MODELING ELECTRONEGATIVE PROCESSES IN PLASMAS*

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AGENDA

- Physics of electronegative plasmas…What is different?
- Modeling strategies for electronegative plasmas.
- Examples from low pressure systems
- Examples from high pressure systems
- Concluding remarks

MODELING ELECTRONEGATIVE PLASMAS

- **This could be a very short talk…..**
- **There is nothing fundamentally different about modeling electronegative plasmas from electropositive plasmas.**
- **You just need to account for "all the physics"…..**
- **The better your awareness of the physics, the more accurate your model will be.**
- **However…..**

MODELING ELECTRONEGATIVE PLASMAS

- **Modeling electronegative plasmas is all about *plasma chemistry*.**
- **To some degree, all electropositive plasmas look alike.**
- **To model electronegative plasmas well, one must address the unique molecular physics of your feedstock gases, their fragments and products.**
- **This is what we also call physical chemistry; the physics of bonds in molecules.**
- **The better your awareness of the physical chemistry, the more accurate your model will be.**
- **Let's begin with how the bonds in molecules determine your negative ion plasma chemistry.**

DISSOCIATIVE ATTACHMENT

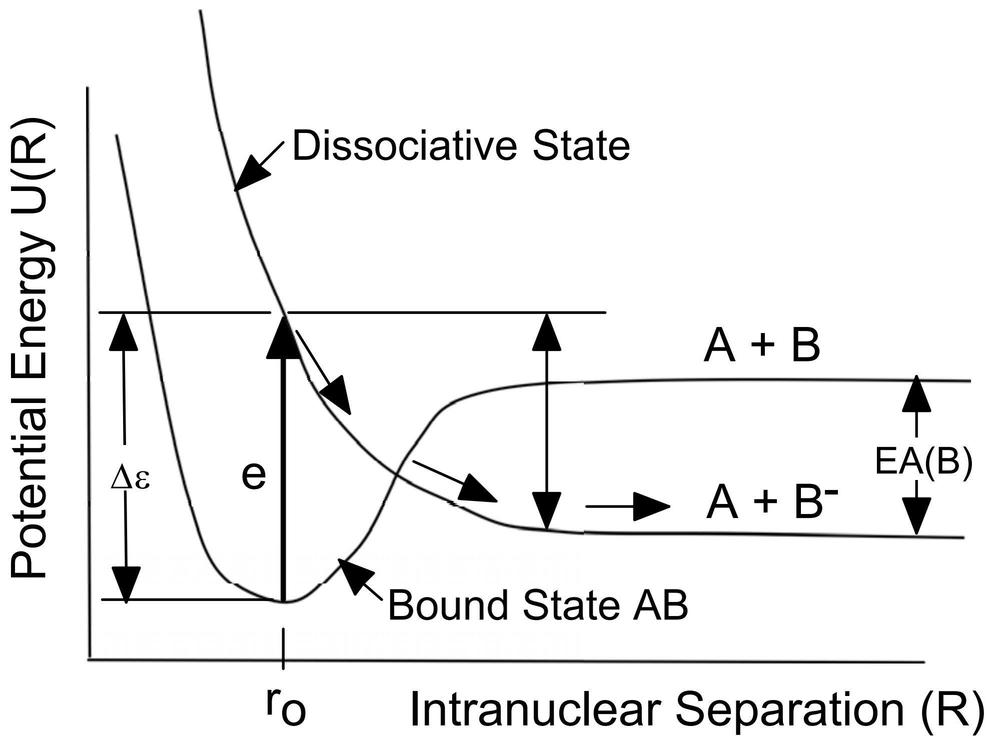
- **The majority of negative ions formed in low pressure plasmas are by dissociative excitation of molecular species.**

e + AB → A + B-

Δε = electron threshold energy

ΔT = kinetic energy of fragments

EA(B) = Electron affinity of B



- **The molecule is excited to either a real or virtual state which has a curve crossing with a dissociative state. The fragments may be produce with significant kinetic energy.**

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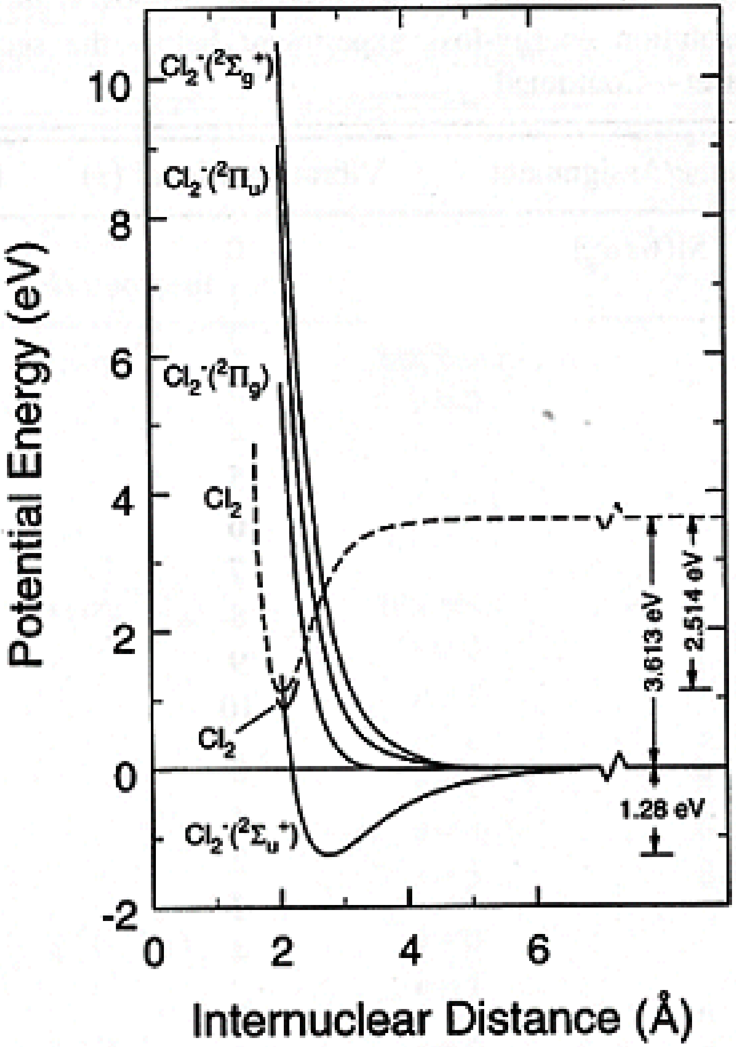
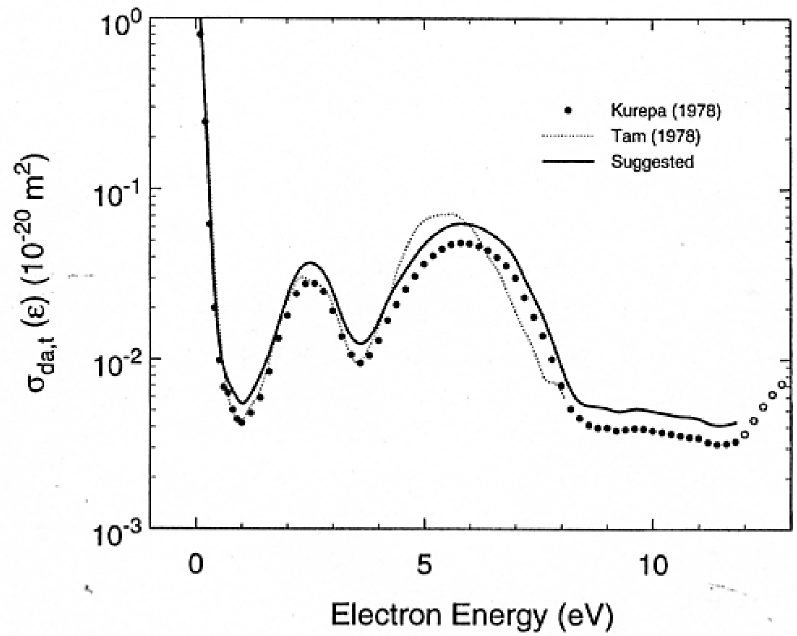
THERMAL DISSOCIATIVE ATTACHMENT



- If the dissociative curve cuts through the bottom of the bound state potential well ($r=r_o$), electrons of "zero" energy can initiate the dissociative attachment.
- Example: $e + Cl_2 \rightarrow Cl + Cl^-$



- Ref: Christophorou, J. Phys. Chem. Ref. Data 28, 131 (1999)

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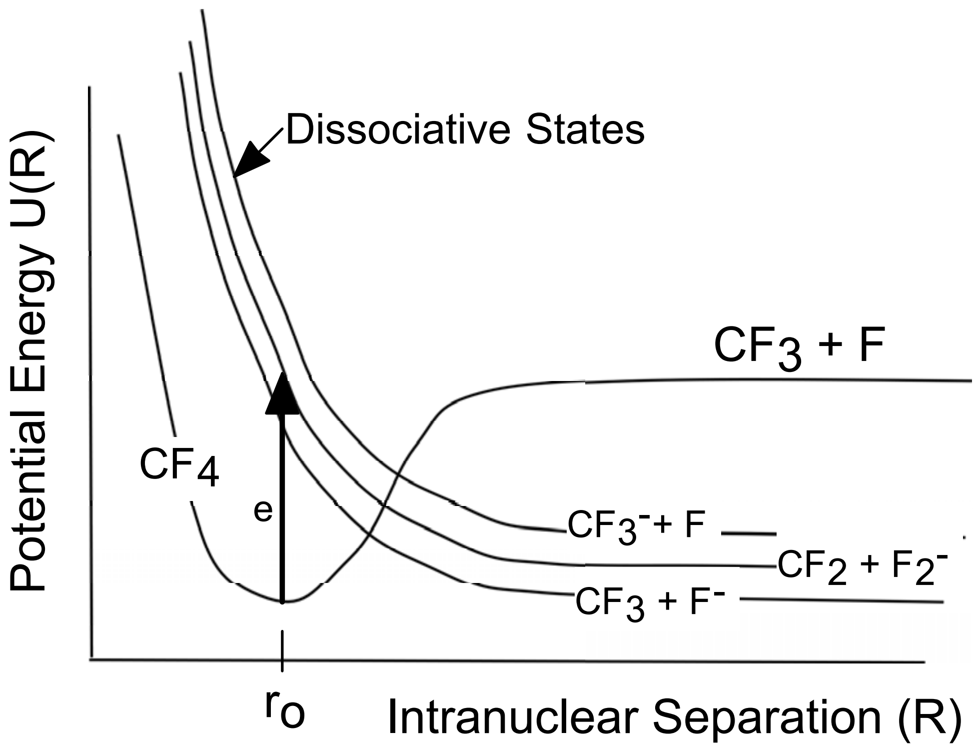
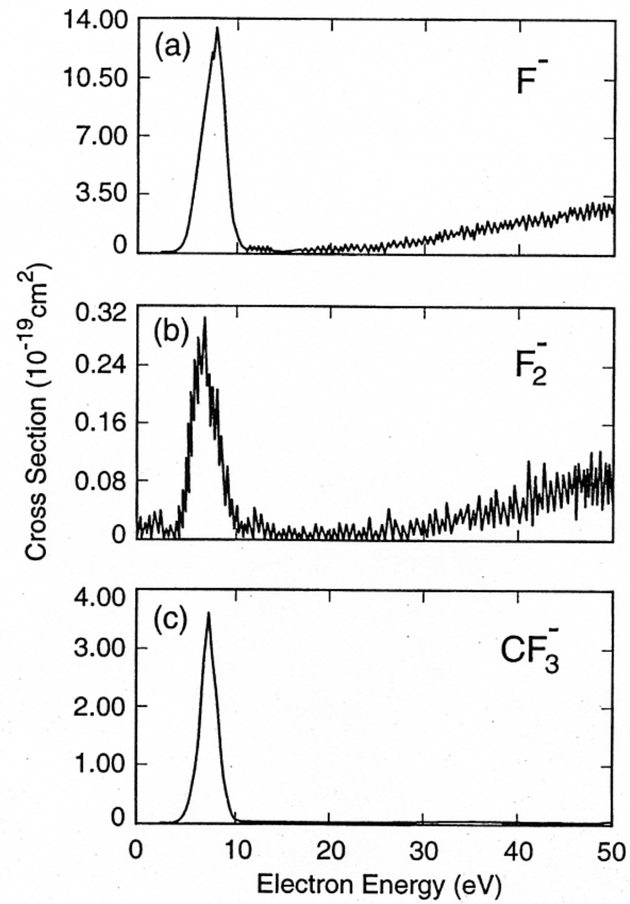
INELASTIC DISSOCIATIVE ATTACHMENT

- **Dissociative curve intersects potential well at $r > r_o$. Conservation of momentum ($\Delta r=0$) results in a finite threshold energy.**

- **Example: $e + CF_4 \rightarrow$ F-, CF_3-, F_2-**





- **Ref: Christophorou, J. Phys. Chem. Ref. Data 25, 1341 (1996)**

3-BODY NON-DISSOCIATIVE ATTACHMENT

- When the attachment is non-dissociative (e.g., $e + O_2 \rightarrow O_2^-$) a 3[rd] body is usually required to dissipate the momentum of the incoming electron.

- The actual attachment process is a series of 1[st] and 2[nd] order events.

$$e + O_2 \xrightarrow{k_1} \left(O_2^-\right)^*$$ ***Attachment***

$$\left(O_2^-\right)^* \xrightarrow{\tau} e + O_2$$ ***Autodetachment***

$$\left(O_2^-\right)^* + M \xrightarrow{k_2} O_2^- + M$$ ***Stablization***

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3-BODY ATTACHMENT: EFFECTIVE 2-BODY RATE

- **The effective two body rate coefficient demonstrates the low pressure regime where stablization is slow; and the high pressure limit where autodetachment is not important.**

$$\frac{d\left[\left(O_2^-\right)^*\right]}{dt} = [e][O_2]k_1 - \left[\left(O_2^-\right)^*\right]\left(\frac{1}{\tau} + Mk_2\right) \approx 0$$

$$\left[\left(O_2^-\right)^*\right] \approx \frac{[e][O_2]k_1}{\left(\frac{1}{\tau} + Mk_2\right)}$$

$$\frac{d\left[O_2^-\right]}{dt} = \left[\left(O_2^-\right)^*\right]Mk_2 \approx \frac{[e][O_2]k_1 Mk_2}{\left(\frac{1}{\tau} + Mk_2\right)}\left[\left(O_2^-\right)^*\right] \approx [e][O_2]k'$$

$$k' = \frac{k_1}{\left(1 + \frac{1}{Mk_2\tau}\right)}$$

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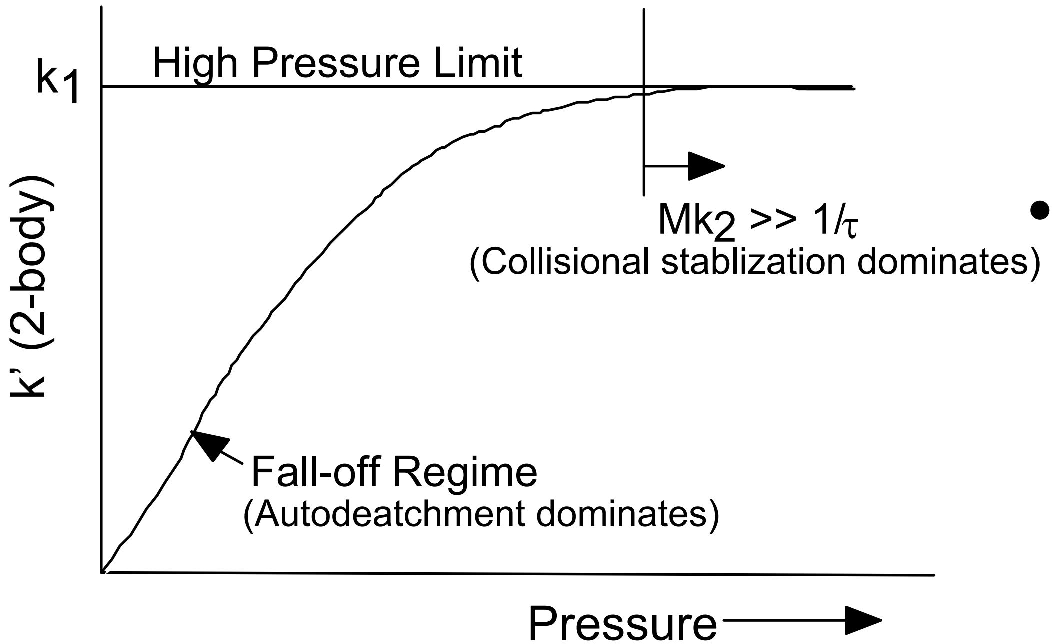
3-BODY ATTACHMENT: EFFECTIVE 2-BODY RATE



- O_2: $k_1 = 3 \times 10^{-11}$ cm^3s^{-1}, $\tau = 0.1$ ns, $k_2 \approx 5 \times 10^{-10}$ cm^3s^{-1} High pressure limit reached at 4 atm
- Almost always acceptable to use 3-body rate coefficient

$$e + O_2 + M \xrightarrow{k_3} O_2^- + M$$

$$k_3 \approx k_1 k_2 \tau \approx 2.3 \times 10^{-30}\, cm^{-6} s^{-1}$$

- For $(C_4F_8^-)^*$, $\tau = 1$ μs, and the high pressure limit is at 0.3 Torr.

- Itikawa, J. Phys. Chem. Ref. Data 18, 23 (1989)
- I. Sauers, J. Chem. Phys. 71, 3016 (1979).
- R. L. Woodin, J. Chem. Phys. 72, 4223 (1980).

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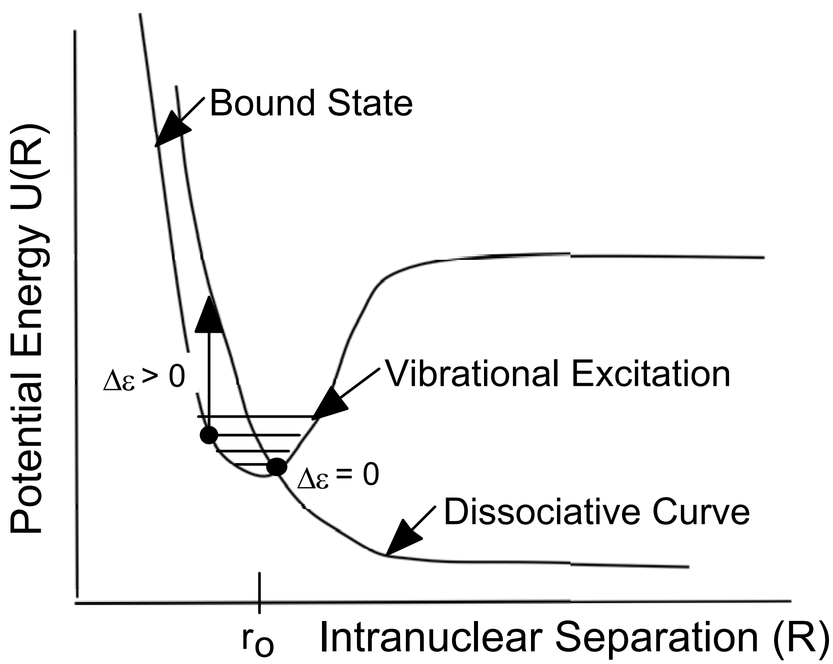
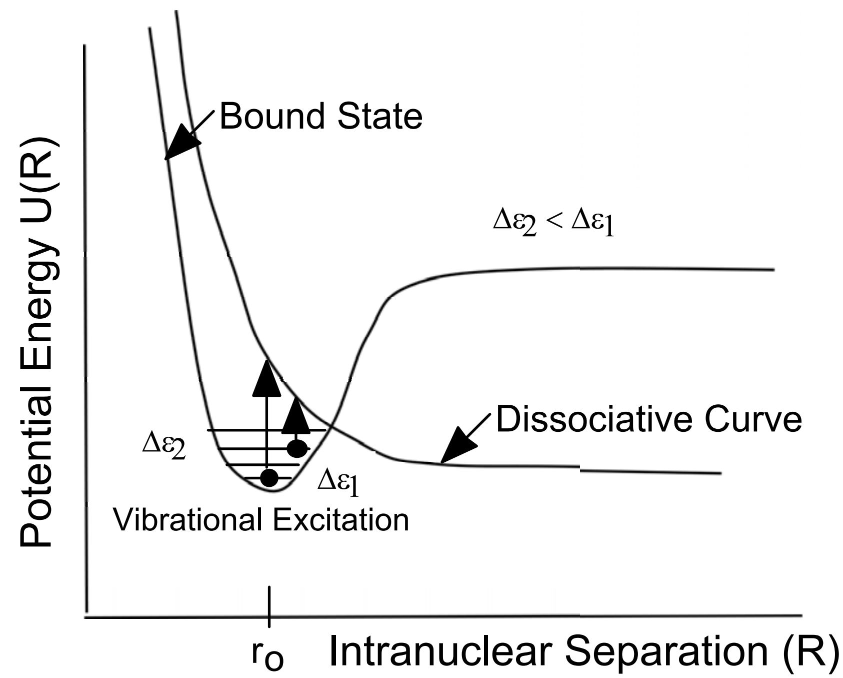
T(gas) DEPENDENCE OF DISSOCIATIVE ATTACHMENT

- **Many rate coefficients for dissociative attachment have a strong dependence on gas temperature due to vibrational-rotational excitation of molecule.**

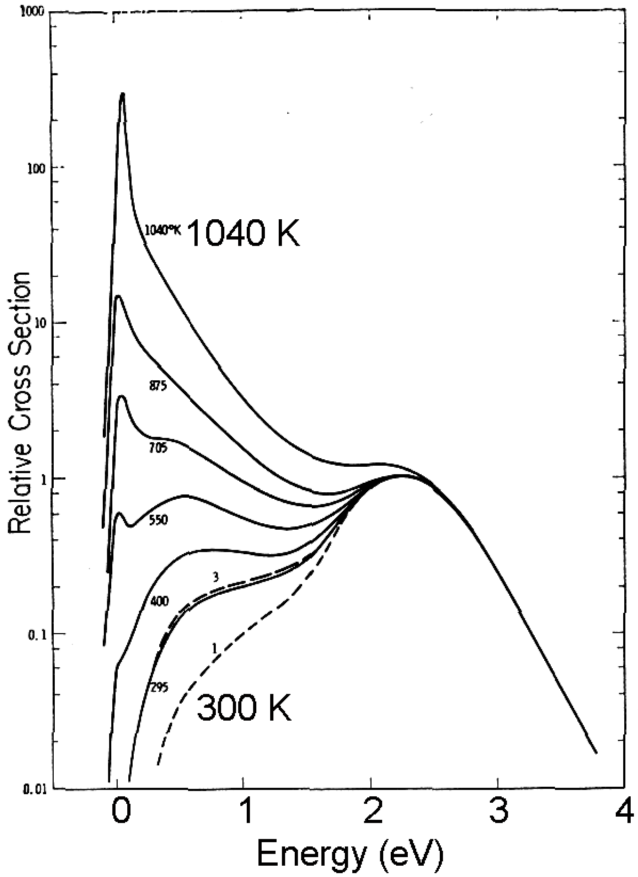




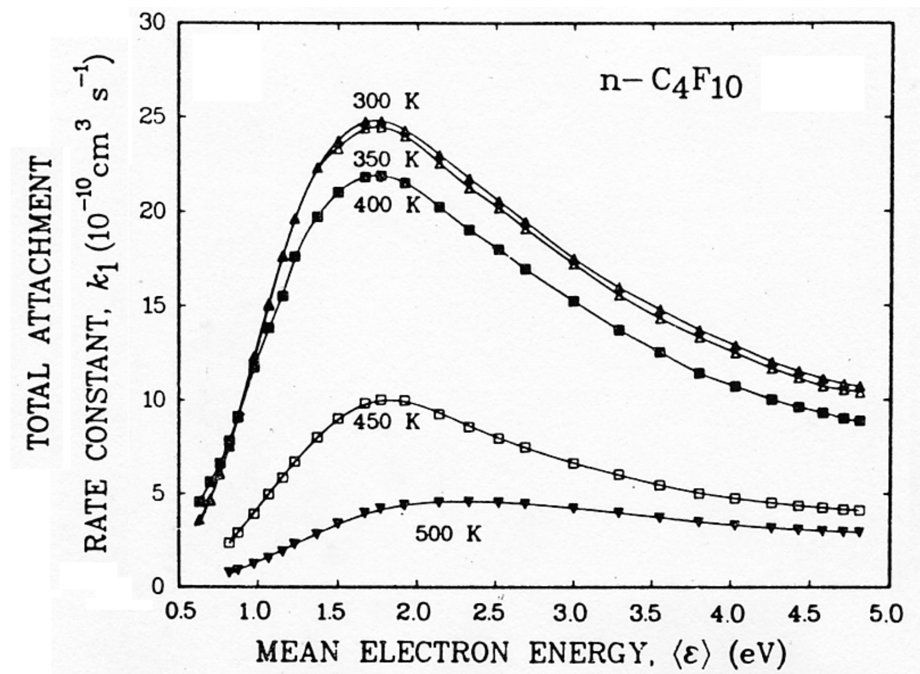
- **Internal energy increases**
  $\Delta\varepsilon$: $dk/dT_{gas} < 0$

