Gas-Surface Interaction Modeling for Carbon Nanotube Deposition

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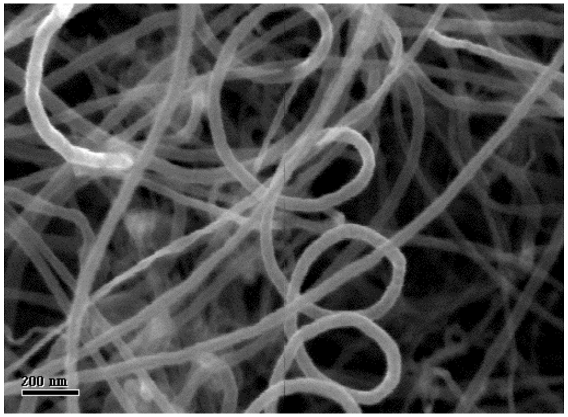
Agenda:
Gas-Surface Interaction in Parts

- Part One: Surface chemical kinetics model

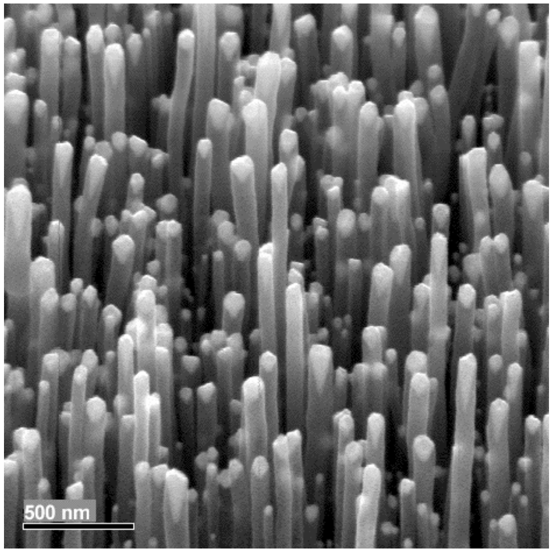
- Part Two: Surface temperature model

Plasma Enhanced CVD for CNTs

- Aligned carbon nanotubes are essential for various potential applications of interest (field-emission devices, biosensors, and interconnects).
- Alignment in PECVD is a result of electrostatic forces generated by strong sheath fields*.



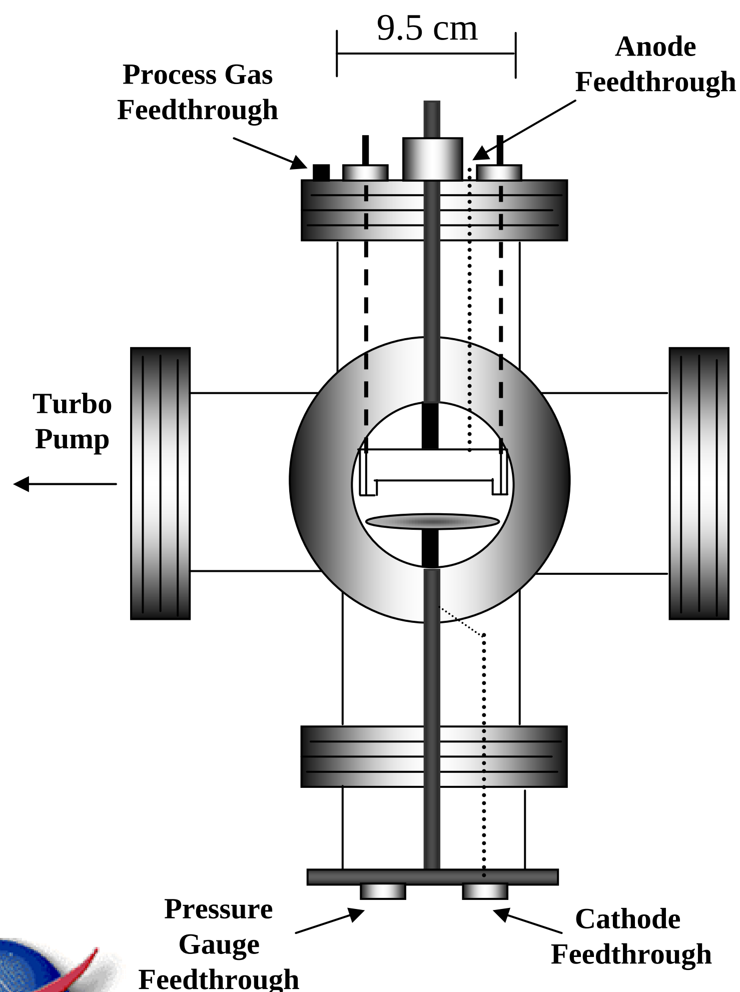
Spaghetti



Aligned

*Merkulov *et al*., Appl. Phys. Lett. **79**, 2970 (2001).

NASA Ames dcPECVD Reactor



- dcPECVD first used by Z. F. Ren† to grow arrays of well-aligned multi-walled carbon nanotubes
- Grounded anode and dc-biased cathode with 3.8 cm separation
- 6.6 cm diameter cathode

†Ren *et al.*, Science **282**, 1105 (1998).

Governing 1-D Equations for SEMS code

Mass: $$\frac{\partial \rho_s}{\partial t} + \frac{1}{A}\nabla \cdot AJ_s = W_s + \frac{2}{R}W_{s,w} + \frac{\rho_{s,i} - \rho_s}{\tau}$$

Neutral Energy: $$\frac{\partial}{\partial t}\left(\rho_n C_{v,n} T\right) + \frac{1}{A}\nabla \cdot A\sum_n q_s = Q_c + Q_{CE} - \sum_n \sum_r W_{s,r}\Delta H_r^\circ + \sum_n \frac{\rho_{s,i}h_{s,i} - \rho_s h_s}{\tau} + \frac{2}{R}Z_w$$

Electron And Ion Energy:

$$\frac{\partial}{\partial t}\left(\rho_e C_{v,e} T_e\right) + \frac{1}{A}\nabla \cdot Aq_e = -\frac{e}{m_e}J_e \cdot E - Q_c - \sum_r W_{e,r}\Delta H_r^\circ$$

$$\frac{\partial}{\partial t}\left(\rho_i C_{v,i} T_i\right) + \frac{1}{A}\nabla \cdot Aq_i = \frac{e}{m_i}J_i \cdot E - Q_{CE} - \sum_r W_{i,r}\Delta H_r^\circ$$

Poisson: $$\nabla^2 \Phi = -\frac{\rho_c}{\varepsilon_0}$$

Drift and Diffusion: $$J_s = \rho_s \mu_s E - \frac{P\mathrm{D}_s}{R_s T_s}\nabla \frac{P_s}{P} - \frac{\mathrm{D}_s^T}{T_s}\nabla T_s$$

Heat Flux: $$q_s = h_s J_s - \kappa_s \cdot \nabla T_s - R_s T_s \mathrm{D}_s^T \cdot \nabla \ln \frac{P_s}{P}$$

Surface Formulation*

$$\sum_s \nu'_{sr}\chi_s = \sum_s \nu''_{sr}\chi_s$$

Surface Production Rate:

$$\dot{S}_s = \sum_r (\nu''_{sr} - \nu'_{sr}) q_r, \quad q_r = k_{f_r} \prod [X_s]^{\nu'_{sr}} - k_{b_r} \prod [X_s]^{\nu''_{sr}}$$

