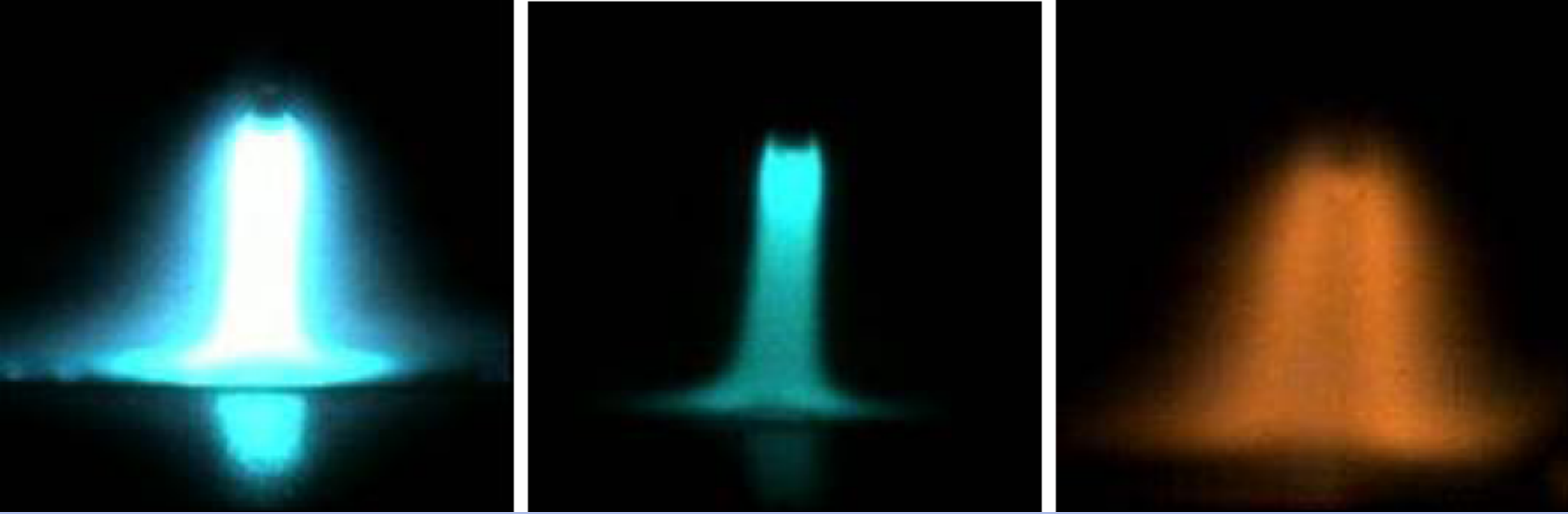


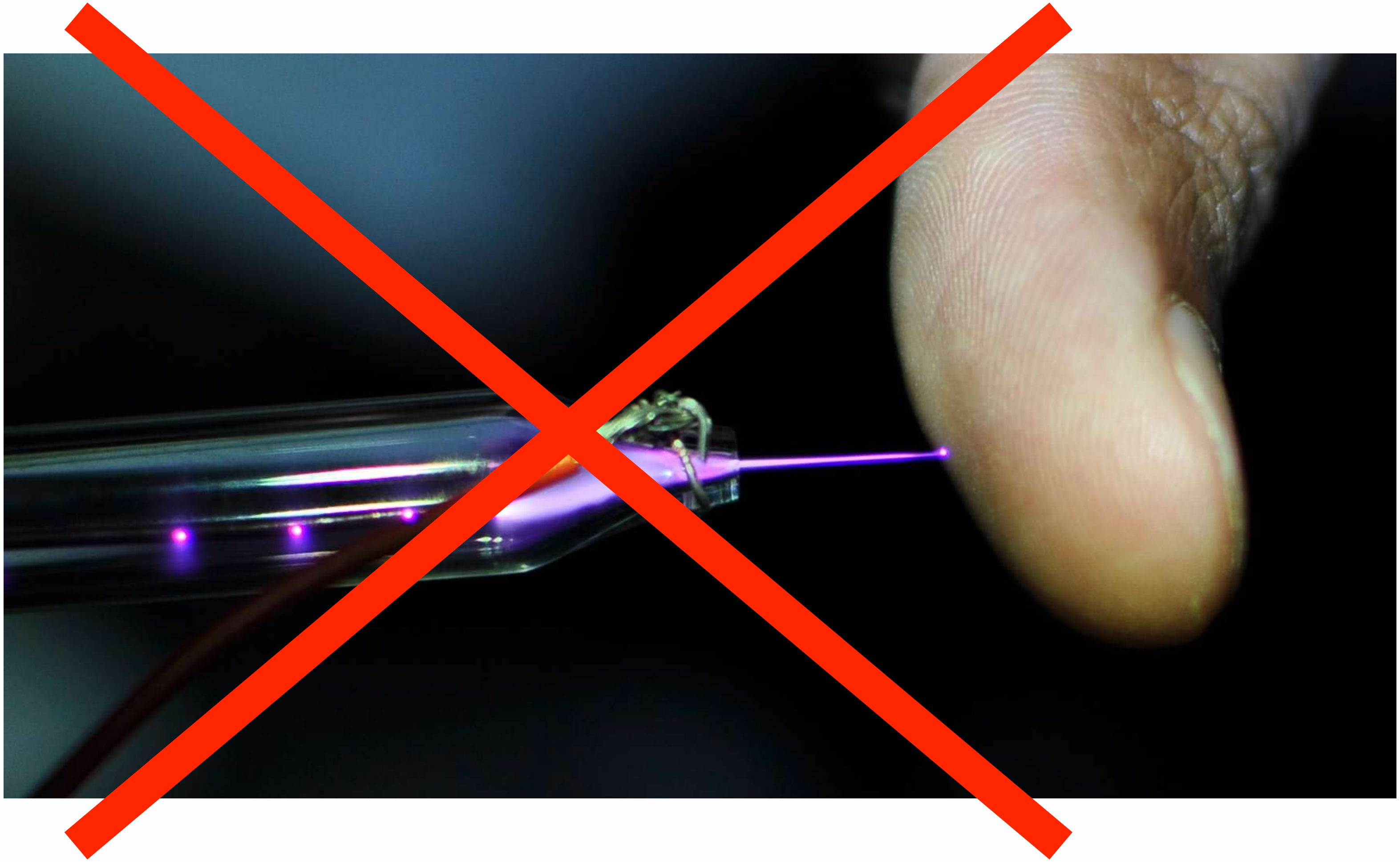
High-Pressure Thermal Plasmas and Sources

Tony Murphy

19th European Summer School, October 2014

"Low Temperature Plasma Physics: Basics and Applications"

What is a Thermal Plasma?



What is a Thermal Plasma?

At or close to atmospheric pressure (at least 0.1 atm)

Temperature ~ 1 to 2 eV (10 000 to 20 000 K) for electrons and heavy species

Formed by dc or ac electric arcs, radio-frequency or microwave electromagnetic fields

Dominated by collisions

Highly ionised (typically 100%, at least 5%)

High electron densities (~ 10^{23} m^{-3})

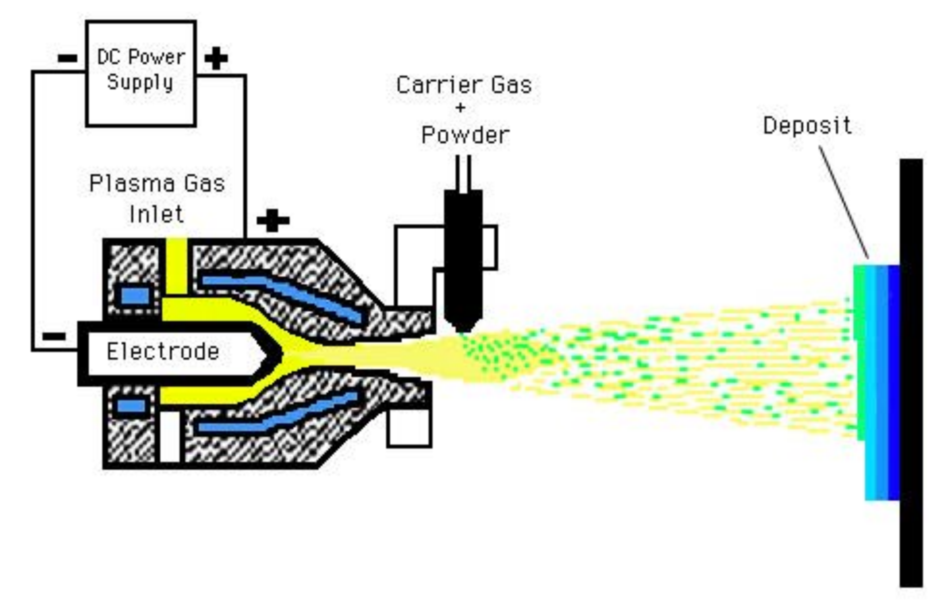
Very widely used in manufacturing and other industries

- High power fluxes
- High fluxes of reactive species
- Strong radiative emission

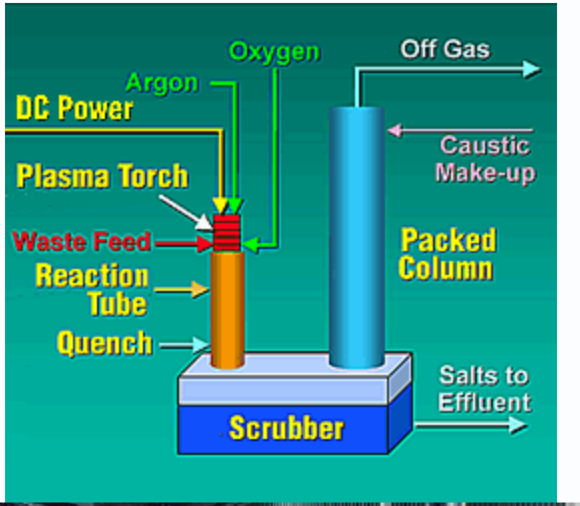
Thermal Plasma Applications: Arc Welding

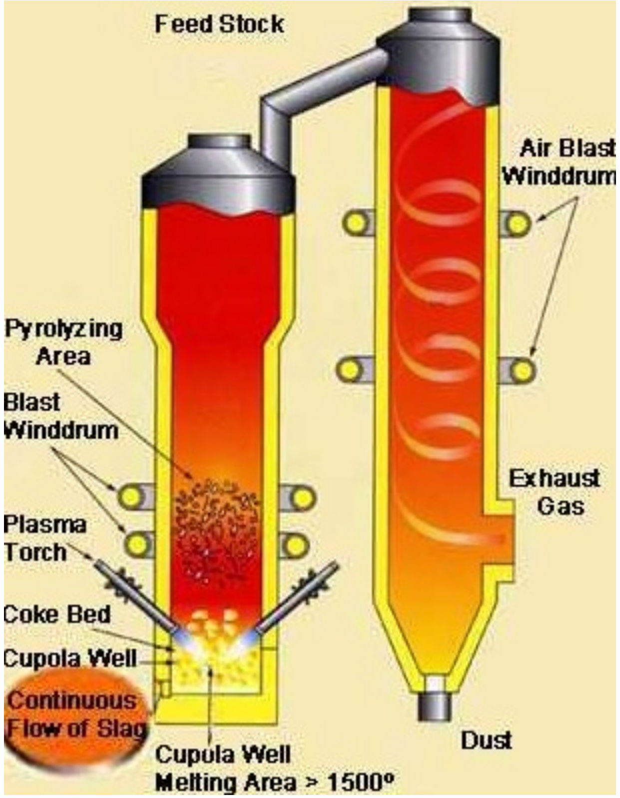
Thermal Plasma Applications: Plasma Cutting

Thermal Plasma Applications: Plasma Spraying



Thermal Plasma Applications: Waste Treatment



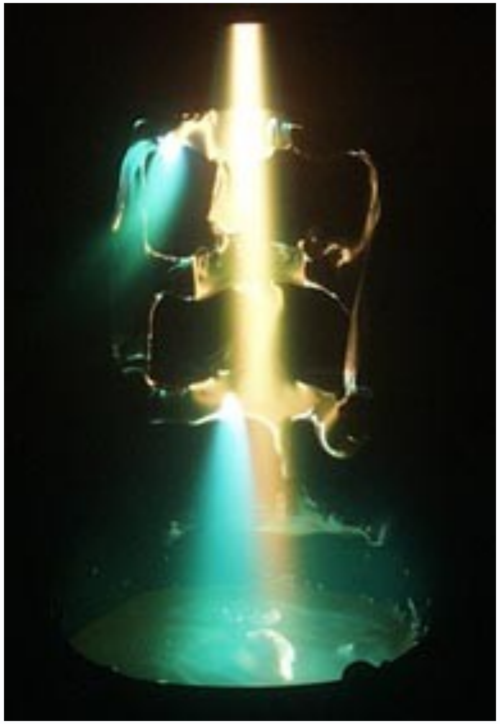


Thermal Plasma Applications: Arc Lighting

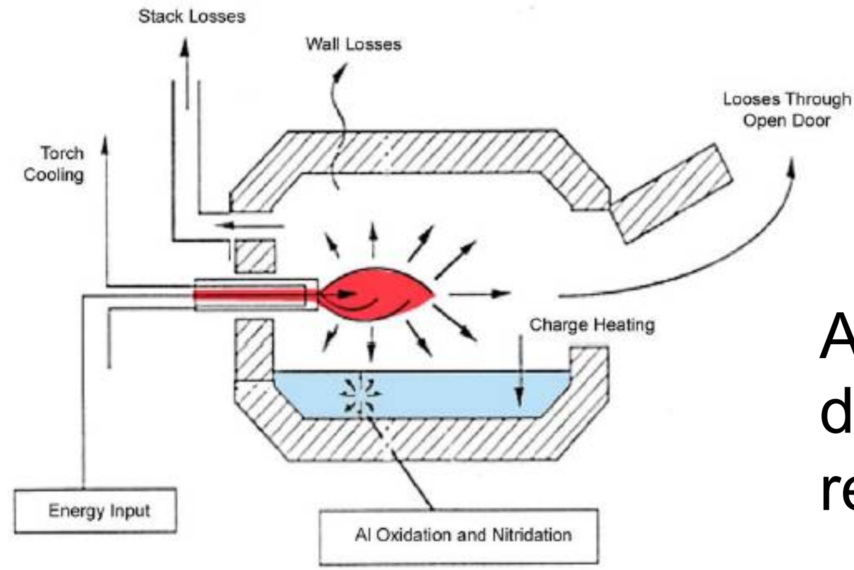
Carbon arc lamp

Xenon arc lamp

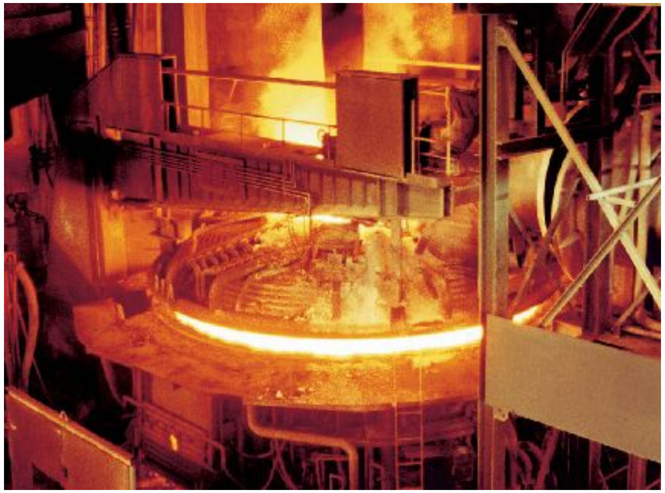
Thermal Plasma Applications: Mineral Processing



Plasma remelting

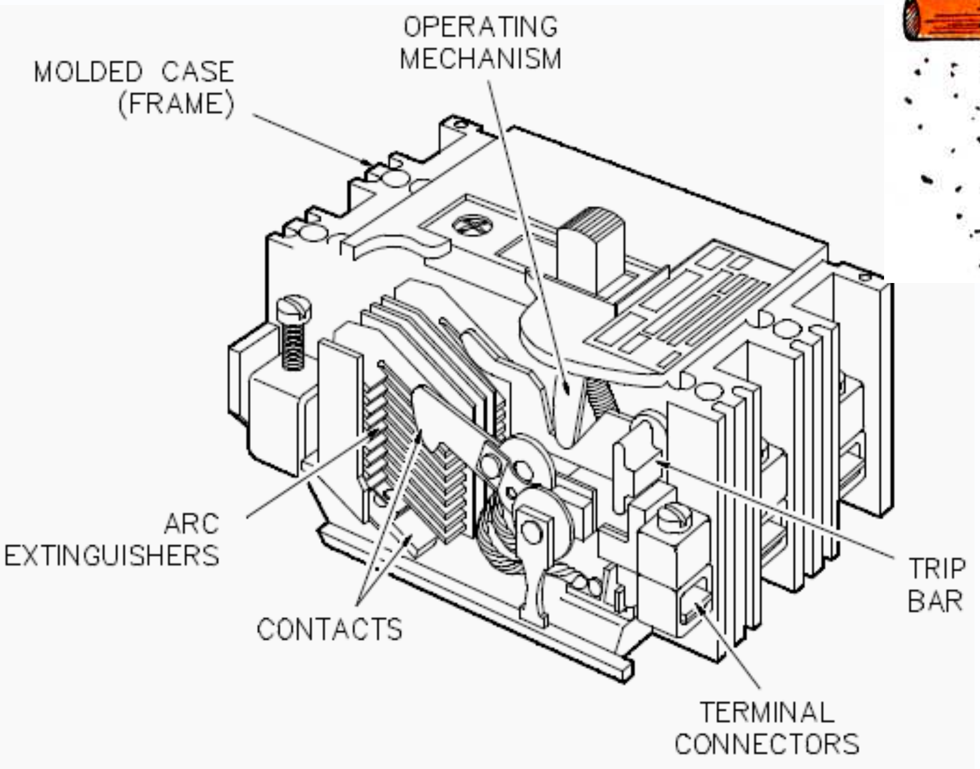


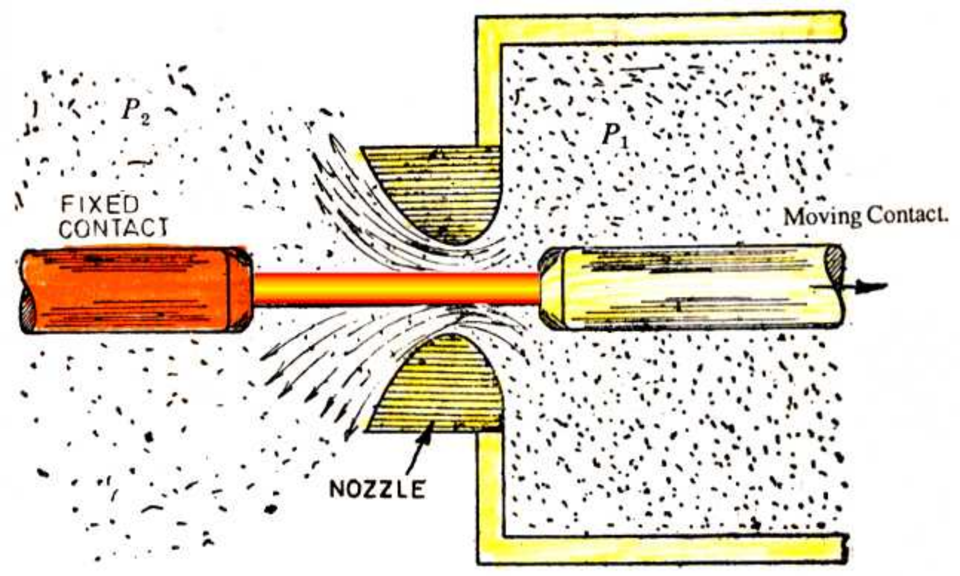
Aluminium dross recovery



Electric arc furnaces

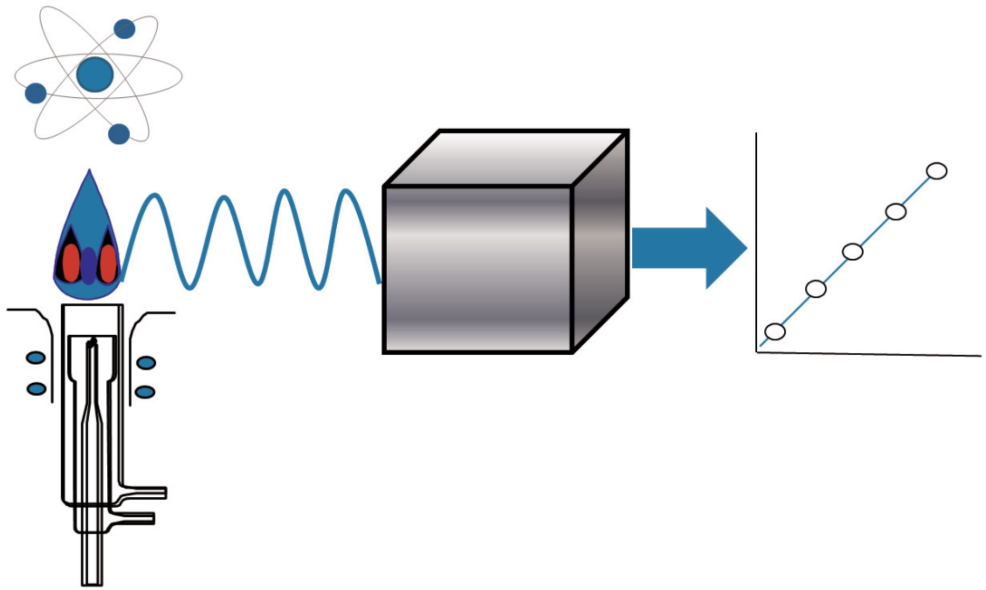
Thermal Plasma Applications: Circuit Breakers



