Plasmas in Liquids: What do we know and what can we still learn?

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DOE Plasma Science Center
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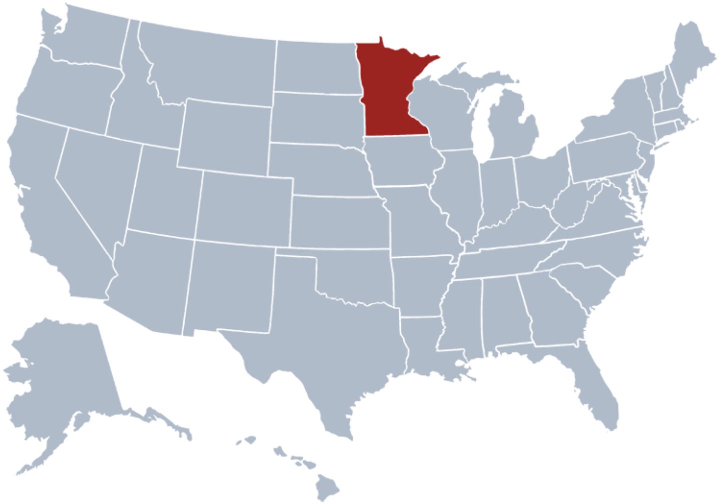
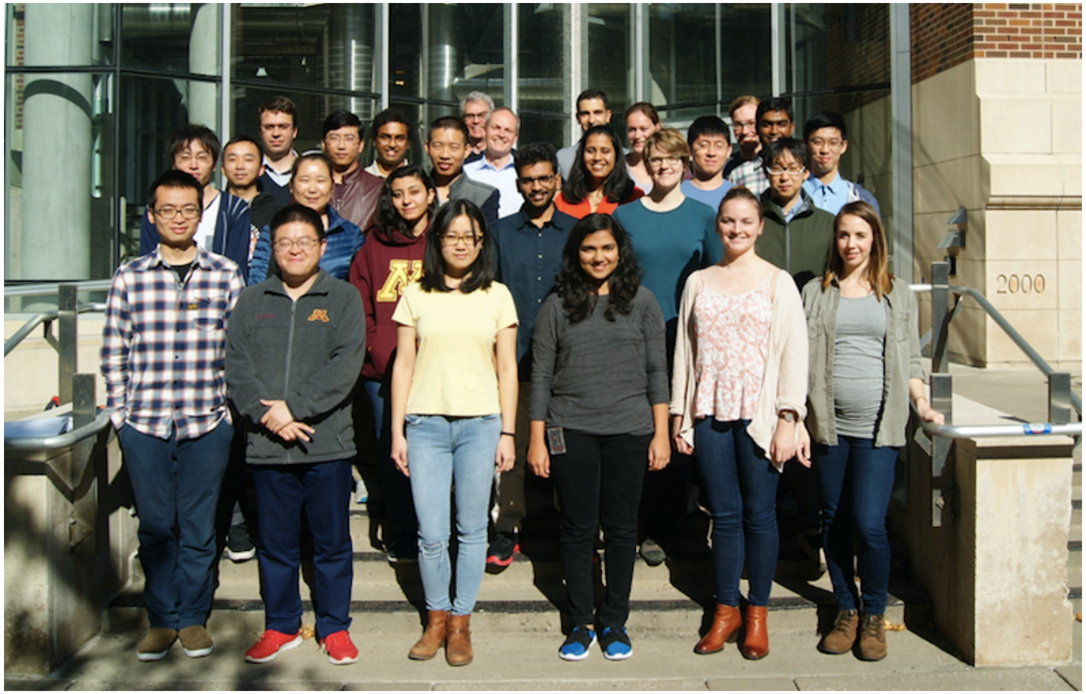
U.S. DEPARTMENT OF ENERGY

NSF

High Temperature and Plasma Laboratory



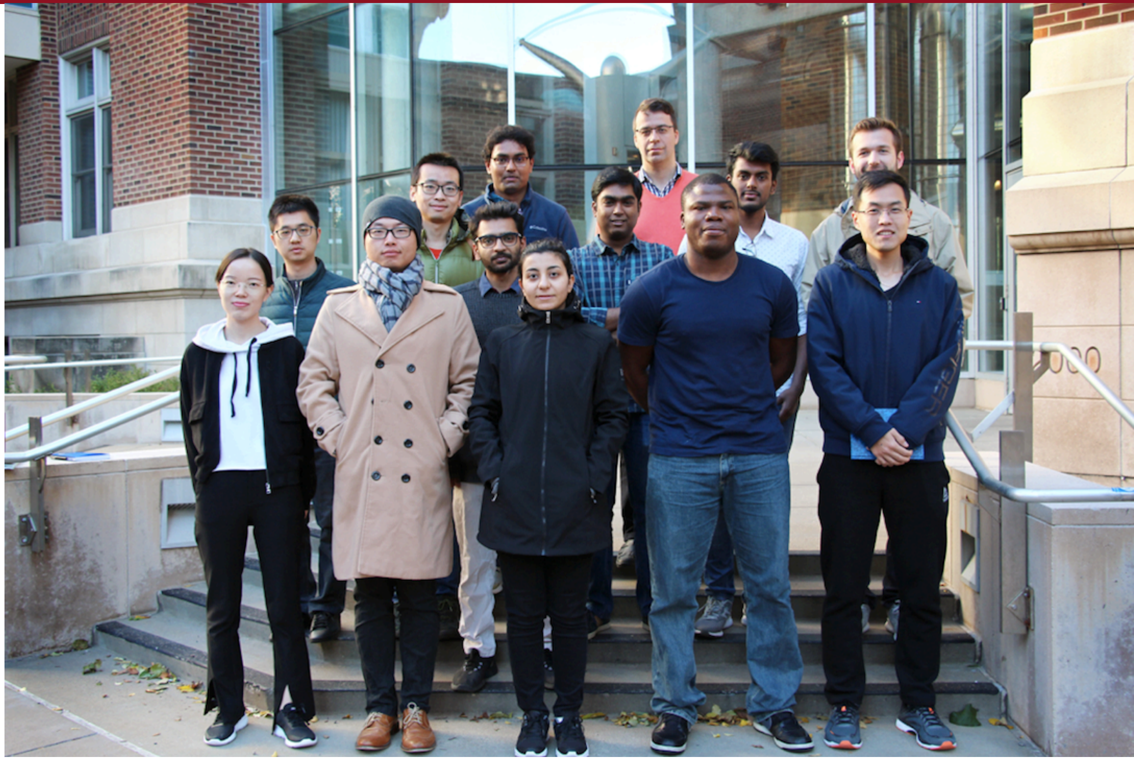


HTPL– September 2017

Acknowledgements

Contributors in my group to this presentation:

- S. Kondeti
- Y. Luo
- Dr. M. Simeni
- Prof. H. Taghvaei
- Dr. S. Yatom

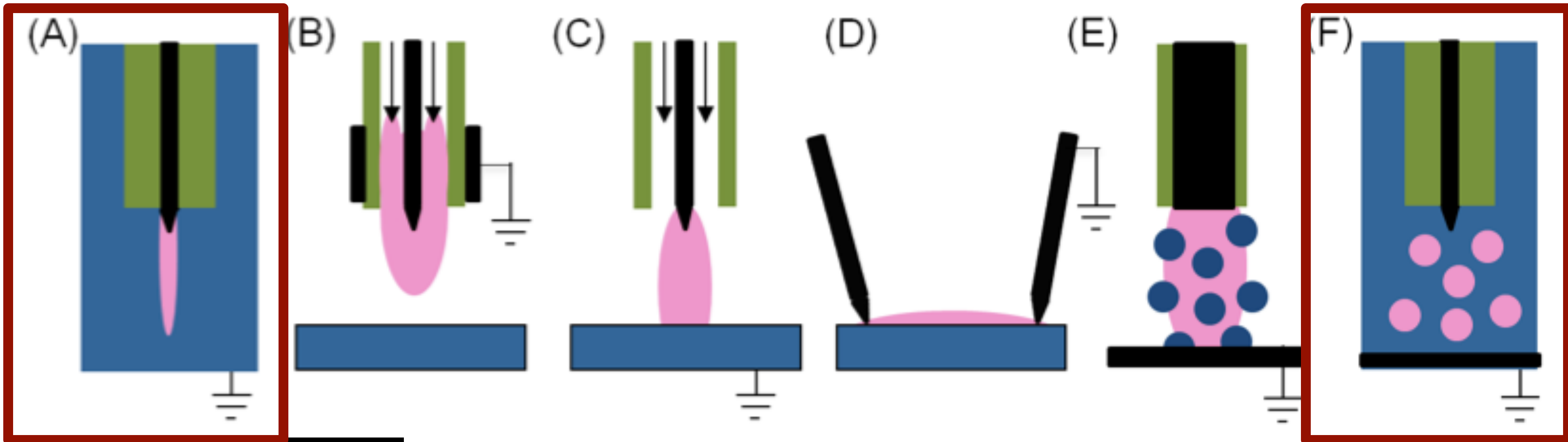


Bruggeman Group – October 2018

Collaborators

- C. Phan, R. Hunter, J. Granick (UMN)
- A. Lietz and M. Kushner (University of Michigan)
- K. Wende, H. Jablonowski (INP), D. Schram (TU/e)

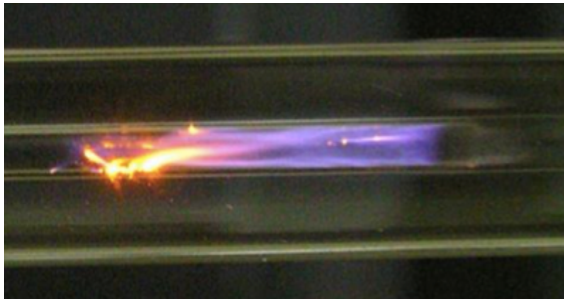
Plasma-liquid interactions



Direct liquid phase discharge

Gas phase discharges

Multi-phase discharges



Are plasmas in liquids are special?

	water	air
breakdown field	1 MV/cm	30 kV/cm
conductivity	conductive	non-conductive
dielectric constant	ε = 80	ε = 1
density ($2.5 \times 10^{25} m^{-3}$)	10^3	1
Life time free electron	1 ps	1 - 20 ns
phase change	yes	no
phases	often dissolved gases	homogeneous
polarization	polar	non-polar

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- Gas phase H_2O vapor kinetics
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Simplified idea about plasmas in liquids

Non-selective oxidizing specie as OH often required.

$$2\,O_3 + H_2O \xrightarrow{OH^-} OH\cdot + O_2 + HO_2\cdot$$

Only for trace compounds!

- **powerful (non-selective) oxidizing species**
- **UV**
- **shockwaves**

• OH^* (2.80 V)
• O_3 (2.07 V)
• H_2O_2 (1.77 V)

Advanced Oxidation Processes

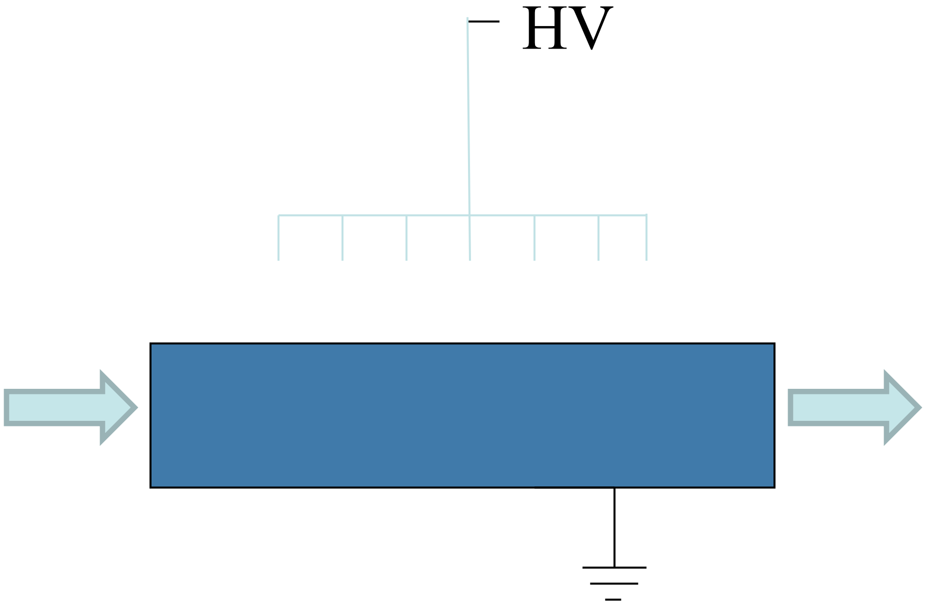
→ **destruction of toxic organic compounds**

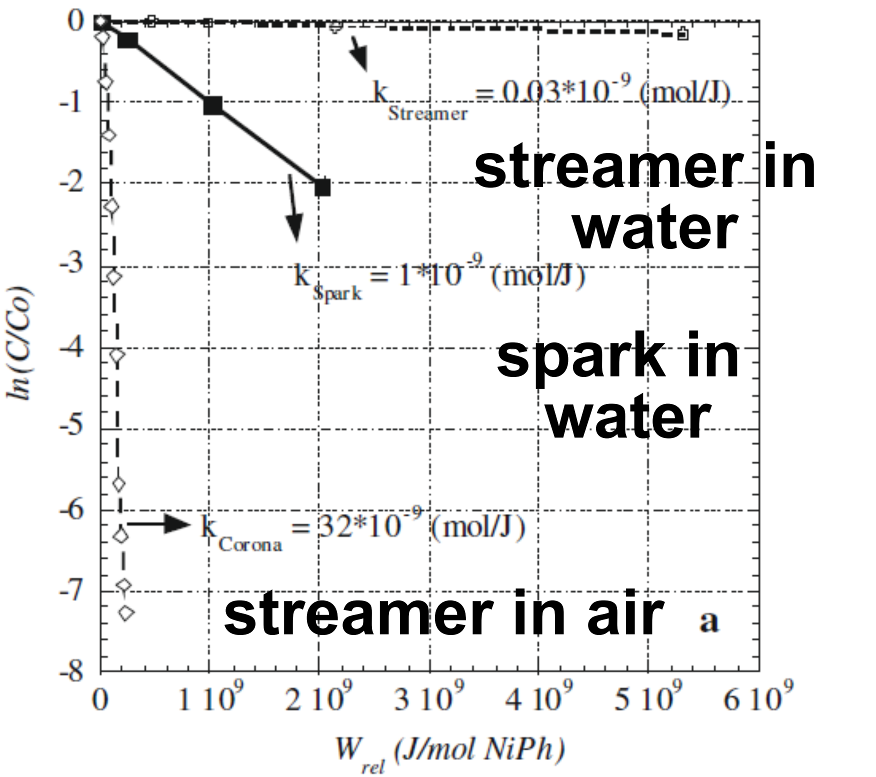
→ **decontamination / sterilisation / purification**

Water treatment with plasmas

→ pulsed corona above water is most efficient!!

removal of phenol / dye

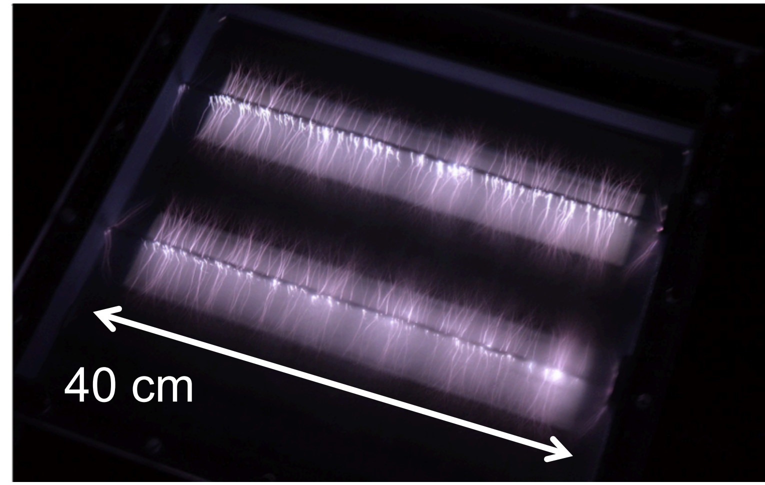




There exist successful applications for thermal arcs in water treatment.

Grabowski, van Veldhuizen et al PCPP, **26**, 1 (2006)
Dang, Denat et al Eur. Phys. J. Appl. Phys. **47,** 22818 (2009)

Degradation of emerging contaminants in wastewater and drinking water



Process	Contaminant	Treatment costs ($/m^3)
Activated carbon	PFOA	0.39
	PFOS	0.45
Plasma	PFOA	0.13
	PFOS	0.07
Sonolysis	PFOA	13.5
	PFOS	32.7

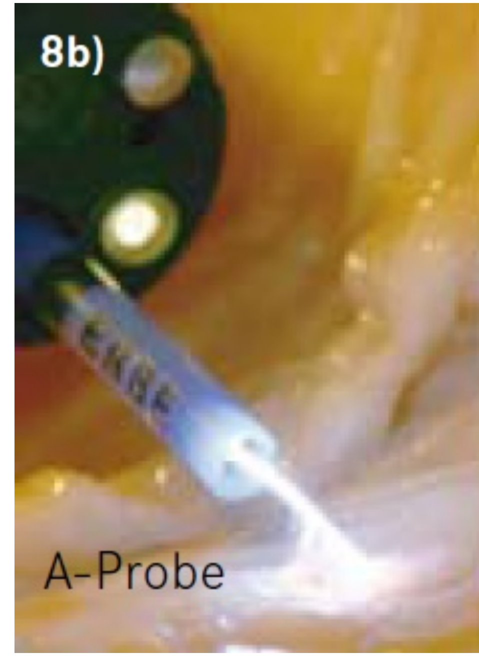
PFOA=Perfluorooctanoic acid
PFOS=Perfluorooctanesulfonic acid

- EPA-regulated cancer-causing compounds are too stable for decomposition by conventional water treatments or by advanced oxidation processes using OH radicals.
- Plasmas produce aqueous electrons and H radicals which are capable of chemically reducing these compounds.
- Plasma water treatment is competitive with the leading conventional and alternative technologies.

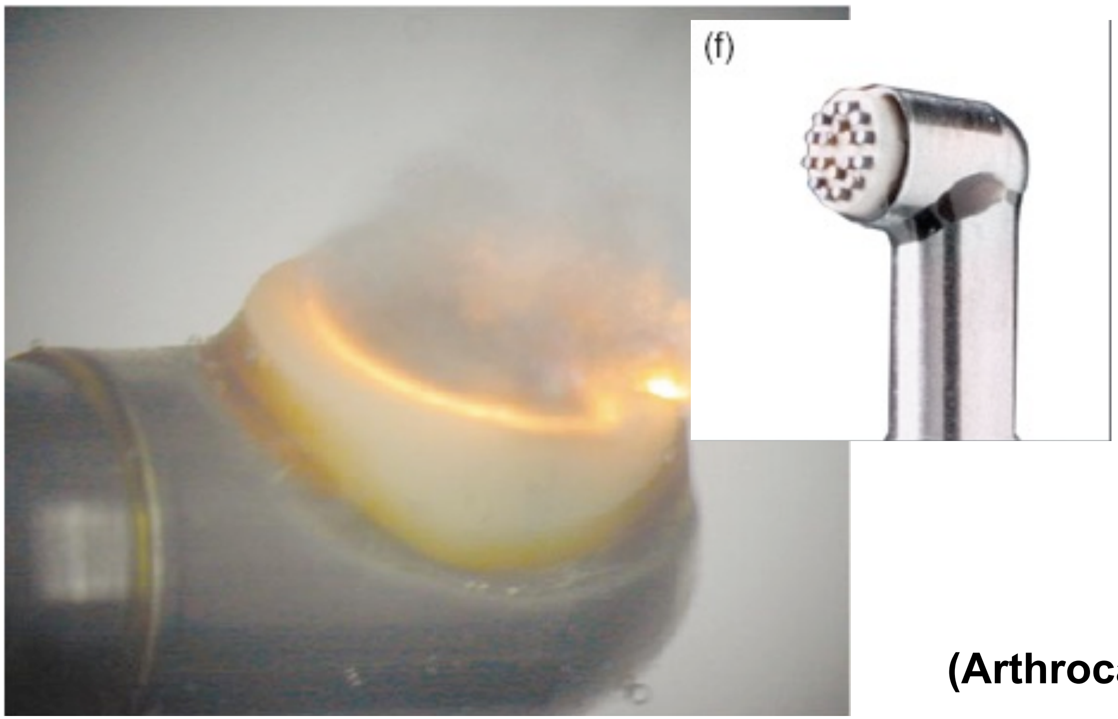
Selma Mededovic Thagard, Chemical and Biomolecular Engineering, Clarkson University

Established medical applications

- Blood coagulation (hemostasis)
- Tissue ablation



(Erbe USA Inc.)



(Arthrocare Inc.)

Decontamination

Sterilization of liquids (water, juices,...)

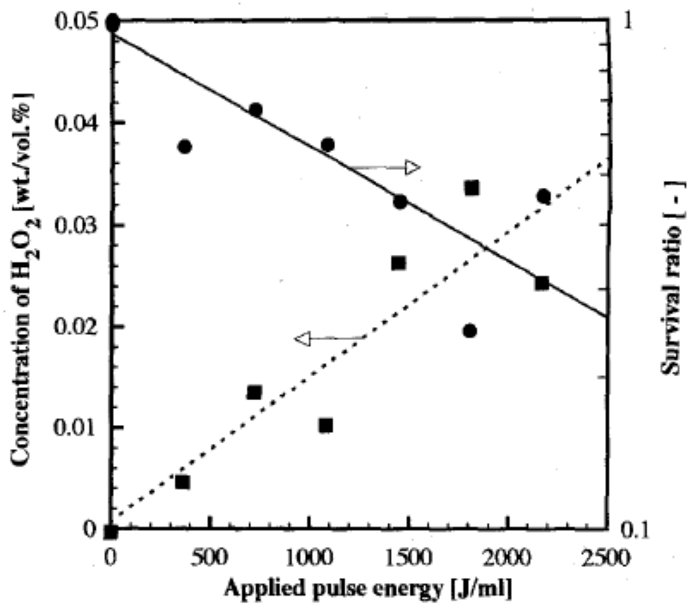


Fig. 9. Cell survival ratio and H_2O_2 concentration in distilled water as a function of total pulse energy applied (pulse voltage: 19 kV).

