Introduction to Low Temperature Plasmas

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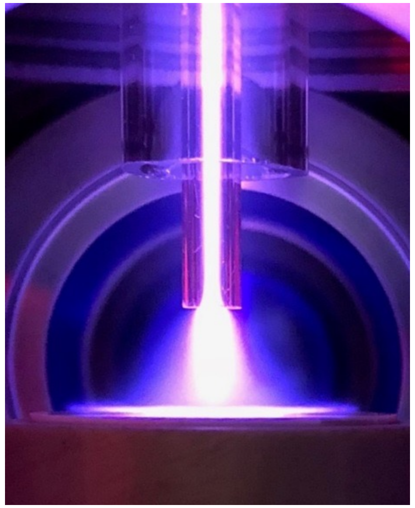
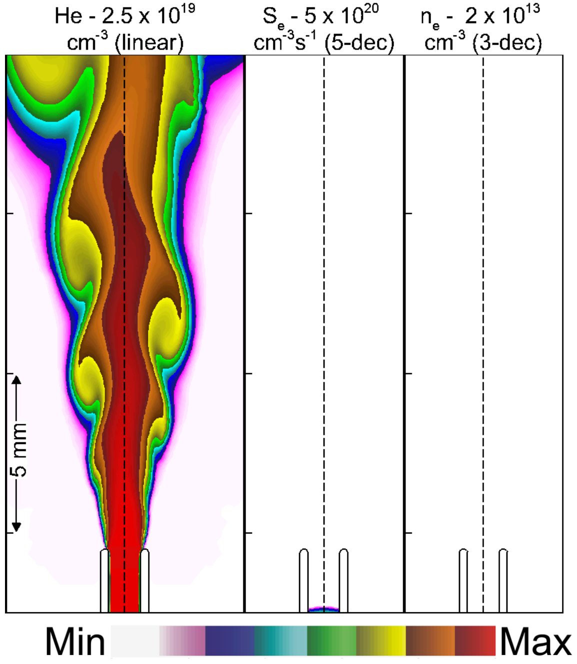
2024 Introduction to Plasma and Fusion Course
June 17, 2024

Dr. Lietz’s Technical Background

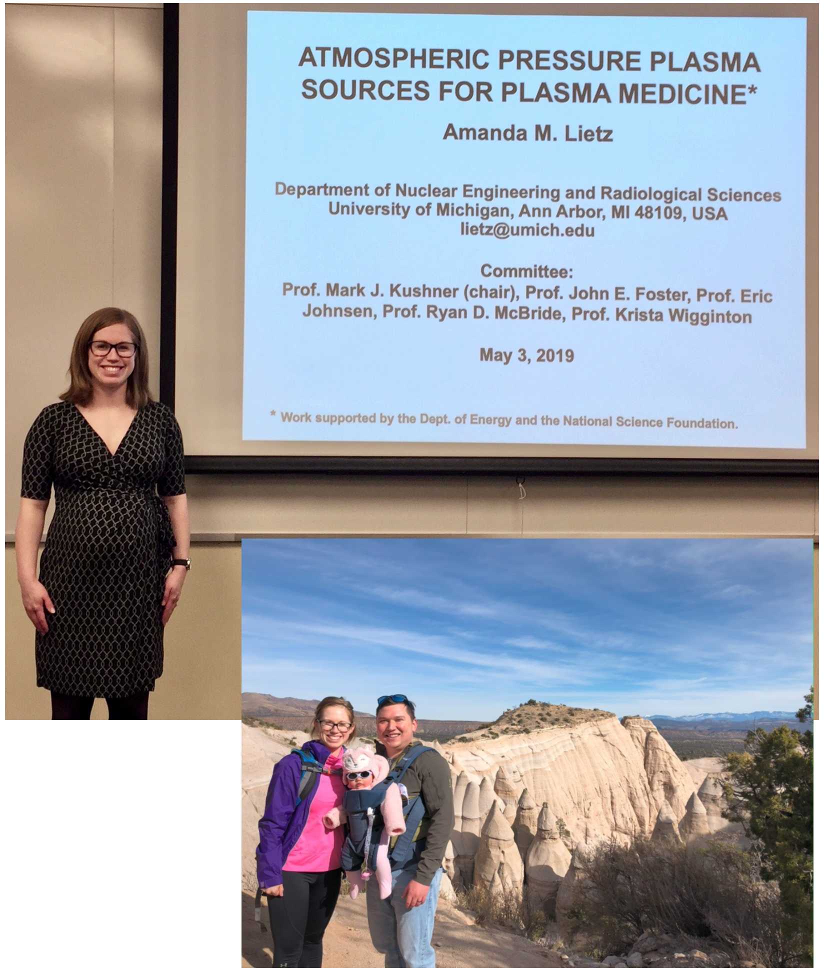
- Assistant Professor in NCSU Nuclear Engineering Department since August 2022.
- B.S., Nuclear Plasma and Radiological Engineering from University of Illinois at Urbana-Champaign
- PhD, Nuclear Engineering and Radiological Sciences at University of Michigan
  - Atmospheric Pressure Plasma Sources for Plasma Medicine
  - Primarily fluid and global modeling
  - Laser diagnostics
- Postdoctoral Appointee at Sandia National Laboratories
  - Thermionic energy converters, mass spectrometers, validation, semiconductor processing
  - Primarily particle-in-cell simulations





Dr. Lietz's Personal Background

- Participated in this course in 2012!



ATMOSPHERIC PRESSURE PLASMA SOURCES FOR PLASMA MEDICINE*

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May 3, 2019

* Work supported by the Dept. of Energy and the National Science Foundation.

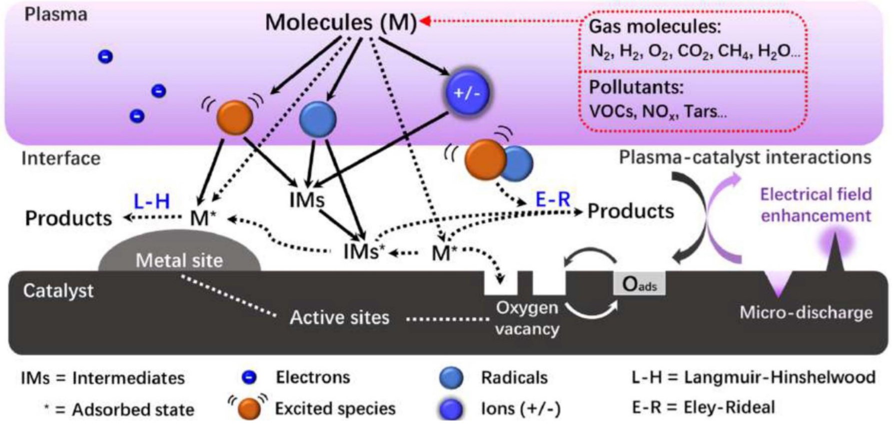
Computational Plasma Science (ComPS) Group

- Modeling Low Temperature Plasmas.
- Established in August 2022.
- Tackling these problems involves using existing tools and developing new tools.

- Application Areas of Interest:
  - Semiconductor Processing
  - Fusion Technologies
  - Biomedical Applications
  - Chemical Conversion
  - Laser-produced Plasmas

G. Xu, X. Shi, J. Cai, S. Chen and P. Li, Wound Repair Regen. 23, 878 (2015).

“Plasma Process Metrology” www.nist.gov

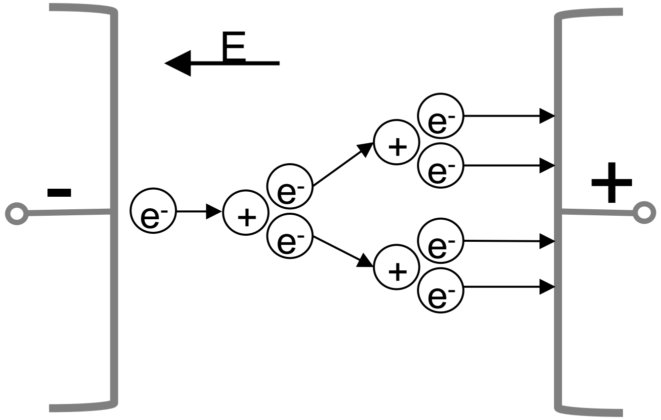


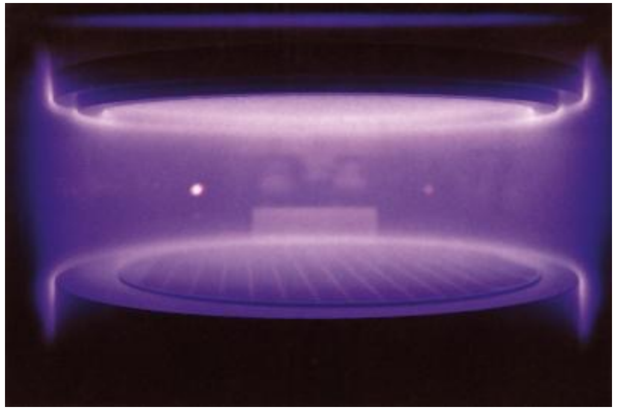
Agenda

- Defining a Low Temperature Plasma (LTP)
- Conceptual Derivation of a Sheath
- Non-equilibrium and non-Maxwellian in LTPs
- Applications of LTPs
- The Role of Computational Modeling

- Learning objectives:
  - Explain why $T_e >> T_{gas}$.
  - Name several applications of LTPs.
  - Describe a sheath.

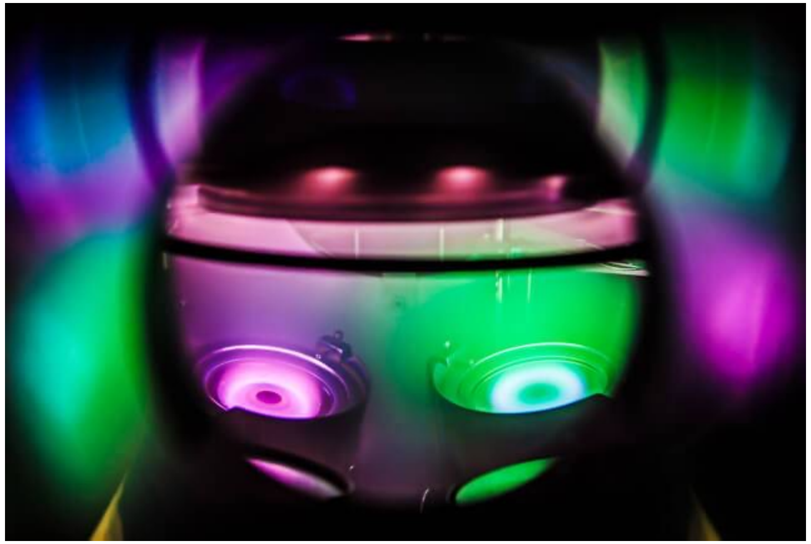
What is a Low-Temperature Plasma?



