Physics of Low Temperature/Non-Equilibrium Plasmas

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June 22nd 2022, SULI Introduction to Fusion Energy and Plasma Physics Course

UNIVERSITY OF MINNESOTA
Driven to Discover®

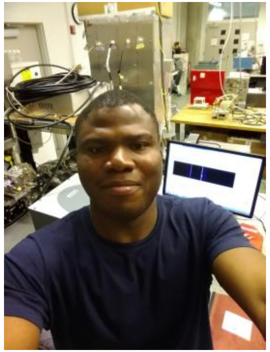
About me

Yaoundé, Cameroon: Up to end of high school

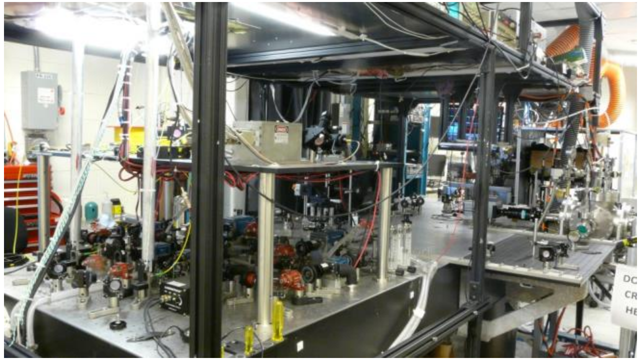
France (Troyes and Paris): Undergrad and Grad Studies

THE Ohio State University: Postdoc

University of Minnesota: Research Associate



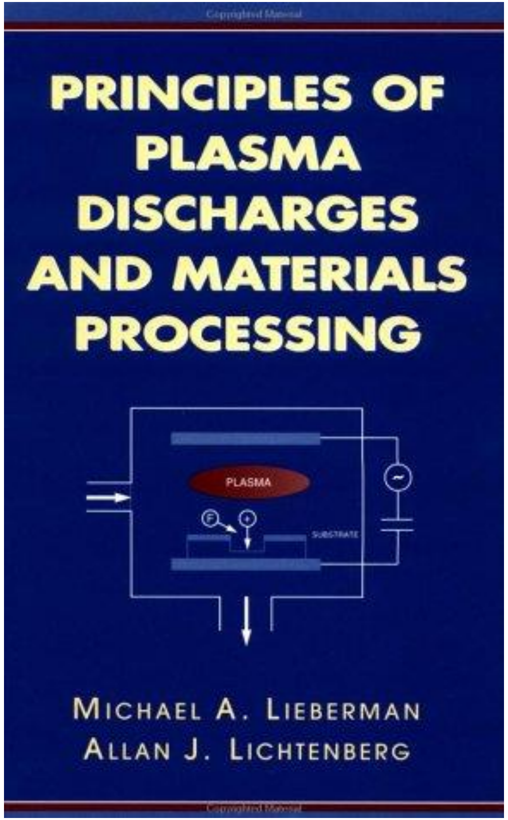
PPPL: Associate Research Physicist

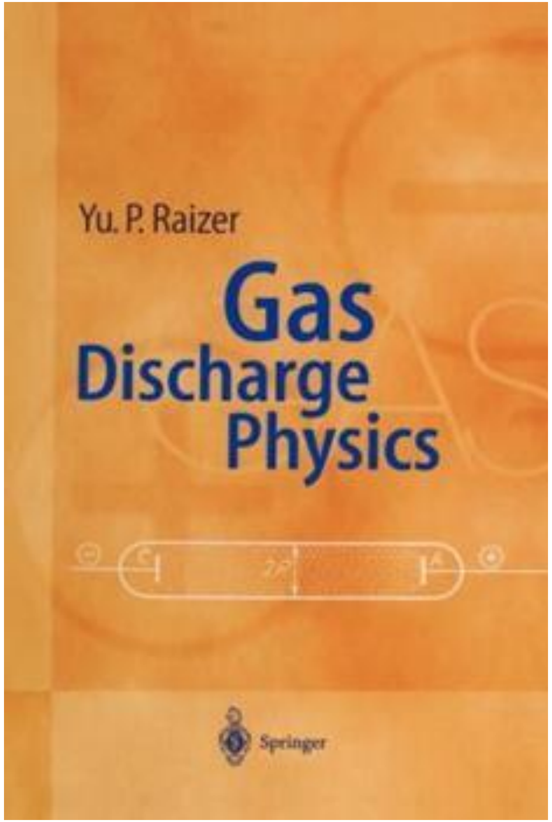


What time is it? *Game time!!*

- **I am a huge fan of team sports, especially basketball and football (soccer in the US)**
- **I believe there are many similarities between how scientists and athletes prepare/operate**
- **Living on 3 continents, I have a strong interest in history of civilizations and cultures, as well as history of science**

Some Good References





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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

I Adamovich[1], S D Baalrud[2], A Bogaerts[3], P J Bruggeman[4], M Cappelli[5], V Colombo[6], U Czarnetzki[7], U Ebert[8,9], J G Eden[10], P Favia[11], D B Graves[12], S Hamaguchi[13], G Hieftje[14], M Hori[15], I D Kaganovich[16], U Kortshagen[4], M J Kushner[17], N J Mason[18], S Mazouffre[19], S Mededovic Thagard[20], H-R Metelmann[21], A Mizuno[22], E Moreau[23], A B Murphy[24], B A Niemira[25], G S Oehrlein[26], Z Lj Petrovic[27], L C Pitchford[28], Y-K Pu[29], S Rauf[30], O Sakai[31], S Samukawa[32], S Starikovskaia[33], J Tennyson[34], K Terashima[35], M M Turner[36], M C M van de Sanden[9,37] and A Vardelle[38]

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Plasma Sources Science and Technology
Plasma Sources Sci. Technol. 26 (2017) 123002 (17pp)
https://doi.org/10.1088/1361-6595/aa97af

Topical Review

Foundations of atmospheric pressure non-equilibrium plasmas

Peter J Bruggeman[1], Felipe Iza[2] and Ronny Brandenburg[3]

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[2] Wolfson School of Mechanical, Electrical and Manufacturing Engineering, Loughborough University, Loughborough LE11 3TU, United Kingdom
[3] Leibniz Institute for Plasma Science and Technology (INP Greifswald), Felix-Hausdorff-Strasse 2, D-17489 Greifswald, Germany

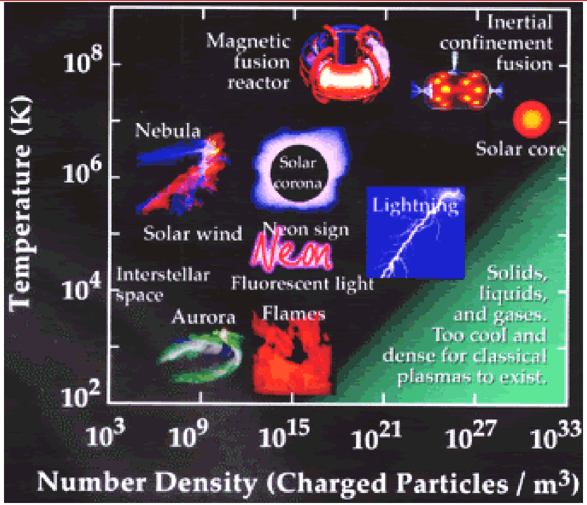
Outline

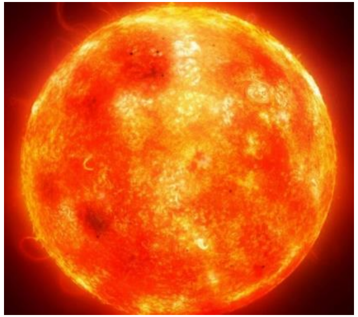
- ✓ Low Temperature Plasmas and Applications
- ✓ Generation of Low Temperature Plasmas and Basic Properties
- ✓ Energy Partition and Transfer in Low Temperature Plasmas
- ✓ Case Study #1: Plasma-Assisted Ignition
- ✓ Case Study #2: Inactivation of Viruses and Bacteria
- ✓ Case Study #3: Polymer Etching
- ✓ Extra: Atmospheric Reentry
- ✓ Conclusion

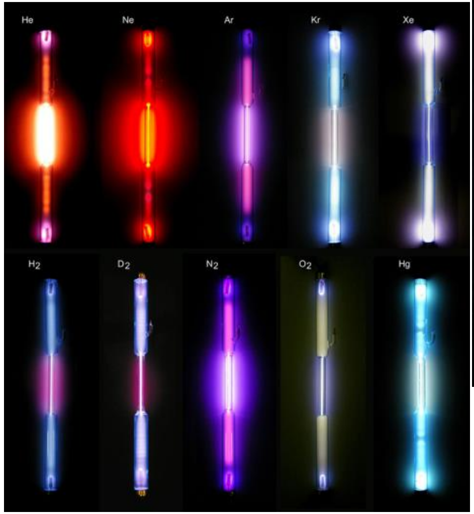
Low Temperature Plasmas and Applications

Plasmas?