Sato M et al (1996) IEEE Trans. Ind. Appl. **32** (1) 1996

Algae treatment

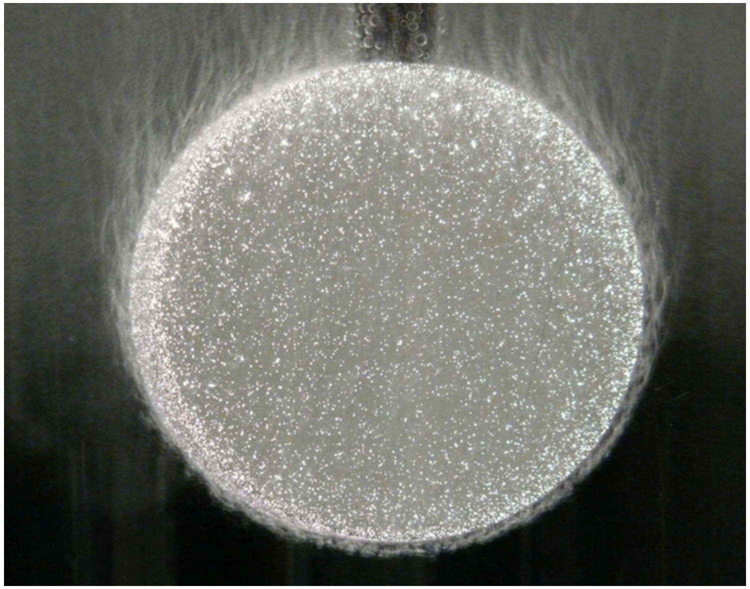
group of prof. H. Akiyama, Kumamoto University

Material synthesis and processing

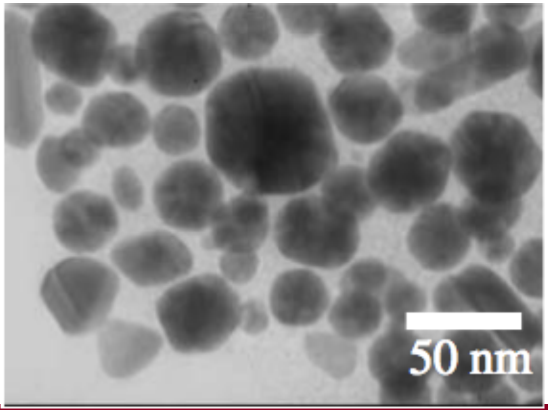
Plasma-polishing of metallic surfaces

Beckmann-Institut für Technologieentwicklung

Plasma Electrolytic Oxidation



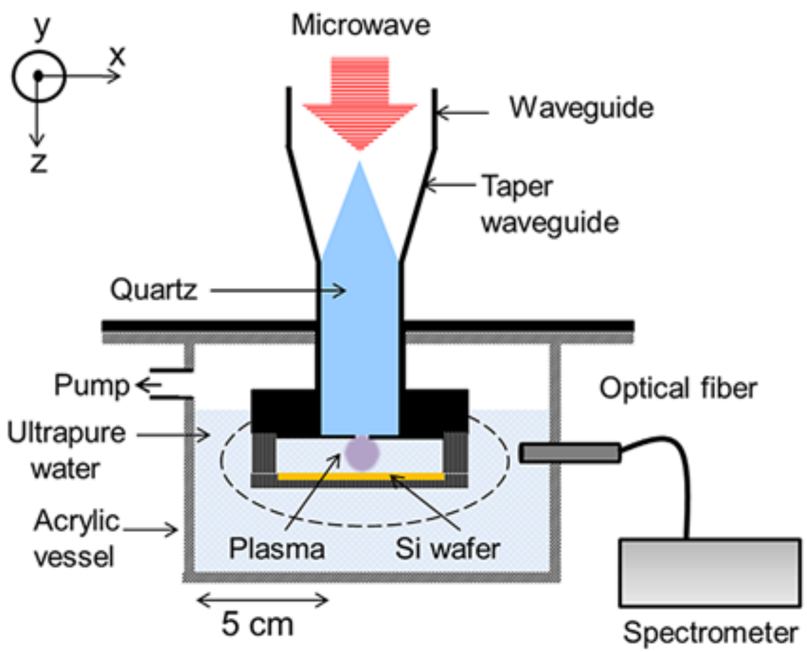
Material synthesis (nanomaterials)

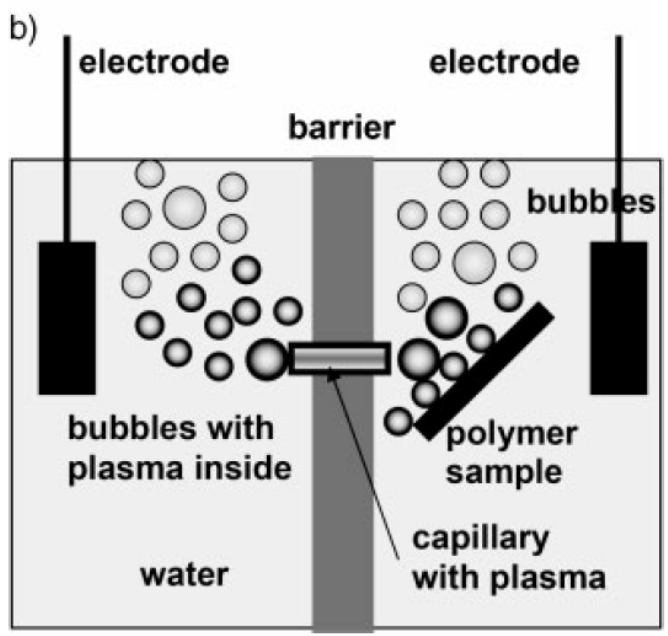


Takai et al , JVSTA 26 (4) (2008)
- Belmonte et al

Image: IBC Coatings Technologies Ltd
- Yerokhin, Henrion

Surface treatment - Polymer treatment





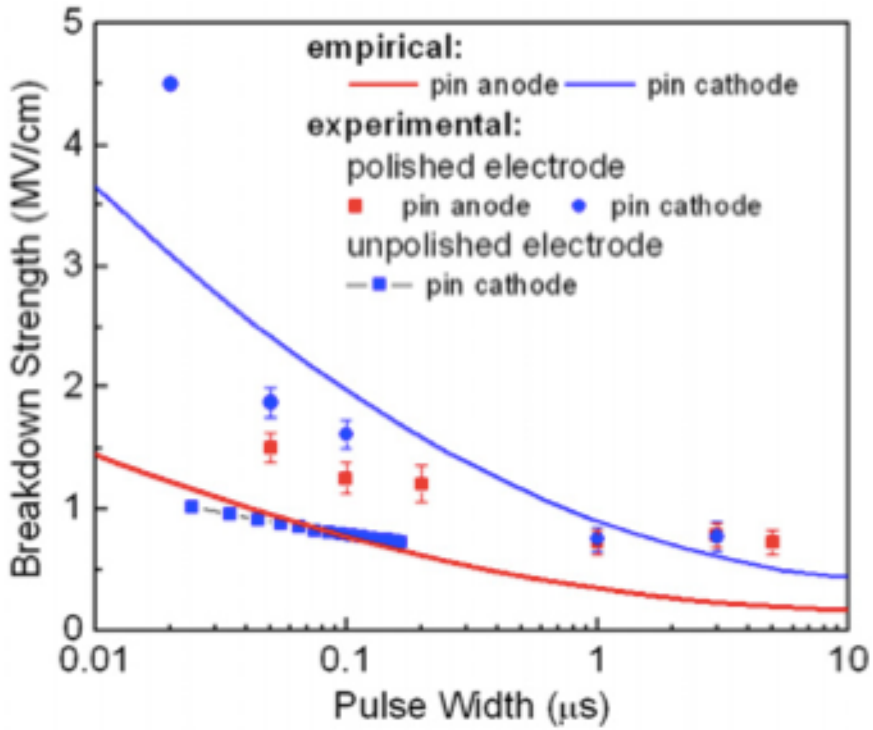
Photoresist etching
(high speed ~ 100 nm/s)

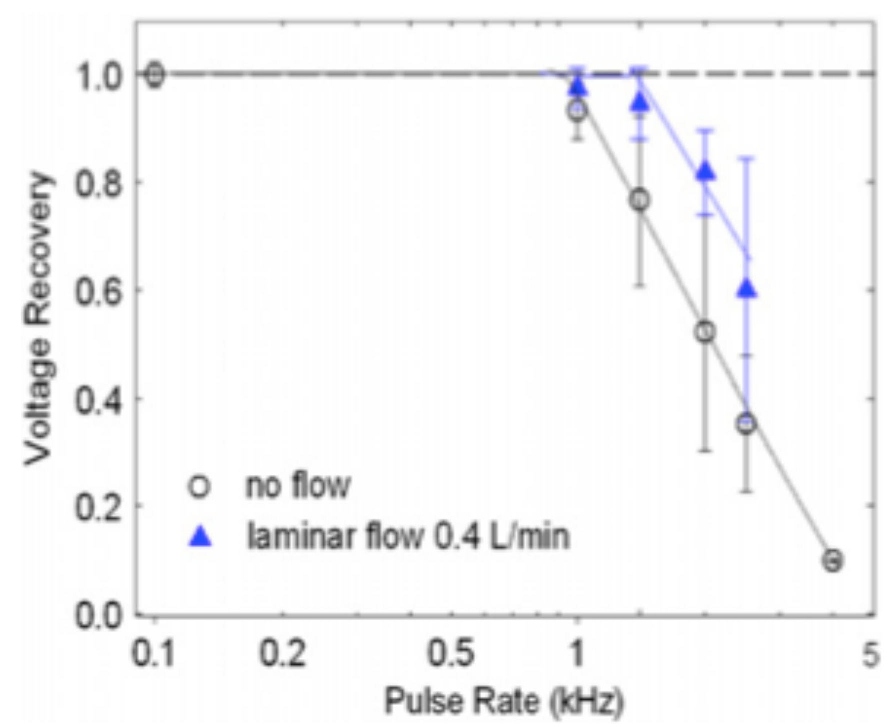
Polymer surface functionalization
with high yield and selectivity
water is energy moderator

Ishijima et al, APL, 103 (2013) 142101

Friedrich et al, PPP, 5 (2008) 407-423

High voltage switching





Switches in dielectric liquids (water, oils)
Importance of breakdown strength and recovery after breakdown

Schoenbach et al PSST 17 (2008) 024010

Increasing complexity: engineering approach

empirical

Plasma treatment

Setting plasma parameters
P, V(t), gas, p, t_{treat}

[redacted]

Characterization of treatment outcome

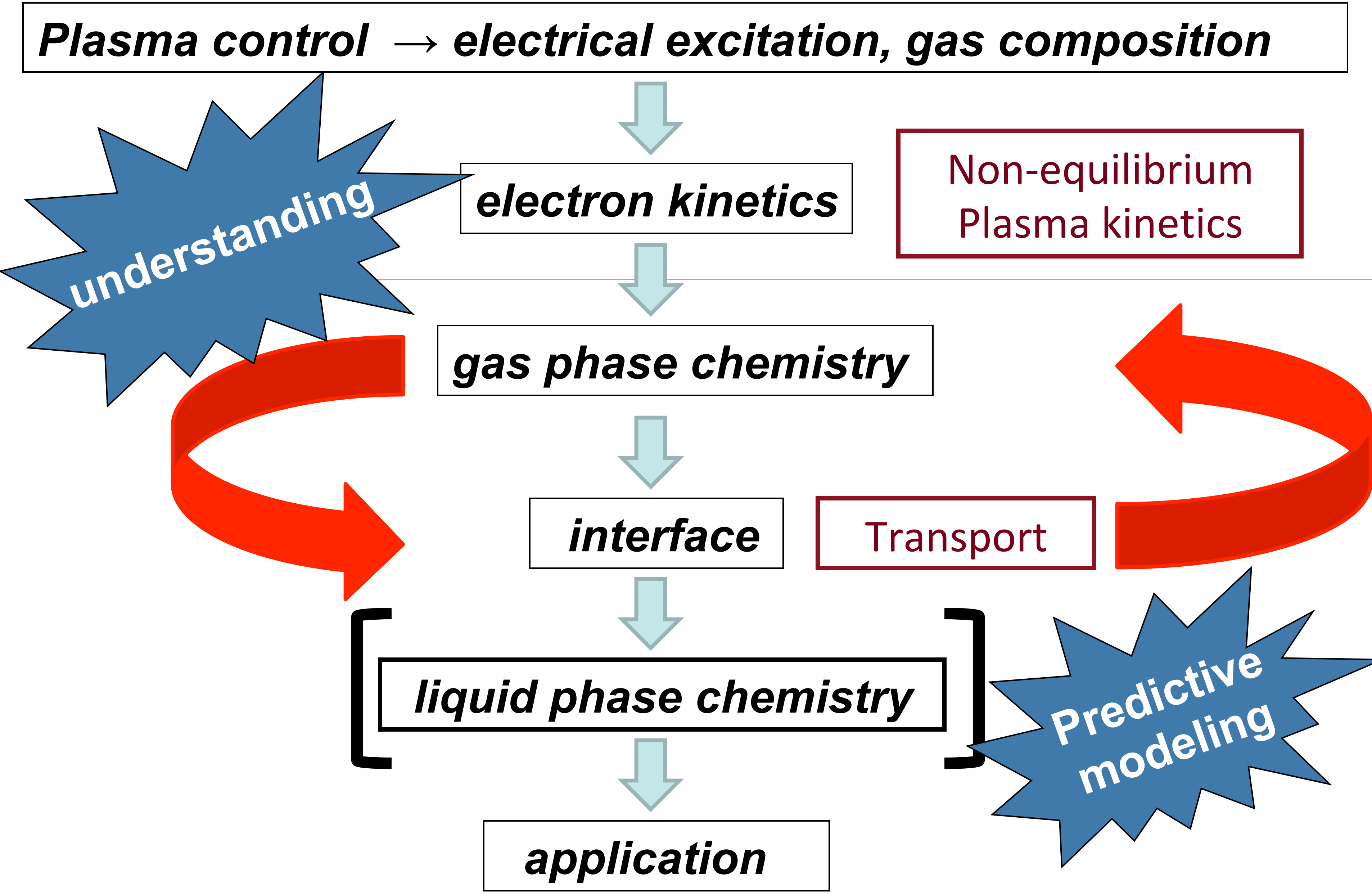
$F(P, V(t), \text{gas}, p, t_{treat})$

$\boldsymbol{F(T_{gas}, T_e(\text{EEDF}), \text{IEDF}, n_e, n_{rad})}$

$n_e \sim 10^{12}$-10^{25} m^{-3}
T_e = 300 K - 10 eV
T_g = 300 K - 2 eV
t = 1 ns - minutes

Plasmas span an excessive parameter range…

From plasma processes to applications



What to know to control applications?

- Plasma-induced reactivity
  - Plasma kinetics
  - Reactivity transport (interfacial and convective)
  - Liquid phase chemistry
- Electrical breakdown
- Mechanics/fluid dynamics
  - Shockwave dynamics
  - Plasma-electrode/substrate interaction
  - Heat release

‘The Unkowns’

IOP Publishing — Journal of Physics D: Applied Physics
J. Phys. D: Appl. Phys. 45 (2012) 253001 (37pp) — doi:10.1088/0022-3727/45/25/253001

REVIEW ARTICLE

The 2012 Plasma Roadmap

OPEN ACCESS
IOP Publishing — Journal of Physics D: Applied Physics
J. Phys. D: Appl. Phys. 50 (2017) 323001 (46pp) — https://doi.org/10.1088/1361-6463/aa76f5

Topical Review

The 2017 Plasma Roadmap: Low temperature plasma science and technology

IOP Publishing — Plasma Sources Science and Technology
Plasma Sources Sci. Technol. 25 (2016) 053002 (59pp) — doi:10.1088/0963-0252/25/5/053002

Review

Plasma–liquid interactions: a review and roadmap

Published Online: 25 July 2018 Accepted: May 2018

Plasma physics of liquids—A focused review

Applied Physics Reviews 5, 031103 (2018); https://doi.org/10.1063/1.5020511

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Understanding (and controlling)

- breakdown processes and mechanisms in liquids
- physical and chemical processes occurring at the plasma–liquid interface

Overview

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  - Applications and “The unknowns”
- **Discharge initiation**
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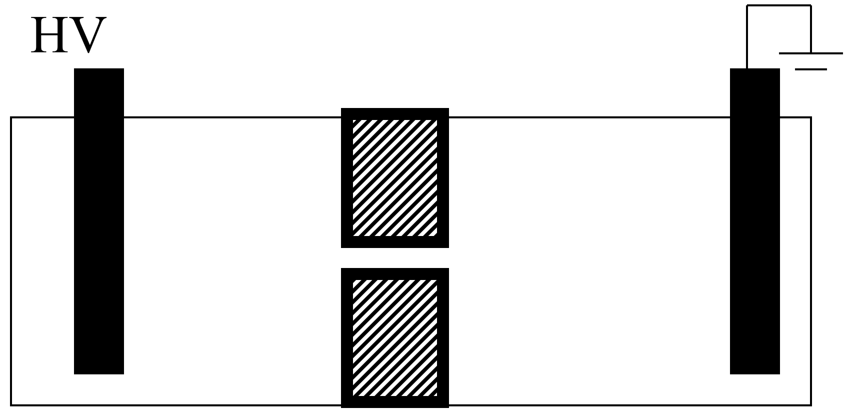
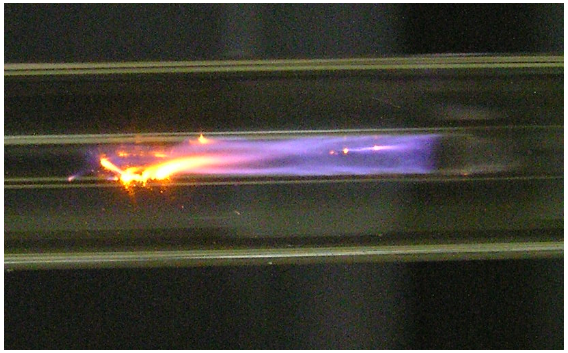
Discharges preceded by evaporation

AC discharge in saline

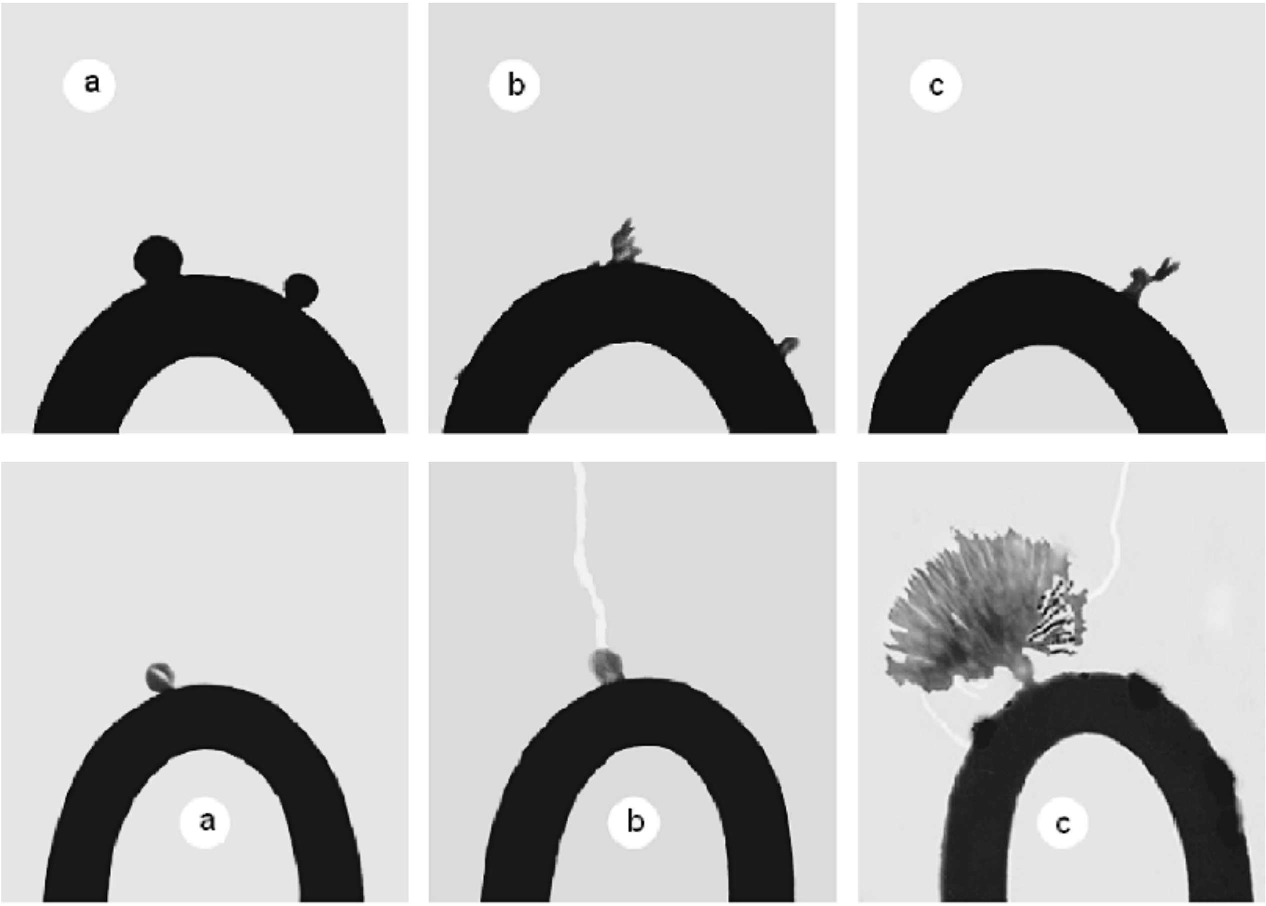
capillary discharge





constriction of pre-discharge current → strong thermal effects (bubble formation, localized boiling) → breakdown

Discharges in pre-existing micro-bubbles



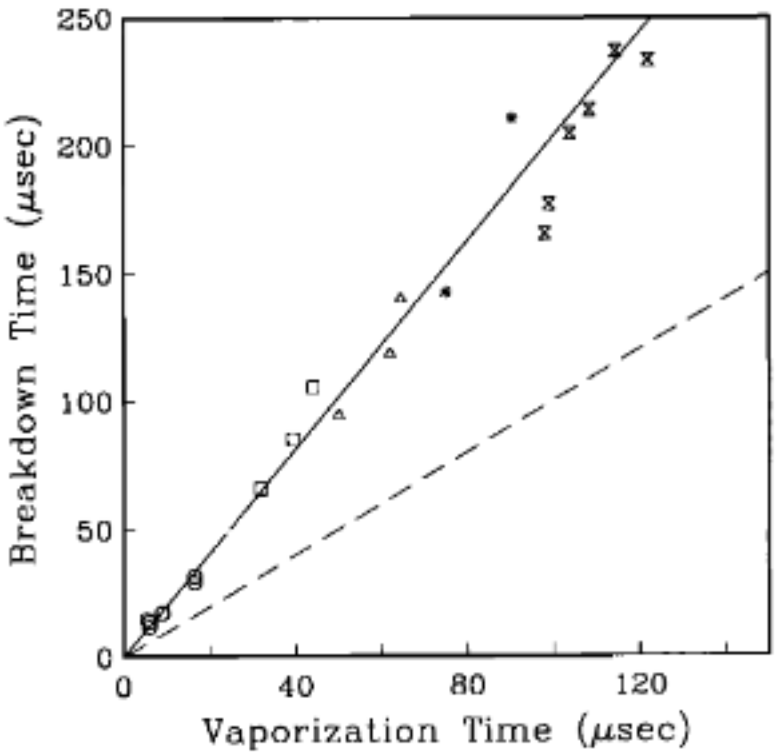
Ushakov et al, Impulse breakdown of liquids.

cathode

anode

When bubbles are not attached to the cathode no discharge formation is observed! Indication for the need of electron injection in the bubble from the cathode.