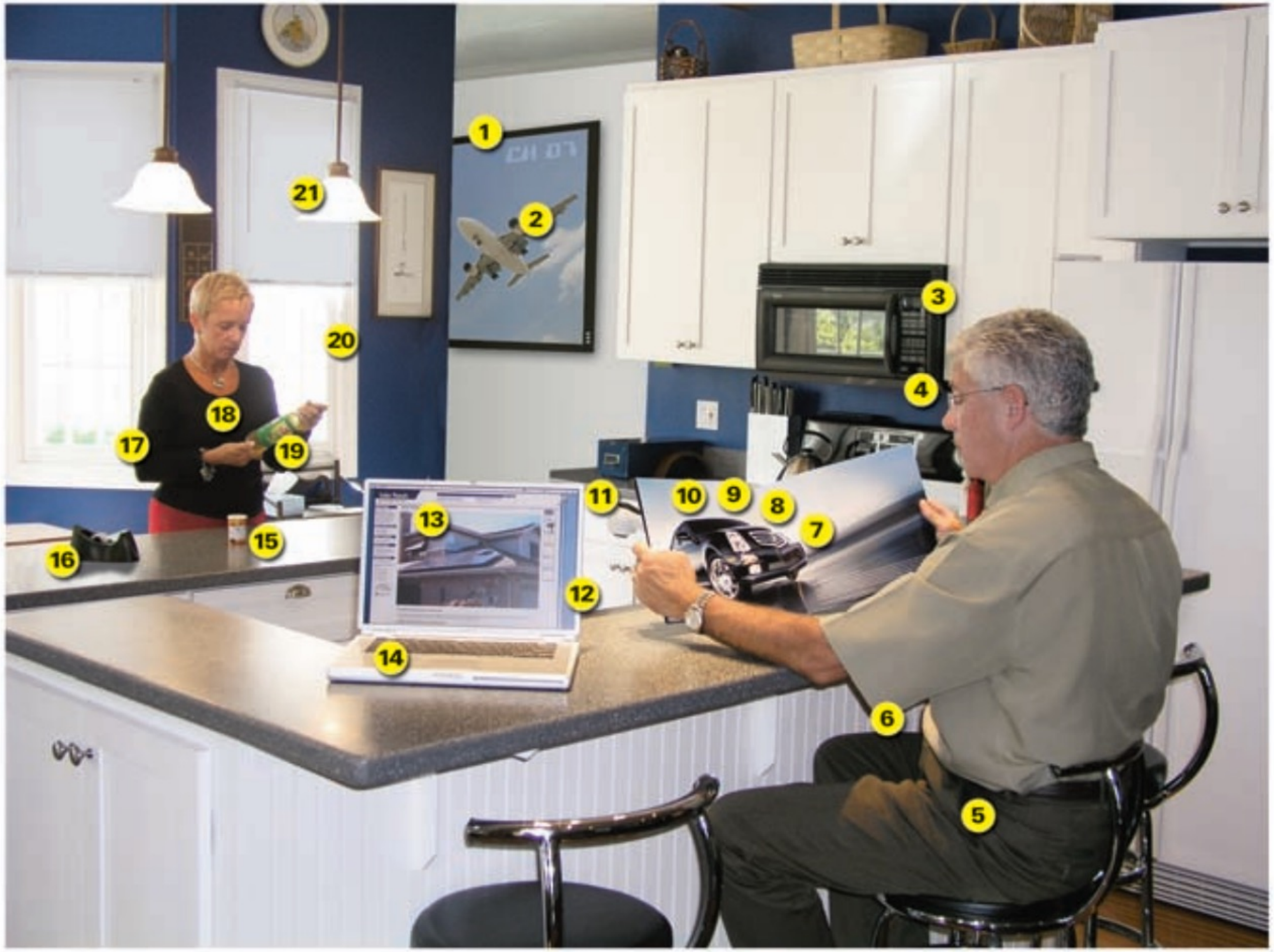


Solvay

- Low temperature plasma – plasmas with a gas temperature much less than what would cause ionization.
- Electrons are heated by an electric field.
  - $T_e >> T_{gas}$
- Sustained by electron-impact ionization.
  - $e + M \rightarrow M^+ + e + e$



Angstrom engineering



01—Plasma TV

02—Plasma-coated jet turbine blades

03—Plasma-manufactured LEDs in panel

04—Diamondlike 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 microelectronics

15—Plasma-sterilization in pharmaceutical production

…

“Plasma Science: Advancing Knowledge in the National Interest”
National Research Council of the National Academies Report (2007).

Low-Temperature Plasmas

- In order to have a plasma, some energy needs to be high enough to cause an ionization.
- In a thermal plasma (i.e. the sun) : $T_{gas} \sim E_{iz}$ (10 eV, 110,000 K)
- Low-temperature plasmas use E-fields, which selectively accelerate electrons.
  - *m* = mass,
  - *v* = velocity,
  - *e* = elementary charge,
  - *E* = constant electric field
- Ignoring collisions.
- Low temperature plasmas also tend to be *weakly ionized* – only a ppb/ppm is charged species.

Electrons	Ions
$m_e \frac{dv_e}{dt} = -eE$	$m_i \frac{dv_i}{dt} = eE$
$v_e = -\frac{eE}{m_e} t$	$v_i = \frac{eE}{m_i} t$

$$\frac{3}{2} k_b T = \frac{1}{2} m \langle v^2 \rangle$$

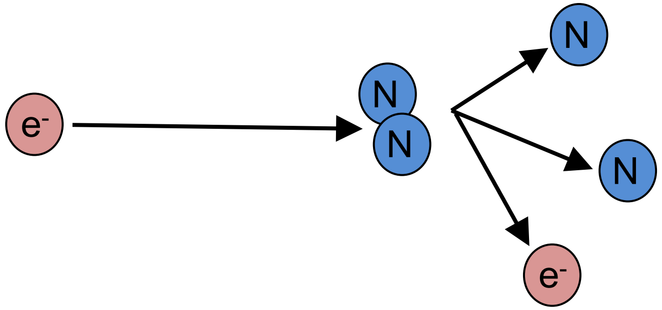
$$\frac{3}{2} k_b T_e = \frac{1}{2} m_e \left(\frac{eE}{m_e} t \right)^2 \qquad \frac{3}{2} k_b T_i = \frac{1}{2} m_i \left(\frac{eE}{m_i} t \right)^2$$

$$T_e \propto \frac{1}{m_e} \qquad T_i \propto \frac{1}{m_i}$$

$$m_e \ll m_i \quad \therefore \quad \boxed{T_e \gg T_i}$$

Plasma Chemistry: Electron Impact Reactions

- Energetic electrons collide with neutral atoms/molecules.
- Elastic Collision (all energies)
  - $e + He \rightarrow He + e$
  - Billiard balls, electron loses energy to gas heating
- **Ionization (4 – 25 eV)**
  - **$e + He \rightarrow He^+ + e + e$**
- Electronic excitation (1-10 eV)
  - $e + He \rightarrow He^* + e$
  - Can emit a photon
- Vibrational excitation (0.1-1 eV)
  - $e + N_2(v=0) \rightarrow e + N_2\ (v \geq 0)$

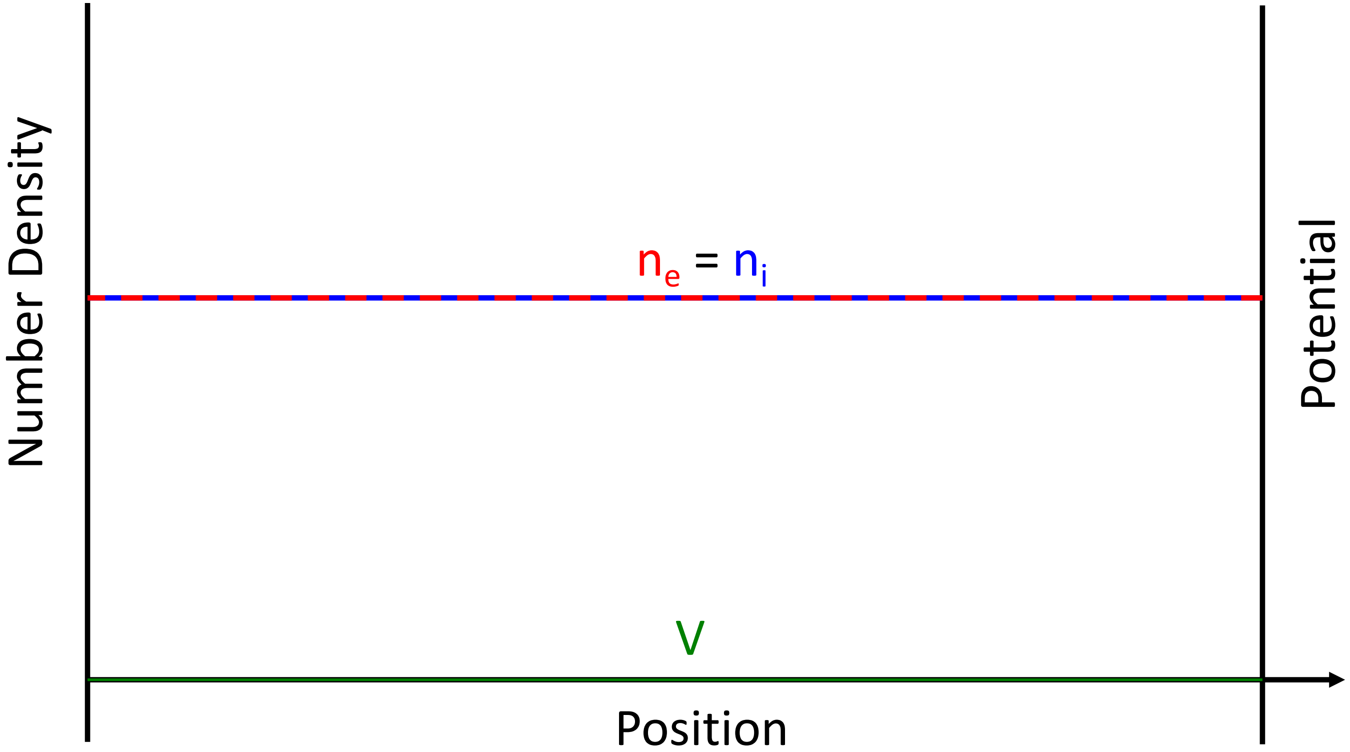


- **Dissociation** (1-15 eV)
  - $e + N_2 \rightarrow N + N + e$
- Dissociative ionization (10-20 eV)
  - $e + N_2 \rightarrow N + N^+ + e + e$
- Attachment (low energy)
  - $e + O_2 + M \rightarrow O_2^- + M$
- Dissociative attachment (low energy)
  - $e + O_2 \rightarrow O^- + O$
- Superelastic collision (low energy)
  - $e + He^* \rightarrow He + e$

SHEATHS

Start with an “ideal” plasma

- Let’s initialize a perfectly uniform plasma
- In a gap between two infinite surfaces.
- n_e = electron number density
- n_i = ion number density



Fluxes to Surfaces

- Flux – the number of particles passing through a surface, per unit area, per unit time.
- The thermal flux in a gas is