- **Internal energy decreases**
  $\Delta\varepsilon$: $dk/dT_{gas} > 0$

T(gas) DEPENDENCE OF DISSOCIATIVE ATTACHMENT



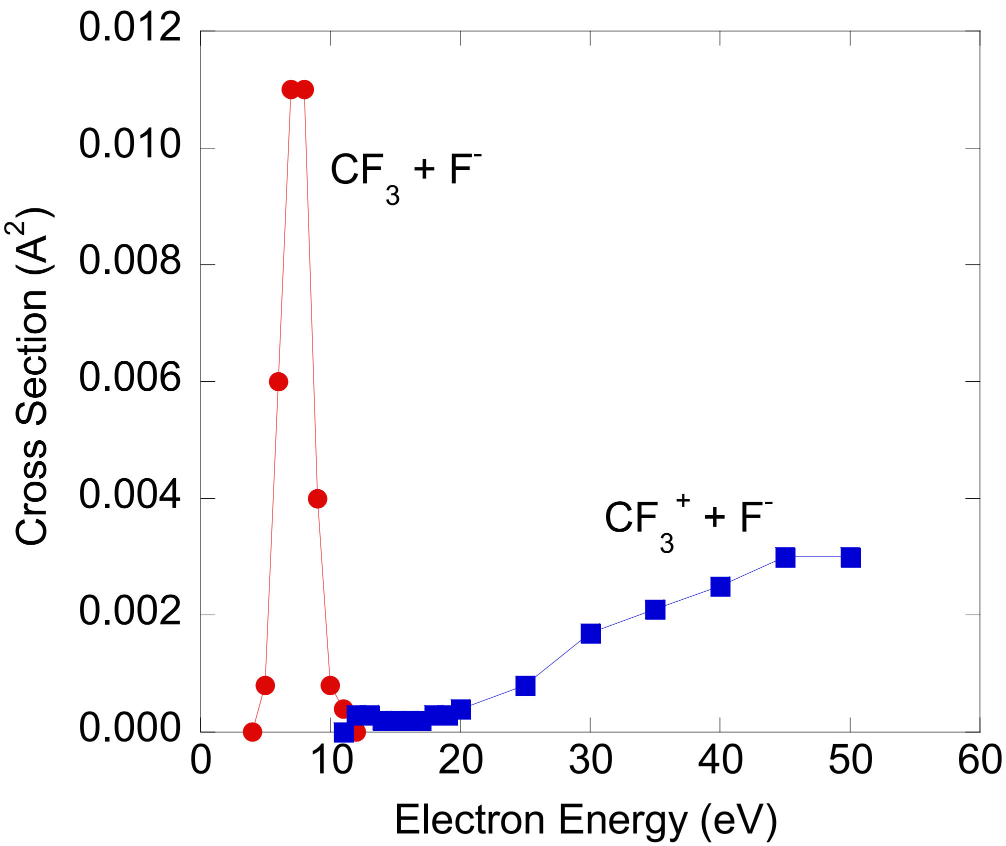
- e + $N_2O \rightarrow N_2$ + O-
  (P. Chantry, J. Chem. Phys. 51, 3369 (1969))



- e + $C_4F_{10} \rightarrow C_4F_{10}$-
  (L. Christophorou, Cont. Plasma Phys. 27, 237 (1987))

ION PAIR FORMATION

- **Although not usually a large source of negative ions, ion-pair formation typically occurs at higher electron energies.**
- **Example: e + $CF_4 \rightarrow CF_3^+$ + F- + e**



- **R. A. Bonham, Jpn. J. Appl. Phys. 33, 4157 (1994)**

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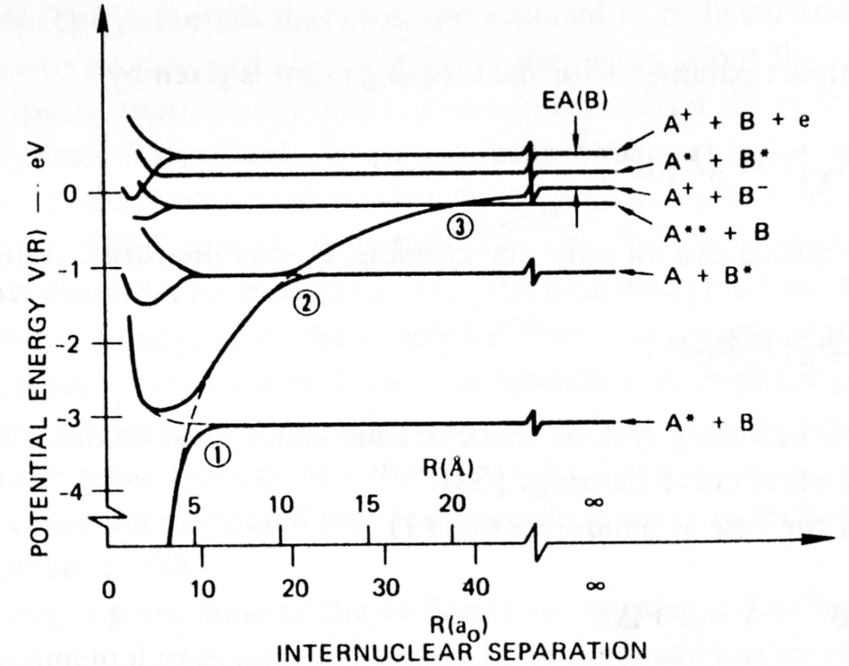
LOSS PROCESSES: ION-ION NEUTRALIZATION

- Negative ions are consumed in the volume of plasmas primarily by ion-ion neutralization

$$A^- + B^+ \rightarrow A + B \quad (\text{or } A^* + B \text{ or } A + B^*)$$

- Requirement: (Ionization Potential)$_B$ > (Electron Affinity)$_A$
- Since the Coulomb forces between are long range; atomic structure of the core is not terribly important.



- Rate coefficients generally depend on IP, EA, reduced mass and scale as $T^{-0.5}$. Typical values 10^{-7} $cm^3 s^{-1}$ (300K)
- J. T. Moseley, Case Studies in Atomic Physics 5, p. 1 (1975)

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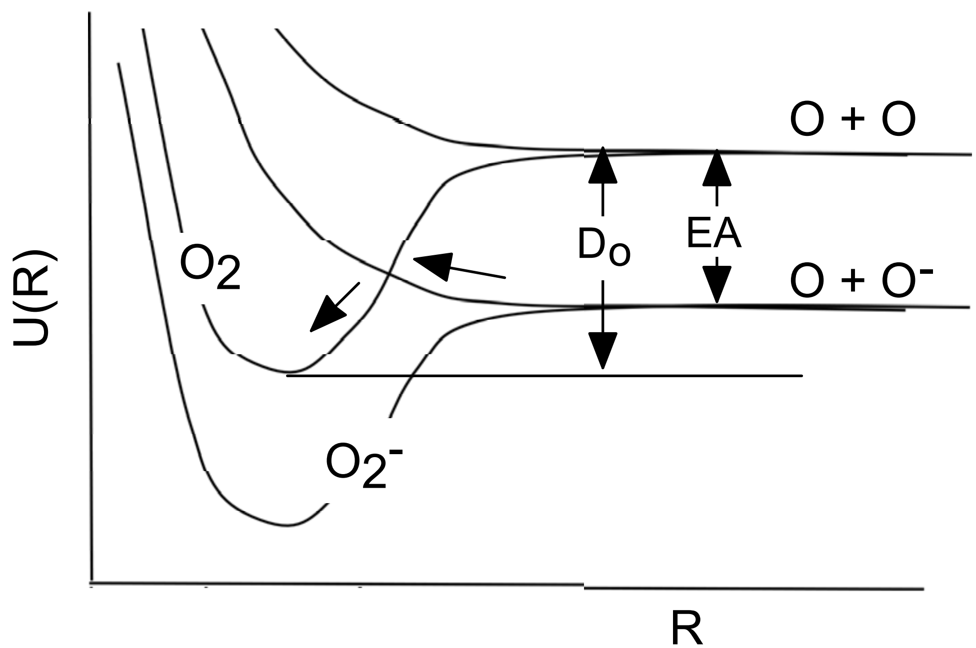
LOSS PROCESSES: ASSOCIATIVE DETACHMENT

- **Association of small radicals to form parent molecules can be accelerated by detachment as the liberated electron carries off excess momentum**

$$O^- + O \rightarrow O_2 + e, \quad k = 2 \times 10^{-10}\ cm^3s^{-1}$$



- **Requirement:**

Bond Energy (D_o) > Electron Affinity

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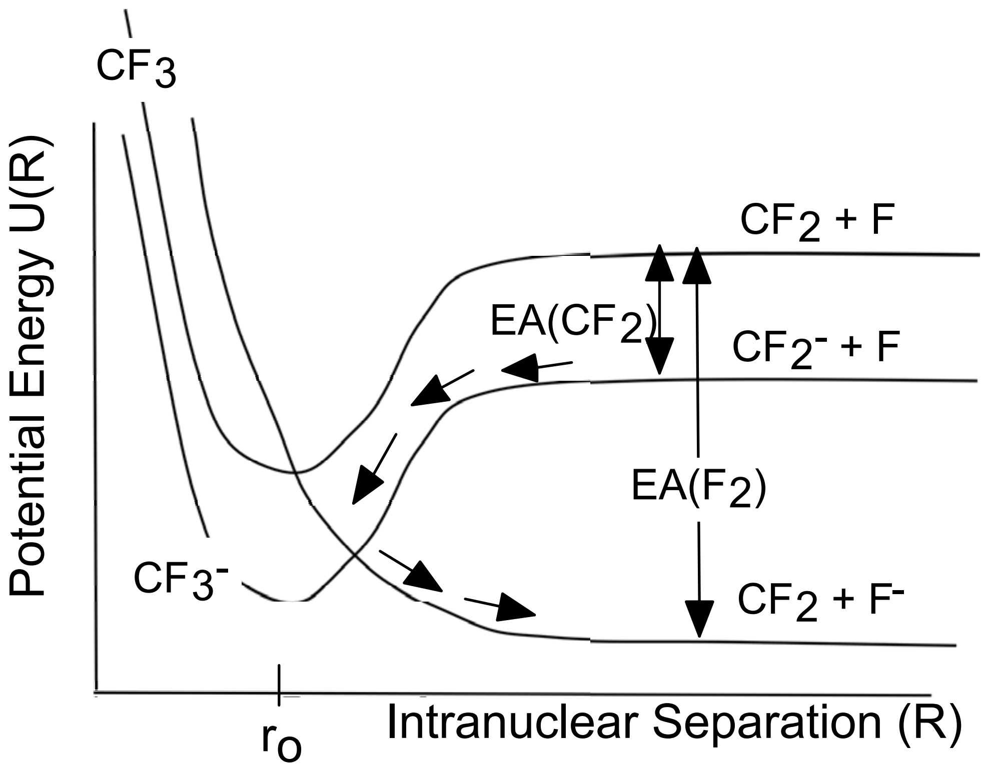
LOSS PROCESSES: CHARGE EXCHANGE

- **Just as positive ions undergo charge exchange if energetically allowed ($A^+ + B \rightarrow A + B^+$, IP(A) > IP(B)), negative ions undergo charge exchange.**



A- + B → A + B-

- **Requirement: EA (B) > EA(A)**
- **Example: CF_2- + F → CF_2 + F-**
- **Process could be stablized.**

$$F + CF_2^- \xrightarrow{k_1} \left(CF_3^-\right)^*$$

$$\left(CF_3^-\right)^* \xrightarrow{\tau} F^- + CF_2$$

$$\left(CF_3^-\right)^* + M \xrightarrow{k_2} CF_3^- + M$$

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SECRET FOR MODELING ELECTRONEGATIVE PLASMAS: DO NOTHING SPECIAL

- **Most approximation methods for electronegative plasmas breakdown somewhere along the way and require fixes. Including all the physics really helps….For example:**

$$\frac{dn_e}{dt} = \underbrace{n_e O_2 k_1}_{\text{ionization}} - \underbrace{n_e O_2^+ k_2}_{\text{recombination}} - \underbrace{n_e O_2 k_2}_{\text{attachment}} - \underbrace{\nabla \cdot \vec{\phi}_e}_{\text{transport}}$$

$$\frac{dO_2^+}{dt} = \underbrace{n_e O_2 k_1}_{\text{ionization}} - \underbrace{n_e O_2^+ k_2}_{\text{recombination}} - \underbrace{O_2^- O_2^+ k_2}_{\text{ion-ion neutralization}} - \underbrace{\nabla \cdot \vec{\phi}_{O_2^+}}_{\text{transport}}$$

$$\frac{dO_2^-}{dt} = \underbrace{n_e O_2 k_2}_{\text{attachment}} - \underbrace{O_2^- O_2^+ k_2}_{\text{ion-ion neutralization}} - \underbrace{\nabla \cdot \vec{\phi}_{O_2^-}}_{\text{transport}}$$

$$\vec{\phi}_i = q_i \mu_i N_i \vec{E} - D_i \nabla N_i$$

$$\nabla \cdot \vec{E} = \frac{q}{\varepsilon_o}\left(O_2^+ - O_2^- - n_e\right)$$

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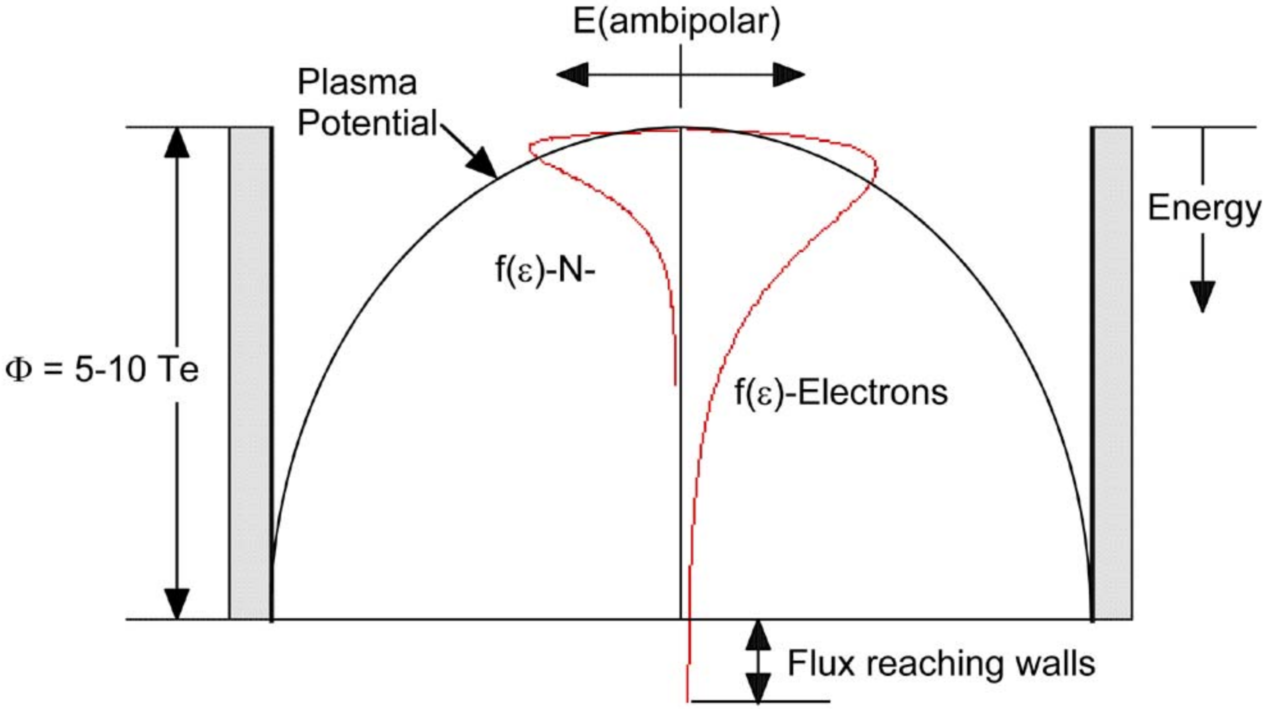
TRANSPORT OF NEGATIVE IONS

- **In principle, negative ions are simply heavy, cold electrons (T_I << T_e) and obey the same kinetic and transport laws.**
- **In practice, N- cannot climb the plasma potential barrier created by ambipolar fields and so are trapped in the plasma.**



- **For conventional plasmas, N- are almost exclusively lost by volumetric processes.**

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AMBIPOLOAR TRANSPORT WITH NEGATIVE IONS

- In ambipolar transport, typically used with global models, the total flux of charged particles leaving the plasma is zero.

$$\vec{\phi}_e = \underbrace{-\frac{D_e}{\Lambda} n_e}_{\text{free diffusion}} - \underbrace{\mu_e n_e E_A}_{\text{ambipolar drift}}$$

$$\vec{\phi}_i^+ = \underbrace{-\frac{D_i^+}{\Lambda} N_i^+}_{\text{free diffusion}} + \underbrace{\mu_i^+ N_i^+ E_A}_{\text{ambipolar drift}}$$

$$\vec{\phi}_j^- = \underbrace{-\frac{D_j^-}{\Lambda} N_j^-}_{\text{free diffusion}} - \underbrace{\mu_j^- N_j^- E_A}_{\text{ambipolar drift}}$$

$$\sum_i \vec{\phi}_i^+ = \sum_j \vec{\phi}_j^- + \vec{\phi}_e$$

$$E_A = \frac{-\sum_i \frac{D_i^+}{\Lambda} N_i^+ + \frac{D_e}{\Lambda} n_e + \sum_j \frac{D_j^-}{\Lambda} N_j^-}{\sum_i \mu_i^+ N_i^+ + \mu_e n_e + \sum_j \mu_j^- N_j^-}$$

- Since $D_e >> D_I$, the ambipolar electric field typically accelerates positive ions, slows electrons (and negative ions)

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AMBIPOLAR TRANSPORT WITH NEGATIVE IONS

- **Problem: Since…..**

$$D_e >> D_I, \quad T_e >> T_I, \quad \mu_e >> \mu_I, \quad \text{then } E_A >> \frac{kT_I}{q\Lambda}$$

which usually results in the unphysical result….

$$\vec{\phi}_j^- = \frac{D_j^-}{\Lambda} N_j^- - \mu_j^- N_j^- \vec{E}_A < 0$$

- **Many work-arounds (all approximations). One example is:**

$$E_A = f\left(N^+, N^-, n_e, D^+, D^-, D_e\right) \rightarrow \phi_j^- \xrightarrow{>0} \textit{good solution}$$

$\phi_j^- \xrightarrow{< 0}$ *neglect* ϕ_j^- $\rightarrow$ back to E_A

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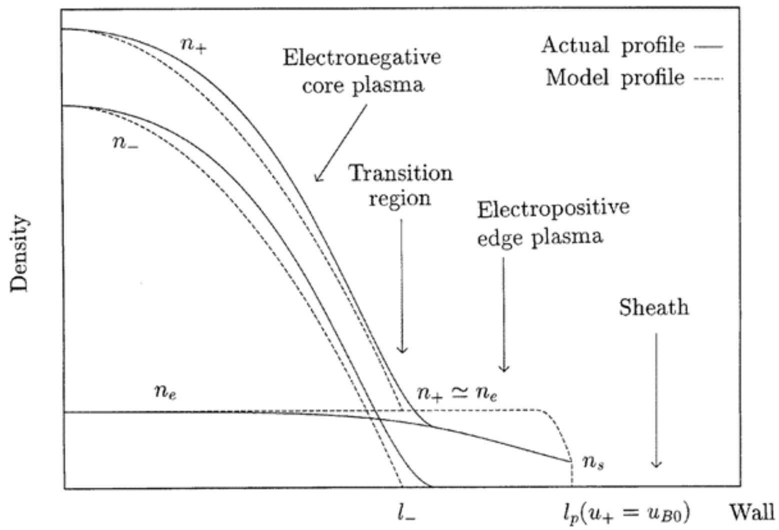
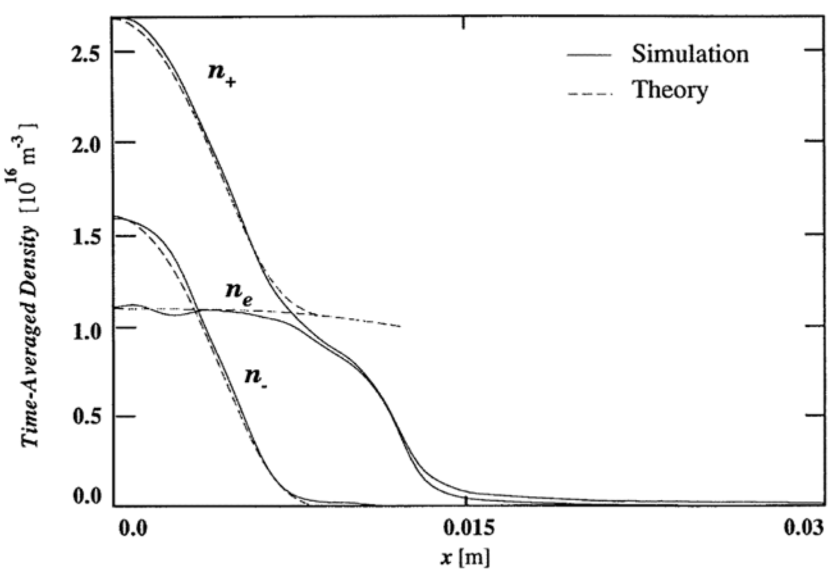
ELECTRONEGATIVE CORE





- **Low pressure plasmas have "cores" which can be dominated by negative ions; surrounded by boundary regions and sheaths where negative ions are excluded.**

