

Electrostatic theory of metal whiskers

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FIG. 1. Scanning electron microscope (SEM) pictures of tin (left) and zinc (right) whiskers. Courtesy of the NASA Electronic Parts and Packaging (NEPP) Program [6].

Thank you, NEPP for
inspirational pictures
and presentations, and
for your courtesy!

Presenting a recent publication: V. G. Karpov “Electrostatic Theory of Metal Whiskers”
PHYSICAL REVIEW APPLIED 1, 044001 (2014)

Disclaimer

- Some may find the explanations insufficient, and some excessive, and some both. It is often this way when looking into areas of science that are to an excessive degree unknown or ill-understood, and many unknown elements are themselves unknown. (*Steve Smith, private communication*)
- Two parts: (A) up to slide 25–introducing some underlying concepts; (B) slides 26-54 to be delivered next time, more closely whisker related.
- Several complimentary slides by the end
- Ask questions at any time

Part A

Outline

- Motivation
 - Facts as seen by a novice
 - Hypotheses as seen by a novice
- Birdseye view of the proposed
- Background: phase transformations (minimalistic overview)
 - Classical (Gibbs) nucleation theory
 - Homogeneous and inhomogeneous nucleation
 - Post-nucleation stages: growth and ripening
 - Field induced nucleation
- Charged patches on metal surfaces
- Electric field distribution near metal surfaces
- Nucleation of whiskers
- Growth of whiskers
- Whisker statistics
- Predictions and suggested mitigation strategies
- Conclusions: what is/isn't understood, possible future work

Motivation (facts are many)

- "...there are many phenomena that produce roughly the same thing: a tin whisker." *Bill Rollins, private communication*
- Lack of remedies means lack of sufficient understanding of cause and effect relations
- Correlations observed:
 - Stresses (external or internal)
 - Oxidations
 - Interfacial defects and grain boundaries
 - Contaminations
- Always with metals (semiconductor/nano whiskers are different)
- Aspect ratios unseen with other physical objects, up to 10,000
- Broad statistical distributions of parameters (randomness)
- Significant effects of additives (at least Pb) and ambient (Ag, etc.)
- Contradictory reports on electric field effects
- In spite of significant damages -- amazingly long time (60+) since observation [exceeding that for superconductivity (1911-1957)!]

Motivation (hypotheses)



- Mainstream: whiskers relieve stress
(challenged: Jadhav et. al. 2009)
- External stresses (bending, squeezing)
- Internal stresses (intermetallic compounds, dislocations, etc.)
- Stress related to hydrogen embrittlement; H is omnipresent
(Ashraf Jafri, 1969)
- Reaction with oxygen introducing stress; O is omnipresent
(M.W. Barsoum et. al 2004)
- Ionic contaminations; omnipresent
(possibly translated into stresses; Zn, Ag, etc., esp., T. Munson, P. Solis, 2010?)
- Stress gradients (M. Sobiech et. al. 2008)
- Multiple grain boundary features and diffusion processes that may be relevant and yet generate strong informational noise
- A mystery of high aspect ratios: why wouldn't they collapse into 'spheres', as other droplets do to minimize surface energy?
- What is a long range force that drives them up?
- Is their relation to metals of essence?
- What is behind their randomness?
- What does Pb do?

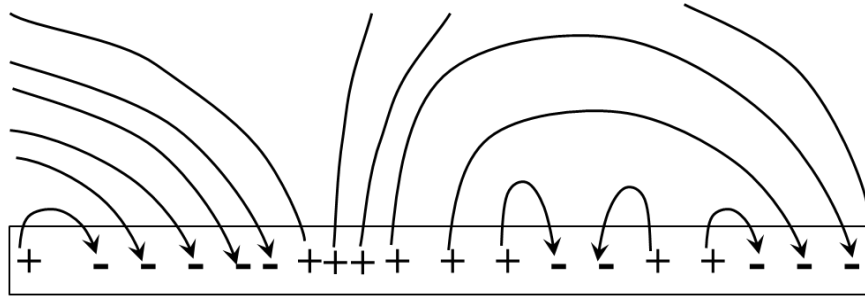
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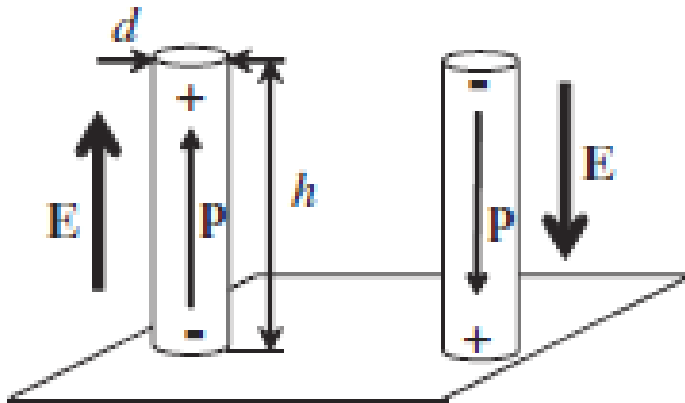
Birdseye view

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Electric forces are omnipresent and long-ranged



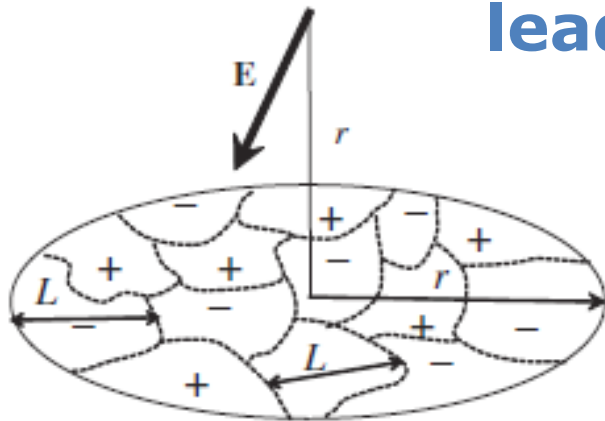
Imperfect metal surfaces contain random charged patches that create significant electric fields, up to 1 MV/cm



Like charges repel producing an outward stress. Where the material is weak enough, whiskers can grow. They provide polarization electrostatic energy gain $-\mathbf{p} \cdot \mathbf{E}$

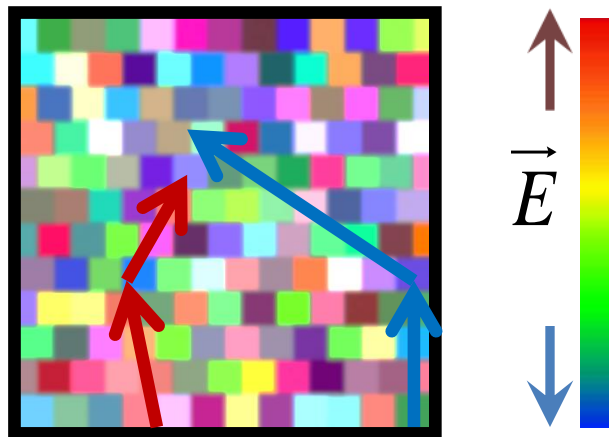
Birdseye view

In addition, these electric forces are random leading to whisker statistics



Beyond the patch size ($r \gg L$) whiskers grow in a random field by many oppositely charged patches

L is the patch size



- Rapid growth while either **+** or **-** fields dominate along the length.
- For large lengths, **+** and **-** fields start balancing each other.
- Whiskers *stop growing* at certain random lengths (*statistics*)
- Can resume growth after a while

Whiskers along predominantly reddish **+** or bluish **-** paths

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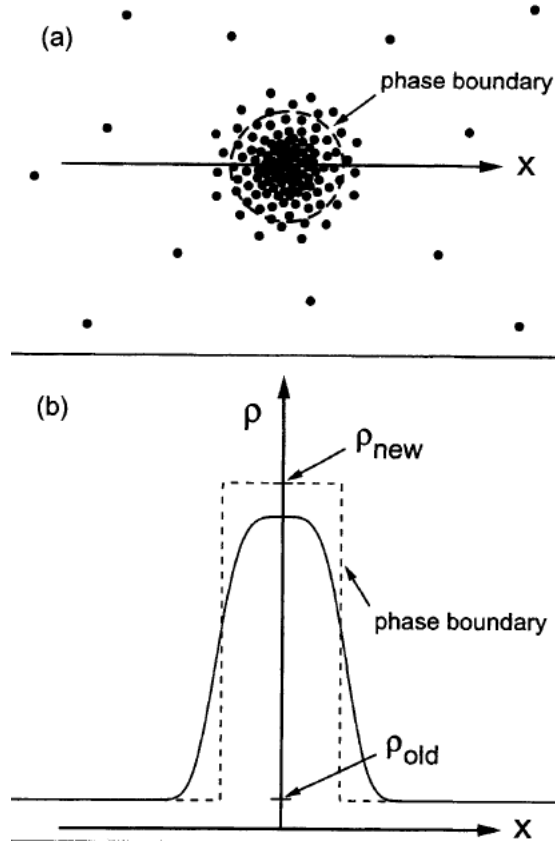
Three stages of the 1st order phase transitions

- 1st order refers to PT, in which changes take place for thermodynamic quantities: volume, internal energy, chemical potential, etc. (2nd order refers to PT where these quantities remain, however their derivatives change, say, heat capacity, $C=dU/dT$).
- Examples: water droplets forming from vapor, steam bubbles forming in a hot water, ice crystals forming in a water, crystalline particles forming in a glassy host, etc.
- The kinetics of 1st order PT includes three stages:
 - (1) nucleation, where particles of a new phase are formed having minimum allowed radii,
 - (2) growth, where these particles grow not yet affecting each other, and
 - (3) coalescence (aka as ripening or Ostwald ripening) where particles compete for the material, and large particles grow at the expense of smaller ones.

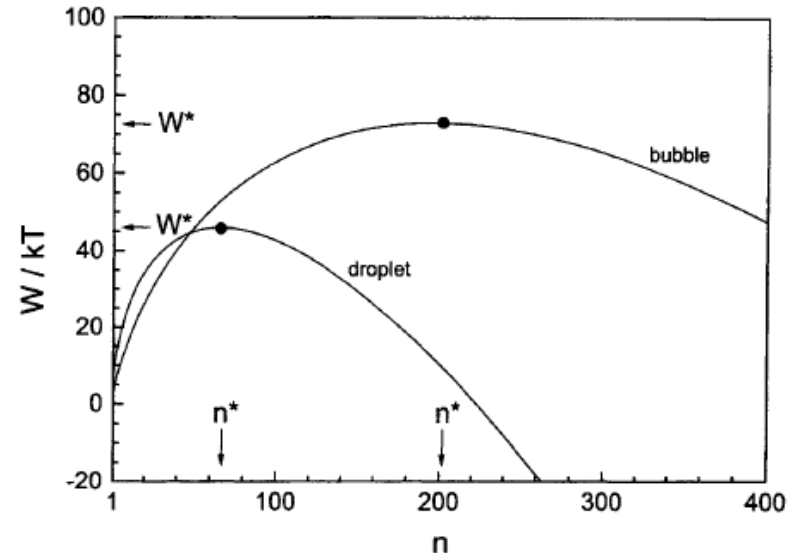
More general view of nucleation and growth

- **Nucleation** is the process of forming a nucleus. It is the process in which ions, atoms, or molecules arrange themselves in a pattern... (*Wikipedia*)
- Can be applied to processes where there is no new phase, but rather shape transformations: nucleation of dry spots in the process of wet film evaporation, nucleation of voids in crystals under radiation,... nucleation of whiskers as distinct patterns.
- Can be applied outside physics: nucleation of ethnic communities in NY and Chicago, nucleation of gangs..
- In all cases, a nucleus above some finite size become stable
- Most often, nuclei assume a shape with a minimum surface area (roundish) to minimize surface energy
- The process by which that nucleus evolves is called growth

Phase boundary and cluster size



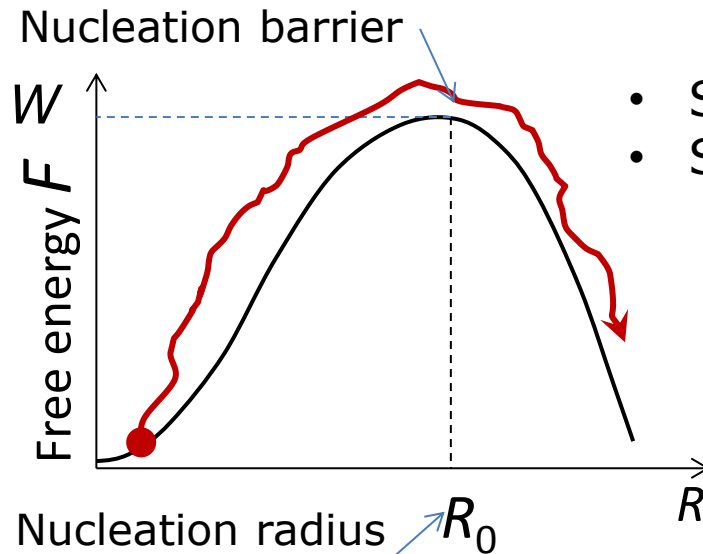
Nanoscopical formation of a condensed phase according to (a) the cluster, and (b) the density-functional approach. The dashed line visualizes the phase boundary (classical approach) between the cluster and old phase.



Dependence of the work for cluster formation on the cluster size: curve 'droplet'-for water droplets in vapor at $T = 300$ K and $P/P_e = 4$; curve 'bubble' - steam bubbles in water at $T = 583$ K and $P_e/P = 4$. Note $n \gg 1$ in both cases.

Classical (Gibbs) nucleation theory: energy loss due to interface, energy gain due to bulk

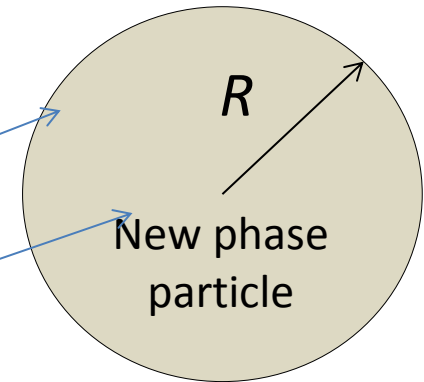
Nucleation time, $\tau = \tau_0 \exp\left(\frac{W}{kT}\right)$, $\tau_0 \sim 1$ ps for solids



- Spherical nuclei
- Surface vs. bulk

$$A = 4\pi R^2$$

$$V = 4\pi R^3 / 3$$



Proved adequate in a variety of applications (gas/fluid, liquid/solid, glass/crystal, etc.)

$$F = 4\pi R^2 \sigma - 4\pi R^3 \mu / 3, \quad \frac{dF}{dR} = 0 \quad \mapsto$$

$$R_0 = \frac{2\sigma}{\mu} \sim 1-3 \text{ nm}, \quad W = \frac{16\pi\sigma^3}{3\mu} \sim 1-10 \text{ eV}$$

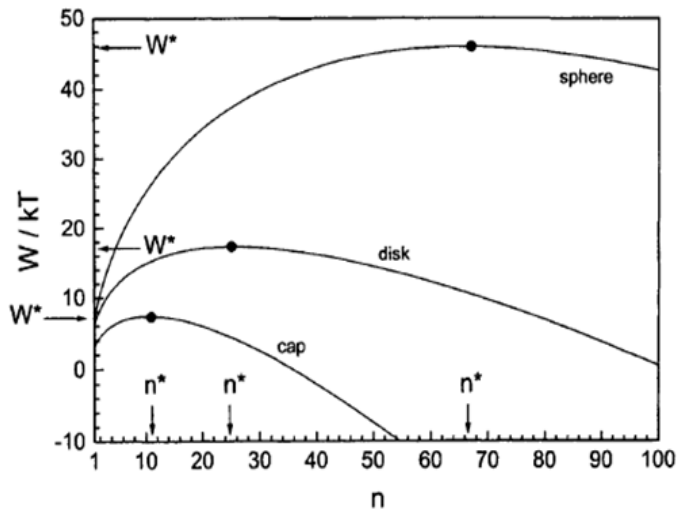
σ – surface energy, μ – change in the chemical potential,

Classical nucleation theory will be used in what follows

D. Kaschiev, Nucleation: Basic Theory with Applications (Butterworth-Heinemann, Oxford, Amsterdam, 2000). K. F. Kelton, in Solid State Physics, edited by H. Ehrenreich and D. Turnbull (Academic Press, Boston, 1991), Vol. 45, p. 75.