Breakdown in conductive liquids (μs pulse)?



- Breakdown time correlations with time needed to dissipate enough energy to vaporize locally the liquid.
- Input power is in good agreement with the power required to vaporize the liquid contained within the volume of the streamers.

Olson and Sutton *J. Acoust. Soc. Am.* **94** 2226–31 (1993)

Lisitsyn, Akiyama et al, *IEEE Trans. Dielectr. Electr. Insul.* **6** 351–6 (1999)

Plasma formation in dense liquid media

	water	air
E_{break}	1 MV/cm	30 kV/cm

Nanosecond breakdown in a liquid

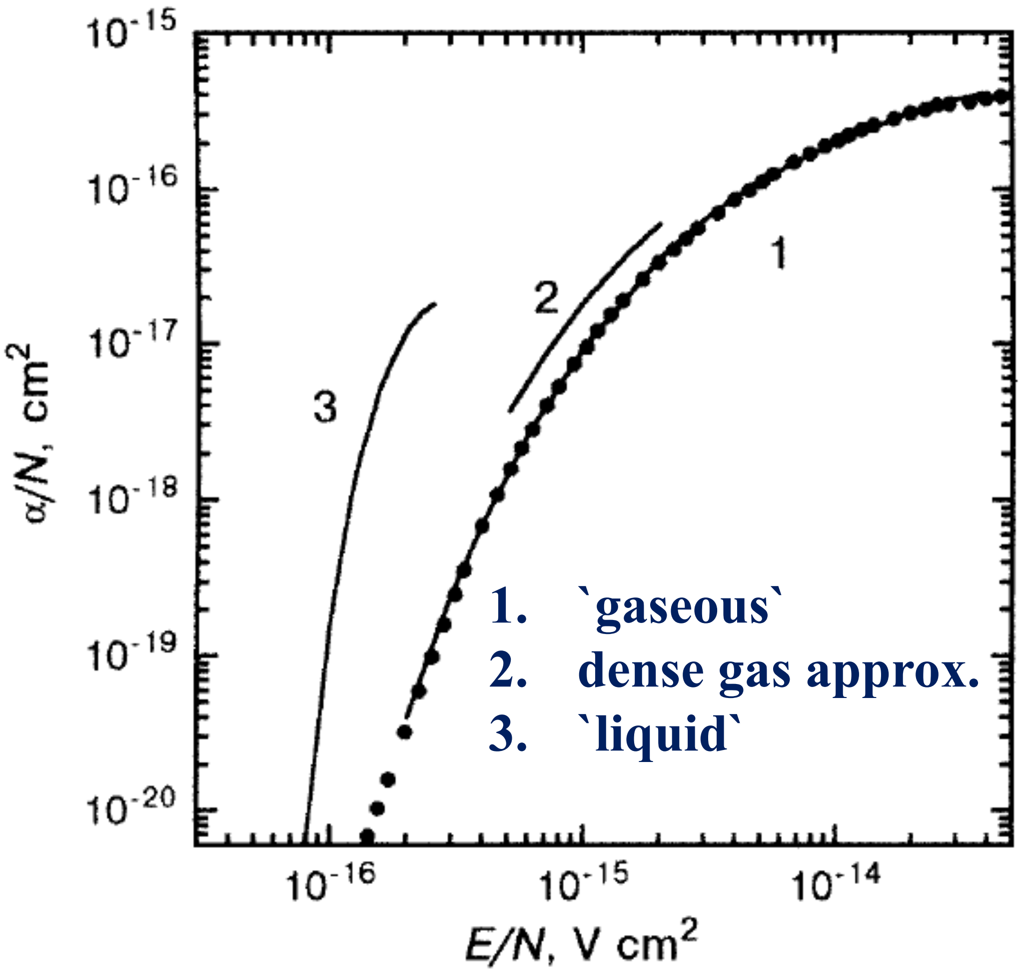
Electron multiplication in the liquid?

Phase change mechanism neccessary?

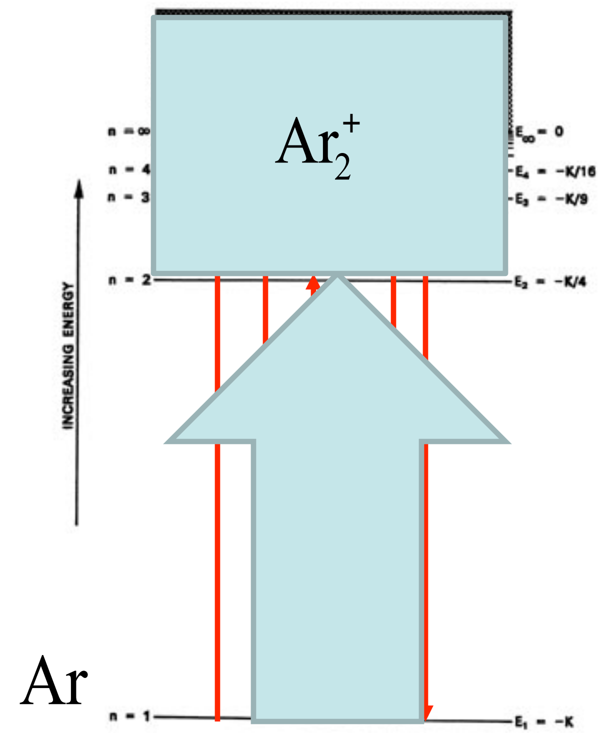
- **in liquid Xe, Ar, He, ... directly in liquid.**
- **life time of electron in water ~ 1 ps (hydrated electron)**
- **nanosecond HV pulse – no time for phase change**
- **many mechanisms proposed...**

O Lesaint, J. Phys. D: Appl. J. Phys.D: Appl. Phys. 49 (2016) 144001

From gaseous to liquid Ar?

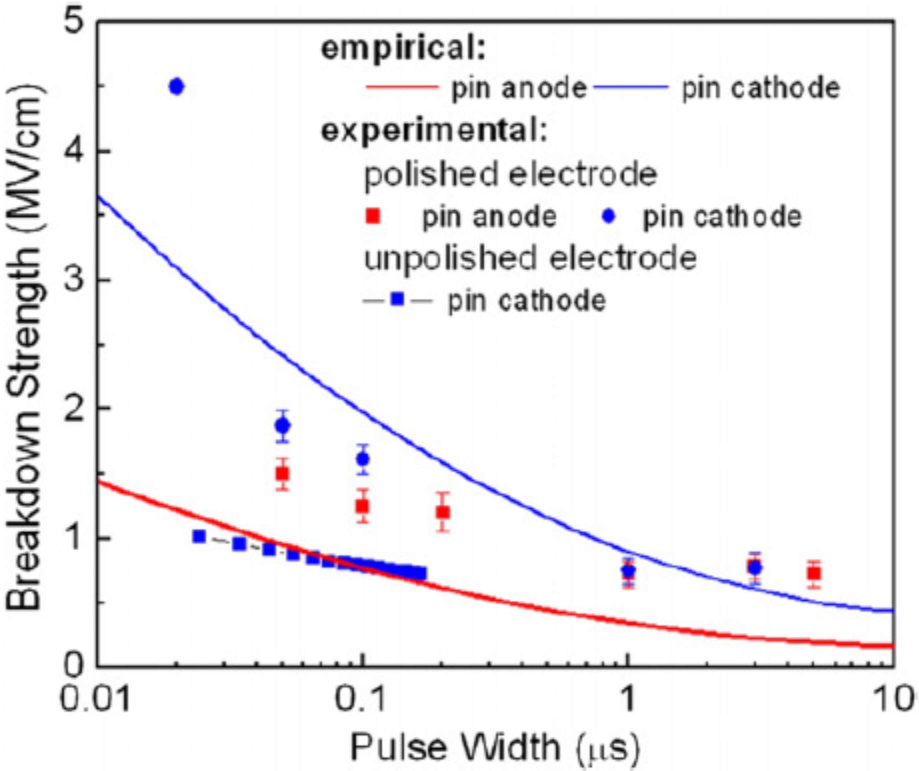


In the limit of very high neutral densities, everything which is excited gets ionized.



Bonifaci, Denat and V Atrazhev, 1997 J. Phys. D: Appl. Phys. 30 2717

Breakdown strength?

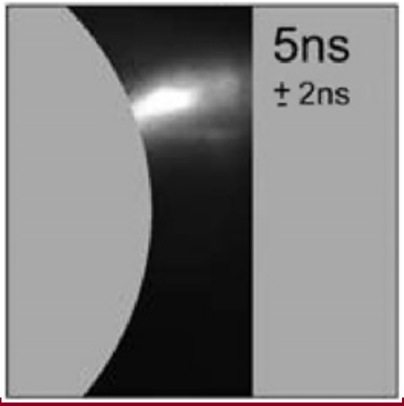


$$E_{\rm a} = \alpha 0.23 A^{-0.058} t^{-1/3}$$

Depends on:

- **pulse duration (t)**
- **electrode area (A)**

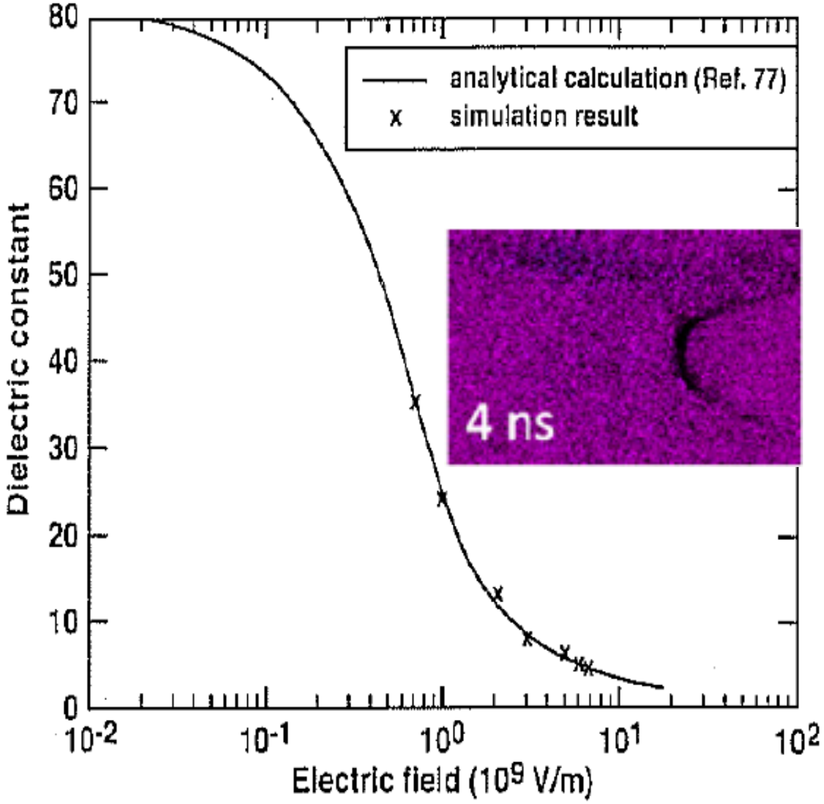
Ecton − explosive emission centers (micro-explosions of imperfections/micro-protrusions at the cathode)

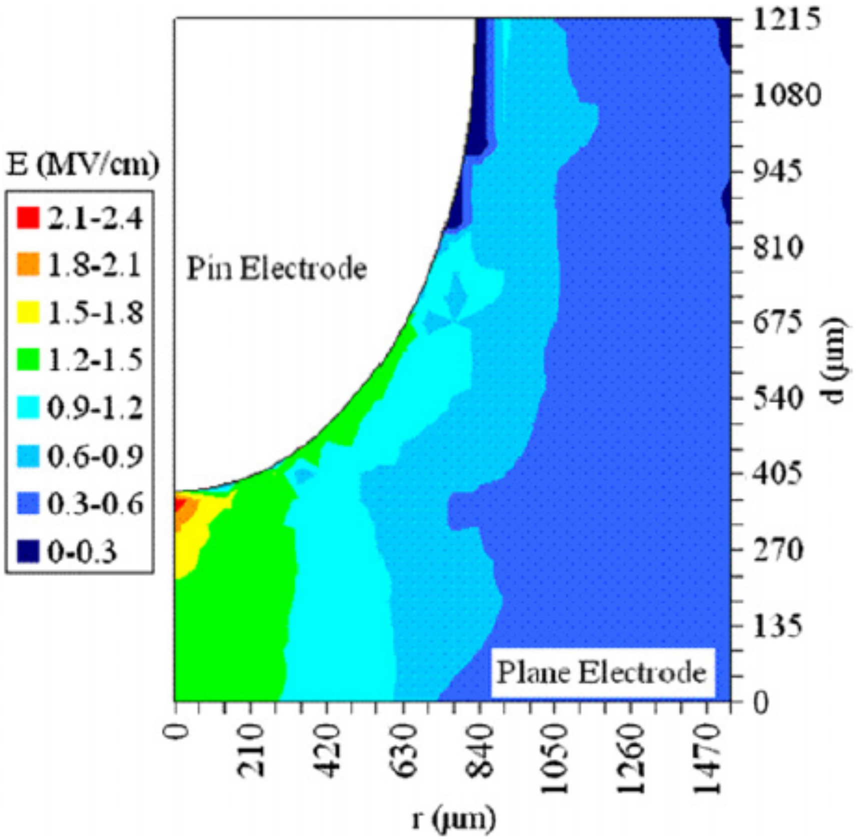


How smooth can an electrode be?
Preferentially breakdown at anode.

Schoenbach, Kolb et al, Plasma Sources Sci. Technol. **17** (2008) 024010
Mesyats G A 1995 Phys.—Usp. **38** 567–91

Local electric field enhancement?



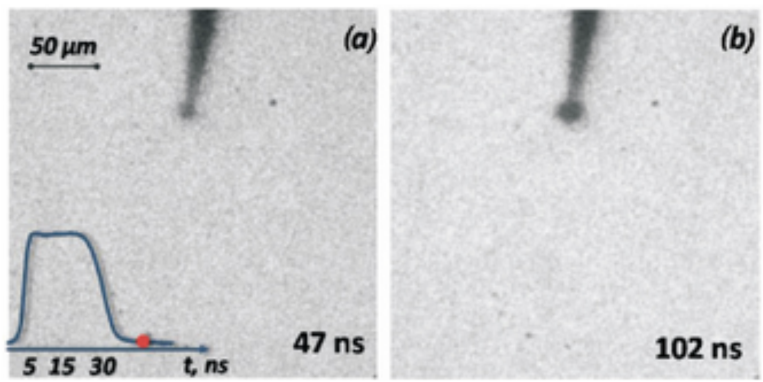


- **Reduction of the dielectric constant for high fields (is important)**
- **Field measurement (the Kerr effect, by interferometery $n_{par} - n_{perp} \sim E^2$)**
- **Positive feedback for E field due to reduction of ε for E>1MV/cm**

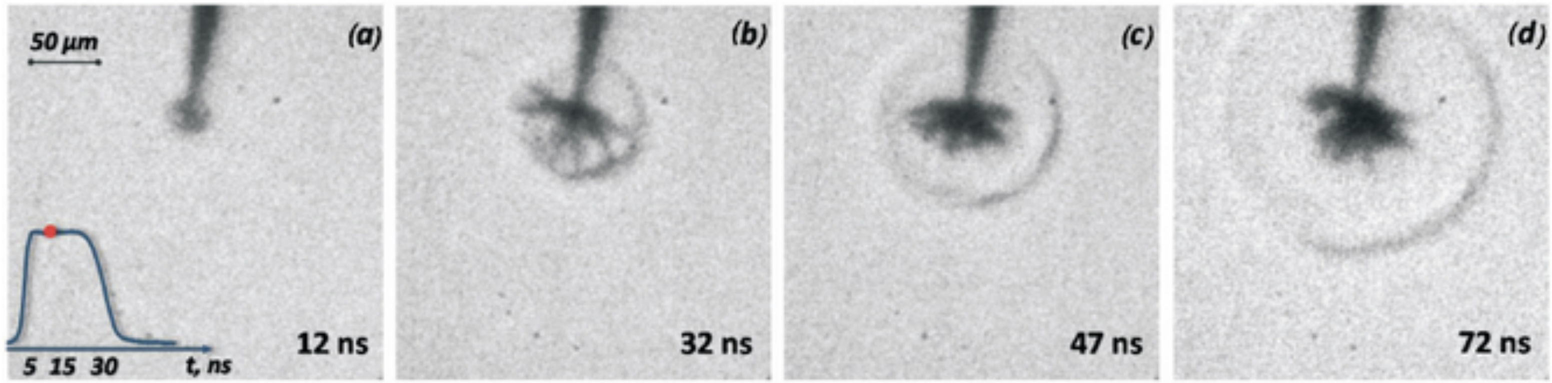
Schoenbach, Kolb et al, Plasma Sources Sci. Technol. **17** (2008) 024010
Schlieren image: Fridman group

Bubble formation in ns pulsed discharges?

4 kV



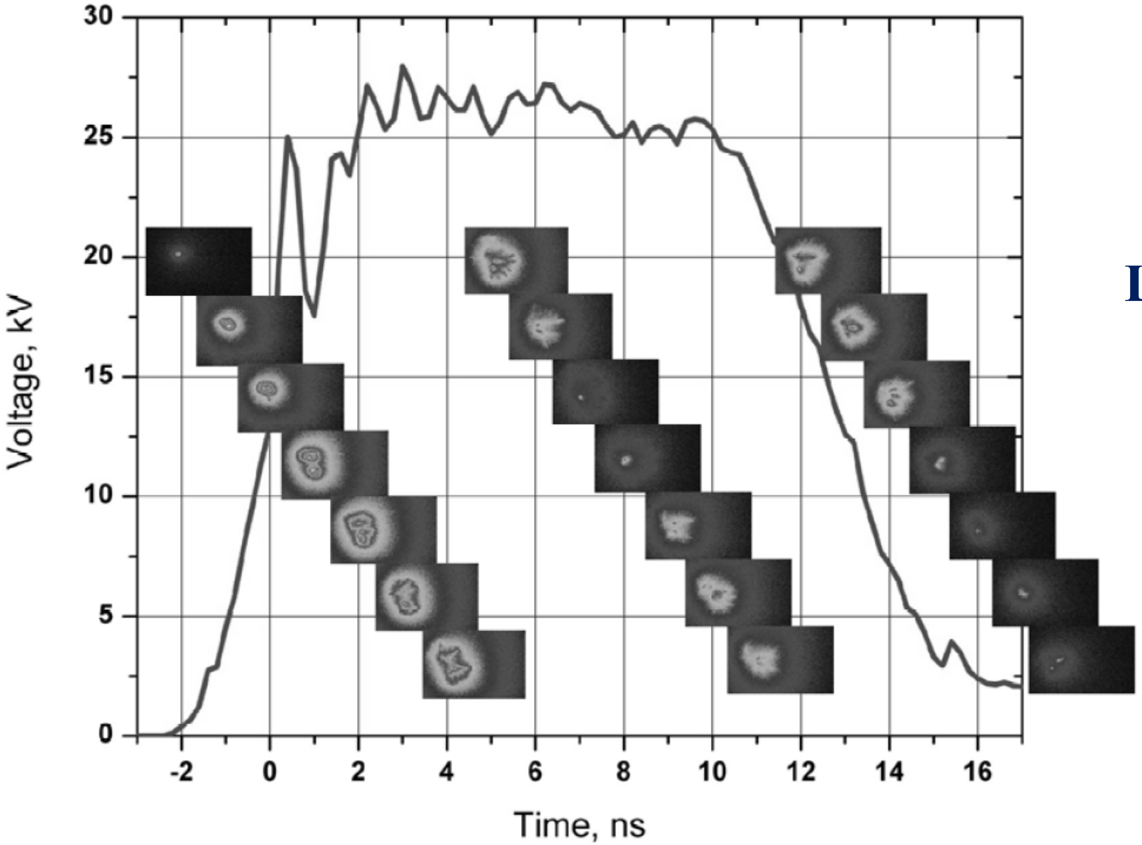
Stochastic process
(not every voltage pulse
leads to discharge)



- Clearly zone with lower refractive index observed – bubble
- > 4×10^8 V/m → dipole alignment can lead to refractive index change

I. Marinov et al PSST, 22, 042001 (2013), J. Kolb, IEEE PPS, 2015

Direct discharges in water possible?



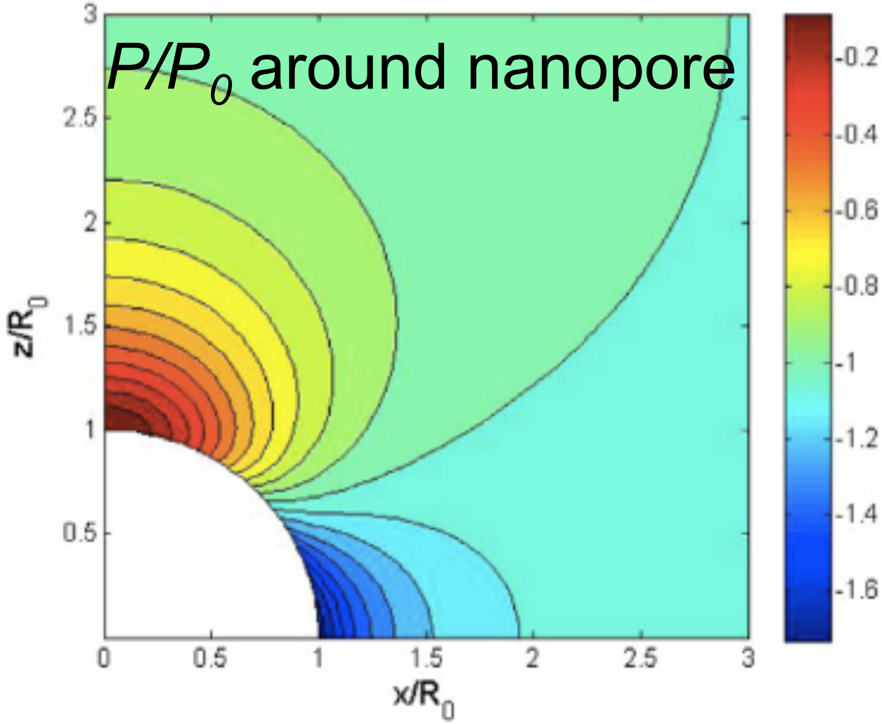
Starikovskyi et al

Life time free electron = 1ps

(sub-)nanosecond rise time are necessary!