- **PIC simulation of plane parallel O_2 plasma (10 mTorr)**

- **Ref: I. Kouznetsov, Plasma Sources Sci. Technol. 5, 662 (1996)**

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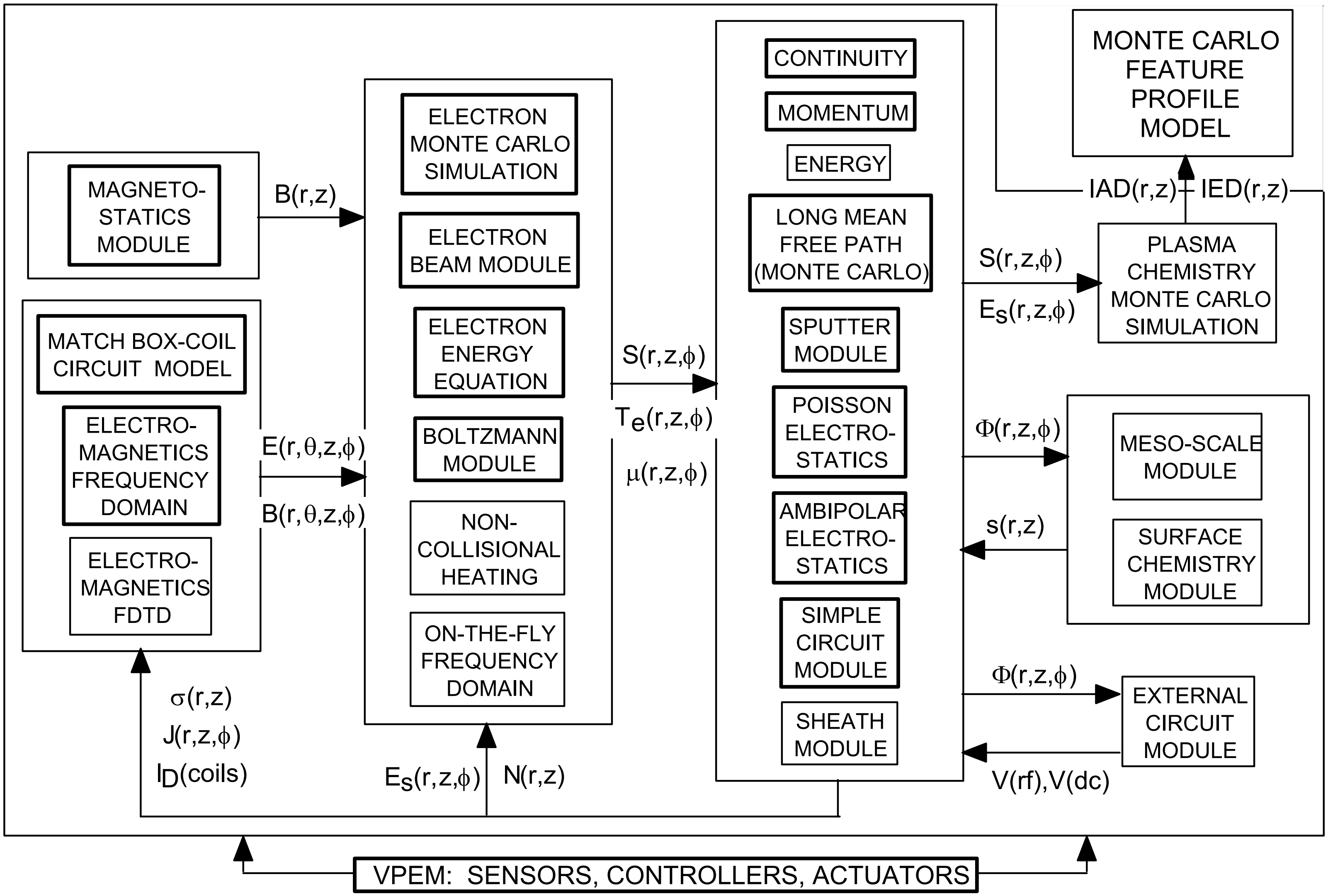
HYBRID PLASMA EQUIPMENT MODEL



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ELECTROMAGNETICS MODULE

- **The wave equation is solved in the frequency domain using sparse matrix techniques:**

$$-\nabla\left(\frac{1}{\mu}\nabla\cdot\overline{E}\right)+\nabla\cdot\left(\frac{1}{\mu}\nabla\overline{E}\right)=\frac{\partial^2\left(\varepsilon\overline{E}\right)}{\partial t^2}+\frac{\partial\left(\overline{\overline{\sigma}}\cdot\overline{E}+\overline{J}\right)}{\partial t}$$

$$\vec{E}(\vec{r},t)=\vec{E}'(\vec{r})\exp(-i(\omega t+\varphi(\vec{r})))$$

- **Conductivities are tensor quantities:**

$$\overline{\overline{\sigma}}=\sum_j\sigma_j\frac{m_j\nu_{jm}}{q_j\alpha_j}\frac{1}{\left(\alpha^2+\left|\vec{B}\right|^2\right)}\begin{pmatrix}\alpha^2+B_r^2 & \alpha B_z+B_rB_\theta & -\alpha B_\theta+B_rB_z\\ -\alpha B_z+B_rB_\theta & \alpha^2+B_\theta^2 & \alpha B_r+B_\theta B_z\\ -\alpha B_\theta+B_rB_z & -\alpha B_r+B_\theta B_z & \alpha^2+B_z^2\end{pmatrix}$$

$$\vec{j}=\overline{\overline{\sigma}}\cdot\vec{E}\qquad\qquad \alpha_j=\frac{\left(i\omega+\nu_{jm}\right)}{q_j/m_j},\quad \sigma_j=\frac{q^2n_j}{m_j\nu_{jm}}$$

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ELECTRON ENERGY TRANSPORT

- **Continuum:**

$$\partial\left(\frac{3}{2}n_e kT_e\right)/\partial t = S(T_e) - L(T_e) - \nabla\cdot\left(\frac{5}{2}\Phi kT_e - \overline{\overline{\kappa}}(T_e)\cdot\nabla T_e\right) + S_{EB}$$

where	**$S(T_e)$**	**=**	**Power deposition from electric fields**
	$L(T_e)$	**=**	**Electron power loss due to collisions**
	Φ	**=**	**Electron flux**
	$\kappa(T_e)$	**=**	**Electron thermal conductivity tensor**
	S_{EB}	**=**	**Power source source from beam electrons**

- **Power deposition has contributions from wave and electrostatic heating.**

- **Kinetic: A Monte Carlo Simulation is used to derive $f(\varepsilon, \vec{r}, t)$ including electron-electron collisions using electromagnetic fields from the EMM and electrostatic fields from the FKM.**

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PLASMA CHEMISTRY, TRANSPORT AND ELECTROSTATICS

- **Continuity, momentum and energy equations are solved for each species (with jump conditions at boundaries).**

$$\frac{\partial N_i}{\partial t} = -\nabla \cdot (N_i \vec{\mathrm{v}}_i) + S_i$$

$$\frac{\partial \left(N_i \vec{v}_i\right)}{\partial t} = \frac{1}{m_i}\nabla\left(kN_i T_i\right) - \nabla \cdot \left(N_i \vec{v}_i \vec{v}_i\right) + \frac{q_i N_i}{m_i}\left(\vec{E} + \vec{v}_i \times \vec{B}\right) - \nabla \cdot \overline{\mu}_i - \sum_j \frac{m_j}{m_i + m_j} N_i N_j \left(\vec{v}_i - \vec{v}_j\right)\nu_{ij}$$

$$\frac{\partial \left(N_i \varepsilon_i\right)}{\partial t} + \nabla \cdot \mathrm{Q}_i + P_i \nabla \cdot \mathrm{U}_i + \nabla \cdot (N_i \mathrm{U}_i \varepsilon_i) = \frac{N_i q_i^2 \nu_i}{m_i(\nu_i^2 + \omega^2)} E^2 + \frac{N_i q_i^2}{m_i \nu_i} E_s^2 + \sum_j 3 \frac{m_{ij}}{m_i + m_j} N_i N_j R_{ij} k_B (T_j - T_i) \pm \sum_j 3 N_i N_j R_{ij} k_B T_j$$

- **Implicit solution of Poisson's equation:**

$$\nabla \cdot \varepsilon \nabla \Phi\left(t + \Delta t\right) = -\left(\rho_s + \sum_i q_i N_i - \Delta \mathrm{t} \cdot \sum_{\mathrm{i}} \left(\mathrm{q}_{\mathrm{i}} \nabla \cdot \vec{\phi}_i\right)\right)$$

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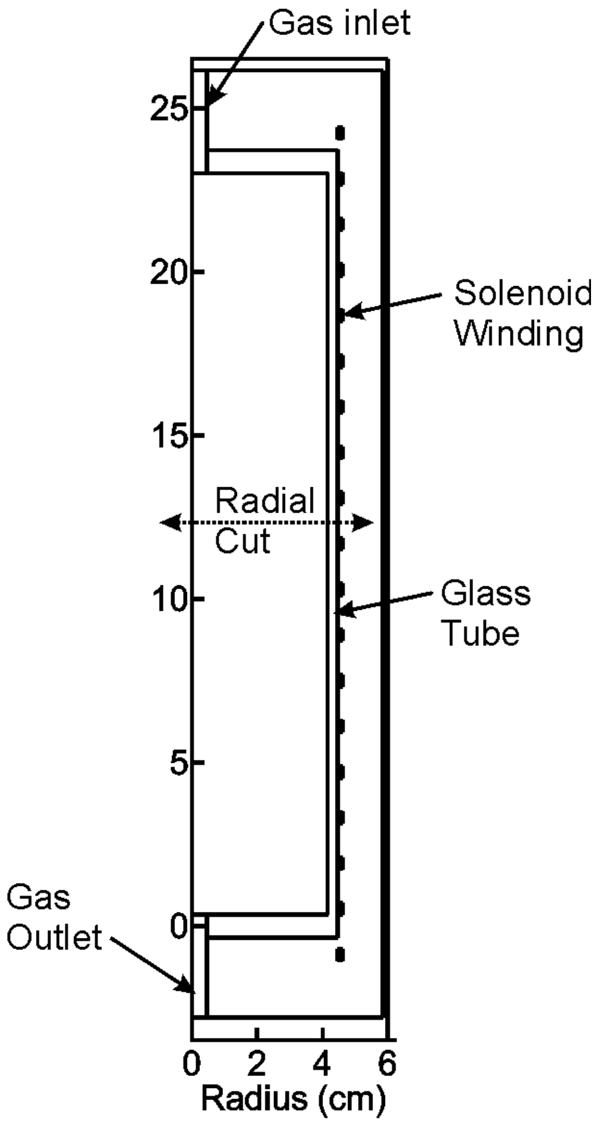
DEMONSTRATION OF CONCEPTS: SOLENOID ICP



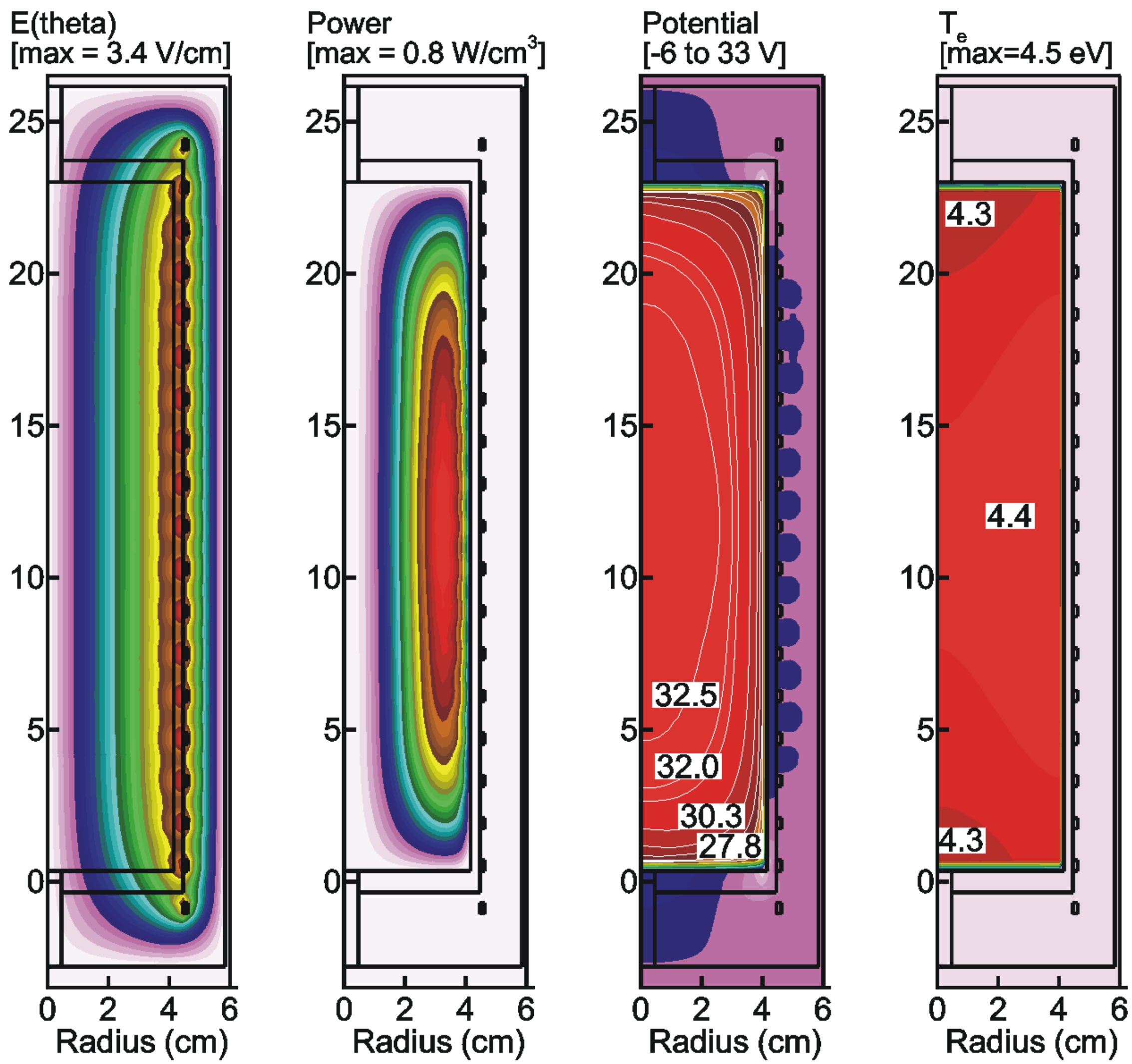
- **Demonstrate concepts with low pressure solenoidal inductively coupled plasma.**
- **Narrow tube produces high T_e and large negative-ion trapping plasma potentials.**
- **1-d radial cuts are taken through maximum in negative ion density**
- **He/O_2 = 90/10, 10-100 mTorr, 30-300 sccm, 50 W**
- **Species:**

  He, He*, He^+

  O_2, $O_2(^1\Delta)$, $O_2(^1\Sigma)$, O_2^+, O_2^-,

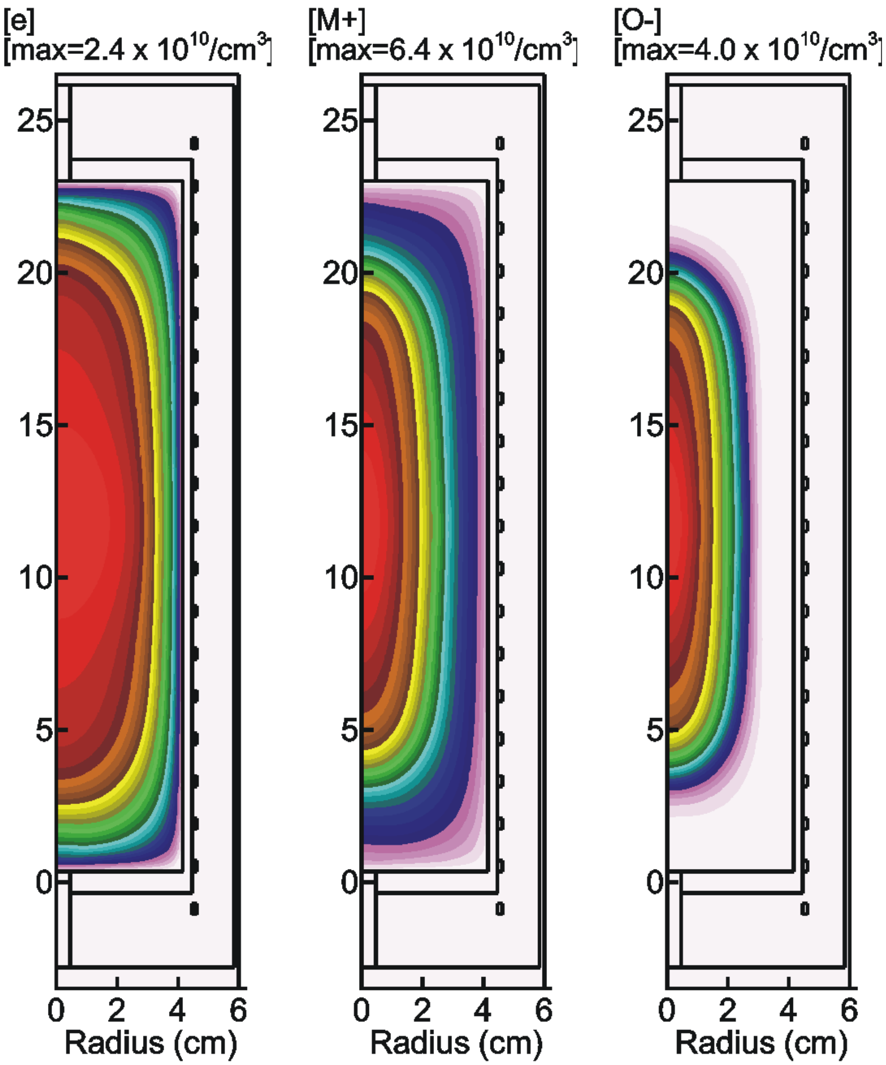
  O, $O(^1D)$, $O(^1S)$, O^+, O^-

SOLENOID ICP: He/O_2 = 90/10, 50 mTorr, 50 W



- **High specific power deposition in a narrow tube and high plasma density produces a large and uniform T_e.**
- **The resulting plasma potential > 30 V.**

SOLENOID ICP: He/O_2 = 90/10, 50 mTorr, 50 W



- **[e] extends to boundaries, [O-] is restricted to the core of the plasma.**
- **T(O-) does not exceed an eV and so is not able to climb the plasma potential.**
- **The distribution of positive ions (dominated by O_2^{+}) is less uniform than electrons as M^+ shields O^- in the center of the plasma.**

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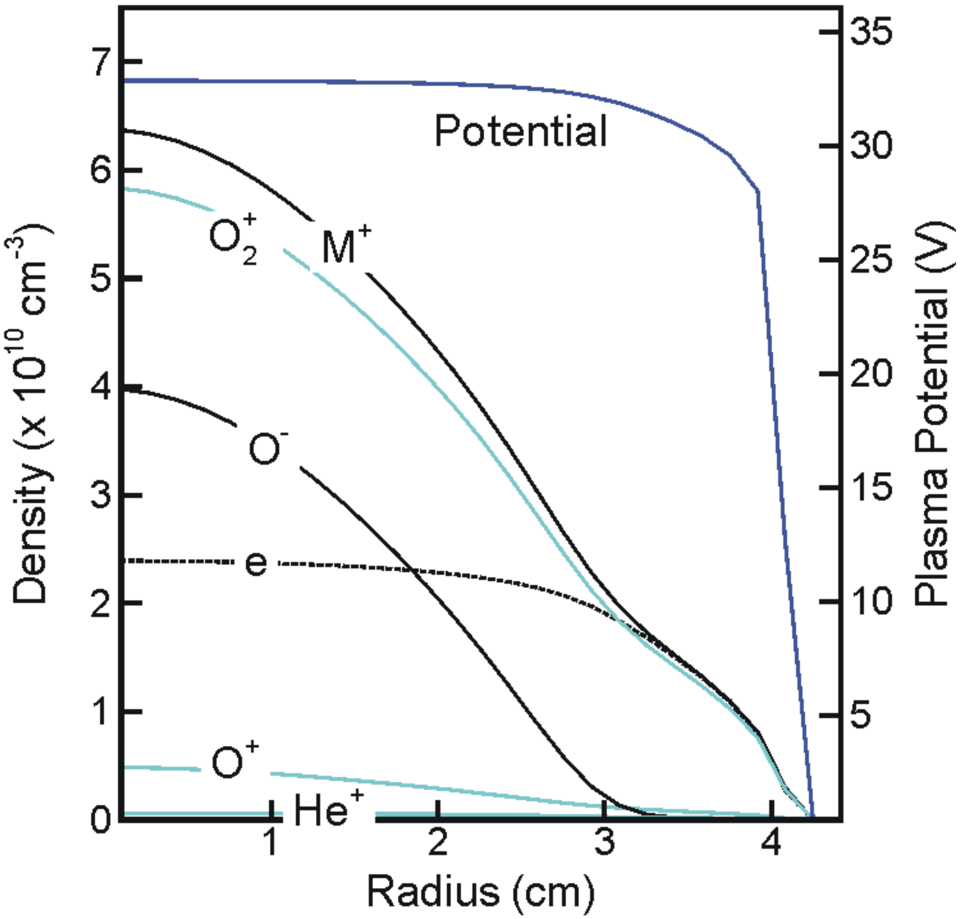
SOLENOID ICP: He/O_2 = 90/10, 50 mTorr RADIAL PROPERTIES



- 3 regions define the plasma.
  - Electronegative core
  - Electropositive “halo”
  - Sheath

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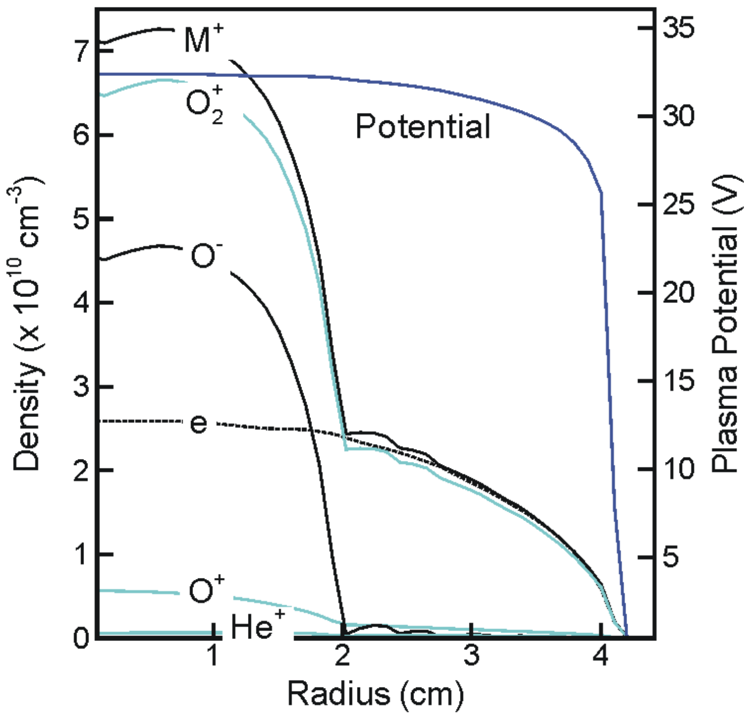
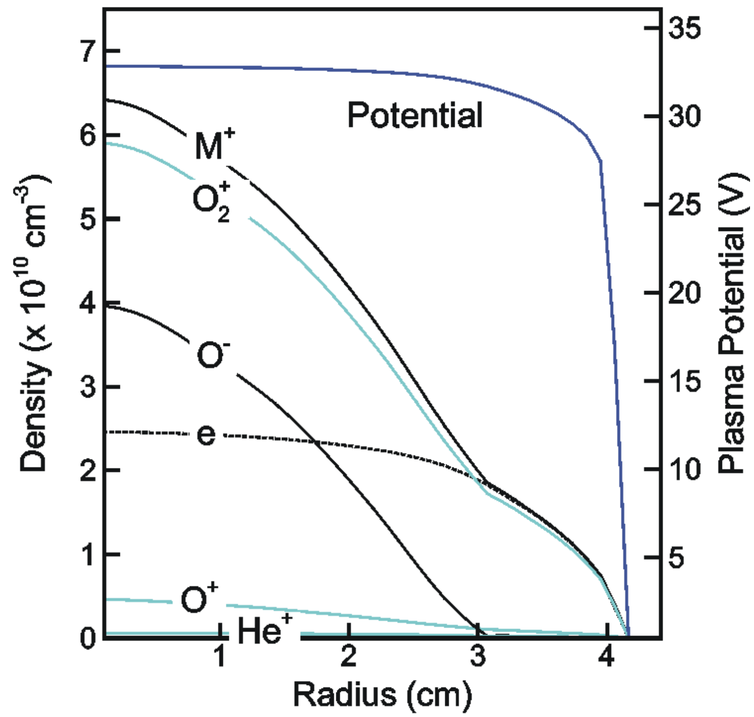
SOLENOID ICP: He/O_2 = 90/10, 50 mTorr vs T(O^-)



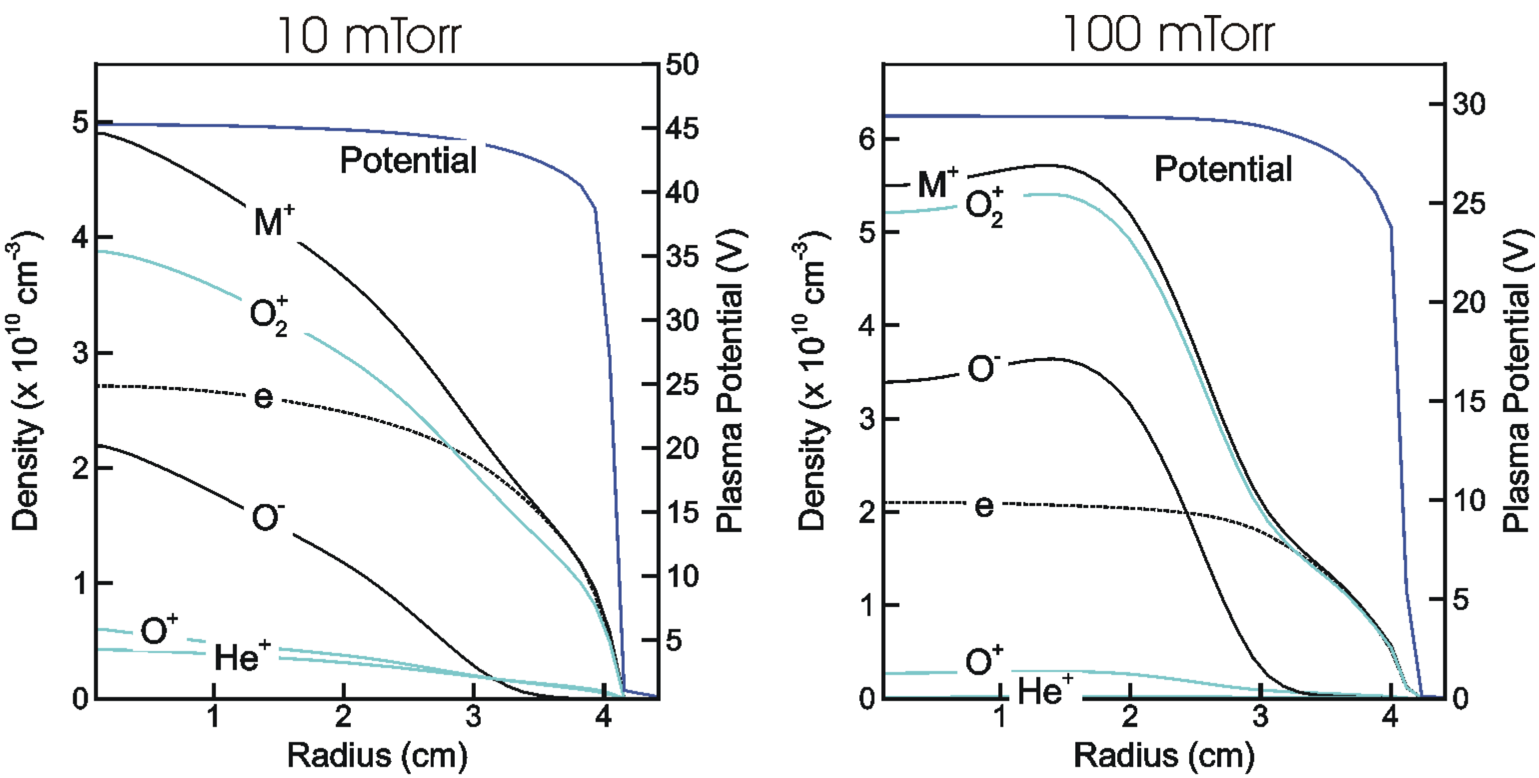
- T(O-) = T(gas)



- T(O-) = 20 x T(gas)

- Artificially constraining T(O-) restricts (or expands) the region of plasma accessible to negative ions.