Gas Phase Concentrations: $[X_s] = \rho_s / M_s$

Surface Concentrations: $[X_s] = \dfrac{Z_s \Gamma}{\sigma_s}$

Gas-phase species: $J_s = \dot{S}_s M_s$

Surface species: $\dot{S}_s = 0$

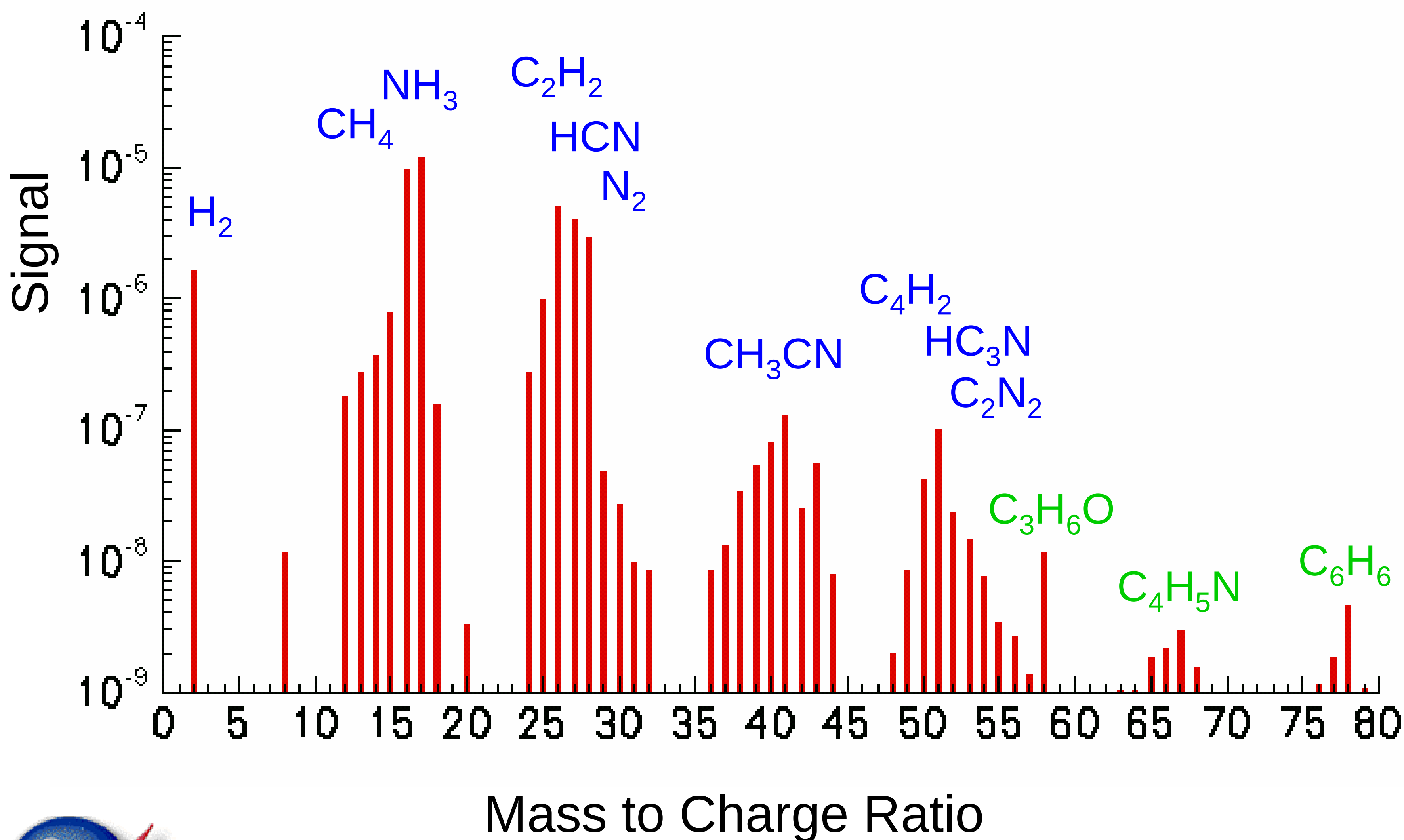
Deposited species: $G_s = \dfrac{\dot{S}_s M_s}{\rho_s}$

*Coltrin, Kee, Rupley, and Meeks, SURFACE CHEMKIN-III, SAND96-8217, 1996.

dcPECVD Reactor Conditions

- Flow Rates: 22.5 sccm C_2H_2, 80 sccm NH_3
- 22 Neutral Species: H_2,H,CH_4,CH_3,CH_2,C_2H_4,C_2H_3,C_2H_2,C_2H,C_3H_3,C_3H_2,C_4H_2,N_2,N,NH_3,NH_2,NH,HCN,CN,HC_3N,CH_3CN,C_2N_2
- 7 Charged Species: NH_3^+,NH_4^+,$C_2H_2^+$,$C_2H_3^+$,H_3^+,H_2^+,e
- 9 Surface Species: Ni(S),H(S),C(S,R_3),CH(S,R_2),CH_2(S,R),CH_3(S),C_2(S,R_2),C_2H(S,R),C_2H_2(S)
- 148 Gas-Phase Reactions, 17 Surface Reactions
- DC Voltage Bias: 525 V Pressure: 4 Torr
- Anode: $450^\circ C$ Cathode: $700^\circ C$

Downstream Residual Gas Analysis Results



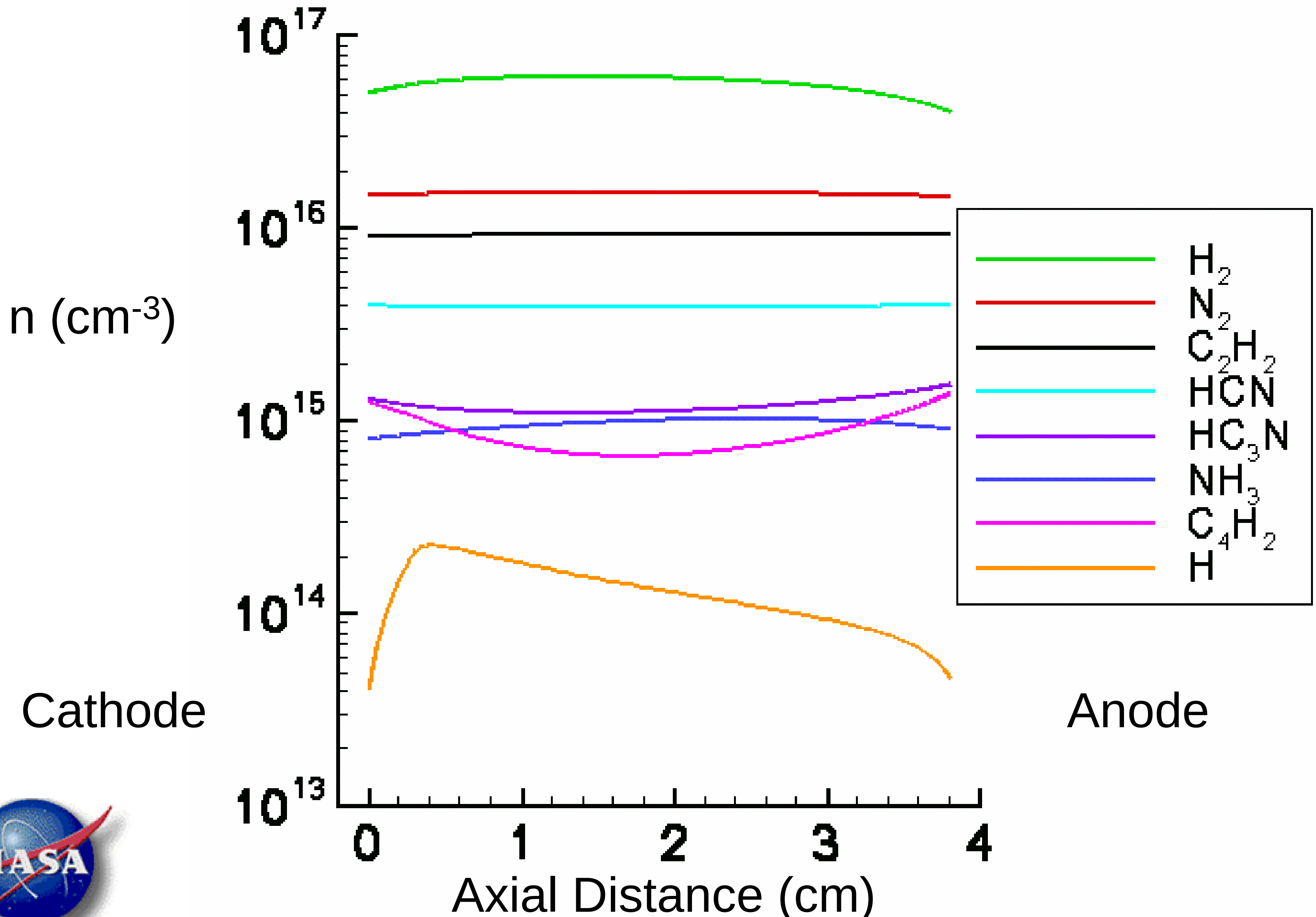
Surface Reactions*: Supply-Limited Growth‡

Chemisorption	
$H + Ni(S) \Leftrightarrow H(S)$	1×10^{13}
$CH_3 + Ni(S) \Leftrightarrow CH_3(S)$	5×10^{12}
$C_2H_2 + Ni(S) \Leftrightarrow C_2H_2(S)$	$8 \times 10^{10} \exp(-3.878 / T_s)$
Recombination	
$H + H(S) \Leftrightarrow H_2 + Ni(S)$	$1.3 \times 10^{14} \exp(-3.676 / T_s)$
$H + CH_2(S,R) \Leftrightarrow CH_3 + Ni(S)$	3×10^{13}
Hydrogen Abstraction/Addition	
$CH_3(S) + H \Leftrightarrow CH_2(S,R) + H_2$	$2.8 \times 10^{7} T_s^2 \exp(-3878 / T_s)$
$CH_2(S,R) + H \Leftrightarrow CH_3(S)$	1×10^{13}
$CH_2(S,R) + H \Leftrightarrow CH(S,R_2) + H_2$	$2.8 \times 10^{7} T_s^2 \exp(-3878 / T_s)$
$CH(S,R_2) + H \Leftrightarrow CH_2(S,R)$	1×10^{13}
$CH(S,R_2) + H \Leftrightarrow C(S,R_3) + H_2$	$2.8 \times 10^{7} T_s^2 \exp(-3878 / T_s)$
$C(S,R_3) + H \Leftrightarrow CH(S,R_2)$	1×10^{13}
$C_2H_2(S) + H \Leftrightarrow C_2H(S,R) + H_2$	$9 \times 10^{6} T_s^2 \exp(-2518 / T_s)$
$C_2H(S,R) + H \Leftrightarrow C_2H_2(S)$	2×10^{13}
$C_2H(S,R) + H \Leftrightarrow C_2(S,R_2) + H_2$	$9 \times 10^{6} T_s^2 \exp(-2518 / T_s)$
$C_2(S,R_2) + H \Leftrightarrow C_2H(S,R)$	2×10^{13}
Carbon Nanotube Formation	
$C_2(S,R_2) \Leftrightarrow Ni(S) + 2\ C(CNT)$	∞
$C(S,R_3) \Leftrightarrow Ni(S) + C(CNT)$	∞