Is this a proof of a discharge in water without phase change?

Electrostriction?



$$P_{\text{total}} = P_{\text{hydr}} - \rho\varepsilon_0 \left(\frac{\partial \varepsilon}{\partial \rho}\right) E^2$$

- a stretching tension occurs in the fluid → nanopores
- Liquid inertia does not lead to recovery on ns timescale
- Breakdown: $2R \times E$ >12.6 eV

  → E >10^{10}V/m]

Secondary cavitation could lead to the appearance of chains of nanopores, aligned along the electric field lines, in which the breakdown may develop.

M. Pekker and M.N. Shneider J. Phys.D 48 (2015) 424009

The view of Nikuradse (1934) and Kolb (2008)

'It is difficult to compare the results of different authors, since their experimental conditions are entirely different. [. . .] A comprehensive theory does not exist. Each one only deals with a fraction of the causes, which could lead to breakdown. Therefore they will be able to exist beside each other until a general theory can be developed.'

(A Nikuradse **1934** *Das flussige Dielektrikum (Berlin: Verlag Julius* Springer) p 165, translated from German)

Recited in:
J F Kolb, R P Joshi, S Xiao and K H Schoenbach, Streamers in water and other dielectric liquids, J. Phys. D: Appl. Phys. 41 (**2008**) 234007

... or we can directly measure the phenomenon without assumptions in the interpretation of the data.

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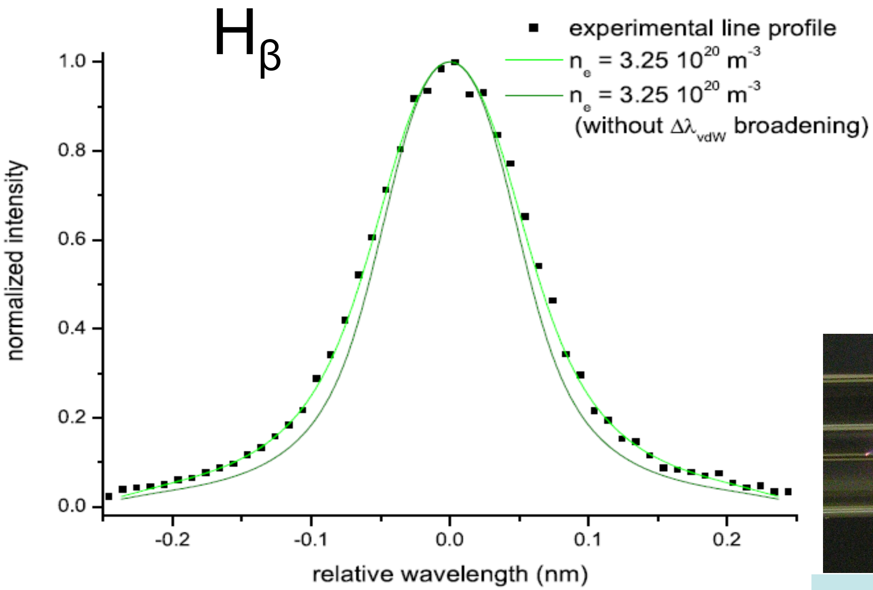
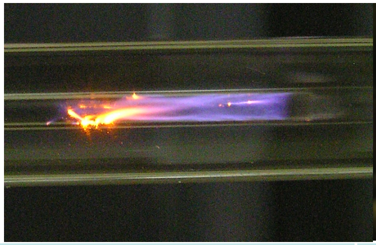
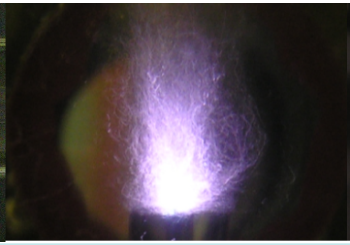
n_e of filamentary H_2O discharges



$$\Delta\lambda_{Stark} \propto n_e^{\frac{2}{3}}$$

$$\Delta\lambda_{vdW} \propto \frac{p}{T_g^{0.7}}$$



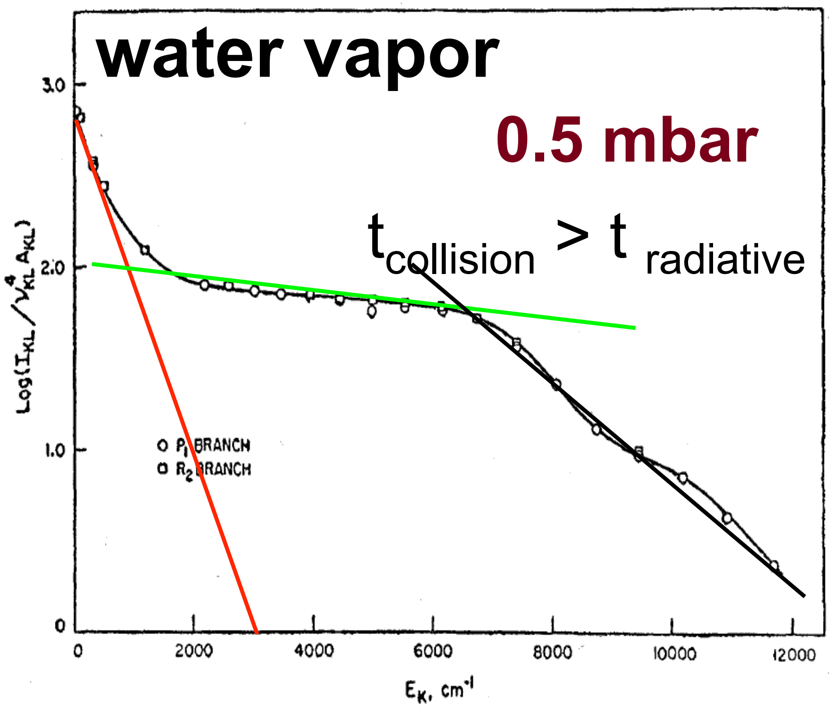


Filamentary (streamer like)	Strongly driven discharges in bubbles	Direct liquid
10^{20}-10^{21} m^{-3}	10^{21}-10^{23} m^{-3}	10^{23}-10^{25} m^{-3} (pressure broadening!!!)

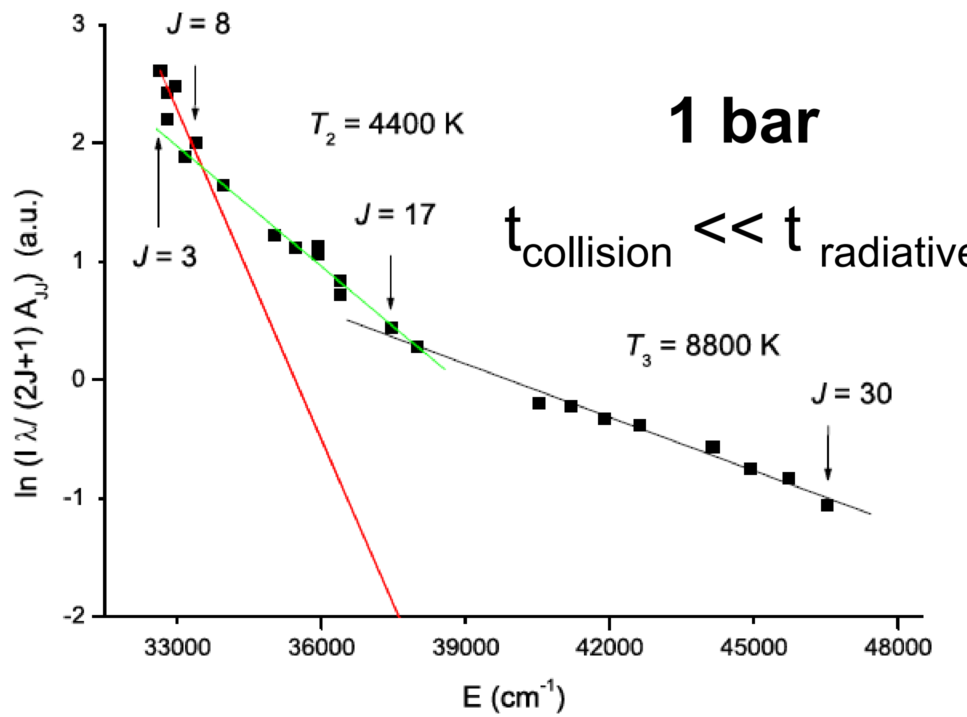
H_β Balmer line is very reliable but *p* and *T_g* needs to be know!

(Bruggeman et al. J. Phys. D **42** 053001, 2009
(Bruggeman et al PSST **18**, 025017, 2009

Gas temperature: OH(A-X) emission



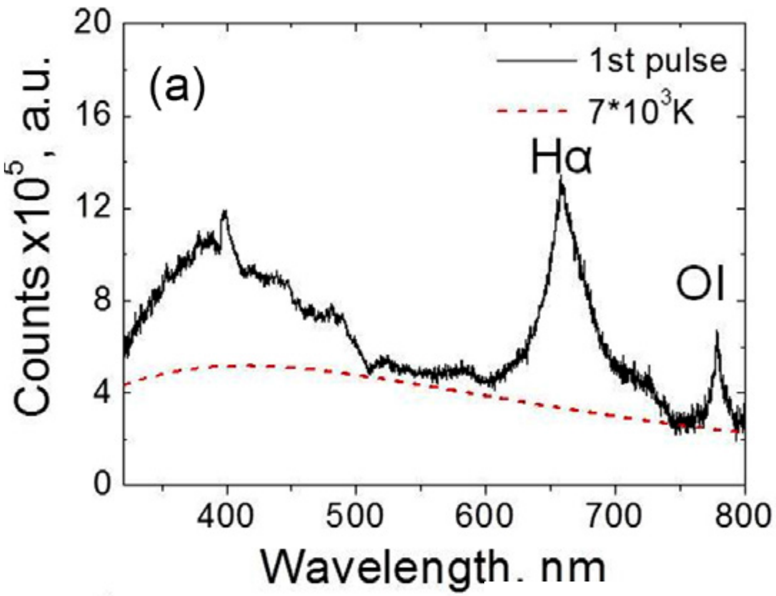
Broida and Krane, *Phys Rev* **89** (1953)



Bruggeman et al, *J. Phys D* **41** (2008)

Rotational distribution is an image of the formation process and does not represent the gas temperature !!

Exotic discharges in liquid (water)



- high electron density (10^{24}-10^{25} m^{-3})
- 2-3ns pressure pulses of 2-3GPa

(all properties deduced from indirect measurements)

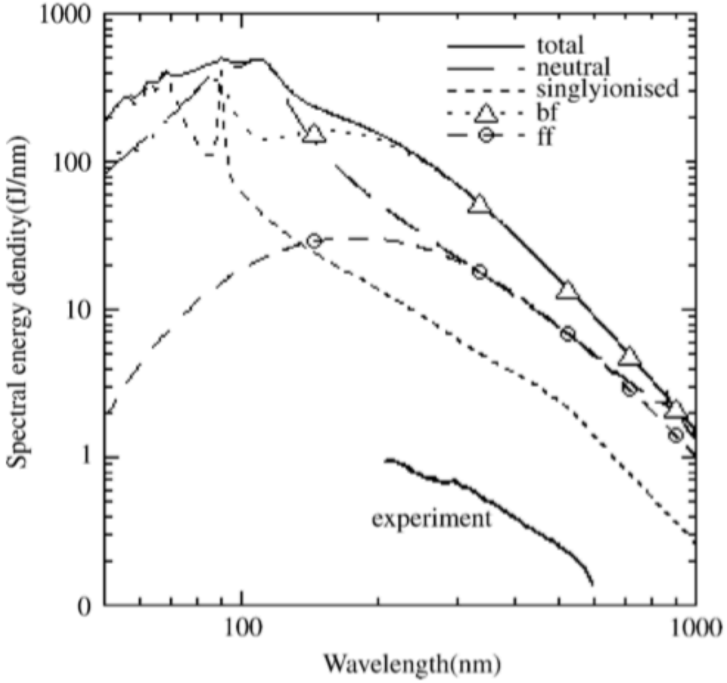
correlated plasma ??

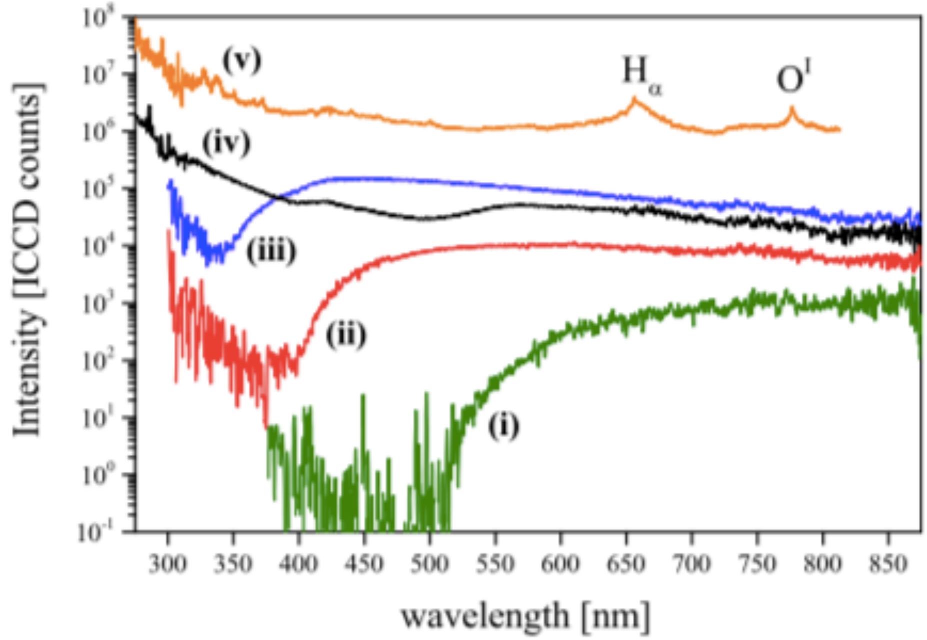
Coupling parameter:

$$\Gamma = \frac{E_{coulomb}}{kT_e} \approx \Lambda^{-3/2} \sim 1$$

Bruggeman, J. Phys. D 2009
An et al JAP 101, 053302, 2007
PhD thesis Paul Ceccato
Marinov et al, J. Phys. D: Appl. Phys. 47 (2014) 224017

Broad band emission



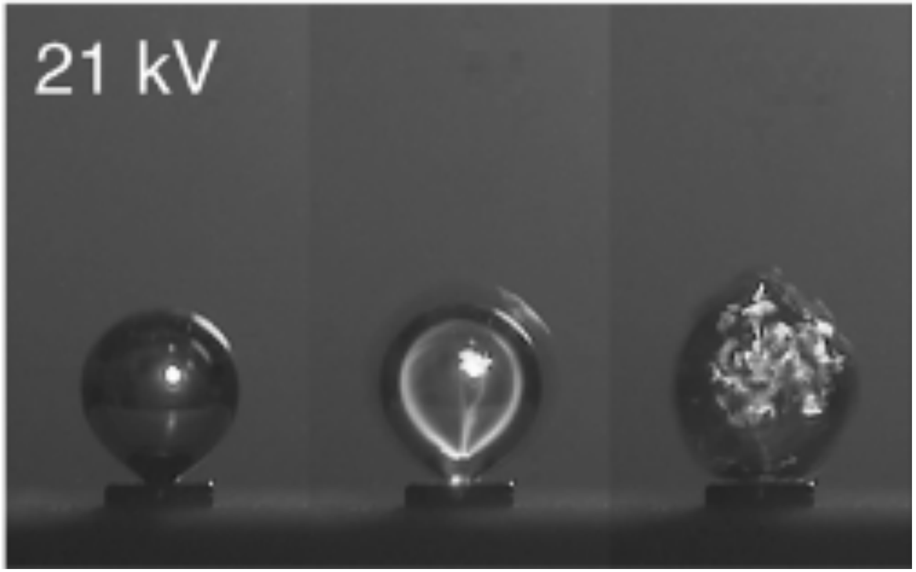


Studied in detail in arcs and sonoluminescence

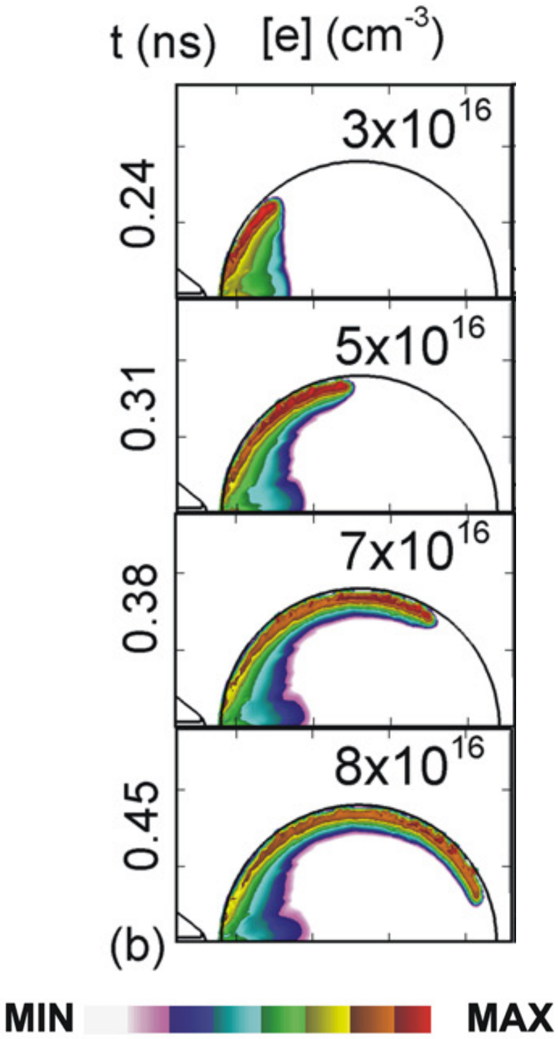
- Planck emission (optical thick plasma)
- Free-free, free-bound and H_2 continuum emission

Burnett et al, JQSRT 71 (2001) 215-223
Simek et al, Plasma Sources Sci. Technol. 26 (2017) 07LT01

Discharge in bubbles: surface discharges



Surface hugging effect increases with ε↑ and σ ↑ (confirmed by modeling)



Babaeva and Kushner J.Phys.D **42**, 13, 132003 (2009)
Bruggeman et al PSST, **18**, 025017 (2009)
Tachibana et al, PSST, **20**, 034005 (2011)

Overview of typical plasma properties

Plasma	T_g (K)	T_e (eV)	n_e (m^{-3})	Radical Densities	UV	Shock Waves
Corona-like in liquid water	1,500–7,000	1–10	10^{21}–10^{25}	+	+	+
Capillary/diaphragm in liquid water	500–3,000	2–10	10^{20}–10^{21}	+	+	(+)
Diffuse glow-like	300–1,000	1–4	10^{16}–10^{19}	+	+	–
Filamentary DBD-like	300–500	2–5	10^{20}–10^{21}	+	++	–
Pulsed corona (gas phase)	300–500	2–10	10^{20}–10^{21}	+	+	–
Spark*	500–5,000	1–3	10^{20}–10^{24}	++	++	+++
MW	500–5,000	1–3	10^{20}–10^{22}	++	++	–
Arcs	3,000–20,000	~1	10^{23}–10^{25}	+++	++++	++++
Plasma jets (cold)	300–600	1–10	10^{17}–10^{21}	+	+	–
Gliding arc	2,500–10,000	1–2	10^{17}–10^{19} (averaged)	++	++	–

- **For most discharges in water – electron density is high!**
- **High density hot plasma typically produce significant UV.**

Bruggeman and Locke, Low Temperature Plasma Technology, 2012

Overview

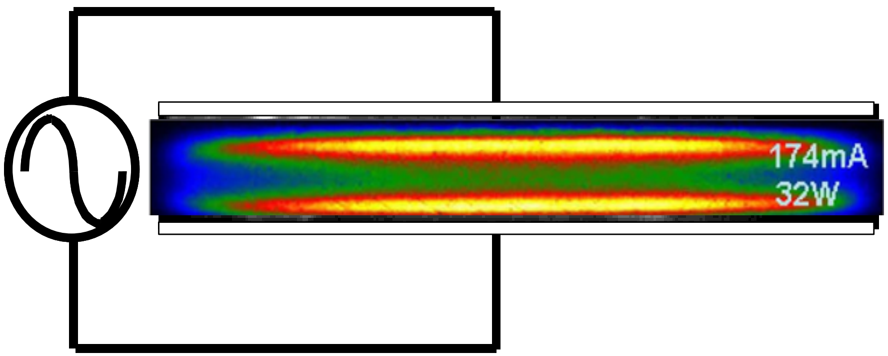
- Introduction
  - Applications and “The unknowns”
- Discharge initiation
- Discharge properties
  - Direct discharges in liquid
  - Discharges in bubbles
- **(Gas phase) H_2O vapor kinetics**
- Plasma-liquid interface and transport
- Liquid phase analyses
- Conclusions

He-H_2O chemistry reaction set

He-H_2O reaction set:

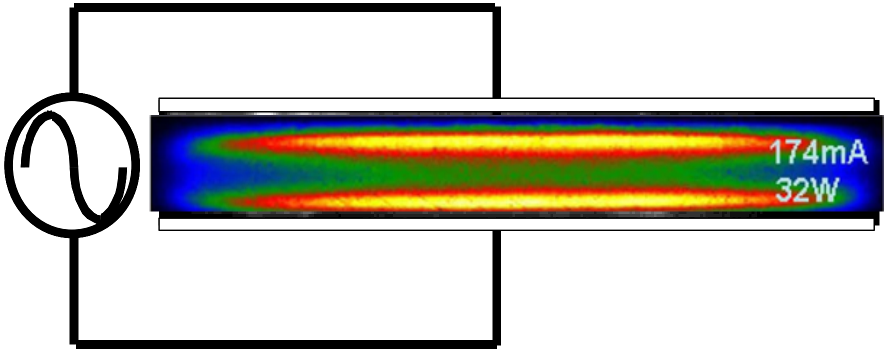
Liu, Bruggeman, Iza, Rong, Kong, Plasma Sources Sci. Technol. 19 (2010) 025018