- Ionized gases
- 4^{th} state of matter
- 99.9% of the visible universe
- Made of neutral particles, free electrons, ions, electric fields, photons
- Span over several orders of magnitude of densities and temperatures





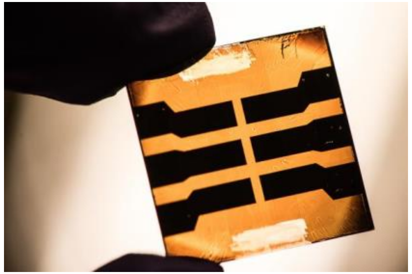


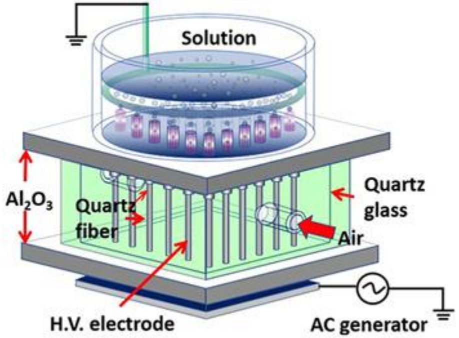
Current Grand Challenges of Engineering

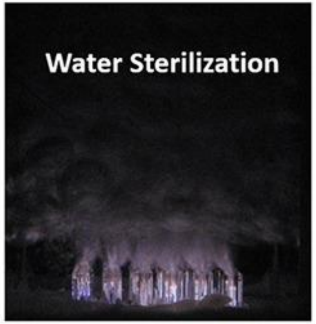
US Academy of Engineering

- Make solar energy economical
- Provide access to clean water
- Provide energy from fusion
- Manage the nitrogen cycle
- Engineer the tools for scientific discovery
- Improve CO_2 sequestration

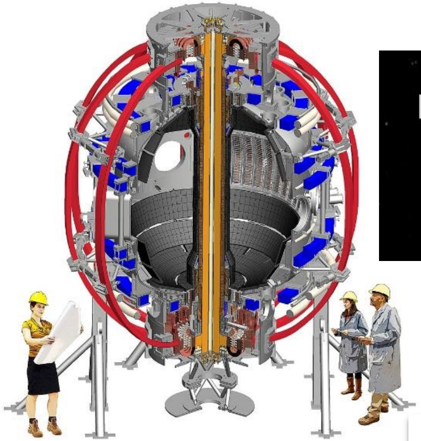
Perovskite solar cell



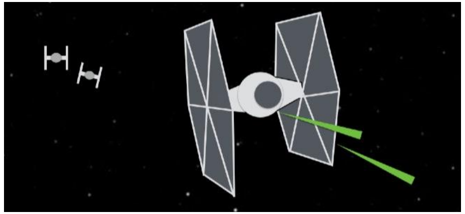




Spherical Tokamak at PPPL



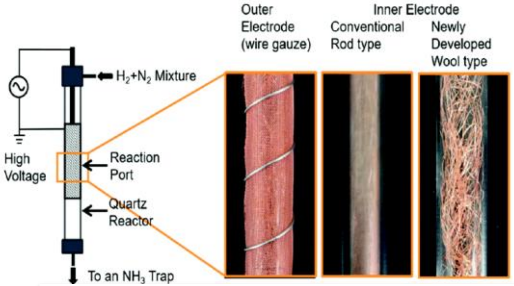
Electric propulsion for spacecraft



Star Wars twin ion engine fighters

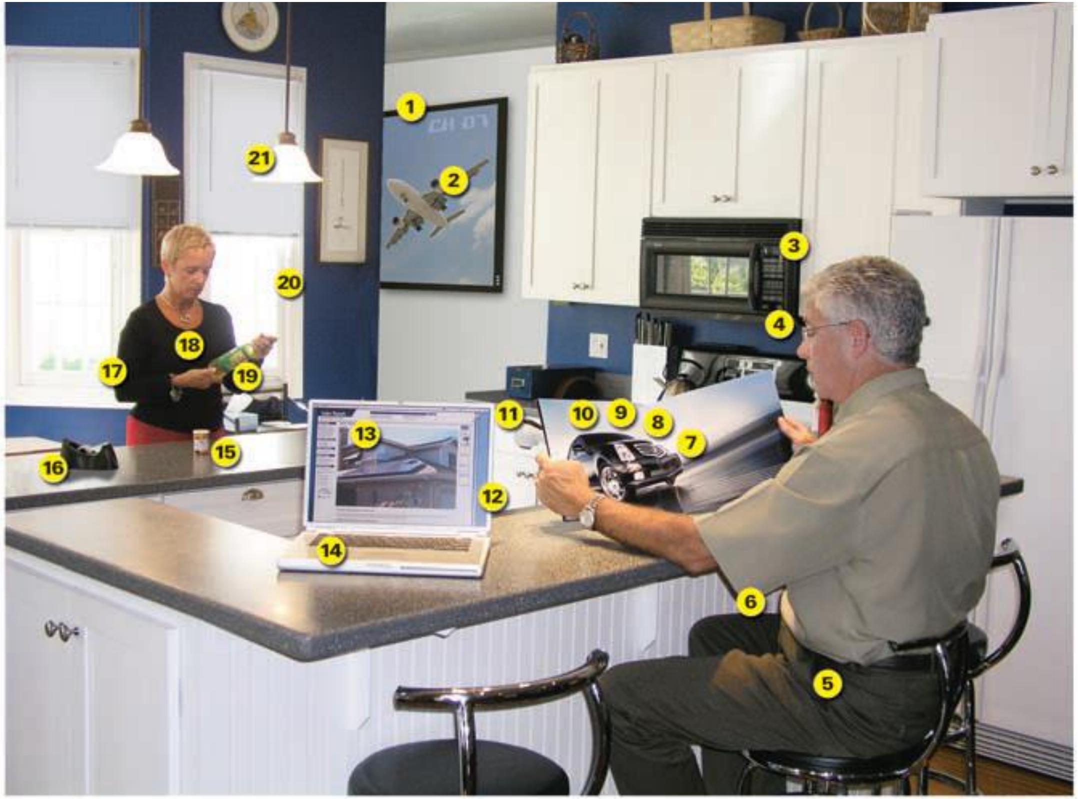
Aihara *et al.* ChemComm(2016)

Plasma-assisted ammonia synthesis



Zhang *et al.* ACS Plasma Proc Polym (2018)

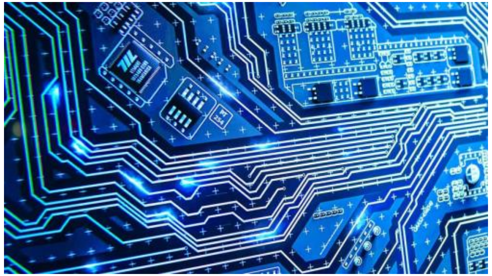
LT Plasmas Impact our Every-day Life



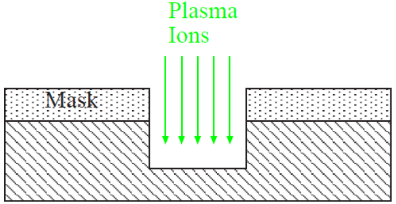
Plasma Science: Advancing Knowledge in the National Interest, National Research Council (US, 2007)

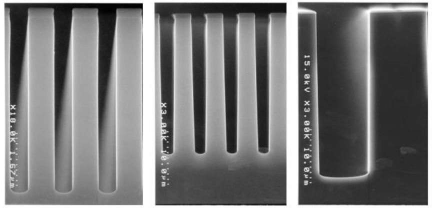
01 — Plasma TV
02 — Plasma-coated jet turbine blades
03 — Plasma-manufactured LEDs in panel
04 — Diamond-like plasma CVD eyeglass coating
05 — Plasma ion-implanted artificial hip
06 — Plasma laser-cut cloth
07 — Plasma HID headlamps
08 — Plasma-produced H_2 in fuel cell
09 — Plasma-aided combustion
10 — Plasma muffler
11 — Plasma ozone water purification
12 — Plasma-deposited LCD screen
13 — Plasma-deposited silicon for solar cells
14 — Plasma-processed microelectronic
15 — Plasma-sterilization in pharmaceutical production
16 — Plasma-treated polymers
17 — Plasma-treated textiles
18 — Plasma-treated heart stent
19 — Plasma-deposited diffusion barriers for containers
20 — Plasma-sputtered window glazing
21 — Compact fluorescent plasma lamp

