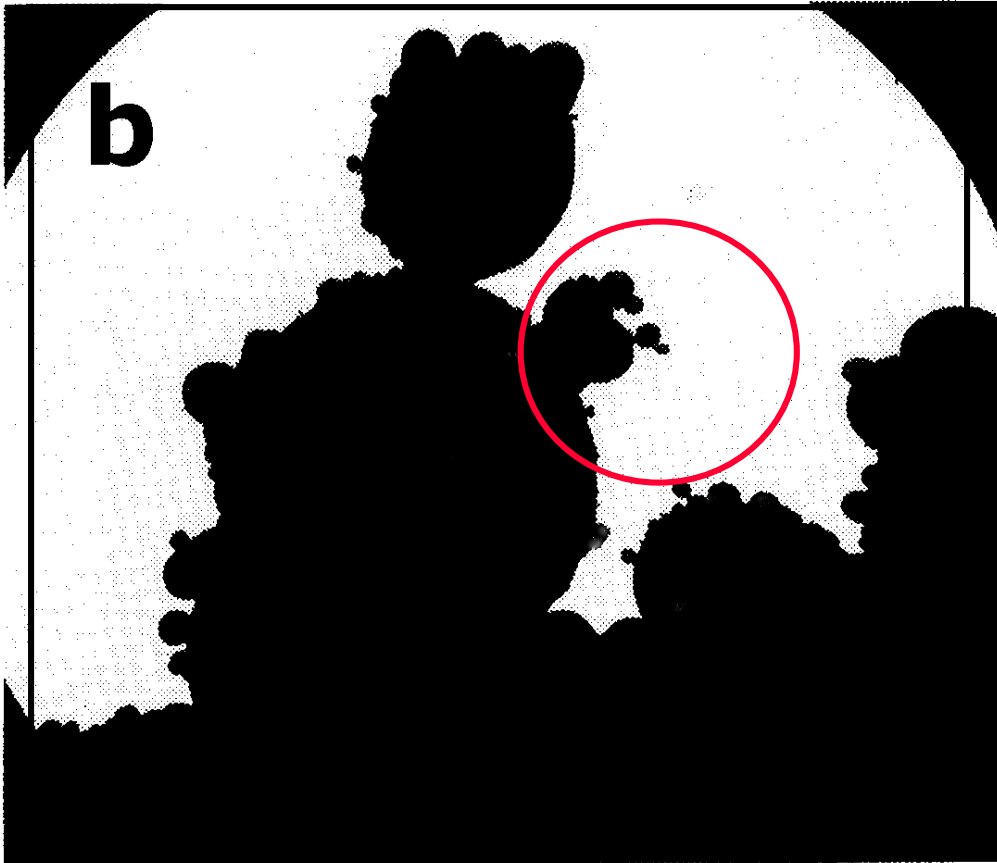


Diagram courtesy: H. Niedrig, W. Driesel & B. Praprotnik.

Extracted from video recording provided privately by H. Niedrig.



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.


  
10  $\mu\text{m}$

Diagram courtesy:

B. Praprotnik, W. Driesel, Ch. Dietsch & H. Niedrig, Surf. Sci. 314, 353 (1994), Fig. 7 (e).

The Helmholtz free-energy  $\mathcal{F}$  has to contain:

- a bulk term;
- a zero-field surface-energy term, which involves the (zero-field) surface free energy per unit area  $\gamma^0$  (also called “surface tension”);
- field-dependent surface terms;
- a classical electrostatic-capacitance ( $C$ ) term, which can alternatively be interpreted as a field-stress term or as an electrostatic vacuum-field-energy term.

The Helmholtz free-energy  $\psi$  has to contain:

- a bulk term;
- a zero-field surface-energy term, which involves the (zero-field) surface free energy per unit area  $\gamma^0$  (also called “surface tension”);
- field-dependent surface terms;
- a classical electrostatic-capacitance ( $C$ ) term, which can alternatively be interpreted as a field-stress term or as an electrostatic vacuum-field-energy term.

The contribution due to field-dependent surface terms is sometimes described as due to **polarization and partial ionization (PPI)**, and can be denoted by  $\psi_{PPI}$ . For a single atom, we can write:

$$\psi_{PPI} = \mu_{PPI} F + \frac{1}{2} C_{PPI} F^2$$

where  $F$  is an appropriate field,  $\mu_{PPI}$  is the **linear-term coefficient** and  $C_{PPI}$  is the **quadratic-term coefficient**.