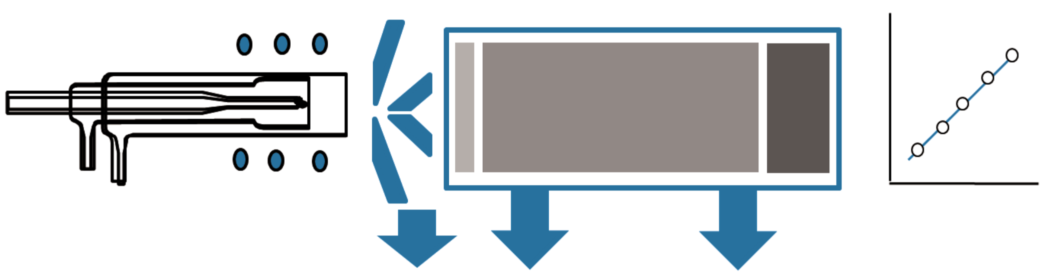


Thermal Plasma Applications: ICP-OES, ICP-MS

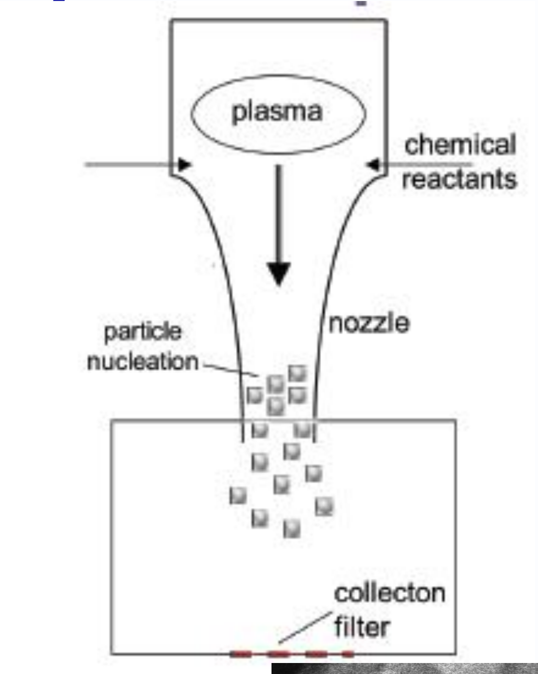
Inductively-coupled plasma – optical emission spectroscopy

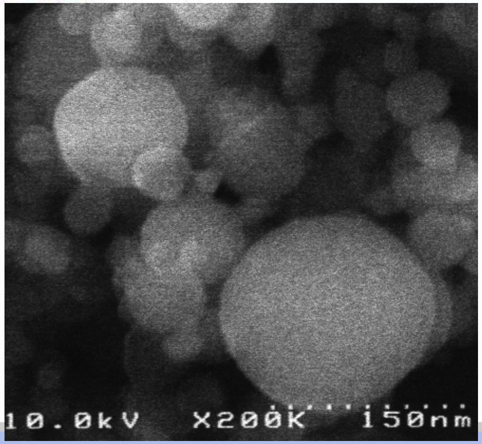


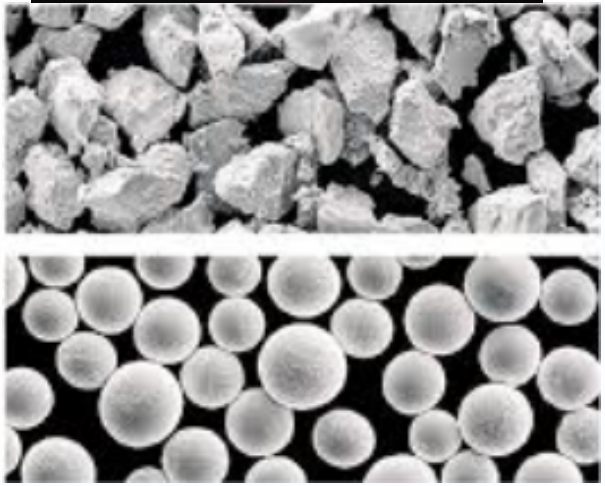
Inductively-coupled plasma – mass spectroscopy



Thermal Plasma Applications: Nanoparticle Synthesis and Particle Spheroidization

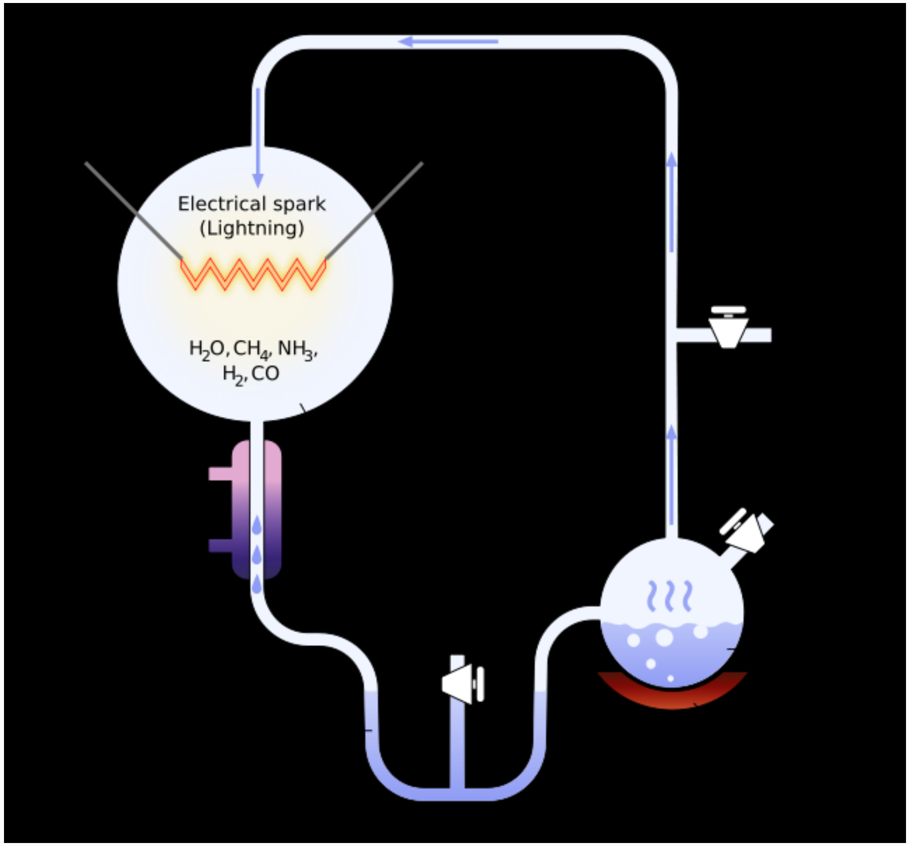






Thermal Plasmas in Nature: Lightning

The First Thermal Plasma Application?

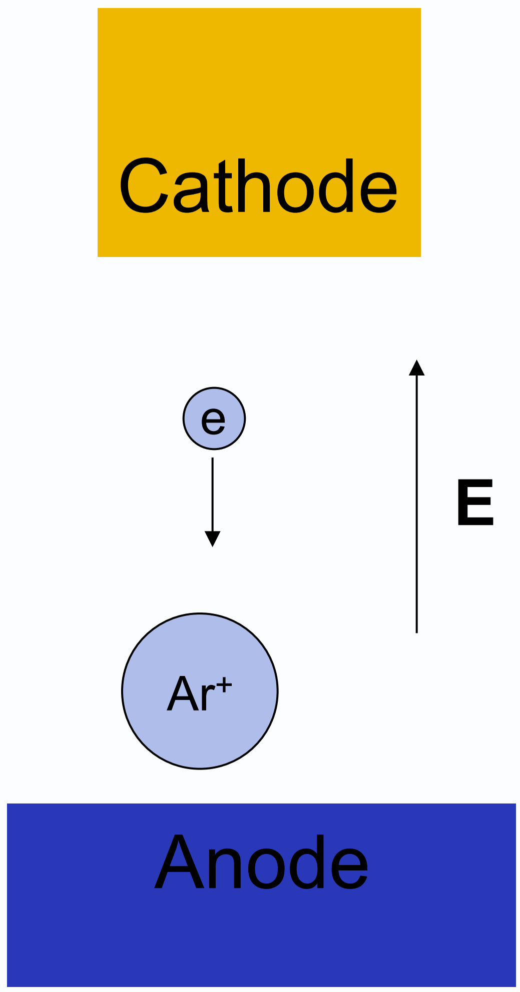


The Miller-Urey experiment

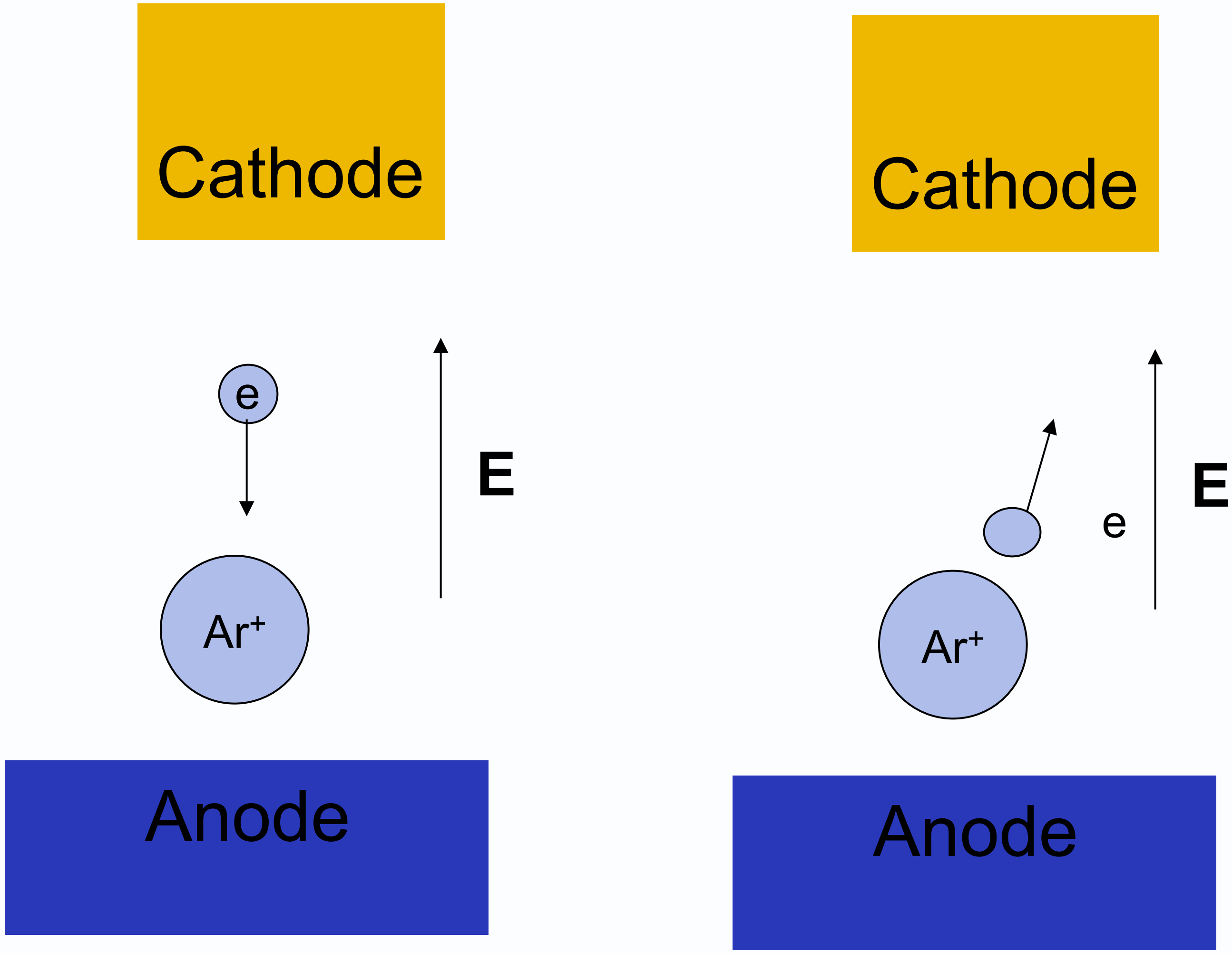
Outline

1. Thermal plasma properties
   - Local thermodynamic equilibrium (LTE)
   - Composition
   - Thermodynamic and transport properties
   - Radiative emission
   - Deviations from LTE
2. Generation of thermal plasmas
   - Transferred arcs
   - Non-transferred arcs
   - RF inductively-coupled plasmas
   - Microwave plasmas
   - Types of plasma flow
3. Modelling of thermal plasmas
   - Equations
   - Turbulence, electrode sheaths, gas mixtures
4. Thermal plasma diagnostics
   - Enthalpy probes
   - Emission spectroscopy
   - Laser scattering
5. Thermal plasma applications
   - Plasma waste destruction

Collisions between Electrons and Ions

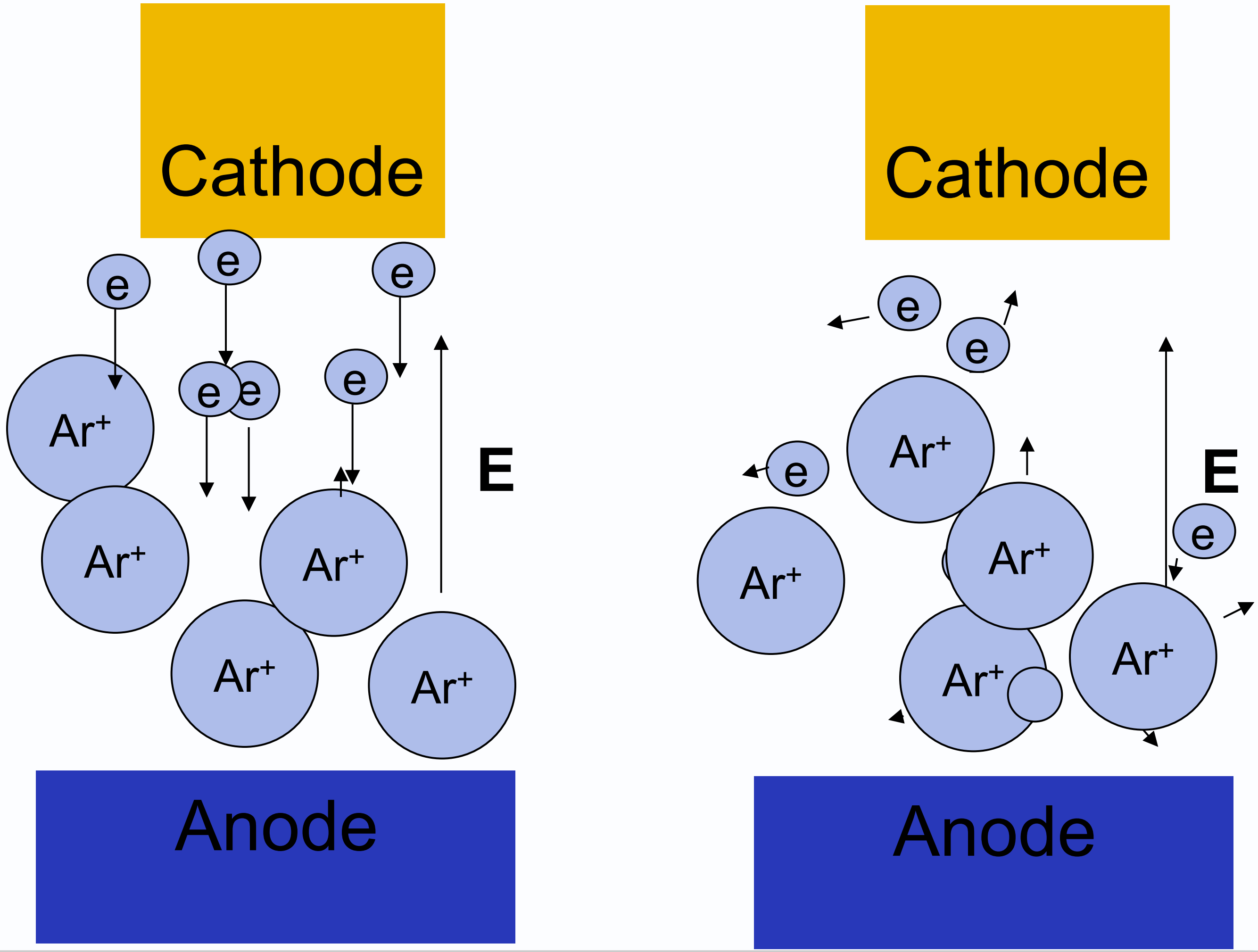


Collisions between Electrons and Heavy Species Transfer Little Energy



$$\Delta E_{\mathrm{kin}} \approx 2m_e / m_h$$

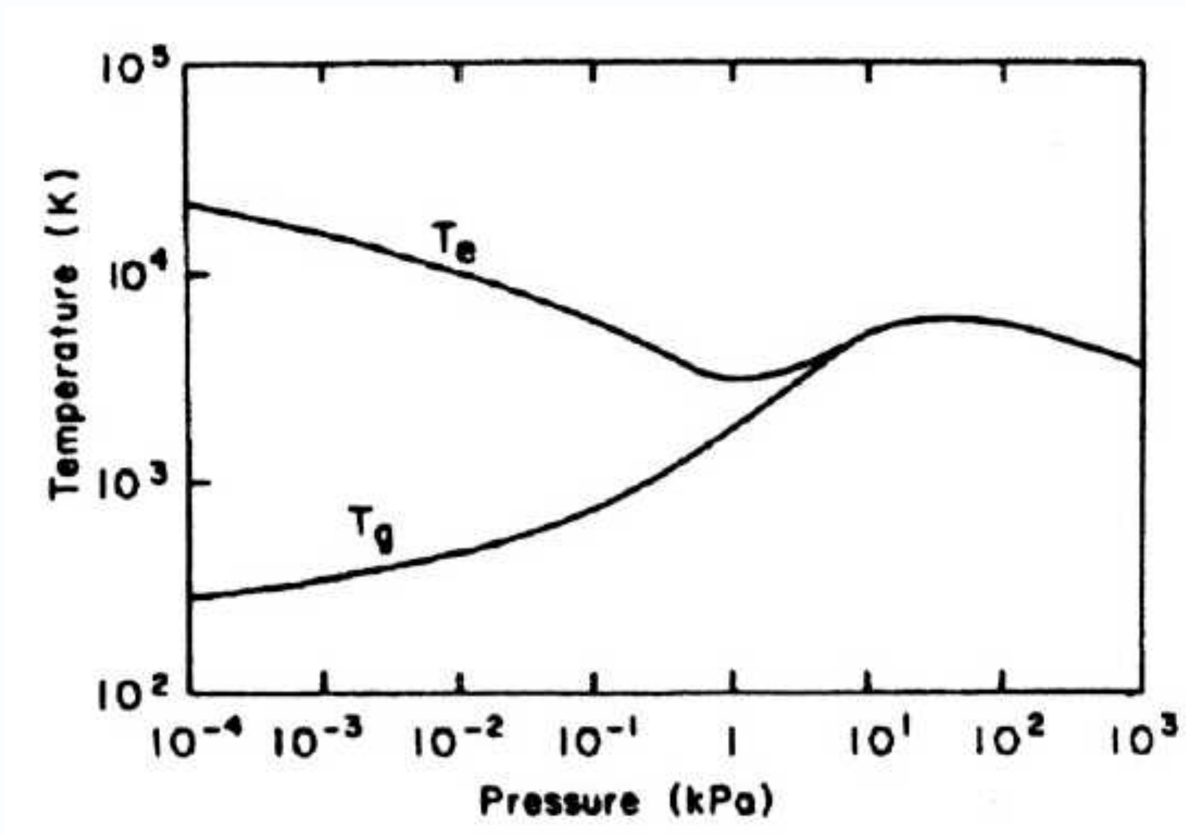
Lots of Collisions between Electrons and Ions Transfer A Lot of Energy