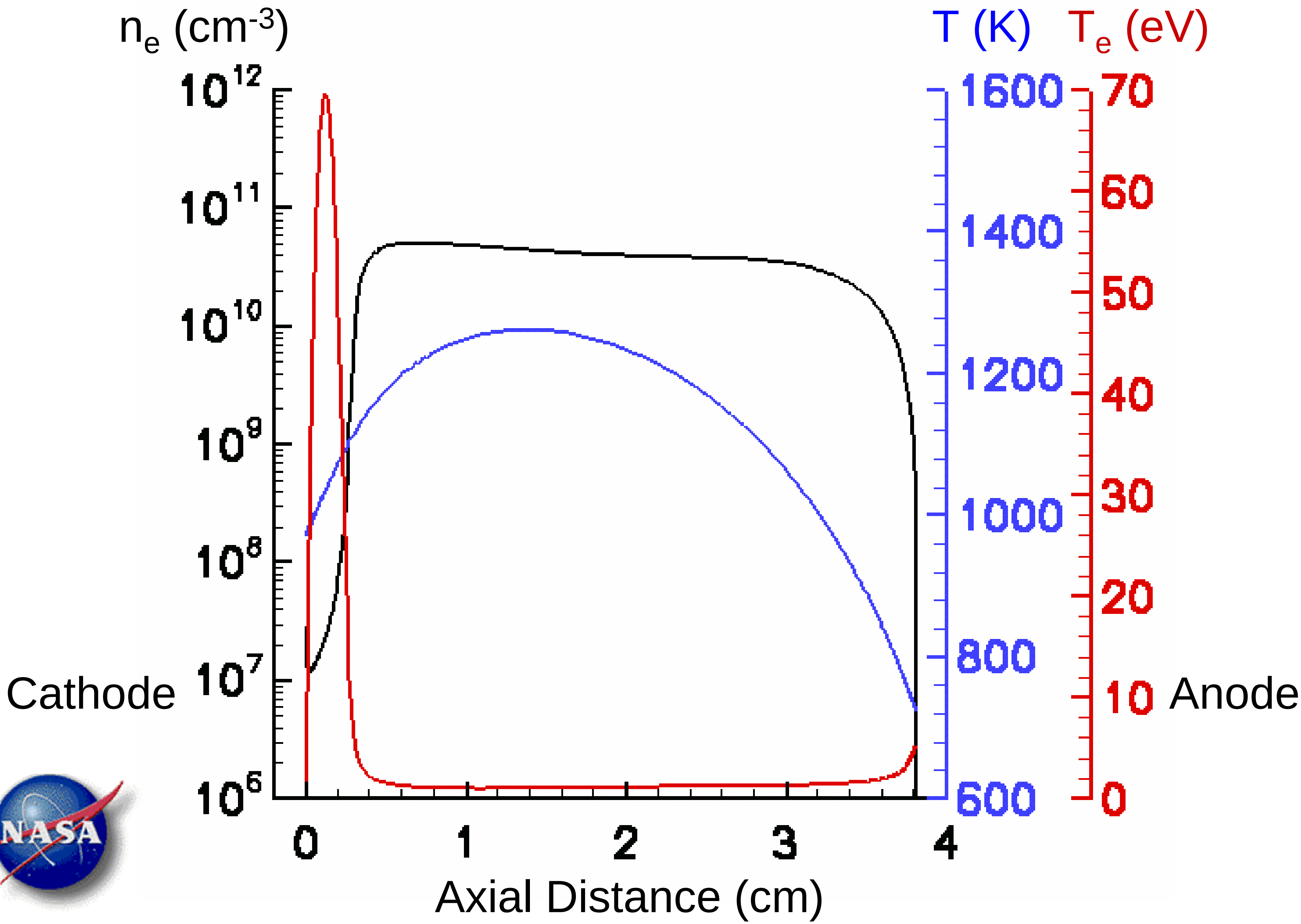
‡Merkulov *et al*., J. Phys. Chem. B **106**, 10570 (2002).

*Grujicic, Cao, and Gersten, Appl. Surf. Sci. **199**, 90 (2002) & J. Mater. Sci. **38**, 1819 (2003) .