## **B: The possible role of carbon in electrical breakdown**

- [R1] V. Jansson, E. Baibuz, A. Kyritsakis & F. Djurabekova, "Adatom diffusion in high electric fields", arXiv:1708.04694.
- [R2] J.W. Wang & G.A. Loew, "Field emission and RF breakdown in high-gradient room-temperature Linac structures", SLAC-PUB-7684 (SLAC, October 1997).
- [R3] K. Almaksour, M.J. Kirkpatrick, Ph. Dessante, E. Odic, A. Simonin, H.P.L. de Esch, B. Lepetit, D. Alamarguy, F. Bayle & Ph. Teste, "Experimental studies of the reduction of field emission by gas injection in vacuum for accelerator applications", Phys. Rev. Sp. Topics Accel. Beams. 17, 103503 (2014).
- [R4] M. Márquez-Mijares, B. Lepetit & D. Lemoine, "Carbon adsorption on tungsten and electronic field emission", Surface Sci. 645, 56 (2016).
- [R5] M. Márquez-Mijares, B. Lepetit, D. Lemoine, K. Almaksour, M.J. Kirkpatrick, P. Dessante, E. Odic, D. Alamarguy, F. Bayle, P. Teste & F. Karlicky, "Influence of ambient gas pressure and carbon adsorption on dark current emission from a cathode", J. Vac. Sci. Technol. B 34, 061208 (2016).
- [R6] R.G. Forbes, "Gas field ionization sources", Chap. 3 in: J. Orloff (ed.) Handbook of Charged Particle Optics, 2<sup>nd</sup> Edition (CRC Press, Boca Raton, 2009), pp. 87-128, see Appendix A.
- [R7] Y. Sugiyama et al., "Numerical simulations on capture area of gas molecules for high brightness gas field ion source", J. Vac. Sci. Technol. B 28, C2A83 (2010).



**End of file**

## Particular arguments about equilibrium shapes

$$\delta G^{el} = \gamma^0 \delta A - \frac{1}{2} V^2 \delta C$$

In the special ideal case where  $\gamma^0$  is assumed uniform and the system is a sphere of radius  $r$ , surrounded by a spherical counter-electrode of very large radius, then: **area**  $A = 4\pi r^2$ ,  $C \approx 4\pi\epsilon_0 r$ , and **surface field**  $F = V/r$ .