The Semiconductor Success Story



Anisotropic Plasma Etching

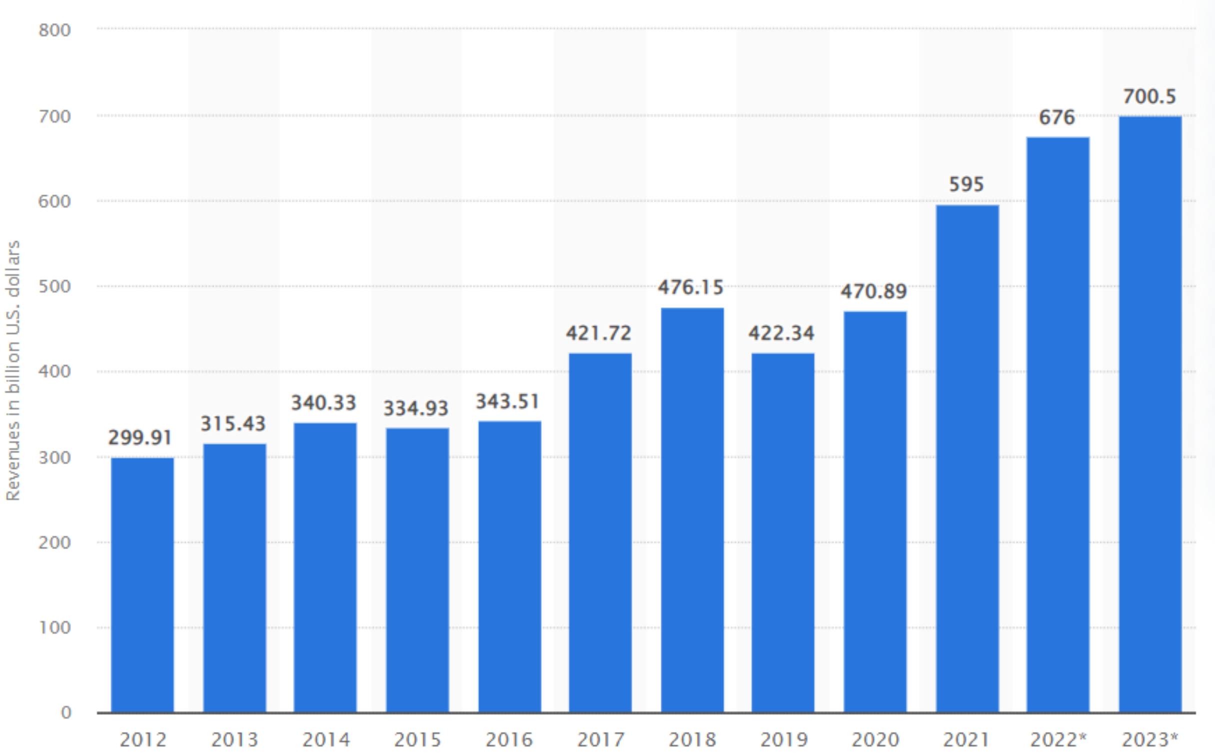




CD =0.6μm
Trench Depth = 5.6μm
E/R = 1.9μm/min.

CD=3μm
Trench Depth = 26μm
E/R = 3.2μm/min.

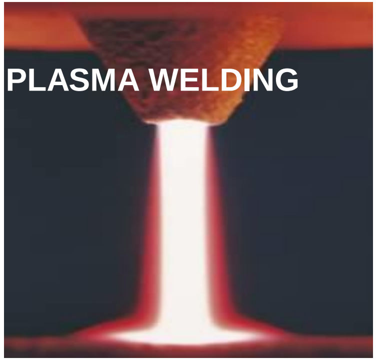
CD=10μm
Trench Depth = 31μm
E/R = 3.9μm/min.

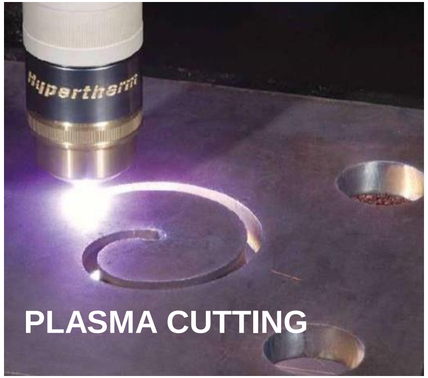


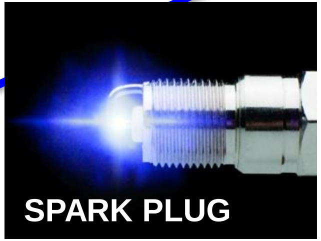
Wu et al, J. Appl. Phys. 108, 051101 (2010)

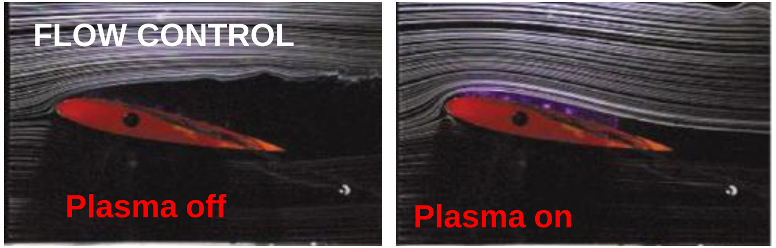
Plasmas and Applications: Thermal VS Non-Thermal

Thermal plasmas:
$T_g \sim T_e$ (2, 000- 10, 000 K)









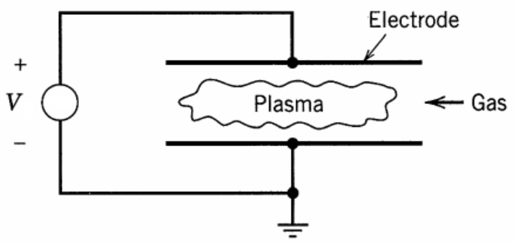
Non-thermal plasmas:
$T_g \ll T_e$ (10, 000 K)

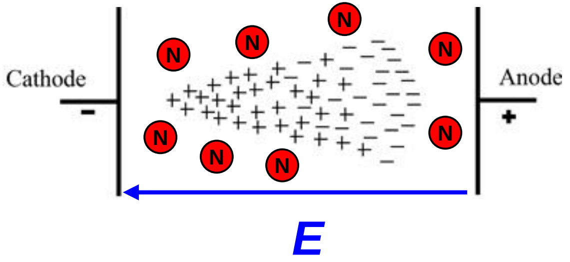
Generation of LT Plasmas and Basic Properties

Gas Discharges as Low Temperature Plasmas

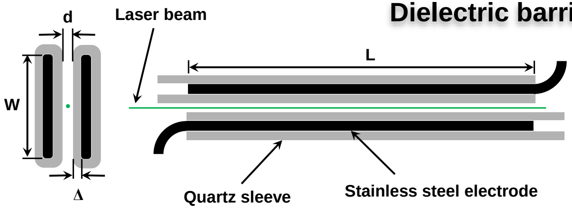
We use electric fields instead of heat!

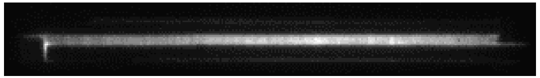
- **Electrically driven**
- **Different excitation sources can be employed: DC, AC, RF, Microwave, nanosecond pulsed,…**
- **The source of energy is the E-field**
- **High E-fields lead to ionizing collisions**
- **Charged particles collisions with neutrals cause the main energy transfer from the electric field energy to the gas**
- **When the energy transfer of electrons to neutral particles is not very fast, the energy of electrons ($=T_e$) can be significant larger than the neutral particles energy ($=T_g$): $T_g << T_e$**