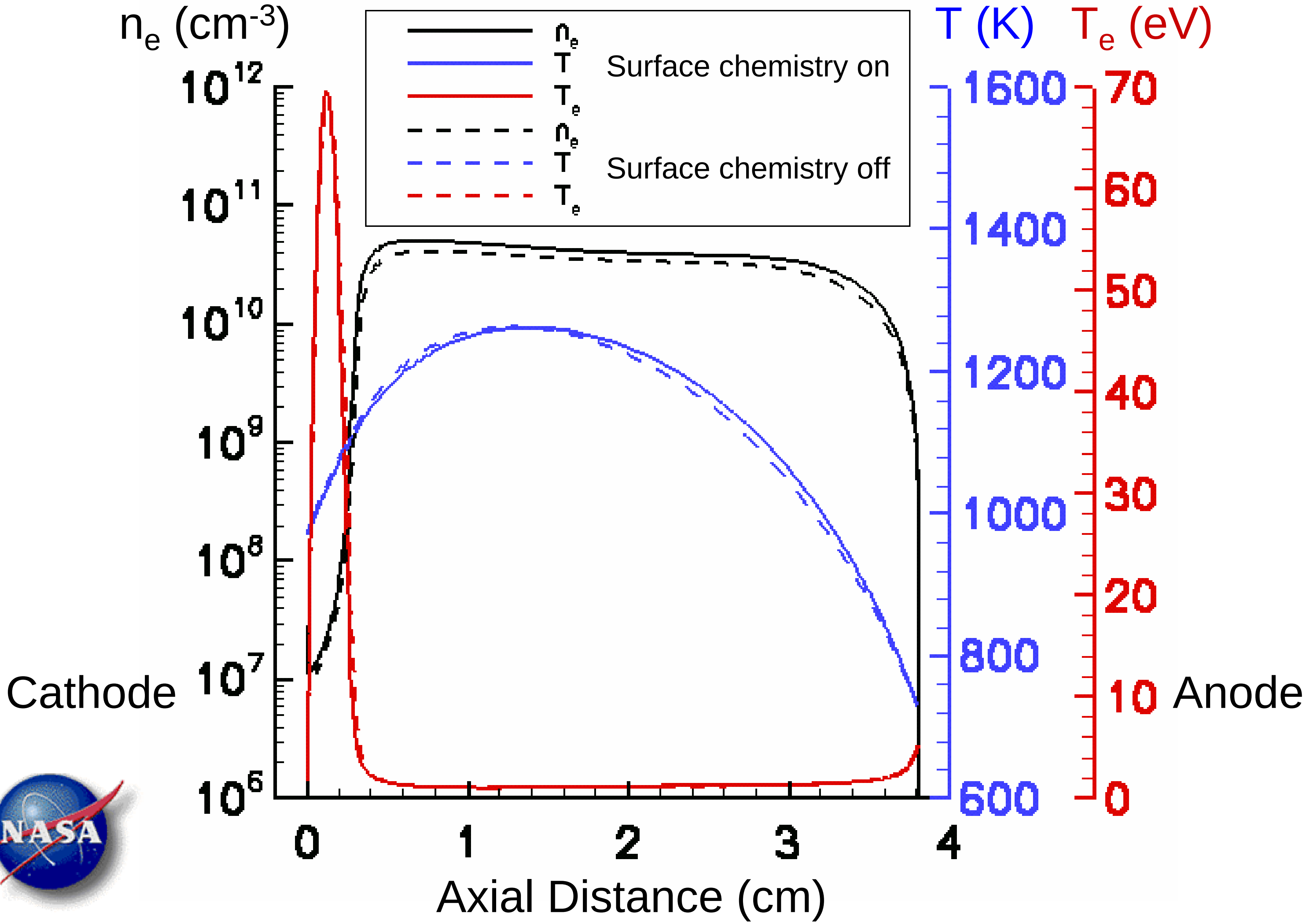
Most Abundant Neutrals from Simulation



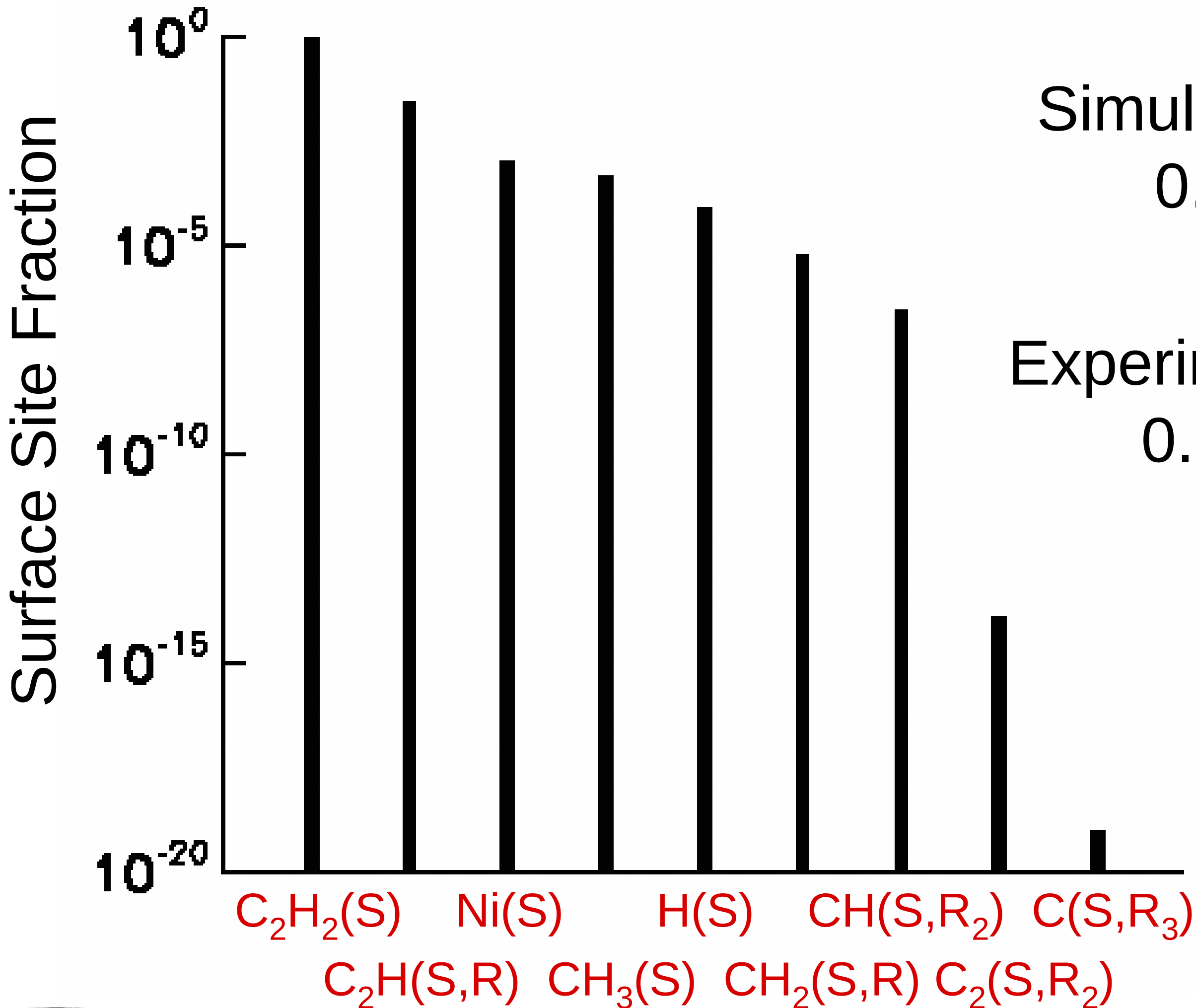
Plasma Profile



Plasma Profile



Surface Species and CNT Growth Rate



Simulated Growth Rate
0.0965 µm/min

Experimental Growth Rate*
0.16-0.25 µm/min

*Cruden, Cassell, Ye, and Meyyappan, J. Appl. Phys. **94**, 4070 (2003).

Part Two: Plasma Heating Effects in Carbon Nanotube Growth

- Recent work* demonstrates aligned growth of CNTs at 200 °C on plastic substrates with dcPECVD
- How significant is plasma heating of the substrate?
- Joint modeling/experimental effort undertaken by the Center for Nanotechnology and the University of Cambridge

*Hofmann *et al*., Appl. Phys. Lett. **83**, 4661 (2003).

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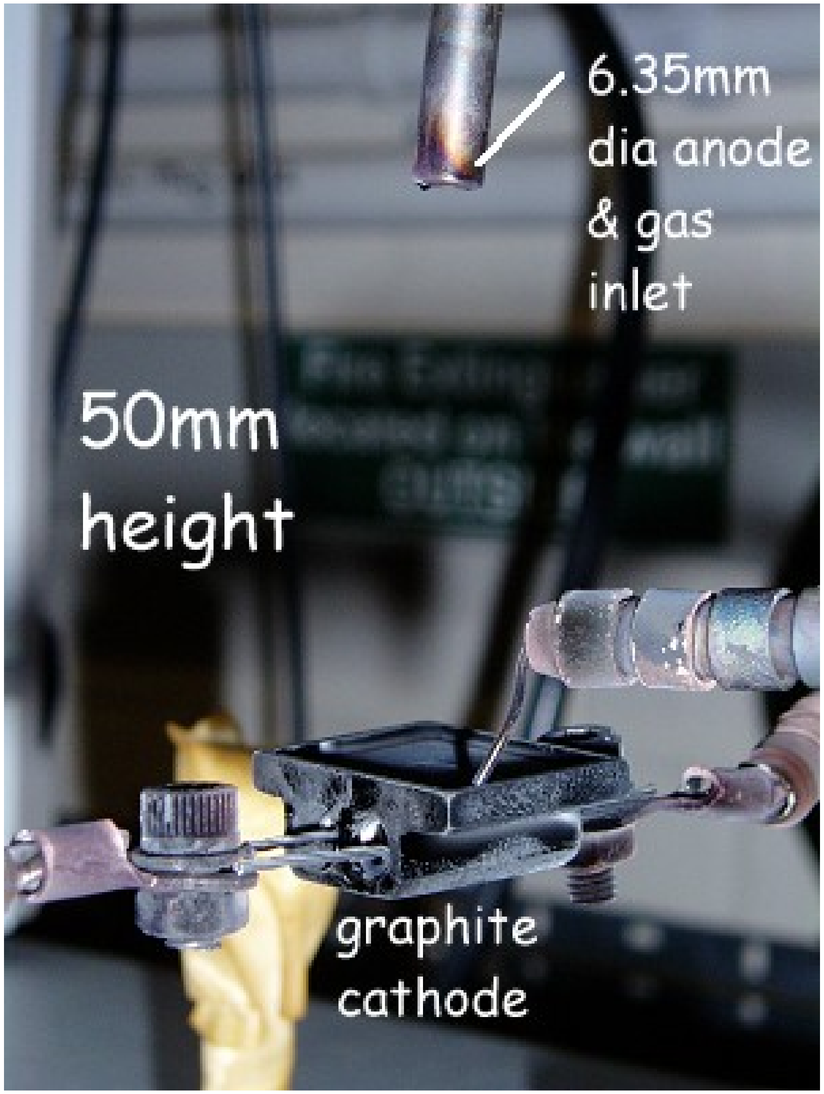
Cambridge dcPECVD Reactor