SOLENOID ICP: He/O_2 = 90/10, 50 W vs PRESSURE



- **In spite of increasing plasma potential, voltage drop in the center of the plasma is not that different, and so extent of O- is about the same…T(O-) also increases with decreasing pressure.**

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ICP: COMPLEX GEOMETRY AND CHEMISTRY

- **Inductively coupled plasmas for microelectronics fabrication often use complex electronegative gas mixtures.**
- **Etch selectivity is obtained from regulating thickness of polymer layers.**
- **Example case:**

10 mTorr, 1000 W, 100 sccm

$Ar/C_4F_8/CO/O_2$=73/7.3/18/1.8

Argon species	Oxygen species	COF_x species
Ar	O_2	CO
Ar(4s)	O_2^+	CO^+
Ar(4p)	O_2^-	CO_2
Ar^+	$O_2(^1\Delta)$	COF
	O	COF_2
	$O(^1D)$	OF
	O^+	
	O^-	

Carbon species	F_x species	CF_x species
C	F	CF
C^+	F^+	CF^+
	F^-	CF_2
	F_2	CF_2^+
	F_2^+	CF_3
		CF_3^-
		CF_3^+
		CF_4

$C_x F_y$ species

$C_2F_3^+$	$C_3F_5^+$	$C_4F_7^+$
C_2F_4	C_3F_6	C_4F_8
$C_2F_4^+$	$C_3F_6^+$	$C_4F_8^-$
C_2F_5	C_3F_7	$C_4F_8^{-*}$
$C_2F_5^+$	$C_3F_7^+$	$C_4F_8^+$
C_2F_6	C_4F_7	
C_3F_5		

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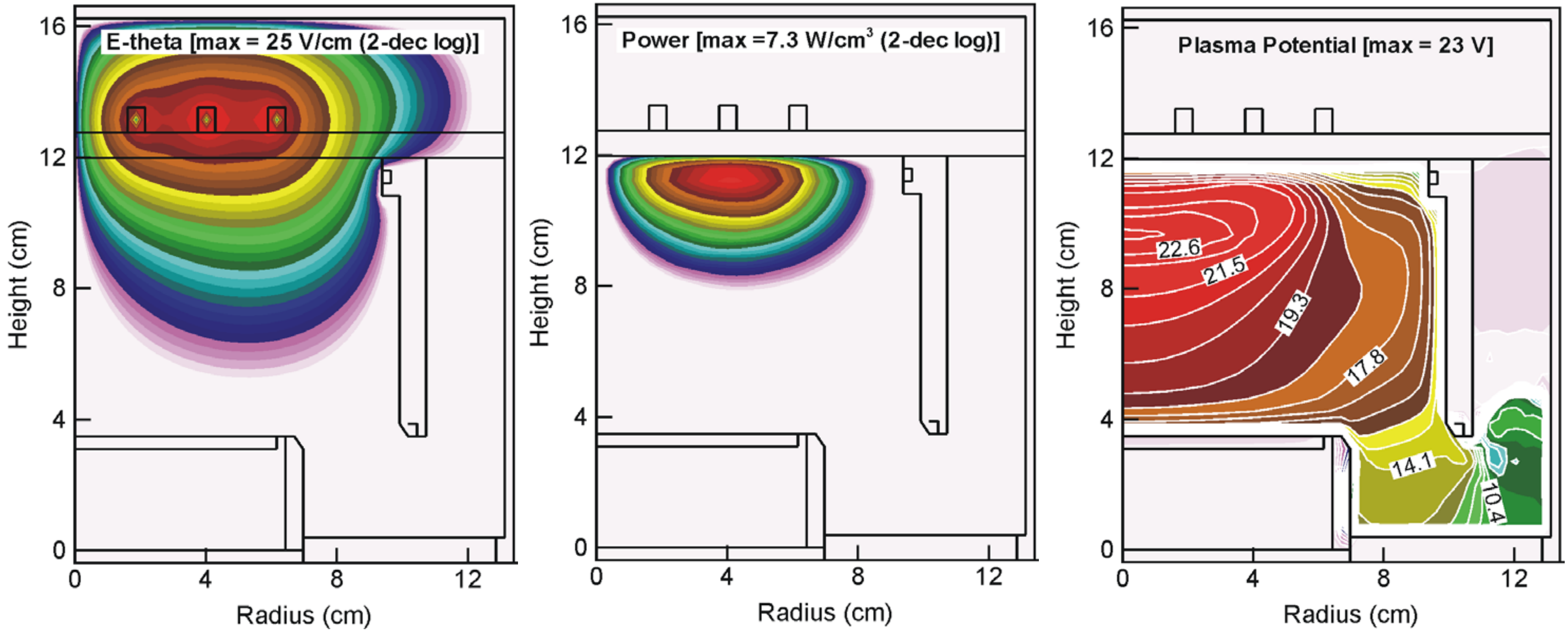
$Ar/C_4F_8/CO/O_2$ ICP: ELECTRIC FIELD, POWER, POTENTIAL



- **Plasma peaks on axis with "pull" towards peak in power deposition where positive ions are dominantly formed.**

- **10 mTorr, 1000 W, 100 sccm $Ar/C_4F_8/CO/O_2$=73/7.3/18/1.8**

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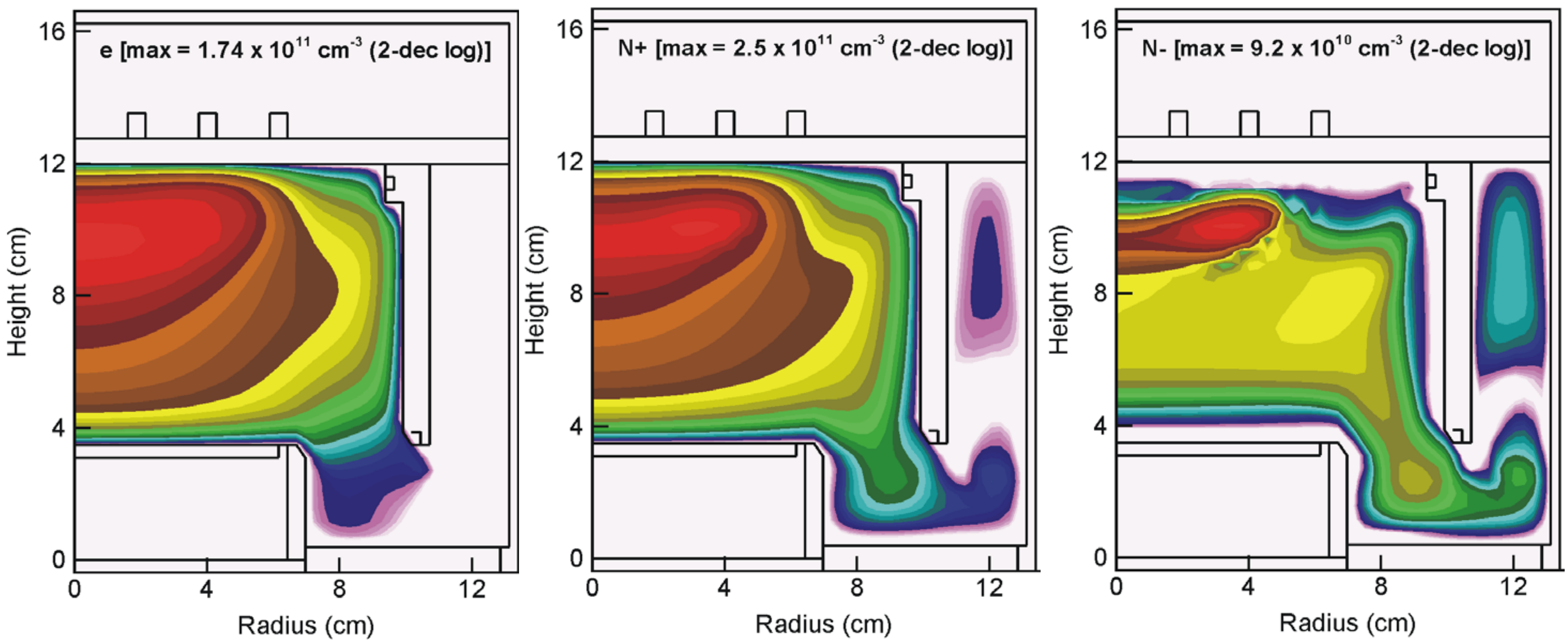
$Ar/C_4F_8/CO/O_2$ ICP: [e], [N^+], [N^-]



- **[e] near maximum in plasma potential. Negative ions "shield" positive ions at their low and high values. Catephoresis displaces negative ions towards boundaries.**

- **10 mTorr, 1000 W, 100 sccm $Ar/C_4F_8/CO/O_2$=73/7.3/18/1.8**

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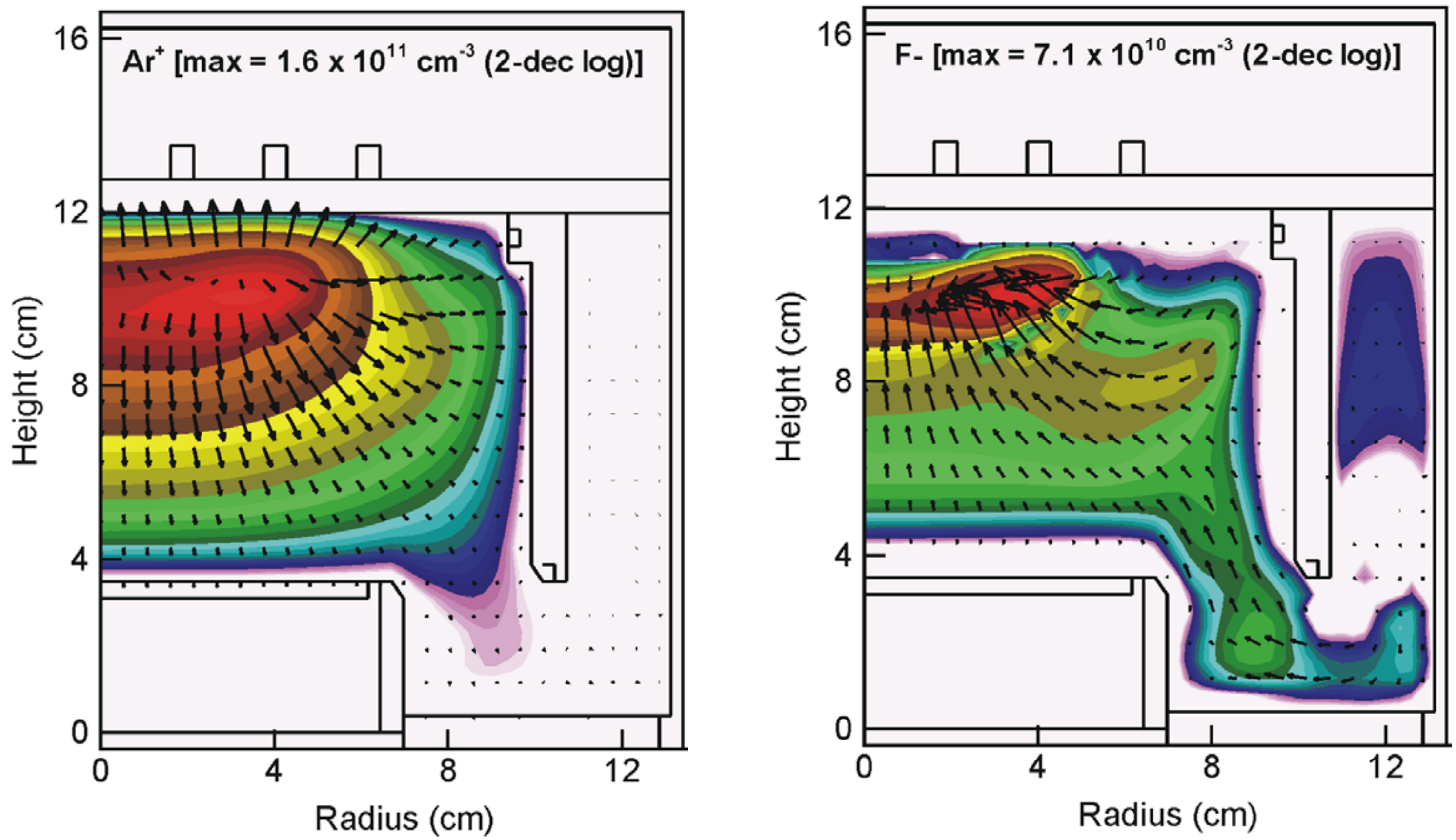
Ar/C_4F_8/CO/O_2 ICP: [Ar^+], [F^-]



- **Negative ions, trapped in the plasma, flow towards peak of plasma potential where they undergo ion-ion neutralization. Positive ions largely flow to boundaries.**

- **10 mTorr, 1000 W, 100 sccm Ar/C_4F_8/CO/O_2=73/7.3/18/1.8**

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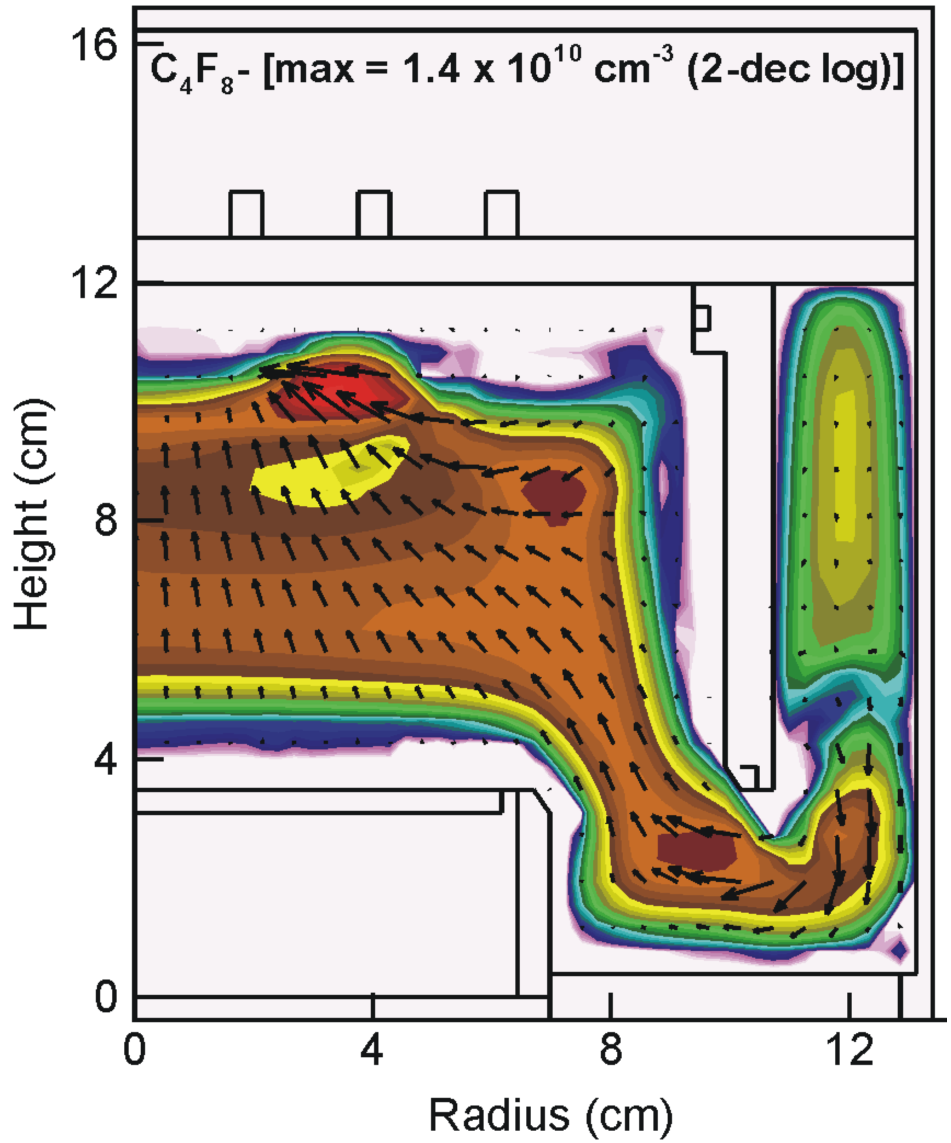
$Ar/C_4F_8/CO/O_2$ ICP: $[C_4F_8^-]$



- C_4F_8-, being heavier and less mobile, is more susceptible to being trapped in small local extrema of the plasma potential.
- These “trapping zones” are often the precursor to dust particle formation.

  - 10 mTorr, 1000 W, 100 sccm $Ar/C_4F_8/CO/O_2$=73/7.3/18/1.8

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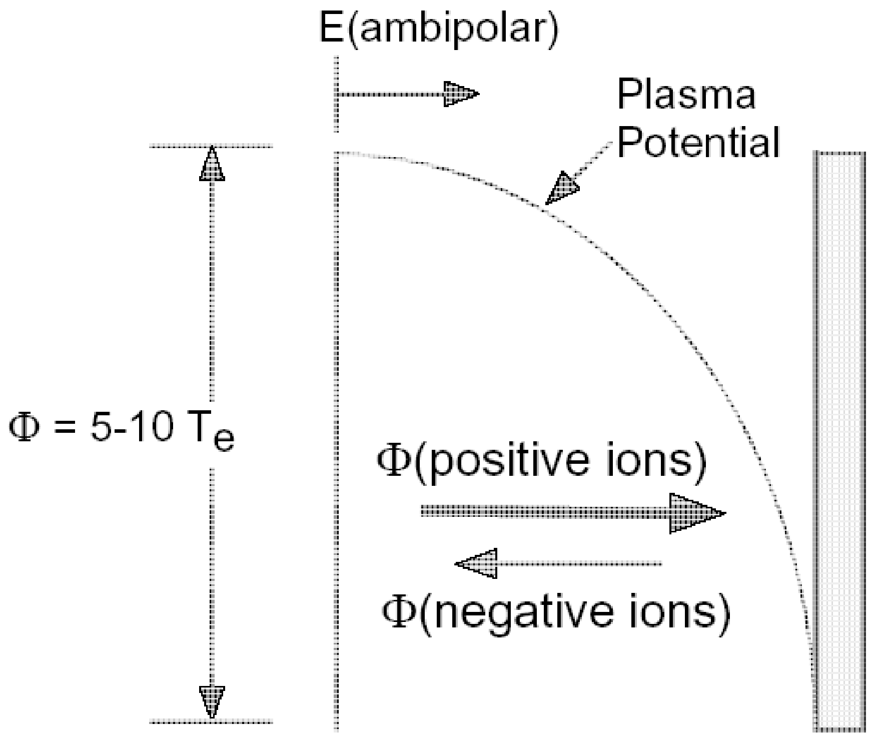
MOMENTUM TRANSFER: CATAPHORESIS

- **Due to the large Coulomb scattering cross section, there is efficient momentum transfer between positive and negative ions.**

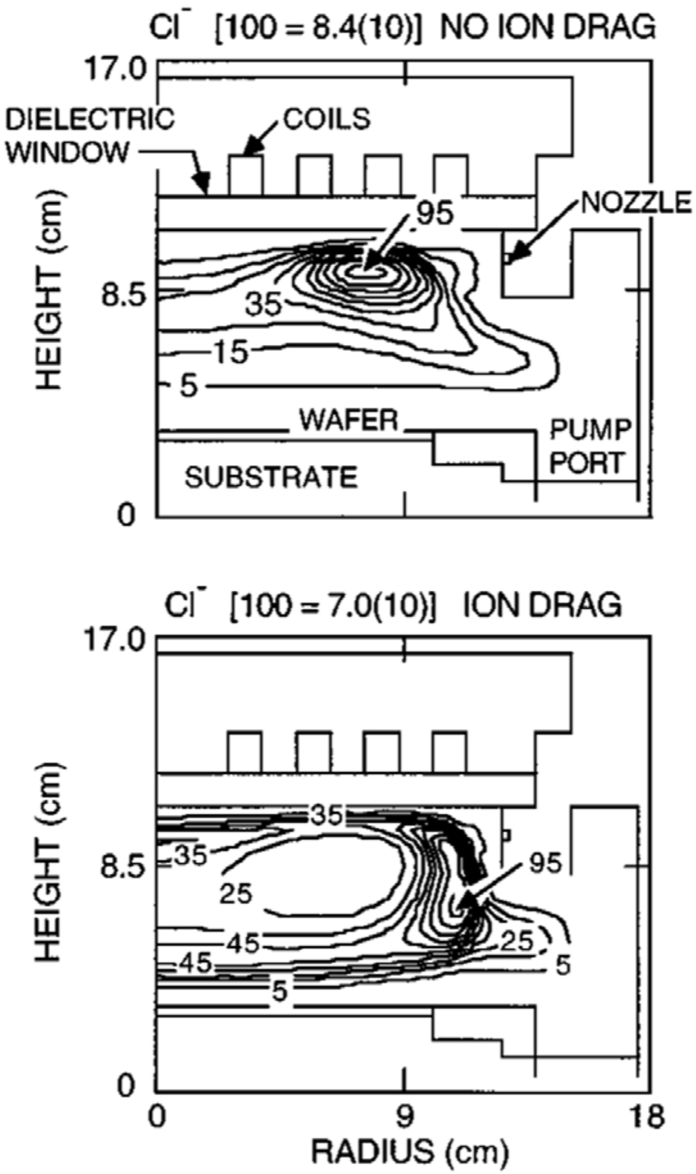


- **Large flux of positive ions moving towards boundaries "pushes" negative ions in the same direction.**

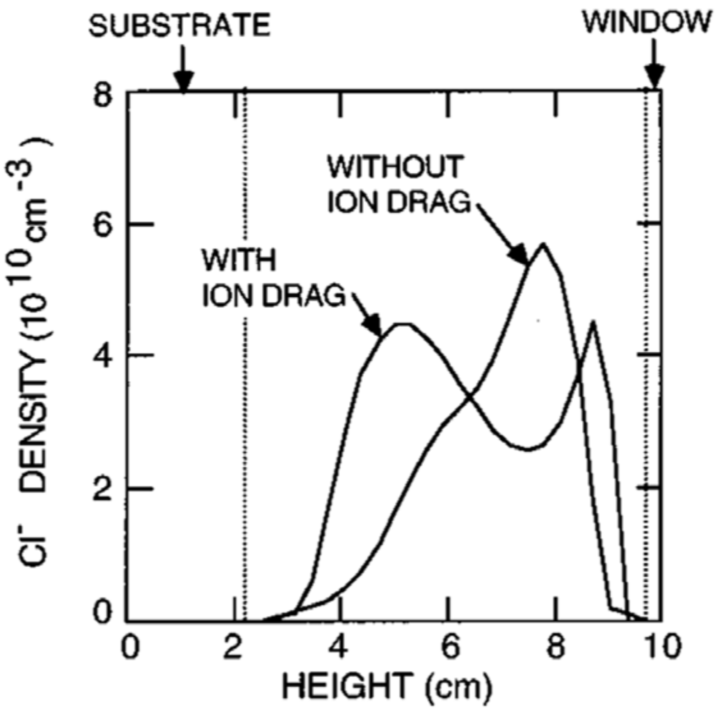
$$\frac{d\vec{\Phi}^-}{dt} = ... + \left|\vec{\Phi}^+\right| N^- \sigma_M \left(\vec{v}_+ - \vec{v}_+\right)$$

- **This is a particularly important process when negative ions are charged dust particles ("ion-drag")**

CATAPHORESIS IN ICPs



- When the flux of positive ions is large and electronegativity (N^-/N^+) small, momentum transfer from N^+ to N^- can be important.