Heterogeneous Nucleation

$$\tau = \tau_0 \exp\left(\frac{W}{kT}\right), \quad W = \frac{16\pi\sigma^3}{3\mu} \sim 1-10 \text{ eV}, \quad kT \approx 0.025 \text{ eV}$$

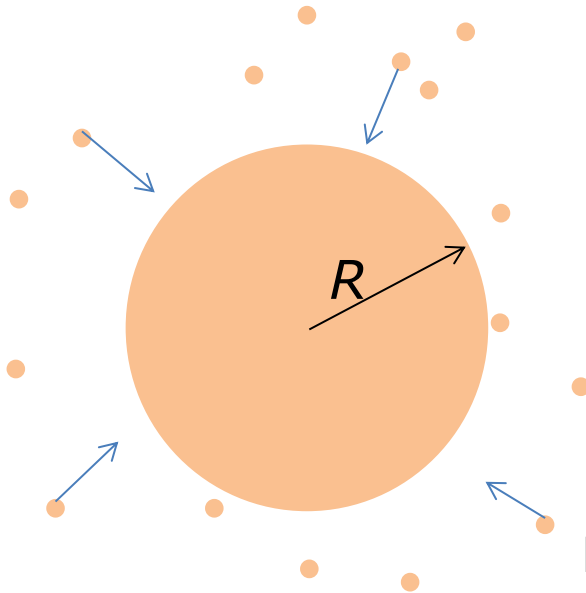


Dependence of the work for cluster formation on the cluster size in the case stand alone droplets in vapor, for caps on a substrate, and disks on a substrate. D. Kaschiev, Nucleation: Basic Theory with Applications (Butterworth-Heinemann, Oxford, Amsterdam, 2000).

- Small variations in surface energy σ (and or μ) will exponentially affect nucleation rate \rightarrow
- Surfaces, surface imperfections will serve as efficient nucleation centers \rightarrow heterogeneous nucleation
- Gibbs theory introduces the concept of nucleation and its important parameters in general
- Heterogeneous nucleation is system/defect specific; general trends limited
- **In most cases, nucleation is heterogeneous**

V. G. Karpov and D. W. Oxtoby, Phys. Rev. B 54, 9734 (1996);
M. Castro, Phys. Rev. B **67**, 035412 (2003), V. G. Karpov et. al.
J. Appl. Phys. 104, 054507 (2008).

Post-nucleation stages. Growth



- Growth by accretion
- Achieved in many steps of attaching new molecules
- Described kinetically
- A compact approach can be developed through the **Fokker-Planck equation**

For 1D growth

$$\frac{dR}{dt} = -b \frac{\partial F}{\partial R}$$

t is time, b is the mobility in the radii space (proportional to the diffusion coefficient or reaction rate), F is the free energy.

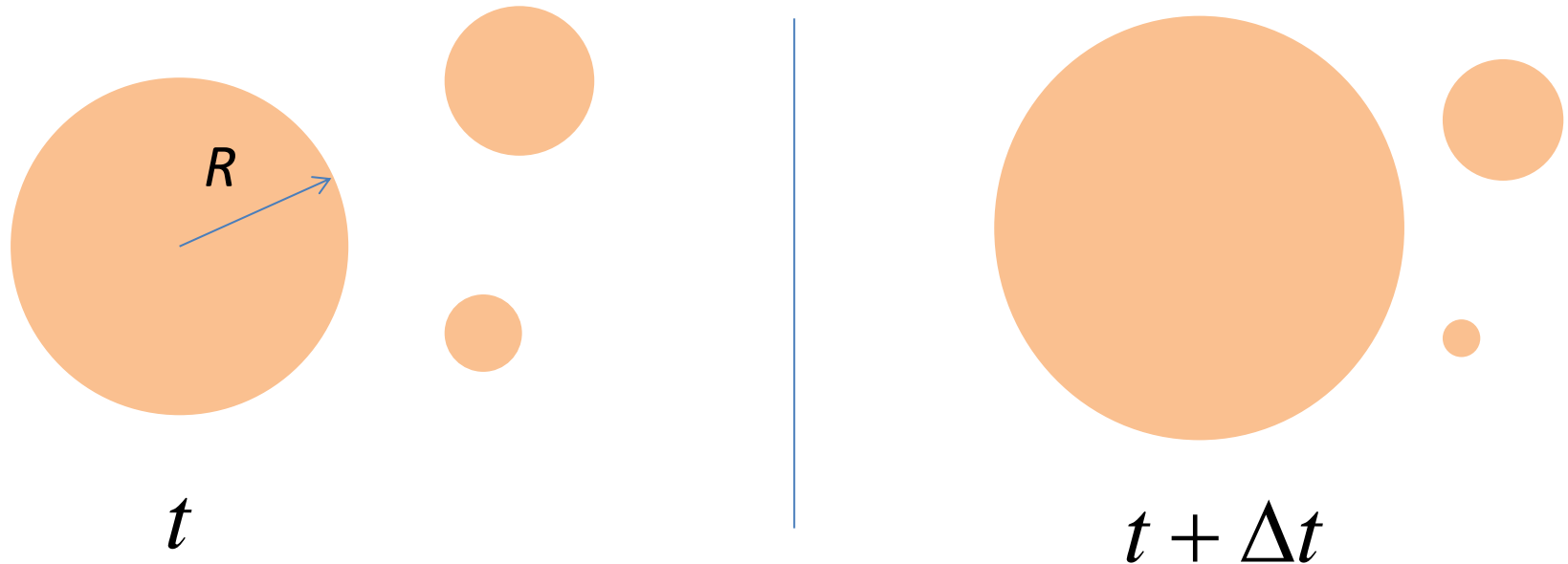
Similar to the relation between velocity and force ($v=bF$)

[Can be amplified with heat transfer, T-effects on diffusion and surface tension, and other factors, as, e. g. water droplets in clouds.]

Fokker-Planck equation will be used in what follows

E. M. Lifshitz and L. P. Pitaevskii, *Physical Kinetics* (Elsevier, Amsterdam, Boston, 2008); V. G. Karpov, et. al. *J. Appl. Phys.*, 109, 114507 (2011).

Post-nucleation stages. Ostwald ripening



Large particles grow at the expense of small ones.

Average radius, $\langle R \rangle \propto t^{1/3}$

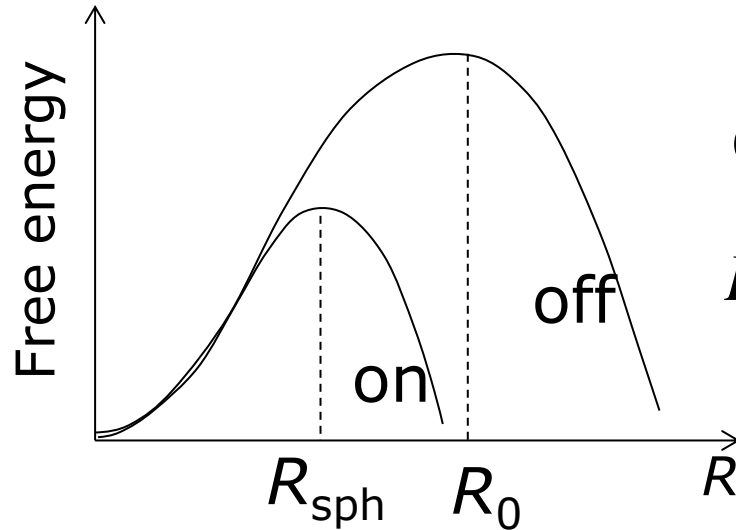
This stage will not be analyzed in what follows for whiskers

E. M. Lifshitz and L. P. Pitaevskii, *Physical Kinetics* (Elsevier, Amsterdam, Boston, 2008).
V. G. Karpov, *Phys. Rev. B* **52**, 15846 (1995).

Field Effect. Spherical Nuclei

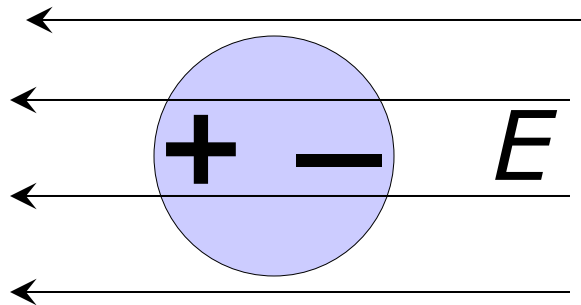
Field decreases nucleation barrier

Previously known for fields < 10 kV/cm



Classical nucleation theory

$$F = 4\pi R^2 \sigma - 4\pi R^3 \mu / 3 - R^3 E^2 \epsilon / 2$$

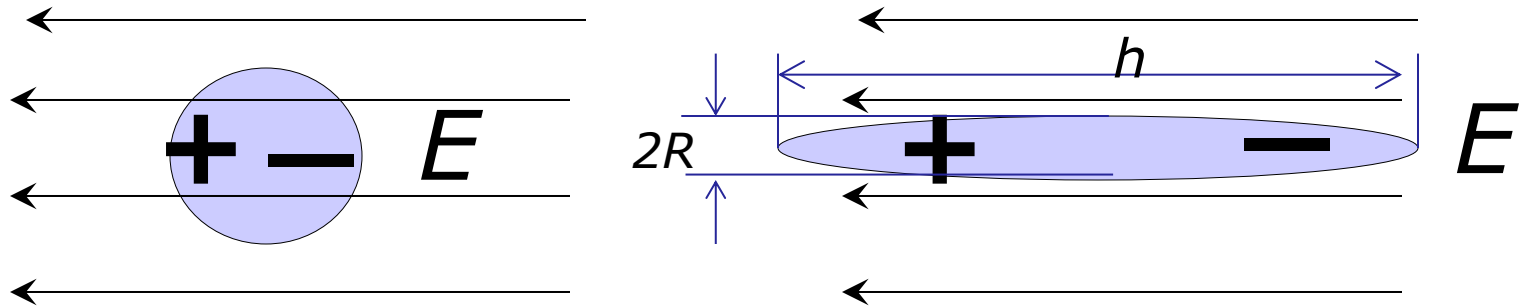


Physical mechanism:
electrostatic polarization
and dipole energy $W = -pE$

W. Liu, *et al.* J. Phys. D: Appl. Phys. **30**, 3366 (1997);

C.C. Koch, *et al.* Material Science and Engineering, A **287**, 213 (2000)

Field Induced Nucleation: Needle-shaped Particles



The same volume needle has much bigger dipole moment

$$p_{needle} \approx p_{sphere} \left(\frac{h}{R} \right)^2 \gg p_{sphere}$$

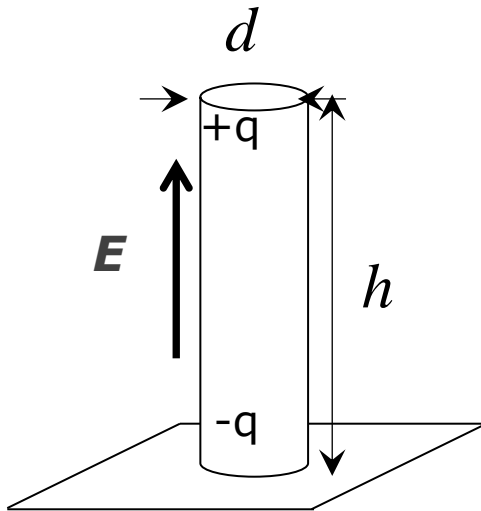
Electrostatic energy gain $W = -pE$ much stronger for needles

Nucleation of needle shaped nuclei will dominate

V. G. Karpov, et. al: Appl. Phys. Lett., **90**, 123504 (2007); Phys. Rev. B **78**, 052201 (2008);
Phys. Rev. B **86**, 075463 (2012)

Gigantic polarizability of a metal filament

The induced charges $\pm q$ create field to cancel E inside a metal \rightarrow



$$\frac{q}{h^2} \sim E \Rightarrow q \sim Eh^2 \Rightarrow p = qh \sim h^3 E \Rightarrow$$

$$\alpha \sim h^3 \sim V \left(\frac{h}{d} \right)^2, \quad V = \pi d^2 h / 4 - \text{volume}$$

$$\left(\frac{h}{d} \right)^2 \gg 1 \text{ enhancement compared to sphere.}$$

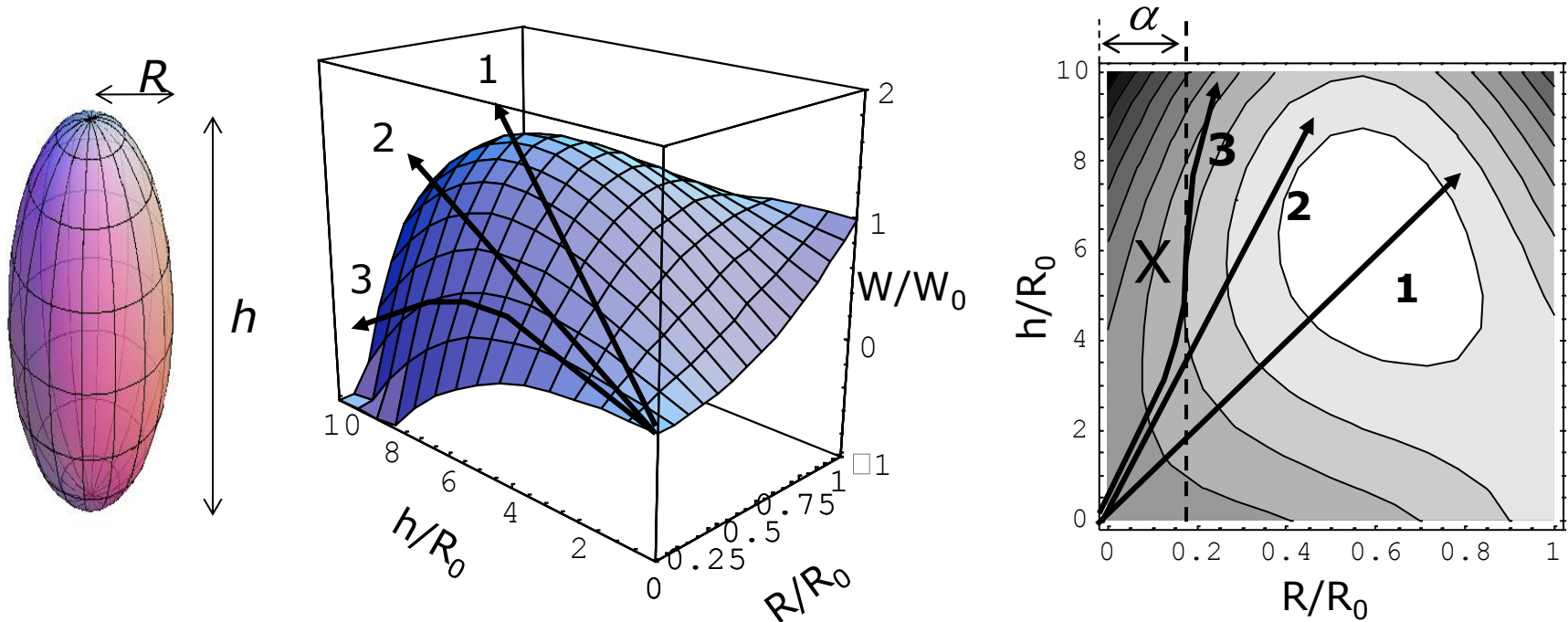
$$\text{Rigorous result: } \alpha = 2h^3 [3\ln(4h/d) - 7]^{-1}$$