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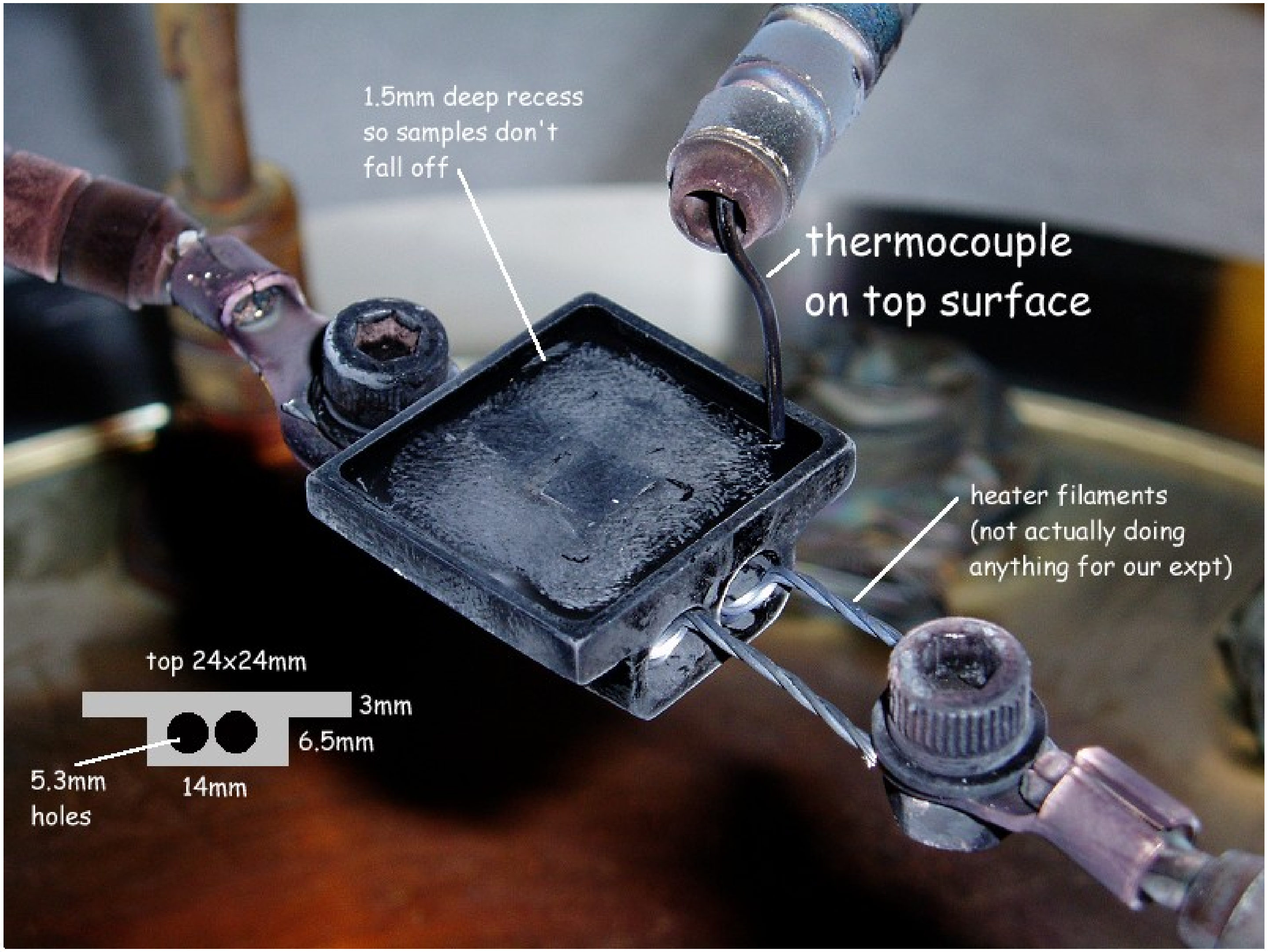
Cambridge dcPECVD Cathode Stage



Cambridge dcPECVD Reactor Conditions and Modeling Details

- Flow Rates: 72.5 sccm C_2H_2, 200 sccm NH_3
- 9 Neutral Species: H_2,H,C_2H_2,C_2H,N_2,N,NH_3,NH_2,NH
- 3 Charged Species: NH_3^+,$C_2H_2^+$,e
- 43 Gas-Phase Reactions
- dc Power Range: 0-200 W
- Pressure: 3.75 Torr

Stage - Gas Energy Balance

Gas:

$$\sum_n \left(\kappa_s \cdot \nabla T + R_s T D_s^T \cdot \nabla \ln \frac{P_s}{P} \right) - (1 - f) h_i J_i = \frac{\rho \overline{c'}}{4} \frac{2\alpha}{(2-\alpha)} C_p (T - T_s)$$

Neutral Energy Flux **Reflected Ion Energy** **Energy Transferred To Stage***

*Leroy *et al*., J. Phys. D: Appl. Phys. **30**, 499 (1997).

Stage:

$$-f h_i J_i + \frac{\rho \overline{c'}}{4} \frac{2\alpha}{(2-\alpha)} C_p (T - T_s) = \sigma \varepsilon (T_s^4 - T_a^4) + h_c (T_s - T_a)$$

Ion Bombardment Energy† **Energy Transferred From Gas** **Thermal Radiation** **Conduction Through Stage Apparatus**

$$f = \frac{1}{1 + (E_i / a)^{-b}}$$

†Winters *et al*., Phys. Rev. B **41**, 6240 (1990).

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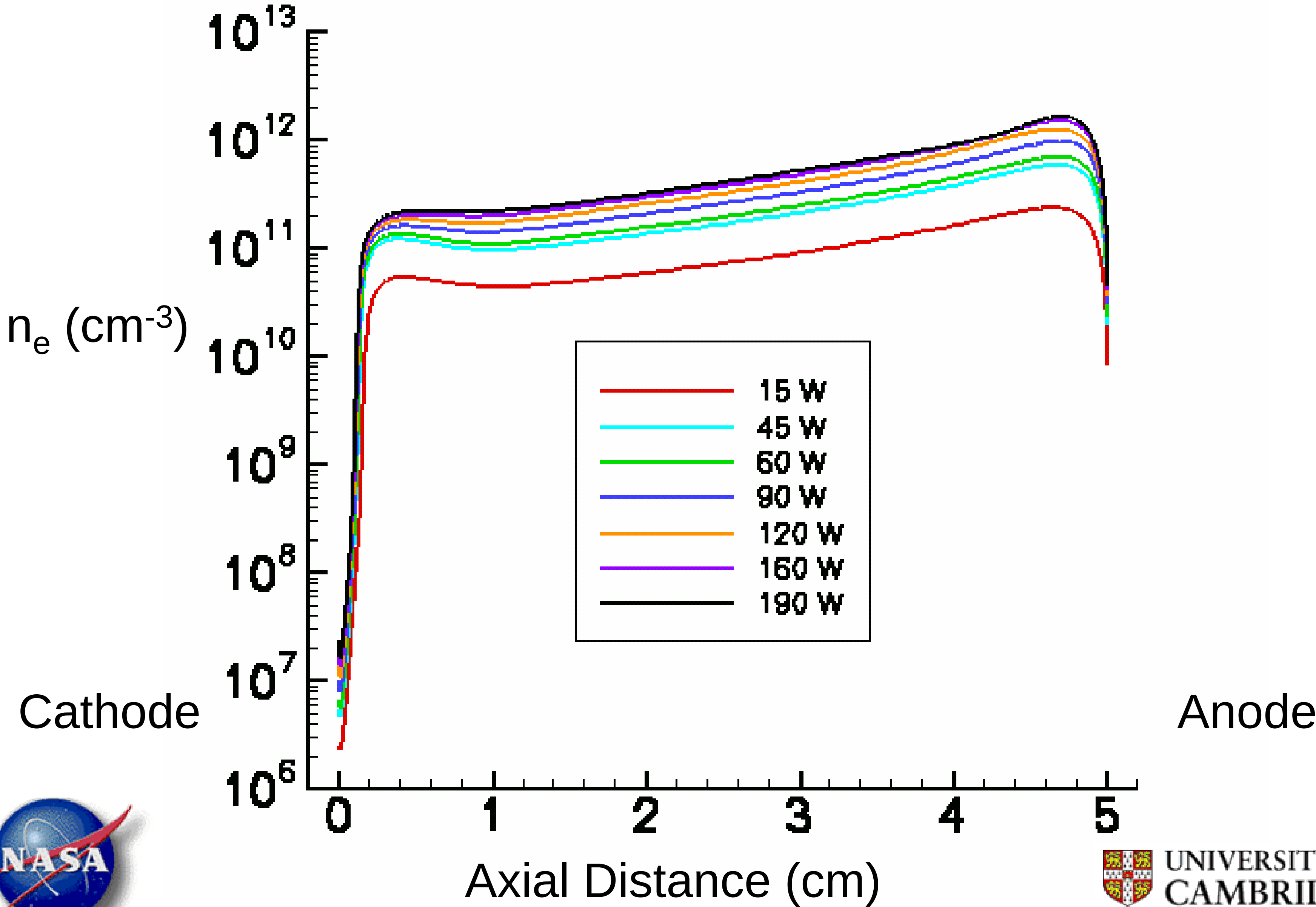
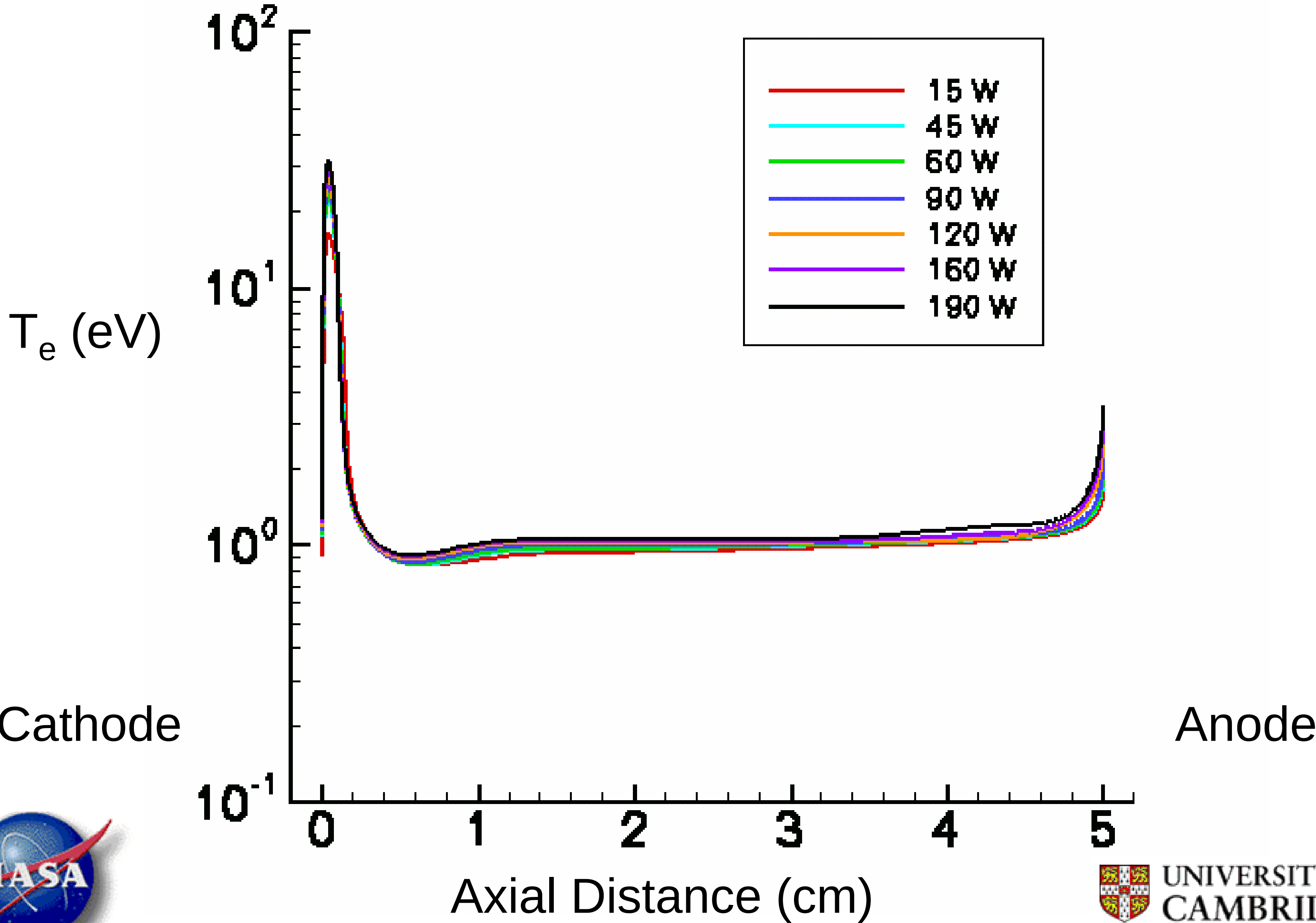
Plasma Profile



