Physics of Low Temperature/Non-Equilibrium Plasmas

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June 22nd 2022, SULI Introduction to Fusion Energy and Plasma Physics Course
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
PRINCIPLES OF PLASMA DISCHARGES AND MATERIALS PROCESSING

Michael A. Lieberman
Allan J. Lichtenberg

Topical Review

The 2017 Plasma Roadmap: Low temperature plasma science and technology

Yu. P. Raizer

Topical Review

Foundations of atmospheric pressure non-equilibrium plasmas

Peter J Bruggeman, Felipe Iza and Ronny Brandenburg
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
- 4th 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 Spherical Tokamak at PPPL
- Manage the nitrogen cycle
- Engineer the tools for scientific discovery
- Improve CO₂ sequestration

Perovskite solar cell

Electric propulsion for spacecraft

Star Wars twin ion engine fighters

Plasma-assisted ammonia synthesis

Aihara et al. ChemComm(2016)
LT Plasmas Impact our Every-day Life

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 H₂ 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

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

Anisotropic Plasma Etching

Plasmas and Applications: Thermal VS Non-Thermal

Thermal plasmas:
\[ T_g \sim T_e \ (2,000\text{-}10,000 \ \text{K}) \]

Non-thermal plasmas:
\[ T_g \ll T_e \ (10,000 \ \text{K}) \]
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 ($T_g$): $T_g << T_e$
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: $T_e \sim 1-10\ eV$
- 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 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:

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

\[
\lambda_{De} = \left(\frac{\varepsilon_0 T_e}{en_e}\right)^{\frac{1}{2}}
\]

\[
\lambda_{De}(cm) = 740\sqrt{\frac{T_e}{n_e}}
\]

- For \( T_e = 4 \text{ eV} \) and \( n_e = 10^{10} \text{ cm}^{-3} \), \( \lambda_{De} \approx 148 \mu\text{m} \) (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

<table>
<thead>
<tr>
<th></th>
<th>JET Tokamak</th>
<th>Atmospheric pressure plasmas</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Power</strong></td>
<td>~16 MW</td>
<td>10^{-2} – 10 W</td>
</tr>
<tr>
<td><strong>Volume</strong></td>
<td>~ 100 m³</td>
<td>~ 10^{-8} m³ (10 mm³)</td>
</tr>
<tr>
<td><strong>Power density</strong></td>
<td>10⁶ W m⁻³</td>
<td>10⁶-10⁹ Wm⁻³</td>
</tr>
<tr>
<td><strong>Ionization degree</strong></td>
<td>FULL</td>
<td>10⁻⁵ – 10⁻²</td>
</tr>
<tr>
<td><strong>Temperature</strong></td>
<td>T_e = T_g =10⁸ K</td>
<td>T_e = 10³-10⁴ K</td>
</tr>
<tr>
<td></td>
<td></td>
<td>T_g = 300 – 3000 K</td>
</tr>
<tr>
<td><strong>Pulse duration</strong></td>
<td>~1 s</td>
<td>~ 10 ns up to DC</td>
</tr>
</tbody>
</table>
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**: $e^- + \text{Ar} \rightarrow \text{Ar} + e^-$
- **Electronic excitation collisions**: $e^- + \text{Ar} \rightarrow \text{Ar}^* + e^- \rightarrow \text{Ar} + e^- + \text{photons}$
- **Ionizing collisions**: $e^- + \text{Ar} \rightarrow \text{Ar}^+ + e^- + e^-$
- **Cross sections from different databases are compiled on the LXCAT website**: https://us.lxcat.net/
  - Databases: IST-Lisbon, Morgan, Phelps, Itikawa, Triniti, Hayashi, …
  - $1 \text{ eV} \sim 1.6 \times 10^{-19} \text{ J}$
Where does the energy from the electrons go?

- **E/N**, electric field divided by total number density

- 1 Td (Townsend) = $10^{-17} \, \text{V.cm}^2$

- 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

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:

\[ W_L = \text{final energy for particle } m_2 \]
\[ W = \text{initial energy for particle } m_1 \]

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

\[ \theta_2 = \frac{\pi}{2} - \frac{\theta_{CM}}{2} \]

• 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: \(T_e \gg T_g\)

- 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: \(T_{\text{ion}} \sim T_g\)
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

- 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 $\frac{3}{2}$ eV
Rate Coefficients

Electron-Argon Rate Coefficients

- Rate coefficient is the average of the cross section $\sigma (V_R)$ of the process over the Maxwellian distribution

- $K(T_e) = <\sigma V_R>_{\text{Maxwellian}}$

- $V_R$ = 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
• About 12 orders of magnitude in timescales
• Integrating timestep (stability, accuracy): $\Delta t$
• Dynamic timescale (to resolve the evolution of plasma phenomena): $\Delta T$
Case Study #1: Plasma-Assisted Ignition
C$_2$H$_4$ Ignition below Auto-ignition Temperature

- 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

OH emission from plasma and flame

Case Study #2: Inactivation of Viruses and Bacteria
RONS from Air Plasmas for Virus Inactivation

- Reactive components from plasma chemistry: \( \text{O}_3, \text{NO}_x, \text{OH}, \text{O}, \text{H}_2\text{O}_2, \text{N}_2^+, \text{O}_2^+, \text{O}_2^-, \text{UV light, e}^- \)
- Comparison of surface decontamination efficiency of 4 different plasmas
- Strong correlations between generation of gas phase \( \text{N}_2\text{O}_5 \) and inactivation

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

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$_2$O 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

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

<table>
<thead>
<tr>
<th>Species</th>
<th>$\beta$</th>
<th>$\gamma$</th>
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<tbody>
<tr>
<td>O$^-$</td>
<td>$10^{-4}$</td>
<td>$(1.9 \pm 0.1) \times 10^{-5}$</td>
</tr>
<tr>
<td></td>
<td>$10^{-3}$</td>
<td>$(3.2 \pm 0.2) \times 10^{-5}$</td>
</tr>
<tr>
<td></td>
<td>$10^{-2}$</td>
<td>$(1.4 \pm 0.2) \times 10^{-4}$</td>
</tr>
<tr>
<td>H$^+$</td>
<td>$10^{-5}$</td>
<td>$&lt;8.3 \times 10^{-6}$</td>
</tr>
<tr>
<td></td>
<td>$10^{-3}$</td>
<td>$&lt;1.8 \times 10^{-5}$</td>
</tr>
<tr>
<td>OH</td>
<td>$10^{-3}$</td>
<td>$(2.8 \pm 0.1) \times 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>$10^{-2}$</td>
<td>$(5.750 \pm 0.001) \times 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>$10^{-1}$</td>
<td>$(3.5 \pm 0.1) \times 10^{-2}$</td>
</tr>
</tbody>
</table>

Luan et al, J. Phys. D: Appl. Phys. 50 (2017) 03LT02
Kondeti et al, J. Vac. Sci. Technol. A 38(3)
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

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!