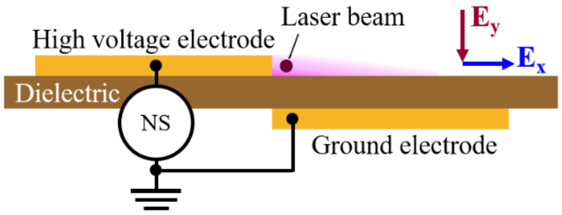


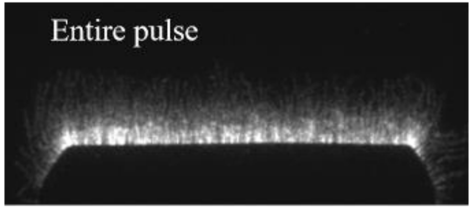
Dielectric barrier discharge



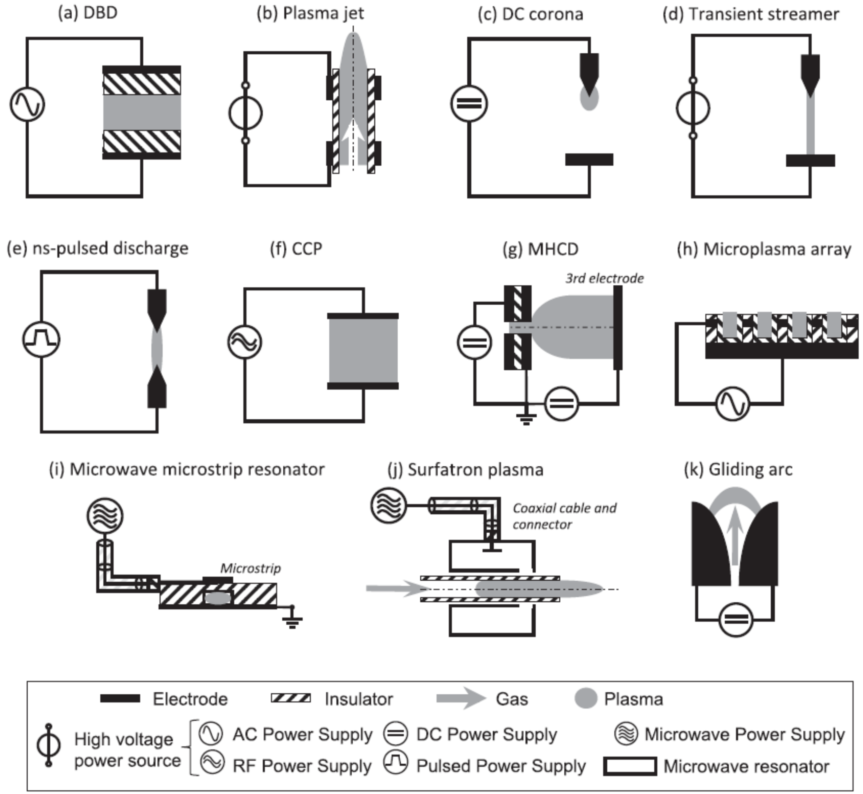


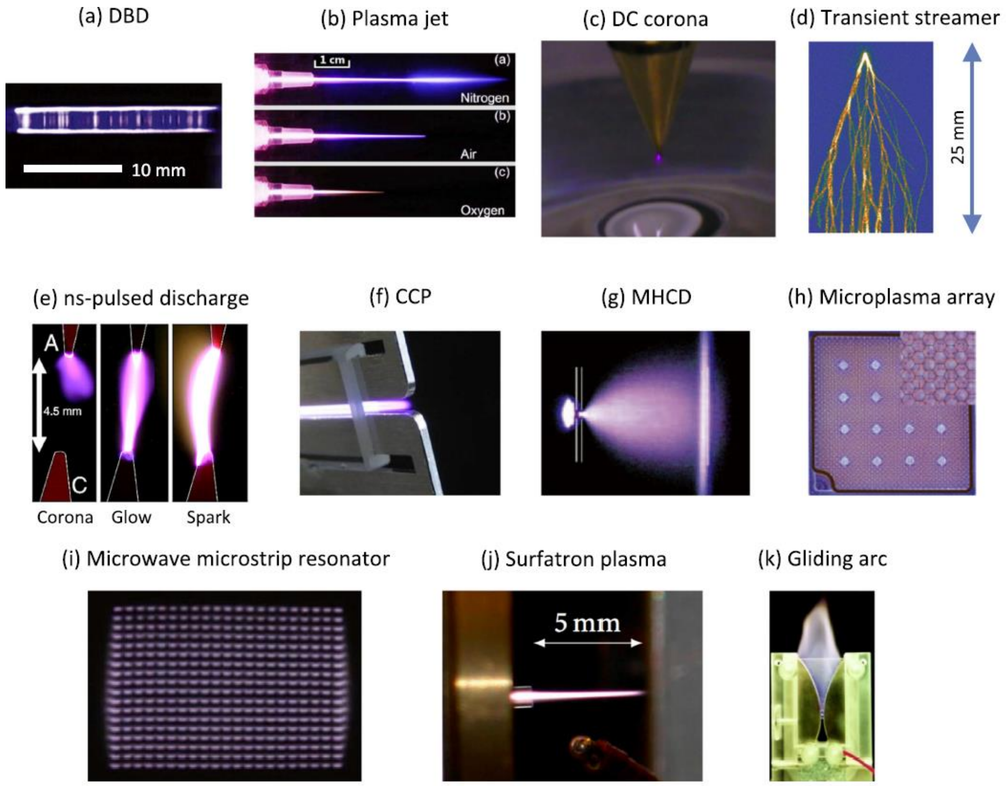
Surface dielectric barrier discharge





Overview of Atmospheric Pressure LT Plasmas





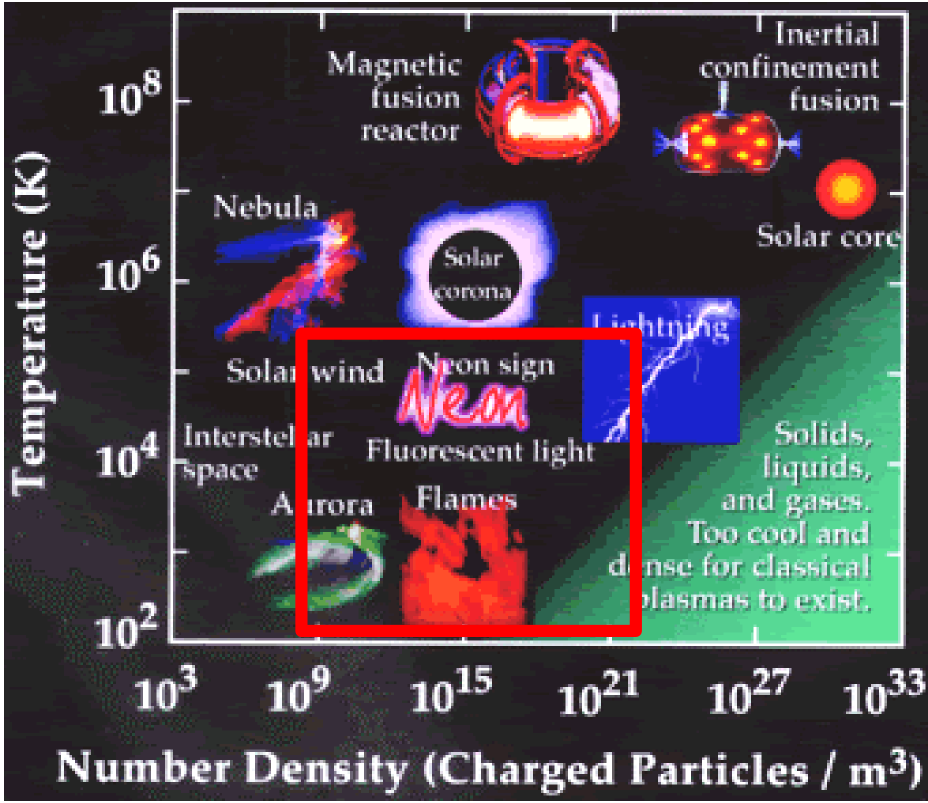
Bruggeman et al, Plasma Sources Sci. Technol. 26 (2017) 123002

LT Plasmas are Rich of Physics and Chemistry

- Span over 12 orders of magnitude for n_e
- Often low ionization fraction (degree): $\frac{n_e}{N} < 1\%$
- Ions and neutrals temperatures are near room temperature: $T_i \sim T_g \sim \frac{1}{40}$ eV
- Electron temperature can reach several eV: T_e ~ 1-10 eV

1 eV ≈ 11,606K

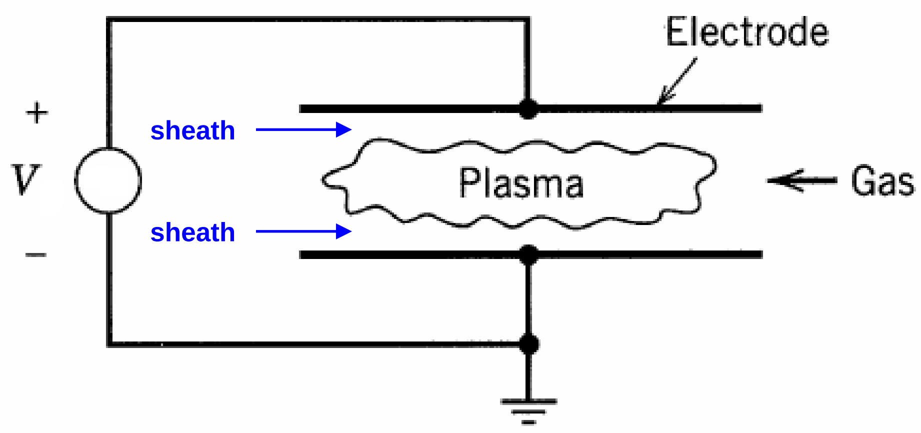
- Highly non-equilibrium
- Highly reactive plasmas can be generated near room gas temperatures
- In presence of molecular gases, dissociation can occur generating a very rich and complex electrons-driven chemistry: LT plasma = chemical processor

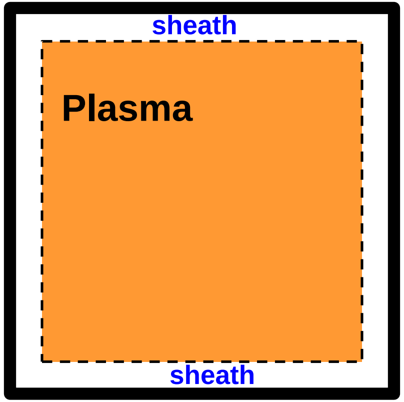


Plasma Interactions with Surfaces: Formation of Sheaths

Plasma are surrounded by Sheaths!

- The sheath is the boundary layer between a plasma and a solid surface (electrodes, substrate, container walls, …)
- It acts to balance electron and ion currents lost from a plasma
- Sheaths are characterized by a strong E-field, low electron density
- Sheaths form as ions are accelerated into surfaces
- Sheaths have an important role for applications relevant to: removal of surface material and ion implantation





Sheaths size depends on the plasma density (pressure)

The Debye length is the characteristic length scale of a plasma

- **It's the distance scale over which significant charge densities can spontaneously exist**

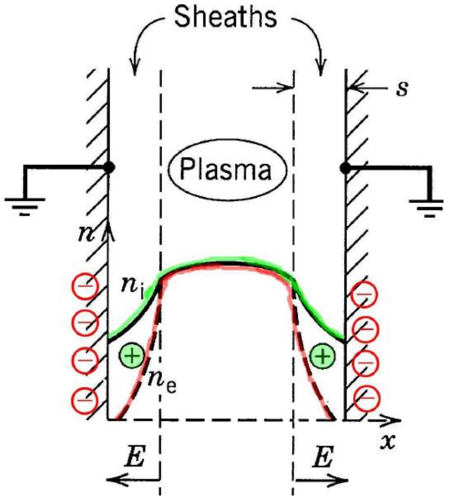
Using Poisson's equation:

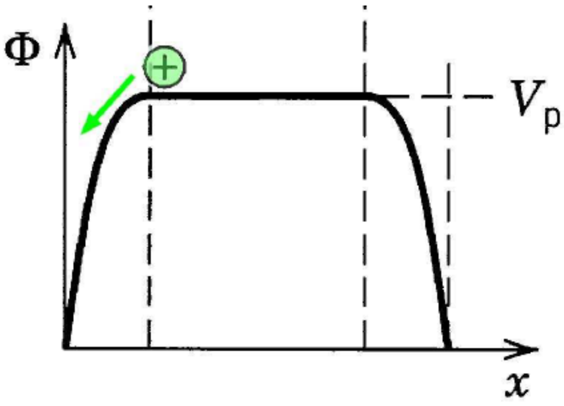
$$\phi = \phi_0 e^{-|x|/\lambda_{De}}$$

$$\lambda_{De} = \left(\frac{\varepsilon_0 T_e}{e n_e}\right)^{\frac{1}{2}}$$

$$\lambda_{De}(cm) = 740\sqrt{T_e/n_e}$$

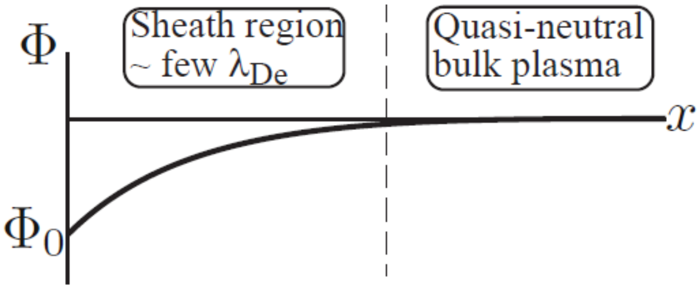
T_e in eV and n_e in cm^{-3}





$$\boldsymbol{E} = -\nabla\boldsymbol{\phi}$$

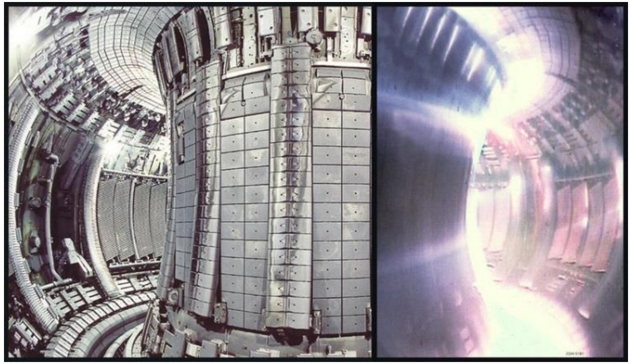
- **For T_e = 4 eV and n_e = 10^{10} cm^{-3}, λ_{De} ~ 148 µm (quite small!)**



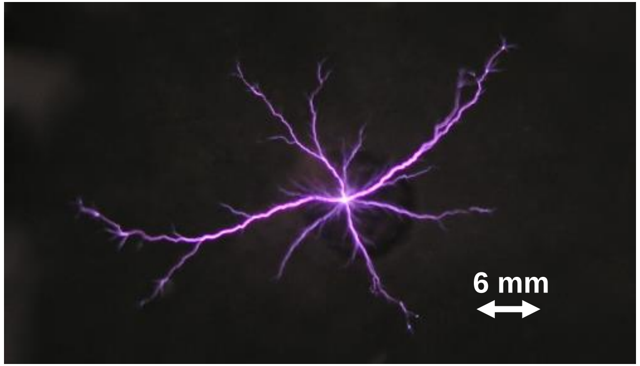
- **Sheath thickness l_s provided by Child-Langmuir sheath model:**

$$\frac{l_s}{\lambda_{De}} = \frac{\sqrt{2}}{3}\left(\frac{2e\Delta\phi}{T_e}\right)^{3/4}$$

Comparison between Hot and Cold Plasmas



EFDA JET: Joint European Torus



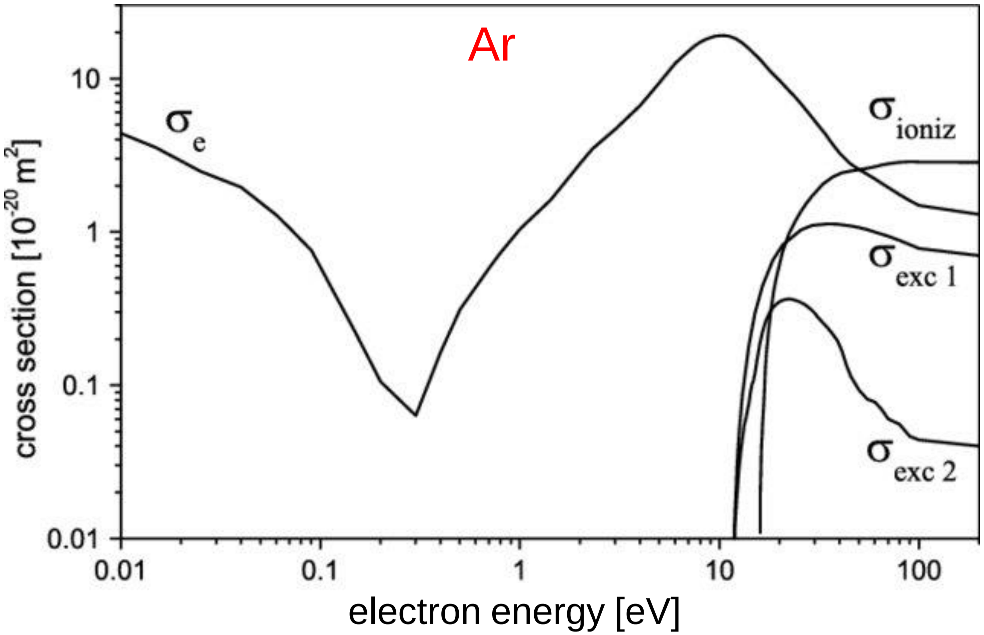
	JET Tokamak	Atmospheric pressure plasmas
Power	~16 MW	10^{-2} – 10 W
Volume	~ 100 m^3	~ 10^{-8} m^3 (10 mm^3)
Power density	**10^6 W m^{-3}**	**10^6-10^9 Wm^{-3}**
Ionization degree	FULL	10^{-5} – 10^{-2}
Temperature	T_e = T_g =10^8 K	T_e = 10^3-10^4 K T_g= 300 – 3000 K
Pulse duration	~1 s	~ 10 ns up to DC

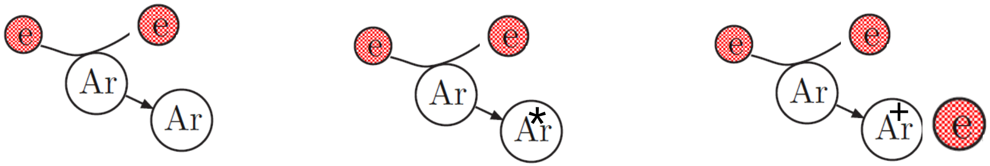
Energy Partition and Transfer in LT Plasmas

Collisions and Elementary Reactions: Atomic Gas

We use cross sections to quantify the probability that a process may occur

- **Elastic collisions:** $e^- + Ar \rightarrow Ar + e^-$
- **Electronic excitation collisions:** $e^- + Ar \rightarrow Ar^* + e^- \rightarrow Ar + e^- +$ photons
- **Ionizing collisions:** $e^- + Ar \rightarrow Ar^+ + e^- + e^-$
- **Cross sections from different databases are compiled on the LXCAT website:** https://us.lxcat.net/
- **Databases: IST-Lisbon, Morgan, Phelps, Itikawa, Triniti, Hayashi, …**
- **1 eV ~ 1.6×10^{-19} J**



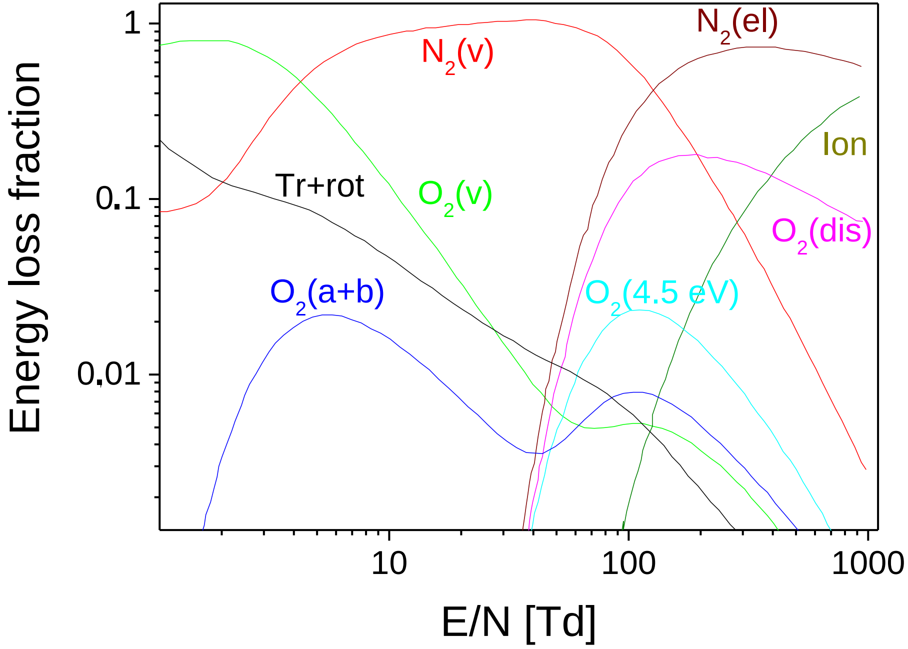


Energy Partition in a Molecular Gas: Air

Where does the energy from the electrons go?