Image charge effect \uparrow

L. D. Landau, et. al., *Electrodynamics of Continuous Media* (Pergamon, Oxford, 1984).

R. Maltby et.al., ms. under preparation

Needle Nucleation: 2D Space (h, r)



Nucleus can evolve in \mathbf{R} or \mathbf{h} along the **transition coordinate X**
Given this **extra freedom**, nucleation occurs via **lower barriers**

Ideally, $R=0$. Practically, minimum radius stable metal filament,
 $\mathbf{R}=\alpha\mathbf{R}_0$, $\alpha \sim 0.1$ – dimensionless empirical coefficient

Spherical Vs. Needle Nuclei

Characteristic field, nucleation barrier and dimensions

Spherical

$$E_0 = \sqrt{W_0 / R_0^3 \varepsilon} \approx 10^6 \text{ V/cm}$$

$$W = W_0 [1 + (E/2E_0)^2]^{-2},$$

$$R = R_0 [1 + (E/2E_0)^2]^{-1}$$

Needle-shaped

$$E_c = 2\sqrt{\alpha^3 W_0 / R_0^3 \varepsilon} \approx 10^4 \text{ V/cm}$$

$$W = W_0 E_c / E,$$

$$h = R_0 E_c / \alpha E \gg R,$$

$$R = \alpha R_0, \quad \alpha \sim 0.1$$

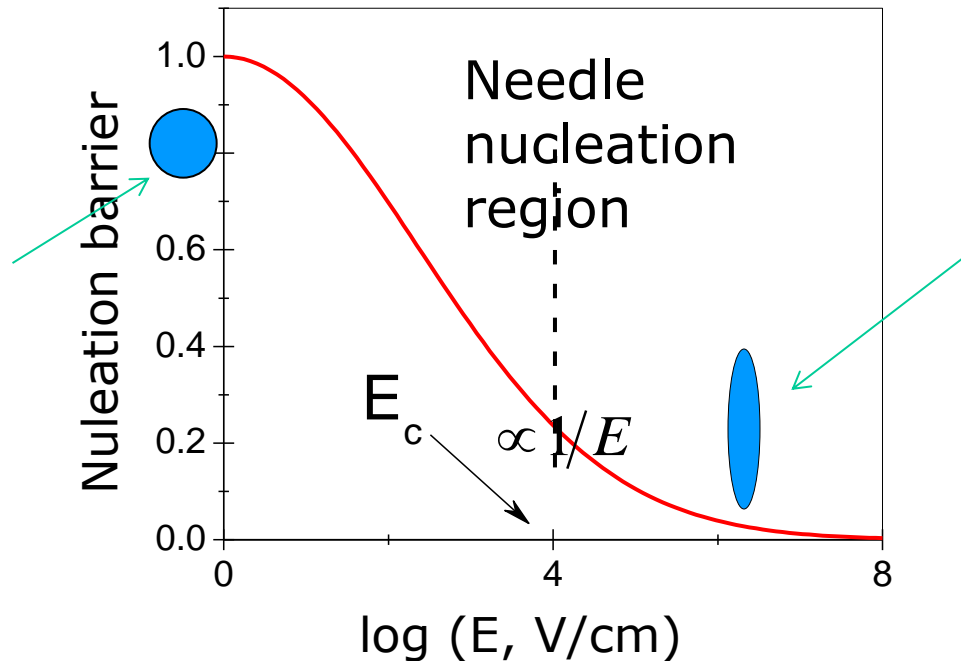
αR_0 is a minimum radius of a continuous metallic cylinder

V. G. Karpov, et. al: Appl. Phys. Lett., **90**, 123504 (2007); Phys. Rev. B **78**, 052201 (2008); Phys. Rev. B **86**, 075463 (2012); M. Nardone et.al, Phys. Chem. Chem. Phys., **14**, 13601 (2012)

Crossover from Sphere to Needle

Crossover field $E_c = 2\alpha^{3/2} E_0 \approx 10^4 \text{ V/cm}$

- Energy gain due to smaller surface area
- Energy loss due to smaller polarizability



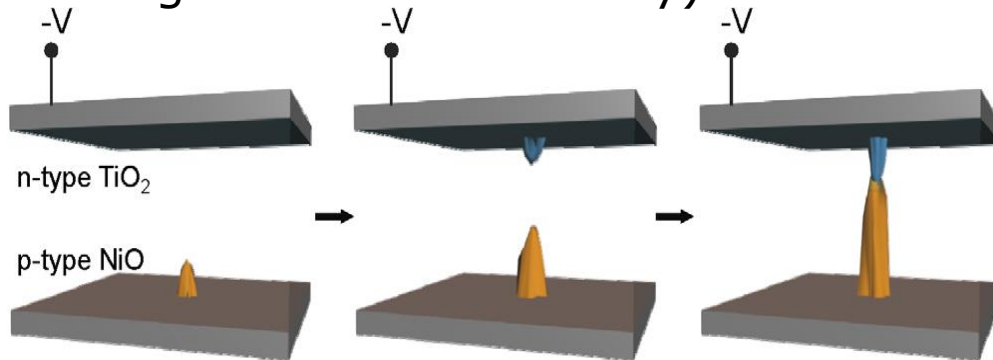
- Energy gain due to better polarizability
- Energy loss due to larger surface area

Needle nucleation dominates strong field region!

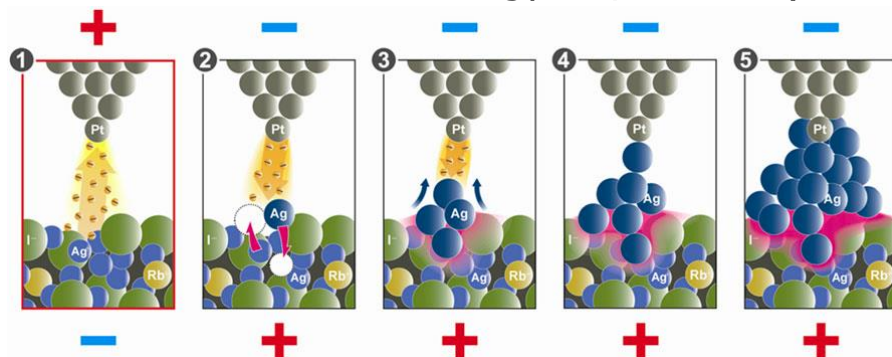
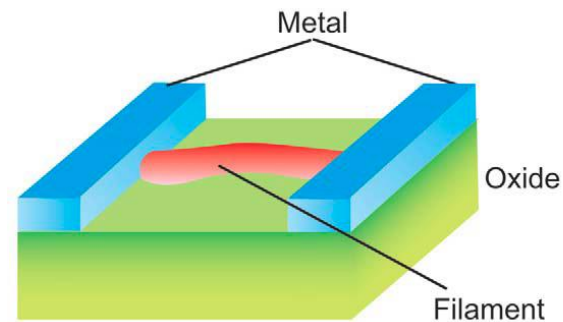
Verification of the field induced nucleation in the phase change memory included in the complimentary slides

Examples of conducting filaments forming in strong electric fields I

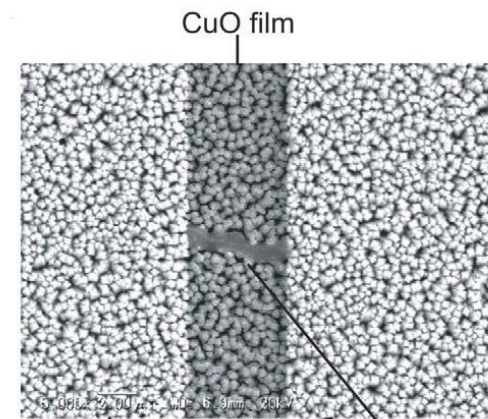
Many examples of filament formation under electric bias include both detrimental effects (shunting) and useful applications (switching in resistive memory)



K. M. Kim et. al. Nanotechnology **22**, 254002(2011)



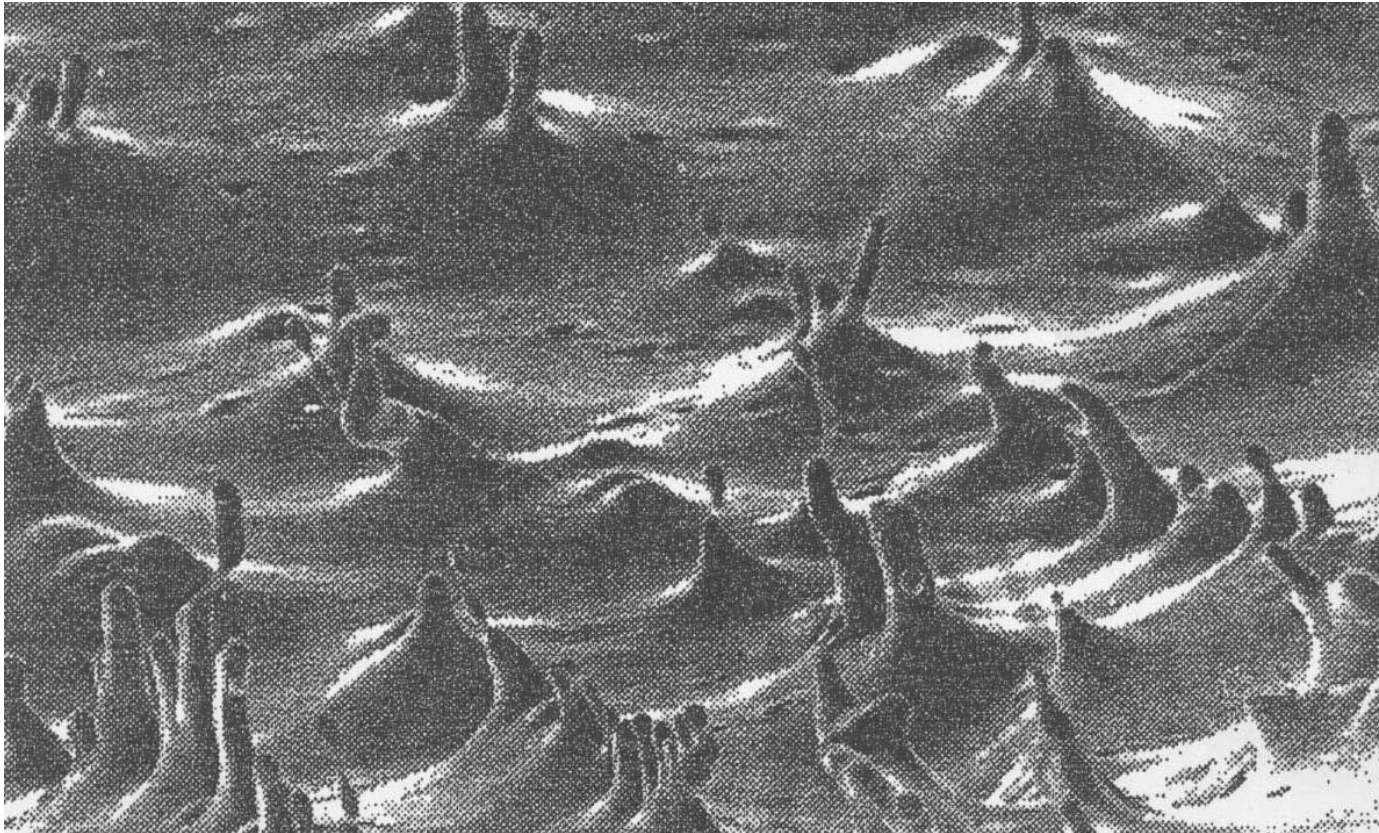
I. Valov et. al., J Solid State Electrochem, **17**,365(2013)



Pt electrodes Filamentary conducting path
A.Sawa, Materials Today, **11**, 28 (2008)

The theory of field induced nucleation shows that it is the field (rather than bias or current) driving the filament formation

Examples of conducting filaments forming in strong electric fields II



Structures pulled up by a strong electric field on the surface of a molten metal [G. A. Mesyats, *Explosive Electron Emission*, URO-Press, Ekaterinberg, (1998); p.29].

Part B

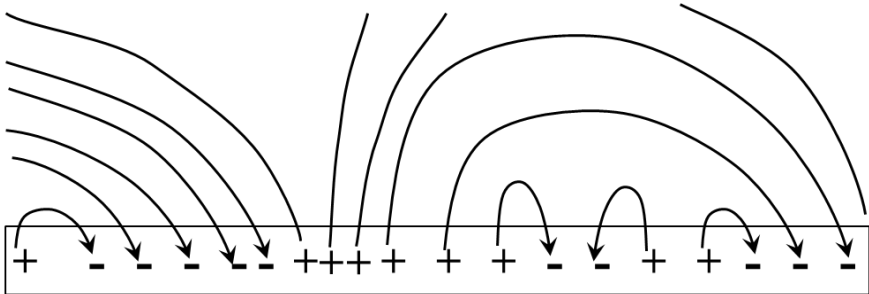
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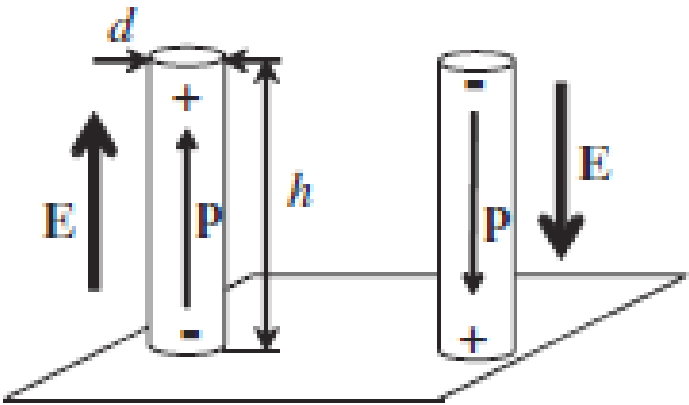
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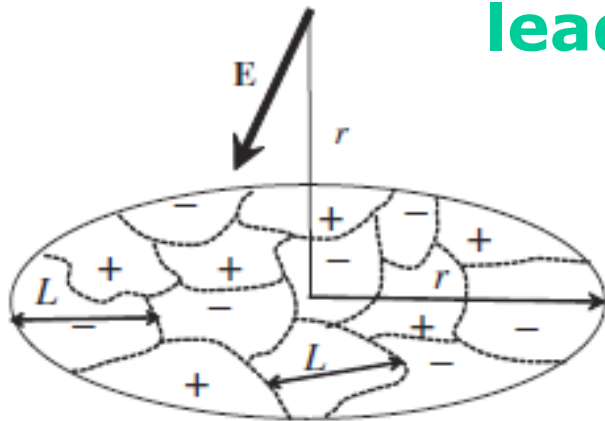
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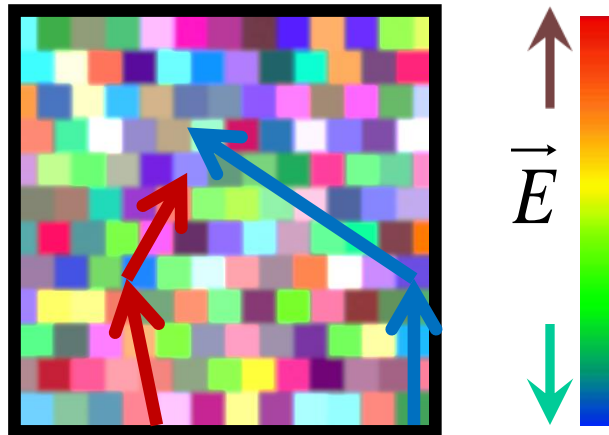
Birdseye view

