Thermal Mode Nonequilibrium in Gas Dynamic and Plasma Flows

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• What is thermal mode nonequilibrium?  
  Emphasis on high density, collision-dominated flows, cold molecular plasmas

• Environments  
  i) Cool Electric Discharge Plasmas  
     Self-Sustained vs. Preionized  
  ii) Optically Pumped Plasmas  
     Excitation of Vibrational States  
     Kinetics and Energy Transfer Studies  
  iii) Gas Dynamic Flows  
     Supersonic Expansions of High Enthalpy Gases  
     Strong Shock Waves

• Applications  
  i) Plasma Wind Tunnels  
  ii) Gas Lasers  
  iii) Chemistry: Isotope Separation

• Summary: Where do we go with this?
What is thermal mode equilibrium?

\[ \frac{n_i}{g_i} \sim \exp \left( -\frac{E_i}{kT} \right), \]

\[ N = \sum n_i, \] and \[ E = \sum n_i E_i \]

If we know the energy levels, \( E_i \), and the gas temperature, \( T \), we can calculate the whole ideal gas thermodynamic table:

**Table 1**  Air at Low Pressures (for One Pound)

<table>
<thead>
<tr>
<th>T</th>
<th>t</th>
<th>h</th>
<th>( p_r )</th>
<th>u</th>
<th>( v_r )</th>
<th>( \phi )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>540.3</td>
<td>240.98</td>
<td>12.298</td>
<td>172.43</td>
<td>30.12</td>
<td>.75042</td>
</tr>
<tr>
<td>1001</td>
<td></td>
<td></td>
<td></td>
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<td>1002</td>
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<td>1003</td>
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<td>1004</td>
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</tbody>
</table>
Thermal nonequilibrium exists whenever:

- The populations, \( \frac{n_i}{N} \), of one or more modes are distributed according to the Boltzmann law, but the temperature, \( T \), of at least one mode differs from that of the others. 

OR

- The populations, \( \frac{n_i}{N} \), of one or more modes are not distributed according to the Boltzmann law.
Fraction of Power into each Mode, as a function of \( E/N \). \( E/N \) is approximately proportional to the mean energy of the free electrons.

1. Rotational mode
2. Vibrational mode
3. Electronic mode
4. Ionization

\[
\frac{E}{N} \text{ is approximatively proportional to the mean energy of the free electrons.}
\]

<table>
<thead>
<tr>
<th>Plasma Tube</th>
<th>Ratio of Electric Field, ( E ), to total number density of molecules, ( N )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Electric Field = Voltage/Electrode Separation ( E = V/L )</td>
</tr>
</tbody>
</table>
Environments: Preionized Electrical Glow Discharge
Short Pulse HV Ionizer, D.C. Sustainer - Geometry

Pulser electrodes in top and bottom walls
DC electrodes in side walls
Flow direction left to right

Dimensions: 1 cm x 5 cm, 10 cm long
Mach number: M~0.2
Discharge pressure: up to 160 torr
(O₂-He, O₂-Ar)
Mass flow rate: up to 12 g/sec
Environments: Preionized Electrical Glow Discharge
Short Pulse HV Ionizer, D.C. Sustainer - Performance

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On the left, species concentrations after the ionizing pulse, on the right, schematic of the pulsed and d.c. discharge operation. \( P=0.1 \text{ atm}, \ T=300 \text{ K}, \ E/N_{max}=350 \text{ Td}, \ E_{max}=8.5 \text{ kV/cm}, \tau_{pulse}=10 \text{ nsec} \)
Environments: Preionized Electrical Glow Discharge
Short Pulse HV Ionizer, D.C. Sustainer - Photos

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P=300 torr, 10 kHz  
P=500 torr, 10 kHz

\[
\frac{k_k}{k_r} = \exp \left( \frac{\Delta E_{v,v-1} - \Delta E_{w,w+1}}{T} \right) > 1
\]

\[\text{CO}(v) + \text{CO}(w) \rightarrow \text{CO}(v-1) + \text{CO}(w+1)\]

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![Graph showing vibrational distribution function](image)

- Emission [arb. units]
- cm$^{-1}$
- Relative population
- T=1200 K
- Measured nonequilibrium distribution
- Boltzmann distribution at T=4100 K

Vibrational quantum number
Each peak is from a successive vibrational state, \( v \), ground state signal on the right. The time delay between the pump and probe pulse is (a) 150 ns, (b) 1 ms, (c) 5 ms, (d) 10 ms.
Optically Pumped Plasmas: Kinetics Studies
Experimental Setup for CO Plasma

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Optically Pumped Plasmas: Kinetics Studies
Energy Transfer and Kinetics Processes in a CO Plasma

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Relative population

Ionization:
\[ \text{CO}(v)+\text{CO}(w) \rightarrow (\text{CO})_2^+ + \text{e}^- \]

V-E:
\[ \text{CO} (X^1\Sigma,v\sim40) + \text{M} \rightarrow \text{CO} (A^1\Pi) + \text{M} \]