- Ar/Cl_2=50/50, 100 sccm, 500 W, 10 mTorr

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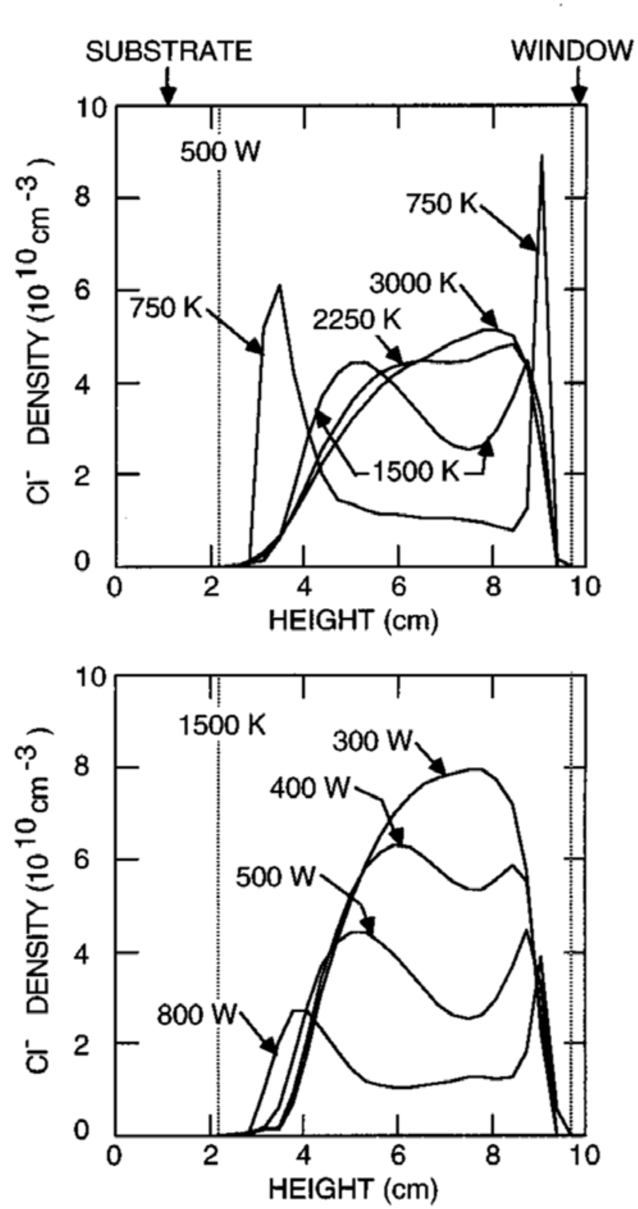
CATAPHORESIS IN ICPs



- **The Coulomb momentum transfer cross section between N^- and N^+ scales inversely with energy.**

$$\sigma_{ij} = \frac{5.9\times10^{-6}\, ln\,\Lambda}{\Psi_{ij}(K)}\,\mathrm{cm}^{-2},$$

$$\frac{3}{2}k\,\Psi_{ij} = \frac{3}{2}kT_I + \frac{1}{2}\eta_{ij}\left|\vec{v}_i - \vec{v}_j\right|$$

- **Ion drag is therefore sensitive to temperature and speed of interaction; decreasing in importance as both increase.**

- **Ar/Cl_2=50/50, 100 sccm, 500 W, 10 mTorr**

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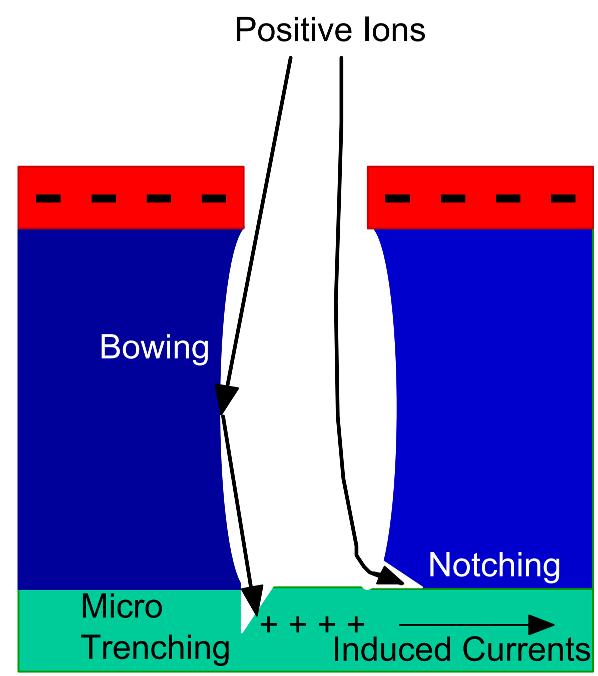
CHARGING DAMAGE IN MICROELECTRONICS FABRICATION

- **In microelectronics fabrication, trenches are etched into silicon substrates**
- **Ions arrive with vertical trajectories. Electrons arrive with broad thermal trajectories.**
- **The top of the trench is charged negative; the bottom positive.**
- **Ion trajectories are perturbed by electric fields in the trench.**
- **Plasma induced damage such as notching, bowing, microtrenching can then occur.**
- **Charge in the bottom of the trench can be neutralized accelerating negative ions into the wafer**



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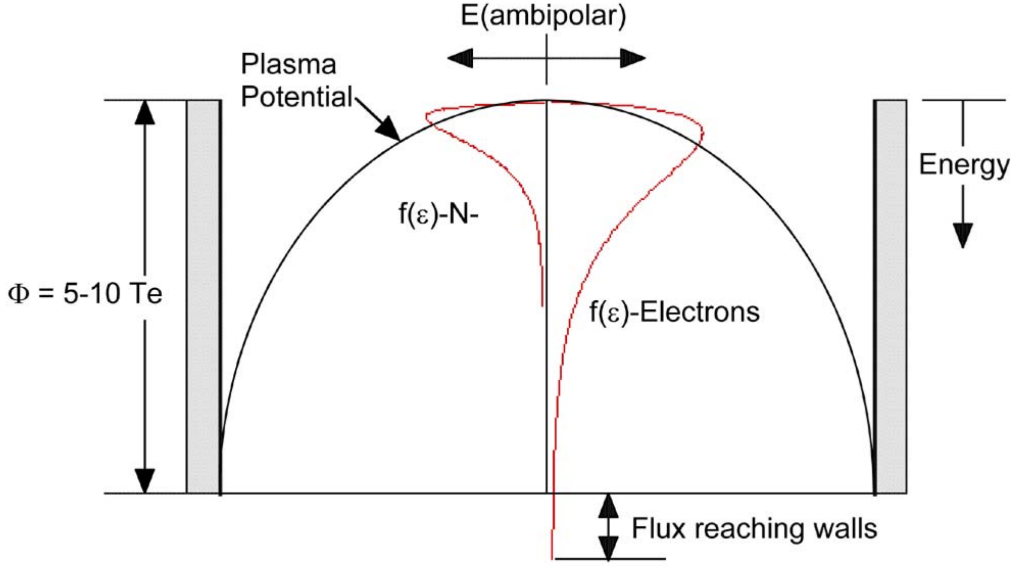
PULSED PLASMAS FOR NEGATIVE ION EXTRACTION

- During cw operation of ICPs, negative ions cannot escape the plasma.
- By pulsing the plasma (turn power on-off), during the off period (the “afterglow”)…
  - The electron temperature decreases
  - Plasma potential decreas
  - Negative ion formation (usually) increases
  - Negative ions can escape…



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PULSED PLASMAS: Ar/Cl_2 GAS CHEMISTRIES

- The ideal gas mixture is low attaching at high T_e (power-on) and highly attaching at low T_e (power-off)

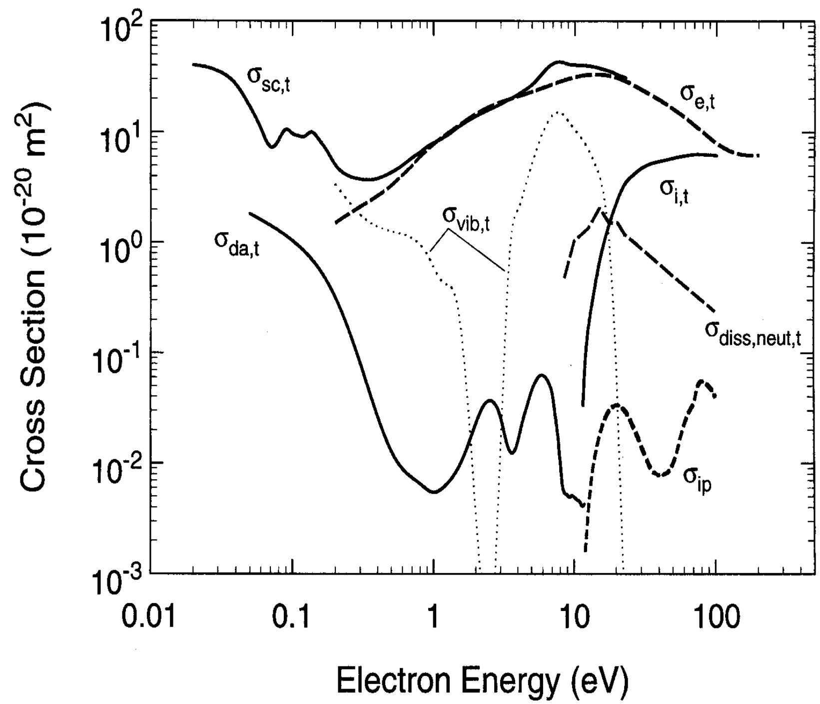
- Ar/Cl_2 mixtures have these properties.

- Dissociative attachment cross section peaks at thermal energies.

$$e + Cl_2 \rightarrow Cl + Cl^-$$

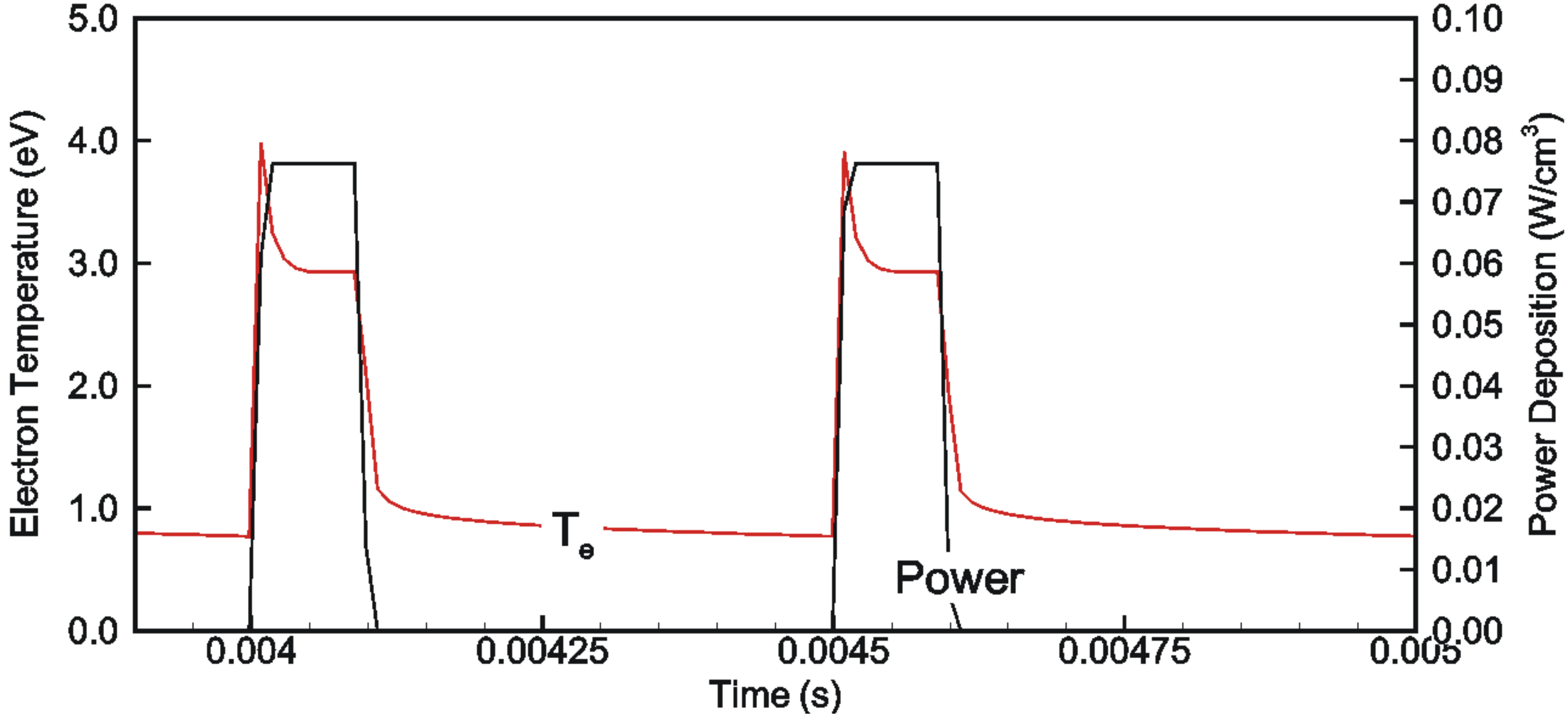
- Rapid attachment occurs in the afterglow.

Ref: J. Olthoff, Appl. J. Phys. Chem. Ref. Data, 28, 130 (1999)



- Electron impact cross sections for Cl_2.

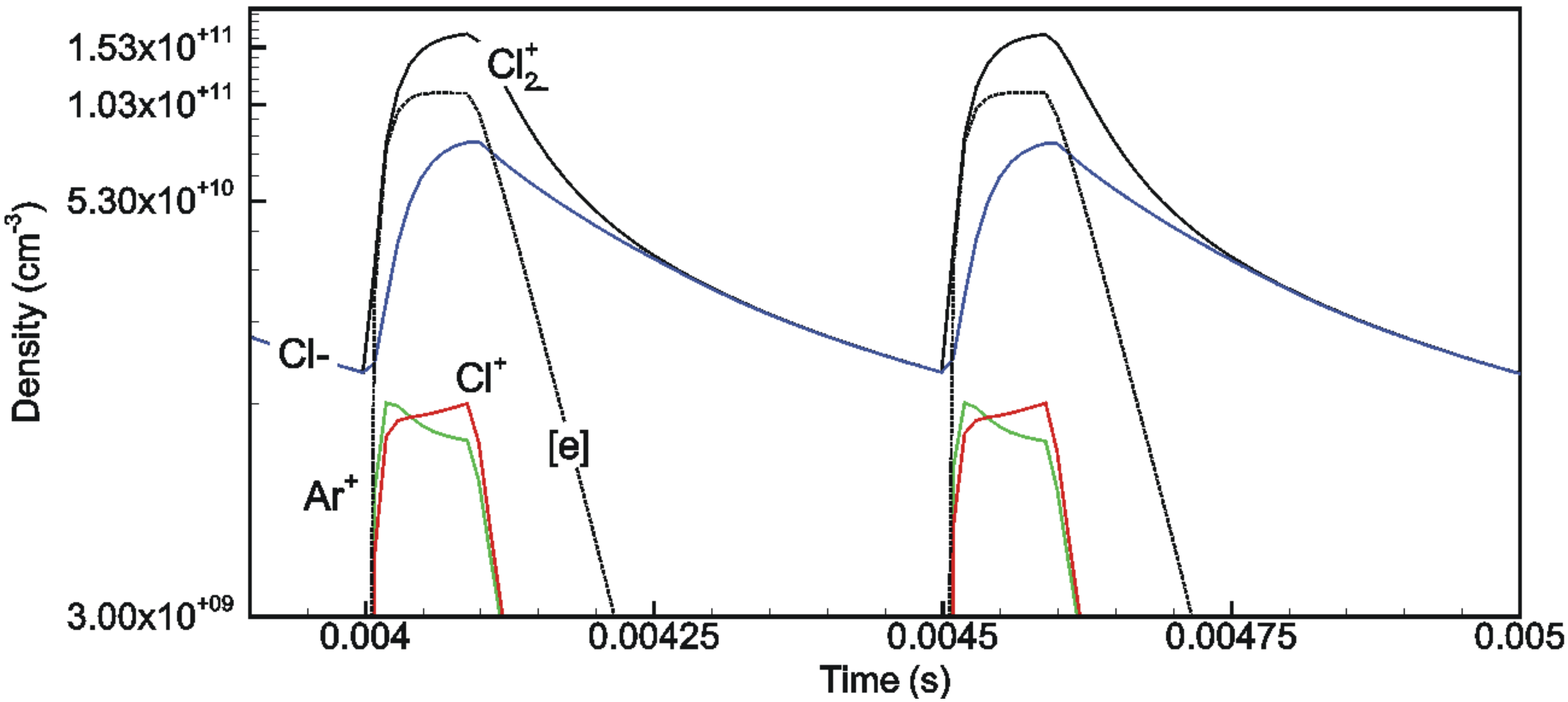
GLOBAL MODELING: PULSED Ar/Cl_2 ICPs



- **Spiking of T_e occurs at leading edge of power pulse as electron density is low producing rapid ionization. Rapid thermalization in afterglow turns off ionization; increases attachment.**

- **Ar/Cl_2 = 70/30, 15 mTorr, 2 kHz, 20% duty cycle.**

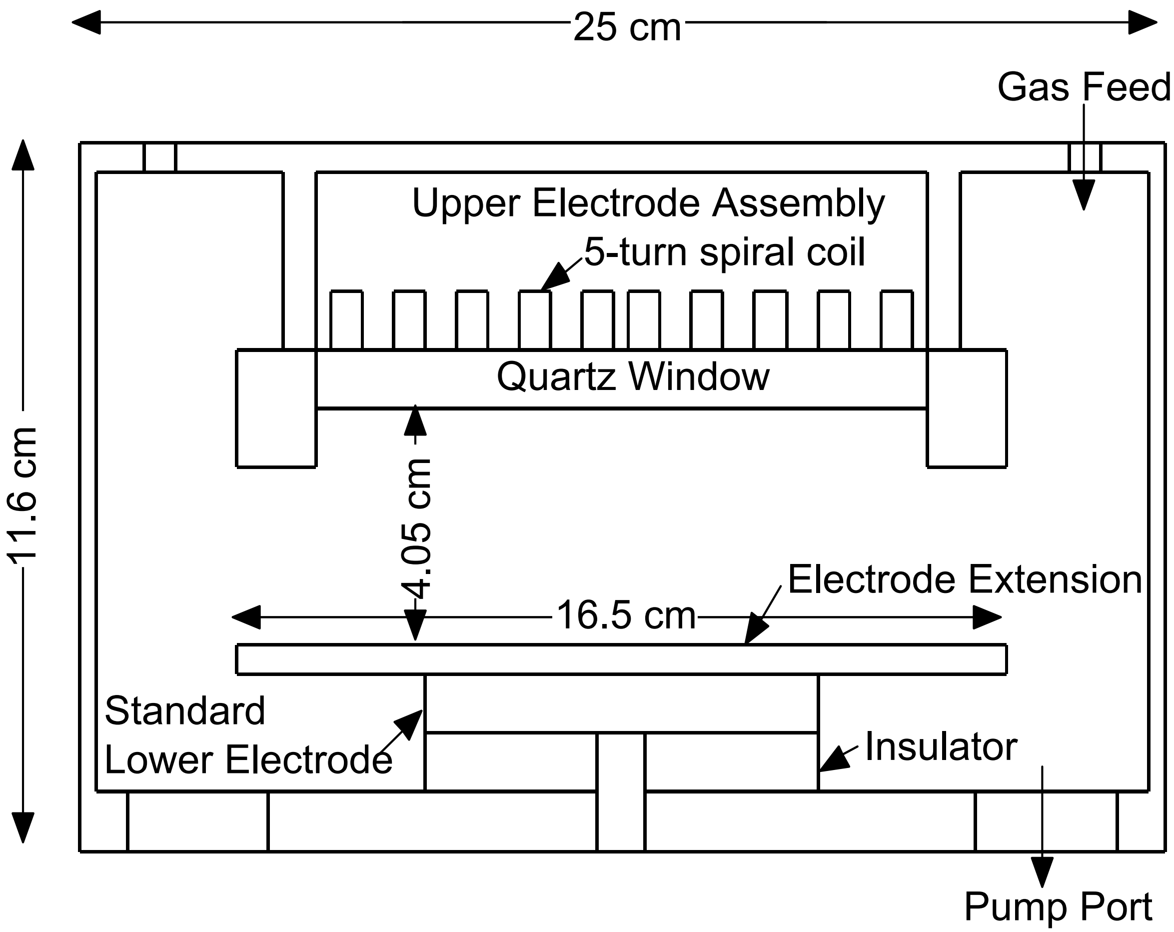
GLOBAL MODELING: PULSED Ar/Cl_2 ICPs



- **Rapid attachment in the afterglow produces an ion-ion plasma; charge balance is met by negative ions, not electrons. Ambipolar fields dissipate and negative ions can escape.**

- **Ar/Cl_2 = 70/30, 15 mTorr, 2 kHz, 20% duty cycle.**

REACTOR AND CONDITIONS



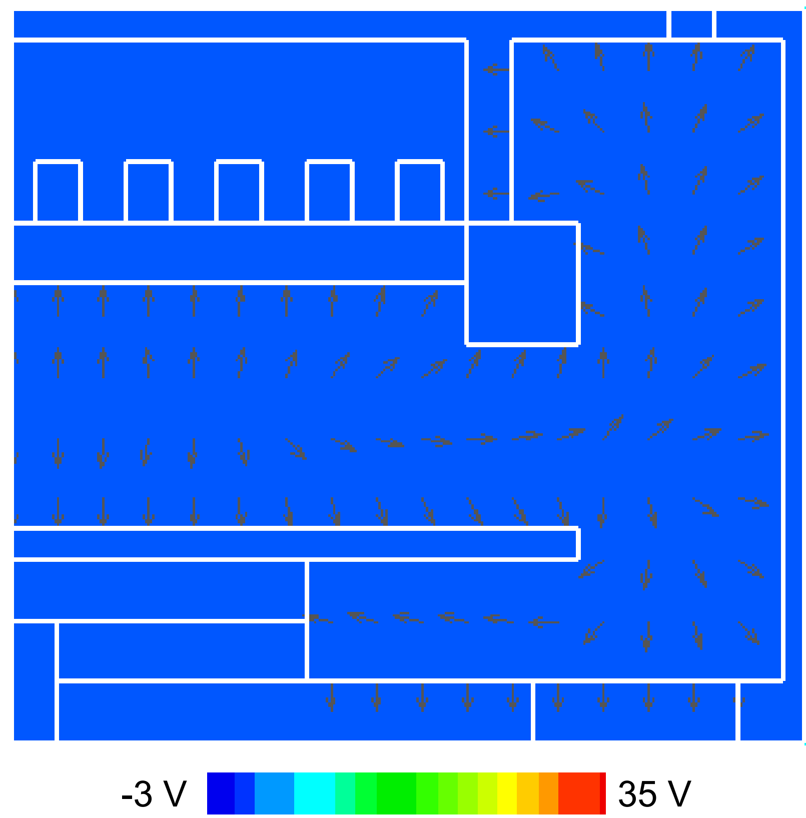
- **Simulations were performed in a GECRC**

- **Peak input power : 300 W**
- **Pulse repetition frequency : 10 kHz**
- **Pressure : 20 mTorr**
- **Inlet gas flow rate : 20 sccm**
- **Ar, Ar/Cl_2 = 80/20**

2-D DYNAMICS IN Ar/Cl_2 : PLASMA POTENTIAL AND Cl^- FLUX VECTORS

- As the pulse begins, the peak plasma potential migrates to under the coils.
- As the steady state is reached, the peak plasma potential moves towards the center.
- Cl^- flux vectors point towards the peak plasma potential when plasma potential is large.
- It takes about 25 μs for the ions to move from periphery to the center.
- When the plasma is turned off, Cl^- flux vectors reverse, pointing towards boundaries.