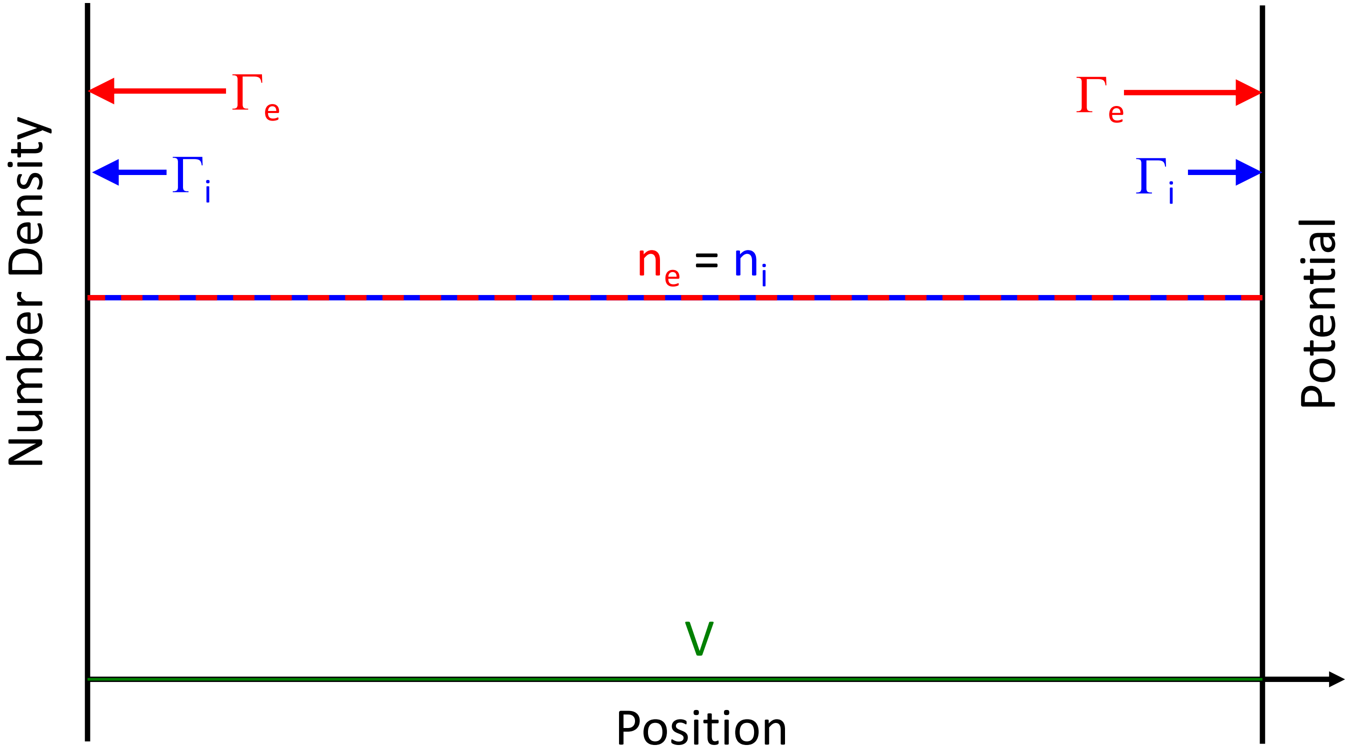
$$\Gamma = \frac{1}{4} n v_{th}$$

- n = number density
- v_{th} = average thermal speed

$$v_{th} = \sqrt{\frac{8k_B T}{\pi m}}$$

- Even if $T_e = T_i$,

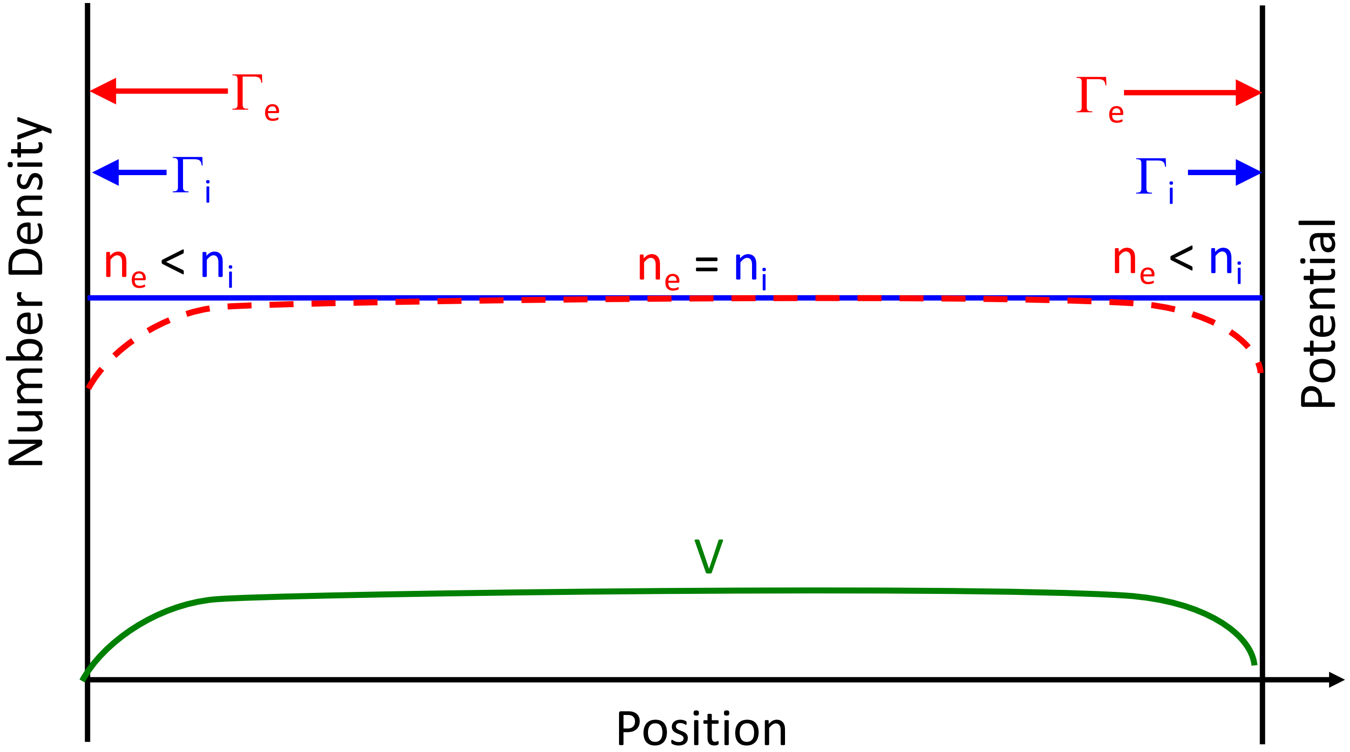
$$m_e \ll m_i \therefore v_{th,e} \gg v_{th,i}$$
$$\Gamma_e \gg \Gamma_i$$



Lose e⁻ faster because they're moving faster!

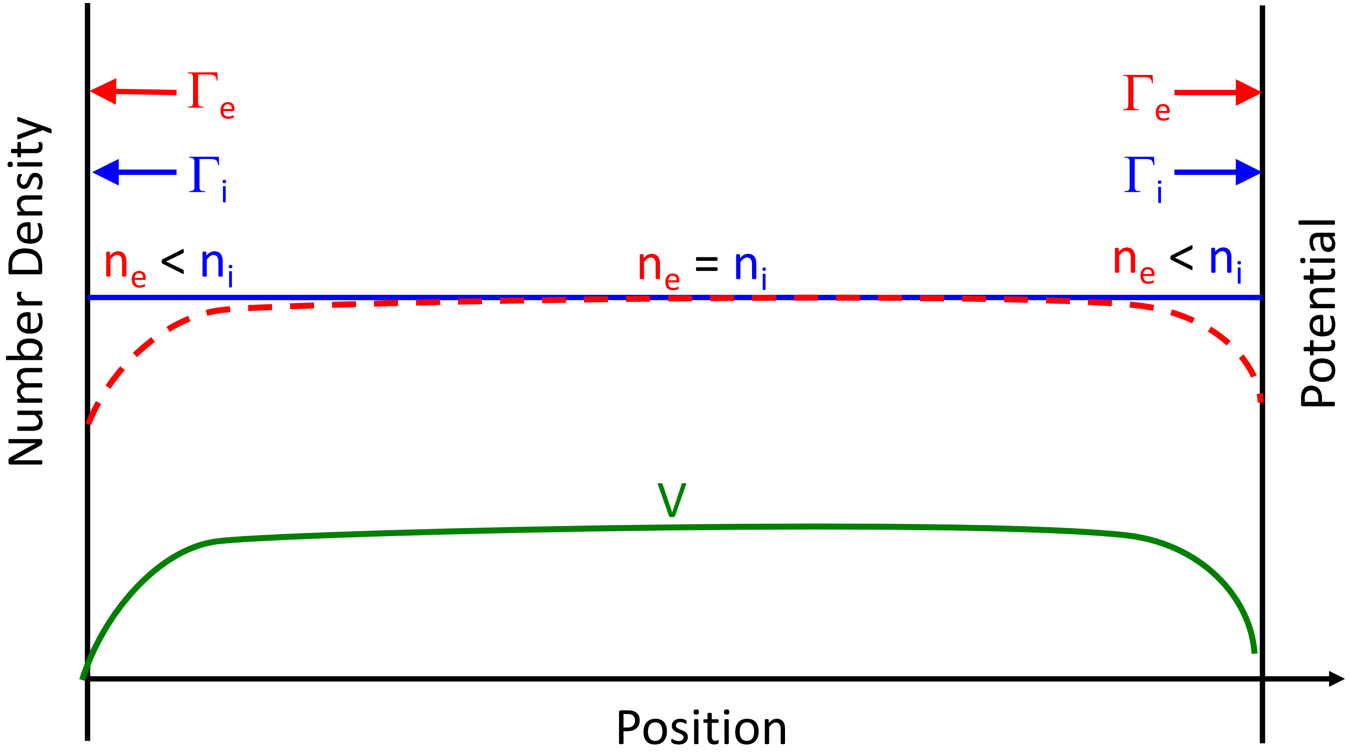
Plasma Potential Develops

- An instant later…
- You only need to lose a very small fraction of the electrons to create a significant electric potential.
- This electric field near the walls changes the fluxes.



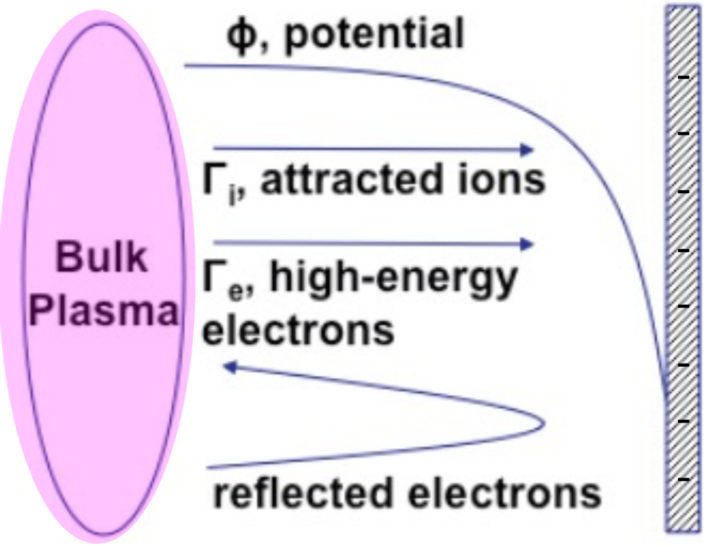
Steady State – Sheath!