- 46 species and 577 reactions
- Global model
- Reduced plasma chemistry models (1/10)
- Diffuse RF glow discharge



n_e/n_g	10^{-7}-10^{-8}
T_g	300 - 400 K
T_e	1-3 eV
n_e	10^{17}-10^{18} m^{-3}
gas	He + 0.1-1% H_2O
Freq.	13.56 MHz

Validation of He-H_2O chemistry



EXPERIMENTALLY

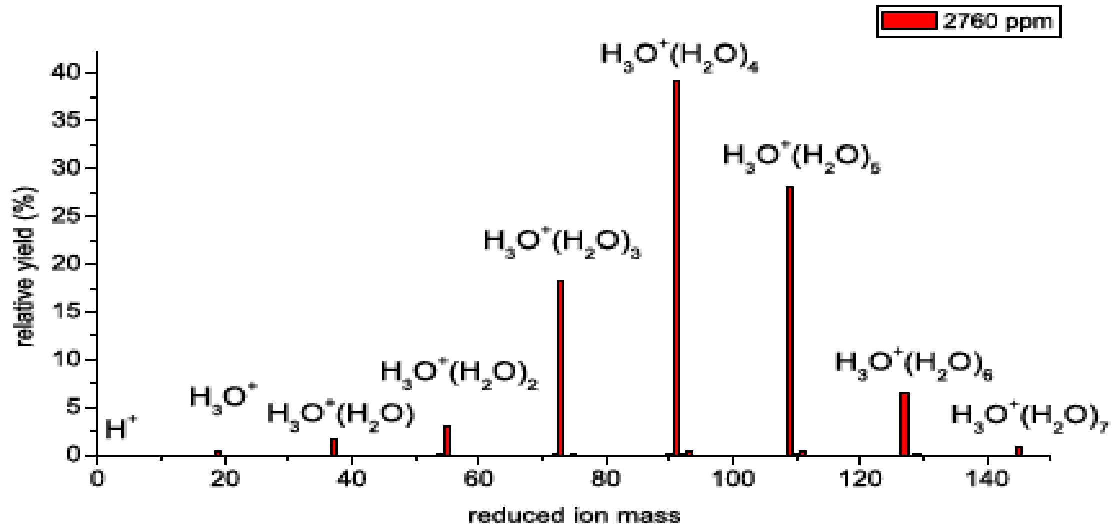
- Plasma dissipated power
- Gas temperature
- OH, H_2O_2 density

Density (cm^{-3})	Experiment	1 D fluid model
$n_{H_2O_2}$	1.3×10^{14}	3.2×10^{14}
n_{OH}	$0.7 - 1.5 \times 10^{14}$	2.2×10^{14}

n_{OH} and N_{H2O2} correspond within accuracy of measurement and reaction rates and experiment

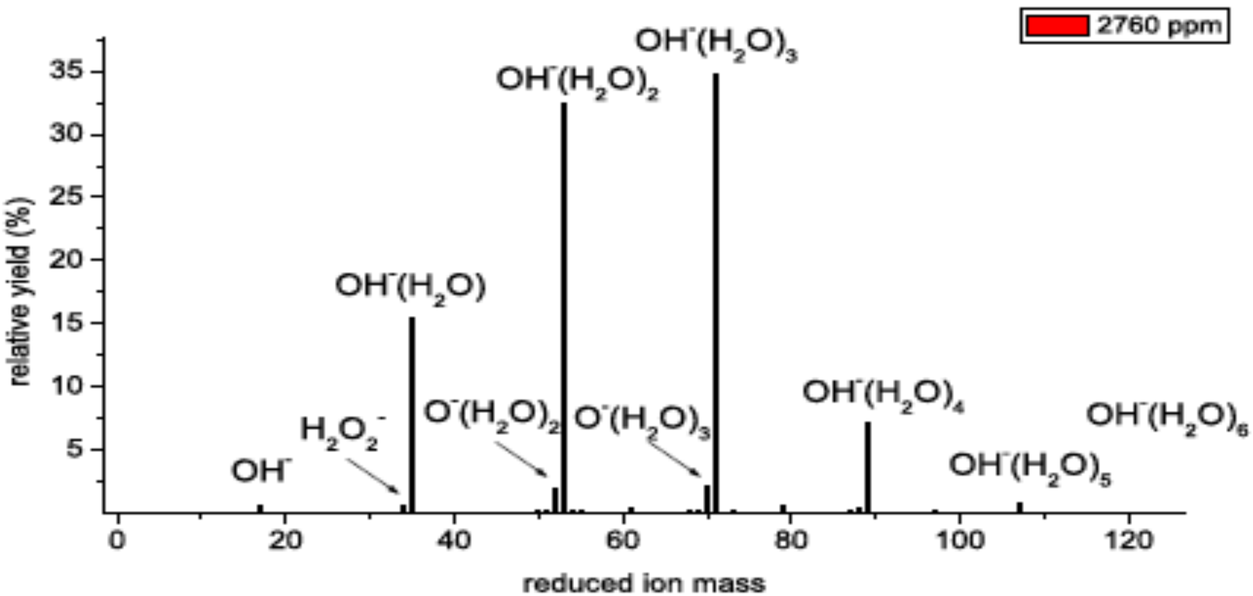
Vasko, Liu, van Veldhuizen, Iza, Bruggeman, PCPP (2014)

Ion hydration



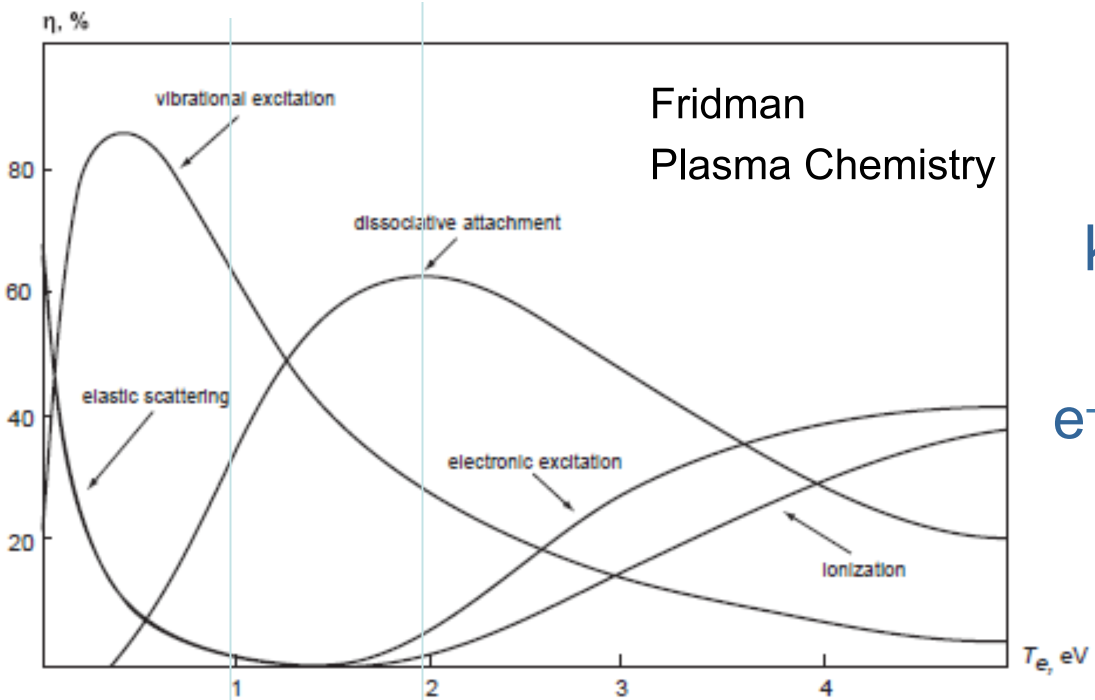
H_3O^+ and clusters!

OH^- and clusters!



Bruggeman, Iza, Lauwers and Aranda Gonzalvo, J.Phys.D 2010 (012003).

Vibrational excitation in water



$H_2O + H_2O^* \rightarrow OH(X) + H$

$k \sim 10^{-20}$ m^3/s (T_v=0.5 eV)

$e^- + H_3O^+ \rightarrow OH(X/A) + H_2 + e$

$k \sim 10^{-13}$ m^3/s

V-T relaxation rate is very high ($k_{VT} \sim 10^{-18}$ m^3/s)

→ vibrational induced dissociation can only be possible when:

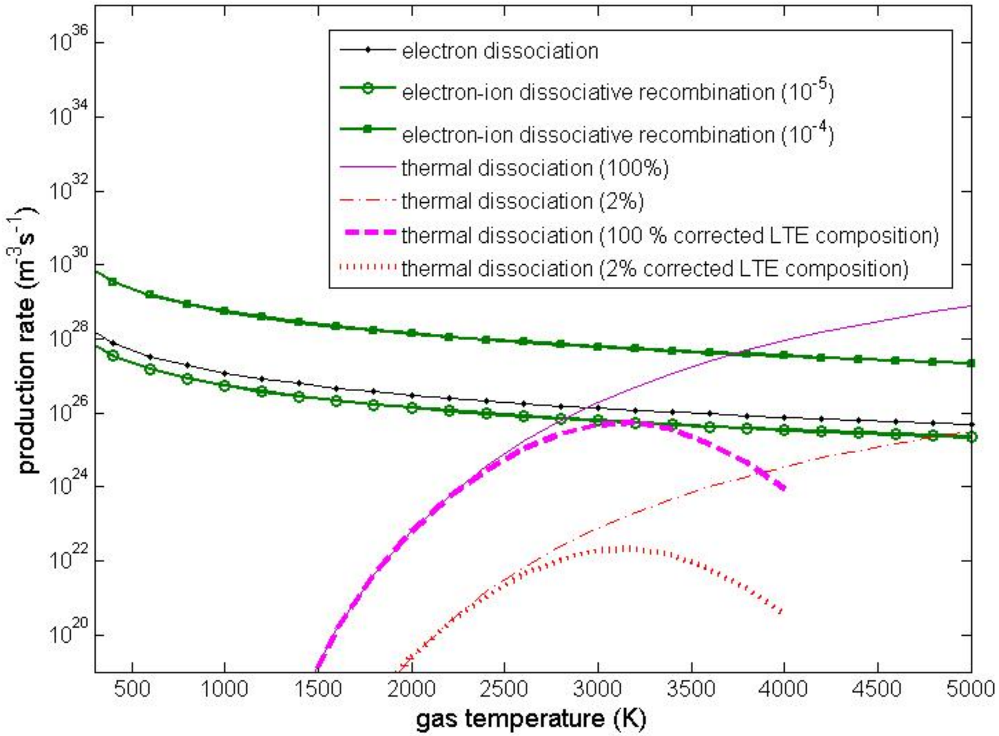
$n_e\, k_{eV}(T_e) > n_g\, k_{VT}(T_g)$ or $n_e/n_g > 10^{-4}$ → DR pathway

→ contributes to delayed gas heating

High density H_2O plasmas: OH formation

- Gas temperature is often overestimated !!!
- Plasmas with large T_g have high ionization degree !
- Dissociative recombination rate is very fast (k ~ 10^{-13} m^3/s)

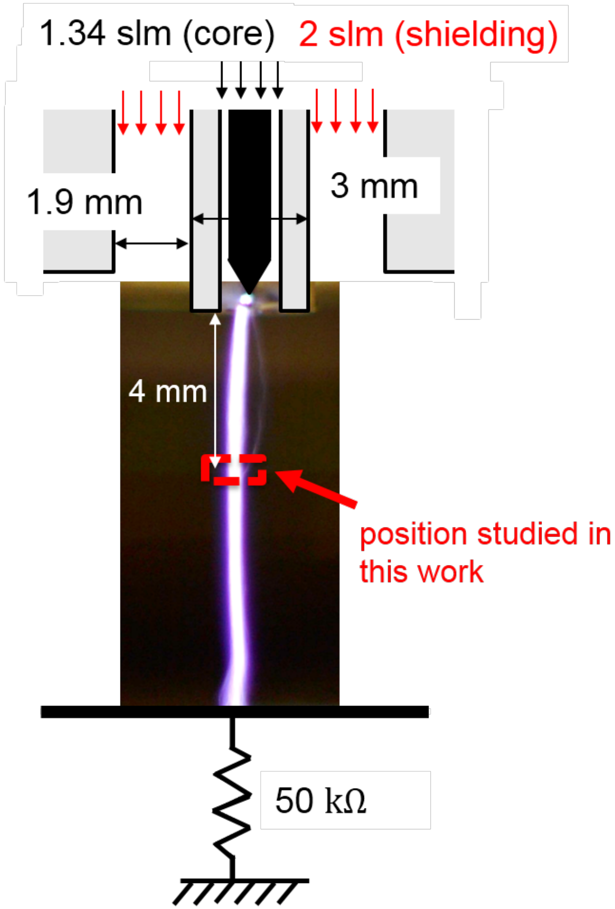
1 exception is perhaps O_2 containing plasmas



In most non-thermal plasmas used in applications thermal dissociation can at most only become as important as dissociative recombination even for T_{gas} > 3000 K

Bruggeman and Schram, PSST 2010 **19** 045025

High n_e density filaments: $Ar\text{-}H_2O$ kinetics



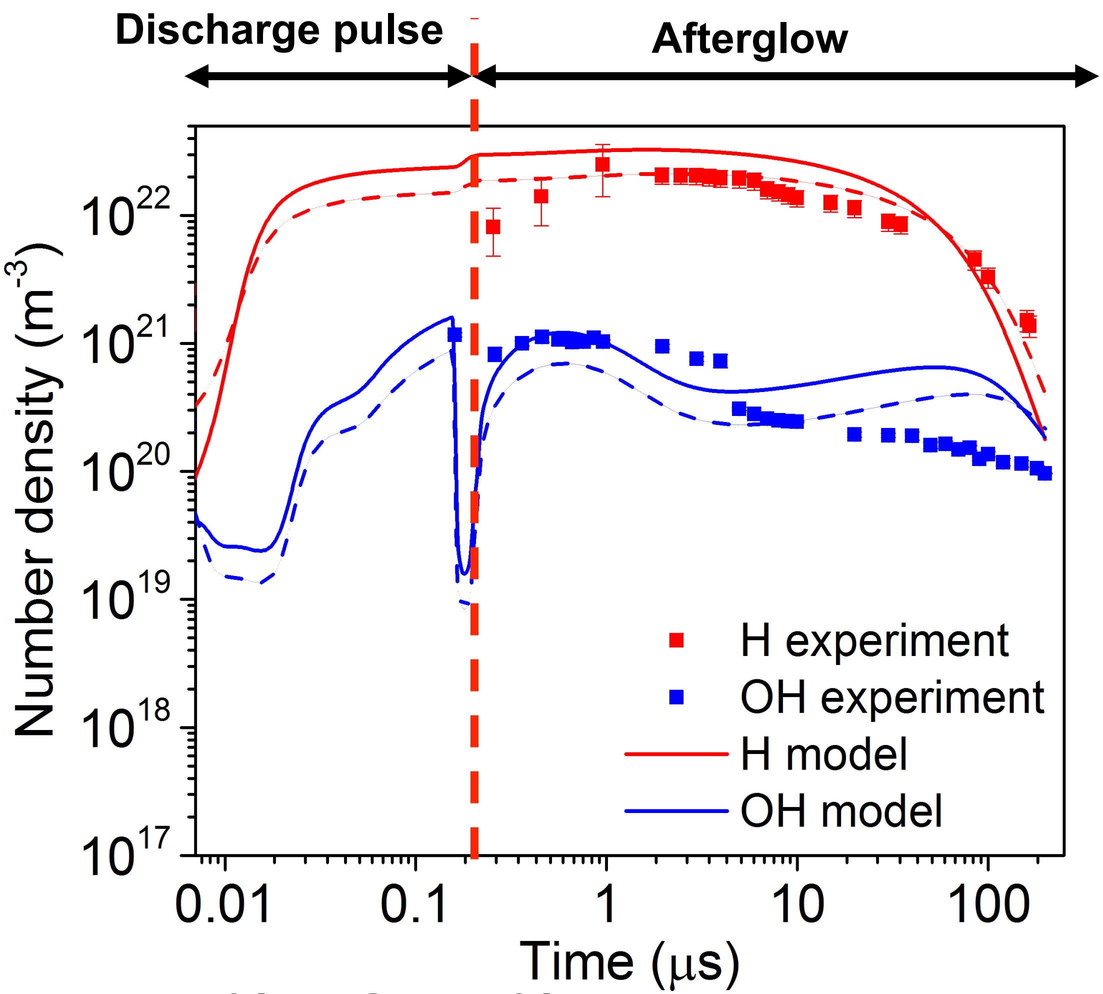
- **Nanosecond pulsed discharge**
- **LIF AND TaLIF for H and OH densities + 0-D kinetics modeling (Global Kin)**

RESEARCH QUESTION:

What is the dominant kinetics and most abundant radicals in high density water containing discharges?

Luo, Lietz, Yatom, Kushner, Bruggeman (submitted)

Validation of 0-D model with H and OH (Ta)LIF



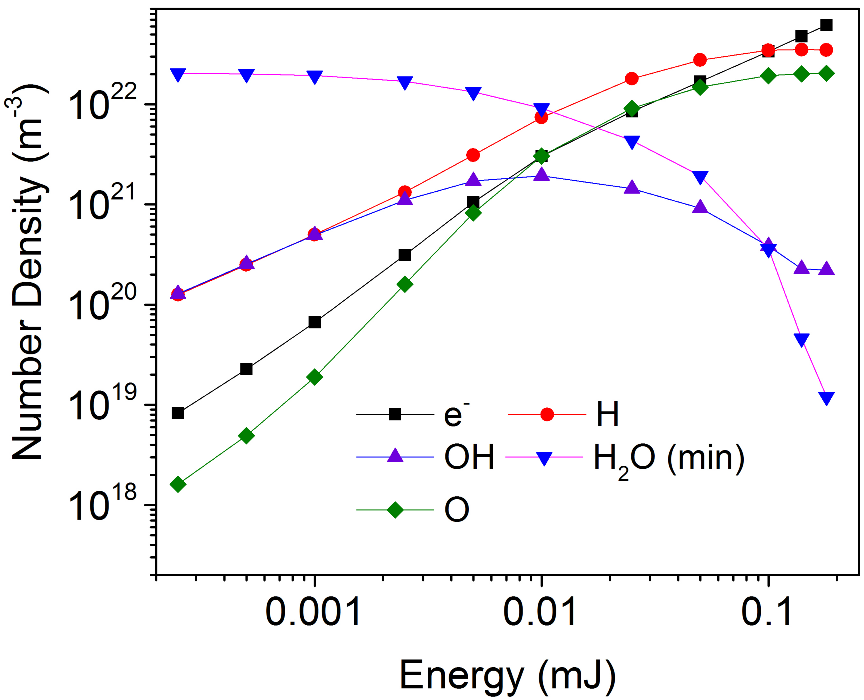
Ar+0.1%H_2O + 1% air

- **Absolute densities predicted well by model**
- **$n_H >> n_{OH}$**
- **High dissociation degree**
- **Measured H and OH densities well represented by model**

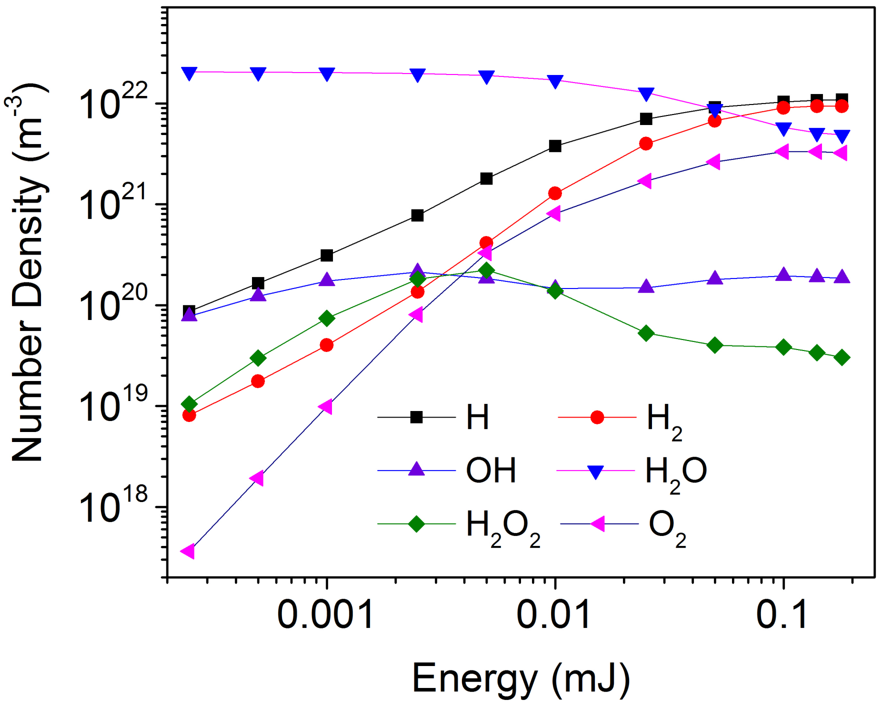
Luo, Lietz, Yatom, Kushner, Bruggeman (submitted)

Effect of energy deposition (Ar + 0.1% H_2O)