Chem. Reactions:
\[ \text{CO}(v)+\text{CO}(w) \rightarrow \text{CO}_2+C \]

T = 600 K
\( T_v = 3300 \text{ K} \)

2 Torr CO, 100 Torr Ar, CO laser power 10 W c.w.
Optically Pumped Plasmas: Kinetics Studies
Optically Pumped CO Plasma Photo
Vibrational energy level populations for an optically pumped air plasma. If energy were equilibrated, temperature of vibrational modes would be ~ 2000K. Measured as kinetic temperature is only 500 K. Extreme nonequilibrium is created in a steady state, atmospheric pressure, molecular gas plasma. Gas mixture is CO/N2/O2=5/75/20, P=1 atm. Pump laser power is 10 W.

Raman Spectra

Experimental Vibrational State Populations
Inferred from Raman Spectra. Calculated State Populations from Master Equation Kinetic Model
Optically Pumped Plasmas: Kinetics Studies

Associative Ionization in Optically Pumped Plasmas I

\[
\text{CO}(v) + \text{CO}(w) \rightarrow (\text{CO})_2^+ + e^- , \ E_v + E_w > E_{\text{ion}}
\]

Thomson discharge

Microwave absorption

Electron production rate:

\[ k_{\text{ion}} \approx 10^{-13} \text{ cm}^3/\text{s} \]

Electron density:

\[ n_e \approx 10^{11} \text{ cm}^{-3} \]
Optically Pumped Plasmas: Kinetics Studies

Associative Ionization in Optically Pumped Plasmas II

$\text{CO}(v) + \text{CO}(w) \rightarrow (\text{CO})_2^+ + e^- , E_v + E_w > E_{\text{ion}}$

Current-voltage characteristics of the DC Thomson discharge at different helium partial pressures

Vibrational distribution functions of carbon monoxide at different helium partial pressures
Optically Pumped Plasmas: Kinetics Studies
Coupling of Vibrational Populations with Free Electrons

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Fig. 11. Electric field influence on different CO vibrational level populations.

Fig. 12. Qualitative demonstration of the $V \rightarrow e \rightarrow V - \Delta V$ effect (strongly exaggerated). $\epsilon$: electron energy; $T_e$: electron temperature.
Optically Pumped Plasmas: Kinetics Studies
Measurements of Electron Density Decay (by microwave attn) for E-beam Created Plasma – Experimental Schematic

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Plasma Power Consumption at $10^{13}$ Electrons/cm$^3$ in 1 Atm, 560 K Air:

**Electron-Ion Recombination**
- $\beta = 2.5 \times 10^{-7}$ cm$^3$ sec$^{-1}$
- Nonequilibrium: $56$ W cm$^{-3}$
- Equilibrium: $450$ W cm$^{-3}$

**Electron Attachment to O$_2$**
- $k_{\text{eff}} = 2.3 \times 10^{-33}$ cm$^6$ sec$^{-1}$
- Nonequilibrium: $1.2$ W cm$^{-3}$
- Equilibrium: $1.4$ kW cm$^{-3}$
Attachment is weakly dependent upon heavy species temperature whereas detachment is highly dependent.

\[ \text{O}_2 + e^- + M \leftrightarrow \text{O}_2^- + M \]

\( \text{O}_2 \) Electron Affinity \(~0.43\) eV (\(~\text{Two Vibrational Quanta}\)
200/18/35  N$_2$/CO/O$_2$ – Optically Pumped
(Diameter of Vibrationally Excited Region ~ 1 mm)
Average energy per molecule in electron Volts.
(0.1 eV = 1,161 °K)

Expansion of a gas mixture of 20% CO, 20% N₂, 60% Ar,
Stagnation Pressure = 100 atm.
Stagnation Temperature = 2,000 °K.
15 ° Half Angle Nozzle,
Expands to M = 10 at 100 cm downstream of throat

Distance from nozzle throat, in centimeters
Gas Dynamic Flows: Thermal mode nonequilibrium behind a hypersonic shock wave

$T_t = \text{translational mode temperature}$

$T_r = \text{rotational mode temperature}$

$T_v = \text{vibrational mode temperature}$

Mode
Temperature
Degrees K

Distance behind shock front, in meters
Plasma Wind Tunnels: A supersonic tunnel with energy loading of selected internal states in the plenum

Schematic of the wind tunnel discharge section / nozzle / test section assembly
Plasma Wind Tunnels: A supersonic tunnel with energy loading of selected internal states – photo of plenum in operation

Photograph of a discharge in the nozzle plenum. Dimensions 4x4x10 cm.
A uniform, cold gas fills the plenum; $O_2$/He mixture shown, similar uniformity for air; $P_0$ to 1 atm.
Plasma Wind Tunnels: A supersonic tunnel with energy loading of selected internal states – objects in a 2-D, M = 3 test section
Plasma Wind Tunnels: Calculated $M = 4$ Flow over a 0.5 cm Dia semicylinder. Vibrationally Excited $N_2$ Expanding from 1 atm.