Manipulation yields

$$\delta G^{el} = (2\gamma^0/r - \frac{1}{2}\epsilon_0 F^2) A \delta r,$$

or 
$$\delta G^{el}/A = (2\gamma^0/r - \frac{1}{2}\epsilon_0 F^2) \delta r,$$

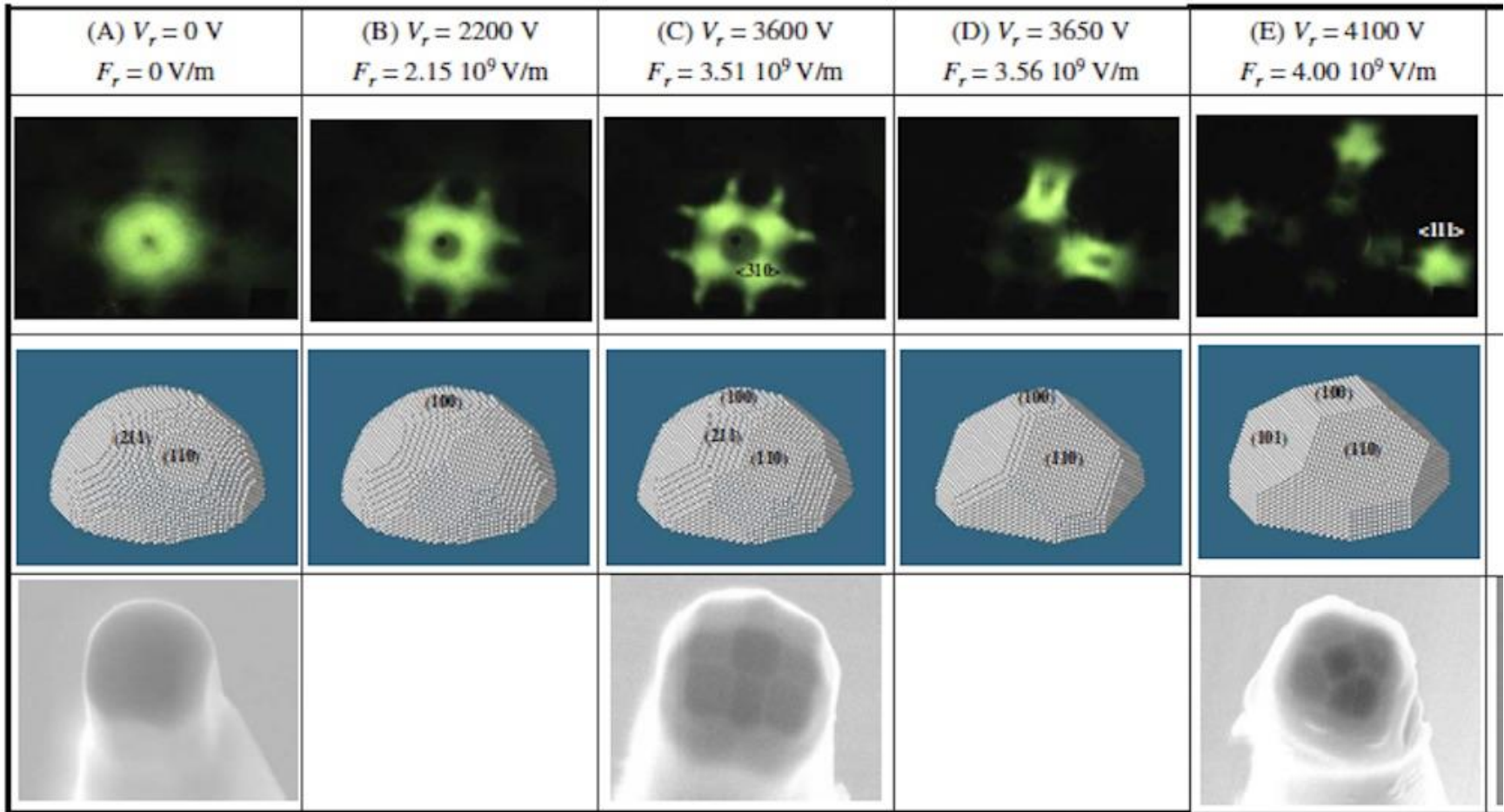
or 
$$\square(G^{el}/A)/\square r = (2\gamma^0/r - \frac{1}{2}\epsilon_0 F^2).$$

The term in brackets may read as “Surface-tension stress inwards less Maxwell stress outwards”.

This is often interpreted as a **stress-based stability condition**. The argument is that  $\delta G^{el}$  becomes negative when the field becomes higher than a **change-over field**  $F_{co}$  at which the Maxwell stress becomes greater in magnitude than the surface-tension stress. Hence, at this change-over, the object tends to become unstable and change its shape.

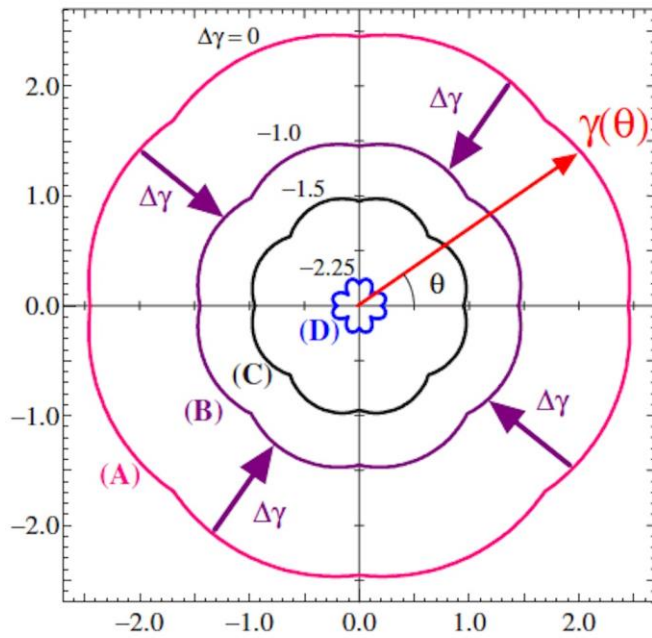
[In reality, this argument is too simple.]