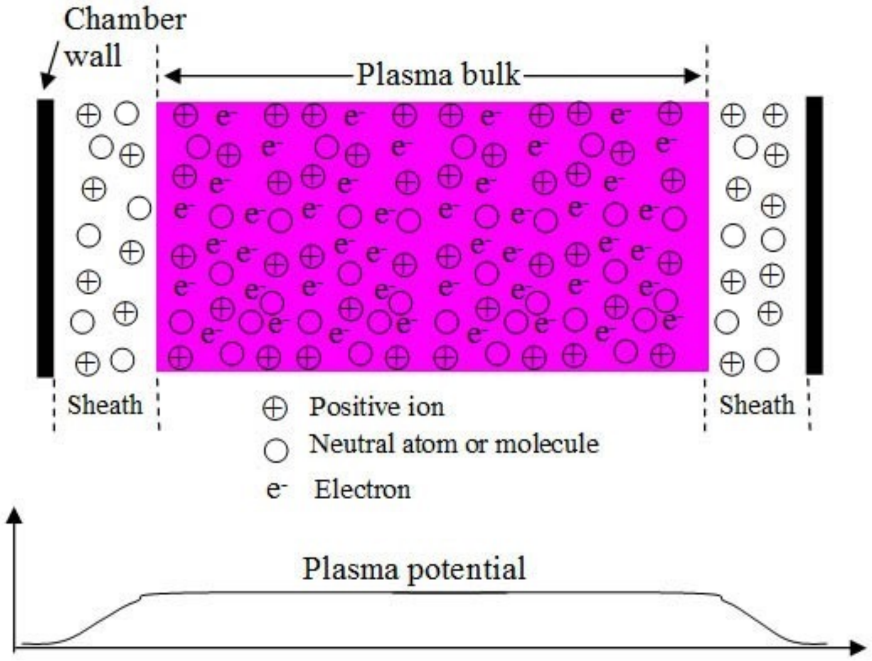
- The self-generated electric field stops growing when the fluxes balance.
- When a charged particle approaches the wall, this potential
    - Decelerates electrons
    - Accelerates ions
- Plasma tends to be the most positive thing in the system.
    - If you apply a positive voltage, the plasma potential will increase above that.



Now we have a sheath!

- Sheath is a few λ_D thick
- Sheaths form at all wall surfaces in contact with the plasma
- The plasma is the most positive thing in the system (“Plasma potential”)
- The potential profile accelerates ions and repels electrons.
- Because electrons are hot, many of them have enough energy to overcome the potential gradient.





ELECTRON ENERGY DISTRIBUTIONS

Plasma Chemistry: Electron Impact Reactions

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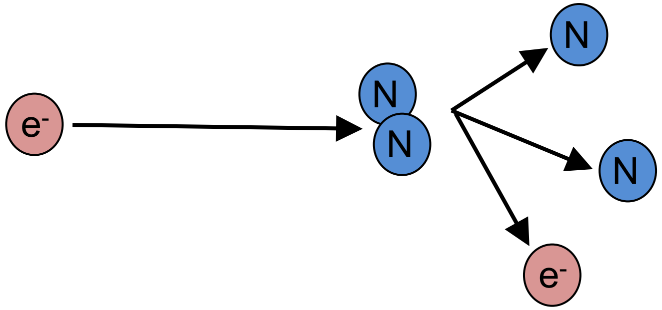

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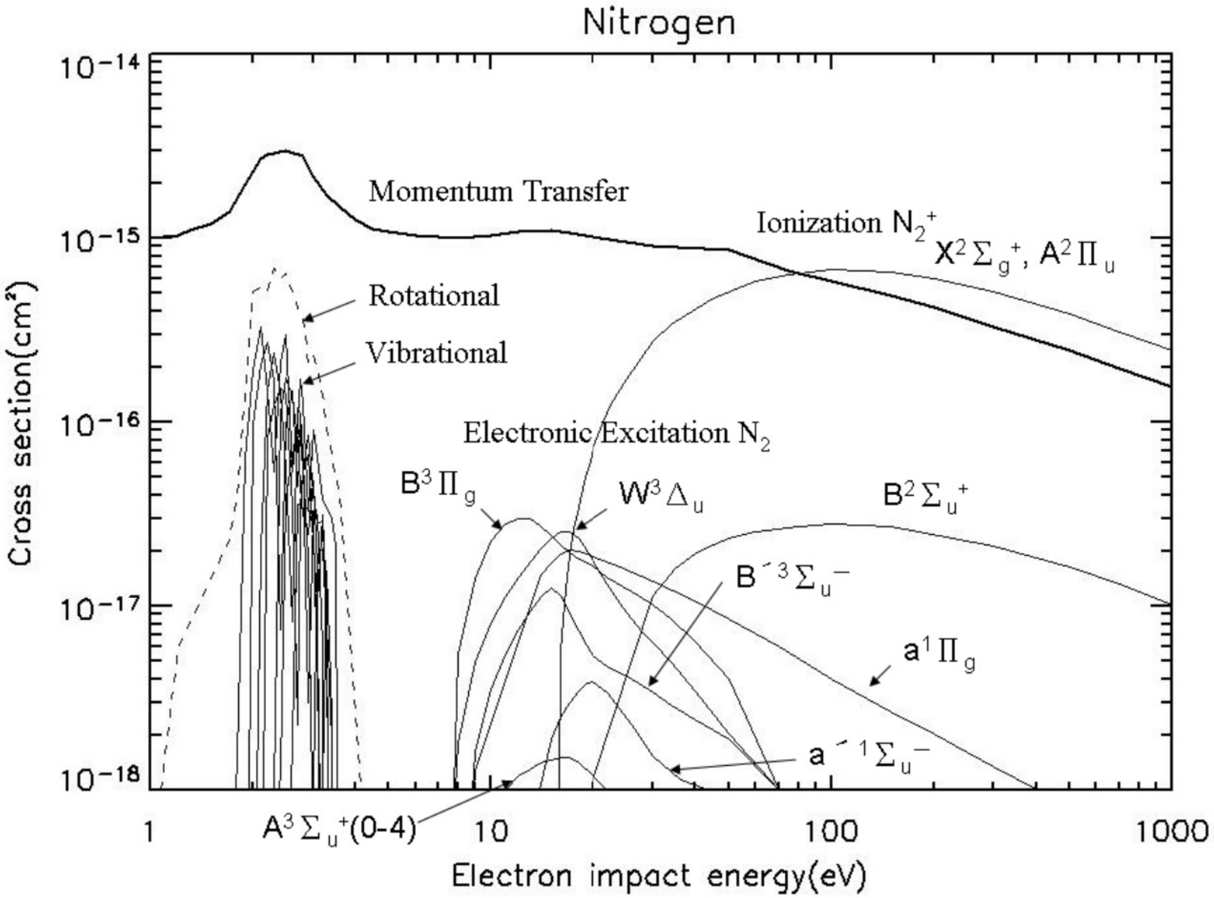
Electron Energy Distribution Functions (EEDFs)

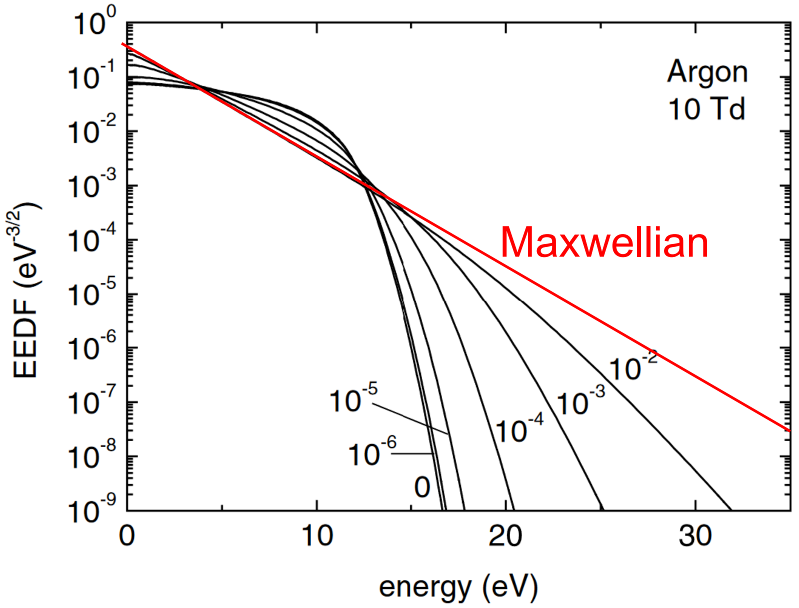


- Must use cross sections (instead of rates) for electron impact reactions.

A. M. Lietz, Introduction to Low Temperature Plasmas

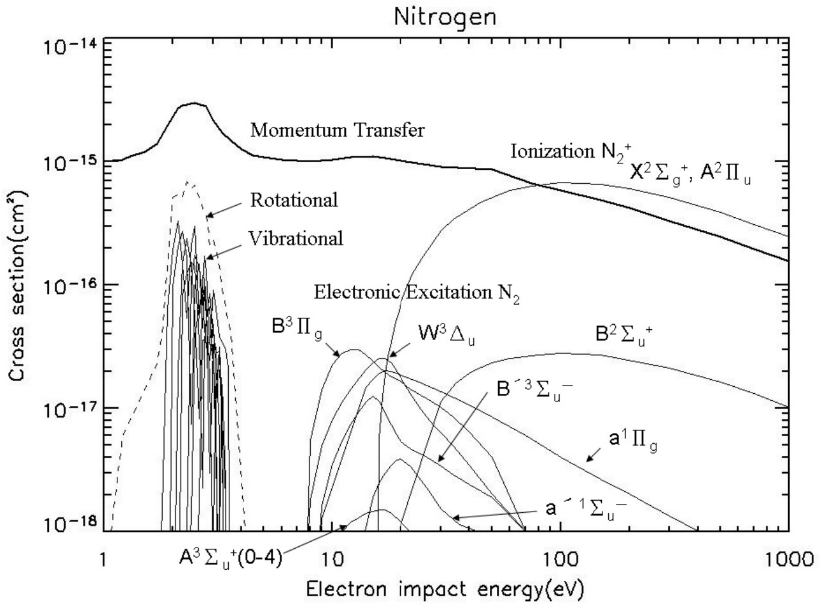
Cheng Ling Kuo, Advances in Spacecraft Systems and Orbit Determination.

Electron Energy Distribution Functions (EEDFs)



Hagelaar, Pitchford. Plasma Sources Sci. Technol. 14, 722 (2005).