Electron Temperature



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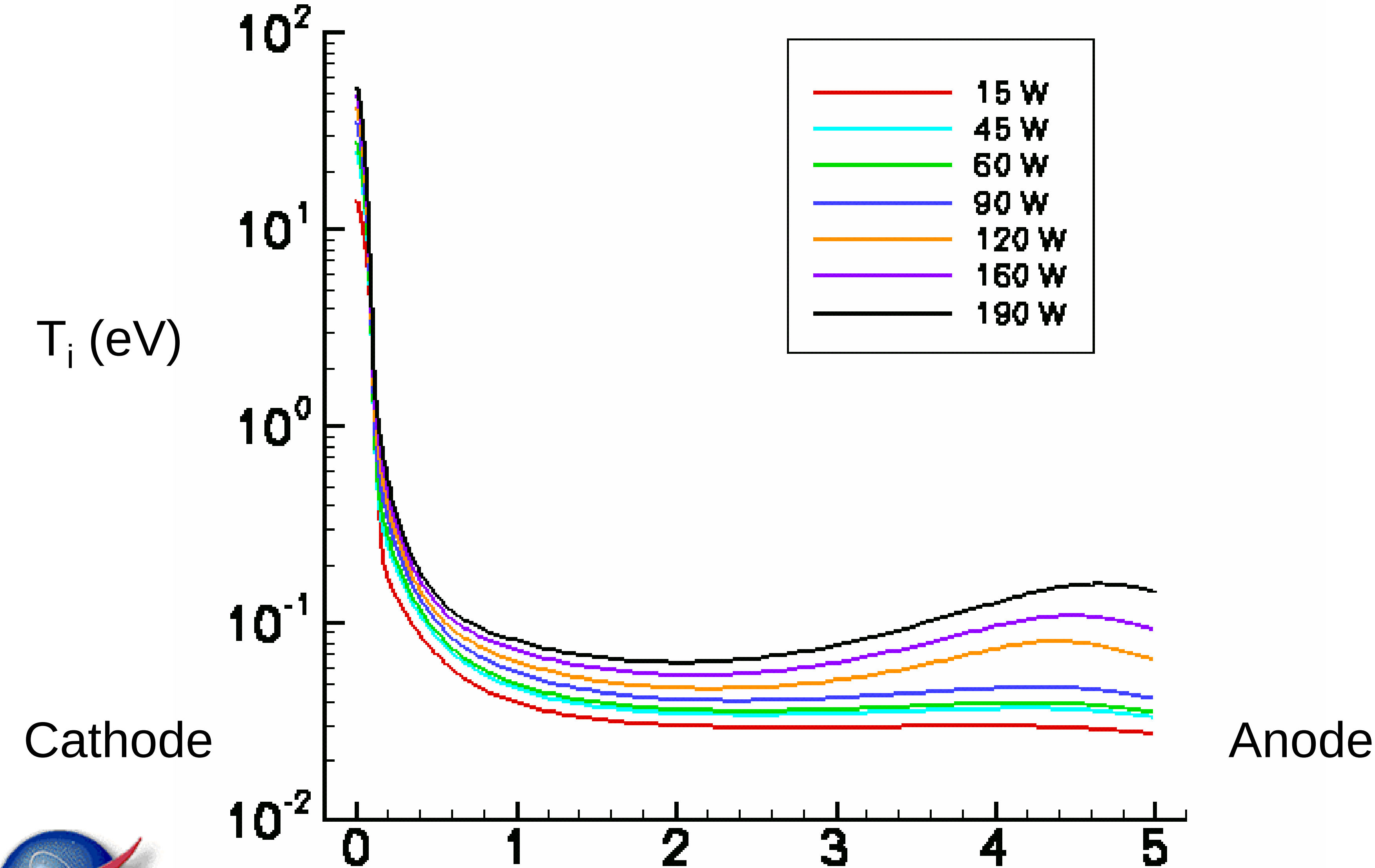
Ion Temperature



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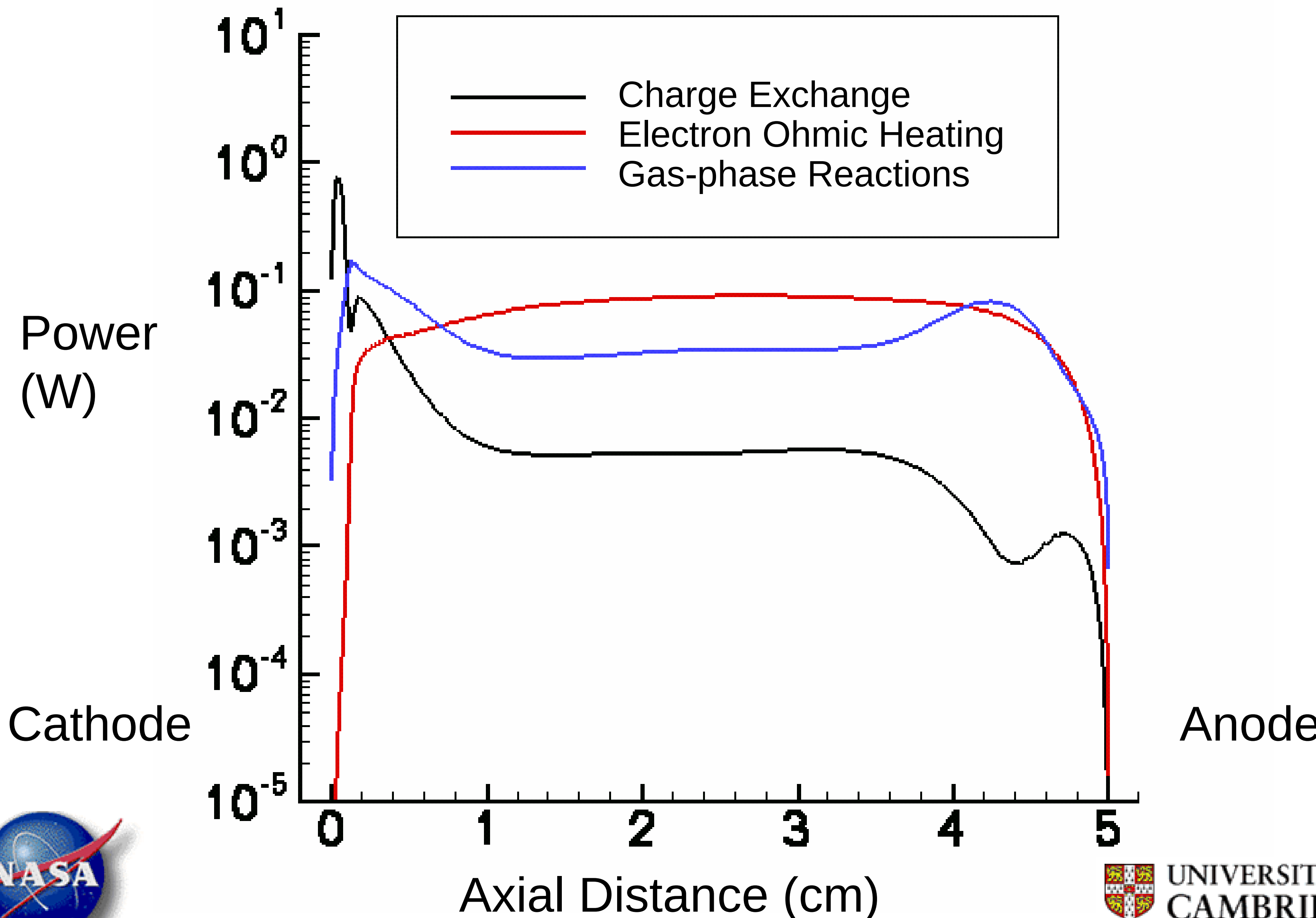
Gas Heating Terms @ 120 W