- Ar/Cl_2 = 80/20, 20 mTorr, 300 W, 10 kHz/50%



Animation Slide

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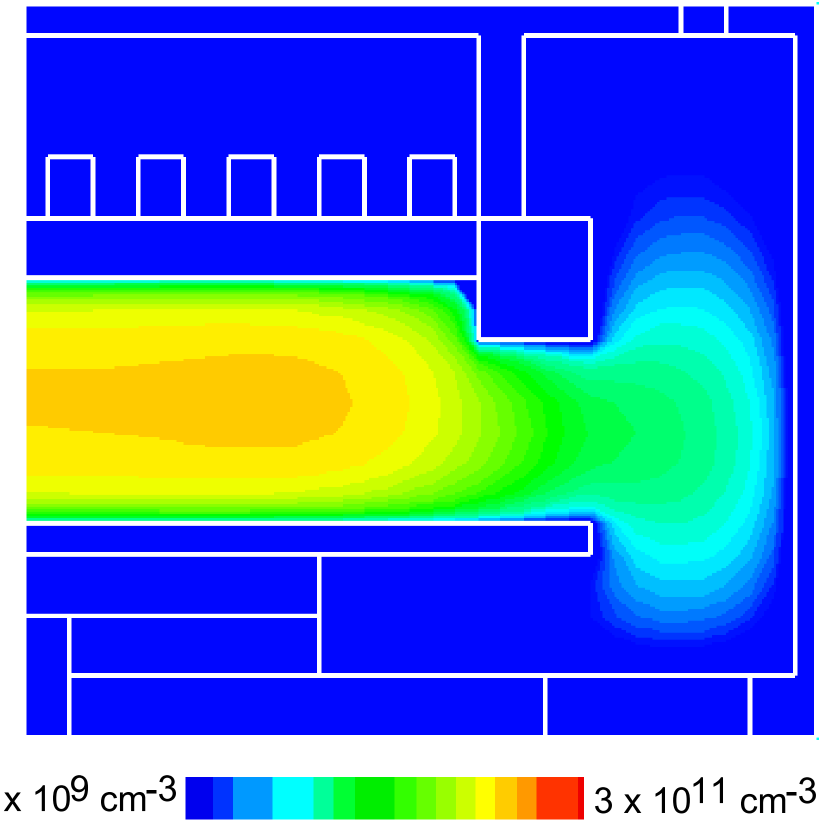
2-D DYNAMICS IN Ar/Cl_2 : Cl^- DENSITY

- **During power on, the plasma potential peaks thereby "compressing" the [Cl^-]**
- **At steady state, [Cl^-] "rebounds" as the plasma potential decreases**
- **Due to inertia, [Cl^-] does not respond to changes in plasma potential immediately.**
- **When the plasma is turned off, the [Cl^-] increases due to a higher rate of dissociative attachment at low T_e.**
- **Later, the plasma potential falls and [Cl^-] spreads**

- **Ar/Cl_2 = 80/20, 20 mTorr, 300 W, 10 kHz/50%**



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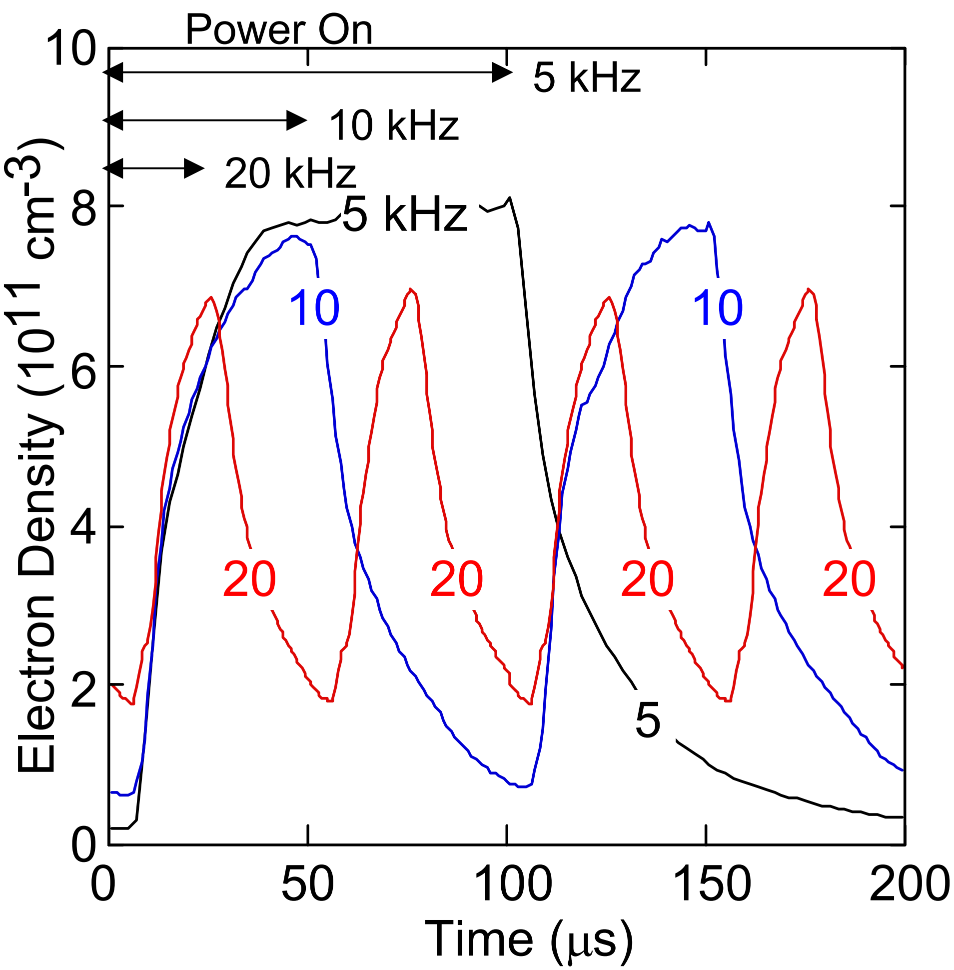
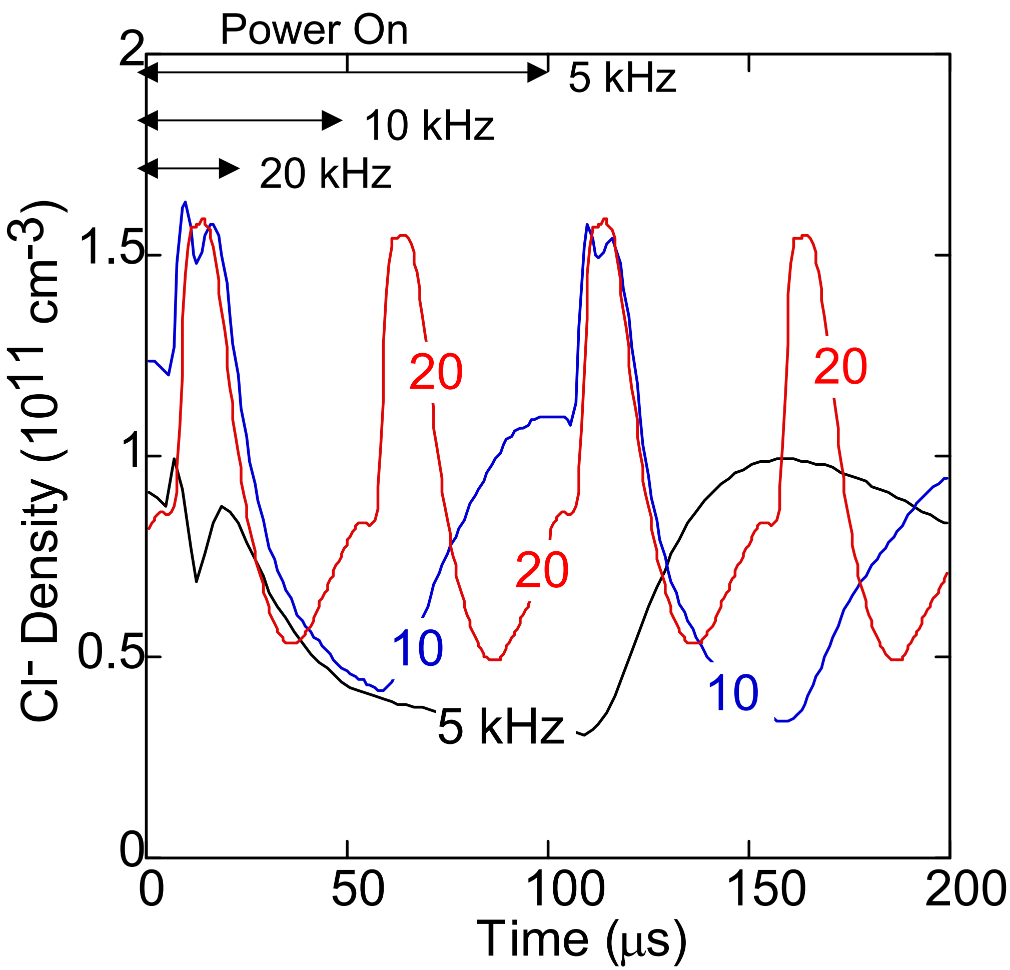
[e] vs PULSE REPETITION FREQUENCY (PRF)



- **Non-monotonic behavior in peak [e].**
- **Lower PRF results in higher rate of dissociation due to higher T_e producing less dissociative attachment.**

- **Ar/Cl_2 = 80/20, 20 mTorr, 300 W, 10 kHz, 50% duty cycle**

[Cl-] vs PULSE REPETITION FREQUENCY (PRF)



- **[Cl⁻] increases at plasma turn on as the Cl⁻ ions move to the center of plasma; and then decrease as recombination occurs.**
- **When power is removed, [Cl⁻] increases with drop in T_e, and then decreases as Cl- diffuses to walls.**

- **Ar/Cl_2 = 80/20, 20 mTorr, 300 W, 10 kHz, 50% duty cycle**

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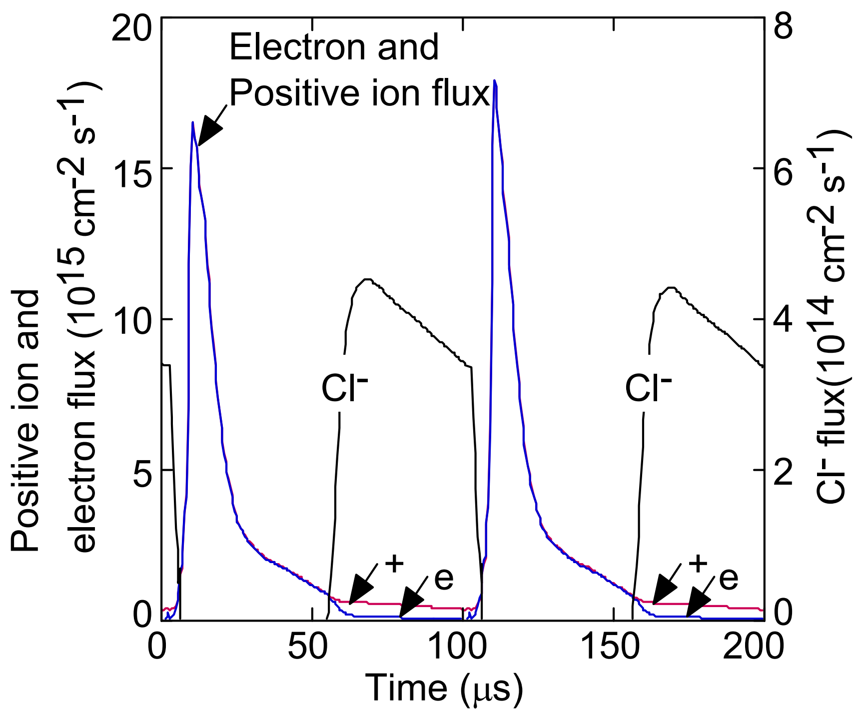
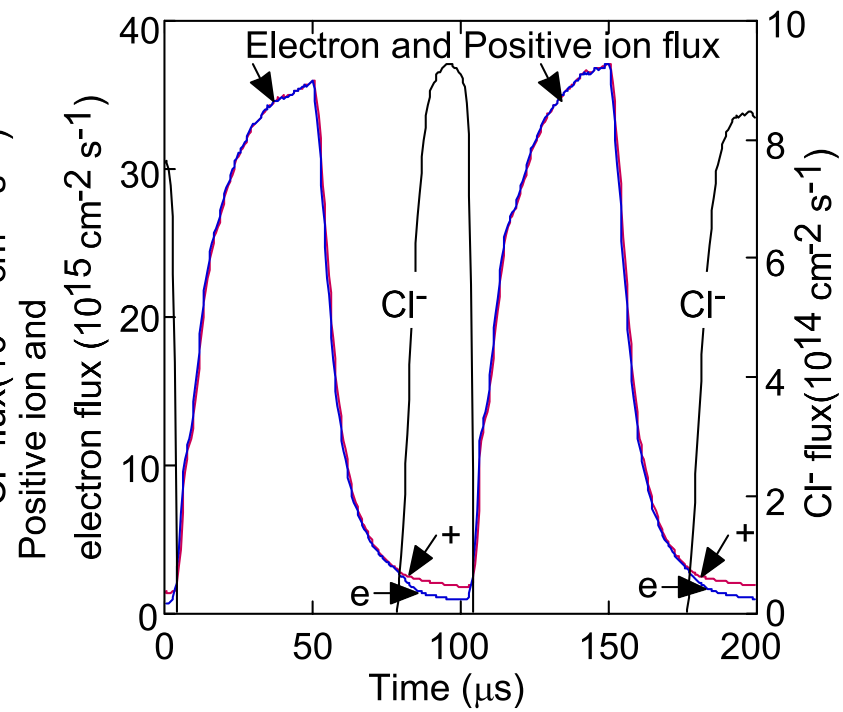
FLUXES TO SUBSTRATE: DUTY CYCLE



- **Duty cycle : 10%**



- **Duty cycle : 50%**

- **A finite time is required to transition to ion-ion plasma in the afterglow with a low plasma potential.**
- **For a give repetition rate, smaller duty cycles (longer afterglow) produces longer pulses of Cl- fluxes to the substrate.**

- **Ar/Cl_2 = 80/20, 20 mTorr, 300 W, 10 kHz**

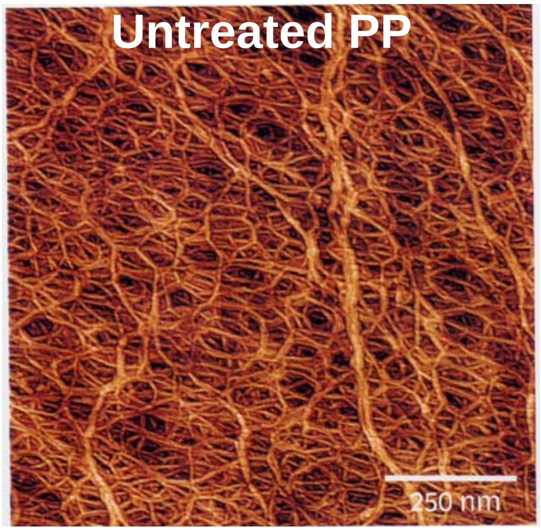
ELECTRONEGATIVE PLASMAS: ATMOSPHERIC PRESSURE

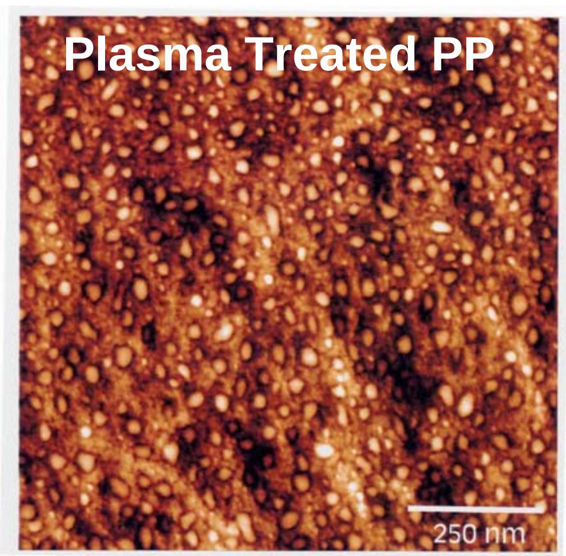
- **The vast majority of atmospheric pressure plasmas having significant electronegativity are pulsed, transient or filamentary.**
- **What changes at atmospheric pressure?**
  - **Availability of 3rd body increases rates of association reactions; and is the basis of excimer formation.**

$$Xe^+ + Cl^- + M \rightarrow XeCl(B) + M$$
$$XeCl(B) \rightarrow Xe + Cl + h\nu$$

  - **Kinetics are "local" in that transport for negative is not terribly important.**
  - **Due to higher gas densities, rates of attachment are higher, making transitions to ion-ion plasmas more rapid.**
  - **"Stationary" negative ions provide local shielding of positive ions, particularly in afterglow situations.**

PLASMA SURFACE MODIFICATION OF POLYMERS

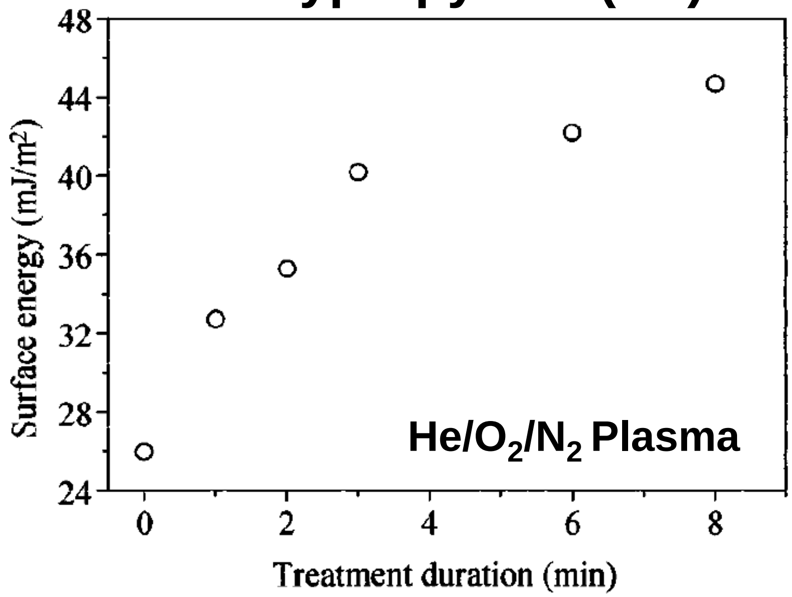




- M. Strobel, 3M

- To improve wetting and adhesion of polymers atmospheric plasmas are used to generate gas-phase radicals to functionalize their surfaces.

- Polypropylene (PP)



- Massines *et al.* J. Phys. D 31, 3411 (1998).

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FUNCTIONALIZATION OF POLYPROPYLENE

- Untreated PP is hydrophobic.
- Increases in surface energy by plasma treatment are attributed to the functionalization of the surface with hydrophilic groups.
  - Carbonyl (-C=O)
  - Alcohols (C-OH)
  - Peroxy (-C-O-O)
  - Acids ((OH)C=O)
- The degree of functionalization depends on process parameters such as gas mix, energy deposition and relative humidity (RH).
- At sufficiently high energy deposition, erosion of the polymer occurs.

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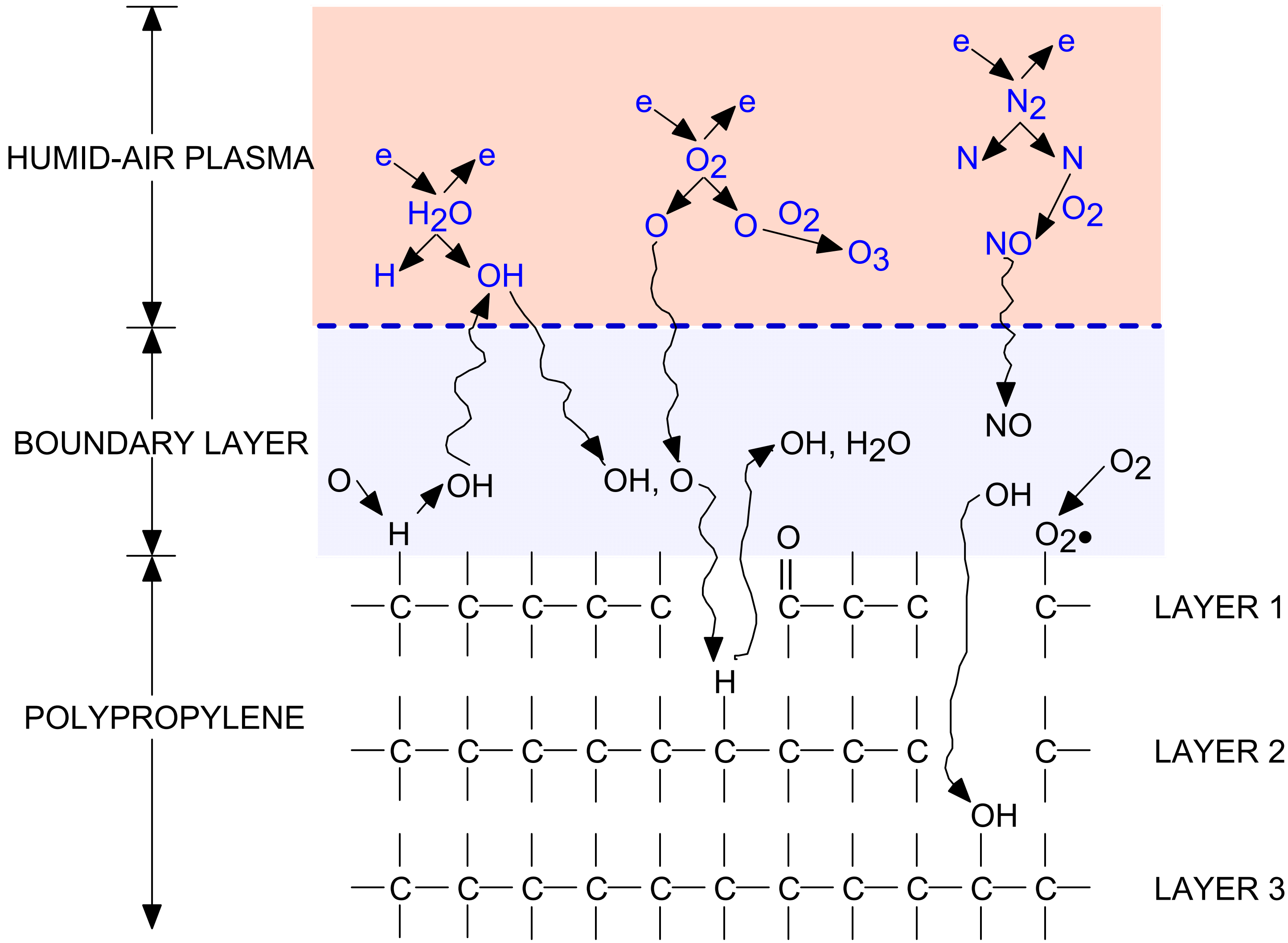
REACTION PATHWAY