# Emitter shape depends on applied field

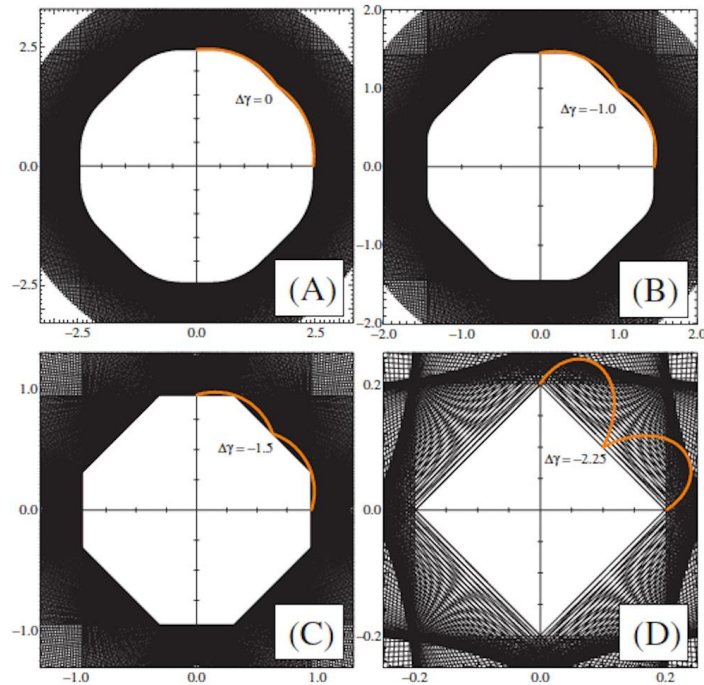


More generally, the equilibrium shape of a field emitter tip depends on the value of the applied field (and, obviously, affects the field electron emission images).

Diagram courtesy: S. Fujiota & H. Shimoyama, Phys. Rev. B 75, 235431 (2007), Fig. 5.