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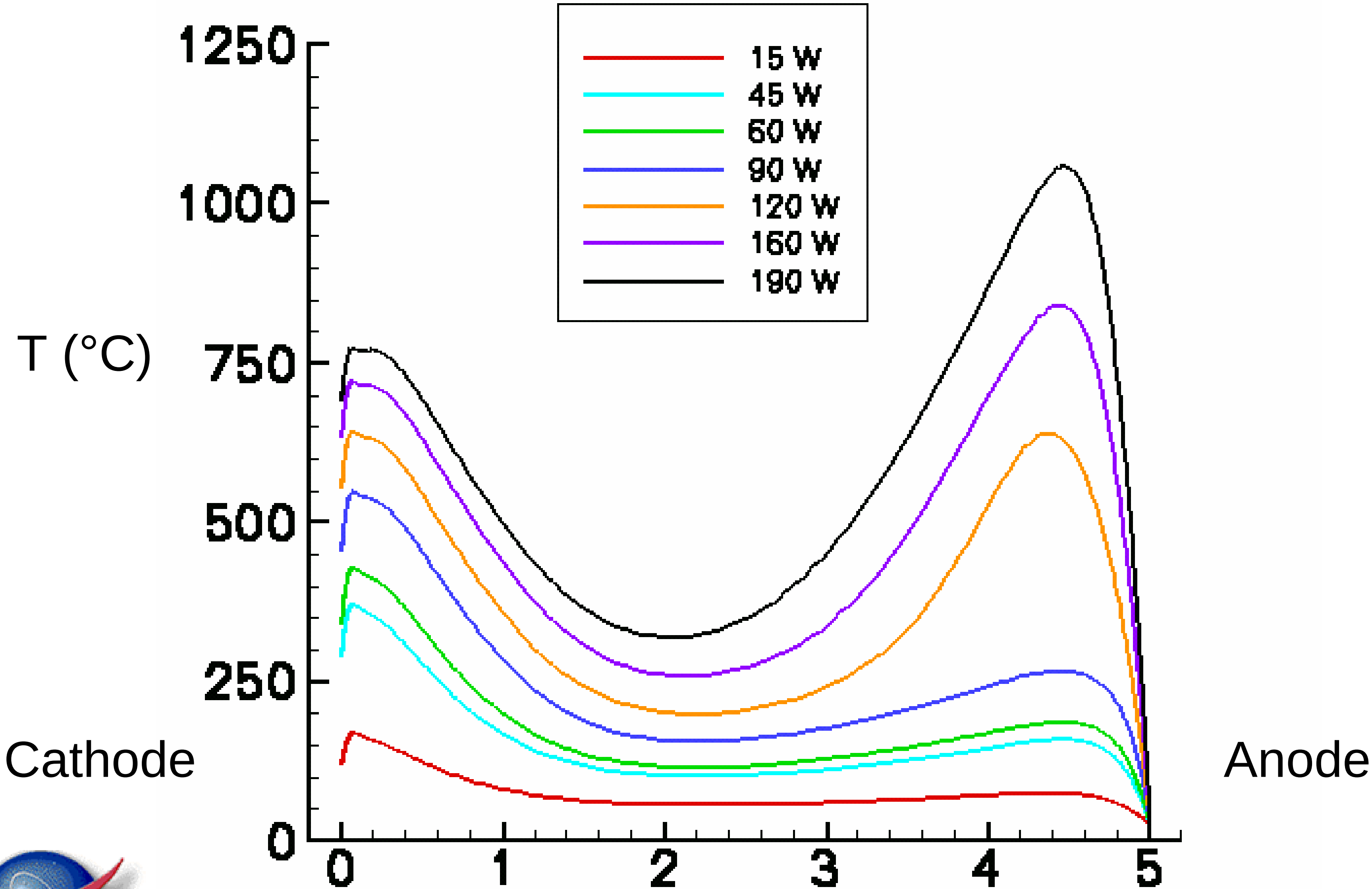
Gas Temperature