For 15 000 K, 1 atm:

$$\overline{\tau_e} = l_e / \overline{v_e} \sim \frac{3\times10^{-6}\ \text{m}}{7\times10^{5}\ \text{m/s}} \sim 5\ \text{ps}$$

Effect of Pressure on Equilibrium



Increasing pressure increases the number density,
and therefore the collision rate and the transfer of energy
from electrons to heavy species

Local Thermodynamic Equilibrium (LTE)

LTE exists if all species satisfy

- Maxwellian distribution for translational temperatures
- Boltzmann distribution for excitation temperatures
- Chemical equilibrium equations for reactions, e.g., ionisation

and all these temperatures are the same

LTE exists if the collision rate is much greater than the rates of diffusion and convection

It is generally valid in the bulk of the plasma (away from the edges and electrodes)

Why We Love LTE

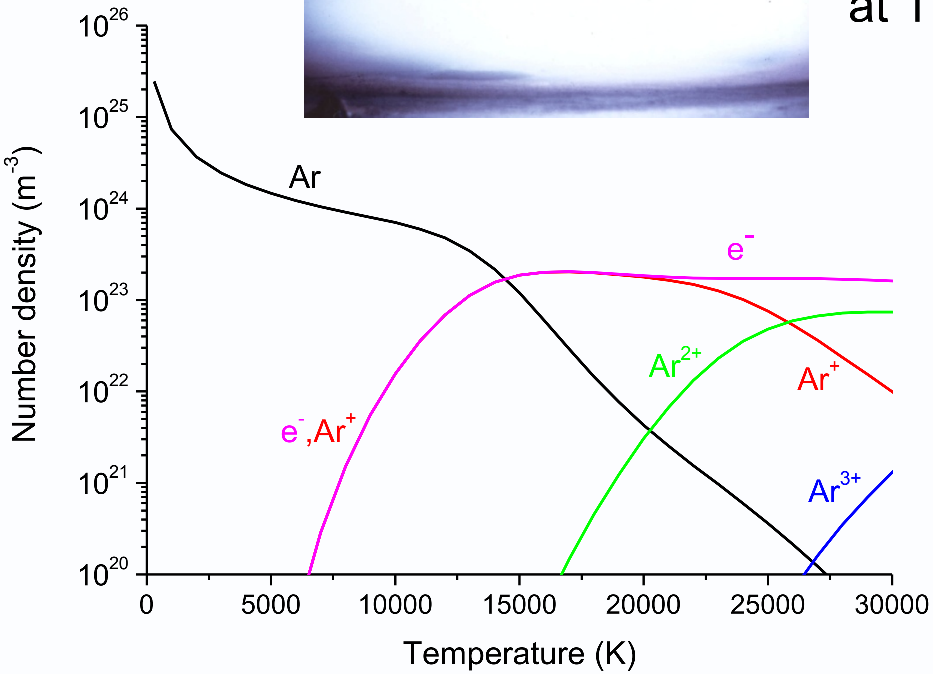
If LTE exists, then if we know (at a given point in the plasma)

- the pressure
- the temperature (or instead the density of any species)
- if there is a mixture of gases, the proportions of each gases

then we can fully describe the composition of the plasma at that point

This greatly simplifies modelling and diagnostics

Example: argon arc at 1 atm



Why Calculate Plasma Properties?

1. They are needed for computational modelling

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \boldsymbol{v}) = 0$$

$$\frac{\partial (\rho \boldsymbol{v})}{\partial t} + \nabla \cdot (\rho \boldsymbol{v}\boldsymbol{v}) = -\nabla P - \nabla \cdot \boldsymbol{\tau} + \boldsymbol{j} \times \boldsymbol{B} + \rho \boldsymbol{g}$$

where $\tau_{rr} = -2\eta \, \partial v_r / \partial r$, etc

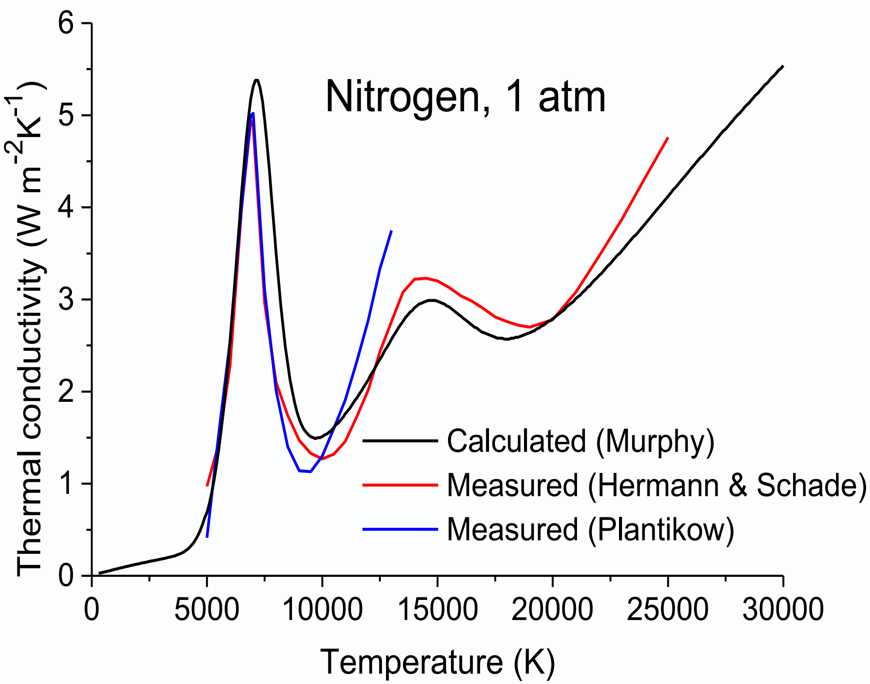
$$\frac{\partial (\rho h)}{\partial t} + \nabla \cdot (\rho \boldsymbol{v} h) = \frac{\boldsymbol{j}^2}{\sigma} - U - \nabla \cdot \left(\frac{\kappa}{c_p} \nabla h \right) + \frac{5k_B}{2ec_p} \boldsymbol{j} \cdot \nabla h$$

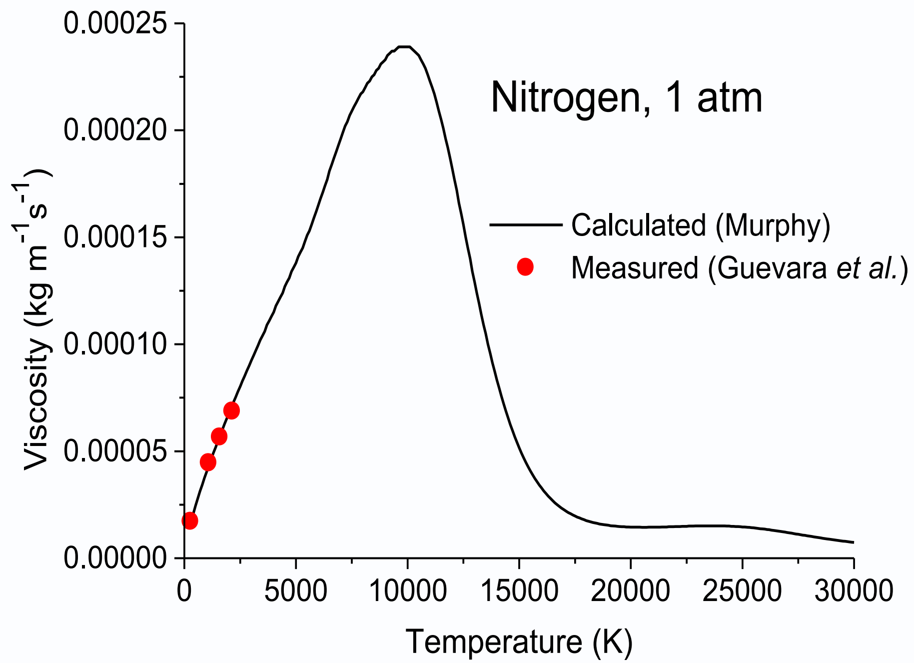
where h is a function of T

$$\nabla \cdot (\sigma \nabla \phi) = 0$$

Why Calculate Plasma Properties?

2. Measurements are inaccurate and inadequate





CSIRO

Classification of Properties

Thermodynamic properties

- Mass density (kg/m^3)
- Specific heat at constant pressure c_p (J/kg/K)
- Specific enthalpy (J/kg)

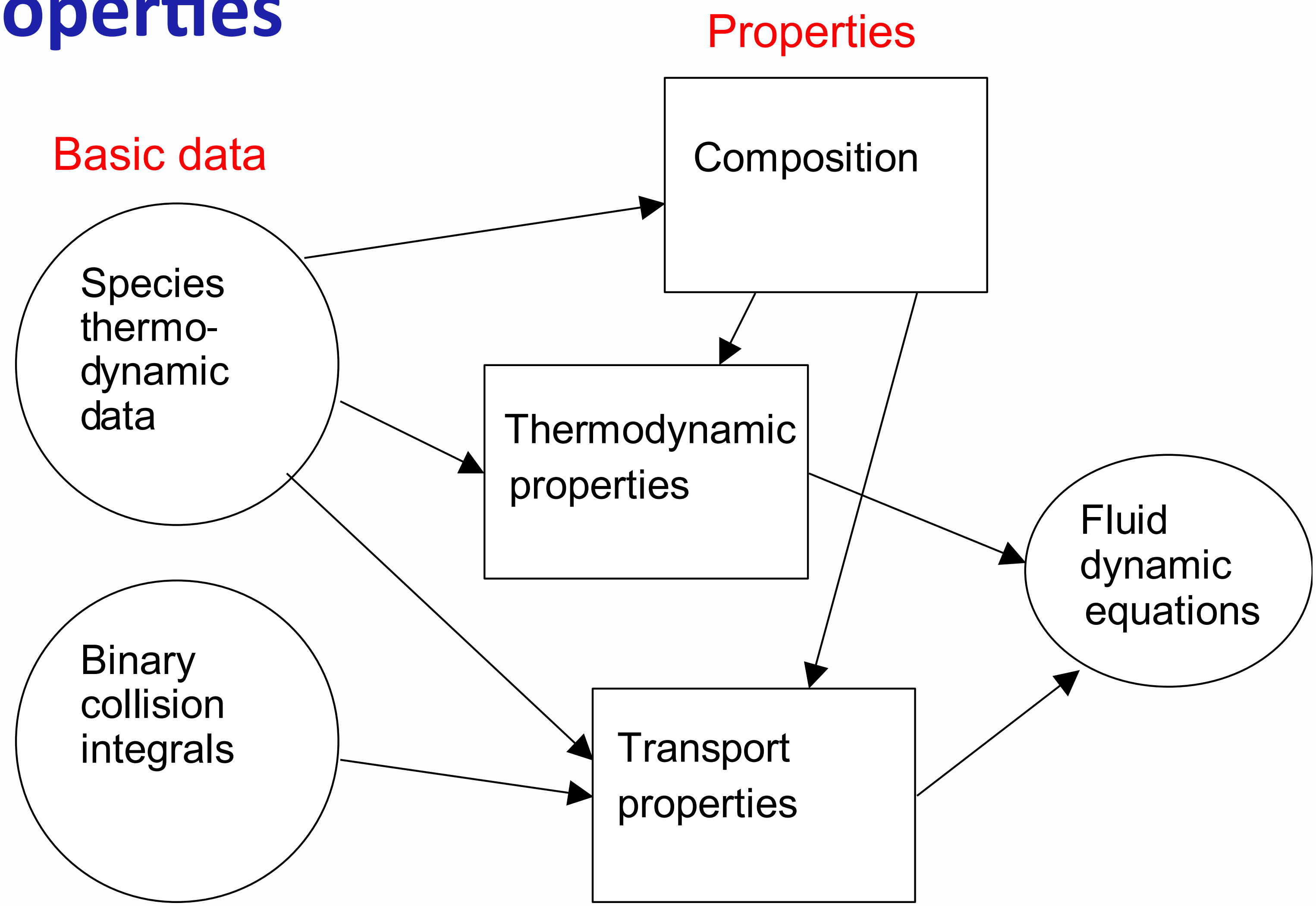
Transport properties (transport coefficients)

- Viscosity (kg/m/s)
- Thermal conductivity (W/m/K)
- Electrical conductivity (S/m)
- Ordinary diffusion coefficient (m^2/s)
- Thermal diffusion coefficient (kg/m/s)

Radiation properties

- Net emission coefficient ($W/m^3/sr$)

Relation between Basic Data and Material Properties



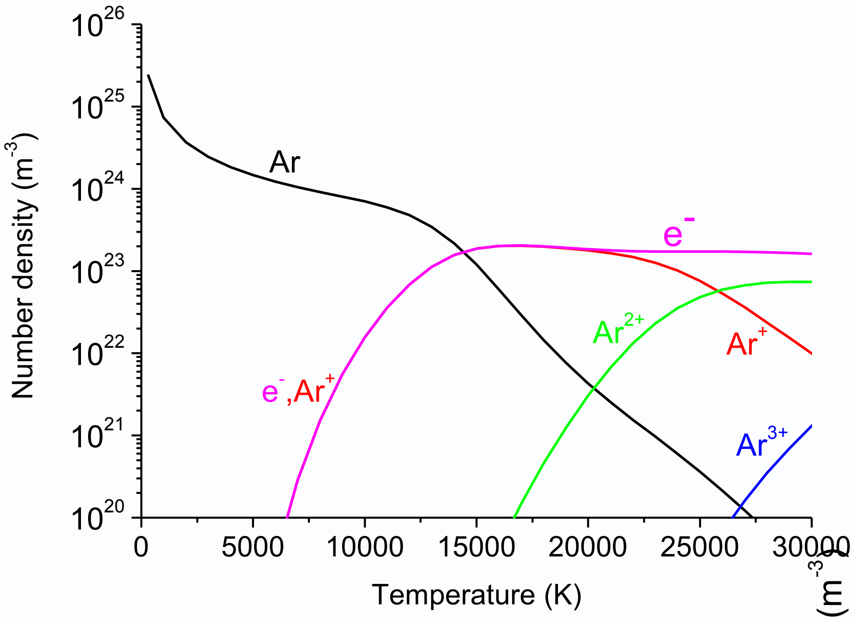
Plasma Composition

Use either:

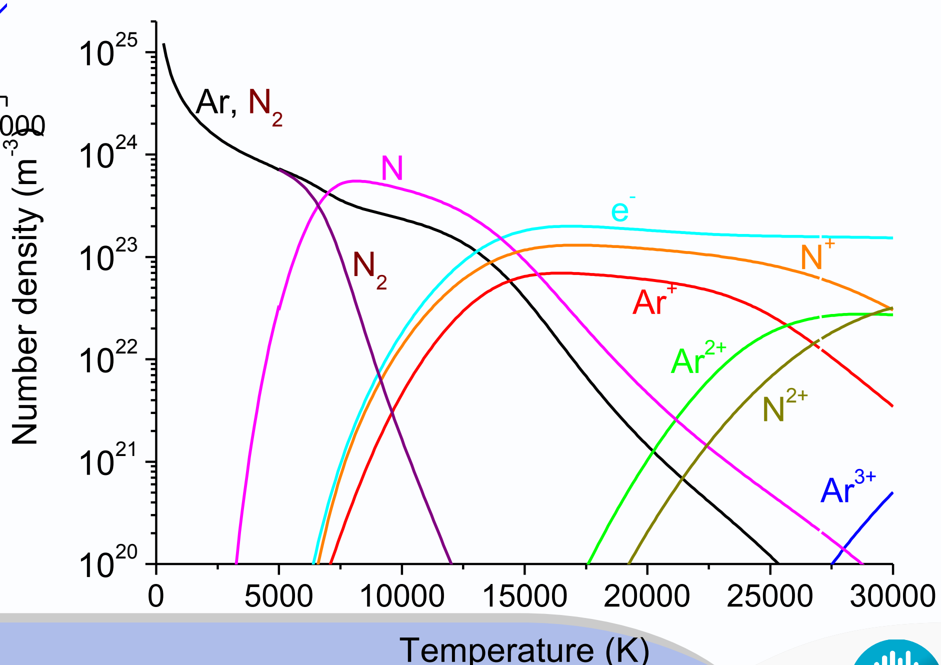
- Saha equations for ionisation reactions & Guldberg-Waage equations for dissociation reactions
  - Solve simultaneously (one equation for each reaction)
- Minimisation of Gibbs free energy $G = H - TS$ (H = enthalpy, S = entropy)
  - Restrictions: chemical elements conserved, charge neutrality
  - Input data (specific heat of each species / partition functions for each species) can be calculated from spectral data, or taken from tables