In addition, these electric forces are random leading to whisker statistics



Beyond the patch size ($r \gg L$) whiskers grow in a random field by many oppositely charged patches

L is the patch size



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Electric charges on metal surfaces (Reflections I)

- **Imperfect nonmetal surfaces have electric charges:** surface states, Tamm states, oxides and other chemical modifications, deformations, polycrystalline structure, etc.
- We want to say that **the same is true for metal surfaces**. In spite of a common intuitive belief that free electrons would level out any electric nonuniformity.
- From the charge point of view, the **difference between metals and nonmetals is purely quantitative**, in the characteristic time to level out electric nonuniformities (=Maxwell or dielectric time, $\tau_M = 4\pi\rho$ where ρ is the resistivity; Gaussian system).
- Over long times, dielectric = metal. No catch: **metal surfaces can bear electric charges as well.**

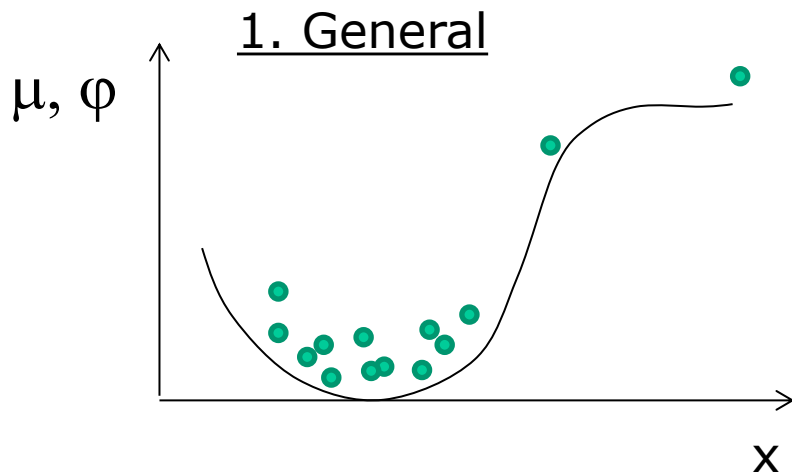
Electric charges on metal surfaces (Reflections II)

- We are used to think that electric fields at metal surfaces do not exist in statics because otherwise they would force currents...
- Our physics instructors forget to tell us that it is only true for uniform metals where chemical potential is constant.
- Indeed, we know from the physics of semiconductors: zero currents does not mean constant electric potential (zero field).
- Think of p-n junctions: in equilibrium there is no currents in spite of strong built-in electric fields
- The minimum free energy requires that it is not the electric potential φ , but rather electro-chemical potential Φ that must be constant to guarantee zero currents

$$\Phi = \varphi + \frac{\mu}{e}, \quad \mu = \text{chemical potential, } e = \text{electron charge}$$

- In nonuniform metals, $\mu = \mu(\vec{r}) \Rightarrow \vec{E}(\vec{r}) = -grad \left[\mu(\vec{r}) / e \right] \neq 0$

Models of chemical potential I

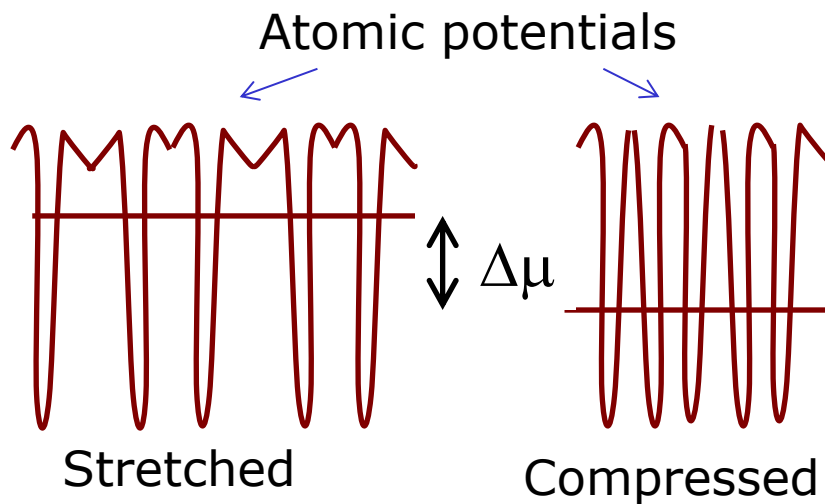


Diffusion current from high concentration region is balanced by drift current from the low concentration region

$$-D \frac{dn}{dx} = bnE, \quad b = \text{mobility}$$

$$\text{Total current} = 0, \quad \vec{E} \neq 0$$

2. Deformation



$$D = \frac{d\Delta\mu}{du} - \text{deform. potential,}$$

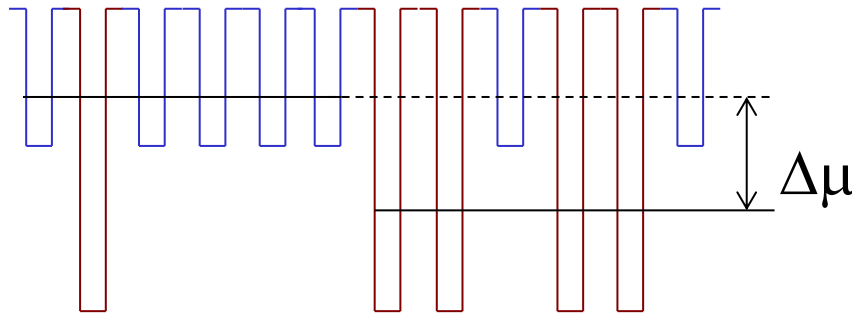
$$u = \text{dilation}$$

$$|D| \sim 1 \text{ eV}$$

External stress, internal stress (dislocations, other defects, intra-grain pressure, other), incommensurate phases,

Models of chemical potential II

2. Fluctuations in chemical composition

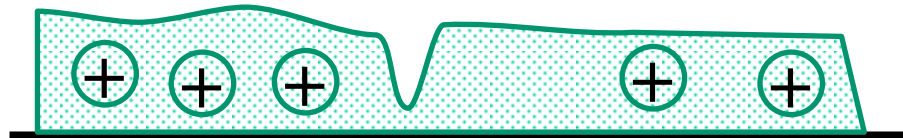


Alloys,
Contamination,
Grain boundaries vs. grains
Cottrell atmospheres around
dislocations (impurity atoms
attracted to the core of a
dislocation)

3. Wrong grain facets orientation



4. Oxides or other dielectric layers capable of charge accumulation



5. Direct ionic contamination (soup applications, etc.)

6. Grain boundaries that are certainly charged

7. Anything else making metals imperfect

Intermediate summary

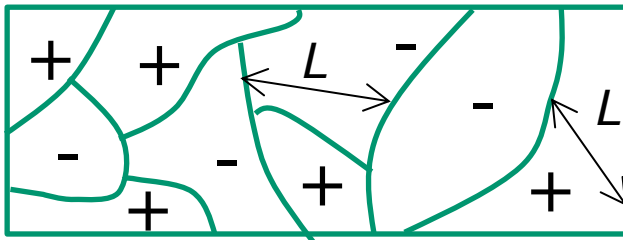
- A common belief that metal surface cannot have local charges is wrong.
- The condition of electro neutrality is not among laws of nature. Instead, electrons distribute themselves in such a manner as to minimize the total free energy, not the total charge.
- In real metals, there are many factors leading to surface imperfections: external or internal stresses (and their related deformations), fluctuations of chemical composition, polycrystallinity, oxidation, ionic contaminations –with the same **common denominator** that they are conducive of **surface charges** accumulation.

Charge patch model

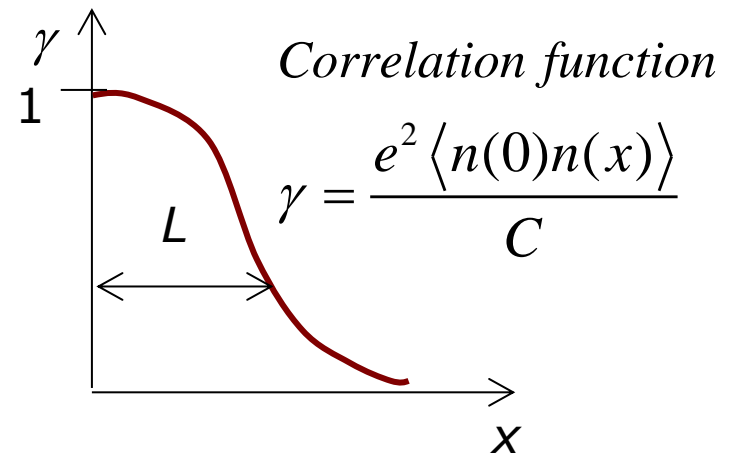
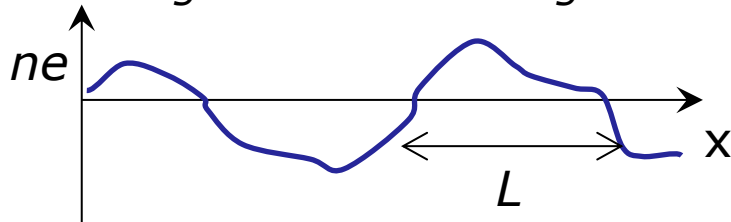
(the simplest random surface charge model)

- The surface must be neutral overall (zero electric flux): hence, combination of positively and negatively charged domains similar to a chess board, but not that ordered.
- Characterized by a single geometrical dimension L .
- Uncorrelated, rms value of charge density, $\sqrt{\langle (ne)^2 \rangle} = C$

Charge patches top view



Charge variations along a line



Charge patch model

(some data and numerical estimates)

- Direct measurements, using AFM Kelvin probe, field emission, and admittance characterization:

Electric potential variations of tenths of Volt per 1 micron in lateral directions →

$$E_{\parallel} \sim 1 - 10 \text{ kV/cm}$$

patch size $L \sim 10$ micron

- Indirect estimates assuming the same order of magnitude surface charge density, $n \sim 10^{12} \text{ cm}^{-2}$ as in many dielectrics.

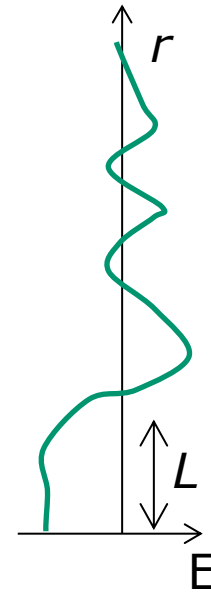
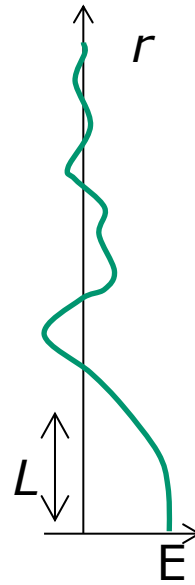
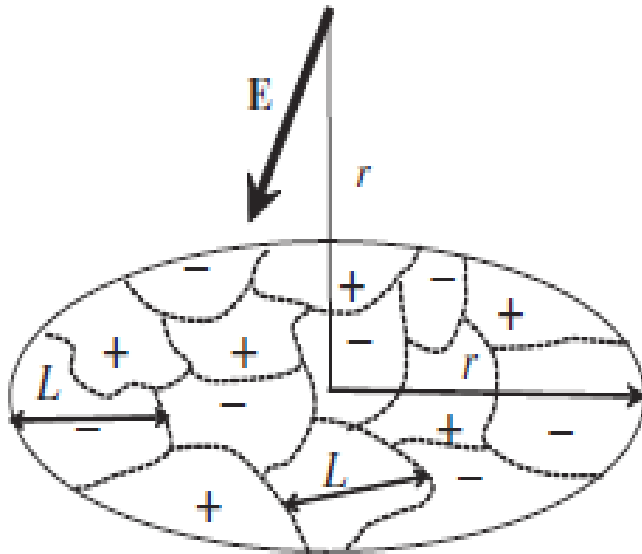
$$E_{\perp} \sim 4\pi n e \sim 1 \text{ MV/cm}$$

(No dielectric breakdown due to micron small distances)

$$\text{Overall, } E \sim 10^4 - 10^6 \text{ V/cm}$$

J. B. Camp, et. al. J. Appl. Phys., 69, 7126 (1991). E. Bano, et. al. Appl. Phys. Lett., 65, 2723 (1994). J. Labaziewicz, et. al., Phys. Rev. Lett. 101, 180602 (2008). R. Dubessy, et. al., Phys. Rev. A 80, 031402R (2009). G. H. Low, et. al., Phys. Rev. A 84, 053425 (2011).

Electric field distribution



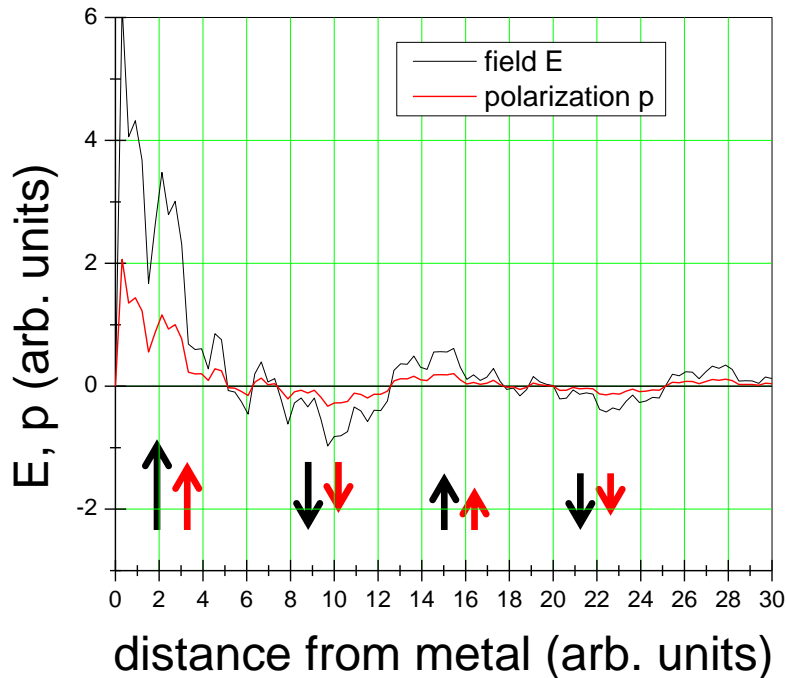
For large $r \gg L$, # of patches seen from distance r ,
 $N \sim (r/L)^2$.