Maximum densities



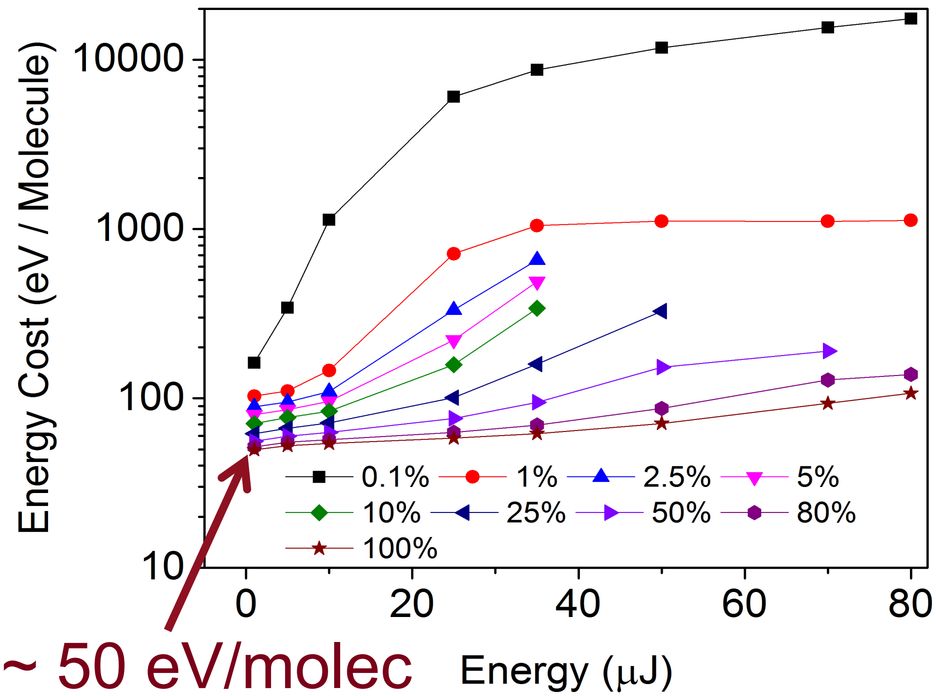
Average densities

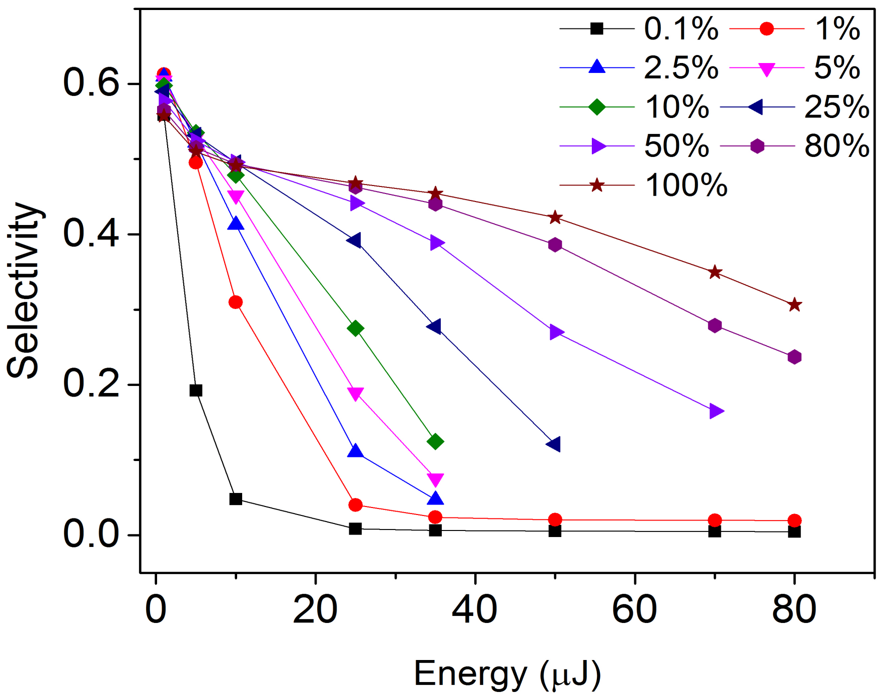


- **At high energies, O and H are dominant radicals**
- **Decomposition at higher energies due:** $e^- + OH \rightarrow e^- + H + O$

Luo, Lietz, Yatom, Kushner, Bruggeman (submitted)

H_2O_2 production in pulsed Ar + xx % H_2O





- **Low energy, pure water nanosecond pulsed discharge is most efficient source of H_2O_2 production.**

- $$\eta_{H_2O_2} = \frac{n_{H_2O_2}}{n_{H_2O_2} + n_{H_2} + n_{O_2}}$$
- **High energy discharge produce H_2, O_2 (and H_2O)!**

H_2O_2 production

	Input	Energy efficiency (g/kWh)
Spark/pulsed corona	Liquid water	0.1-3.64
Discharges in bubbles	Air/ Ar / O_2 in liquid H_2O	0.4-8.4
Gas phase corona / DBD	Air / Ar + water surface	0.04-5
MW	Steam	24
DBD	Humid gas	1.14-1.7
Gliding arc	Water droplets (in Ar)	0.57-80
Electron beam		8.9
Vacuum UV	Vapor or liquid water	13-33
electrolysis		112.4-227.3

$2H_2O \rightarrow H_2O_2 + H_2$

ΔH = 3.2 eV/molec
= 400 g/kWh

80 g/kWh
~ 16 eV/molec

Bruggeman and Locke, Assessment of potential applications of plasma with water, Low temperature plasma technology methods and applications Eds Chu and Lu

Why are discharges in liquids ineffective?

Remember: phenol decomposition efficiency:
Gas phase streamer > > streamer-like liquid

Losses	Liquid discharge	Gas phase discharge
Evaporation	Major	Minimal
Transport	Minimal	Major (interfacial recombination)
Radical-radical recombination	Major	Minimal (low energy loss)

- Energy density is too large in liquid discharges leading to larger radical densities.
- Control of liquid discharge is less straightforward as dynamics is on sub-nanosecond time scale while in gas phase ~ 100ns

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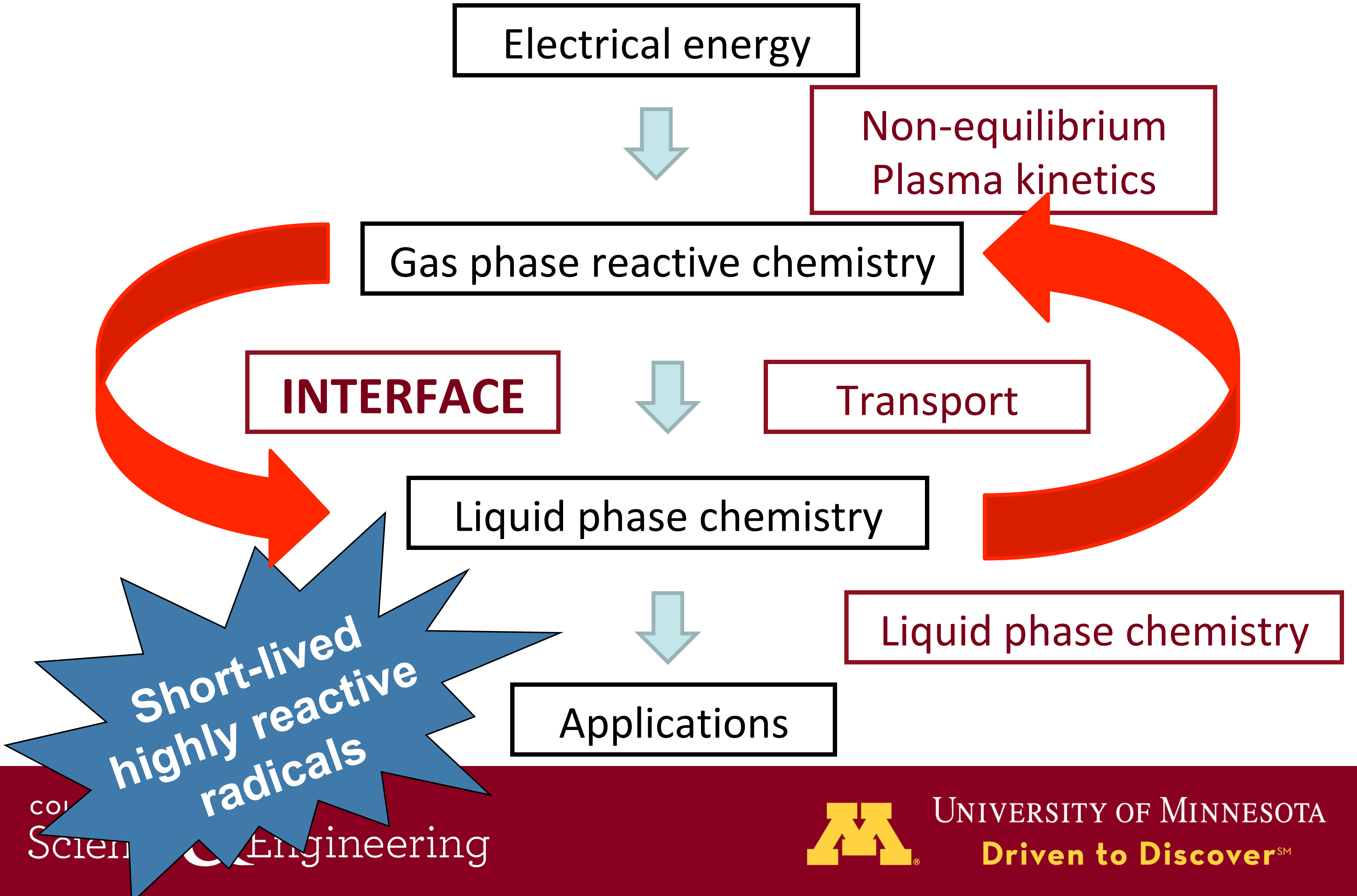
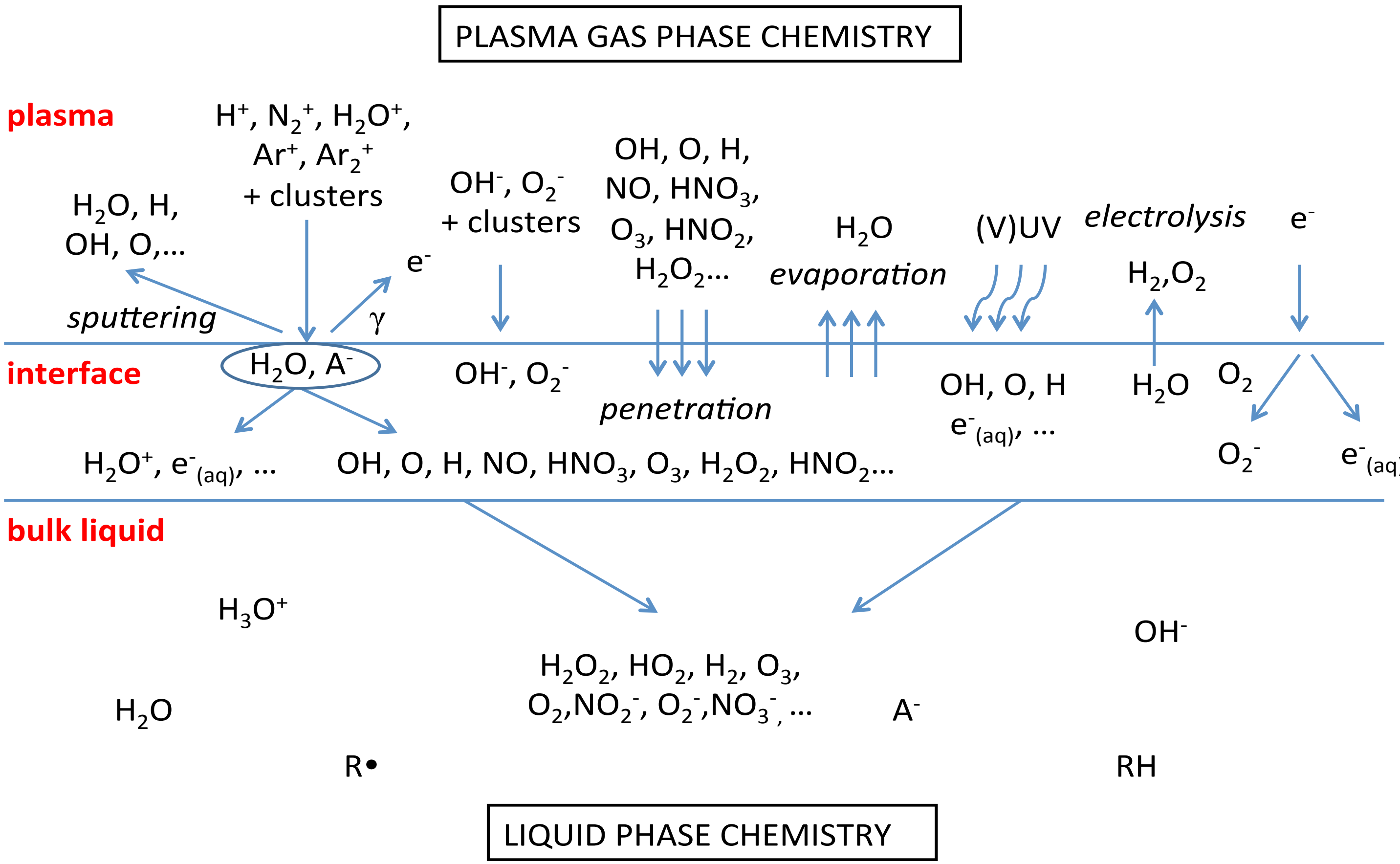
- Liquid phase analyses
- Conclusions

Plasma-liquid interactions (1)

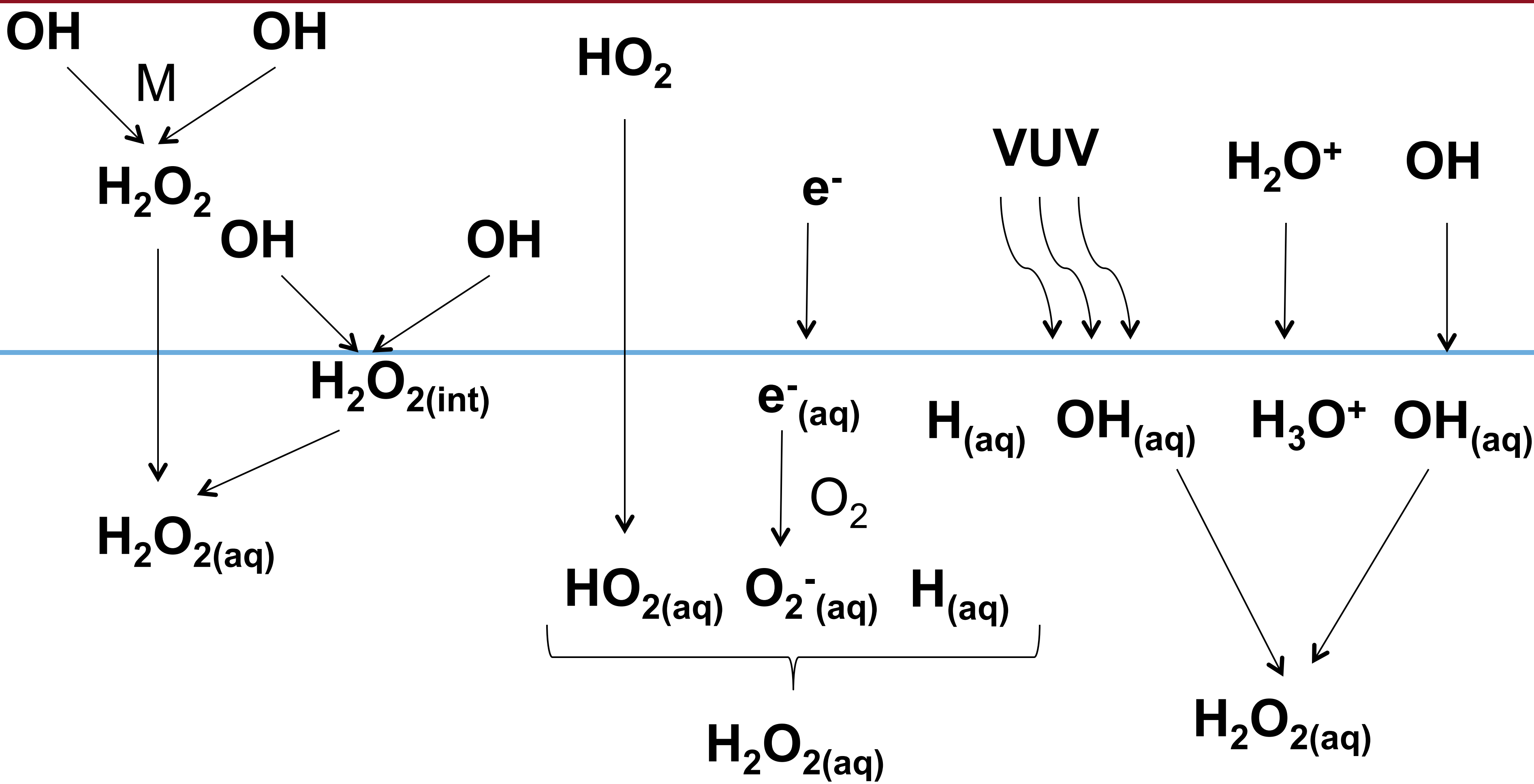


Plasma-liquid interactions (2)



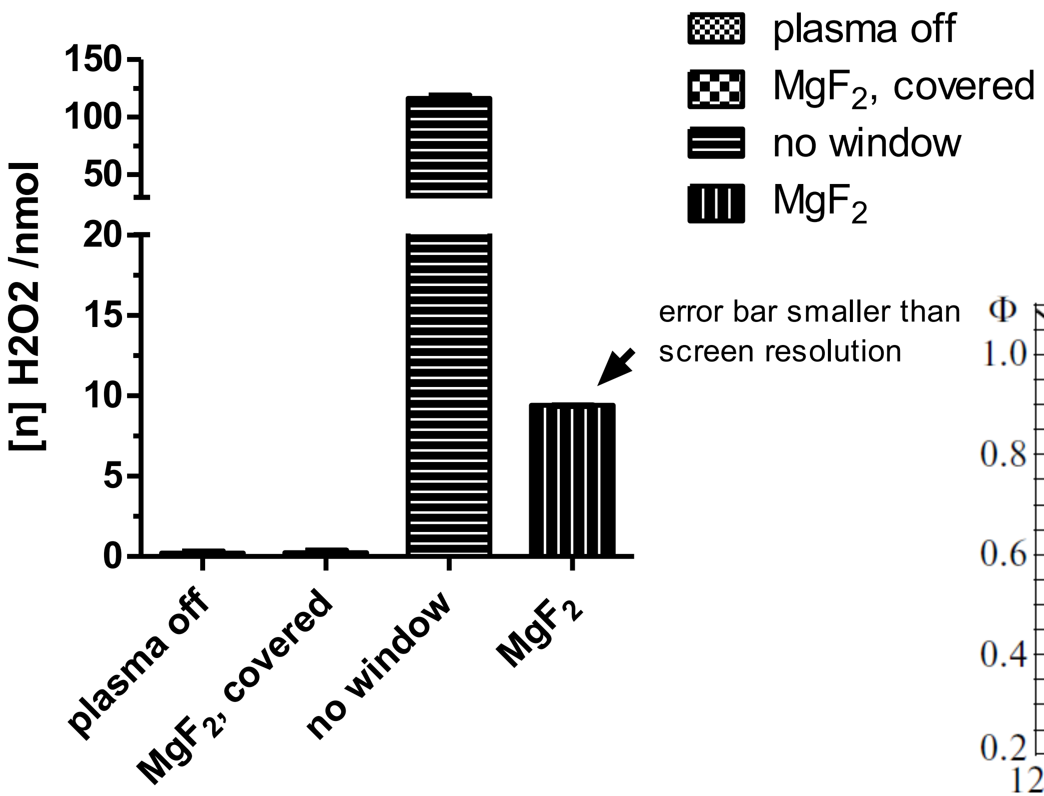
P. Bruggeman et al PSST 2016

Example H_2O_2 production ….



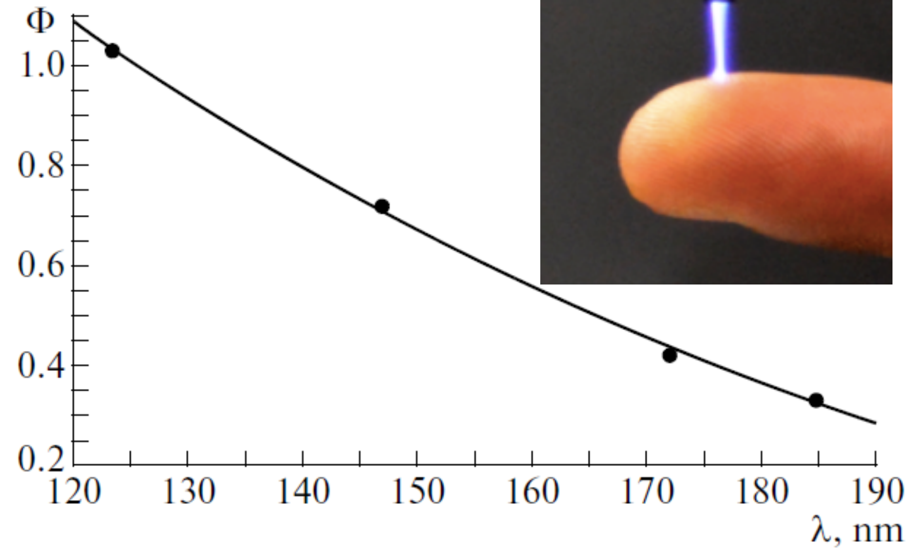
Many different pathways – interfacial reactions !!!

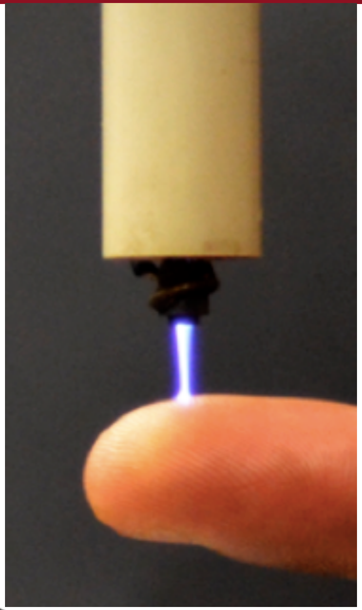
Production of H_2O_2 by excimer radiation



Wende et al (unpublished)

Ar plasma jet



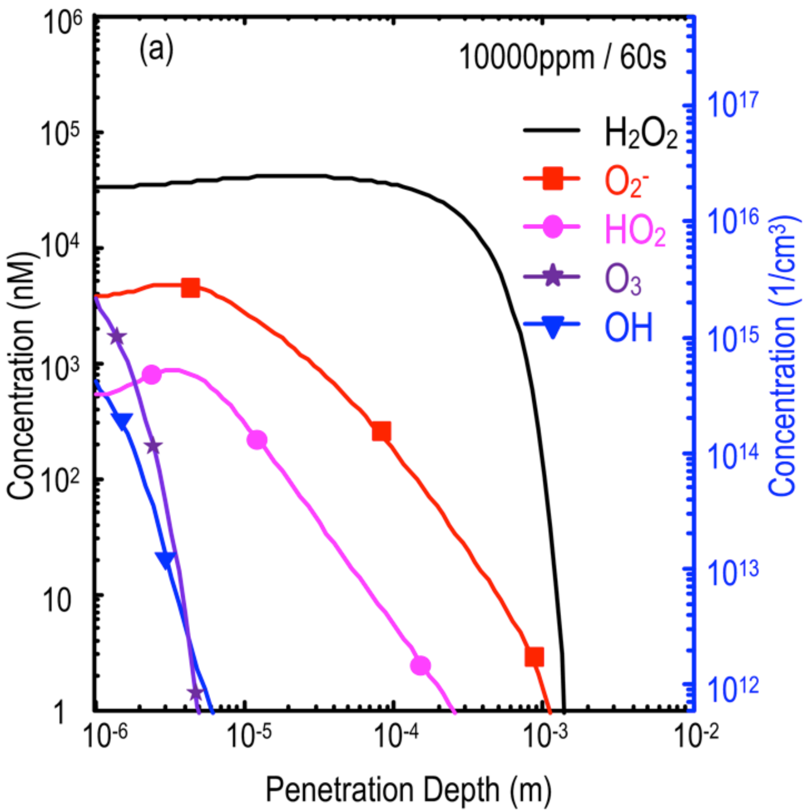


Heit et al, 1998

Significant amount of H_2O_2 produced by Ar excimer radiation (125 nm)

Wende, Bruggeman et al

Surface and bulk OH radicals



Chen et al (2014) *Plasma Chem. Plasma Process.* **34**: 403 – 441.