- **E/N, electric field divided by total number density**
- **1 Td (Townsend) = 10^{-17} V.cm^2**
- **The rates of electron impact processes depend exponentially on E/N**
- **At low E/N values (< 10 Td): Energy coupled preferentially to vibrational excitation of O_2**
- **For 10 Td < E/N < 100 Td: Energy coupled preferentially to vibrational excitation of N_2**
- **For E/N > 100 Td: Energy coupled into electronic excitation of N_2, O_2 dissociation and ionization**

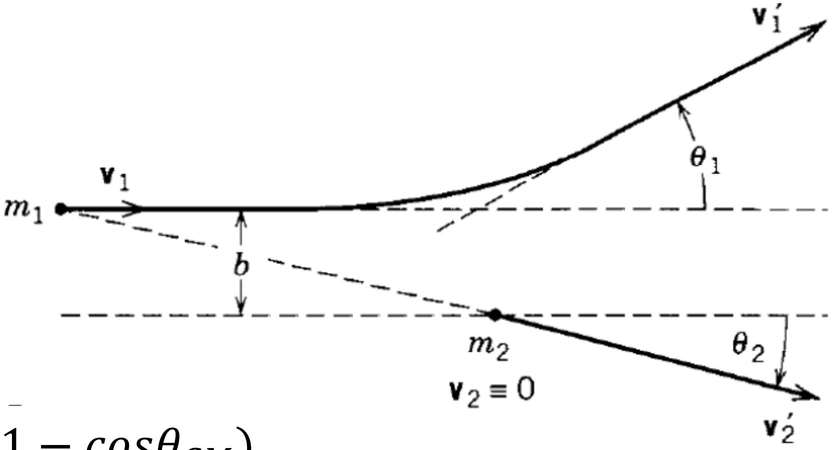
Yuri Raizer: Gas discharge Physics



High E/N values result in high reactivity and rapid electron-driven processes. This is for instance achieved using nanosecond pulsed discharges

Energy Transfer in an Elastic Collision (1)

- **Expressing energy and momentum balances yields:**



W_L = final energy for particle m_2
W= initial energy for particle m_1

$$\frac{W_L}{W} = \zeta_L = \frac{4m_1m_2}{(m_1+m_2)^2}\cos^2\theta_2 = \frac{2m_1m_2}{(m_1+m_2)^2}(1-\cos\theta_{CM})$$

$$\theta_2 = \frac{\pi}{2} - \frac{\theta_{CM}}{2}$$

CM = Center of Mass (given)

- **What is now the average energy transfer per collision?**

Energy Transfer in an Elastic Collision (2)

Fraction of energy transferred in one collision:

- **For electron – neutral collision (hard sphere model)**

$$\frac{2m_1 m_2}{(m_1+m_2)^2} \approx \frac{2m_e}{M} \approx 10^{-4}$$

Electrons transfer little energy in elastic collisions with neutrals: $T_e >> T_g$

- **For ion – neutral collision (with same mass)**

$$\frac{2m_1 m_2}{(m_1+m_2)^2} = \frac{1}{2}$$

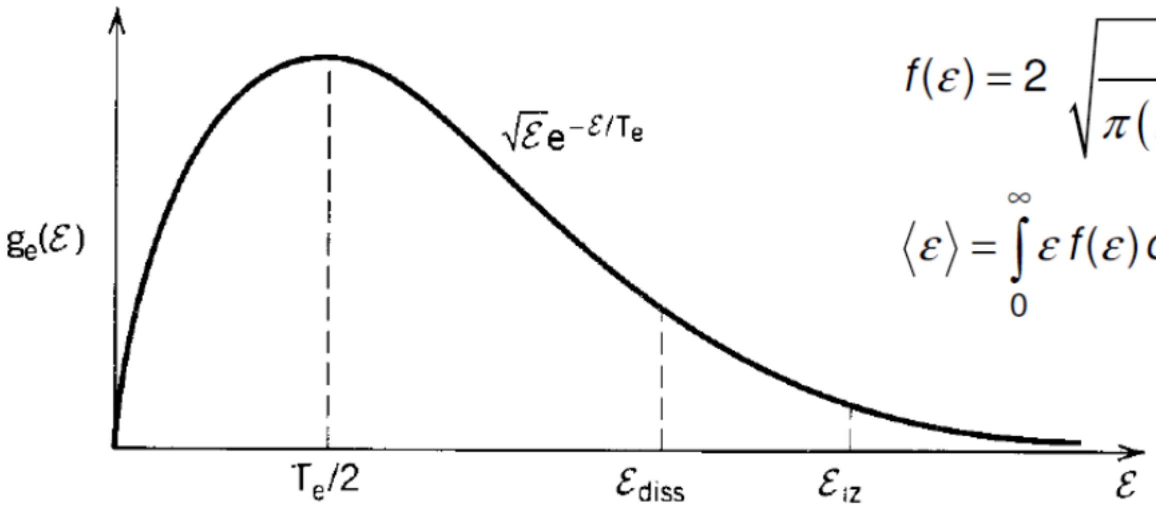
Equilibration rates depend on the mass ratios

Ions neutral collisions transfer significant energy in elastic collisions: $T_{ion} \sim T_g$

What does Temperature mean?

Temperature is actually related to the mean kinetic energy!

Concept of thermal equilibrium in statistical mechanics: Maxwell-Boltzmann distribution function of the particle energy



Particle energy

$$f(\varepsilon) = 2\sqrt{\frac{\varepsilon}{\pi (kT_e)^3}}\exp\left(-\frac{\varepsilon}{kT_e}\right)$$

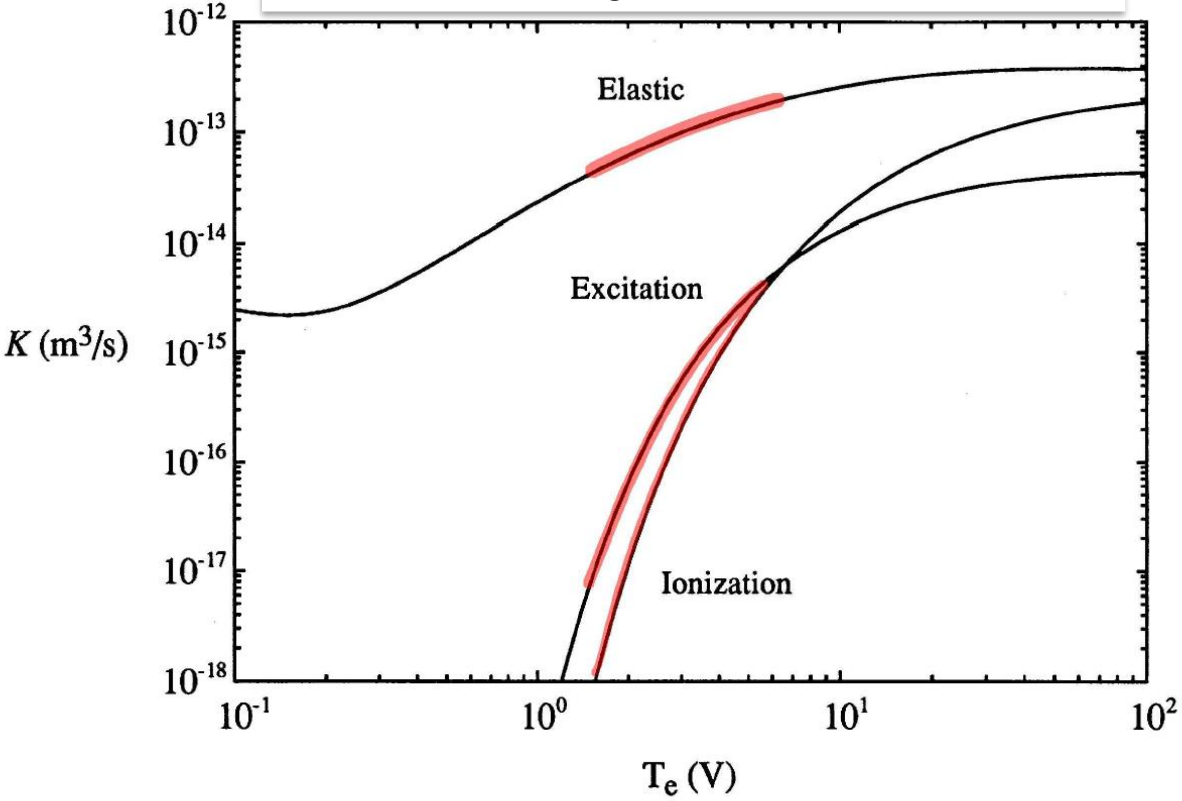
$$\langle \varepsilon \rangle = \int_0^\infty \varepsilon f(\varepsilon)\, d\varepsilon = \frac{3}{2}kT_e$$

- **Ionization is caused by high energy electrons in the tail of the distribution!**

- **An electron temperature (T_e) of 1 eV therefore means that the plasma has an electron energy distribution function (EEDF) with a mean energy of 3/2 eV**