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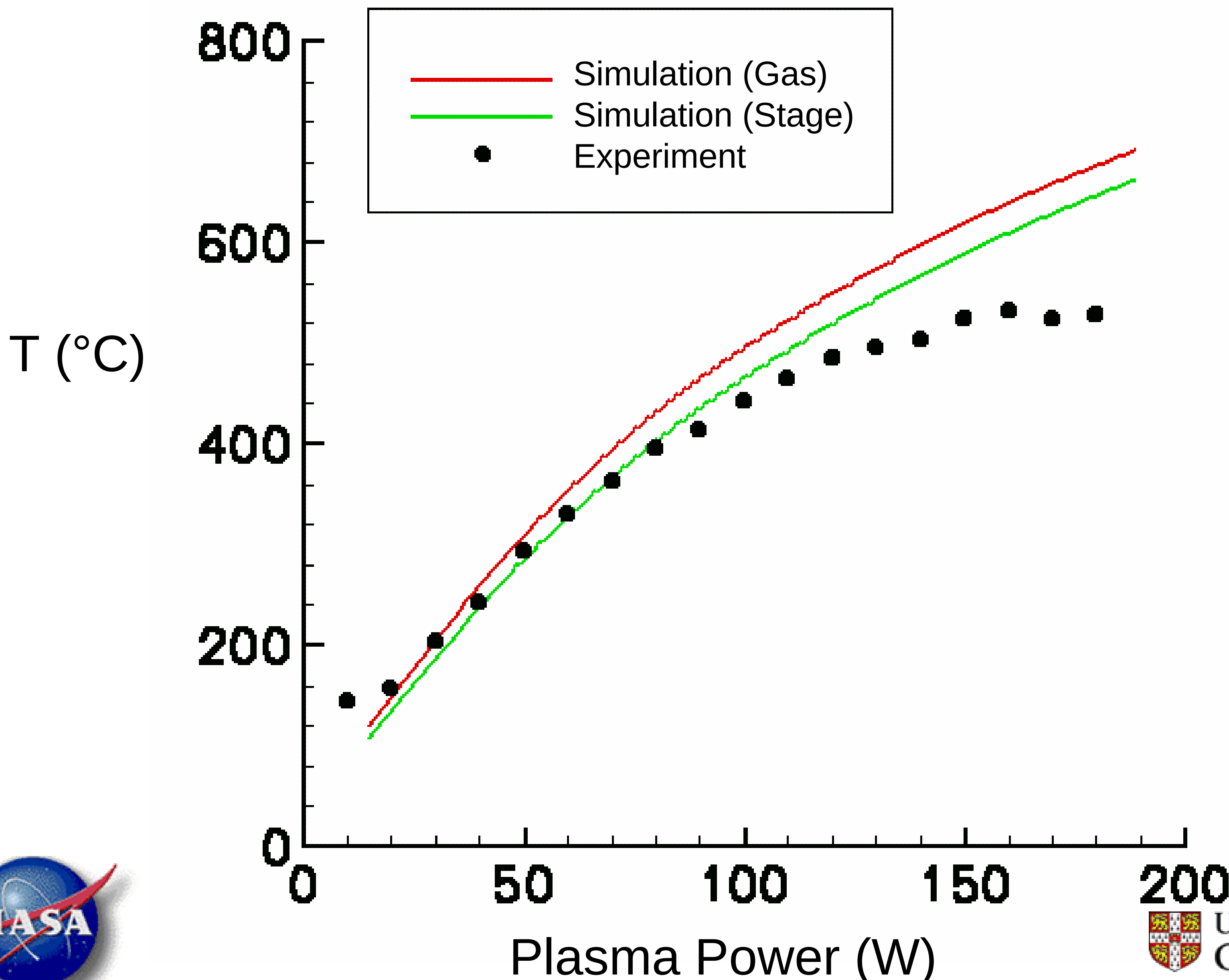
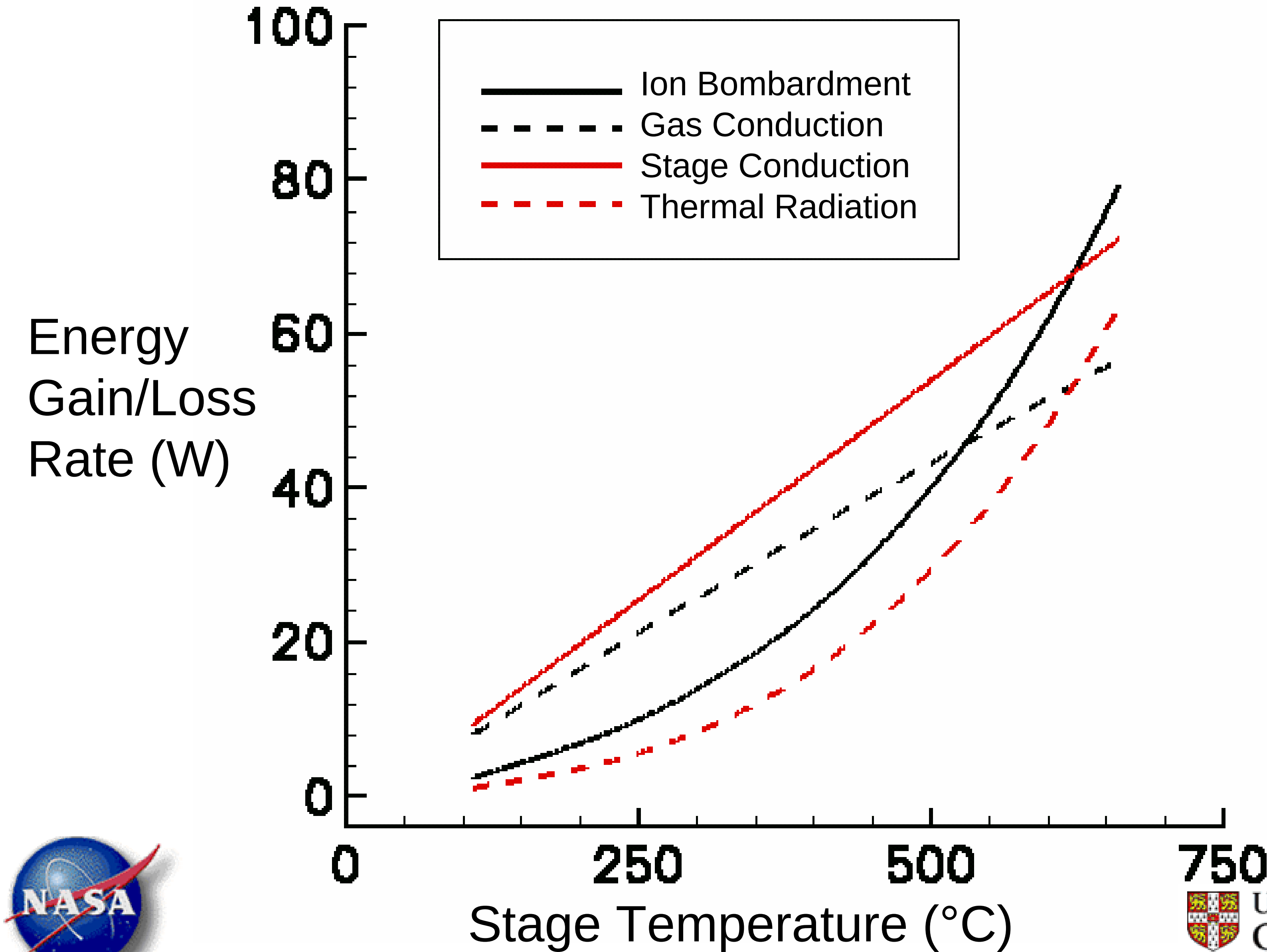
Stage Temperature Predictions



Stage Energy Balance



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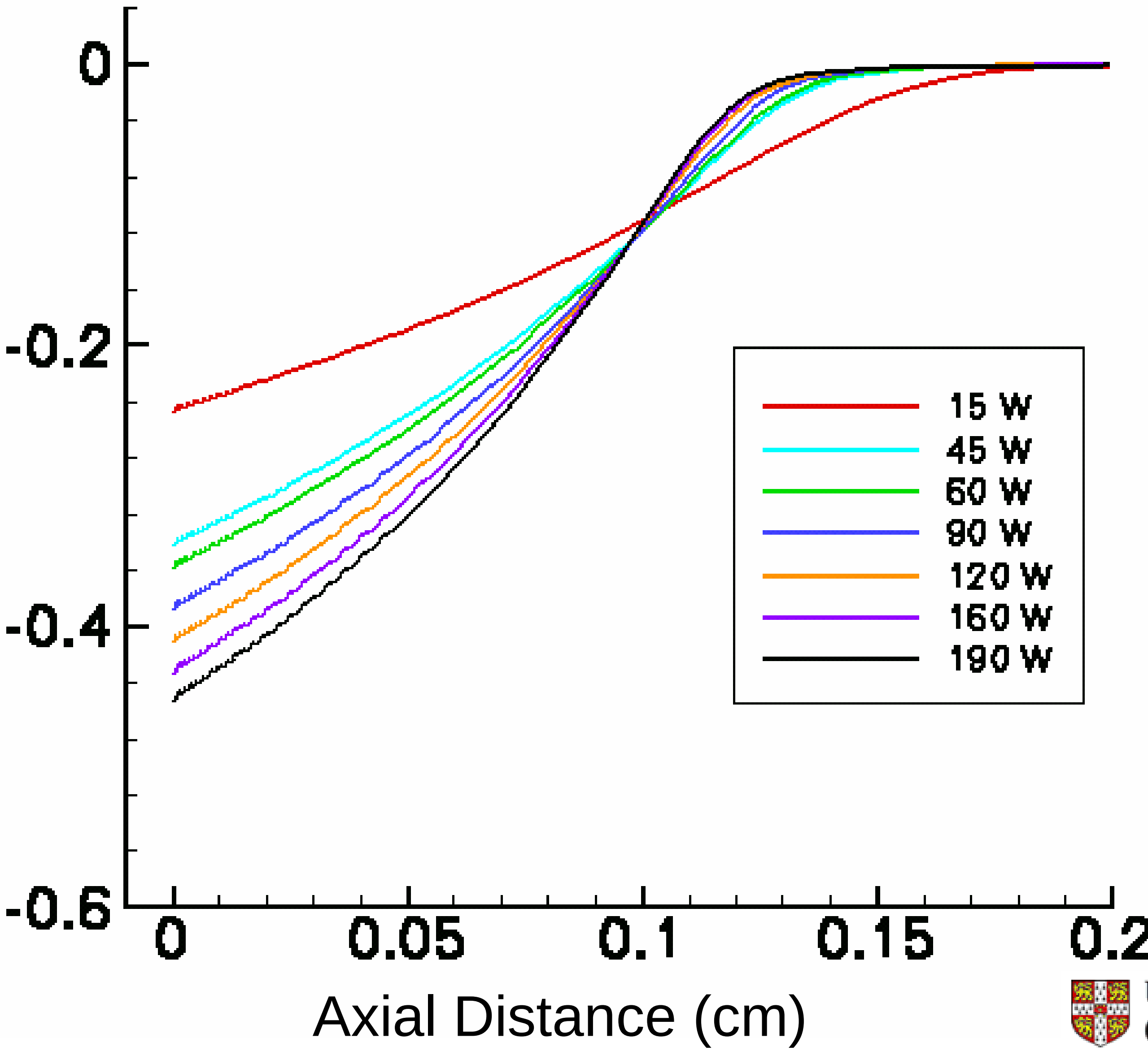
Cathode Sheath Electric Field

E
(V/μm)

-0.15 V/μm required for alignment [Chhowalla *et al*., J. Appl. Phys. **90**, 5308 (2001)]

Cathode



Summary

- A simple surface chemistry model has been incorporated into the NASA Ames SEMS code that provides reasonable agreement with in-house experimental measurements of CNT growth rate.
- Plasma heating in dcPECVD growth of carbon nanotubes can obviate the need for resistive heating of substrates.
- Future work will involve further development of the surface chemistry model and extension of the governing equations to 2-D.

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