Examples

Argon, 1 atm



50% Argon, 50% Nitrogen, 1 atm



Thermodynamic Properties

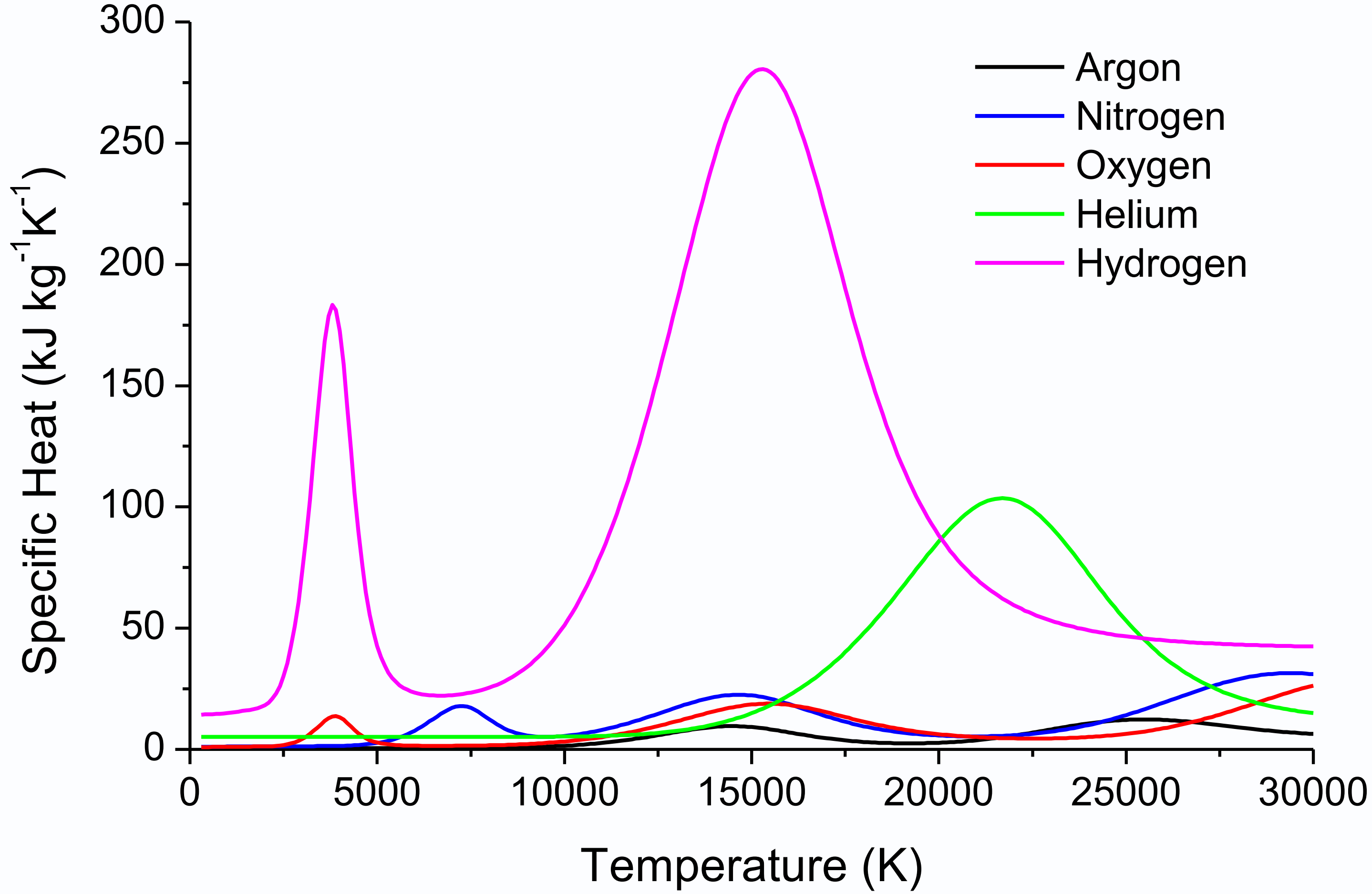
These are easily calculated once the plasma composition is known

Density (kg m^{-3}) $\rho = \sum_{i=1}^{N} n_i m_i$

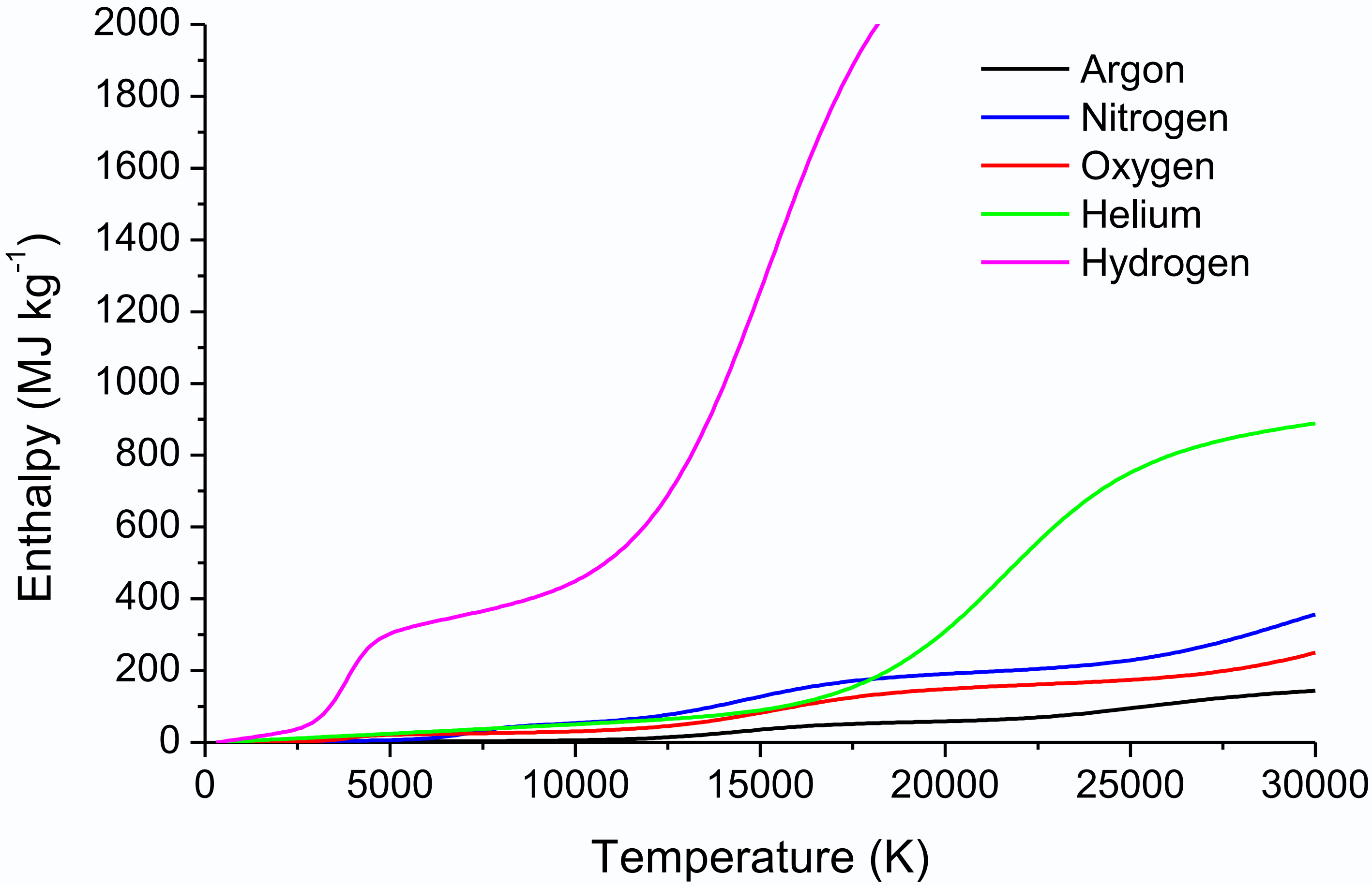
Enthalpy (J kg^{-1}) $h = \dfrac{1}{\rho} \sum_{i=1}^{N} n_i m_i h_i$ (+ minor correction term)

Specific heat (J kg^{-1}K^{-1}) $C_p = \left.\dfrac{\partial h}{\partial T}\right|_P$

Specific Heat for Various Plasmas



Enthalpy for Various Plasmas



Transport Properties

- Viscosity: transport of momentum perpendicular to flow
- Thermal conductivity: transport of heat
- Electrical conductivity: transport of charge
- Diffusion coefficients: transport of mass

Determined by collision cross-sections (mean free paths) of all species

For plasmas, have many species present – need information about collision cross-sections between all pairs of species:
neutral-neutral, neutral-ion, neutral-electron, charged-charged (Coulomb)

References for transport coefficient calculations:

J. O. Hirschfelder, C. J. Curtiss and R. B. Bird 'Molecular Theory of Gases and Liquids, 2nd edn (Wiley: New York, 1964)
M. I. Boulos, P. Fauchais and E. Pfender 'Thermal Plasmas: Fundamentals and Applications' Vol. 1 (Plenum: New York, 1994)
A. B. Murphy and C. J. Arundell *Plasma Chem. Plasma Process.* **14** (1994) 451

Viscosity

To first order: $\eta = \frac{1}{2} k_B T \sum_j n_j b_{j0}$

where $\sum_{j=1}^{q} Q_{ij}^{00} b_{j0} = 5n_i$

$$Q_{ij}^{00} = \frac{16}{3} \frac{n_i m_i}{m_j} \sum_{k=1}^{q} \frac{n_k m_k}{\left(m_i + m_k\right)^2}$$

$$\times \left[5m_j \left(\delta_{ij} - \delta_{jk} \right) \Omega_{ik}^{(1,1)} + \frac{3}{2} m_k \left(\delta_{ij} + \delta_{jk} \right) \Omega_{ik}^{(2,2)} \right]$$

Collision Integrals are Calculated from the Intermolecular Potentials

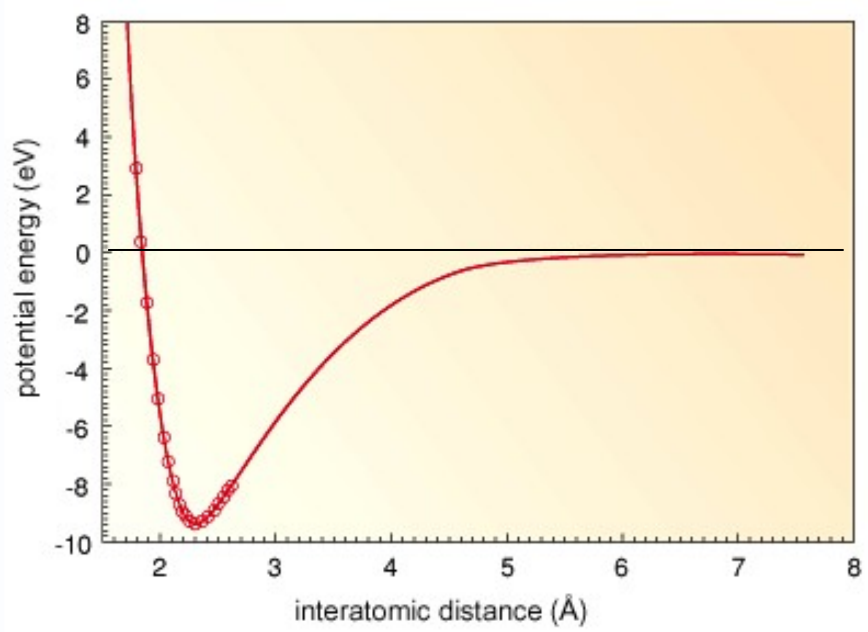
$$\Omega_{ij}^{(l,s)}(T) = \sqrt{\frac{kT}{2\pi\mu_{ij}}} \int_0^\infty \exp\left(-\gamma_{ij}^2\right)\gamma_{ij}^{2s+3} Q_{ij}^{(l)}(g)\, d\gamma_{ij} \quad \text{where} \quad \gamma_{ij} = \sqrt{\frac{\mu_{ij}}{2kT}} g_{ij}$$

are averages over a Maxwellian distribution of the gas kinetic cross-section

$$Q_{ij}^{l}(g) = 2\pi \int_0^\pi \left(1 - \cos^l \chi\right) b\, db$$

where the angle of deflection is

$$\chi(b,g) = \pi - 2b \int_{r_m}^{0} \frac{dr/r^2}{\sqrt{1 - \varphi(r)\big/\tfrac{1}{2}\mu g^2 - b^2/r^2}}$$



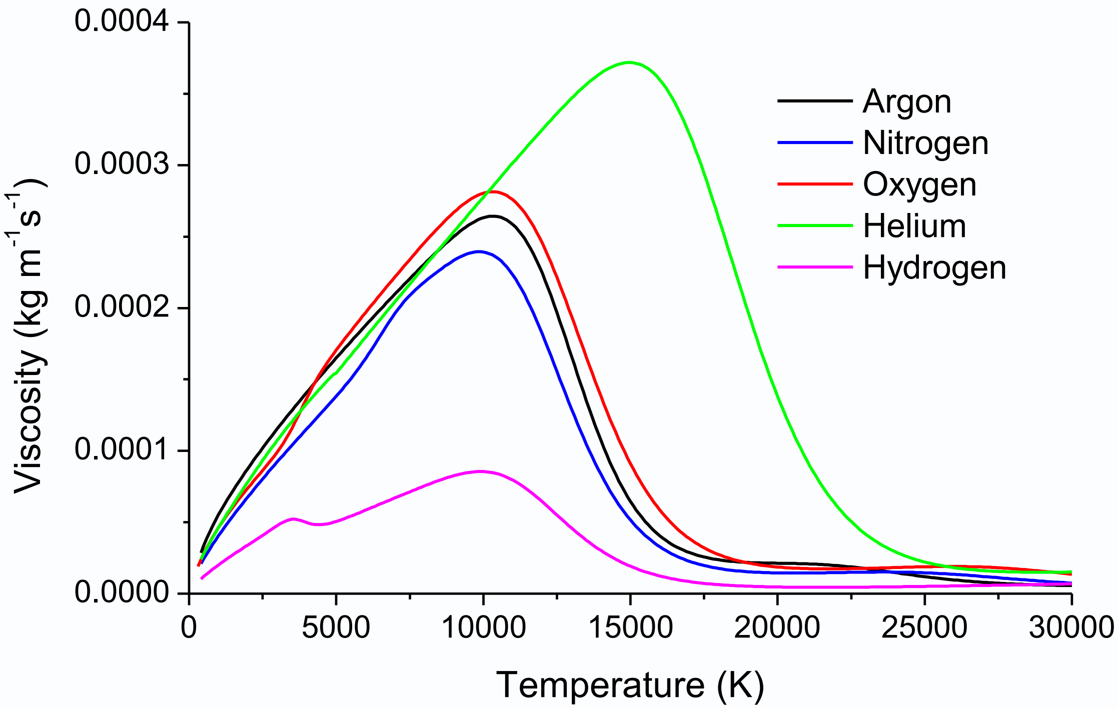
intermolecular potential $\varphi(r)$

reduced mass μ

initial relative speed g

impact parameter b

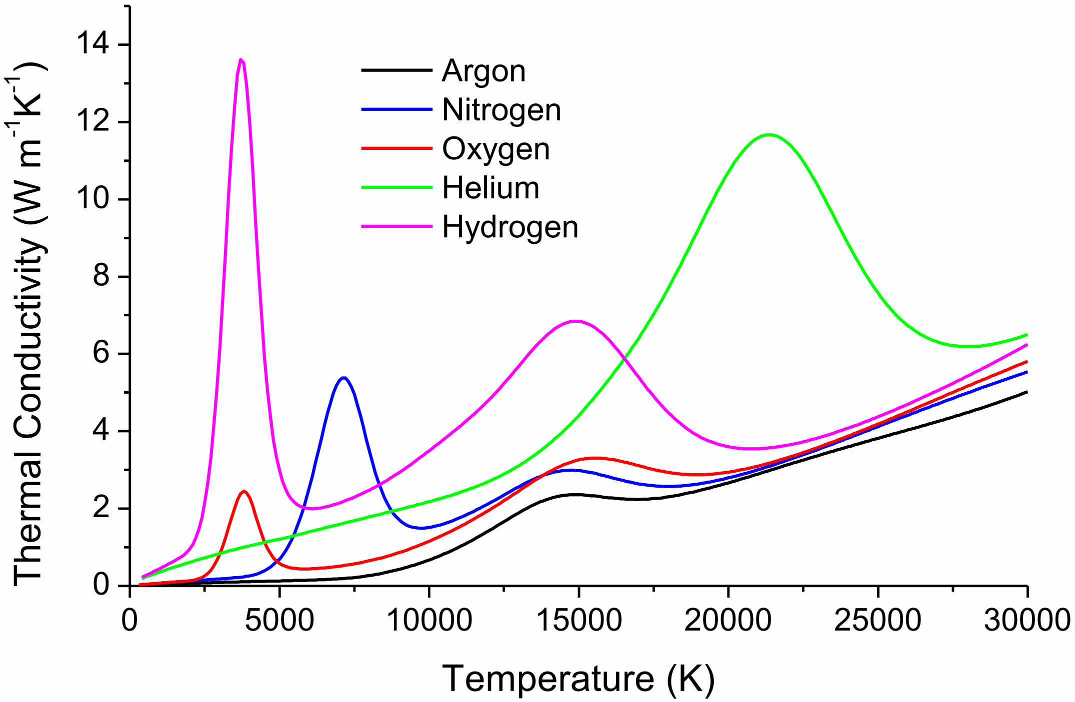
Viscosity for Various Plasmas



Viscosity η describes relationship between shear stress and velocity gradient $F = -\eta \frac{dv_x}{dy}$

$\eta \sim \frac{\sqrt{m_i T}}{\Omega}$, Ω is collision cross section

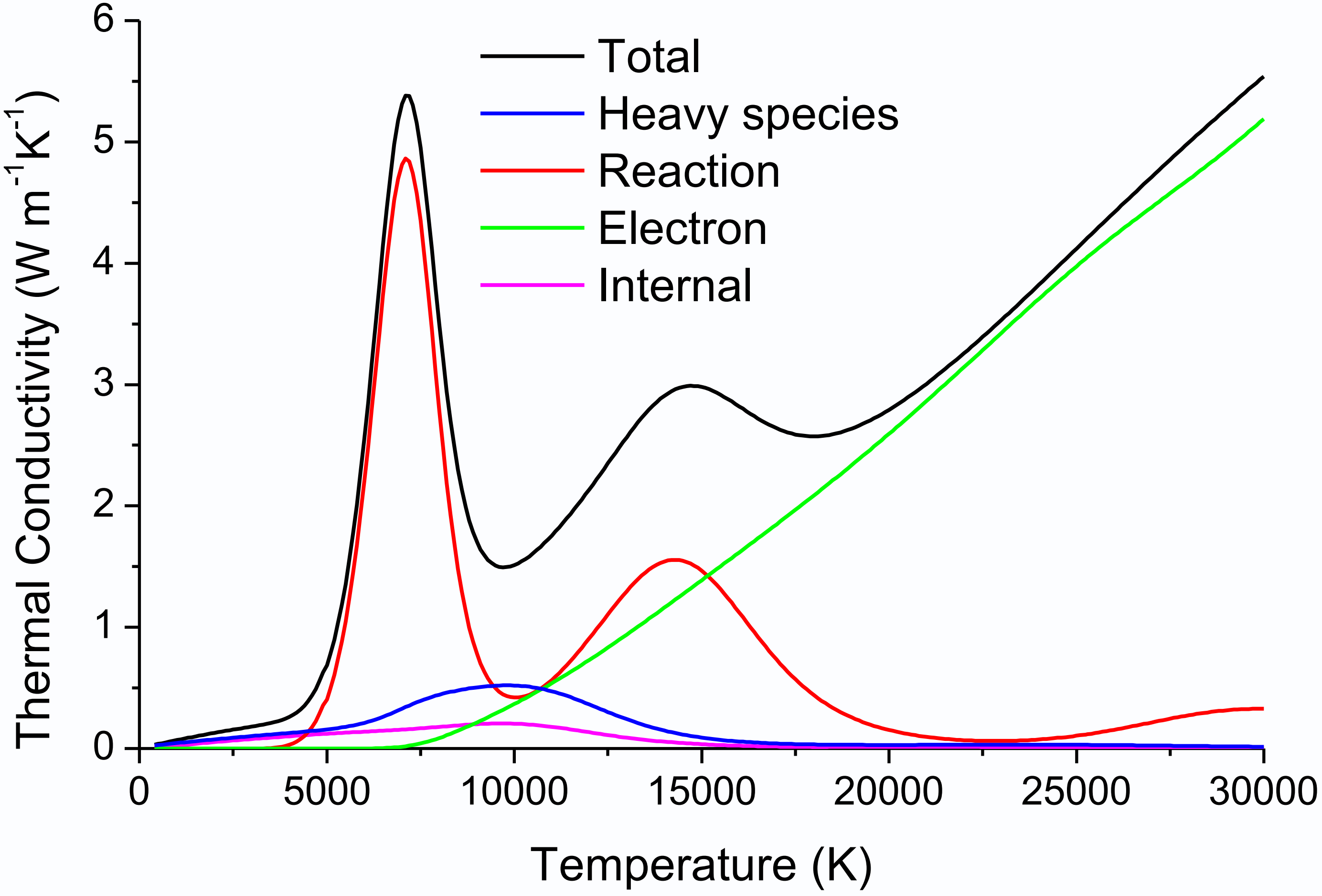
Thermal Conductivity for Various Plasmas