(a) Surface tension reduction by electrostatic field

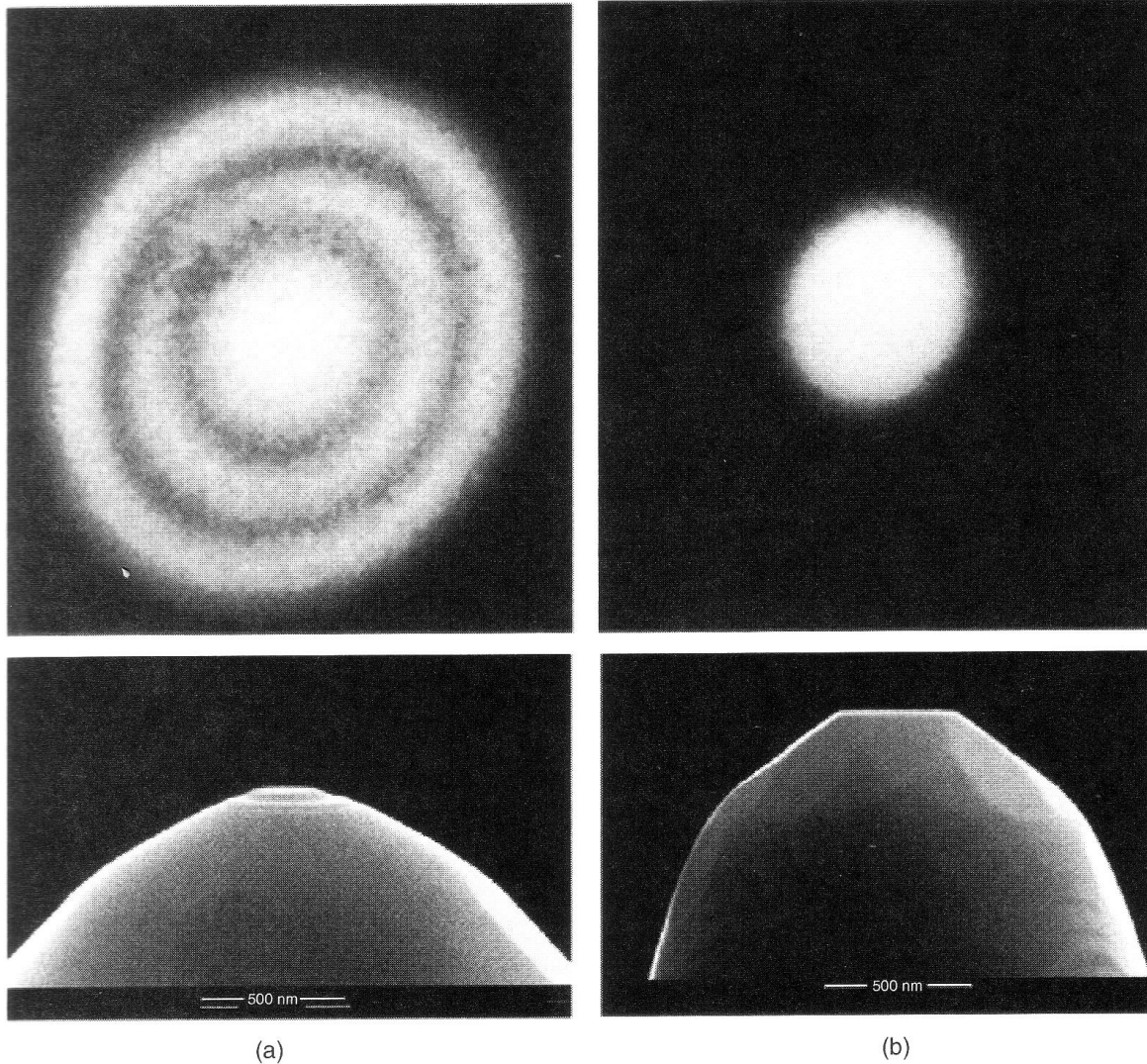


(b) Evolution of Equilibrium Crystal Shape

Effects of this kind can be explained by a Wulff-type methods, with the local "electrical Gibbs function per unit area" taking the place of the local surface free energy per unit area ("local surface tension"). Alternatively, the Gibbs function can be treated as a (reduced) "effective surface tension", as in the diagrams above.

Diagram courtesy: S. Fujitota & H. Shimoyama, Phys. Rev. B 75, 235431 (2007), Fig. 10.

# Schottky-emitter formation



Thermal-field (TF) shaping effects of this kind are used to make commercial "Schottky emitters".

Diagram courtesy: L.W. Swanson & G.A. Schwind, "Review of ZrO/W Schottky cathode", in: J. Orloff (ed.) Handbook of Charged Particle Optics, 2<sup>nd</sup> Edition (CRC Press, Baton Rouge, 2009), Fig. 1.5 .

FIGURE 1.5 Field electron microscope emission patterns (upper) and corresponding scanning electron microscope images of the emitter shapes (lower) for the ZrO/W SE cathode: (a) immediately after thermal processing at 1800 K in a low electric field and (b) after long-term heating at 1800 K in a high electric field.

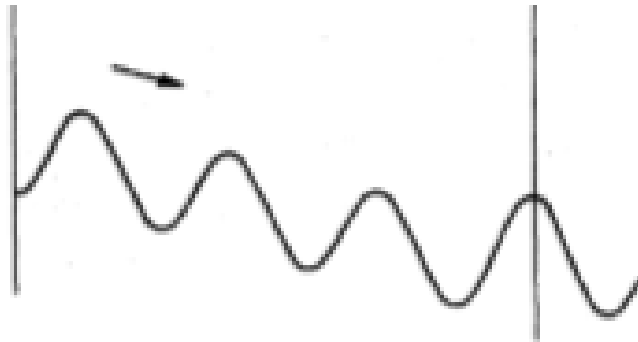
So a fuller atomic-level theory has **THREE** field-related terms

- Linear and quadratic PPI terms and
- A quadratic vacuum-field-energy term

So the scientific issue is: Is one of these terms dominant? Or do we have to include all ? [And, do current DFT codes capture both  $F^2$  terms ?]

A particular context where these issues arise is diffusion across surfaces in the presence of high fields (as per diagram below).

This is relevant both (a) to old experiments (1975) by Tsong and Kellogg\*\*, and (b) to the growth of nanoprotusions.



\*\*T.T. Tsong & G. Kellogg, Phys. Rev. B 12, 1343 (1975).

Taking a  $\mu_{PPI}$  value from the Tsong-Kellogg experiments, and other coefficient values from DFT calculations, Ville Jansson and the Helsinki group [R1] have been able to reproduce the experimental Tsong-Kellogg diffusion results.

On the other hand, I showed long ago that the effect of fields on *average* surface-atom bonding energies can be explained as a vacuum field-energy effect, and gives agreement with experiment within the estimated error limits.

And all the old thermal-field shaping work, described earlier, used field-stress arguments (which are equivalent to vacuum field-energy arguments).

In my view, there are unresolved issues as to precisely which term or terms (effect or effects) are the primary cause(s) that drive: (a) the operation of liquid-metal ion sources (and related electrohydrodynamic effects); (b) the growth of conducting nanoprotusions, and (c) other forms of thermal-field shaping.