Rate Coefficients

Electron-Argon Rate Coefficients



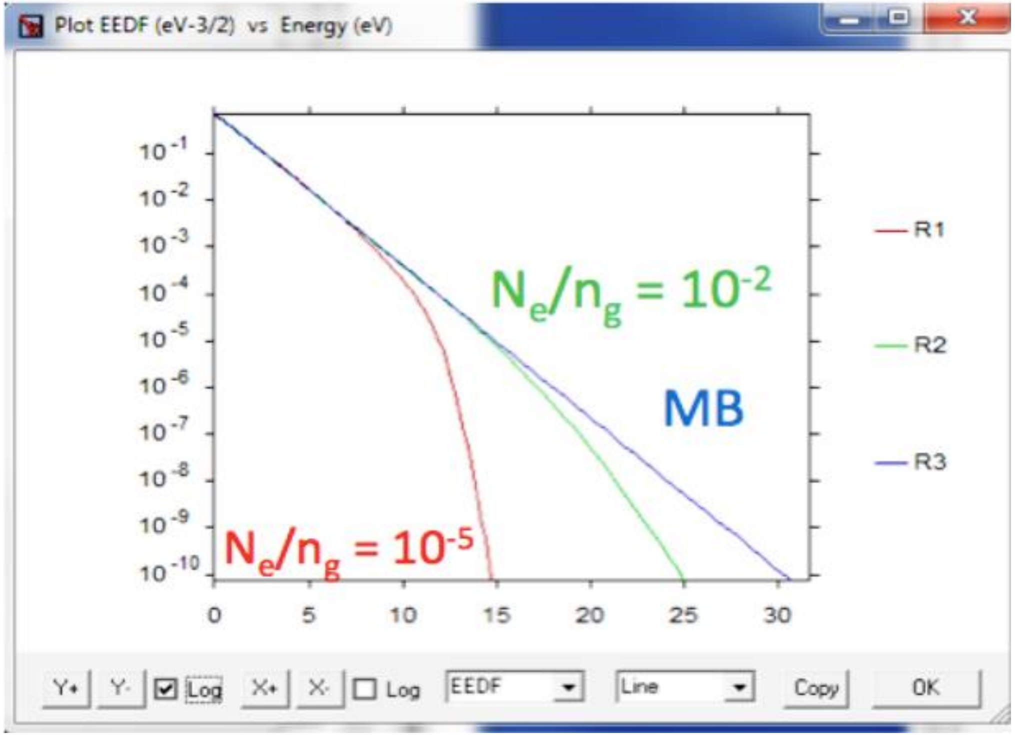
- Rate coefficient is the average of the cross section σ (V_R) of the process over the Maxwellian distribution
- $K(T_e) = \langle \sigma V_R \rangle_{Maxwellian}$
- V_R = relative velocity of colliding particles
- The knowledge of rate coefficients is indispensable for establishing accurate collisional-radiative models of plasmas

Deviation from Maxwell-Boltzmann Distribution

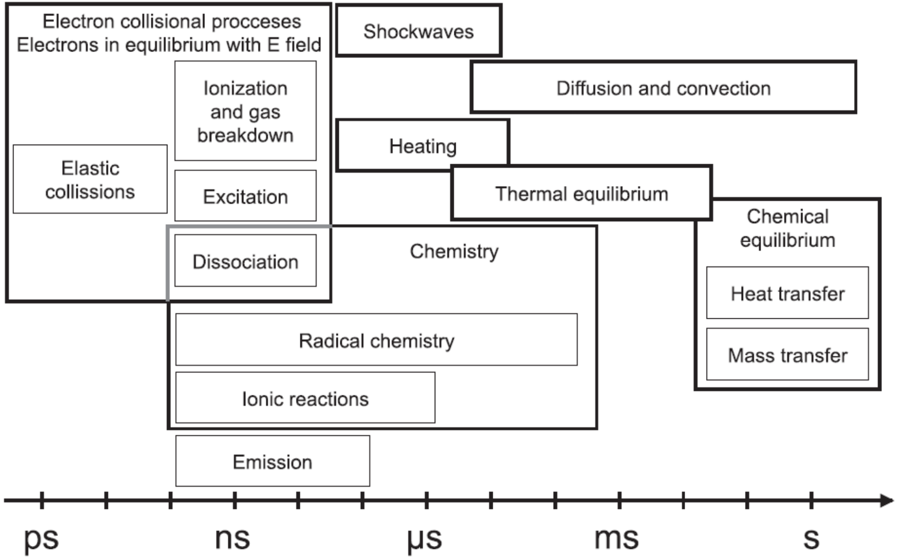
The EEDF is not necessarily Maxwell-Boltzmann!

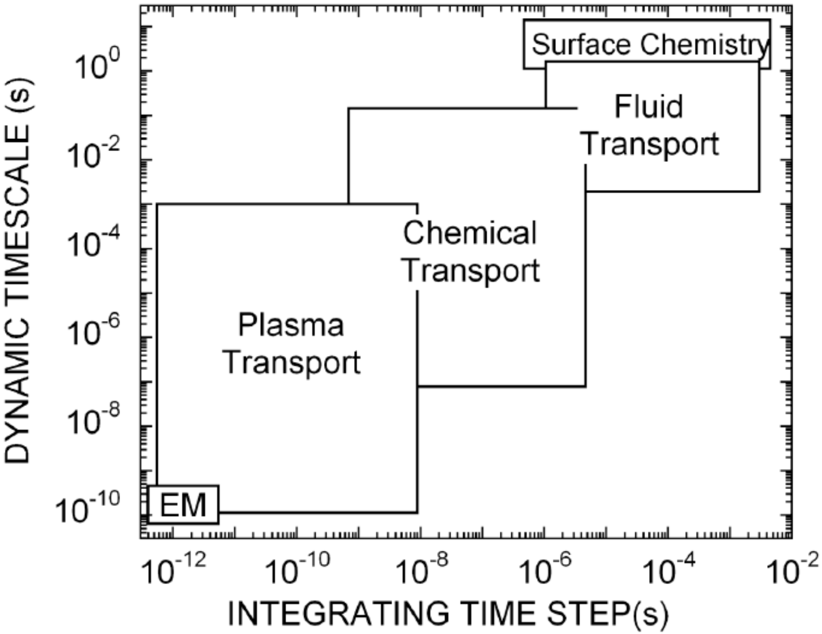
- **It depends on the ionization degree**
- **Assuming M-B when it is not can hugely impact rates with high threshold energy**
- **Plasma codes have a Boltzmann solver (EEDF can depend on gas composition)**

Bolsig+: Boltzmann equation solver



LT Plasmas Modeling and Timescales





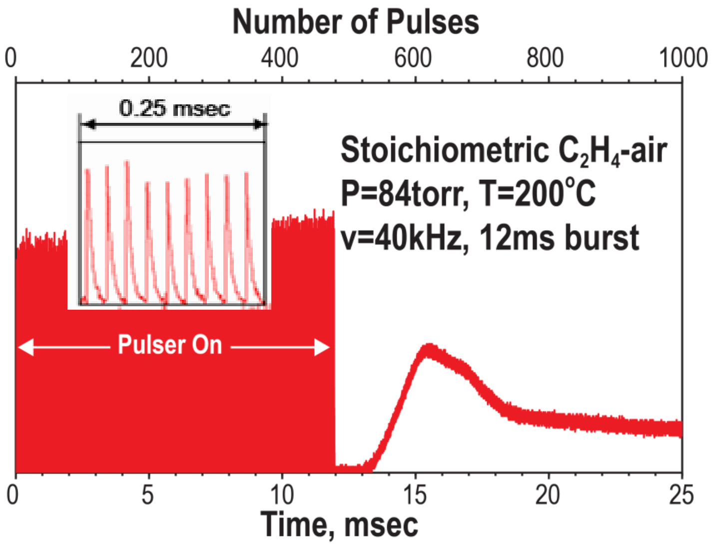
- **About 12 orders of magnitude in timescales**
- **Integrating timestep (stability, accuracy): Δt**
- **Dynamic timescale (to resolve the evolution of plasma phenomena): ΔT**

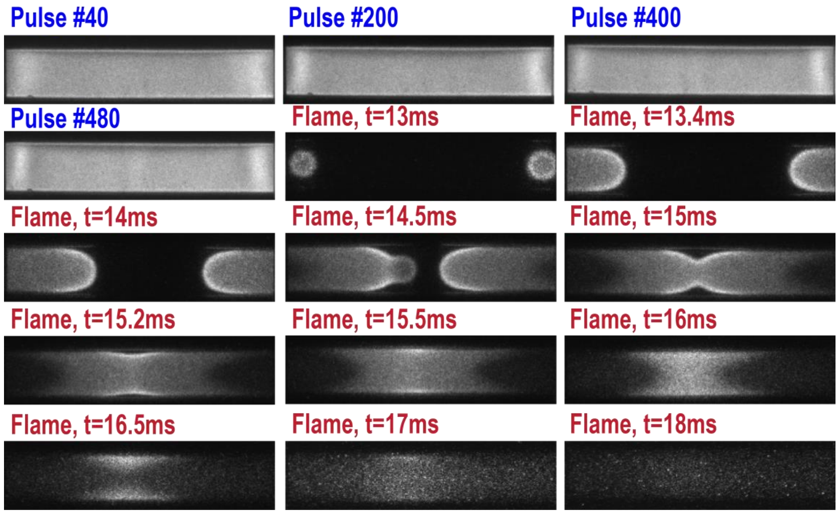
Mark J. Kushner, University of Michigan

Bruggeman et al, Plasma Sources Sci. Technol. 26 (2017) 123002

Case Study #1: Plasma-Assisted Ignition

C_2H_4 Ignition below Auto-ignition Temperature





OH emission from plasma and flame

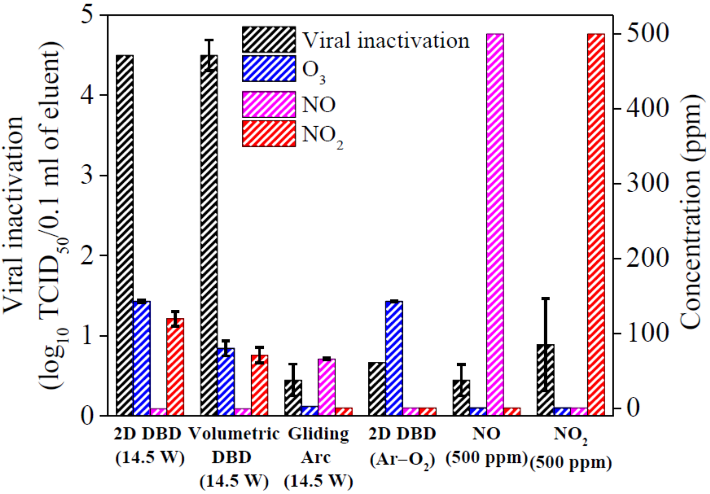
- **Ignition induced by radicals generated in the plasma (primarily O and H atoms)**
- **Ignition occurs at temperature ≈ 200 K below autoignition**
- **Ignition begins near edges of the plasma (higher energy loading)**
- **Flame propagates to the center of the plasma**