- Energy distributions can be significantly non-Maxwellian.
- A Maxwellian distribution is linear in these units.



Cheng Ling Kuo, Advances in Spacecraft Systems and Orbit Determination.

- Must use cross sections (instead of rates) for electron impact reactions.

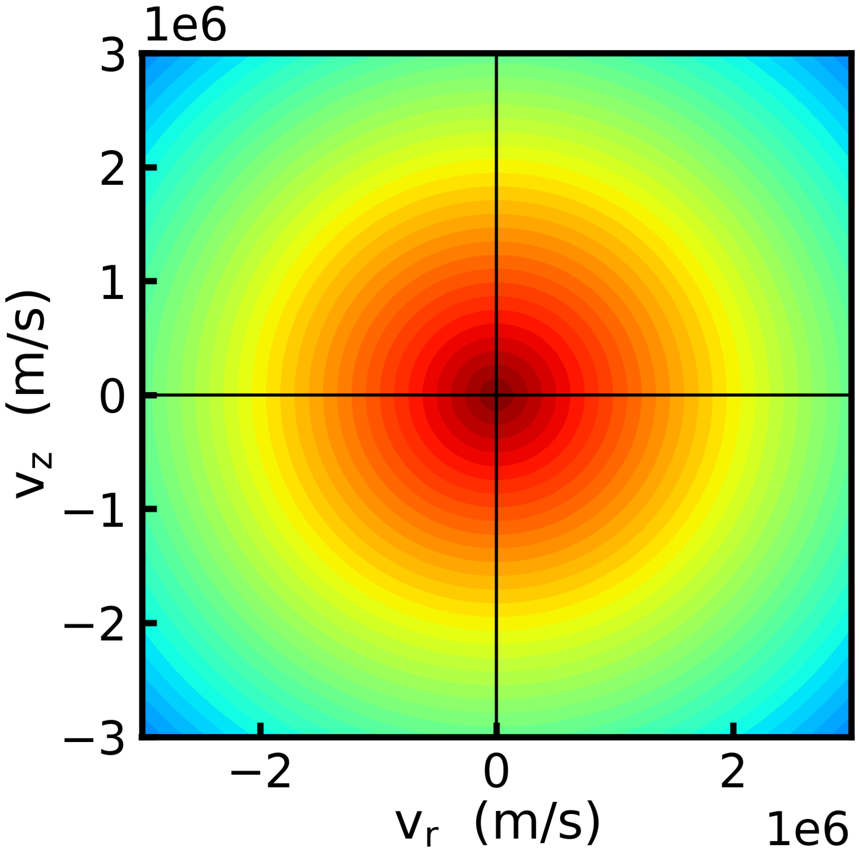
- Solve Boltzmann's equation in 0D using a spherical harmonic expansion of the EEDF:

$$f(\vec{x},\vec{v},t) = f_0(v) + f_1(v)\cos(\theta)$$

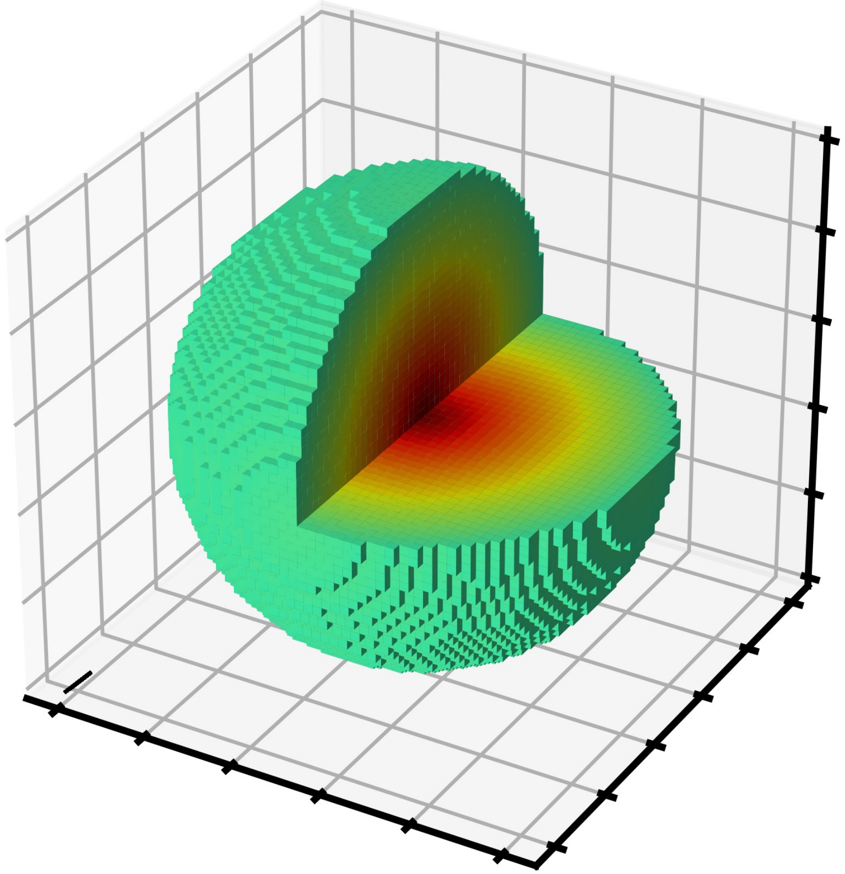
- This is used to calculate reaction rates, $k(T_e)$.
- Sometimes fully kinetic (Monte Carlo) methods are required.

Maxwellian Distribution Function, f(v)