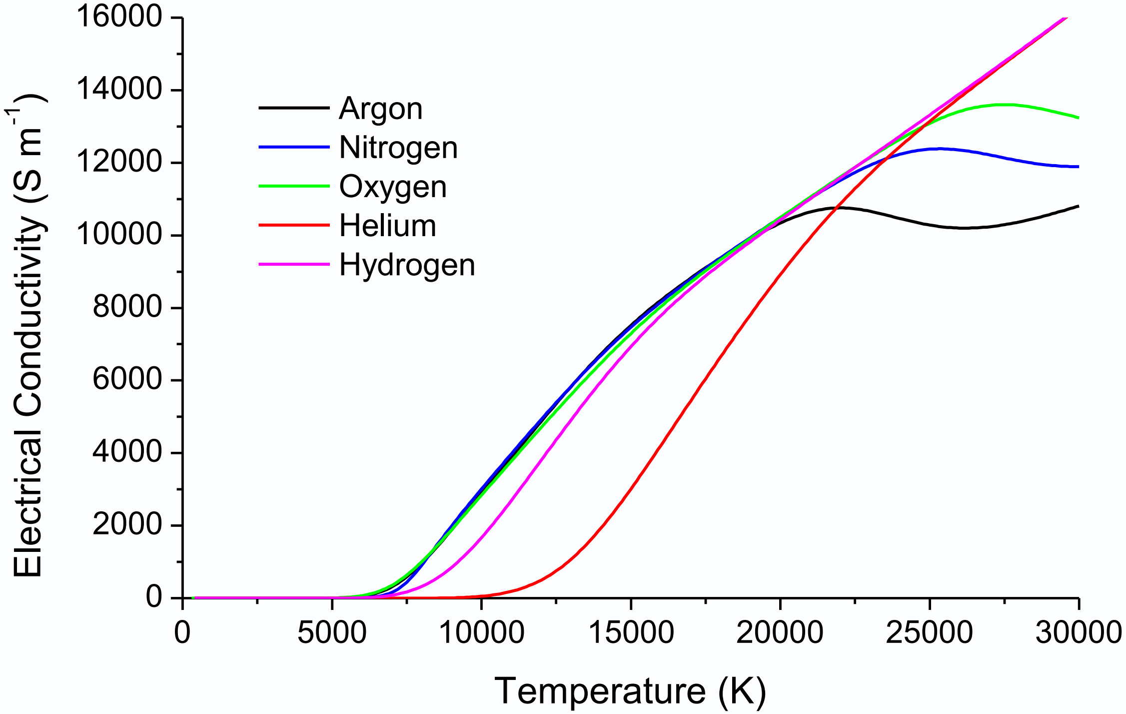
Thermal conductivity k describes relationship between heat flux density and temperature gradient $q = -k\,\dfrac{dT}{dx}$

$k \sim \dfrac{C_p}{\Omega}\sqrt{\dfrac{T_i}{m_i}}$, Ω is collision cross-section

Components of Thermal Conductivity for Nitrogen



Electrical Conductivity for Various Plasmas



Electrical conductivity σ describes relationship between current density and voltage gradient $j = \sigma \frac{dV}{dx}$

$\sigma \sim \frac{n_e}{\sqrt{T} n \Omega}$, n_e is electron density, n is density of other species, Ω is collision cross section

Radiative Emission

Important in thermal plasmas

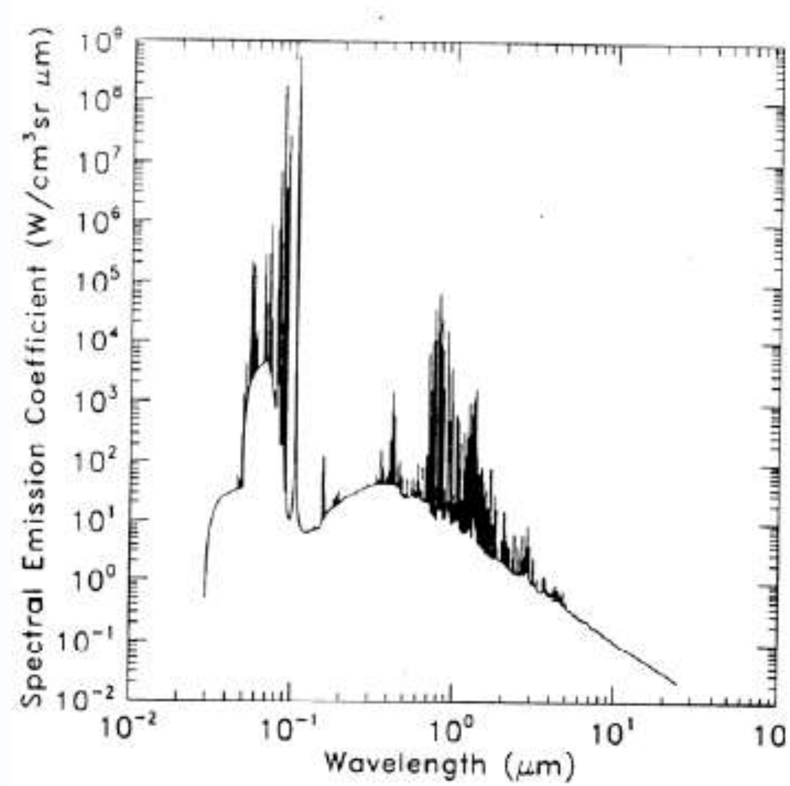
A full treatment is difficult:

- Determine emission and absorption at every volume element
- A large number of wavelength intervals required to cover line and continuum radiation

Net emission coefficients are a very successful approximation

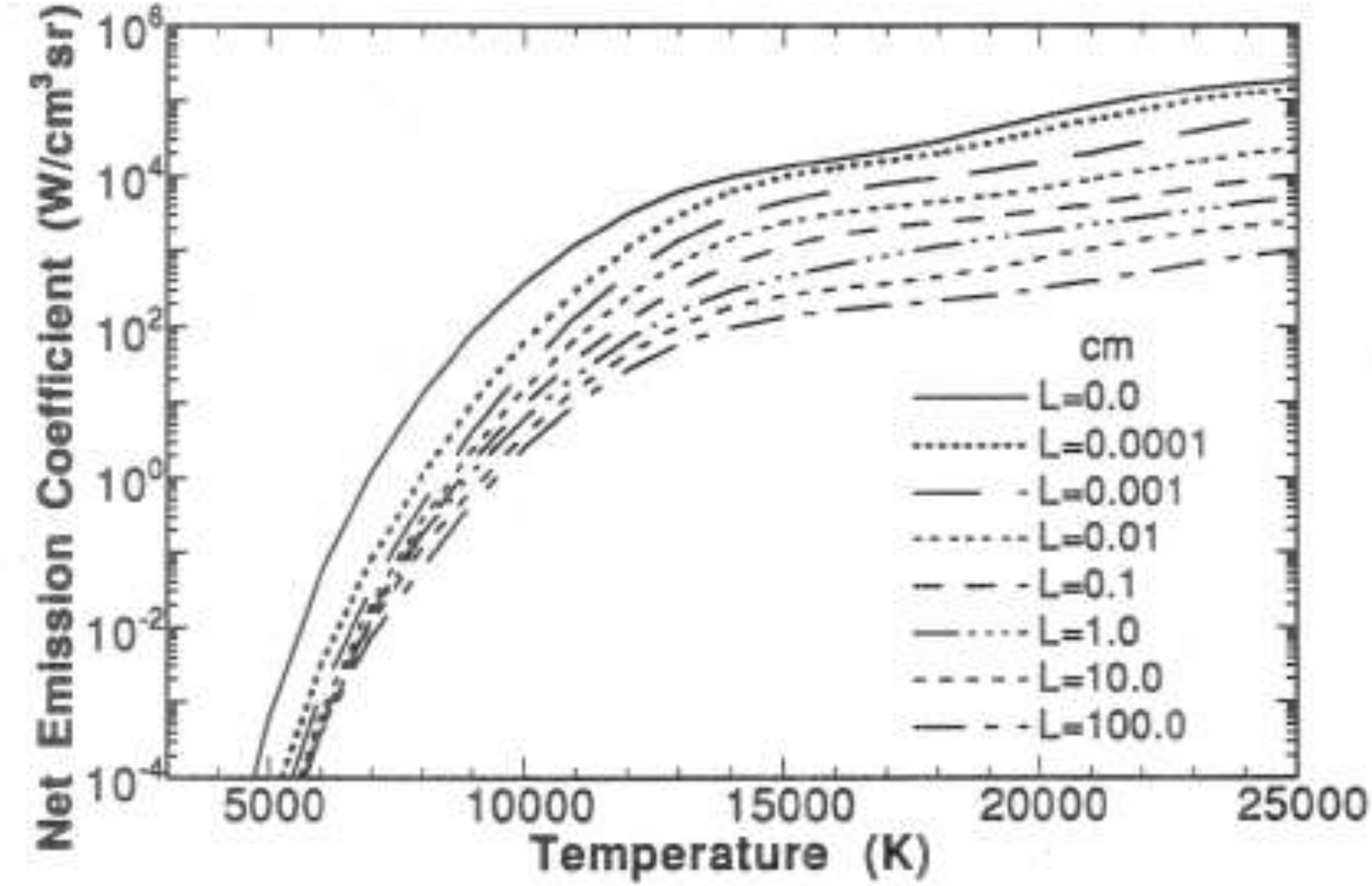
- For a given temperature, integrate emission over all wavelengths
- Take into account absorption in a sphere of a given radius

For applications in which radiation flux at boundary is important, need more complex treatments



J. J. Lowke *J Quant Spectrosc. Radiat. Transf.* **16** (1974) 111
A. Gleizes *et al. J. Phys. D: Appl. Phys.* **26** (1993) 1921

Net Emission Coefficients for Argon at 1 atm



L is the radius of the absorbing sphere

J. A. Menart PhD Thesis Uni. of Minneapolis (1996)

2. Generation of Thermal Plasmas

Electric arcs

- Requires electrodes
- Relatively inexpensive
- The most widely-used method
- Transferred or non-transferred arcs
- Usually DC, but can be AC

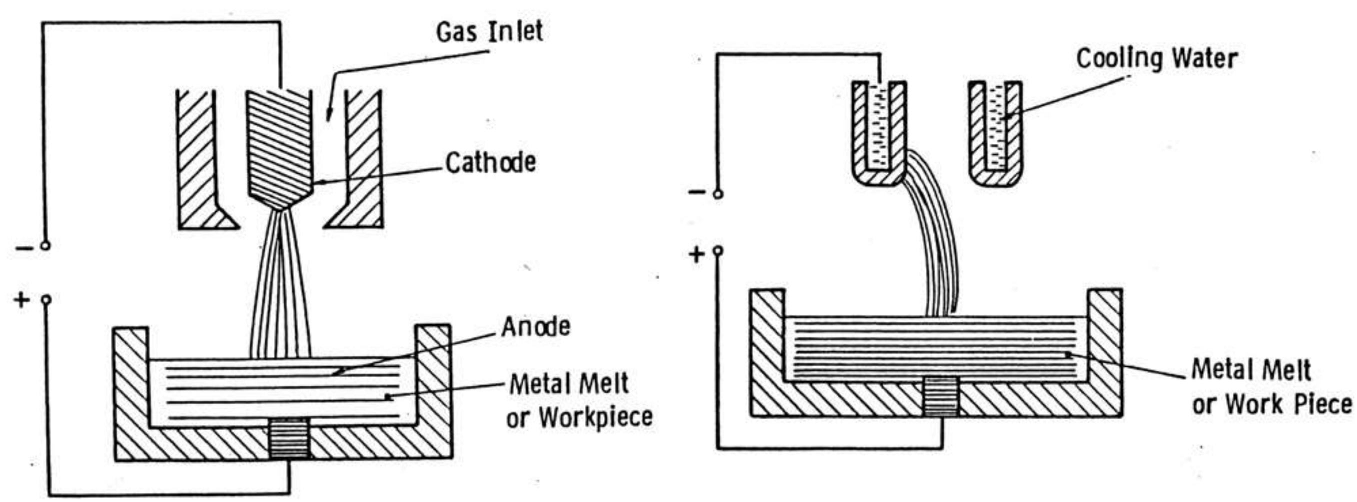
Radiofrequency inductively-coupled discharges

- No electrodes required
- More expensive
- Generates a larger, more uniform, plasma volume
- Lower efficiency
- More sensitive to process variations

Microwave discharges

- No electrodes required
- Relatively small-scale and expensive
- Usually $T_e > T_h$

Electric Arcs: Transferred Arcs



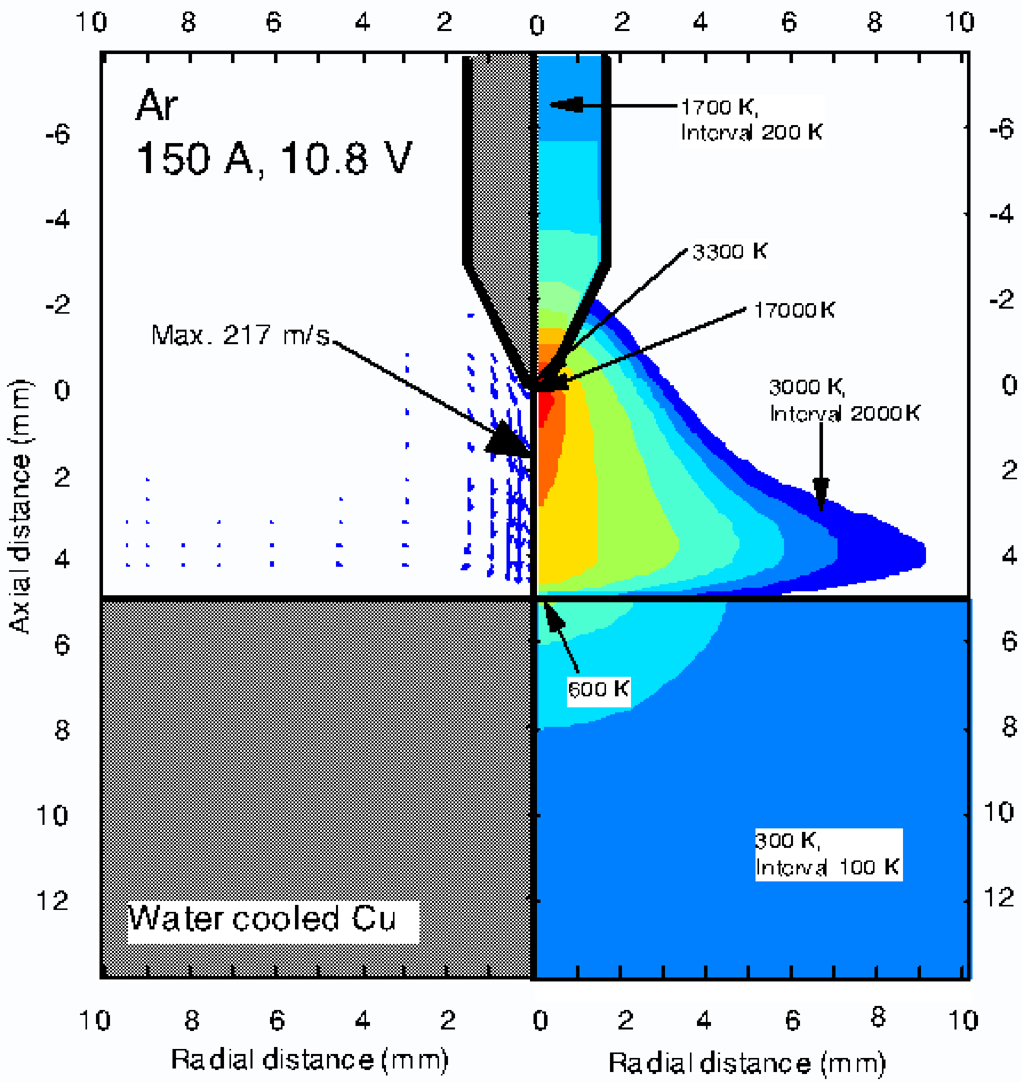
Arc between one electrode (usually cathode) and metal or conducting workpiece

High energy transfer efficiency to workpiece

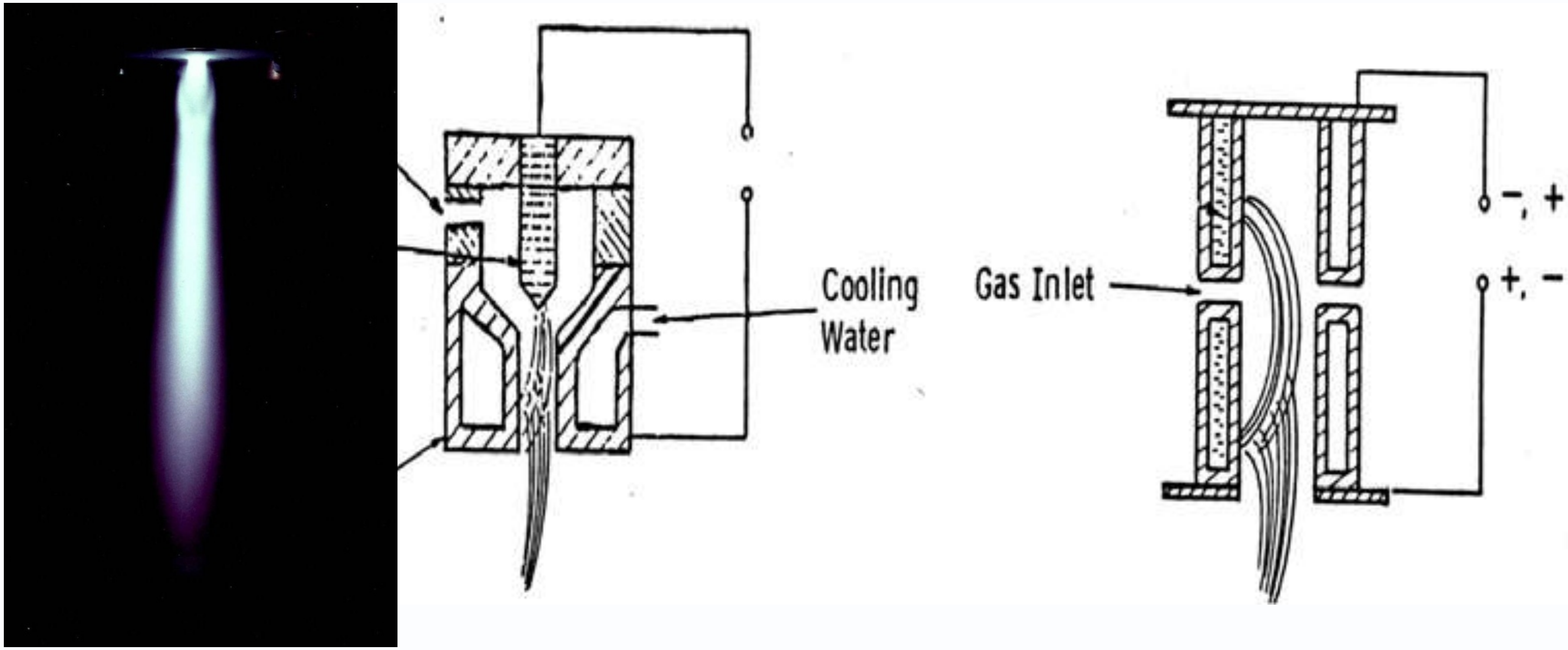
Low gas flow

High peak temperature, narrow distribution

Used in welding, plasma cutting, electric arc furnaces, arc lamps, waste destruction, etc.