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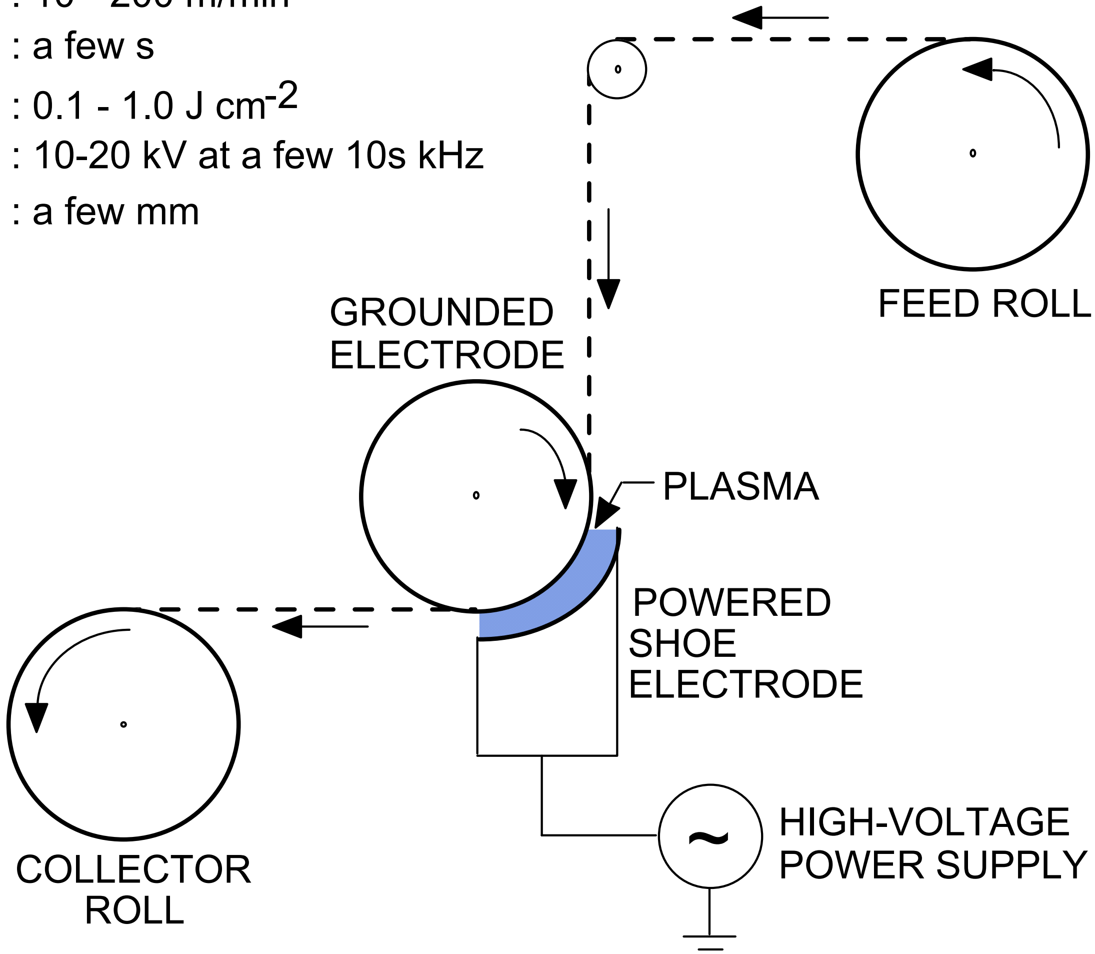
POLYMER TREATMENT APPARATUS

- TYPICAL PROCESS CONDITIONS:

Web speed	: 10 - 200 m/min
Residence time	: a few s
Energy deposition	: 0.1 - 1.0 J cm^{-2}
Applied voltage	: 10-20 kV at a few 10s kHz
Gas gap	: a few mm



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COMMERCIAL CORONA PLASMA EQUIPMENT

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HIGH PRESSURE PLASMA SIMULATION: non-PDPSIM

- 2-d rectilinear or cylindrical unstructured mesh
- Implicit drift-diffusion for charged and neutral species
- Poisson's equation with volume and surface charge, and material conduction.
- Circuit model
- Electron energy equation coupled with Boltzmann solution for electron transport coefficients
- Optically thick radiation transport with photoionization
- Secondary electron emission by impact
- Thermally enhanced electric field emission of electrons
- Surface chemistry.
- Monte Carlo Simulation for secondary electrons
- Compressible Navier Stokes for hydrodynamic flow
- Maxwell Equations in frequency domain

DESCRIPTION OF MODEL: CHARGED PARTICLES, POTENTIAL

- **Continuity with sources due to electron impact, heavy particle reactions, surface chemistry, photo-ionization and secondary emission.**

$$\frac{\partial N_i}{\partial t} = -\vec{\nabla} \cdot \vec{\phi} + S_i$$

- **Charged particle fluxes by modified Sharfetter-Gummel expression for drift-diffusion. Assuming collisional coupling between ions and flow field, v_f, advective field is included:**

$$\vec{\varphi}_{i+\frac{1}{2}} = \frac{\alpha \overline{D}(n_{i+1} - n_i \, exp(\alpha \Delta x))}{(1 - exp(\alpha \Delta x))}, \;\; \alpha = -q\overline{\mu}(\frac{\Phi_{i+1} - \Phi_i}{\Delta x}) + v_f$$

- **Poisson's Equation for Electric Potential:** $-\nabla \cdot \varepsilon \nabla \Phi = \rho_V + \rho_S$

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DESCRIPTION OF MODEL: CHARGED PARTICLE SOURCES

- **Photoionization:**

$$S_{Pi}(\vec{r}) = \int \frac{N_i(\vec{r})\sigma_{ij}N_j(\vec{r}\,')\exp\left(\frac{-\left|\vec{r}\,'-\vec{r}\right|}{\lambda}\right)d^3\vec{r}\,'}{4\pi\left|\vec{r}\,'-\vec{r}\right|^2}$$

- **Electric field and secondary emission:**

$$S_{Si} = -\nabla \cdot j, \quad j_E = AT^2\exp\left(\frac{-\left(\Phi_W - \left(q^3\mathrm{E}/\varepsilon_0\right)^{1/2}\right)}{kT_S}\right), \quad j_S = \sum_j \gamma_{ij}\phi_j$$

- **Volumetric Plasma Charge:**

$$\frac{\partial \rho_V}{\partial t} = \sum_i -\nabla \cdot \left(q_i \vec{\phi}_i\right)$$

- **Surface and in Material Charges:**

$$\frac{\partial \rho_S}{\partial t} = \sum_i -\nabla \cdot \left(q_i \vec{\phi}_i \left(1+\gamma_i\right)\right) - \nabla \cdot \left(\sigma\left(-\nabla \Phi\right) + j_E\right)$$

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DESCRIPTION OF MODEL:
ELECTRON ENERGY, TRANSPORT COEFFICIENTS

- **Electron energy equation implicitly integrated using Successive-Over-Relaxation:**

$$\frac{\partial (n_e \varepsilon)}{\partial t} = \vec{j} \cdot \vec{E} - n_e \sum_i N_i \kappa_i - \nabla \cdot \left(\frac{5}{2} \varepsilon \varphi - \lambda \nabla T_e \right), \quad \vec{j} = q \vec{\phi}_e$$

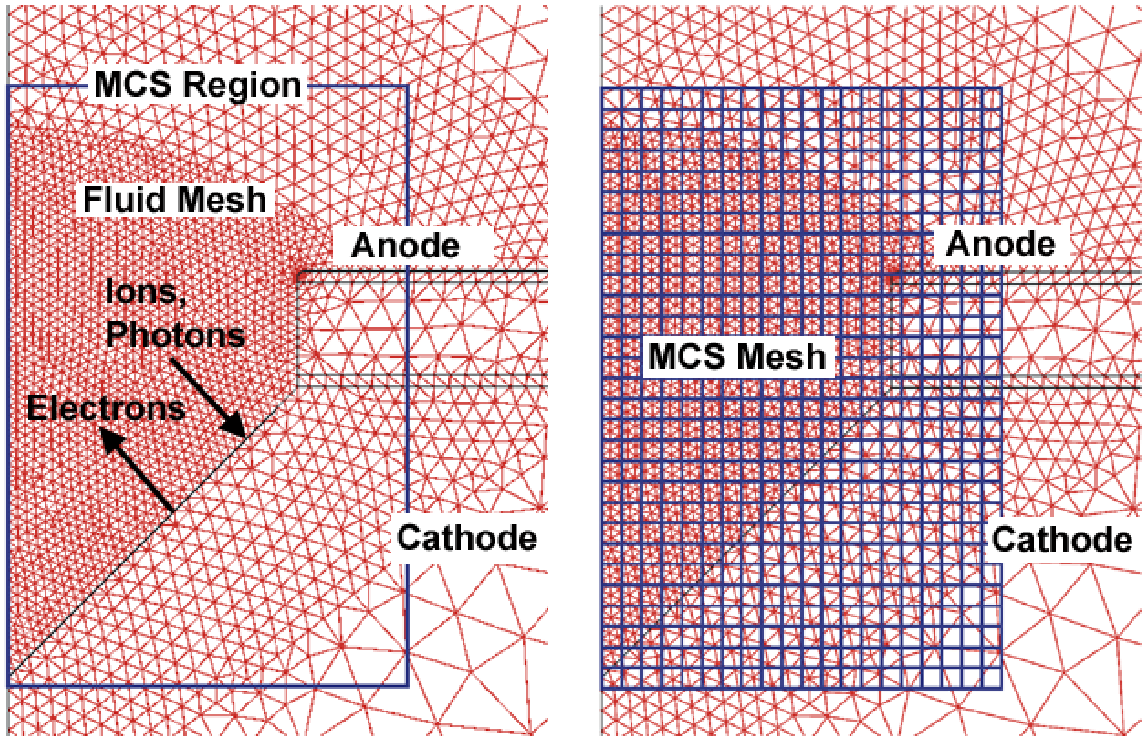
- **Electron transport coefficients obtained from 2-term spherical harmonic expansion of Boltzmann's Equation.**
- **Ion transport coefficients obtained from tabulated values from the literature or using conventional approximation techniques.**

DESCRIPTION OF MODEL:
SECONDARY ELECTRONS-MONTE CARLO SIMULATION

- **Transport of energetic secondary electrons is addressed with a Monte Carlo Simulation.**
- **MCS is periodically executed to provide electron impact source functions for continuity equations for charged and neutral particles.**
- **Algorithms in MCS account for large dynamic range in mesh resolution, electric field, and reactant densities.**

DESCRIPTION OF MODEL: MCS MESHING

- Select regions in which high energy electron transport is expected.



- Superimpose Cartesian MCS mesh on unstructured fluid mesh.
- Construct Greens functions for interpolation between meshes.

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ELECTROMAGNETICS MODEL

- The wave equation is solved in the frequency domain.

$$\nabla \cdot \left(\frac{1}{\mu} \nabla \overline{E} \right) = \frac{\partial^2 \left(\varepsilon \overline{E} \right)}{\partial t^2} + \frac{\partial \left(\sigma \overline{E} + \overline{J}_{antenna} \right)}{\partial t}$$

- All quantities are complex for to account for finite collision frequencies.

- Solved using method of Successive-over-Relaxation

COMPRESSIBLE NAVIER STOKES

- **Fluid averaged values of mass density, mass momentum and thermal energy density obtained in using unsteady algorithms.**

$$\frac{\partial \rho}{\partial t} = -\nabla \cdot (\rho \vec{v}) + (inlets, pumps)$$

$$\frac{\partial (\rho \vec{v})}{\partial t} = \nabla (NkT) - \nabla \cdot (\rho \vec{v}\vec{v}) - \nabla \cdot \overline{\mu} + \sum_i q_i N_i \vec{E}_i$$

$$\frac{\partial (\rho c_p T)}{\partial t} = -\nabla \left(-\kappa \nabla T + \rho \vec{v} c_p T \right) + P_i \nabla \cdot v_f - \sum_i R_i \Delta H_i + \sum_i \vec{j}_i \cdot \vec{E}$$

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DESCRIPTION OF MODEL: NEUTRAL PARTICLE UPDATE

- **Transport equations are implicitly solved using Successive-Over-Relaxation:**

$$N_i(t+\Delta t) = N_i(t) - \nabla \cdot \left(\vec{v}_f - D_i N_T \nabla \left(\frac{N_i(t+\Delta t)}{N_T} \right) \right) + S_V + S_S$$

- **Surface chemistry is addressed using "flux-in/flux-out" boundary conditions with reactive sticking coefficients**

$$S_{Si} = \sum_j \left(\nabla \cdot \vec{\phi}_j \right) \gamma_{ij}$$

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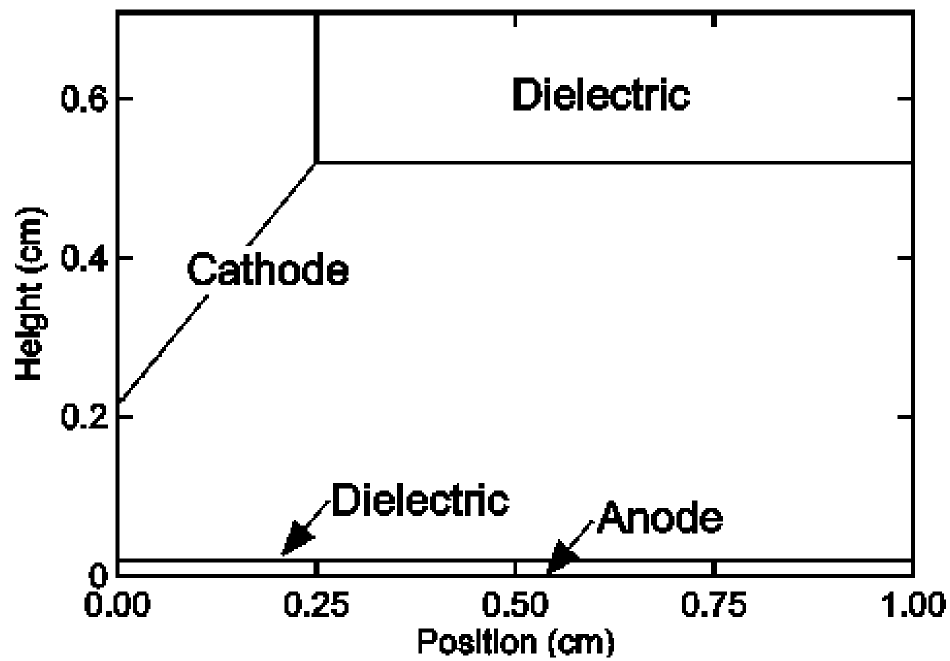
ATMOSPHERIC PRESSURE LINEAR CORONA

- **Demonstrate concepts of pulsed atmospheric pressure electronegative plasma with linear corona discharge as used in polymer functionalization.**
- **Device is functionally a dielectric barrier discharge. Discharge is initiated by field emission from cathode.**



- **Dry Air N_2/O_2 = 80/20, -15 kV, 2 mm gap**

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LINEAR CORONA: NEGATIVE ION DYNAMICS

- **Dissociative attachment ($e + O_2 \rightarrow O^- + O$) has a 5 eV threshold energy. Occurs dominantly in high E/N regions.**
- **3-body non-dissociative attachment ($e + O_2 + M \rightarrow O_2^- + M$) has no threshold. Occurs with frequency 4×10^8 s^{-1} (2 ns lifetime) in atmospheric pressure air.**
- **O_2^- charge exchanges with O ($O_2^- + O \rightarrow O_2^- + O^-$, $k = 1.5 \times 10^{-10}$ cm^3 s^{-1}). With maximum O density (4×10^{16} cm^{-3}), lifetime is 0.1 μs (not very important).**
- **O^- associates by deattachment with O ($O^- + O \rightarrow O_2 + e$, $k = 2 \times 10^{-10}$ cm^3 s^{-1}). With maximum O density (4×10^{16} cm^{-3}), lifetime is 0.1 μs (not very important).**
- **Negative ions are fairly stable (and immobile) until ion-ion neutralization [k(effective-2 body)= 5×10^{-6} cm^3 s^{-1}, lifetime 10's ns].**

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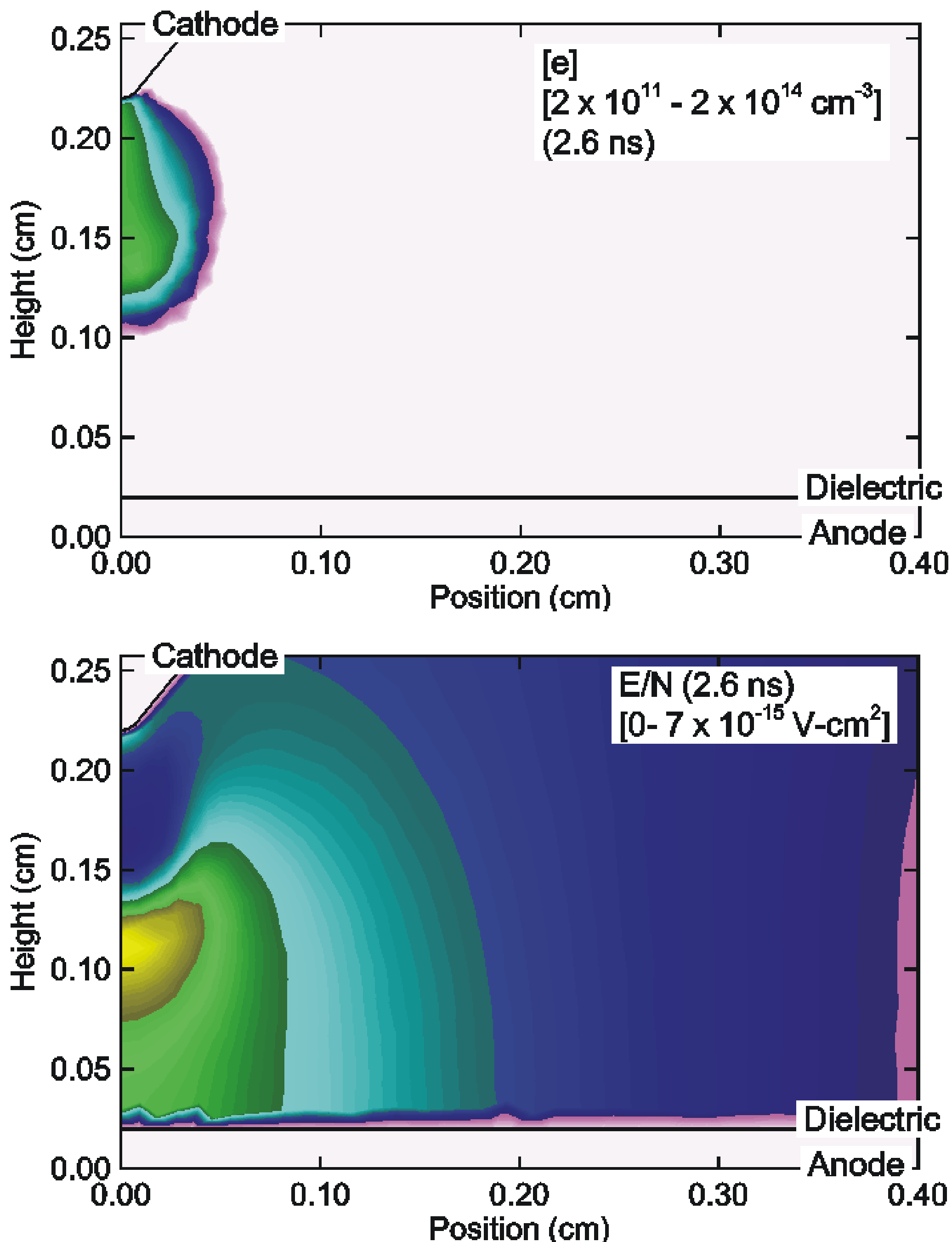
LINEAR CORONA: [e], E/N



NEGPLASMA_0903_49

- **Electron density bridges gap sustained by ionization produced by charge enhanced E/N.**
- **Electrons spread on dielectric web as charge accumulates.**

- **N_2/O_2 = 80/20, -15 kV, 100 ns (log-time)**

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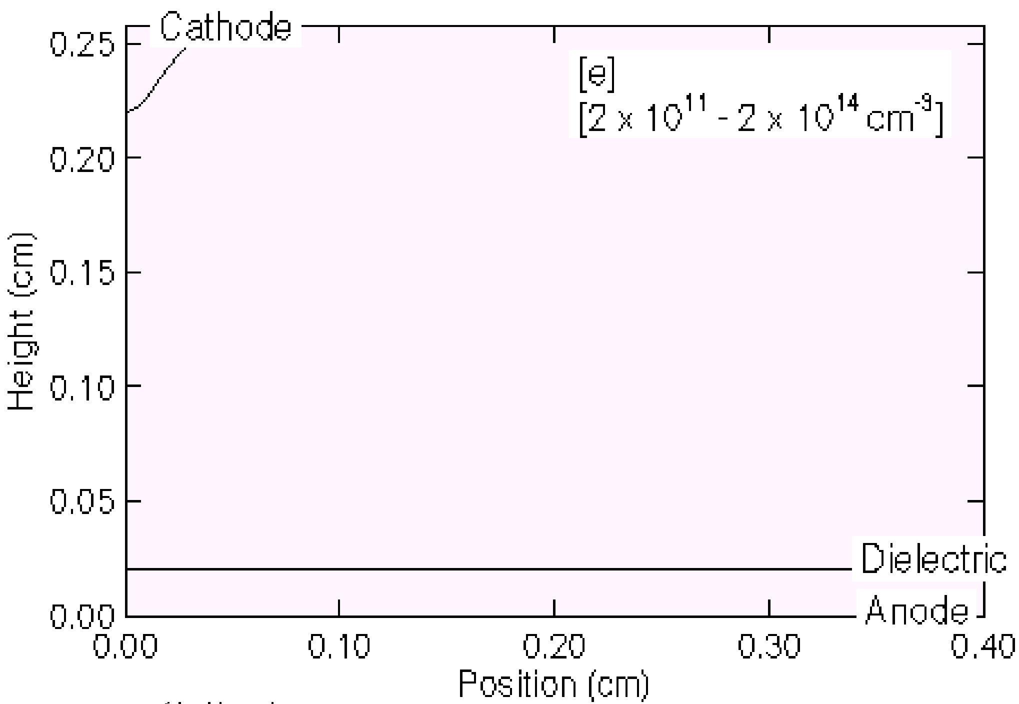

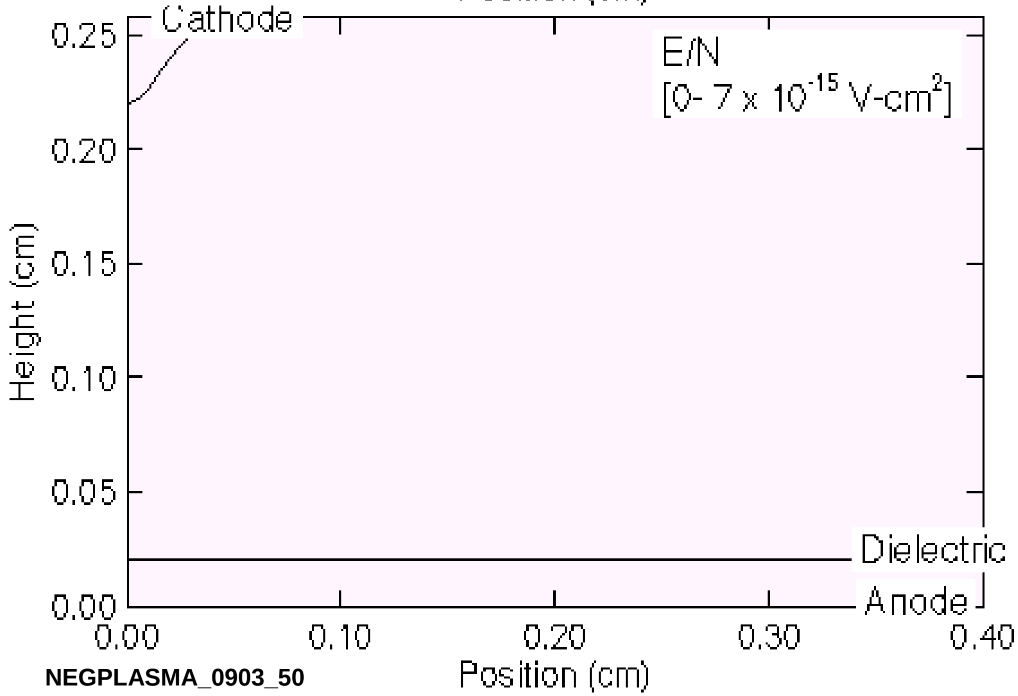

NEGPLASMA_0903_50

LINEAR CORONA: [e], E/N

- **Electron density bridges gap sustained by ionization produced by charge enhanced E/N.**
- **Electrons spread on dielectric web as charge accumulates.**