- 2.5 eV
- Units : s^3/m^3

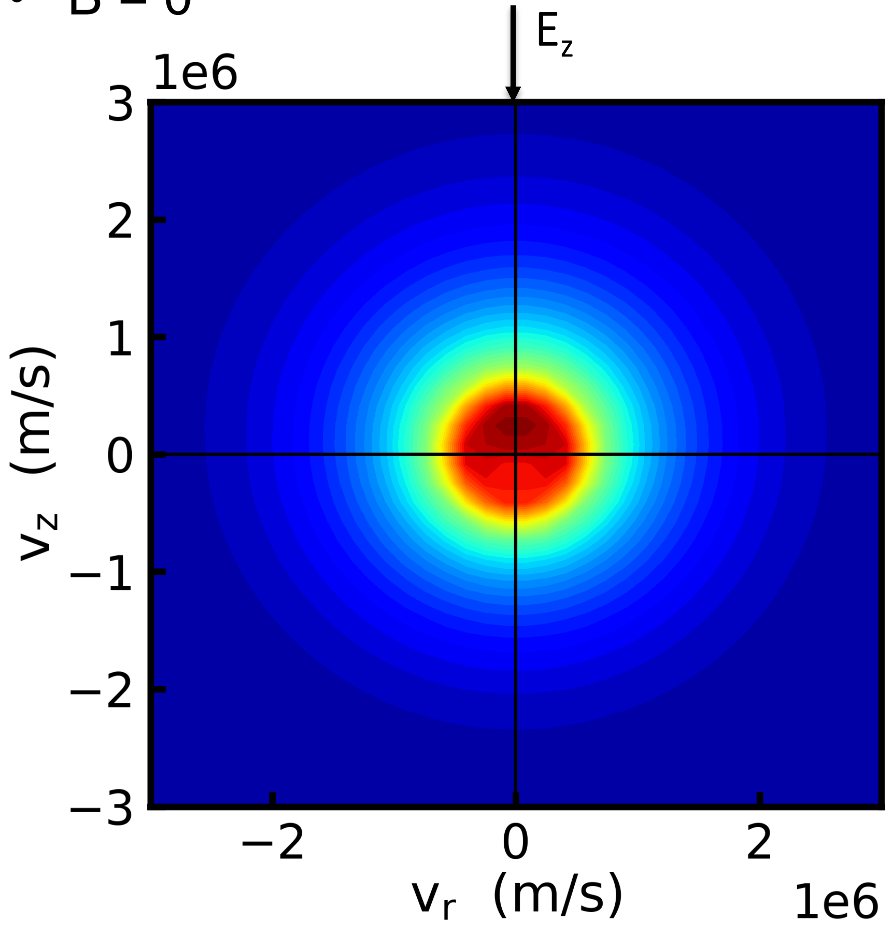


- Same distribution, plotted in 3V space
- Spherical symmetry

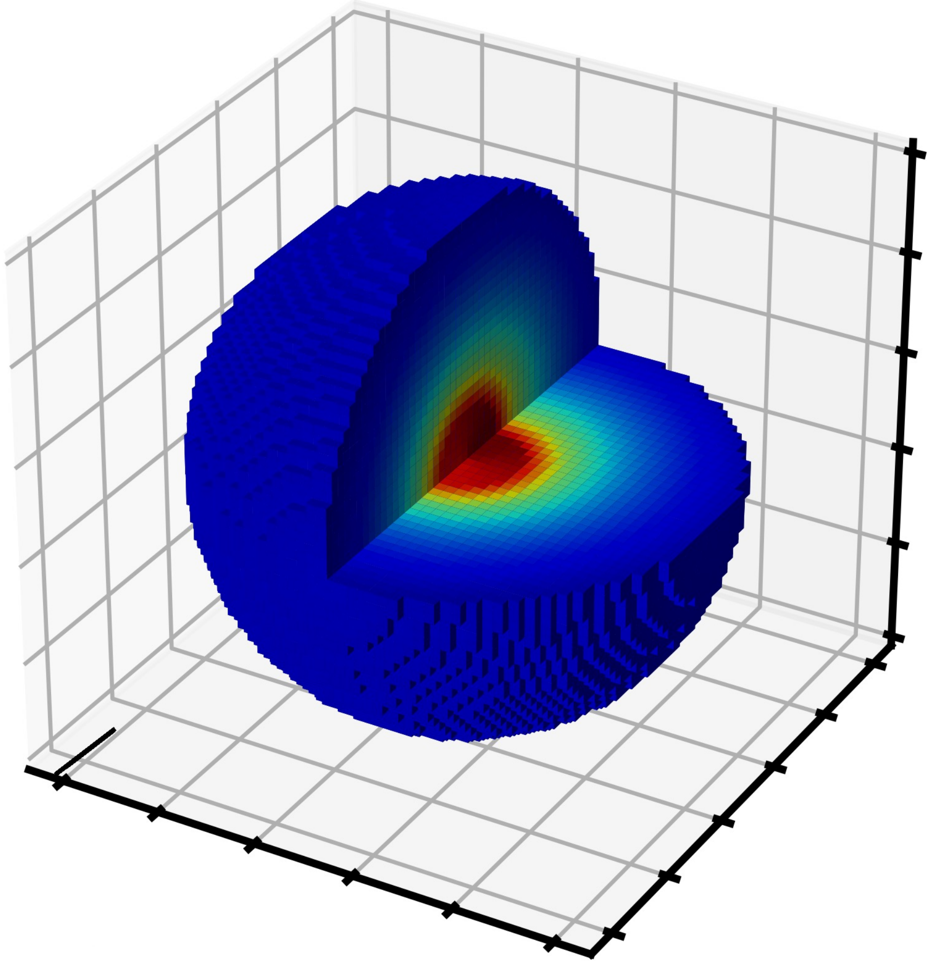


Anisotropic Distribution Functions

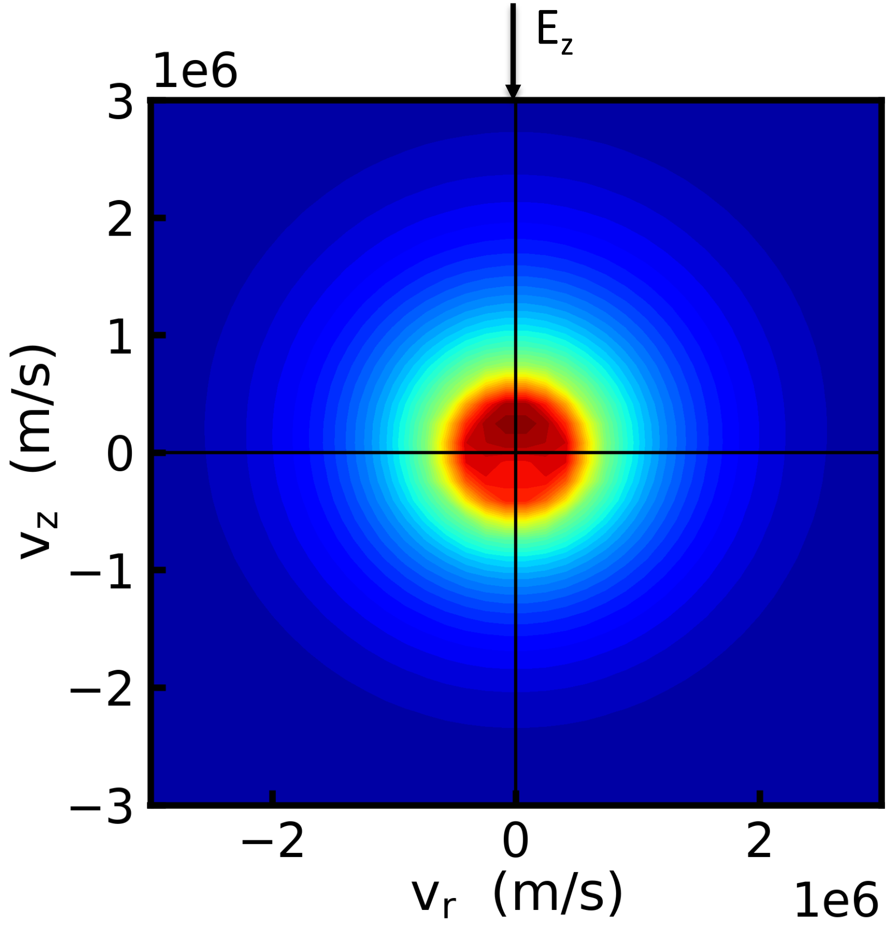
- Add an electric field and neutral collisions
  - Multibolt simulations, 2-term
  - He, Biagi database, E/N = 100 Td
- B = 0



- Same distribution, plotted in 3V space
- Symmetric about E-field axis



What’s the Temperature of this?



- Some say it doesn’t have one.
- Convention in the field:

$$\frac{3}{2}k_B T_e \equiv \int \frac{1}{2} m_e |\vec{v}|^2 f(\vec{v}) d\vec{v}$$

- For Maxwellian, this converges to the standard definition of temperature.

Reduced Electric Field

- E/N is an important parameter in low temperature plasmas.
- E = electric field
- N = gas number density

Electron energy equation

$$\frac{\partial \frac{3}{2} n_e k_b T_e}{\partial t} = \vec{J} \cdot \vec{E} - n_e N k_{elastic}(T_e) \left(\frac{2m_e}{M}\right) \frac{3}{2} k_b \left(T_e - T_g\right) - \sum_i n_e N k_i(T_e) \Delta\varepsilon_i$$

Power Elastic collisions Inelastic collisions

Reduced Electric Field

- E/N is an important parameter in low temperature plasmas.
- E = electric field
- N = gas number density

- The electron energy is a function of E/N (independent of n_e).
  - Based on the assumption that electron neutral-collisions are the main electron energy loss.

- We solve Boltzmann's equation for electrons for a particular E/N in a given gas mixture.
- 1 Td = 10^{-17} Vcm^2

Electron energy equation

$$\cancel{\frac{\partial \frac{3}{2} n_e k_b T_e}{\partial t}} = \vec{j}\cdot\vec{E} - n_e \underset{\uparrow}{N} k_{elastic}(T_e)\left(\frac{2m_e}{M}\right)\frac{3}{2}k_b\left(T_e - T_g\right) - \sum_i n_e \underset{\uparrow}{N} k_i(T_e)\Delta\varepsilon_i$$

Steady state, approximate conductivity

$$T_e = T_g + \frac{2}{3k_b}\frac{M}{2m_e}\left[\frac{e^2}{m_e k^2_{elastic}(T_e)}\left(\frac{E}{N}\right)^2 - \sum_i \frac{k_i(T_e)\Delta\varepsilon}{k_{elastic}(T_e)}\right]$$

NON-EQUILIBRIUM THERMODYNAMICS

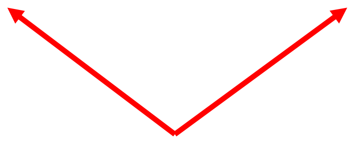
Fighting Thermodynamics

- In most LTPs,

  $T_e >> T_i \sim T_{gas}$
- How do we maintain this high T_e?
- We keep heating the electrons.
- This is much easier in atomic gases (He, Ar) than molecular gases.
- Vibrational/rotation excitation has a low threshold energy, the second term is very large.

Electron energy equation

$$\frac{\partial \frac{3}{2} n_e k_b T_e}{\partial t} = \vec{j} \cdot \vec{E} - n_e N k_{elastic}(T_e) \left(\frac{2m_e}{M}\right) \frac{3}{2} k_b \left(T_e - T_g\right) - \sum_i n_e N k_i(T_e) \Delta\varepsilon_i$$



Decreasing T_e

Fighting Thermodynamics

- Vibrational/rotation excitation has a low threshold energy, the second term is very large.
- Vibrational-translational energy transfer rapidly converts electron energy into gas heating

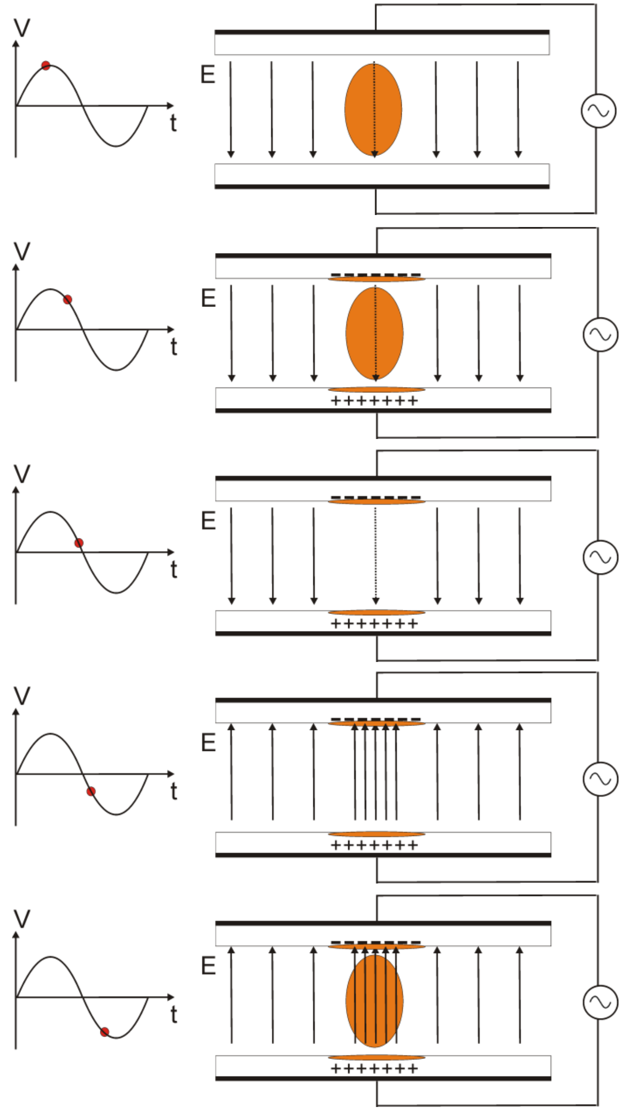
  $N_2(v) + M \rightarrow N_2 + M$
- Short pulses (nanoseconds) can keep $T_{gas} >> T_e$
- Limits total energy deposition so natural heat transfer can keep T_{gas} low.
- The plasma never reaches a steady state.

Electron energy equation

$$\frac{\partial \frac{3}{2} n_e k_b T_e}{\partial t} = \vec{j} \cdot \vec{E} - n_e N k_{elastic}(T_e) \left(\frac{2m_e}{M}\right) \frac{3}{2} k_b (T_e - T_g) - \sum_i n_e N k_i (T_e) \Delta\varepsilon_i$$

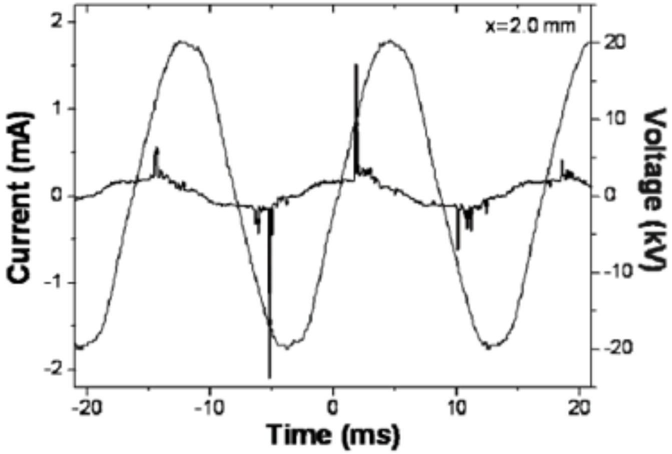
Dielectric Barrier Discharges (DBDs)

- At atmospheric pressure, high collisionality results in short timescales and rapid evolution.
- Need to limit the energy deposition, prevent arc formation and gas heating.
- Dielectric barrier discharges (DBDs) – a pulsed discharge in which at least one electrode is covered by a dielectric.
- Discharges last ~10^{-8} s, repeat every ~10^{-3} s.



J.-C. Wang, PhD Thesis, (Univ. of Michigan, 2014).