Ar
150 A, 10.8 V
Max. 217 m/s
1700 K,
Interval 200 K
3300 K
17000 K
3000 K,
Interval 2000 K
600 K
300 K,
Interval 100 K
Water cooled Cu
Axial distance (mm)
Radial distance (mm)
Radial distance (mm)

Electric Arcs: Non-transferred Arcs



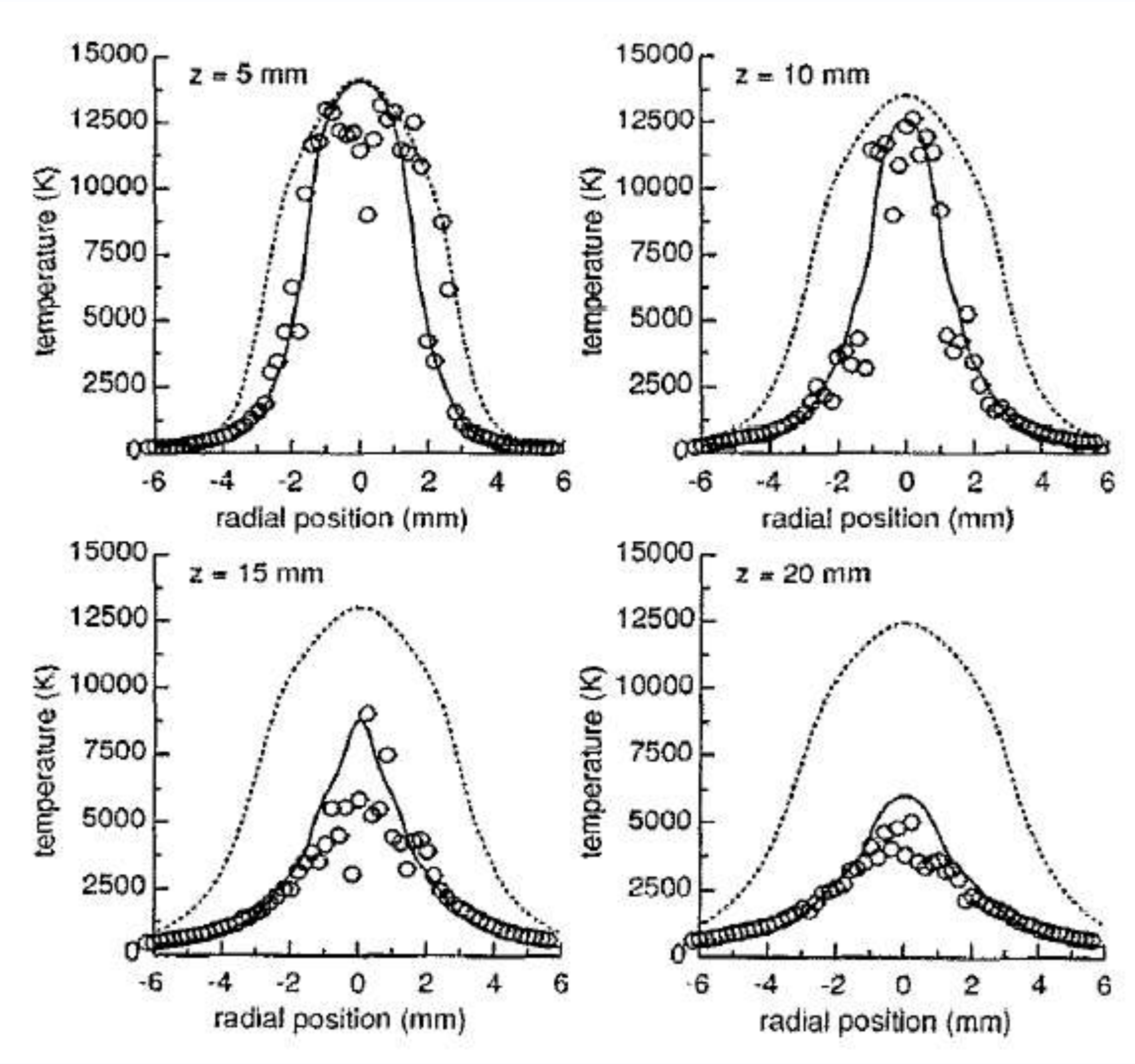
Arc is confined within plasma torch

High efficiency heating of bulk gas (“arc heater”)

High gas flow

Broader heat flux distribution, lower peak temperature

Used in plasma spraying, waste destruction, etc.



400 A, 10 kW argon plasma jet

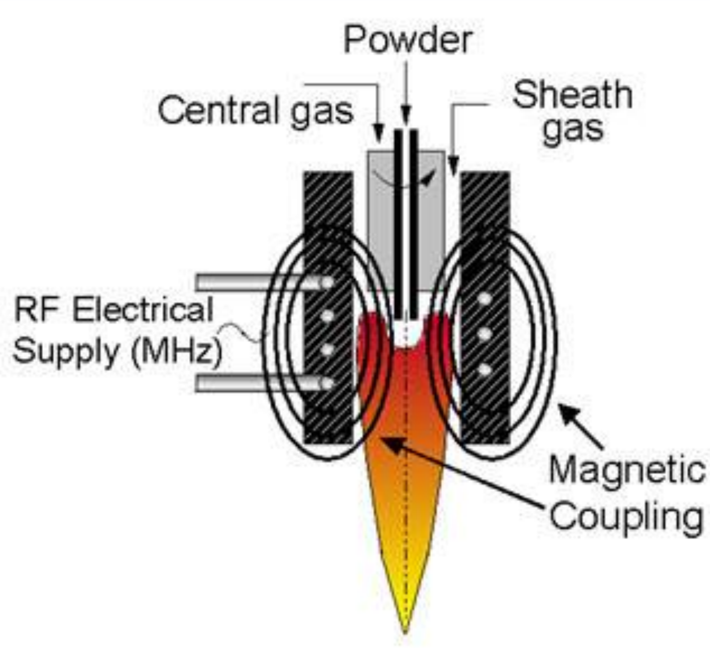
Solid line: calculations for jet into air

Dotted line: calculations for jet into argon

Circles: measurements for jet into air

A. B. Murphy and P. Kovitya, *J. Appl. Phys.* **73** (1993) 4759

RF Inductively-Coupled Plasmas

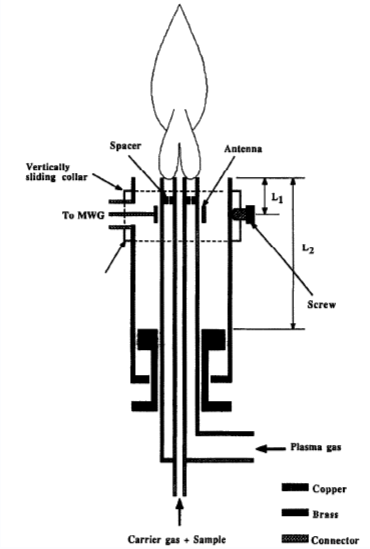


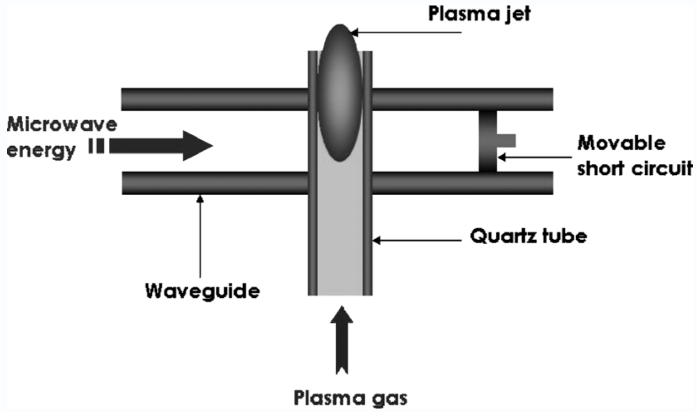
No electrodes, so low contamination

Low gradients

Used for powder processing (densification, spheroidisation), nanoparticle production, etc.

Microwave Plasmas





- No electrodes
- Several different designs
- Strongly non-equilibrium (gas temp. < 5000 K, electron temp. > 10 000 K
- Applications include MP-AES (microwave plasma - atomic emission spectroscopy), gas treatment

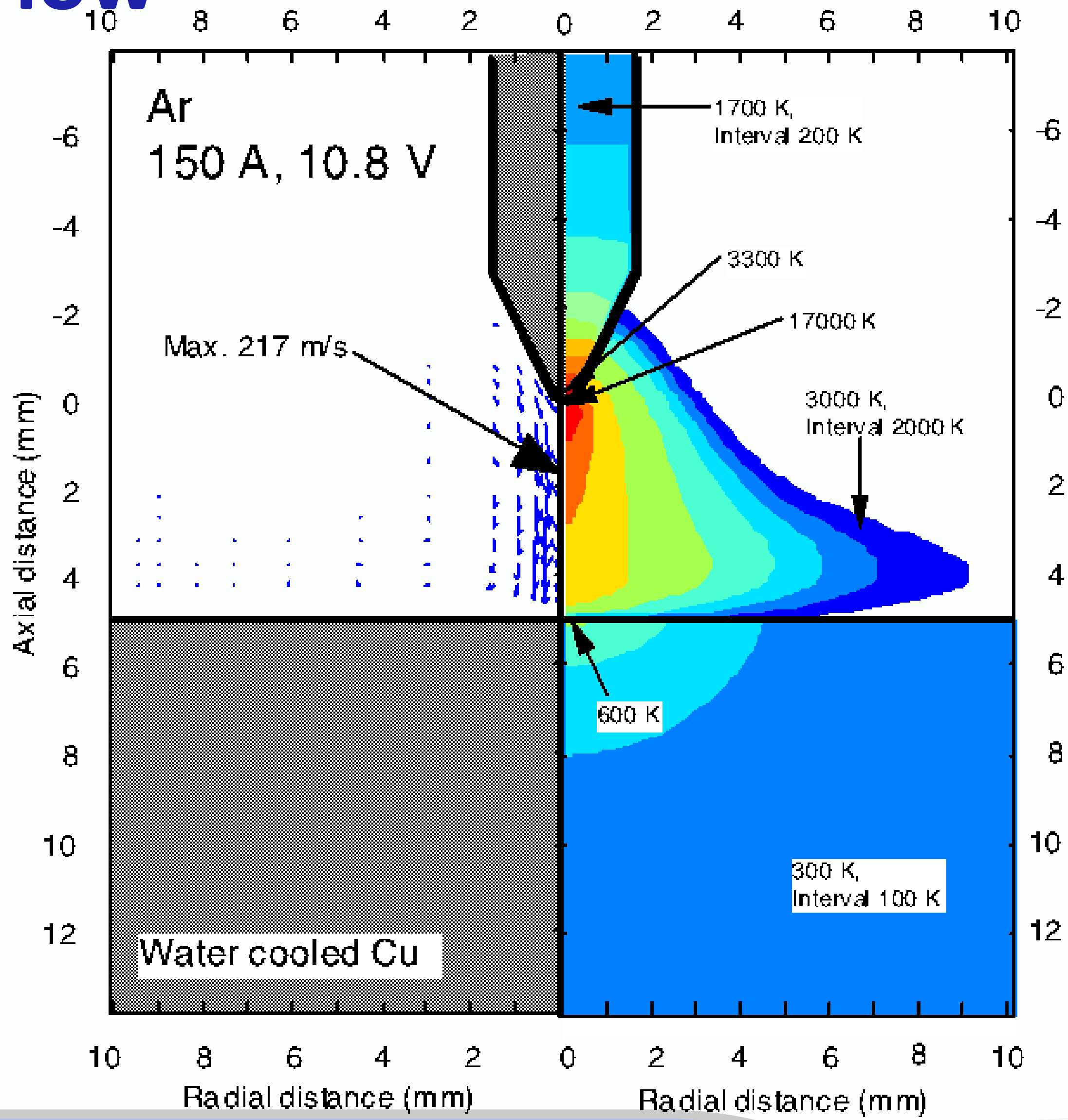
Types of Plasma Flow

Gravity-driven flow

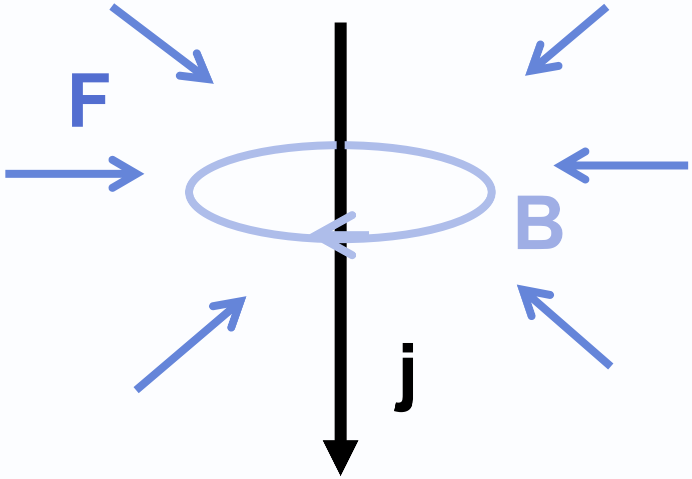
- Low current (< 20 A) arcs
- Flow driven by buoyancy
- Arc lamps

Flow driven by j x B forces

- Higher current (> 30 A) arcs
- Pressure gradient = j x B (the magnetic pinch effect)
- Maximum velocities from 100 to 1000 m/s
- Arcs for welding, plasma cutting, etc



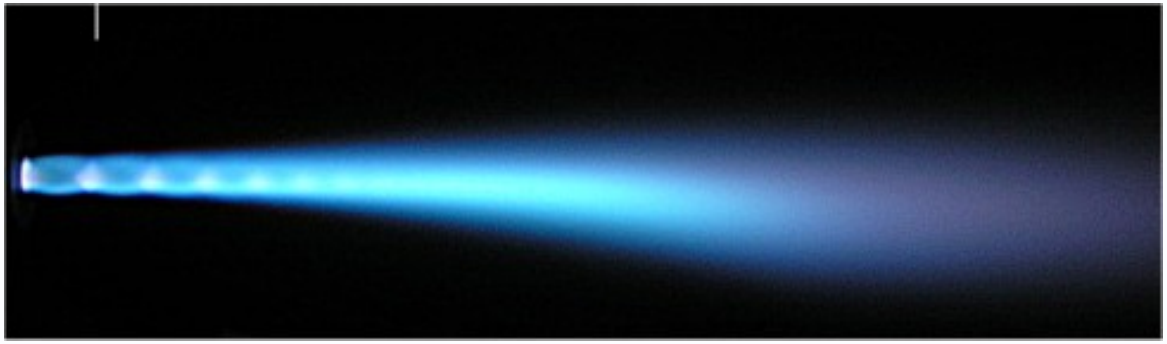
Magnetic Pinch (Lorentz or j x B) Force



Types of Plasma Flow

Flows driven by thermal expansion

- In plasma torches, the arc occurs in a confined region, causing the pressure to rise
- Supersonic velocities (over 2000 m/s) typically achieved
- Arc stabilised by high gas flow and often swirl of gas
- Typical in plasma spraying



Shock diamonds indicating supersonic flow

3. Modelling of Thermal Plasmas

- Use computational fluid dynamic equations for viscous incompressible flow
- A conservation of energy equation is required because the temperature is not constant
- Maxwell’s equations are used to describe current continuity (charge conservation) and magnetic fields
- Additional terms describing ‘plasma’ effects are included (ohmic heating, radiative emission, magnetic pinch effect, electron diffusion)
- The equation of state is implicit in the dependence of thermophysical properties on temperature
- Modifications required for electrode regions, turbulent flows, departures from LTE, high Mach number flow, etc.

Conservation Equations: Single Gas

Time-dependent term
Convective term
Diffusive term
Source term

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \boldsymbol{v}) = 0$$

$$\frac{\partial (\rho \boldsymbol{v})}{\partial t} + \nabla \cdot (\rho \boldsymbol{v}\boldsymbol{v}) = -\nabla \cdot \boldsymbol{\tau} - \nabla P + \boldsymbol{j} \times \boldsymbol{B} + \rho \boldsymbol{g}$$

$$\frac{\partial (\rho h)}{\partial t} + \nabla \cdot (\rho \boldsymbol{v} h) = -\nabla \cdot \left(\frac{\kappa}{c_p} \nabla h \right) + \frac{\boldsymbol{j}^2}{\sigma} - U + \frac{5 k_B}{2e} \boldsymbol{j} \cdot \nabla T$$

$$\nabla \cdot (\sigma \nabla \phi) = 0 \qquad \nabla^2 \boldsymbol{A} = -\mu_0 \boldsymbol{j}$$

Conservation of Mass (Mass Continuity)

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \boldsymbol{v}) = 0$$

ρ mass density

t time

$\boldsymbol{v}$ velocity

Note: if there is a source of mass (e.g., evaporation of a surface) then a source term is required

Conservation of Momentum

Pressure gradient

Magnetic pinch force

Gravity

$$\frac{\partial(\rho \boldsymbol{v})}{\partial t} + \nabla \cdot (\rho \boldsymbol{v}\boldsymbol{v}) = -\nabla \cdot \boldsymbol{\tau} - \nabla P + \boldsymbol{j} \times \boldsymbol{B} + \rho \boldsymbol{g}$$

where $\tau_{ii} = \eta \left(2\frac{\partial v_i}{\partial x_i} - \frac{2}{3}\nabla \cdot \boldsymbol{v} \right), \ \tau_{ij} = \eta \left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} \right), i \neq j$

ρ mass density, t time, $\boldsymbol{v}$ velocity

$\boldsymbol{\tau}$ viscous stress tensor, η viscosity

P pressure

$\boldsymbol{j}$ current density, $\boldsymbol{B}$ magnetic field strength

$\boldsymbol{g}$ acceleration due to gravity

Conservation of Energy

$$\frac{\partial(\rho h)}{\partial t} + \nabla\cdot(\rho \boldsymbol{v} h) = -\nabla\cdot\left(\frac{\kappa}{c_p}\nabla h\right) + \overbrace{\frac{\boldsymbol{j}^2}{\sigma}}^{\text{Ohmic heating}} - \underbrace{U}_{\text{Radiative cooling}} + \overbrace{\frac{5k_B}{2e}\boldsymbol{j}\cdot\nabla T}^{\text{Electron diffusion}}$$

ρ mass density, t time, $\boldsymbol{v}$ velocity, T temperature

h enthalpy, κ thermal conductivity, c_p specific heat

$\boldsymbol{j}$ current density, σ electrical conductivity

U radiative emission coefficient

k_B Boltzmann constant, e elementary charge

For compressible flow (Mach number $\gtrsim 0.5$), need to add

$-(\boldsymbol{\tau} : \nabla \boldsymbol{v}) + \dfrac{Dp}{Dt}$, where $\dfrac{Dp}{Dt} \equiv \dfrac{\partial p}{\partial t} + \boldsymbol{v}\cdot\nabla p$, to right-hand side

Charge Continuity, Magnetic Potential, Maxwell's Equations

$$\nabla \cdot \left(\sigma \nabla \phi \right) = 0$$

$$\nabla^2 \boldsymbol{A} = -\mu_0 \boldsymbol{j}$$

$$\boldsymbol{j} = -\sigma \nabla \phi$$

$$\nabla \times \boldsymbol{B} = \mu_0 \boldsymbol{j}$$

σ electrical conductivity, ϕ electric potential

$\boldsymbol{A}$ magnetic potential, $\boldsymbol{j}$ current density

μ_0 permeability of free space

Complications: Turbulence

Many thermal plasma flows are turbulent

- Plasma jets (e.g., for plasma spraying)
- Plasma cutting arcs

Different approaches

- Direct numerical simulation (DNS)
  - ***Solves*** all the scales of flow
  - Very expensive, and unfeasible for industrial problems
- Large eddy simulation (LES)
  - ***Solves*** for large scales and ***approximately models*** small scales of the flow
  - Turbulence model needed to approximate the small scales
- Reynolds-averaged Navier-Stokes (RANS)
  - ***Approximately models*** all scales of the flow
  - The most common approach for industrial problems
  - Include:
    - 0 equations: Prandtl mixing length
    - 1 equation: Spalart-Allmaras
    - 2 equations: K-ε, K-ε RNG, K-ω