  - **N_2/O_2 = 80/20, -15 kV, 100 ns (log-time)**

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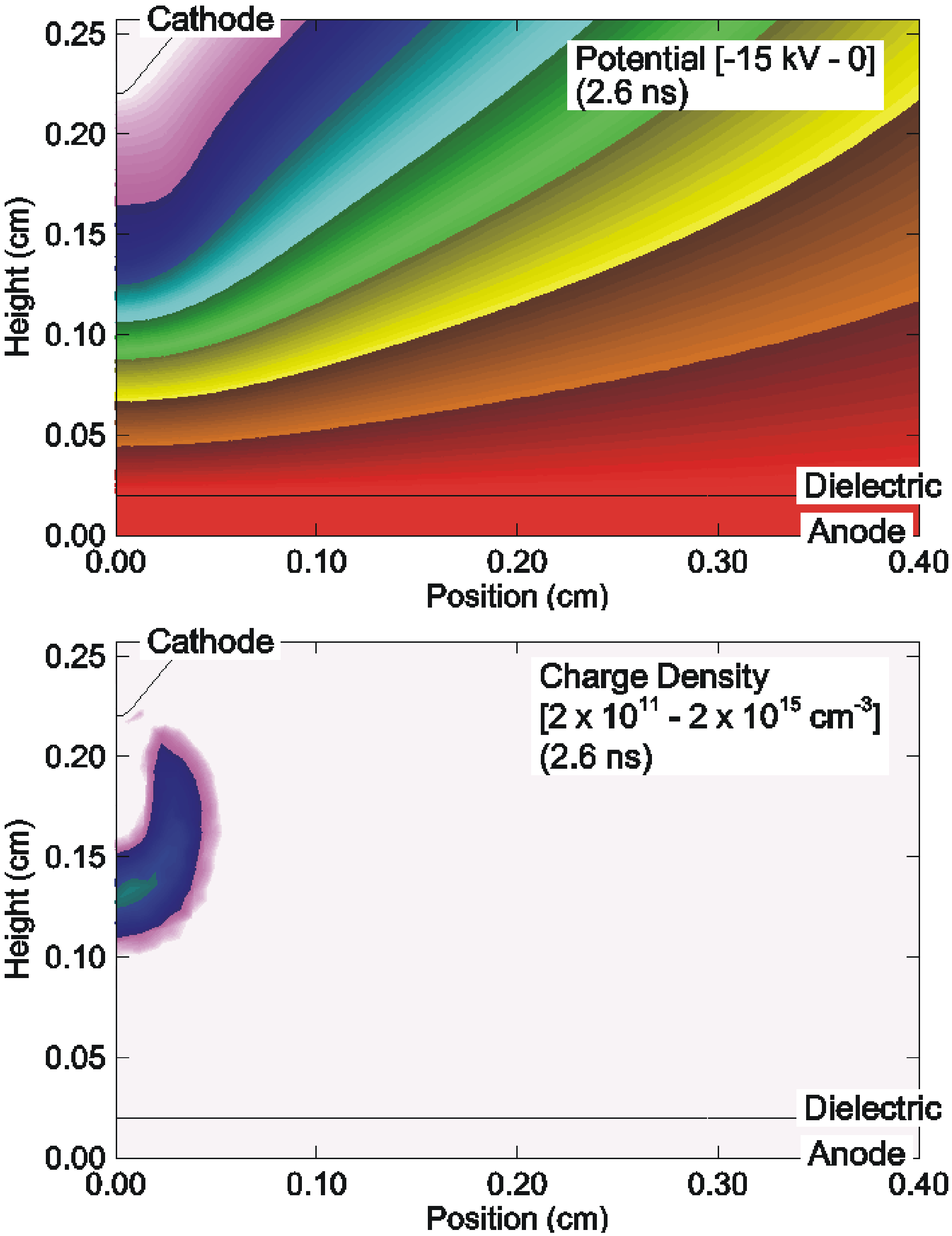
LINEAR CORONA:

POTENTIAL, CHARGE



NEGPLASMA_0903_51

- **Charge density sustains E/N at front of avalanche.**
- **Electric potential is shielded from the gap by charging of the dielectric web.**

- **N_2/O_2 = 80/20, -15 kV, 100 ns (log-time)**

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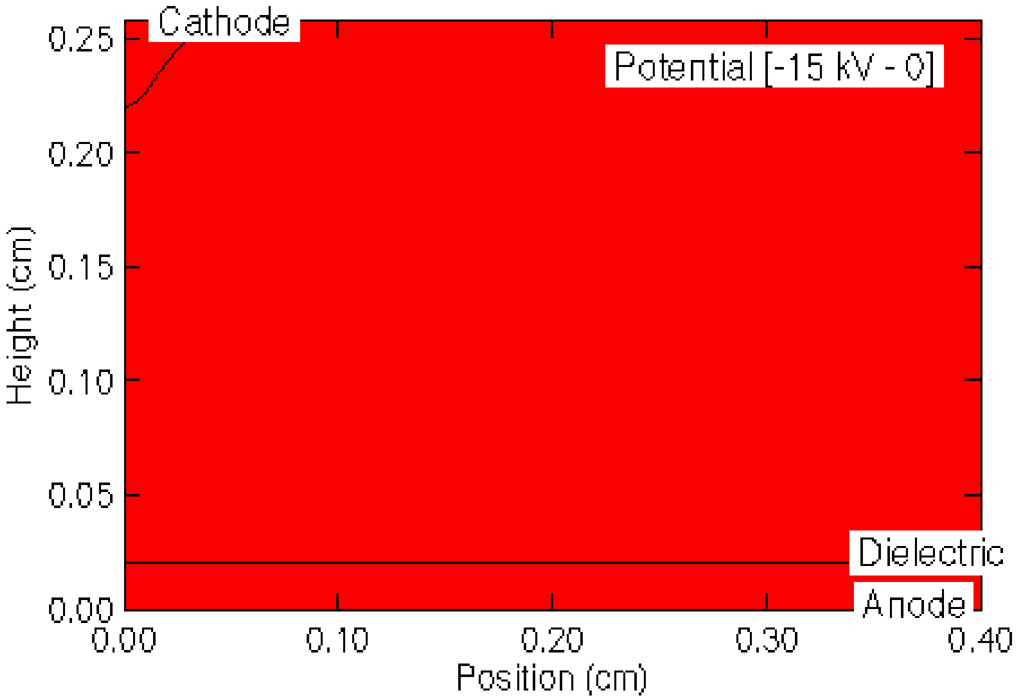

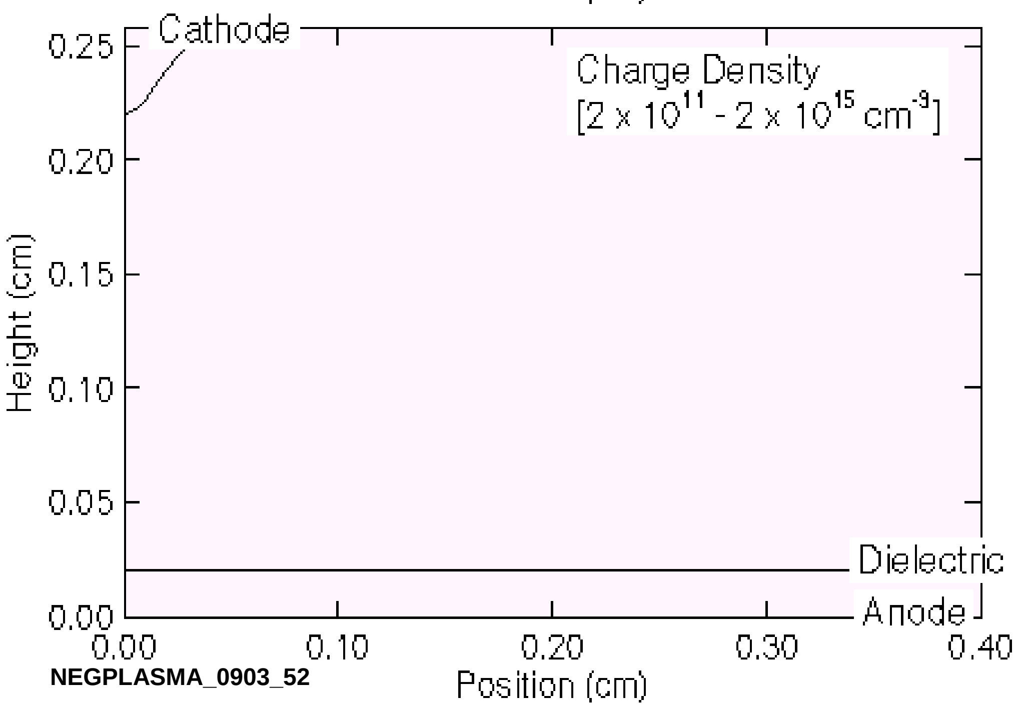

NEGPLASMA_0903_52

LINEAR CORONA:

POTENTIAL, CHARGE

- **Charge density sustains E/N at front of avalanche.**
- **Electric potential is shielded from the gap by charging of the dielectric web.**

- **N_2/O_2 = 80/20, -15 kV, 100 ns (log-time)**

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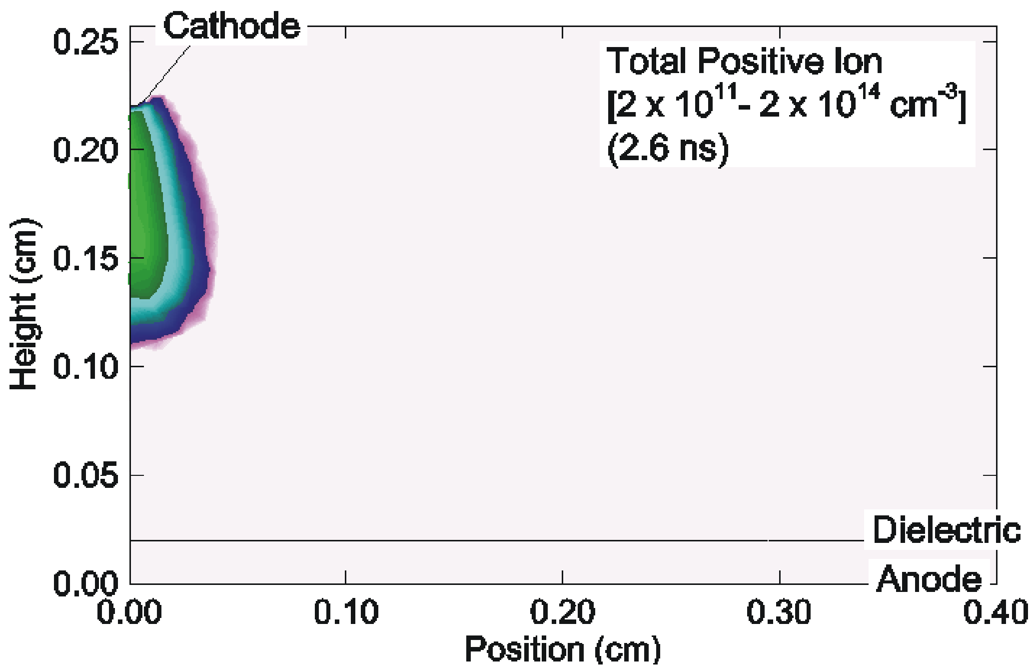

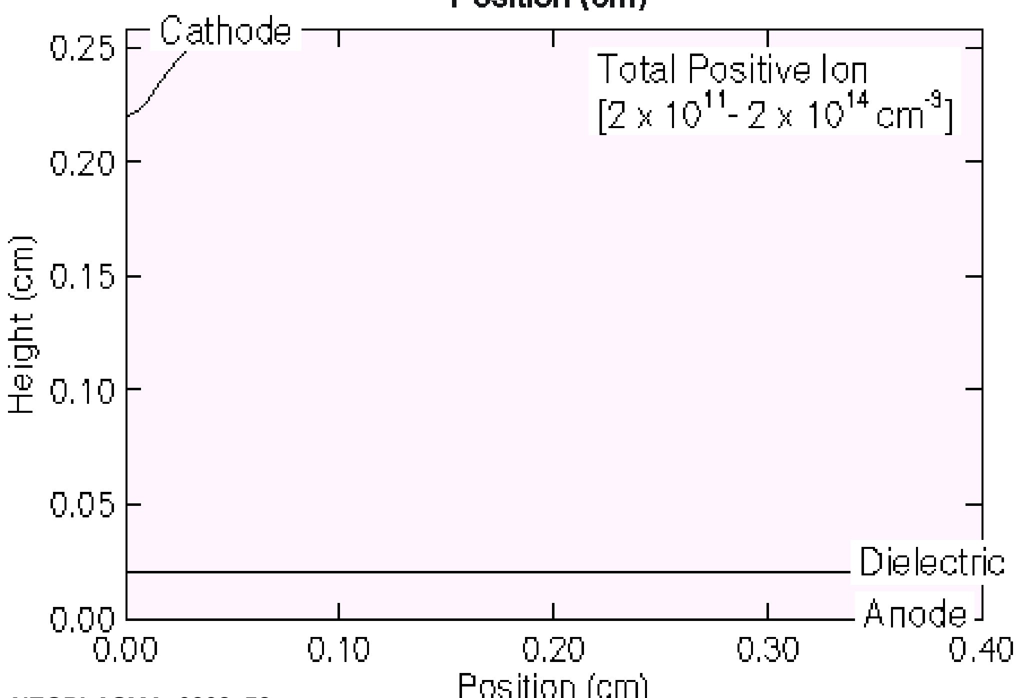

NEGPLASMA_0903_53

LINEAR CORONA: TOTAL POSITIVE ION DENSITY

- **Positive ions: N_2^+, N_4^+, N^+, O^+, O_2^+.**
- **Heavy ions at atmospheric pressure are nearly immobile during short duration of pulse.**
- **Loss is dominantly by local processes (e-ion recombination, ion-ion neutralization).**
  - **N_2/O_2 = 80/20, -15 kV, 100 ns (log-time)**

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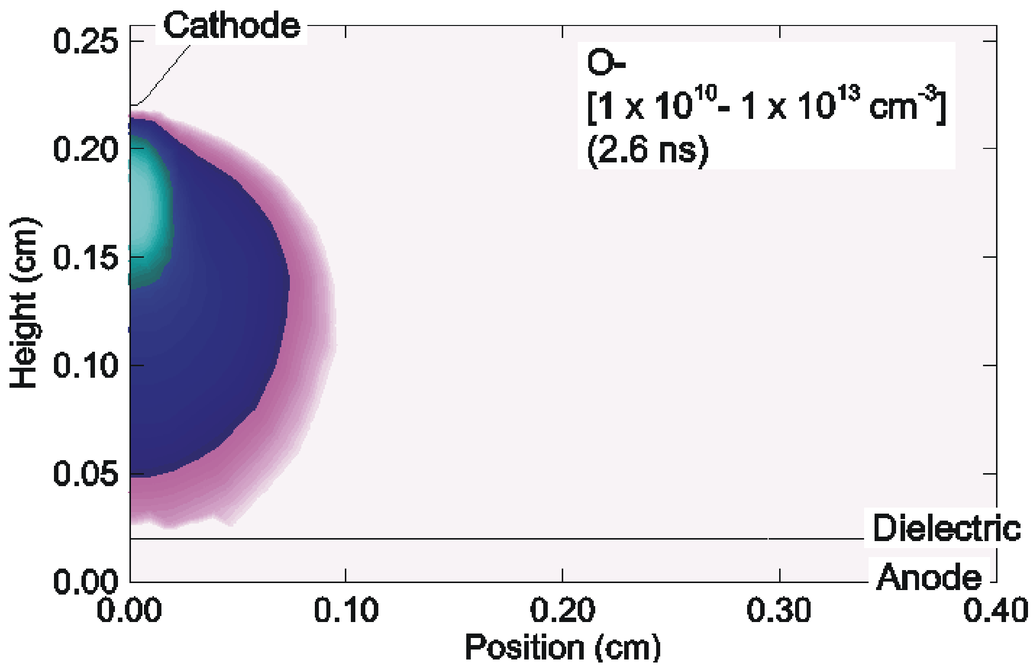
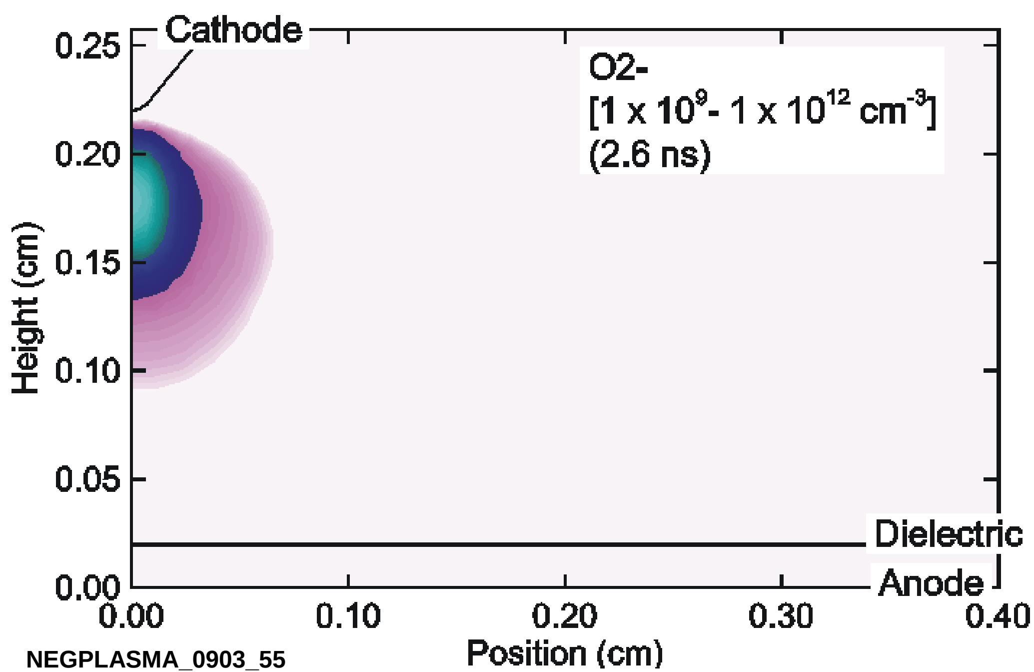
LINEAR CORONA: NEGATIVE IONS O^-, O_2^-





NEGPLASMA_0903_55

- **Rapid conversion of e to O_2^- by 3-body processes produces an ion-ion plasma in afterglow.**
- **Nearly immobile negative ions (μ=2 cm^2/V-s, v_{drift} = 10^5 cm/s) are largely consumed where formed by ion-ion neutralization.**

- **N_2/O_2 = 80/20, -15 kV, 100 ns (log-time)**

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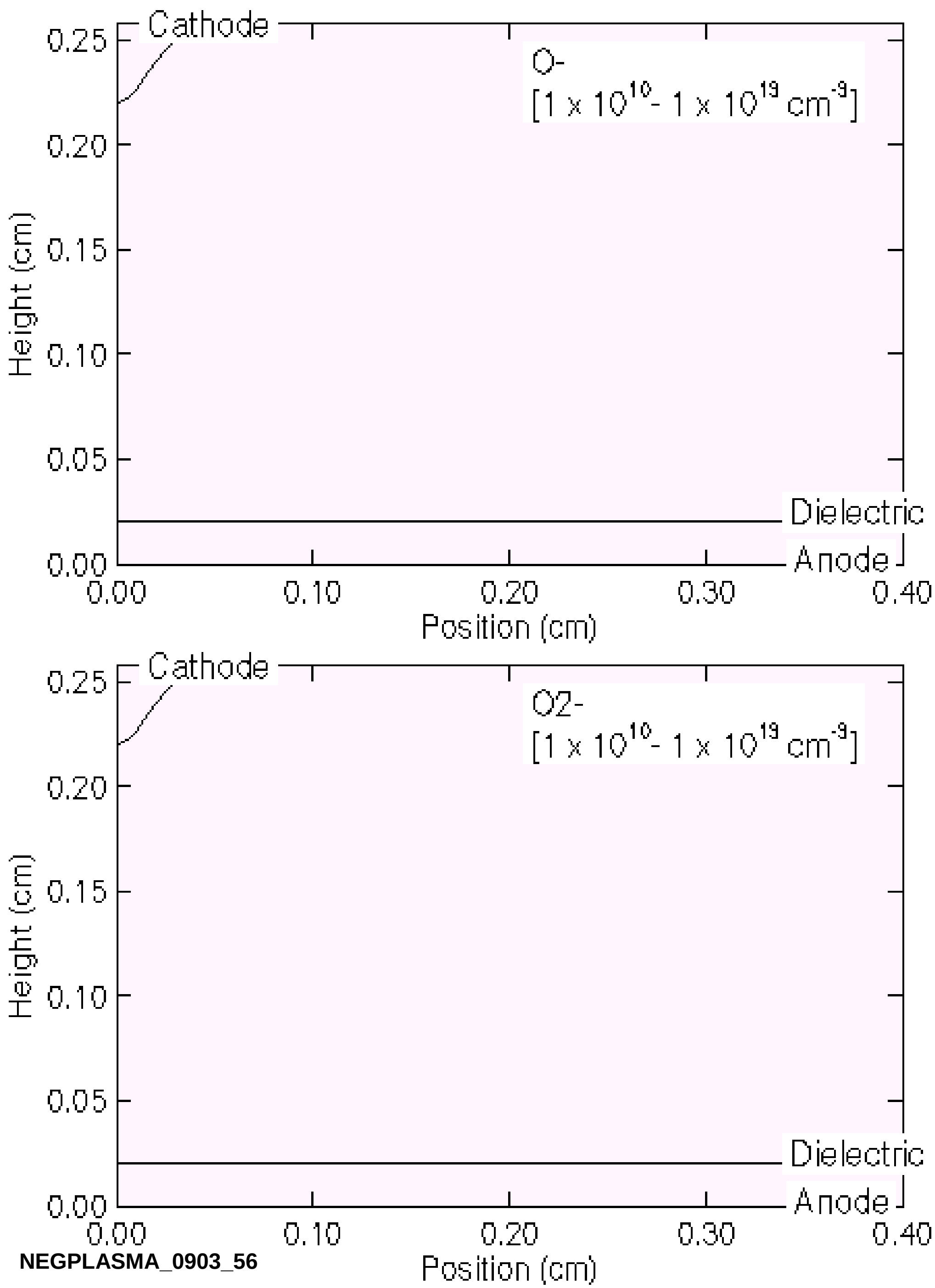
LINEAR CORONA: NEGATIVE IONS O^-, O_2^-



NEGPLASMA_0903_56

- **Rapid conversion of e to O_2^- by 3-body processes produces an ion-ion plasma in afterglow.**
- **Nearly immobile negative ions (μ=2 cm^2/V-s, v_{drift} = 10^5 cm/s) are largely consumed where formed by ion-ion neutralization.**

  - **N_2/O_2 = 80/20, -15 kV, 100 ns (log-time)**

MIN **MAX**

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CONCLUDING REMARKS

- **As you develop you models for electronegative plasmas (or any type plasma)…**
- **Construct your models as *GENERALLY* as possible. *Never, never, never hardwire any species or chemical reaction mechanism in your code*.**
- **Read all options, species, mechanisms as input from *WELL MAINTAINED AND DOCUMENTED DATABASES*.**
- **Develop *STANDARDS* for input, output, use of databases and visualization which *ALL* of your codes obey.**
- ***DOCUMENT, DOCUMENT, DOCUMENT!!!* Every input-variable, every output-parameter, every process. Have "official" versions.**
- **ARCHIVE, ARCHIVE, ARCHIVE!!! Example cases, documentation, best practice, official version.…A computer knowledgeable person should be able to run cases in a day.**

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