Excess + or - charge felt $\sigma L^2 \sqrt{N} \sim \sigma L r \Rightarrow$

Absolute value of field $|E| \sim \frac{\sigma r L}{r^2} = \frac{\sigma L}{r}$

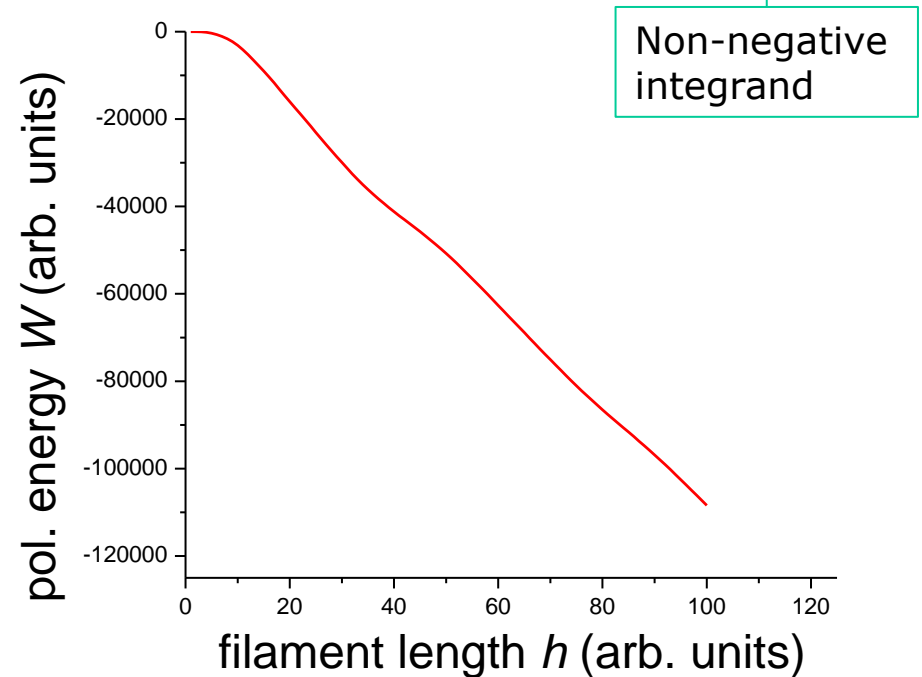
Polarization in a nonuniform field

Field fluctuations do not cancel out polarization energy because the induced polarization fluctuates coherently and $\mathbf{p} \cdot \mathbf{E}$ remains non-negative



Polarization energy of a metal filament can be shown to take the form

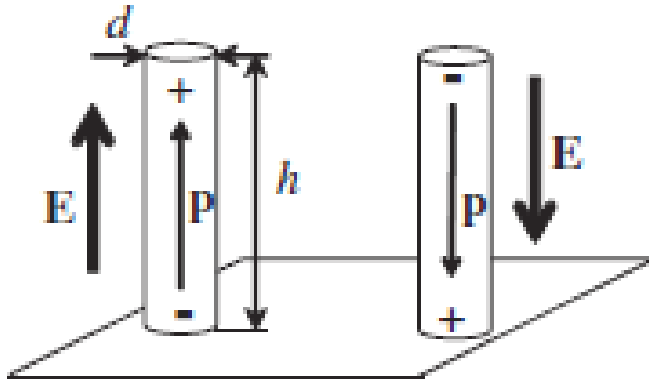
$$F_E(h) = \frac{-1}{2[\ln(4h/d) - 1]} \int_0^h \left[\int_0^x E(x) dx \right]^2 dx$$



Outline

- Motivation
 - Facts as seen by a novice
 - Hypotheses as seen by a novice
- Birdseye view of the proposed
- Background: phase transformations (minimalistic overview)
 - Classical (Gibbs) nucleation theory
 - Homogeneous and inhomogeneous nucleation
 - Post-nucleation stages: growth and ripening
 - Field induced nucleation
- Charged patches on metal surfaces
- Electric field distribution near metal surfaces
- Nucleation of whiskers
- Growth of whiskers
- Whisker statistics
- Predictions and suggested mitigation strategies
- Conclusions: what is/isn't understood, possible future work

Reminder: polarization energy



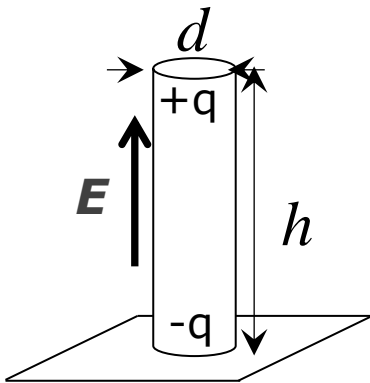
- Polarization of a metal filament makes it a dipole $\mathbf{p} = \alpha \mathbf{E}$ (α = polarizability) with energy gain

$$W = -\mathbf{p} \cdot \mathbf{E} = -\alpha E^2.$$

responsible for filament development.

- It doesn't depend on the field sign
- It is remarkably strong for the filament polarization is gigantic

Gigantic polarizability of a metal filament

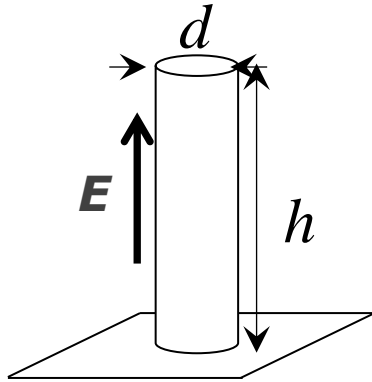


$$\alpha \sim h^3 \sim V \left(\frac{h}{d} \right)^2, \quad V = \pi d^2 h / 4 \text{ - volume}$$

$\left(\frac{h}{d} \right)^2 \gg 1$ **enhancement** compared to sphere.

$$\text{Rigorous result: } \alpha = 2h^3 \left[3 \ln(4h/d) - 7 \right]^{-1}$$

Field induced nucleation of whiskers



Free energy

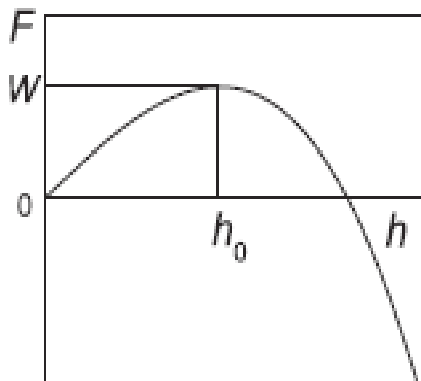
Polarization energy gain

Surface energy loss

$$F = -\alpha E^2 + \sigma h \pi d = -\frac{2h^3}{3\Lambda} E^2 + \sigma h \pi d,$$

$$\Lambda \equiv \ln(4h/d) - 7/3, \quad \frac{dF}{dh} = 0 \Rightarrow$$

$$h_0 = \sqrt{\frac{\pi\sigma\Lambda d}{E^2}}, \quad W = \frac{\pi\sigma d}{3} \sqrt{\frac{\pi\sigma\Lambda d}{E^2}}, \quad \nu \approx d^{-2} \tau_0^{-1} e^{-\frac{W}{kT}}$$



Comparing to data:

Assuming nucleation rate $\nu = 10^{-3} \text{cm}^{-2} \text{s}^{-1}$ yields

$$W = kT \ln(1/d^2 \nu \tau_0) \approx 2 \text{ eV}, \quad (\text{also } h \sim 10 \text{ nm}, d \sim 1 \text{ nm})$$

Requirements:

Even for large $E \sim 1 \text{ MV/cm}$, very small $\sigma \sim 3 \text{ dyn/cm}$ needed*.
 However, $E \sim 10 \text{ kV/cm}$, require abnormally low $\sigma \sim 0.2 \text{ dyn/cm}$ **

Inhomogeneous nucleation becomes a necessary element.

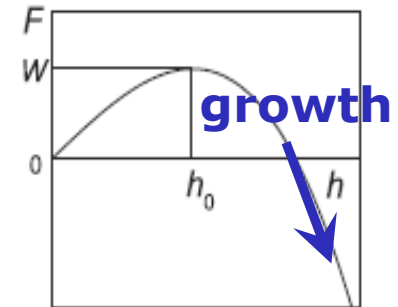
(locally weak surface, defects, etc.)

*For metals, typical $\sigma \sim 100\text{-}1000 \text{ dyn/cm}$: L. Vitos *et. al.* Surface Science **411**, 186 (1998)

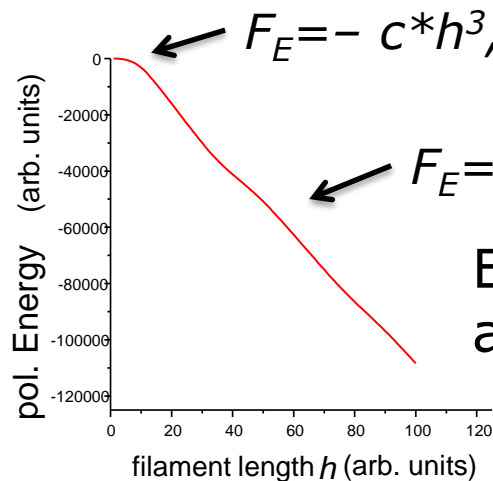
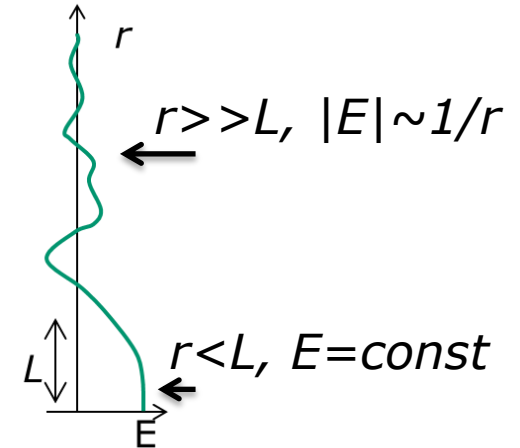
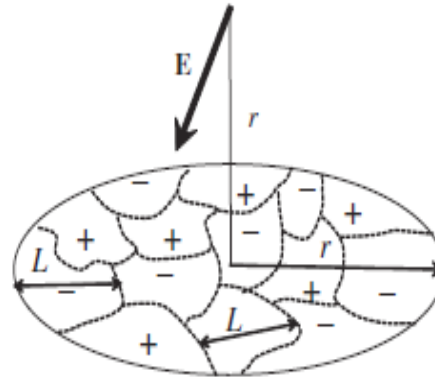
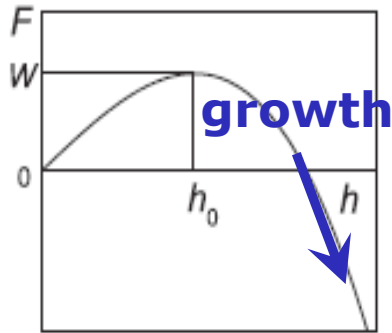
** See complimentary slides

Conclusions from the model of field induced nucleation of whiskers

- Surface field favors nucleation of needle shaped metal nuclei of ~ 10 nm in height and ~ 1 nm in diameter
- Nucleation of spherical particles is less likely
- As nucleated, the needle will retain the tendency of growing with high aspect ratio that minimizes its free energy
- To describe the observed nucleation rates quantitatively, the model has to rely on inhomogeneous nucleation, i. e. existence of weak spots, typical of other nucleation processes



Growth of whiskers. Free energy



$F_E = -c \cdot h^3, c = \text{const}$ when $h < L$

$F_E = a - b \cdot h, a, b = \text{const}$ when $h \gg L$

Electrostatic theory determines the average free energy F vs whisker length h ,

$$F = F_E + \pi\sigma h d$$

Growth of Whiskers. Fokker-Planck I

F-P equation describes kinetics of phenomena evolving in many small steps: diffusion, some types of recombination, particle growth...

Just ignore this

$f(h, d)$, such that $f(h, d)dhdd$ is the number of whiskers with height and diameter in the intervals $(h, h + dh)$ and $(d, d + dd)$, respectively. The Fokker-Planck equation takes the form

$$\frac{\partial f}{\partial t} = -\frac{\partial s_h}{\partial h} - \frac{\partial s_d}{\partial d}.$$

Here, s_h and s_d are the components of the flux in the whisker dimensions space ($s^{-1} \text{ cm}^{-3}$),

$$s_h = -A_h f - B_{hd} \frac{\partial f}{\partial d} - B_{hh} \frac{\partial f}{\partial h},$$

$$s_d = -A_d f - B_{dh} \frac{\partial f}{\partial h} - B_{dd} \frac{\partial f}{\partial d}.$$

$$A_h = \tilde{A}_h + \frac{\partial B_{hd}}{\partial d}, \quad A_d = \tilde{A}_d + \frac{\partial B_{dh}}{\partial h},$$

$$\tilde{A}_h = \sum_i \delta h_i / t, \quad \tilde{A}_d = \sum_i \delta d_i / t,$$

$$B_{hh} = \sum_{ij} \delta h_i \delta h_j / \delta t, \quad B_{dd} = \sum_{ij} \delta d_i \delta d_j / \delta t,$$

$$B_{hd} = B_{dh} = \sum_{ij} \delta h_i \delta d_j / \delta t,$$

where δh_i and δd_i are random changes in h and d at a step i in the course of whisker growth over time δt .

E. M. Lifshitz and L. P. Pitaevskii, Physical Kinetics (Elsevier, Amsterdam, Boston, 2008)

After **all** possible simplifications, F-P yields for the average quantities

$$\frac{\partial h}{\partial t} = -b \frac{\partial F}{\partial h}, \quad \frac{\partial d}{\partial t} = -b \frac{\partial F}{\partial d}, \quad \text{with } b = \frac{B}{kT}$$

With known free energy F

Growth of Whiskers. Fokker-Planck II

$$\frac{\partial h}{\partial t} = -b \frac{\partial F}{\partial h}, \quad \frac{\partial d}{\partial t} = -b \frac{\partial F}{\partial d} \quad \text{with} \quad b = \frac{B}{kT}$$

These equations have simple physical interpretation

$\frac{\partial h}{\partial t}$ and $\frac{\partial d}{\partial t}$ are velocities (of whisker length and diameter growth)

Because F is the (free) energy,

$-\frac{\partial F}{\partial h}$ and $-\frac{\partial F}{\partial d}$ are (thermodynamic) forces along and perpendicular whisker axis,

b has the meaning of mobility linked to diffusivity B through the Einstein relation.

Overall, **(velocity) = (force) × (mobility)**, similar to, say, electrons in solids.

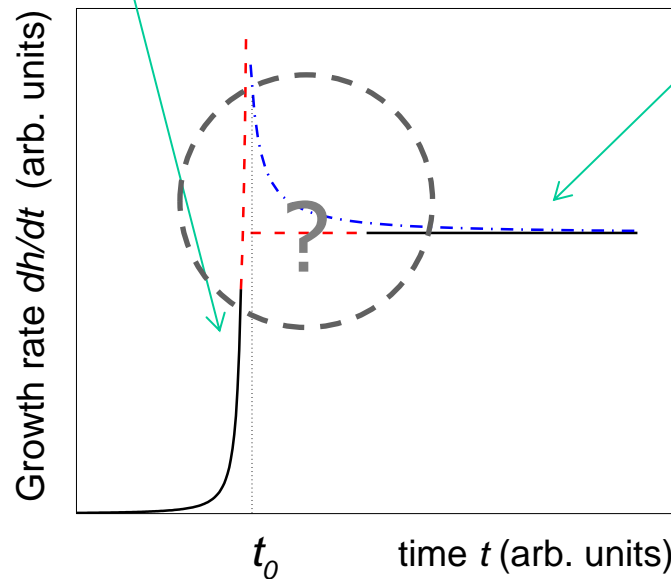
The diffusion coefficient B in whisker parameter space remains unknown.