- OH lifetime ~ few µs
- Penetration depth < 100 µm (Not enhanced by convection)
- Bulk OH production:
  - Fenton`s reaction:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH\cdot$$

  - Ozone decomposition:

$$2\,O_3 + H_2O \xrightarrow{OH^-} OH\cdot + O_2 + HO_2\cdot$$

  - UV decomposition

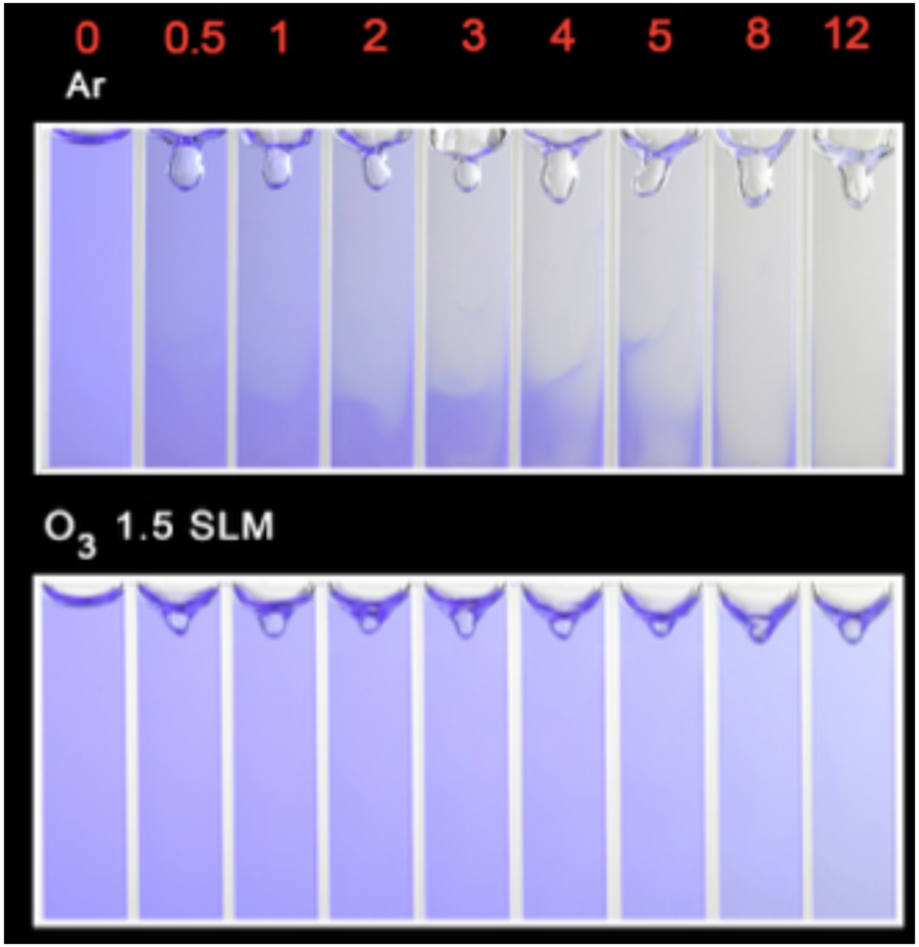
$$H_2O_2 + h\nu \rightarrow 2\,OH\cdot.$$

$$O_3 + h\nu \rightarrow O_2 + O(^1D)$$

$$O(^1D) + H_2O \rightarrow 2\,OH\cdot$$

Crystal violet – spatial decolorization

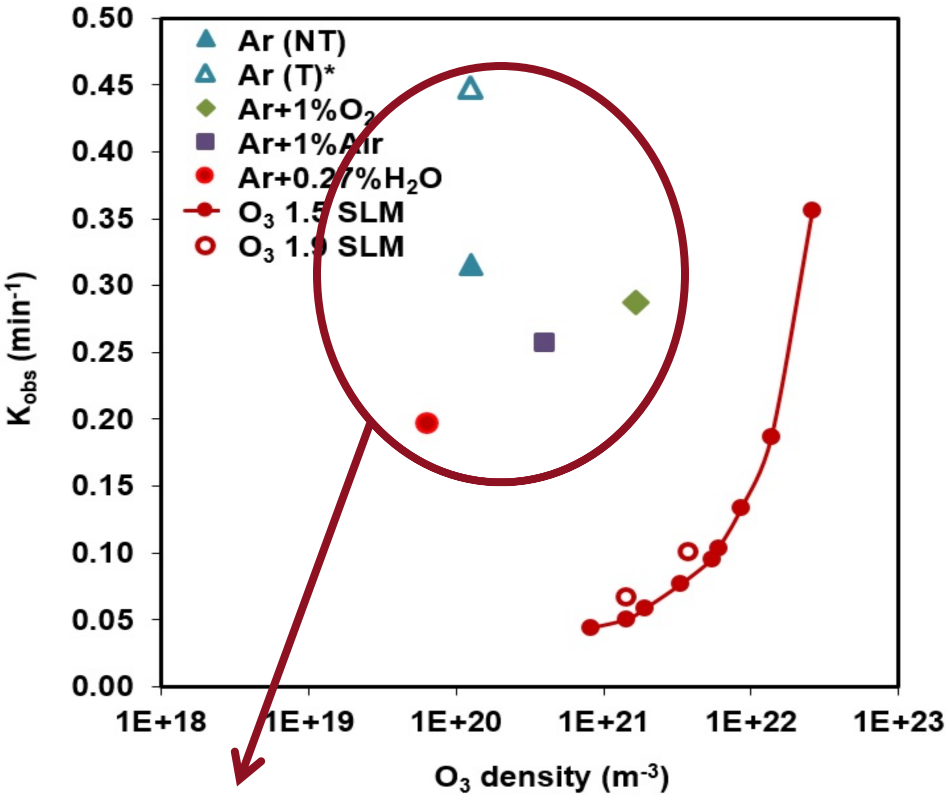
Time (minutes)



- O_3-induced decolorization occurs homogeneously suggesting O_3 is transported through complete solution
- Plasma-induced decolorization of CV is strongly inhomogeneous suggesting short-lived species
- Convection of dye is important

Taghvaei, Kondeti et al (in preparation)

Crystal violet - decomposition rate



Observed crystal violet decomposition rate: 0.2 -0.45 min^{-1}

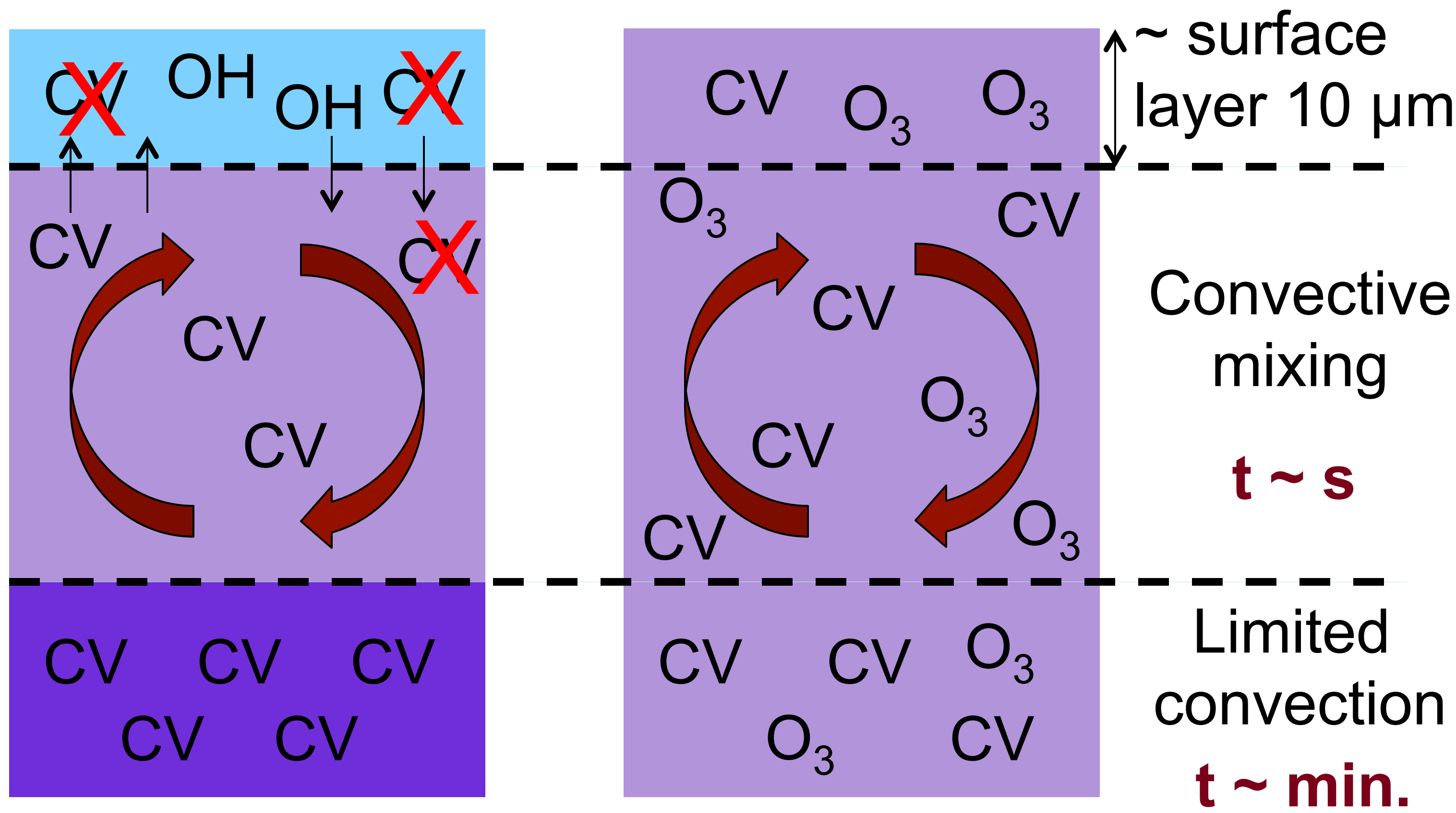
- $K_{obs,touching}$ within 50 % of $K_{obs\ non\text{-}touching}$ while orders of magnitude different radical fluxes!
- K_{ob}^{-1} ~ 100 - 300 s similar to time it takes to make one full vortex filling the upper 1/3 of the cuvette yielding (~ 30-120 s)
- **Reactivity is highly transport limited**

Taghvaei, Kondeti et al (in preparation)

Crystal violet - mechanism

decomposition CV by high OH concentration

t_{OH} ~ ns
t_{O3} ~ min.



convection is of key importance for both O_3 and OH induced reactions (however different mechanism!)

Spark more effective than streamer discharge

- Phenol decomposition: $\eta_{streamer} << \eta_{spark}$
- E coli inactivation in H_2O

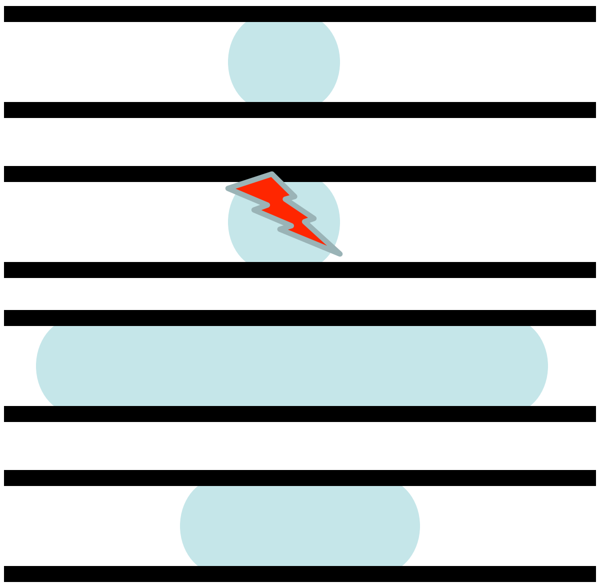
Plasma	D-value* (J/ml)	Liquid conductivity (mS/cm)	Initial bacterial density (CFU/ml)
Pulsed arc in water	18.7		10^7
DBD in air (bubbling)	0.29		
Pulsed corona in water	18- 45	0.1	10^6-10^7
Capillary discharge in water	5.4	0.9 NaCl in H_2O	10^7
PEF	<5	13	10^5
Streamers in air bubbles	13		10^5-10^6
Pulsed corona in air	0.1	0.9	10^7-10^8
Spark discharges in water	0.1-0.4	0.2	10^4-10^6

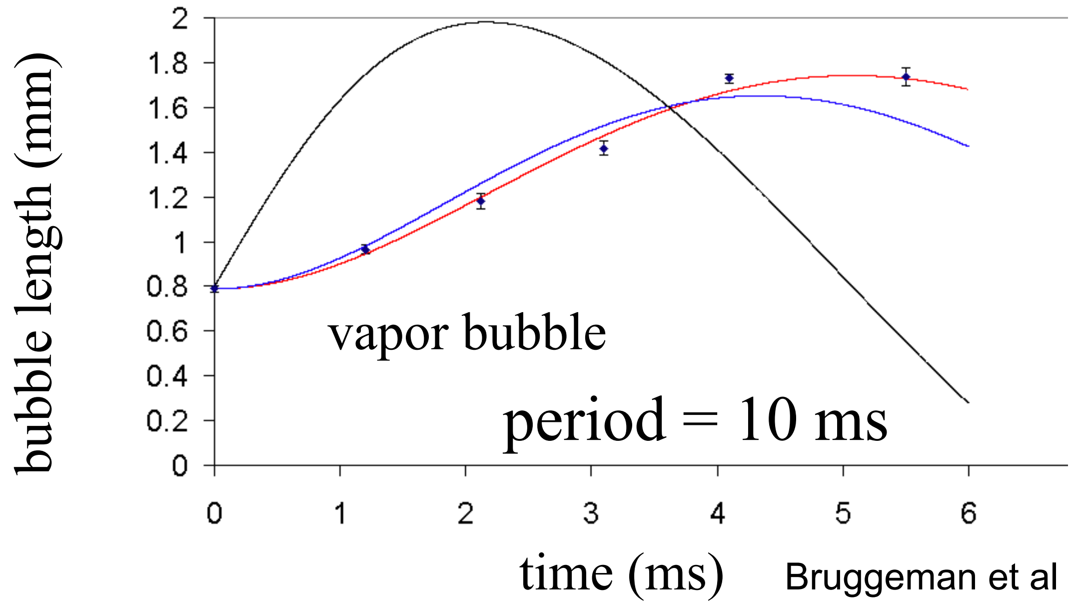
Why?

- Stronger UV
- Shock waves (+ enhancement transport)

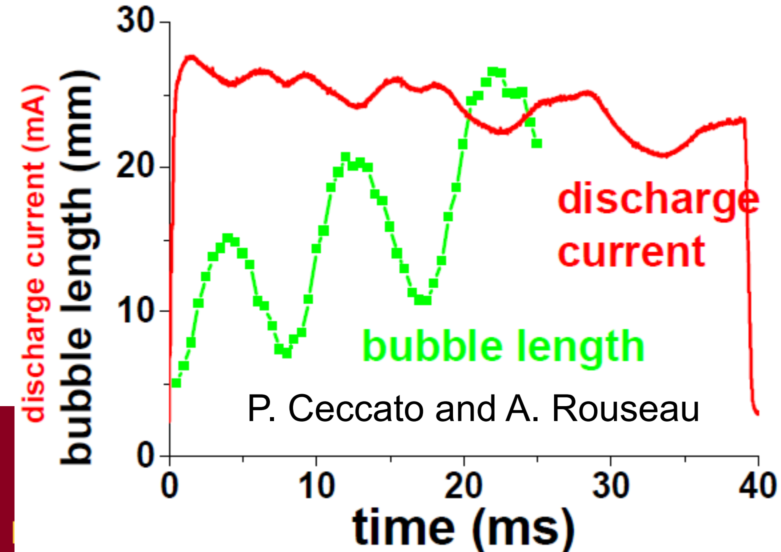
Bruggeman and Locke, Assessment of potential applications of plasma with water, in Low temperature plasma technology methods and applications Eds Chu and Lu

Bubble dynamics (1)





- simulation: $\Delta p \sim 1.5\text{-}1.7$ bar
- $T_{gas,\,max}$ = 550-650 K, $T_{filament} \sim 2000$ K
- effect of evaporation (growth)



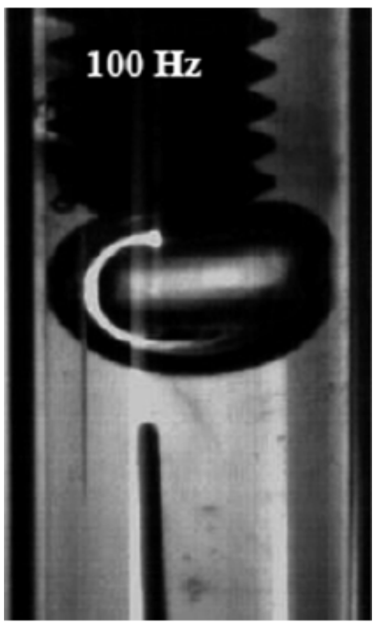
Bubble dynamics (2)

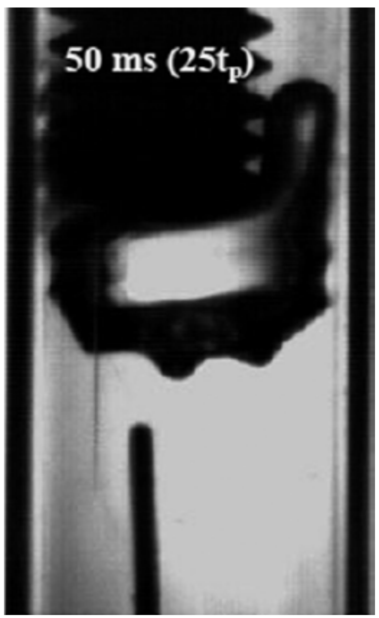
Droplet ejection, break up and surface waves