The K-ε Model

Turbulence is modelled as an additional diffusion mechanism

Solve additional transport equations for K (turbulence kinetic energy) and ε (turbulence energy dissipation), which then give viscosity and thermal conductivity

$$\frac{\partial(\rho K)}{\partial t} + \nabla \cdot (\rho \boldsymbol{v} K) = \nabla \cdot \left[\left(\eta + \frac{\eta_t}{S_K} \right) \nabla K \right] + 2G - \rho\varepsilon$$

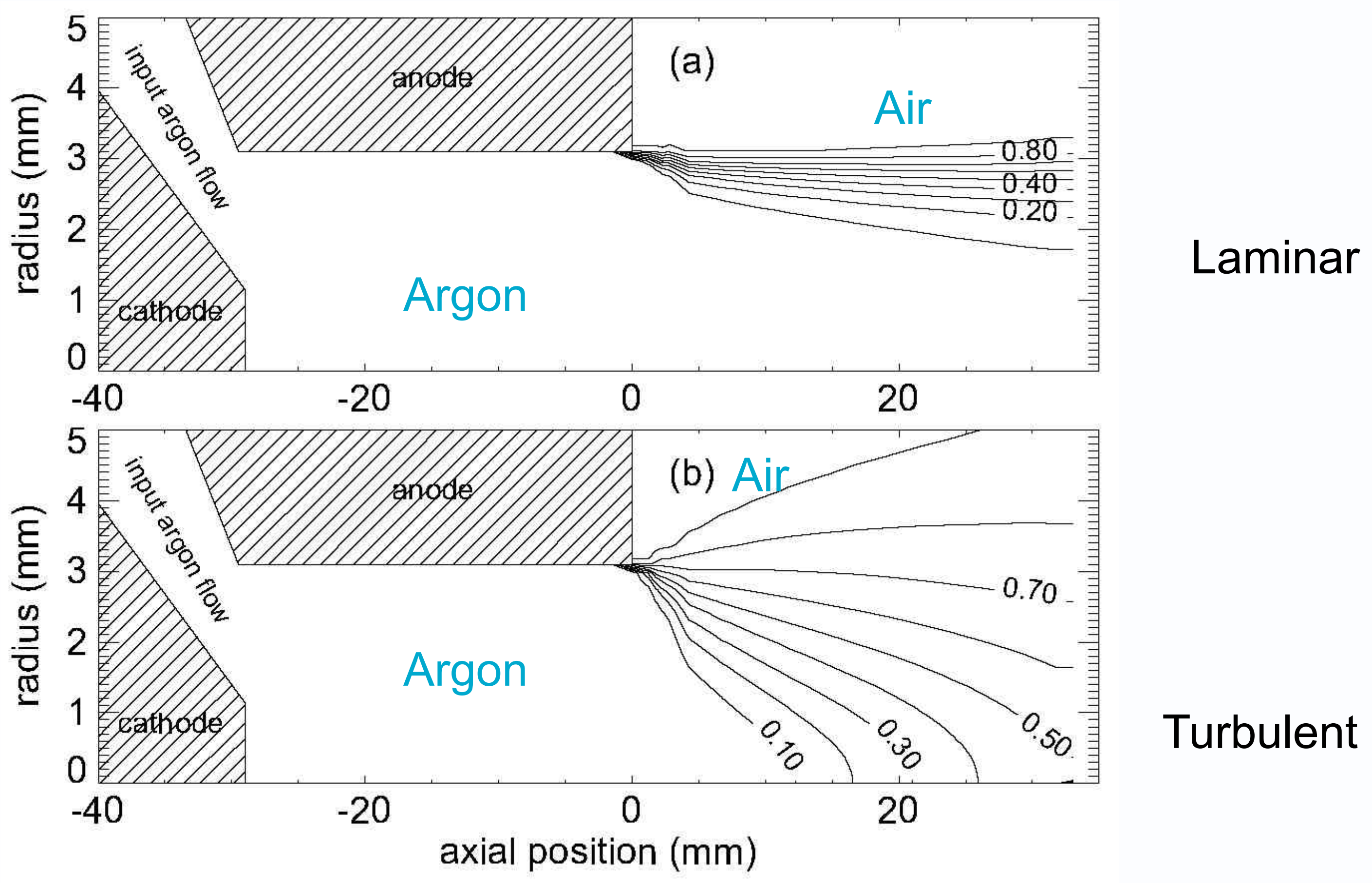
$$\frac{\partial(\rho \varepsilon)}{\partial t} + \nabla \cdot (\rho \boldsymbol{v} \varepsilon) = \nabla \cdot \left[\left(\eta + \frac{\eta_t}{S_\varepsilon} \right) \nabla \varepsilon \right] + 2C_1 \frac{\varepsilon}{K} G - C_2 \rho \frac{\varepsilon^2}{K}$$

$$G = 2\eta_t \left| \nabla \boldsymbol{v} + \nabla \boldsymbol{v}^T \right|^2$$

$\eta_t = C_\eta \rho \dfrac{K^2}{\varepsilon}$ is turbulent viscosity, $\kappa_t = \dfrac{\eta_t C_p}{\Pr_t}$ is turbulent thermal conductivity

S_K, S_ε, C_1, C_2, $\Pr_t$ are constants

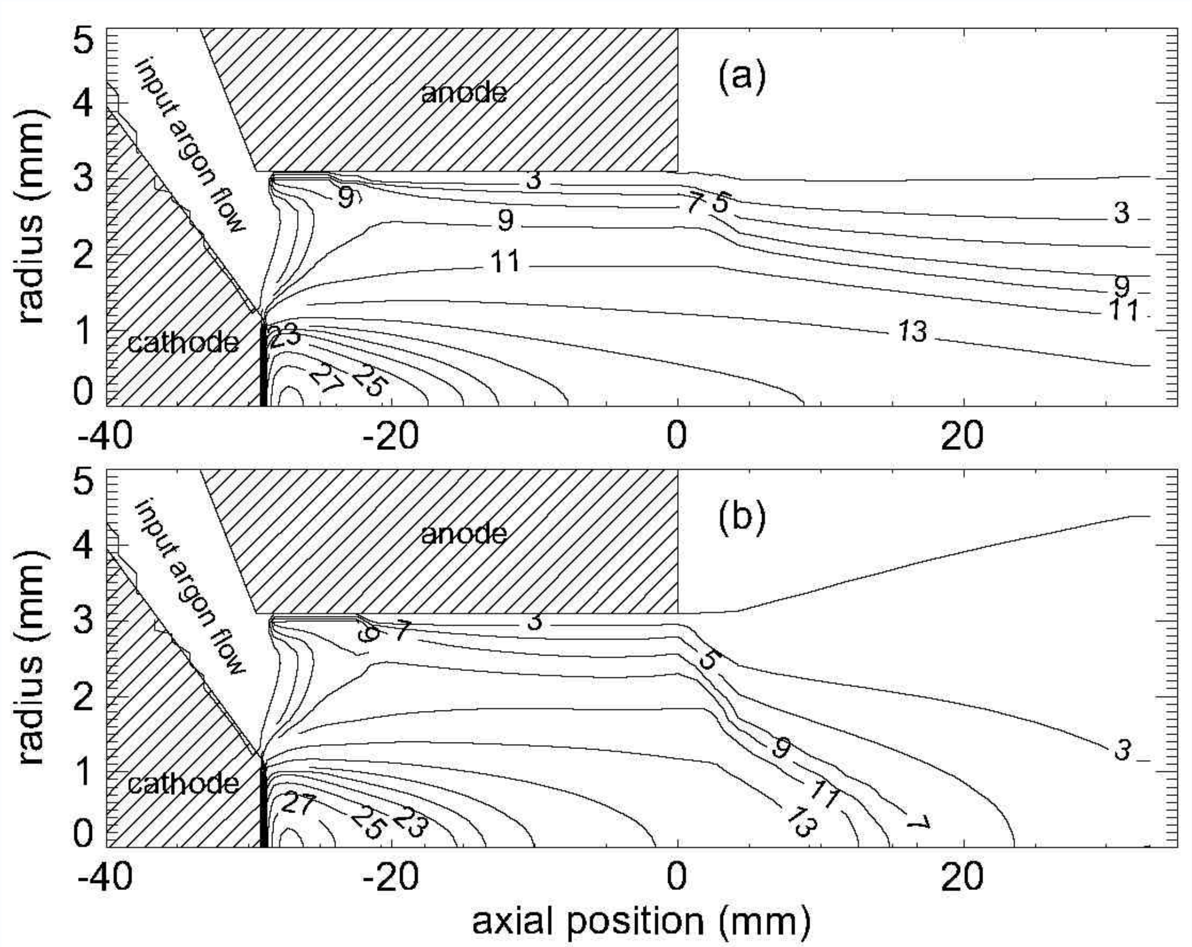
Effect of Turbulence



Mass fraction of air for argon plasma jet discharging into air

A. B. Murphy and P. Kovitya, *J. Appl. Phys.* **73** (1993) 4759

Effect of Turbulence



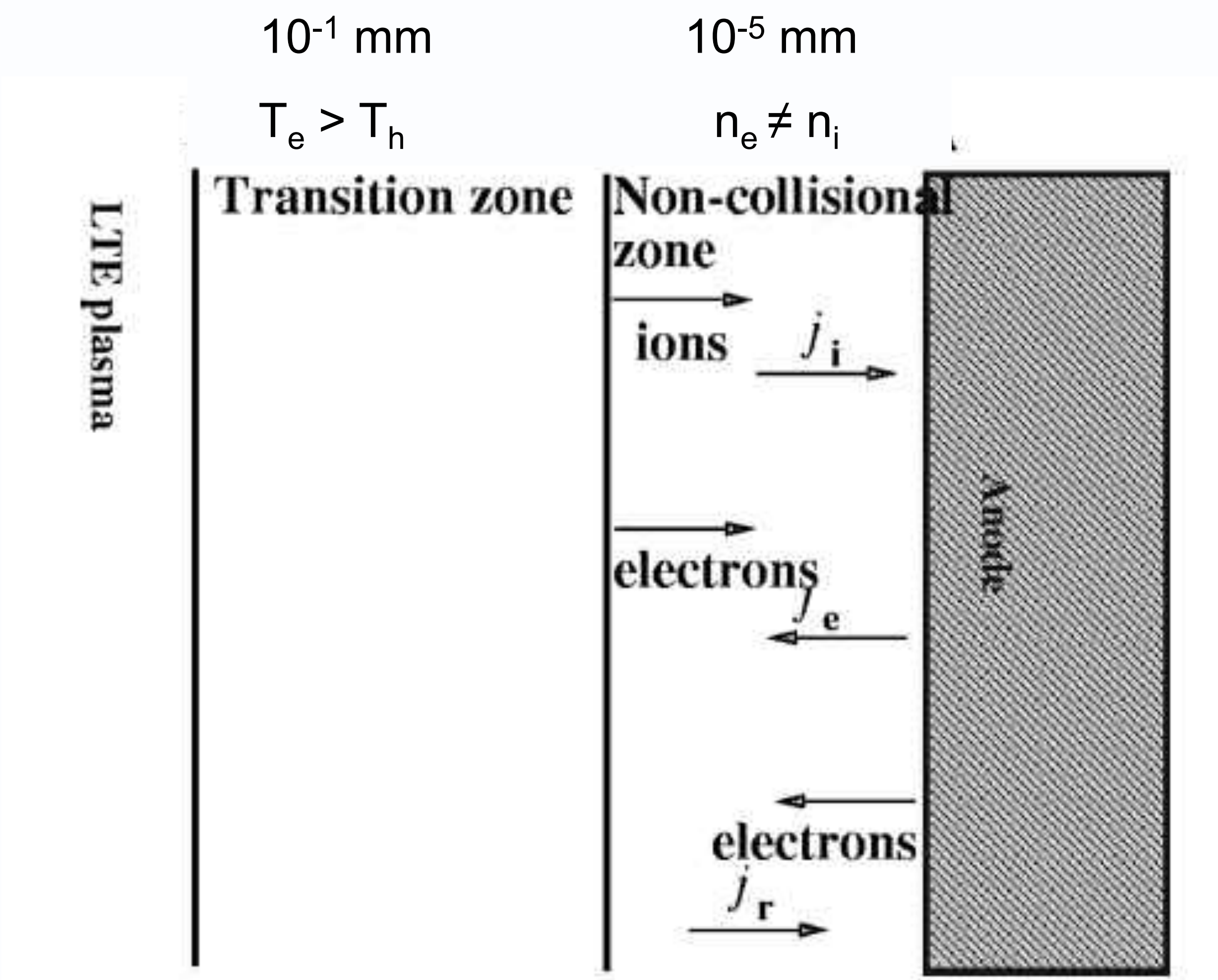
Laminar

Turbulent

Temperature (1000 K) of argon plasma jet discharging into air

A. B. Murphy and P. Kovitya, *J. Appl. Phys.* **73** (1993) 4759

Complications: Electrode Sheath Regions



Anode Treatments

Problem: the temperature adjacent to the anode is low,
so if assume LTE, then $n_e \approx 0 \Rightarrow \sigma \approx 0$

Approach 1: Add electron diffusion term (Sansonnens et al.)

$$\boldsymbol{j} = -\sigma \nabla \phi + eD_e \nabla n_e$$

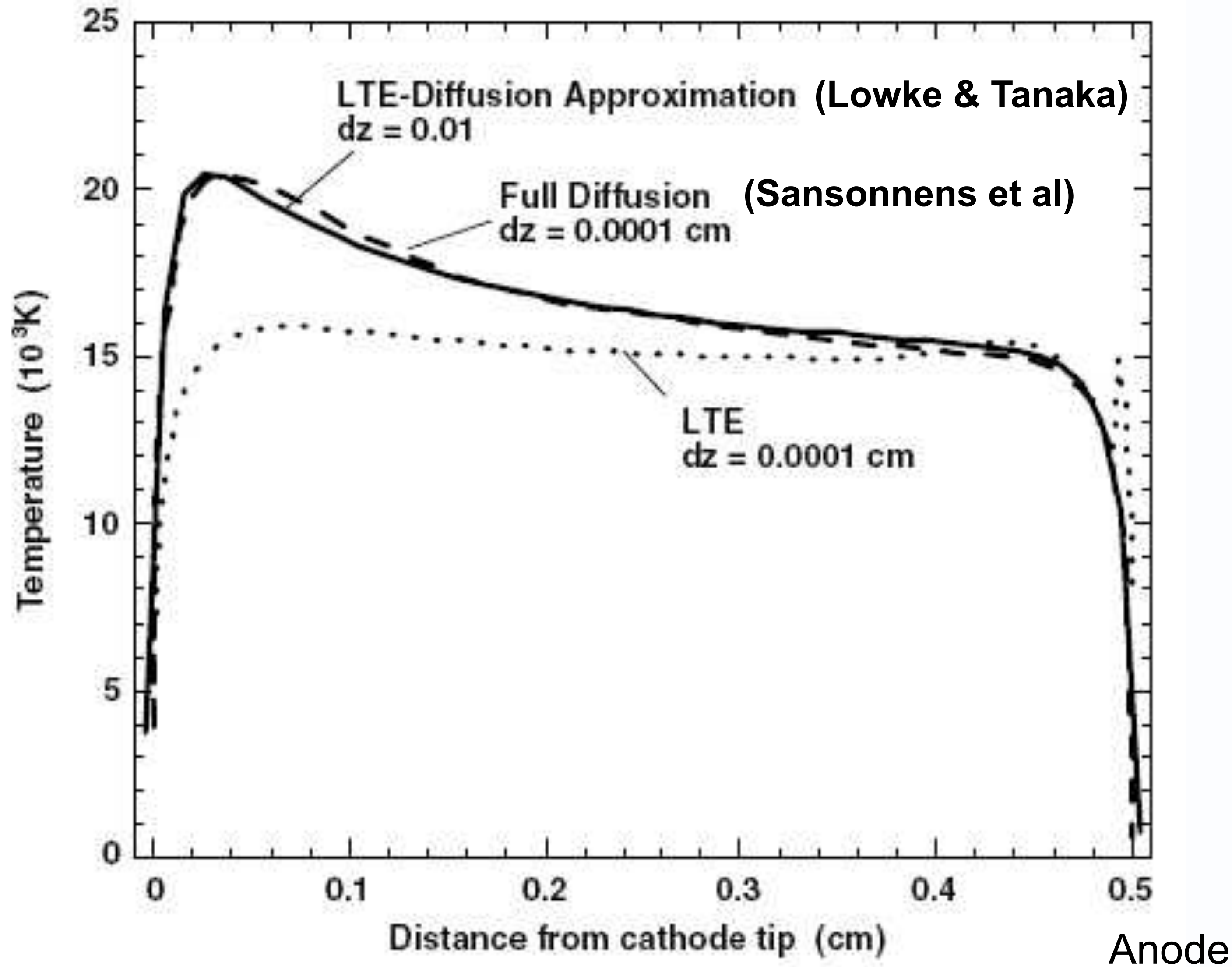
$$\nabla \cdot \left(D_a \nabla n_e \right) + \alpha \left(n_e n_0 \, n_e^{*2} / n_0^{*} - n_e^3 \right) = 0$$

D_e and D_a are electron and ambipolar diffusion coefficients
α is three-body recombination coefficient, * indicates LTE value

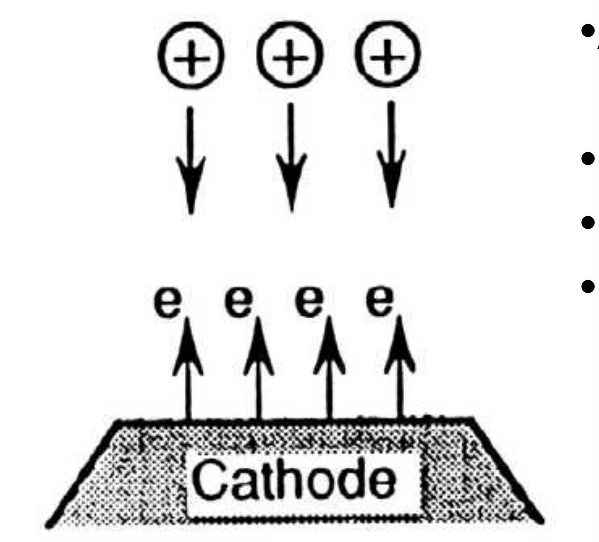
Approach 2: "LTE-diffusion approximation" (Lowke and Tanaka)
Set mesh size near anode to width of region in which
electron diffusion dominates ($\Lambda = k_B T / eE \approx 0.1$ mm).
Then use LTE everywhere.