For simplicity, it is assumed to be equal the tin self-diffusion, $B = D \approx 10^{-18} \text{ cm}^2 \text{ s}^{-1}$.

Growth of Whiskers. Results

$$h = \frac{h_0}{1 - t/t_0}, \quad t_0 \equiv \frac{3\Lambda}{4bE_0^2 h_0} \quad \text{when } h \ll L; \quad h = L \frac{t}{t_L}, \quad t_L \equiv \frac{3\Lambda}{4bE_0^2 L} \quad \text{when } h \gg L.$$

$$d \approx \frac{h}{\sqrt{\Lambda}} \text{ - very sensitive to FP approximations}$$



Absolute values of dormant time t_0 and growth rate L/t_L are in the ballpark (see complimentary slides)

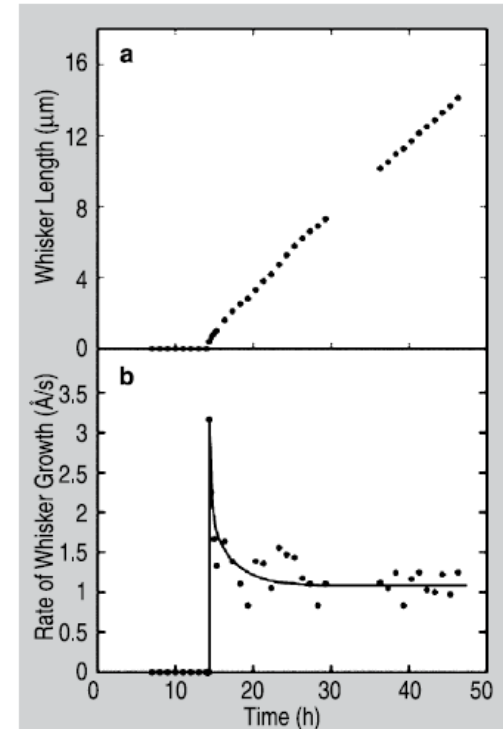
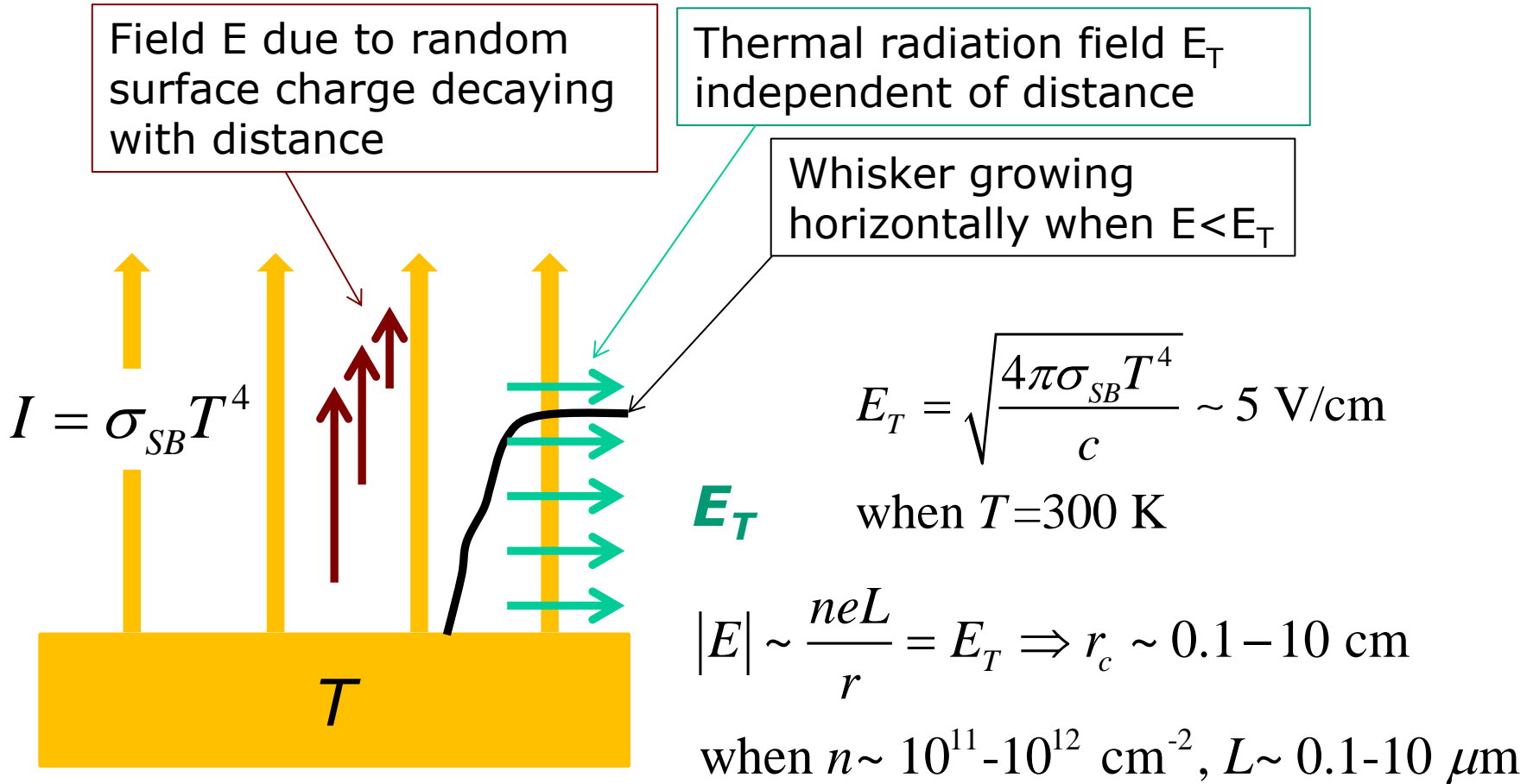


Figure 3. Measurement of: (a) whisker length vs. time; (b) instantaneous growth rate of whisker vs. time.

N. Jadhav, E. Buchovecky, E. Chason, and A. Bower, JOM (2010)

Thermal radiation field



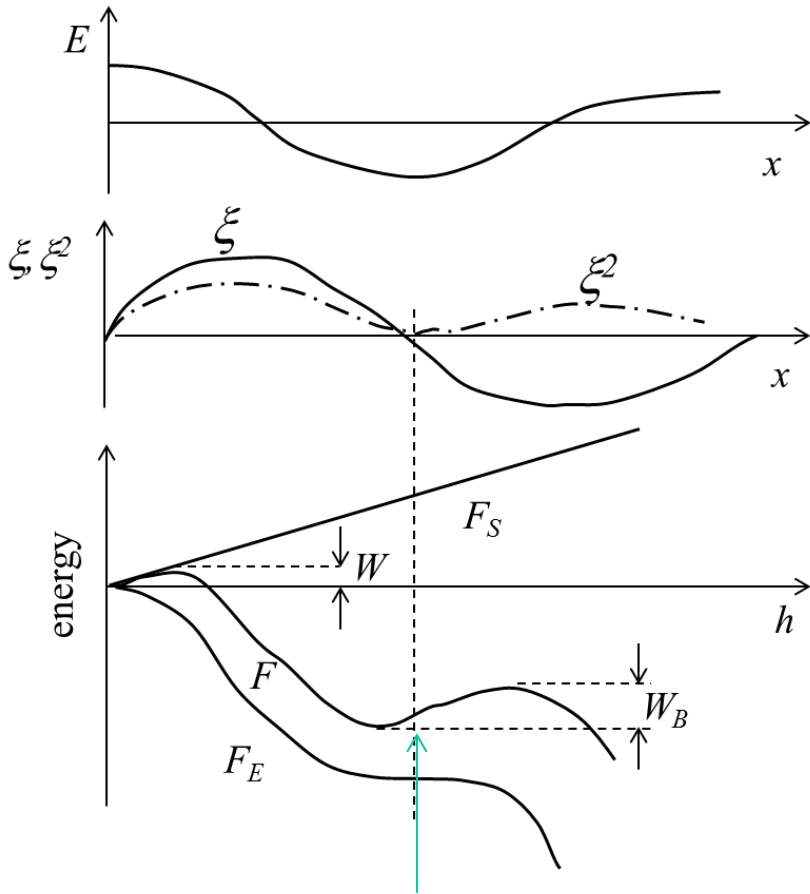
Prediction: if this mechanism works, all whiskers should switch to horizontal growth at about the same distance r_c 47

Conclusions from the electrostatic model of whisker growth

- Whisker length vs. time is described on average:
 - Dormant period t_0
 - Subsequent constant growth rate dh/dt
- Predicts numbers. Generally consistent with experimental data
- Agrees with the data assuming nucleation time $\tau \ll t_0$.
- Less reliable description of whisker diameter growth very sensitive to FP approximations; more work called upon
- Limited to low thermal radiation ($E \sim 5$ V/cm @ room T)
- Long enough whiskers in the domain of thermal radiation are predicted to kink and evolve in horizontal directions
- Growth kinetics have power dependencies on material parameters as opposed to the much stronger exponential dependencies for nucleation kinetics. Therefore, expect
 - Easier ways of killing whiskers at their nucleation stage;
 - Better predict whiskers at their growth stage

Whisker statistics: approach

A whisker stops growing when its tip enters a region of low field, so its further polarization gain is overbalanced by the surface energy loss



It stops here, but can resume growth after quite a while

$$F_E(h) = \frac{-1}{2[\ln(4h/d) - 1]} \int_0^h \left[\int_0^x E(x) dx \right]^2 dx$$

$$F_E(h) = \frac{-1}{2\Lambda} \int_0^h \xi^2 dx, \quad \xi(x) \equiv \int_0^x E(x) dx$$

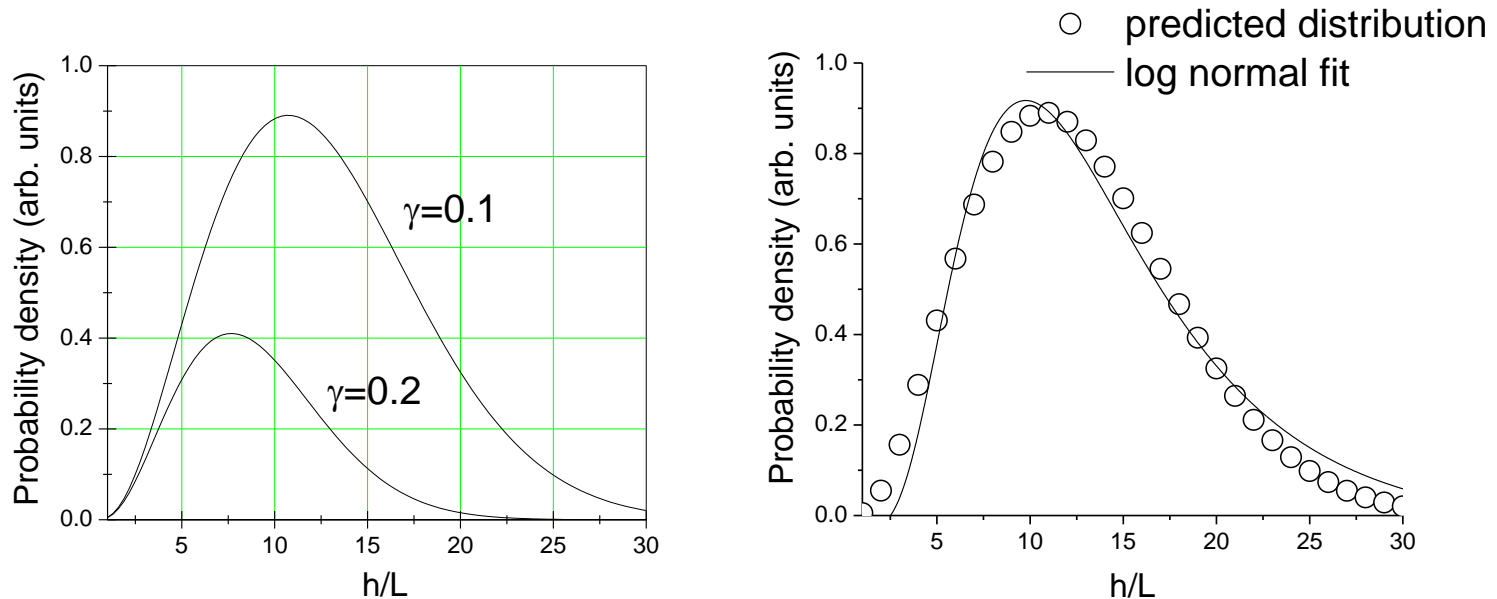
ξ^2 is a sum of many random contributions
Based on the central limit theorem,*

$$g(\xi^2) = \frac{1}{\sqrt{2\pi\Lambda}} \exp \left[-\frac{(\xi^2 - \langle \xi^2 \rangle)^2}{2\Lambda} \right]$$

- \mathbf{E} is a linear functional of surface charge density $n(\mathbf{r})$.
- Statistics of $n \rightarrow$ statistics of $E \rightarrow$ statistics of $\xi^2 \rightarrow$ statistics of $F_E \rightarrow$ statistics of whisker lengths h

*See complimentary slides

Whisker statistics: results



$$g(h) = \beta \frac{h}{L} \exp \left\{ -\gamma \left[\frac{h}{L} \ln \left(\frac{\left[1 + \sqrt{1 + (h/L)^2} \right]^2}{4\sqrt{1 + (h/L)^2}} \right) \right]^2 \right\}$$

β and γ are numerical coefficients not too different from unity

Log-normal provides a close fit in agreement with the data

T. Fang, M. Osterman, and M. Pecht, *Microelectron. Reliab.* **46**, 846, (2006); L. Panashchenko, M.S. thesis, University of Maryland, (2009); D. Susan, J. Michael, R. P. Grant, B. McKenzie, and W. G. Yelton, *Metall. Mater. Trans. A* **44**, 1485 (2013).

Conclusions: what is understood

- Why whiskers are metallic: high electric polarizability
- Why more or less perpendicular to surface: direction of the electric field lines
- Why whiskers parameters are statistically distributed: broad distribution of random electric patches
- Correlations between whiskers and versatile morphology/composition/stress/ambient factors: all producing surface electric charges
- Evolution pattern: long incubation period + constant growth rate reflects E-field distribution
- Numbers are predicted for the first time (?) for whiskers

Conclusions: what is not understood

- Microscopic nature of whiskers, their correlation with specific surface defects, chemical aspects (such as Pb)
- The role of whisker crystalline structure
- Whisker growth in 3D random electric field: winding and kinking.
- Possible role of surface (or grain boundary) diffusion limiting whisker growth.
- Whisker diameters: kinetics and statistics
- Interwhisker interactions limiting their concentration and affecting growth.

Conclusions: possible verifications/future work

- Whisker nucleation and growth in external electric fields (capacitor configuration or inside SEM)
- Whisker nucleation and growth under controlled contamination of metal surface with solutions of charged nanoparticles. This could pave a way to whisker self-healing if a suitable treatment is identified.
- Whisker nucleation and growth under the conditions of strong surface electric fields induced by surface plasmon polariton excitations. This could be used for controlled growth of metal nanowires of desirable parameters on metal surfaces.
- All in all the above is just a sketch of a theory, its multiple components calling upon further work

Acknowledgement

- Useful suggestions from Bill Rollins, Steve Smith, John Barnes, Andrew Kostic, and Ashraf Jafri are greatly appreciated
- The author is grateful to D. Shvydka, A. V. Subashiev, I. V. Karpov, E. Chason, and D. Susan for useful discussions.
- The NASA Electronic Parts and Packaging (NEPP) Program is acknowledged for granting permission to use their figures.
- This work was performed under the auspices of the NSF Grant No. 1066749.