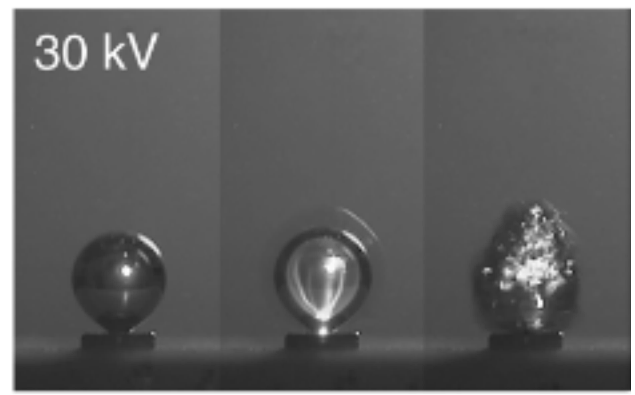
15 kV

Electrical induced (Kelvin`s equation)

$$\omega^2 = \frac{\sigma k^3}{\rho} + gk - \frac{\varepsilon_0 E^2 k^2}{\rho}$$



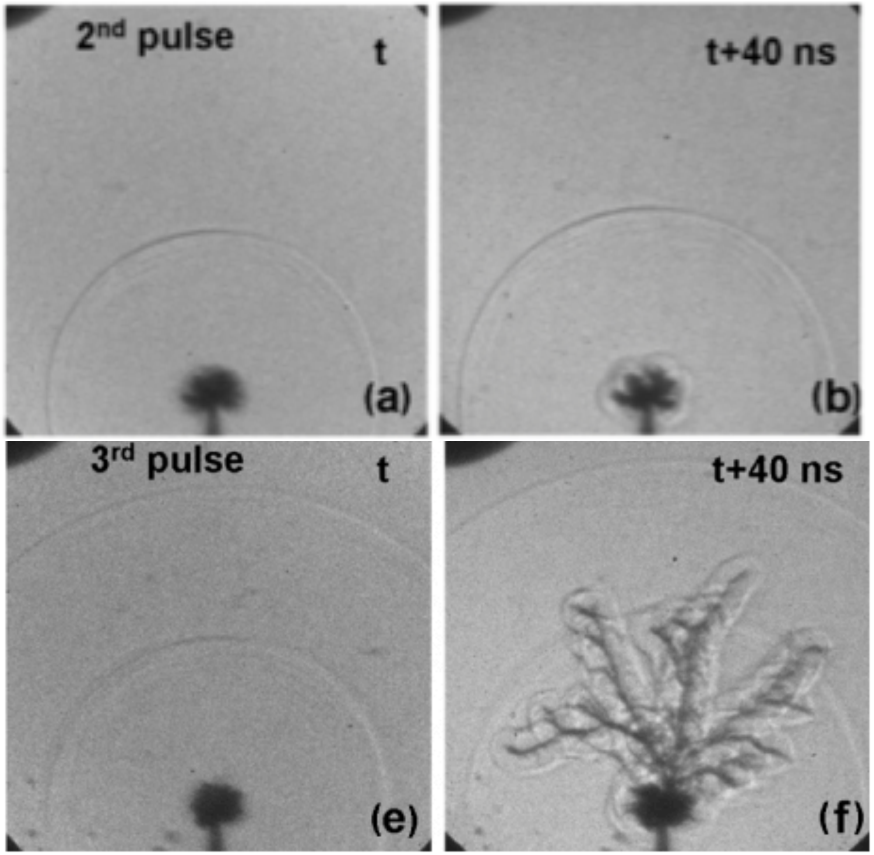


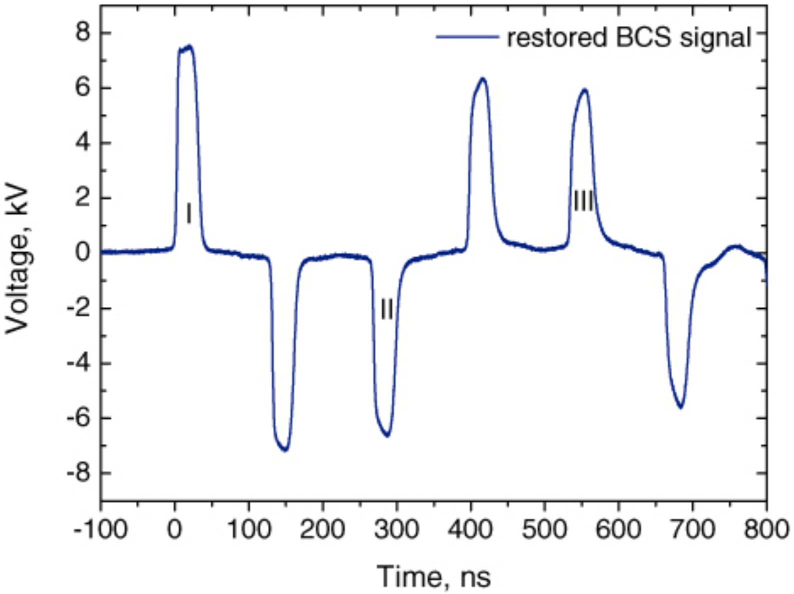


Sommers et al JPD 44 (2011) 082001
Tachibana et al, PSST, 20 (2011) 034005

Direct liquid discharges

Nanosecond pulse with reflections



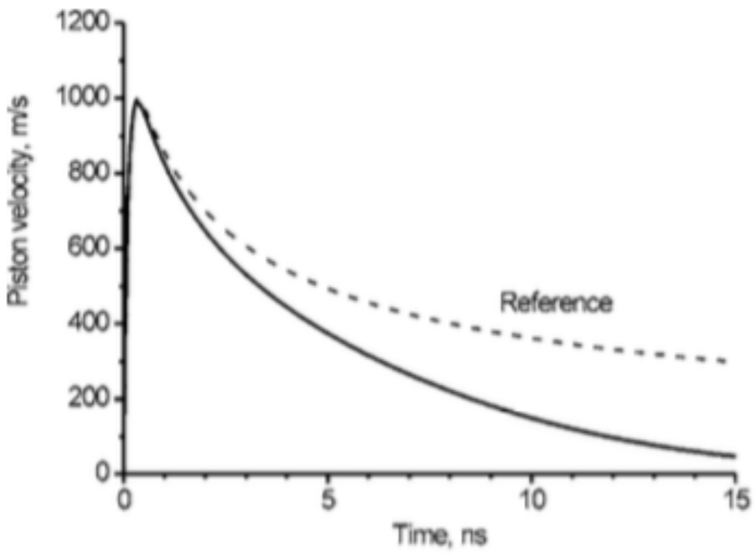


- Shock wave due to large energy injection near electrode
- Shock wave generated by plasma filaments formed in water

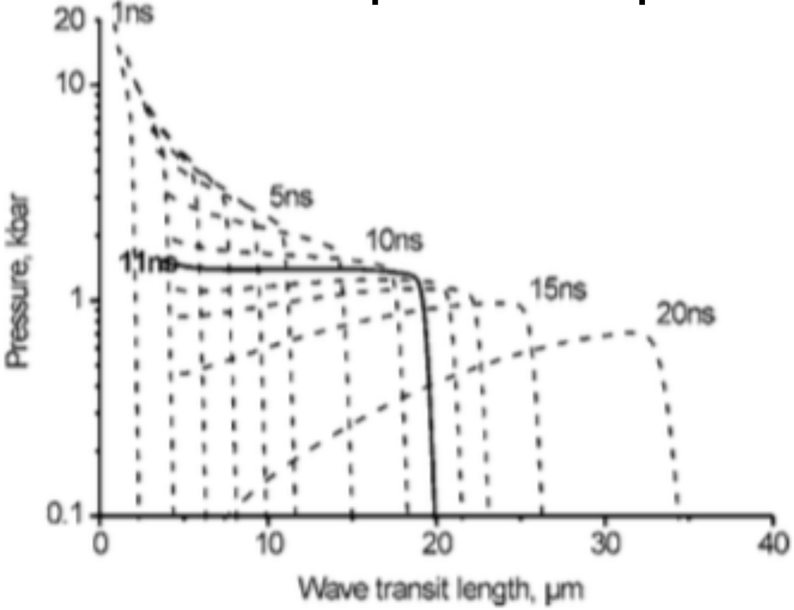
Marinov et al 2013 J. Phys. D: Appl. Phys. 46 464013

Direct liquid discharges

Expansion velocity streamer



Calculated pressure profile



- Mach-Zehnder interferometry and Schlieren imaging
- Pressures up to 2 GPa (short 2-3 ns)
- stepwise propagation (polarity dependent) and re-illuminations

An et al 2007 JAP, 1010, 053302

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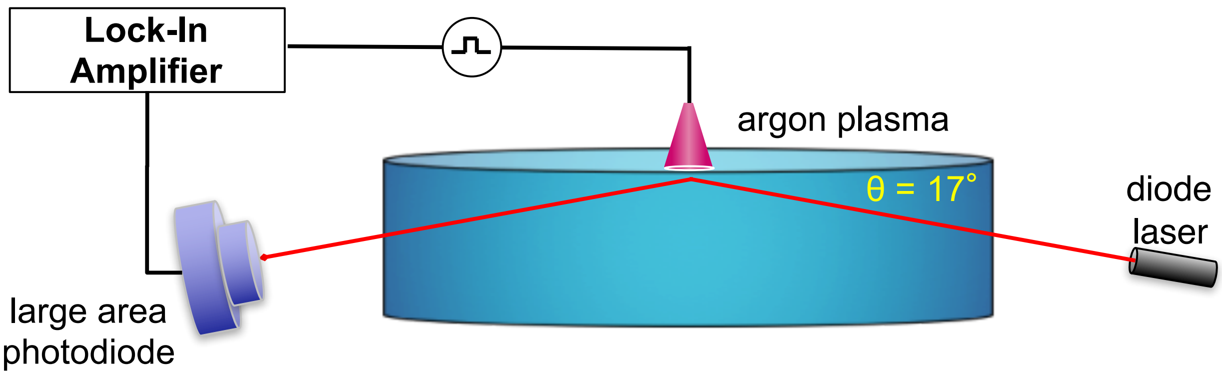
- **Liquid phase chemistry**
- Conclusions

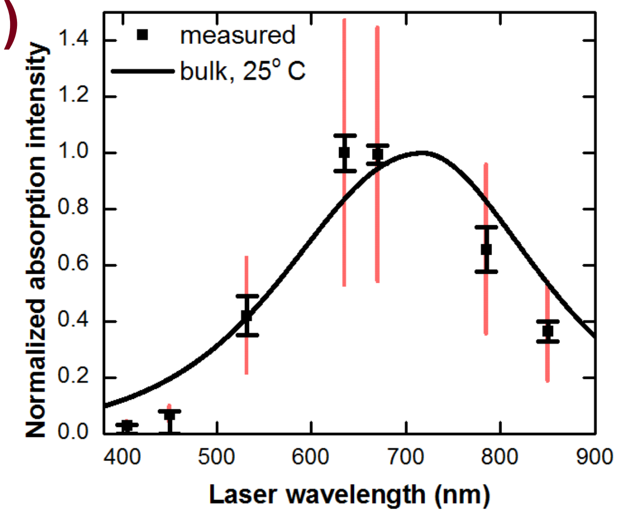
Liquid phase analysis: *challenging!*

"Established methods (of detection of radical species in liquids) often lack the required selectivity or sensitivity or cannot be performed *in situ* with a sufficient spatial or temporal resolution."

2017 Plasma Roadmap (Diagnostics section)

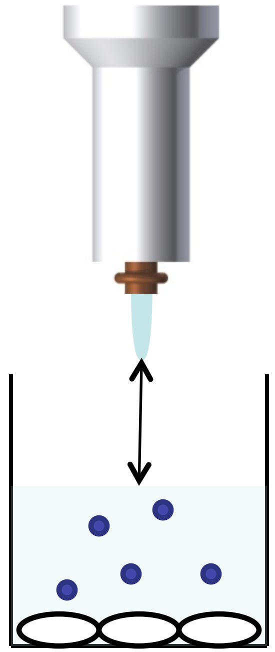
Many methods are indirect measurements but there are exceptions (example solvated electrons)





Rumbach et al., *Nature Comm.* **6**, 7248 (2015)

Example – plasma-liquid interaction

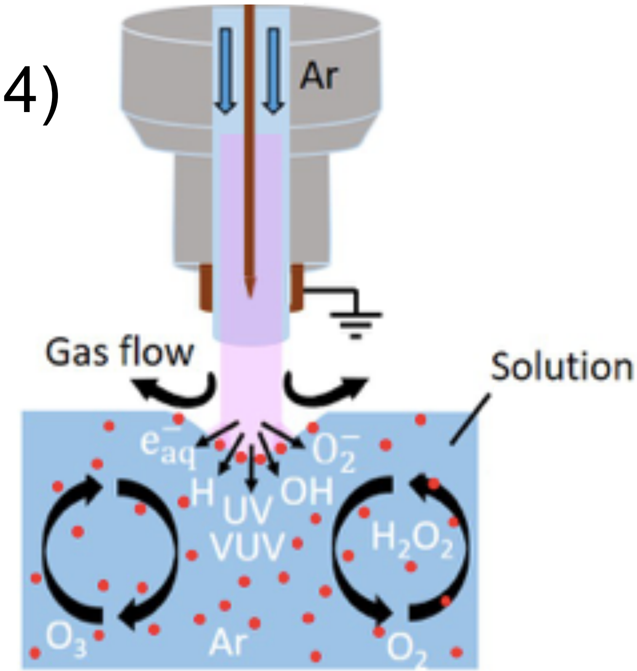


Power = 2.5 W

Pseudomona Aeruginosa (P14)

V = 200 μl

Hofman et al PSST 2011
van Gessel, APL 2013, JPD 2013
Zhang et al JPD 2013, PSST 2014

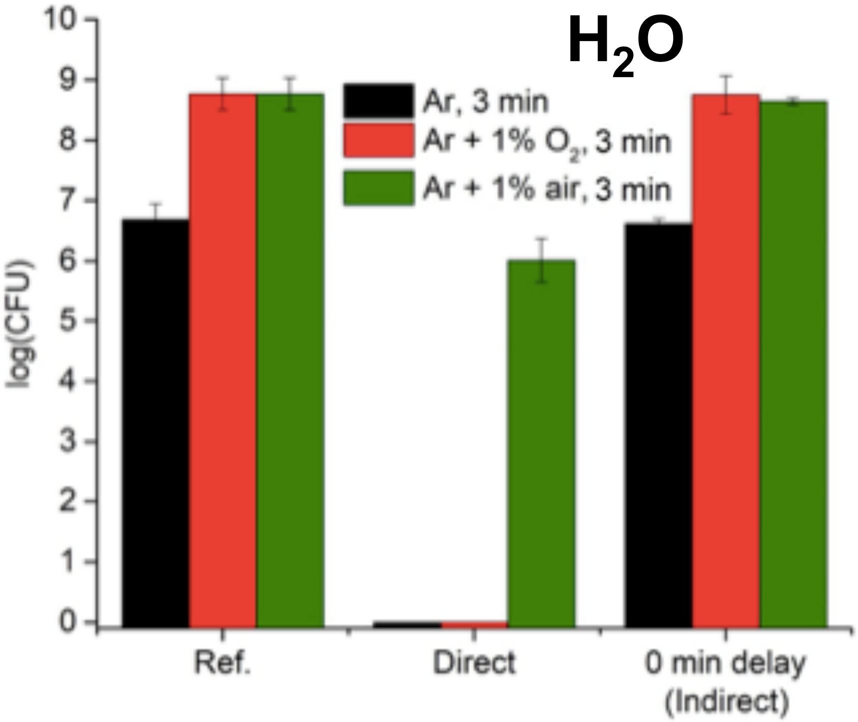


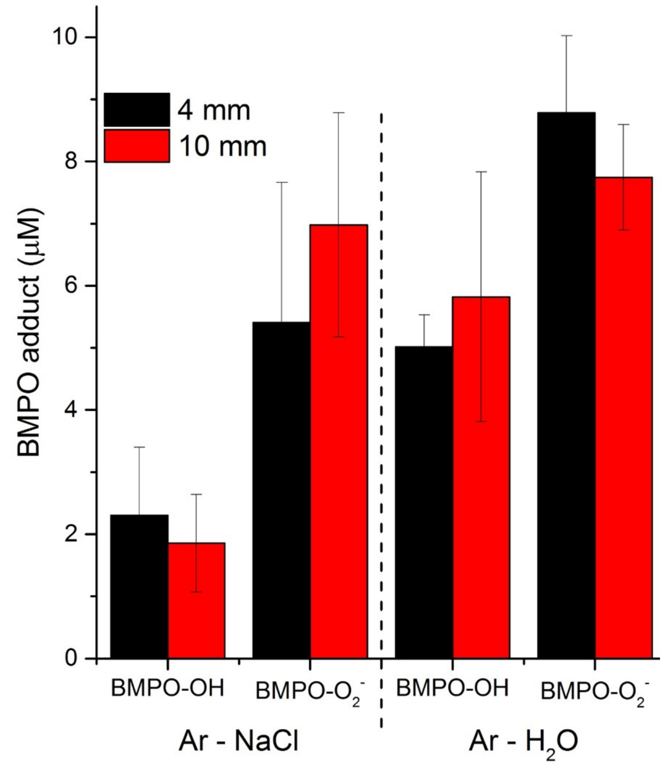
P= 2.5 W
T_e = 1-3 eV
$n_e = 10^{19}\text{-}10^{18}\ m^{-3}$
UV < 2.9mW
$n_{O,max} = 10^{22}\ m^{-3}$

Inactivation only occurs for Ar plasma in contact with the solution suggestion short-lived species induced inactivation

Kondeti et al., *Free Radical Biology and Medicine.* **124**, 275-287 (2018)

Role of short-lived species

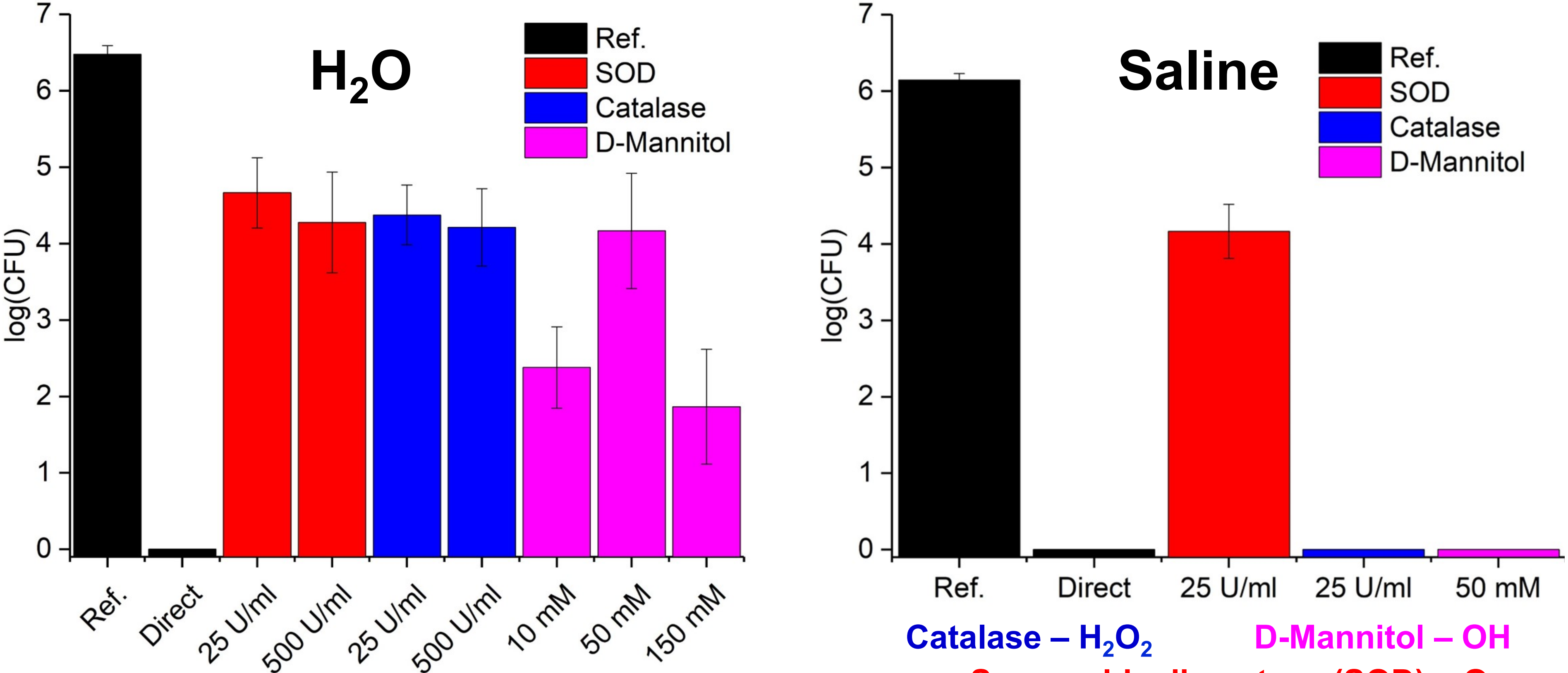




- Only direct treatment inactivates
- Presence of OH, O_2^- in the solution confirmed by ESR.

Kondeti et al., *Free Radical Biology and Medicine.* **124**, 275-287 (2018)

Scavengers: Ar plasma – H_2O vs saline



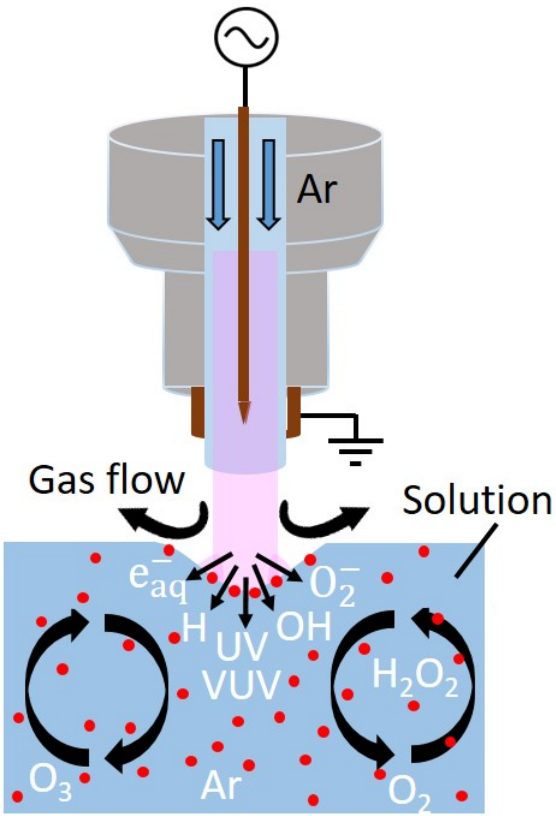
Catalase – H_2O_2　**D-Mannitol – OH**

Superoxide dismutase (SOD) – O_2^-

- O_2^- plays a role in the inactivation in saline.
- Both OH and O_2^- effect in H_2O (OH reacts with Cl^- → Cl^- is a scavenger for OH).

Kondeti et al., *Free Radical Biology and Medicine.* **124**, 275-287 (2018)

Summary of plasma bacteria inactivation



- **Convection important in inactivation of (planktonic) bacteria.**
- **Role of OH and O_2^-**
  - **O_2^- formed by e^- attachment to dissolved O_2.**
  - **OH – transfer of gas phase species to liquid or interfacial generation)**
- **Significant effect of solution on inactivation (NaCl)**

Kondeti et al., *Free Radical Biology and Medicine.* **124**, 275-287 (2018)

Scavengers are never completely selective

Table 2. Reaction rates of L-histidine with some major components produced by the plasma [230].

Reacting species	Reaction rate ($M^{-1}s^{-1}$)
$^1O_2^*$	$3.2–9 \times 10^7$
$e^-_{(aq)}$	6×10^7
$^{\bullet}OH$	4.8×10^9
O_3	3.9×10^3
$O_2^{\bullet -}$	<1
$H^{\bullet}$	2.3×10^8
$HO_2^{\bullet}$	$<2.3 \times 10^8$

- Example of L-histidine (considered scavenger of $^1O_2^*$)
- Effects of transport and concentration gradients can be important (similar for spin traps used in EPR, colorimetric probes etc.).

Bruggeman et al 2016 Plasma Sources Sci. Technol. 25 053002

Overview

- Introduction
  - Applications and “The unknowns”
- Discharge initiation
- Discharge properties
  - Direct discharges in liquid
  - Discharges in bubbles
- Gas phase H_2O vapor kinetics
- Plasma-liquid interface and transport
- Liquid phase chemistry
- **Conclusions**

Conclusions (1)

- Major advances in the last 10 years, particularly in modeling, provided us with an increased but still **incomplete understanding** of discharges in liquids and bubbles.

- **Challenges** preventing a full understanding of breakdown in liquids relate to
  - Limited diagnostics (Schlieren, interferometry, emission)
  - Sub ns time scales – stochastic nature
  - Key processes occur on sub-micrometer length scale
  - Lack of highly controlled experiments (pure liquids,...)
  - Model limitations
  - Lack of general theory and ‘dense gas approximation’

Conclusions (2)

- The plasma-liquid interface has **unique chemical and physical conditions** that provide **many interesting scientific questions** with a direct benefit for society.
- **Controlling plasma processes** might be more about (interfacial) **transport** than optimizing plasma kinetics.
- How do you probe an interfacial plasma-liquid layer of a few μm **time and spatially resolved**?
- **Models with a two-way coupling of plasma kinetics in multi-phase plasmas**, including evaporation, charging, deformation, liquid interface dynamics and liquid phase convection have yet to be fully developed.