Y. Hosokawa et al., J. Phys. D: Appl. Phys., 41, 205418 (2008).

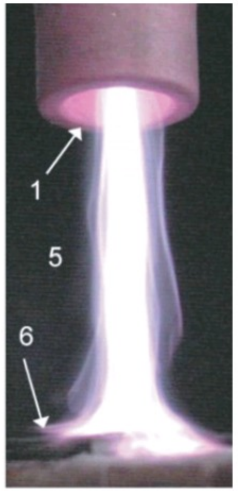


K. G. Kostov, et al., Brazilian J. of Phys. 39, 322 (2009).

LTP APPLICATIONS

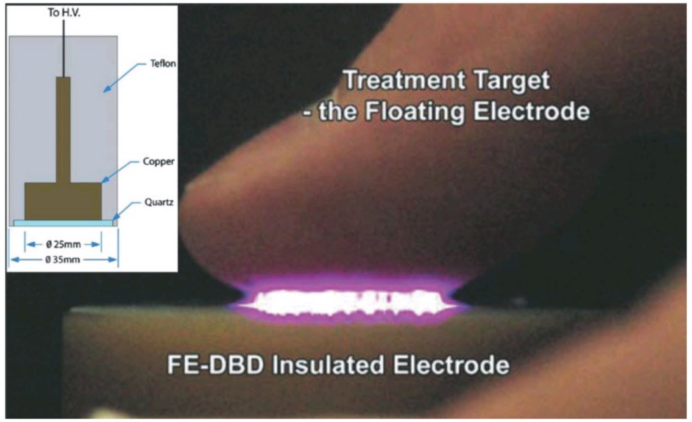
Plasma Medicine

- Atmospheric pressure plasma treatment
  - Improves wound healing
  - Selectively kills cancer cells
  - Kill bacteria
  - Heal dermatological lesions
- Reactive oxygen and nitrogen species are thought to be responsible: OH, O, HO_2, NO, etc.
- Low temperatures are required.
- Dielectric barrier discharges (DBD) and atmospheric pressure plasma jets (APPJs) are popular types of sources.
- Tissue is generally covered in a thin liquid layer of biological liquid.



K. D. Weltmann et al., J. Phys. D: Appl. Phys. 41, 194008 (2008).

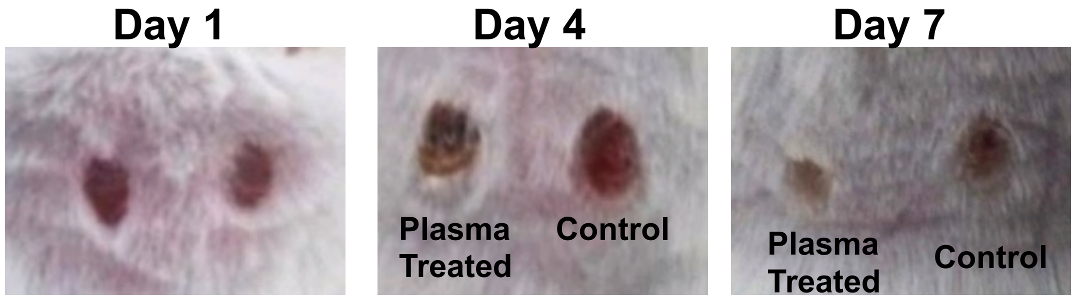
G. Xu, X. Shi, J. Cai, S. Chen and P. Li, Wound Repair Regen. 23, 878 (2015).



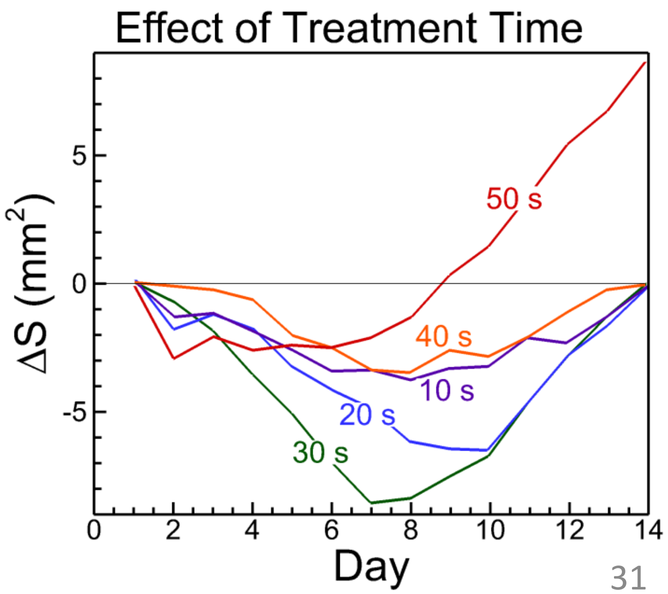
G. Fridman et al., Plasma Chem. Plasma Process. 26, 425 (2006).

Wound Healing

- An example of a typical plasma medicine study.
- Two wounds were generated on each mouse, and one was plasma treated.
- ΔS = area of plasma treated – area of control (averaged over all mice)
- Optimal healing with 30 s of plasma treatment each day.
- Currently these effects cannot be attributed to a single reactive species.

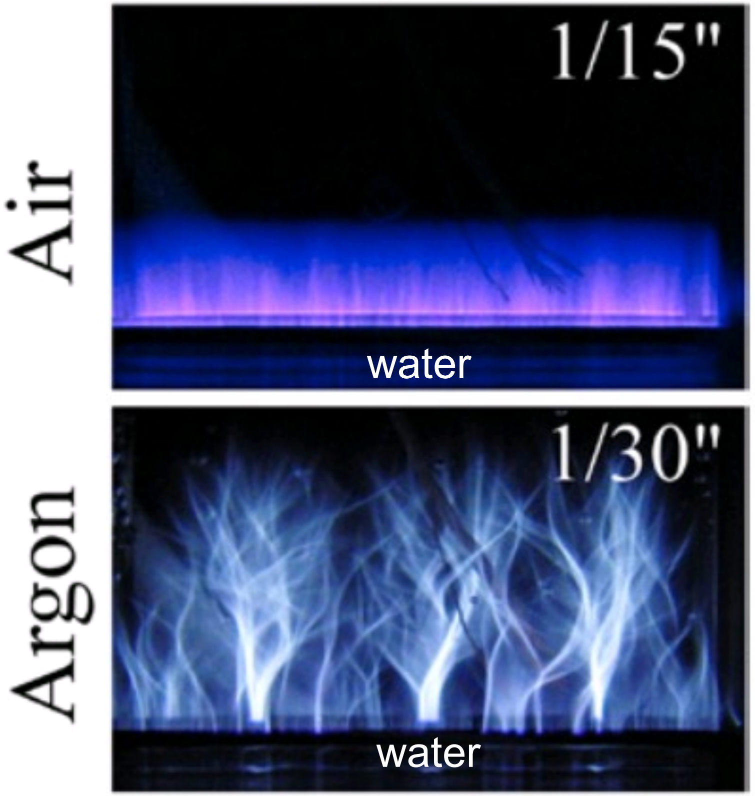


G. Xu, X. Shi, J. Cai, S. Chen and P. Li, Wound Repair Regen. 23, 878 (2015).



Water Treatment

J. E. Foster, Phys. Plasmas 24, 055501 (2017)

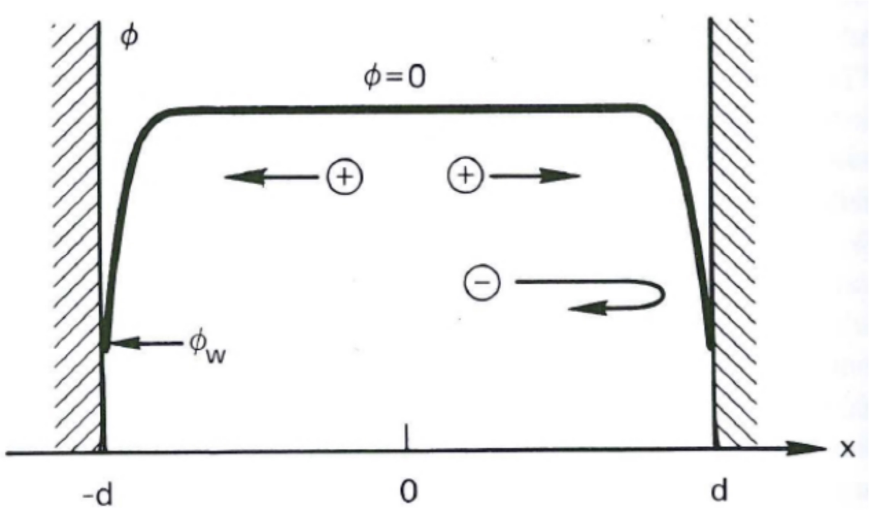


O. Galmiz, et al., J. Phys. D. Appl. Phys. 49, 65201 (2016).

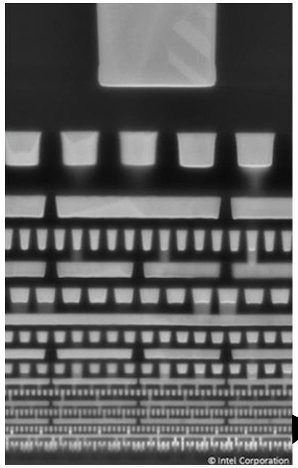
- Plasmas have been used to create O_3 for water treatment since the 1800s.
- Direct treatment of water with plasma is an emerging application.
- Targeting removal of PFAS ‘forever chemicals’.
- For must be extremely scalable, rapid, and inexpensive (usually in air).

Semiconductor Processing

- When a plasma contacts a surface, a sheath develops:
  - Electrons diffuse faster than ions.
  - Plasma potential becomes positive.
  - E-field develops which retains e-, accelerates ions.
- This results in ions reaching the surface with significant energy (a few eV to keV).
- Anisotropy occurs.
- Reactive neutrals (e.g. Cl, F) formed from plasma chemistry work synergistically with ions for rapid etching.
- Plasmas are also used to deposit thin films.
- Without plasmas, computer chips would be stuck in the late 1980s or early 1990s.
- Features are approaching atomic scales: atomic layer etching (ALE) and atomic layer deposition (ALD).



A. Galata, Physics and Technology of the SPES Charge Breeder (2005).



30 nm features

https://www.anandtech.com/show/17448/intel-4-process-node-in-detail-2x-density-scaling-20-improved-performance

Plasma for the Grand Challenges

Make Solar Energy Economical

- Thin film deposition for photovoltaics.
- Nanostructures.
- Use solar power to produce chemical fuels.

Engineer Better Medicines

- Killing drug-resistant pathogens.
- Cancer treatments.
- Wound healing.
- Nanoparticle production.

Provide Access to Clean Water

- Destruction of PFAS.
- Ozone generation.

Provide Energy From Fusion

- Temperatures of 10^5 eV.
- Low temperature plasmas occur near the walls in magnetic confinement fusion.

National Academy of Engineering
http://www.engineeringchallenges.org/challenges.aspx

Plasma for the Grand Challenges

Manage the Nitrogen Cycle

- Plasma nitrogen fixation to produce ammonia.
- Direct production of nitrate.

Develop Carbon Sequestration Methods

- Plasma dissociation of CO_2 into CO.
- Conversion of CO_2 into useful chemicals.

Engineer the Tools of Scientific Discovery

- Mass spectrometers.
- Plasma thrusters for space exploration.
- Quantum computing.