Complimentary slides

- Numerical estimates
- Long-range diffusion
- Central limit theorem
- Verifications of field induced nucleation theory for phase change memory applications
- Surface Plasmon Polaritons
- Example of self-healing electrolyte treatment in photovoltaics

Complimentary slide: numerical estimates

Surface energy. From expression for W , $\sigma \approx \left(\frac{W^2 E^2}{d^3 \Lambda} \right)^{1/3}$.

Set $W=2$ eV= 3.2×10^{-12} erg, $E=10^6$ V/cm ≈ 3000 CGSE, $d=1$ nm= 10^{-7} cm, $\Lambda=3$.

This yields $\sigma \approx 3$ dyn/cm. Assuming $E=10^4$ V/cm makes it $\sigma \approx 0.15$ dyn/cm.

Growth kinetic parameters.

$B = 10^{-18}$ cm²s⁻¹, $kT=0.025$ eV= 4×10^{-14} erg, $b = B / kT=2.5 \times 10^{-5}$ cm²s⁻¹erg⁻¹.

Dormant time, $t_0 \equiv \frac{3\Lambda}{4bE_0^2 h_0} \approx 3$ years, 300 hrs, 3 s

for respectively: $E=10$ kV/cm, 100 kV/cm, 1 MV/cm.

Growth rate $\frac{dh}{dt} = \frac{L}{t_L}$ with $t_L \equiv \frac{3\Lambda}{4bE_0^2 L}$ and $L=10$ μ m= 10^{-3} cm:

$\frac{dh}{dt} = 1$ A/s, 100 A/s, 1 μ m/s for respectively: $E=10$ kV/cm, 100 kV/cm, 1 MV/cm.

Complimentary slide: long-range diffusion

- Whiskers growing from their roots without forming surrounding dents is interpreted as a result of long range uniform drift of material towards whisker roots
- If charges are tightly pinned to the surface material, the system should maintain uniform material density to provide the minimum electrostatic energy; hence, long range drift. (according to the electrostatic theory)
- The charge drift moving the rest of material can be a result of hydrodynamic drag (to be verified yet).
- The property of flat surface and related long-range diffusion can be a separate issue (very often relevant) not necessarily related to whisker thermodynamics

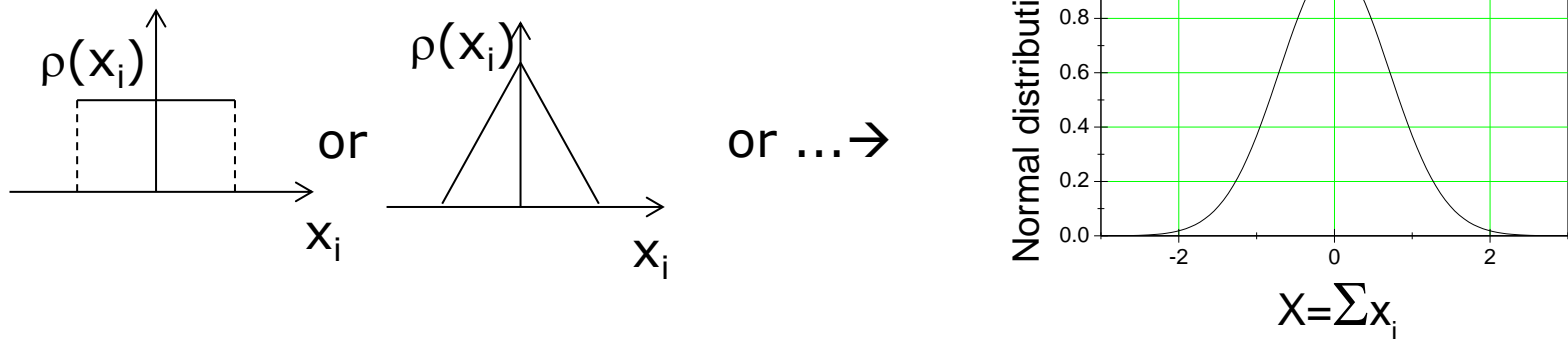
T. A. Woodrow, Proceedings of SMTA International Conference, Rosemont, IL, 2006 (SMTA International, Edina, MN, 2006), pp. 1-50; E. R. Crandall, Ph.D. thesis, Auburn University, Auburn, Alabama, 2012

Complimentary slide: Central limit theorem in general

CLT is a purely mathematical statement that, given certain (reasonable) conditions, the sum of a sufficiently large number of random variables, each with a well-defined expected value and dispersion, will be normally distributed. (*Chebyshev, Lyapunov, Markov 1901-1935*)

... "The huger the mob, and the greater the apparent anarchy, the more perfect is its sway." (F. Galton, French mathematician)

CLT is uniquely significant in random processes because it does not depend on the particularities of probabilistic distributions of individual terms in the sum.



See e. g. C. Kittel "Elementary statistical physics", Dover, NY, 1958, 1986

Complimentary slide: Central limit theorem for whiskers

Need a probabilistic distribution for ξ^2 ,

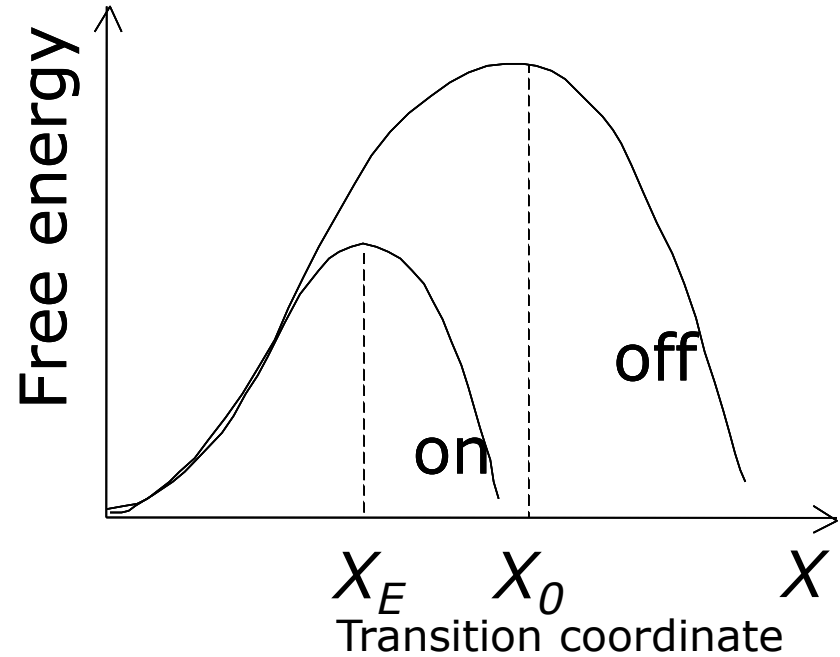
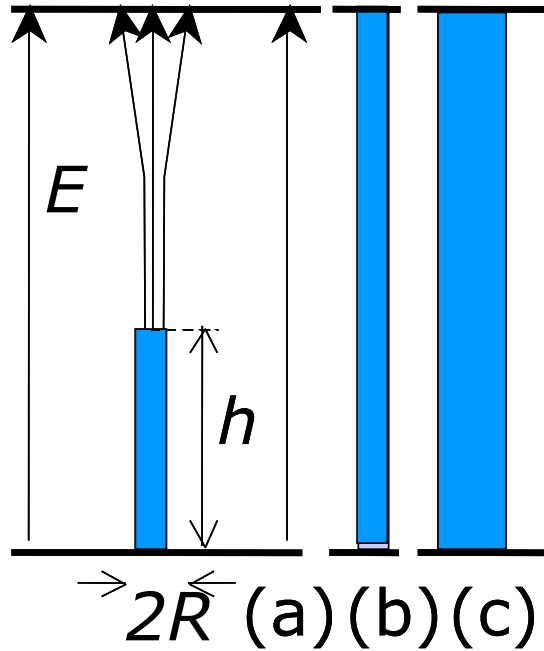
where $\xi(x) \equiv \int_0^x E(x)dx$ and $E(x)$ is a random field.

Representing the integral as a sum, $\xi(x) \equiv \int_0^x E(x)dx \approx \sum_i E(x_i)\Delta x_i$,

$\xi^2 = \sum_{i,j} E(x_i)E(x_j)\Delta x_i\Delta x_j$ is a sum as well.

Hence CLT applicability, $g(\xi^2) = \frac{1}{\sqrt{2\pi\Delta}} \exp\left[-\frac{(\xi^2 - \langle \xi^2 \rangle)^2}{2\Delta}\right]$.

This complimentary slide illustrates verifications of field induced nucleation theory; Switching Mechanism in Phase Change Memory



- Electric field lowers nucleation barrier
- Needle enhances electric field (lightning-rod behavior),
- Subsequent nucleation switches the device

This complimentary slide illustrates verifications of field induced nucleation theory; Phase Change Memory Applications

Threshold voltage and switching time vs. material parameters

$$V_{th} = \frac{V_{max}}{\ln(\tau / \tau_0)}, \quad V_{max} = 2l \frac{W_0}{kT} \sqrt{\frac{\alpha^3 W_0}{\epsilon R_o^3}}$$

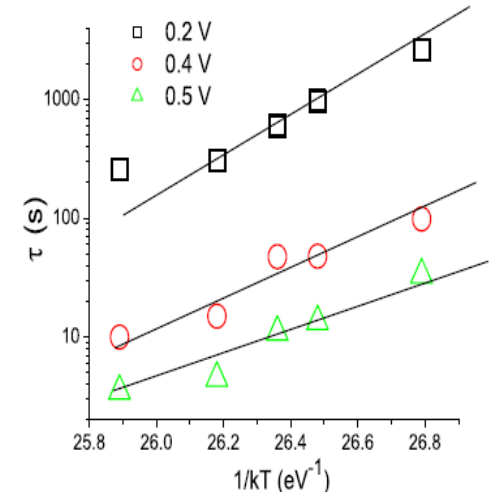
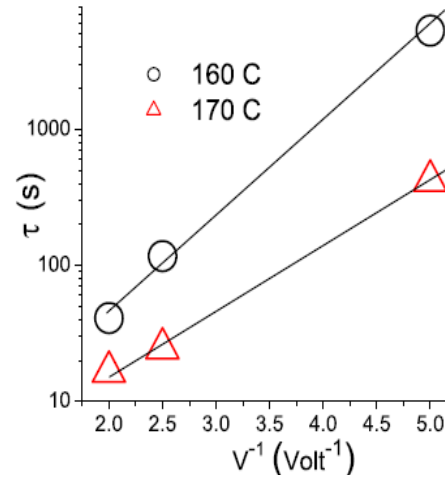
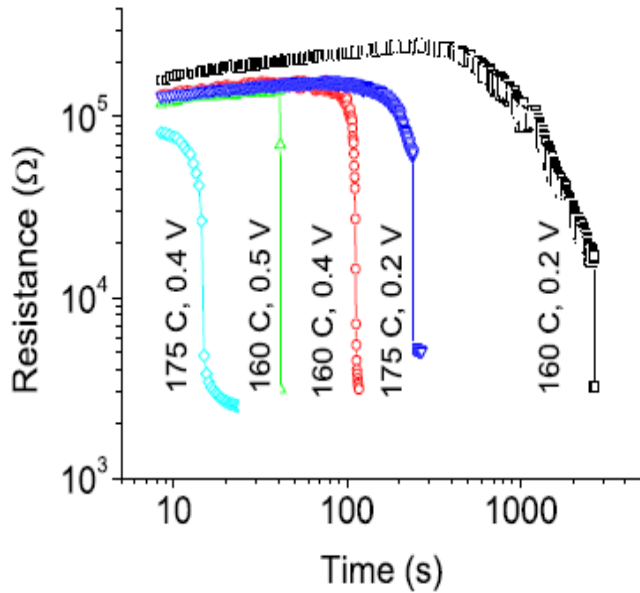
$$\tau = \tau_0 \exp\left(\frac{W_0 \tilde{V}}{kTV}\right), \quad \text{when } V > \tilde{V} \equiv 2l \sqrt{\frac{\alpha^3 W_0}{\epsilon R_o^3}}$$

Switching limits

$$(\text{no S}) \quad V < \tilde{V} \approx 0.2 \text{ V}, (\text{S}) \quad V_{max} \approx 20 \text{ V} < V (\text{fastest S})$$

V. G. Karpov, et. al; Appl. Phys. Lett., **90**, 123504 (2007); Phys. Rev. B **78**,052201 (2008); Phys. Rev. B **86**, 075463 (2012)

This complimentary slide illustrates verifications of field induced nucleation theory; Verification –delay time

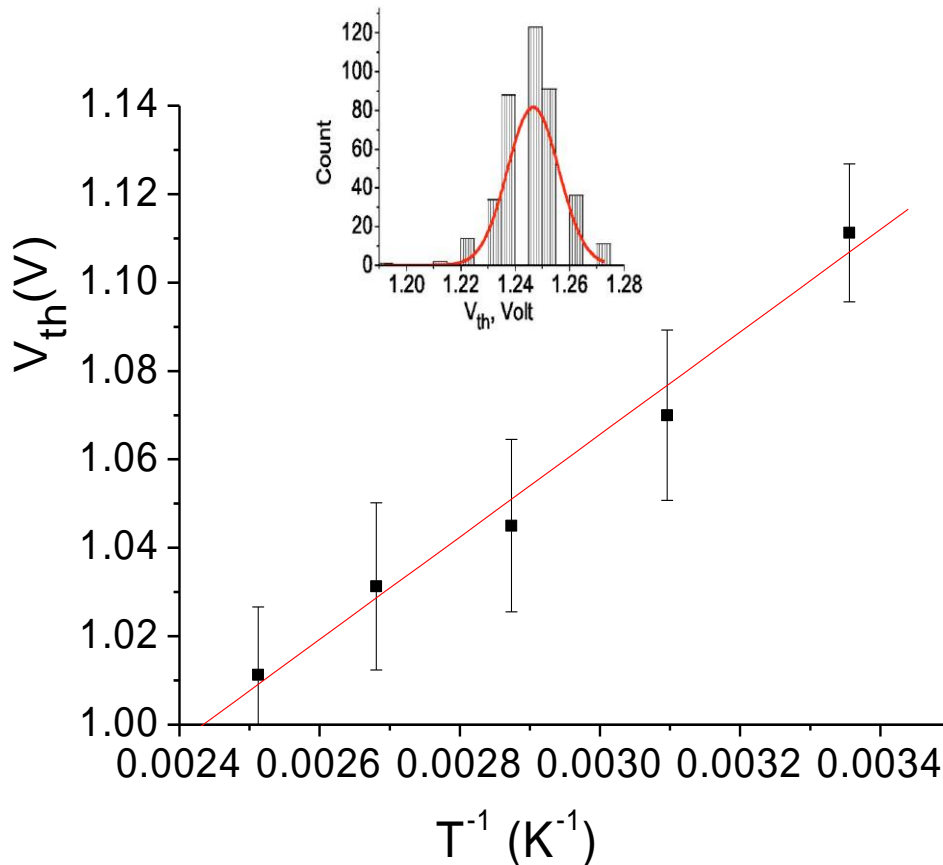


$$\tau = \tau_0 \exp\left(\frac{W_0}{kT} \frac{\tilde{V}}{V}\right) \quad \text{when} \quad V > \tilde{V}$$

V. G. Karpov, et. al: Appl. Phys. Lett., **90**, 123504 (2007); Phys. Rev. B **78**,052201 (2008); Phys. Rev. B **86**, 075463 (2012)