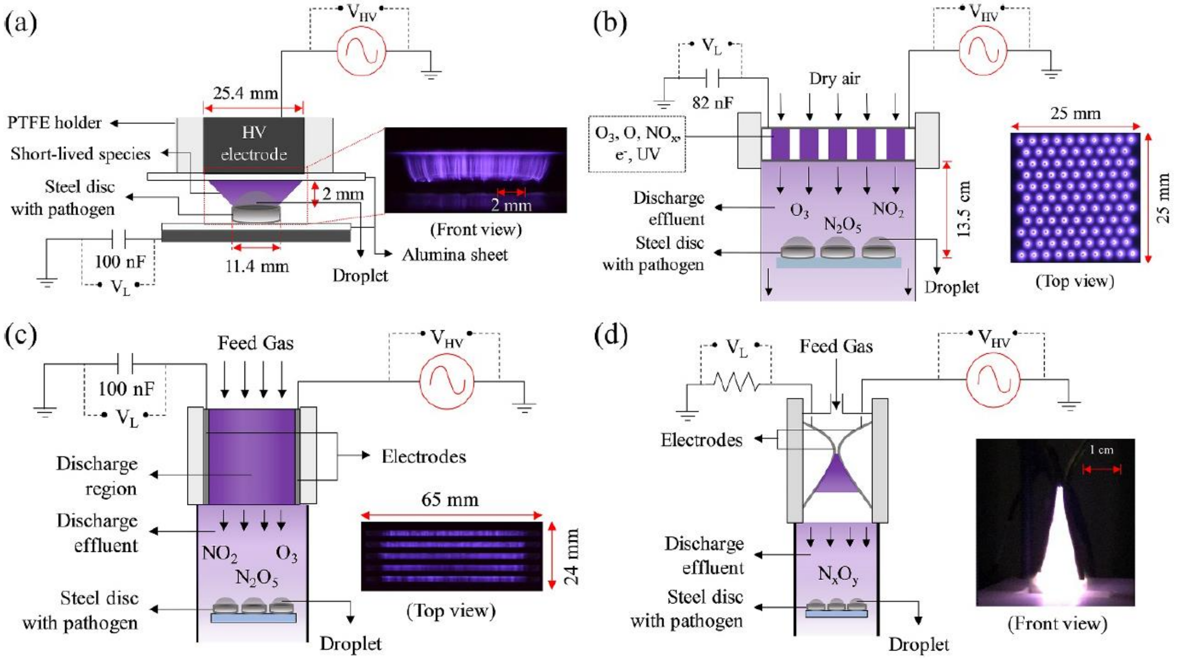
Yin et al, IEEE Trans Plasma Sci. 2011

Case Study #2: Inactivation of Viruses and Bacteria

RONS from Air Plasmas for Virus Inactivation

RONS = Reactive Oxygen Nitrogen Species





- **Reactive components from plasma chemistry: O_3, NO_x, OH, O, H_2O_2, N_2^+, O_2^+, O_2^-, UV light, e^-**
- **Comparison of surface decontamination efficiency of 4 different plasmas**
- **Strong correlations between generation of gas phase N_2O_5 and inactivation**

FCV = Feline CaliciVirus (surrogate of human norovirus = stomach flu)

Moldgy et al, J. Phys. D: Appl. Phys. 53 (2020) 434004

Case Study #3: Polymer Etching

Etching from O, H, OH Produced by a RF Plasma Jet

- **Etching of polystyrene, PMMA (poly methyl methacrylate) and PVA (poly vinyl alcohol)**
- **Ar+1% O_2, Ar+1% air, Ar +1% H_2O plasma jets**
- **Correlation between O flux at the surface and polymer etching rate**
- **Etching probability of polystyrene by OH at least one order of magnitude greater than etching of polystyrene by O radicals**

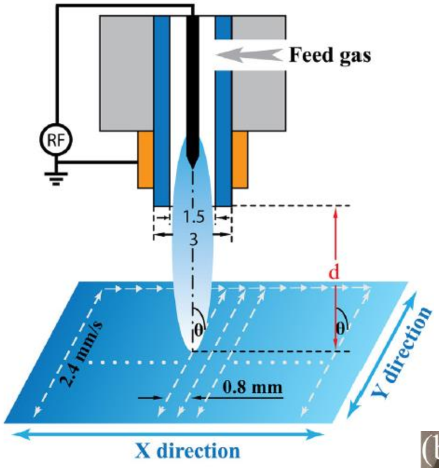
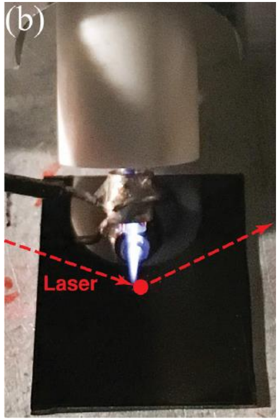


TABLE VI. Obtained etching probability (γ) for different surface loss coefficients (β).

Species	β	γ
O˙	10^{-4}	$(1.9 \pm 0.1) \times 10^{-5}$
	10^{-3}	$(3.2 \pm 0.2) \times 10^{-5}$
	10^{-2}	$(1.4 \pm 0.2) \times 10^{-4}$
H˙	10^{-5}	$<8.3 \times 10^{-6}$
	10^{-3}	$<1.8 \times 10^{-5}$
˙OH	10^{-3}	$(2.8 \pm 0.1) \times 10^{-3}$
	10^{-2}	$(5.750 \pm 0.001) \times 10^{-3}$
	10^{-1}	$(3.5 \pm 0.1) \times 10^{-2}$

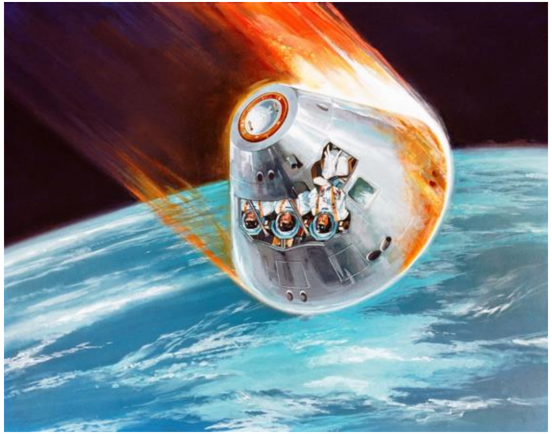


Luan et al, J. Phys. D: Appl. Phys. 50 (2017) 03LT02

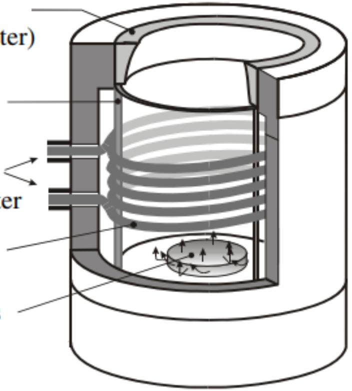
Kondeti et al, J. Vac. Sci. Technol. A 38(3)

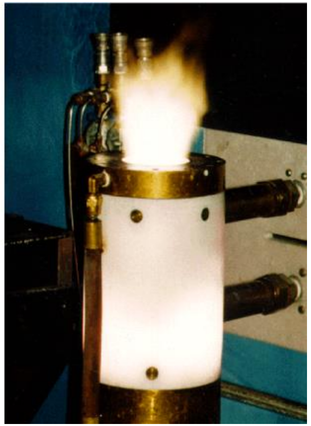
Using plasma to modify surface properties of polymers: Improving adhesion, printing and biocompatibility

Non-equilibrium Flows during Earth Atmospheric Reentry



Plasma Torch Facility at Ecole Centrale Paris





- Earth reentry occurs at hypersonic velocities: 5-20 km.s^{-1}
- Radiative fluxes from the shock-produced plasma account for up to 50% of the total heat encountered by a spacecraft during reentry

MacDonald et al, J. Thermophys. Heat Trans 29.1 (2015)

- The plasma generated is under non-equilibrium conditions
- Designing effective thermal protective systems (TPS) require accurate quantification of these radiative fluxes
- Experiments performed in ground facilities use plasma torches and arc jet plasmas

Summary

- **LT plasmas are everywhere around us**
- **They enable many of our modern technologies**
- **LT plasma physics a multidisciplinary field**
- **Their high non-equilibrium feature provides an almost infinite richness**
- **LT plasmas are relatively easy to generate in the lab. This leads to the research field being exciting and fast-paced**
- **Ongoing work involves theory, modeling, computational and experimental efforts**
- **Come join us!**

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