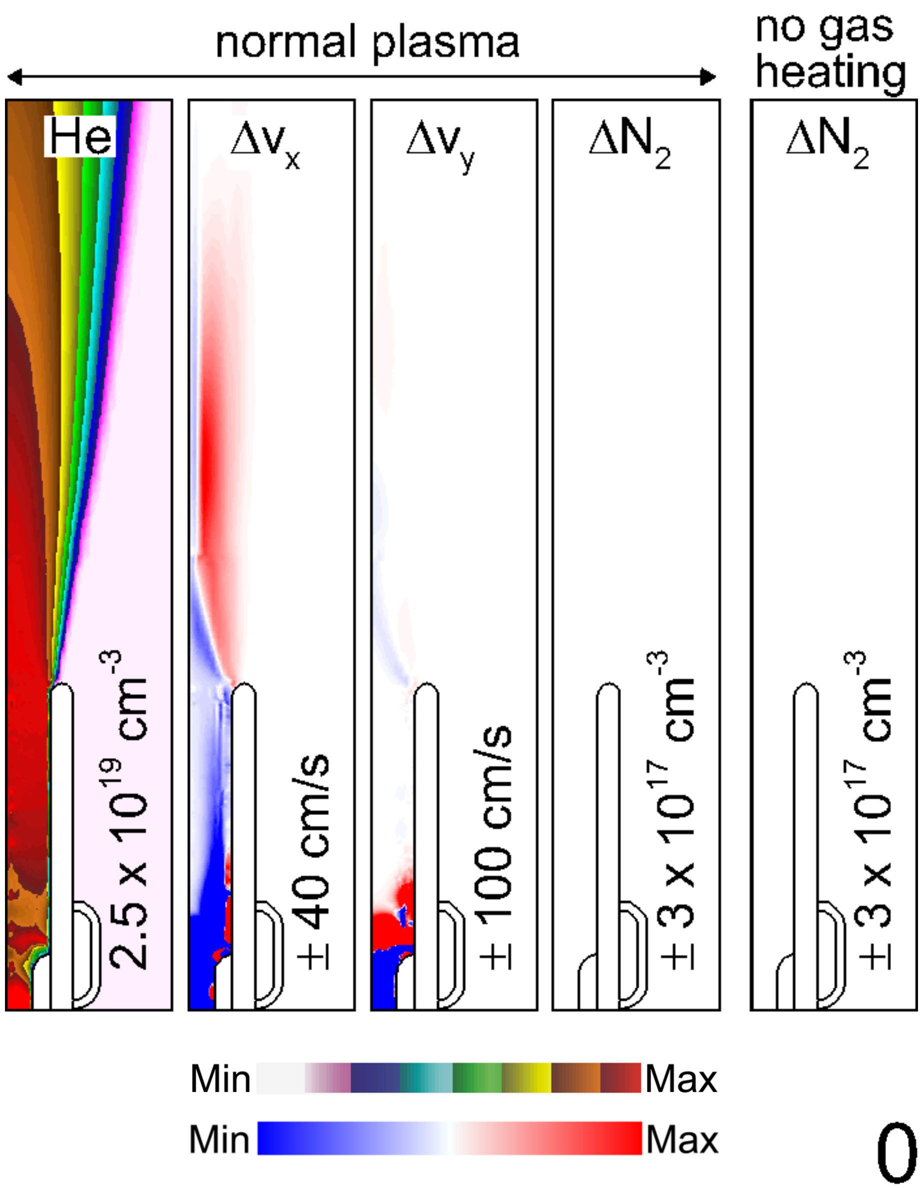
Chips Impact EVERY Challenge

- Advance Personalized Learning
- Enhance Virtual Reality
- Reverse Engineer the Brain
- Advance Health Informatics
- Restore and Improve Urban Infrastructure
- Secure Cyberspace
- Prevent Nuclear Terror

COMPUTATIONAL MODELING

What can we really learn from modeling?

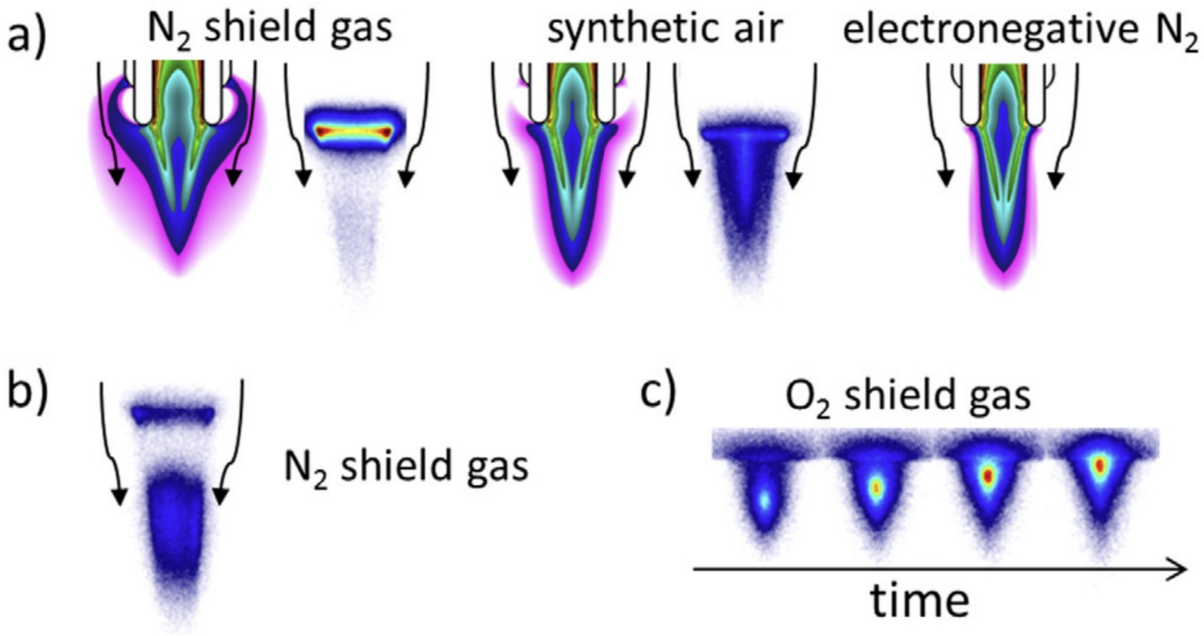
- Helium atmospheric pressure plasma jet.
- Cylindrical symmetry.
- He flows into air.
- Localized heating at the cathode expand launching an acoustic wave.
- Perturbs shear flow.
- We can turn off gas heating!
    - Without changing dissociation, buoyancy, ion wind.



Animation Slide

What can we really learn from modeling?

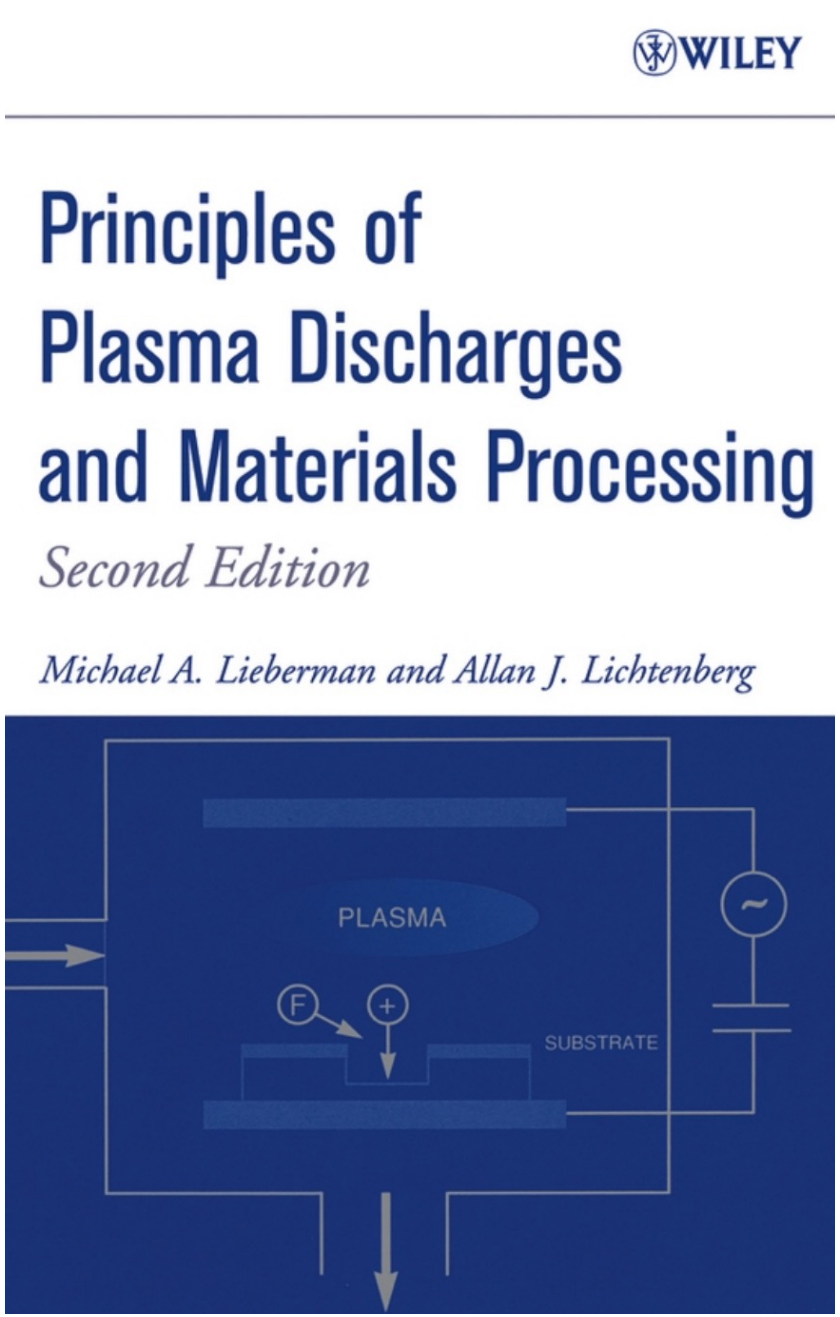
- He atmospheric pressure plasma jet
- Surrounding gas flow (shield gas) observed to influence plasma dynamics from optical emission measurements.
- But why?
- Comparison with a fluid model.



A. Schmidt-Bleker, et al., Plasma Sources Sci. Technol., 24, 035022 (2015).

References

- “Principles of Plasma Discharges and Materials Processing” M. A. Lieberman and A. J. Lichtenerg


WILEY

Principles of Plasma Discharges and Materials Processing

Second Edition

Michael A. Lieberman and Allan J. Lichtenberg

Quick Review

- E/N (Reduced Electric field) is the scaling parameter for LTPs.
  - Acceleration between collisions.
- $T_e >> T_i \sim T_{gas}$
  - Electrons are lighter, more energy is transferred to electrons than ions.
  - We must deposit power to achieve this.
- Sheaths form at surfaces, trapping electrons in the plasma, accelerating ions toward surfaces.
  - These fast ions can be used for etching.
- “Principles of Plasma Discharges and Materials Processing” M. A. Lieberman and A. J. Lichtenerg