This complimentary slide illustrates verifications of field induced nucleation theory;

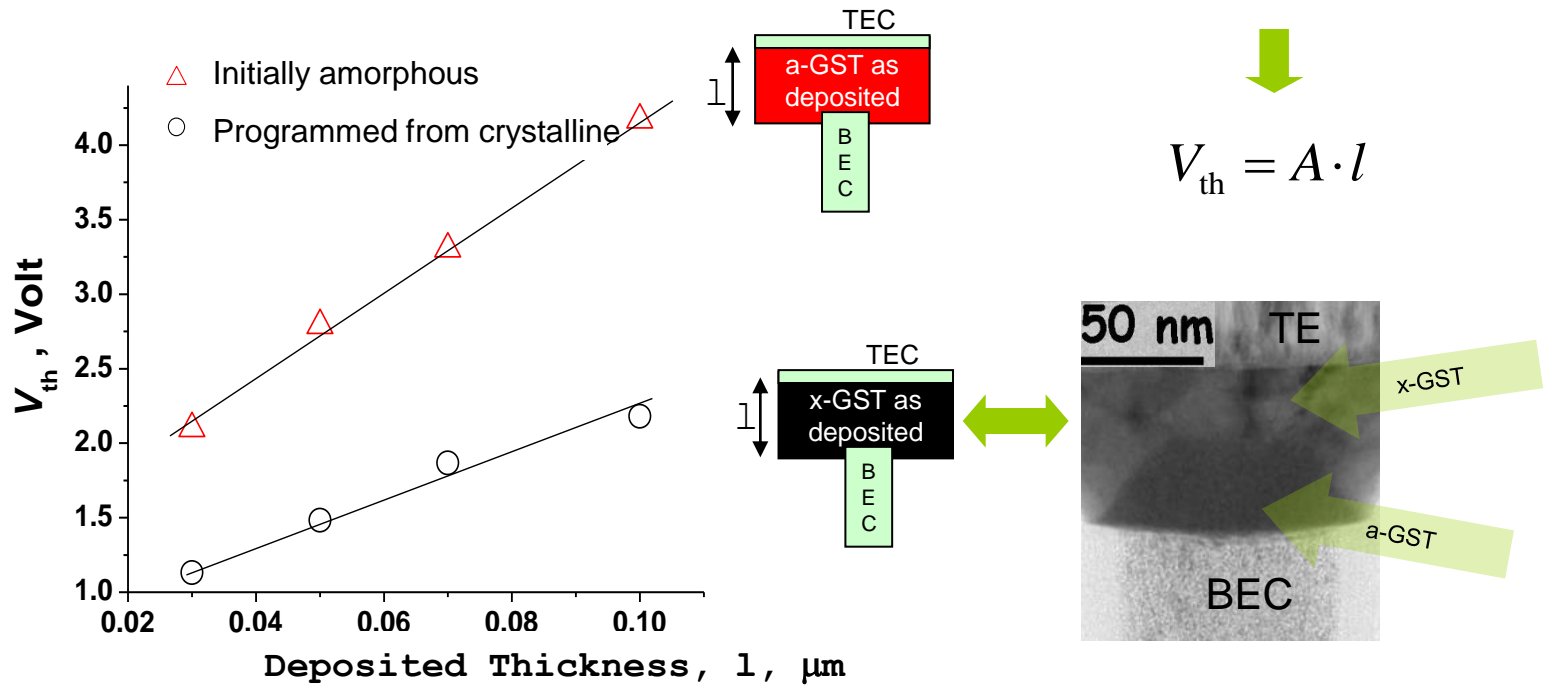
Verification: temperature



$$V_{th} = l \sqrt{\frac{3\pi^2 \alpha^3 W}{32\epsilon R^3}} \left(\frac{W}{kT}\right) \left[\ln\left(\frac{t}{\tau}\right) \right]^{-1}$$

V. G. Karpov, et. al: Appl. Phys. Lett., **90**, 123504 (2007); Phys. Rev. B **78**,052201 (2008); Phys. Rev. B **86**, 075463 (2012)

This complimentary slide illustrates verifications of field induced nucleation theory; Verification: thickness



$$V_{th} = l \sqrt{\frac{3\pi^2 \alpha^3 W}{32\epsilon R^3}} \left(\frac{W}{kT} \right) \left[\ln \left(\frac{t}{\tau} \right) \right]^{-1}$$

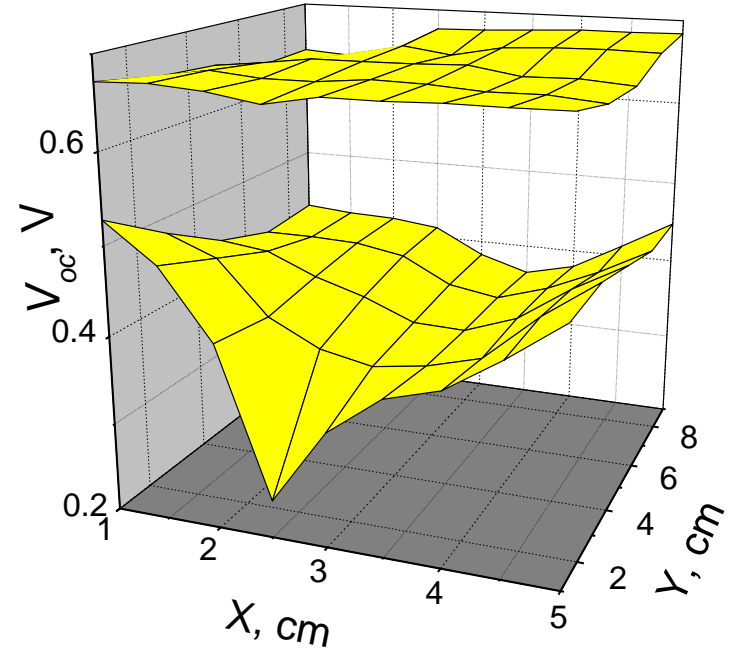
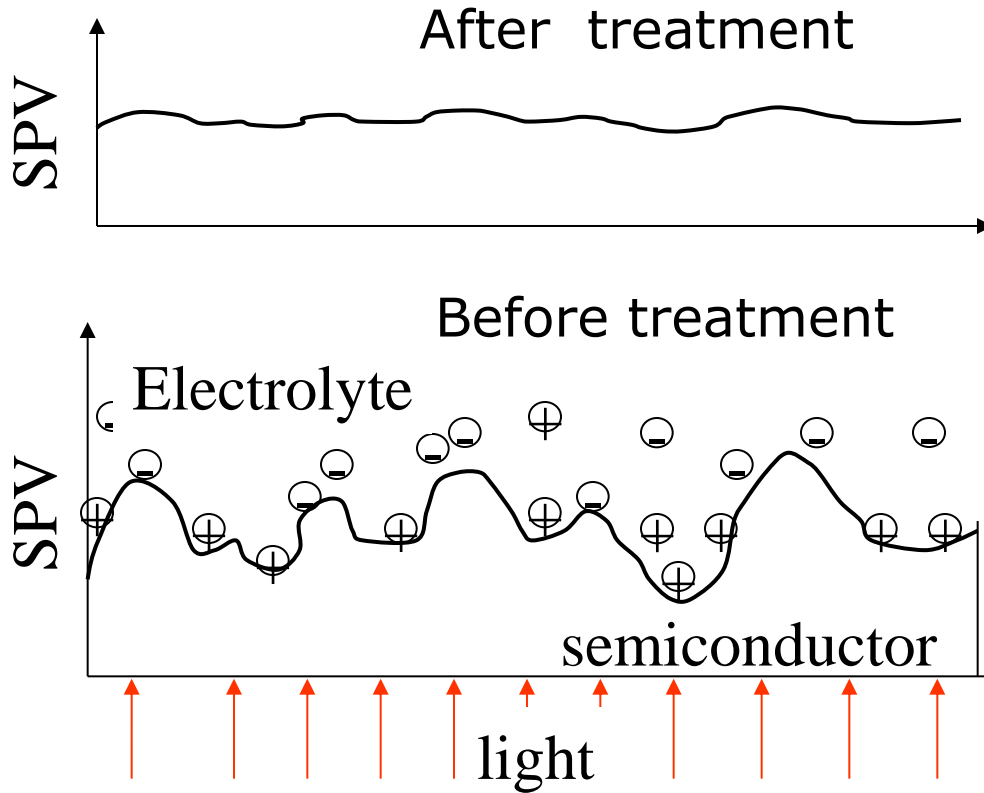
V. G. Karpov, et. al: Appl. Phys. Lett., **90**, 123504 (2007); Phys. Rev. B **78**,052201 (2008); Phys. Rev. B **86**, 075463 (2012)

Complimentary slide: Surface plasmon polariton

- Surface plasmon polaritons (SPPs), are infrared or visible electromagnetic waves, which travel along a metal-dielectric or metal-air interface. They involve both charge motion in the metal (surface plasmons) and electromagnetic waves in the air or dielectric (polaritons).
- SPPs can have tighter spatial confinement and higher local field intensity with the enhancement factors up to ~ 1000
- Coupling of photons into SPPs can be achieved using a coupling medium such as a prism or grating to match the photon and surface plasmon wave vectors.

See e. g.: S. A. Maier, *Plasmonics: Fundamentals and Applications* (2007),
Wikipedia, many other sources

Complimentary slide: “Red wine” effect: self-healing

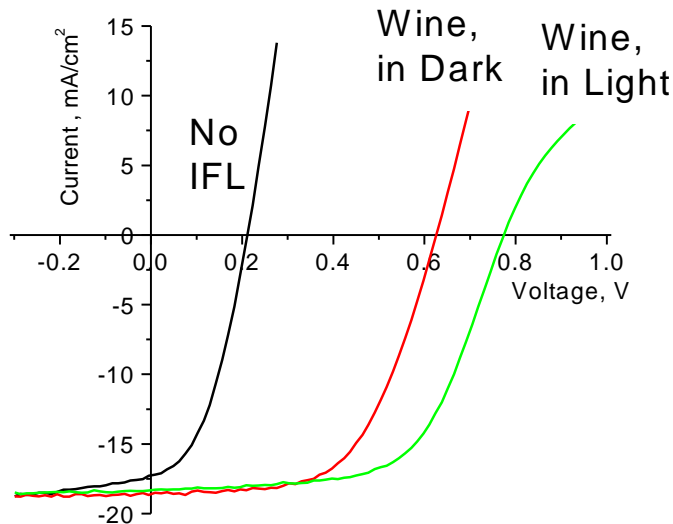


- Patching nonuniformity: act on surface, don't worry about bulk
- Approach differs from classical crystalline PV focused on defects

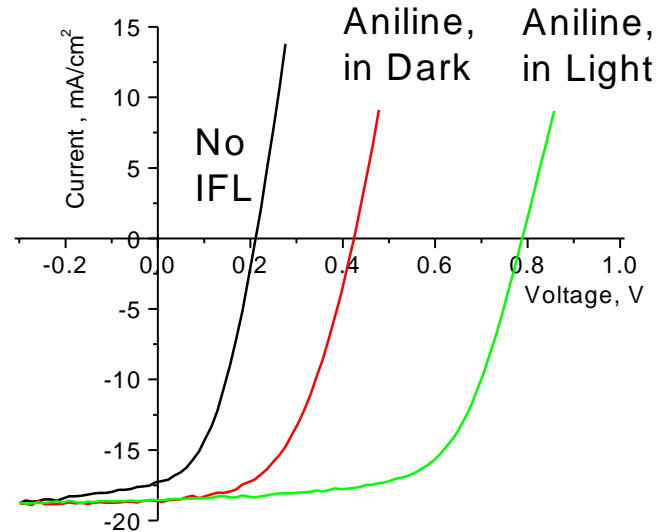
Y. Roussillon et al. Appl. Phys. Lett. (2004); Patent: V. G. Karpov et al. 2006

Complimentary slide: Self-healing: examples

Red wine



Aniline based solution



Self-healing alone increased CdTe PV efficiency
From 2-3% (untreated) **To 10-11%** (treated)

Complimentary slide: Highlighted in the media...

Article published Tuesday, February 10, 2004

Red wine leads UT scientists to juice up potency of solar cells

By **JENNI LAIDMAN**
BLADE SCIENCE
WRITER

Red wine, what can beat it? It reduces your risk of heart disease. It's full of cancer-fighting compounds. And now, researchers at the University of Toledo reveal yet another use for the juice of the grape.

It makes better solar cells.

UT researcher Yann Roussillon didn't expect wine to boost the efficiency of solar



Red Wine Mends Solar Cells

Technology Research News March 19, 2004

University of Toledo researchers have found a way to increase energy production of red wine.

One challenge in making solar cells more efficient is countering the effects of bad spots. These spots drain current, making devices like solar cells less efficient.

The researchers have found a way to use properties of the bad spots to seal the working area of the cell. The researchers used the method to boost the efficiency of a cadmium telluride/cadmium sulfide solar cell from 2 percent to 11 percent.

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Take Sunlight, Add Red Wine, Get More Power

Posted: Tuesday, April 06, 2004

By [Jacob Gaffney](#)

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Wine plays many roles in society -- it's used to make food taste better, to celebrate special occasions, even to benefit one's health. Now researchers at the University of Toledo in Ohio have discovered a truly novel use for the beverage.

A team from the university's chemistry, physics and astronomy departments found that solar panels manufactured with red wine produce up to 12 percent more electricity than solar panels made without it, according to research published in a recent issue of *Applied Physics Letters*.

Red wine, which can conduct electricity, helps solar panels "self-heal" when the flow of electric current is interrupted or slowed down.

Researcher Victor Karpov, a physics professor at the university,

Wine Spectator

Complimentary slide: Patent granted and exclusively licensed ...sadly..



US007098058B1

(12) **United States Patent**
Karpov et al.

(10) **Patent No.:** US 7,098,058 B1
(45) **Date of Patent:** Aug. 29, 2006

(54) **PHOTOVOLTAIC HEALING OF
NON-UNIFORMITIES IN SEMICONDUCTOR
DEVICES**

(75) Inventors: **Victor G. Karpov**, Toledo, OH (US);
Yann Roussillon, Mountain View, CA
(US); **Diana Shvydka**, Toledo, OH
(US); **Alvin D. Compaan**, Holland, OH
(US); **Dean M. Giolando**, Toledo, OH
(US)

OTHER PUBLICATIONS

V. G. Karpov, Diana Shvydka, Yann Roussillon, and A. D. Compaan, "The Mesoscale Physics of Large-Area Photovoltaics", Proceedings of 3d World Conference on Photovoltaic Energy Conversion, Osaka, Japan, May 11-18, 2003 (note: there are no page numbers assigned).

V. G. Karpov, A. D. Compaan, and Diana Shvydka, "Micrononuniformity Effects in Thin-Film Photovoltaics", Proceedings of 29th IEEE Photovoltaic Specialists Conference, New Orleans, May 18-23, 2002, pp 708-711

V. G. Karpov, R. Hajju, and G. Dorer, "Non-Uniform Power

ARTICLE 1 – DEFINITIONS

1.1 "AFFILIATE" means any corporation or other entity that is directly or indirectly controlling, controlled by, or under the common control of [REDACTED] Corporation located at [REDACTED]. For the purpose of this Agreement, "control" means the direct or indirect ownership of at least fifty percent (50%) of the outstanding shares or other voting rights of the subject entity to elect directors, or if not meeting the preceding, any entity owned or controlled by or owning or controlling the maximum control or ownership right permitted in the country where such entity exists.

DSE 1/11

1.2 "FIELD" means cadmium-telluride solar modules.