From E. Josuyla, AFRL
Plasma Wind Tunnels: Calculated $M = 4$ Flow over a 0.5 cm Dia semicylinder. Vibrationally Excited $N_2$ Expanding from 1 atm.

From E. Josuyla, AFRL
Plasma Wind Tunnels: An $M = 4$ MHD Tunnel, with transverse pre-ionized discharge and a 2 Tesla Field in test section
Plasma Wind Tunnels: An M = 4 MHD Tunnel. Lorentz force effect on turbulent boundary layer density fluctuation spectra.

Both B field directions
Laser beam midway

500 W RF, B=1.5 T, U=1500 V (accelerating MHD force)
500 W RF, B=1.5 T, U=1500 V (decelerating MHD force)

Nitrogen, M=3, P0=1/3 atm
Both accelerating and decelerating Lorentz force are created for two possible combinations of B and E fields, as shown.
R is the separation of the C and O nuclei. 

$R_e$ is the equilibrium (nonvibrating) separation.

$V(R) = \frac{1}{2} K(R - R_e)^2$ is the potential energy stored in the oscillator.
Gas Lasers: Carbon Monoxide Electric Discharge Laser - Schematic
Gas Lasers: Carbon Monoxide Electric Discharge Laser – Photo during operation
Gas Lasers: Carbon Monoxide Electric Discharge Laser –
Kinetic Modeling of CO Fundamental Band Laser,
Comparison with OSU Laser Performance

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![Graph showing power output vs. vibrational quantum number with experiment and calculations compared.](image)

- **Power, W**
  - 2.5
  - 2.0
  - 1.5
  - 1.0
  - 0.5
  - 0.0

- **Vibrational quantum number**
  - 0
  - 2
  - 4
  - 6
  - 8
  - 10
  - 12
  - 14
  - 16
  - 18
  - 20

Legend:
- **实验** (experiment)
- **计算** (calculations)

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Theoretically Predicted Output Line Intensities

Experimentally Measured Output Line Intensities
Gas Lasers: An Electric Discharge-Excited Oxygen-Iodine Laser (DOIL) – Boltzmann equation solver results: electron energy balance

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![Graph comparing singlet delta production in O₂-He and O₂-Ar gases with E/N (10^-16 V cm²) as a parameter.]

O₂-He

Highest estimated O₂(1Δ) yield achieved so far ~10 %
Gas Lasers: An Electric Discharge-Excited Oxygen-Iodine Laser (DOIL)

Schematic of Electric Discharge SDO Generator

Advantages of transverse vs. axial discharge: Large volume, stable at high pressures / powers, rapid convective cooling vs. slow wall cooling. Used in most high power electrically excited lasers.

Discharge volume 50 cm³, pressures up to 460 torr, flow rate up to 0.1 mole/sec (O₂), 1 mole/sec (He)
Gas Lasers: An Electric Discharge-Excited Oxygen-Iodine Laser (DOIL)

Gain at Optimized Conditions: 0.12 %/cm at T=100 K (Currently!)

Adding NO: major discharge stabilization factor

Discharge power increased from 1.9 kW to 2.4 kW

\[ P_0=107 \text{ torr}, \ 15\% \ O_2 - \text{He flow, NO 0.2 mmole/sec (550 ppm), } \nu=34 \text{ kHz, } U_{PS}=3.1 \text{ kV, } I=1.54 \text{ A, discharge power 2.4 kW, } I_2 \ 70 \text{ \mu mole/sec (190 ppm).} \]

Gain may be limited by I\(_2\) flow rate
Vibrationally excited CO prepared in cell reacts according to:

\[ \text{CO}(v) + \text{CO}(w) \rightarrow \text{CO}_2 + \text{C} \]
Summary

What have we learned?

• Improved methods to sustain extreme mode disequilibrium in gases: High densities, low gas kinetic temperatures, large volumes
• New data on mechanisms and rates of some critical energy transfer processes in molecular gases of aerospace interest
• Methods for selective excitation of internal energy states
• New applications: improved high power c.w. gas lasers, novel chemical syntheses, new aerodynamic control techniques

Future directions?

• Special purpose supersonic aerodynamic testing
• Modeling code validation
• High power c.w lasers and applications: novel refrigeration?
• More chemistry: new products
Support:
USAF:
AFOSR Space Power & Propulsion Program
AFOSR Unsteady Aerodynamics and Hypersonics Program
AFRL Air Vehicles Directorate
AFRL Directed Energy Directorate
NASA Glenn Research Center
NSF
The Michael A. Chaszeyka Gift

Collaborators:
Univ. of Bonn Physics Dept; Heat and Mass Transfer Institute, Belarussian Academy of Physics; Gas Laser Lab, Lebedeev Physical Institute, Moscow Physical Technical Institute

Kind Listeners