L. Sansonnens, J. J. Lowke and J. Haidar *J. Phys. D: Appl. Phys.* **33** (2000) 148
J. J. Lowke and M. Tanaka *J. Phys. D: Appl. Phys.* **39** (2006) 3634

Comparison of Approaches 1 and 2



Thermionic Cathode Treatment



- Applies to high melting point materials e.g., W, C, Mo, Zr
- Electrons emitted from cathode
- Cathode heated through ion bombardment
- Current densities around 100 A/mm^2

Richardson equation

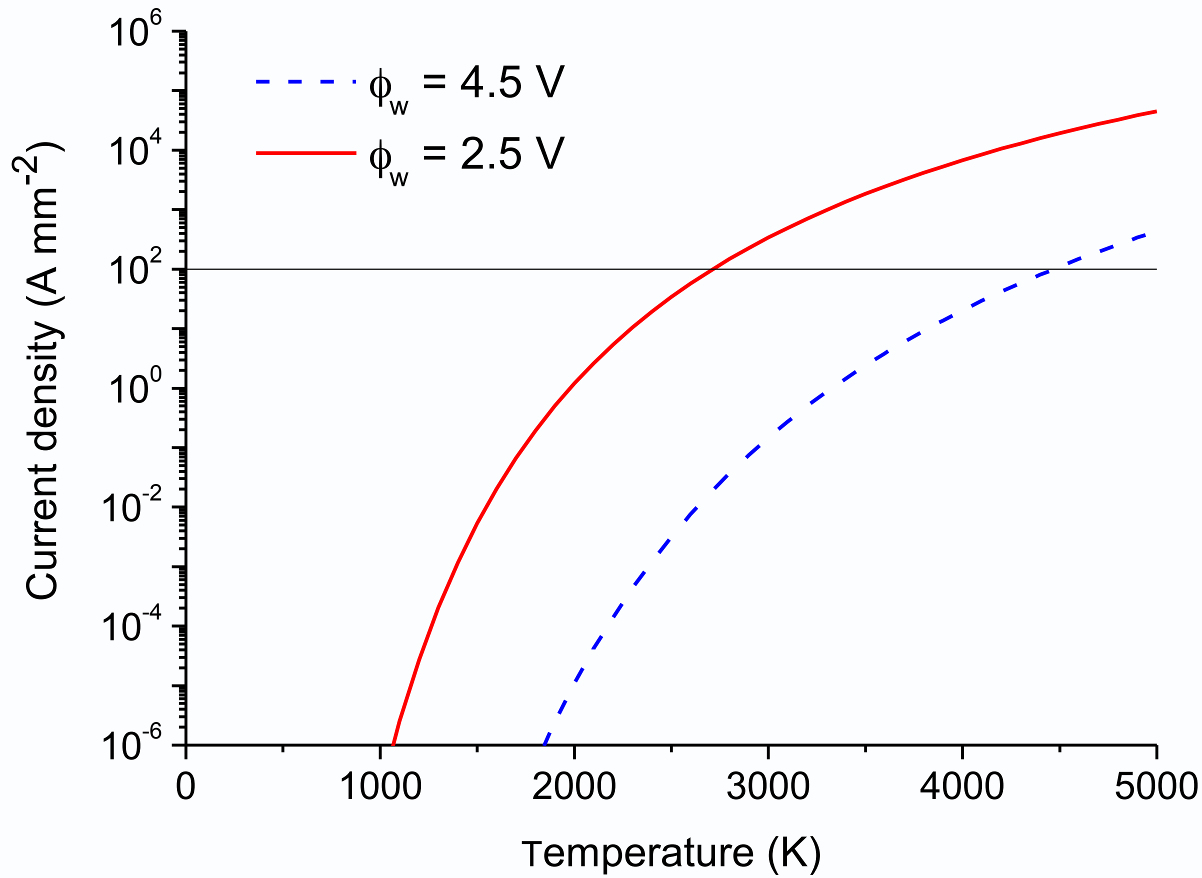
$$j = AT^2 \exp\left(-e\phi_w / k_B T\right)$$

$A \approx 6 \times 10^5$ A mm^{-2} K^{-2} for most metals

ϕ_w (work function) $\approx$ 4.5 V for W

$\approx$ 2.5 V for W(Th)

Thermionic Current Density vs Temperature



Decreasing work function by 2 V reduces the cathode temperature by 1700 K (for 100 A mm^{-2})

Metals that don't have high melting points (Cu, Al, Fe etc) cannot be thermionic emitters

Complications: Plasmas in Gas Mixtures

If more than one gas present, these gases can mix or demix

Even in LTE, need to know their relative fractions

For each species *i*

$$\partial\left(\rho Y_i\right)/dt + \nabla\cdot\left(\rho\,\boldsymbol{v}\,Y_i\right) = -\nabla\cdot\boldsymbol{J}_i + r_i$$

Y_i : mass fraction $\quad r_i$: reaction source term

$\boldsymbol{J}_i$: diffusion mass flux

$$\boldsymbol{J}_i = \frac{n^2 m_i}{\rho}\sum_{j=1}^{q} m_j D_{ij}\nabla x_j - D_i^T\nabla\ \ln T$$

D_{ij} : ordinary diffusion coefficient

D_i^T : thermal diffusion coefficient

x_i : mole fraction

A. B. Murphy *J. Phys. D: Appl. Phys.* **34** (2001) R151

Conservation Equations: Plasmas in Gas Mixtures

$$\frac{\partial(\rho h)}{\partial t} + \nabla\cdot(\rho \boldsymbol{v} h) = \frac{\boldsymbol{j}^2}{\sigma} - U - \nabla\cdot\left(\frac{\kappa}{c_p}\nabla h\right) + \frac{5k_B}{2ec_p}\boldsymbol{j}\cdot\nabla h$$

$$-\nabla\cdot\left(\frac{\kappa}{c_p}\sum_{i=1}^{q} h_i \nabla Y_i\right) - \nabla\cdot\left(\sum_{i=1}^{q} h_i \boldsymbol{J}_i\right)$$

$$\frac{\partial(\rho Y_i)}{\partial t} + \nabla\cdot(\rho \boldsymbol{v} Y_i) + \nabla\cdot\boldsymbol{J}_i = r_i$$

$$\boldsymbol{J}_i = \frac{n^2 m_i}{\rho}\sum_{j=1}^{q} m_j \left[D_{ij}^{a}\nabla x_j - D_{ij}\frac{e x_j Z_j}{k_B T}\boldsymbol{E}\right] - D_i^{Ta}\nabla \ln T$$

Combined Diffusion Coefficients

Group species into gases

E.g., for Ar-He arc

- argon gas = Ar, Ar^+, Ar^{2+}, Ar^{3+}, e^-
- helium gas = He, He^+, He^{2+}, e^-

Model diffusion of helium gas through argon gas

Typically 50 ordinary and thermal diffusion coefficients replaced by two combined diffusion coefficients

Exact for homonuclear gases that do not react for plasmas in LTE

Gas Conservation Equation

Species conservation equations for each species (Ar, Ar^+, Ar^{2+}, Ar^{3+}, He, He^+, He^{2+}, e^-)

$$\nabla \cdot \left(\rho \boldsymbol{v} Y_i \right) = -\nabla \cdot \boldsymbol{J}_i + r_i$$

replaced by a single gas conservation equation

$$\partial\left(\rho \overline{Y_{\mathrm{Ar}}}\right)/\partial t + \nabla \cdot \left(\rho\ \boldsymbol{v} \overline{Y_{\mathrm{Ar}}}\right) = -\nabla \cdot \overline{\boldsymbol{J}_{\mathrm{Ar}}}$$

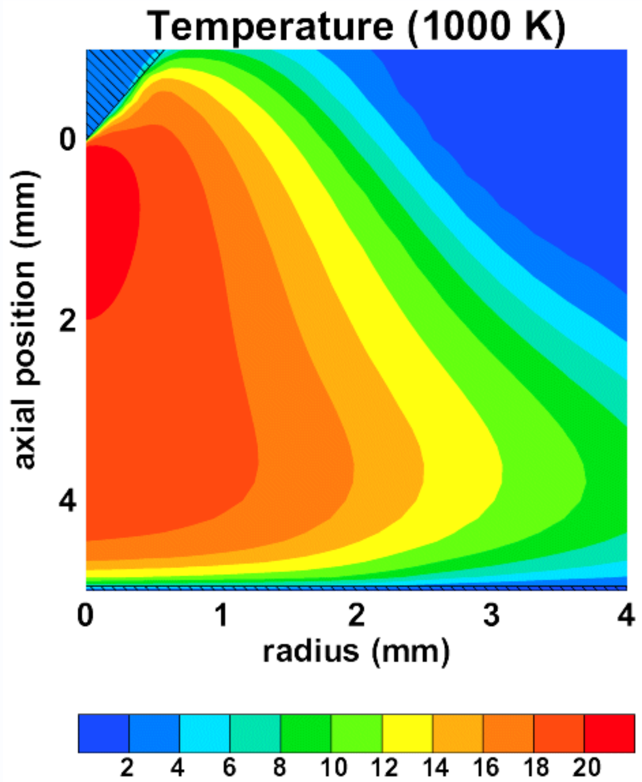
$$\overline{\boldsymbol{J}_{\mathrm{Ar}}} = \left(n^2/\rho\right) \overline{m_{\mathrm{Ar}}}\, \overline{m_{\mathrm{He}}}\, \boxed{\overline{D^x_{\mathrm{Ar,He}}}} \nabla \overline{x_{\mathrm{He}}} - \boxed{\overline{D^T_{\mathrm{Ar}}}} \nabla \ln T$$

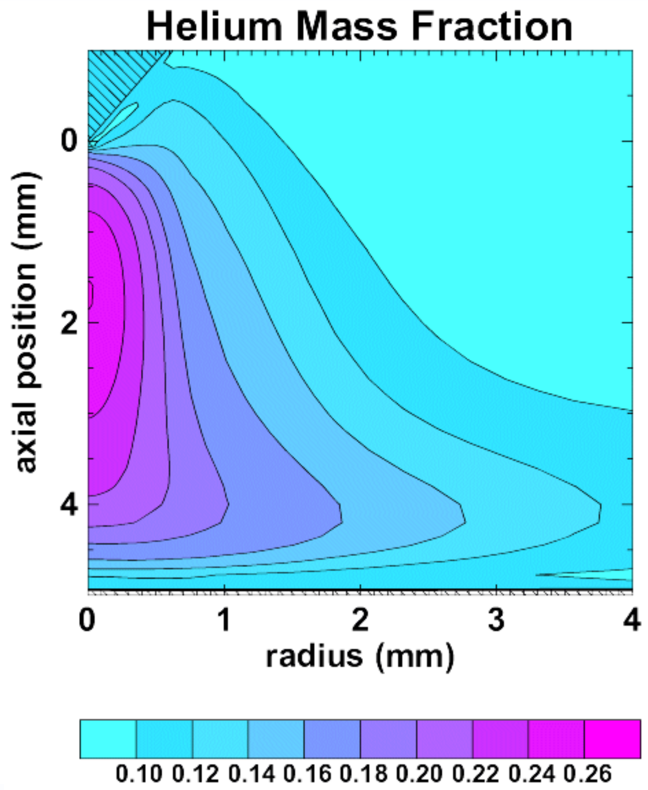
Combined diffusion coefficients

The overbarred quantities are averaged over all species

CSIRO

Example: Demixing in an Argon-Helium Arc



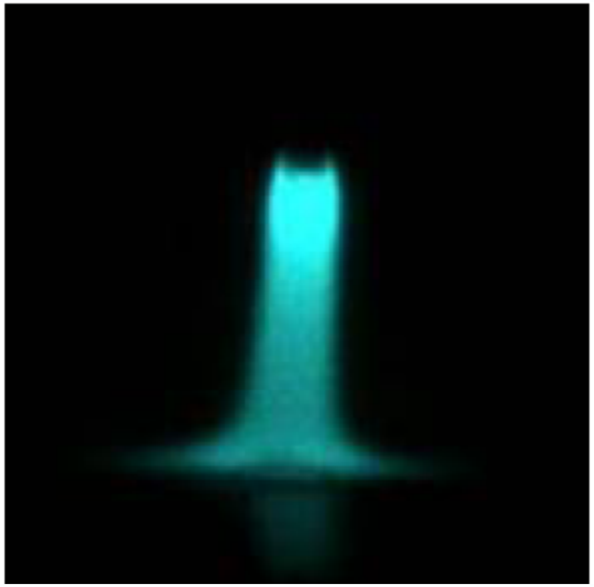


A. B. Murphy *Phys. Rev. E* **55** (1997) 7473

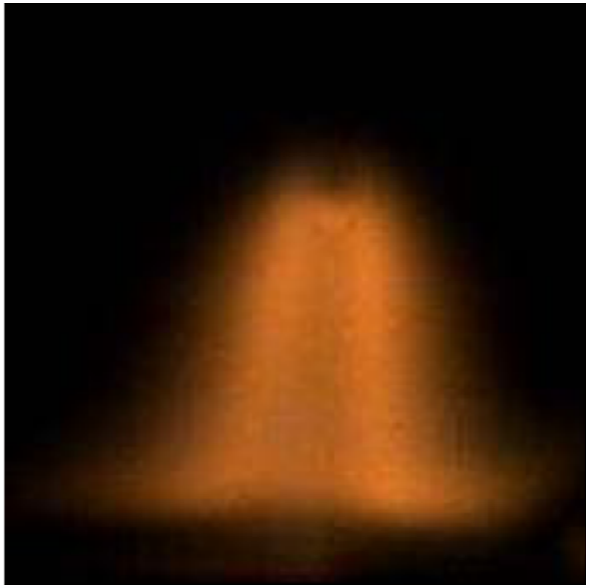
Example 2: Metal Vapour in Welding Arc

Argon arc with steel wire

All emission



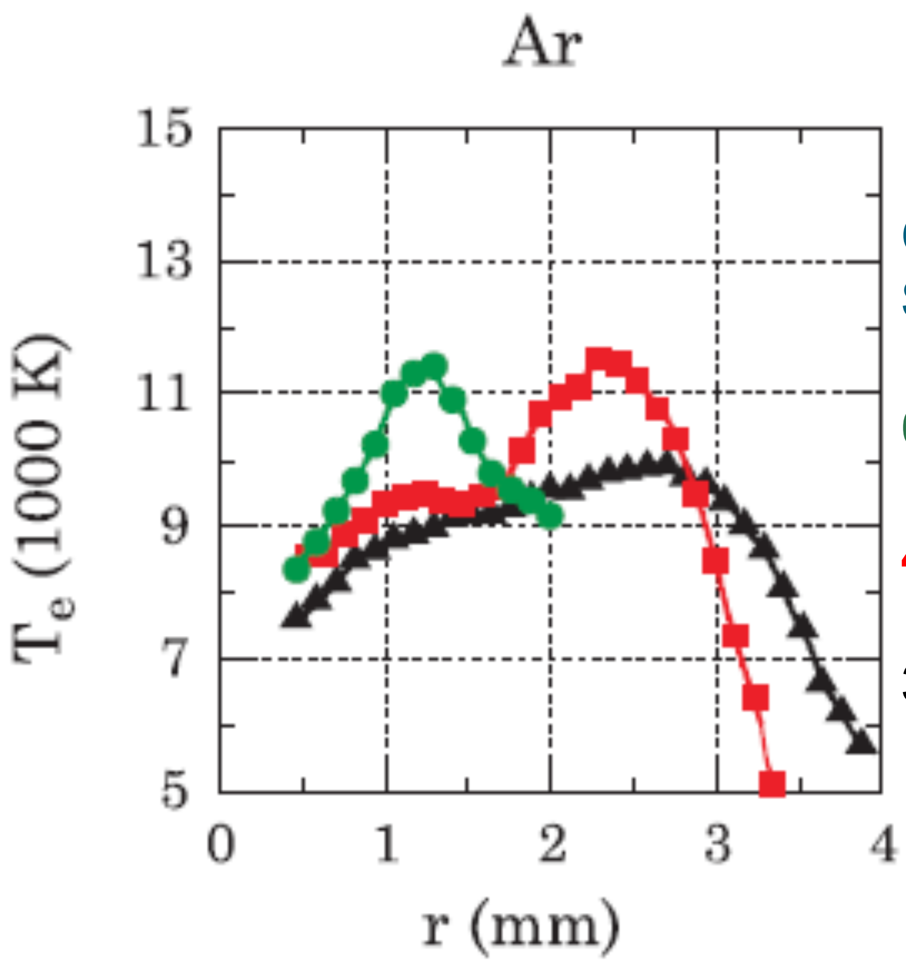
Atomic iron line



Atomic argon line

Goecke S F, Metzke E, Spille-Kohoff A and Langula M 2005
ChopArc. MSG-Lichtbogenschweißen für den Ultraleichtbau (Stuttgart: Fraunhofer IRB)

Measurements Show a Relatively Cool Arc, and a Local Temperature Minimum on Axis



Current = 326 A
Steel wire

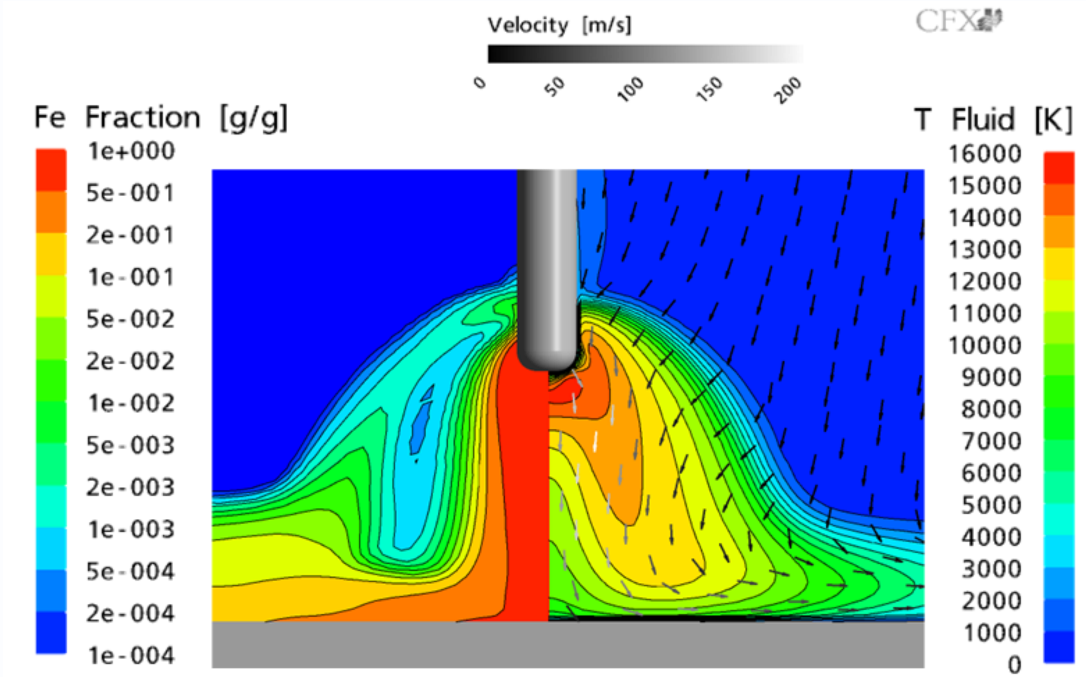
6 mm above workpiece

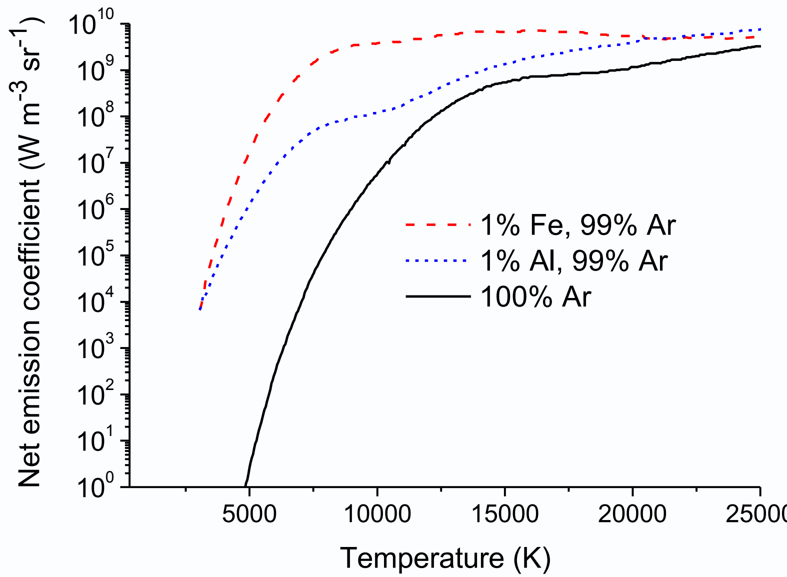
4.5 mm above workpiece

3 mm above workpiece

Zielińska S, Musioł K, Dzierżęga K, Pellerin S, Valensi F, de Izarra C, Briand F
Plasma Sources Sci. Technol. 16 832–8 (2007)

Modelling Indicates Cooling Can Occur due to Increased Radiative Emission from Metal Vapour





Schnick M, Füssel U, Hertel M, Spille-Kohoff A and Murphy A B

J. Phys. D: Appl. Phys. 43 022001 (2010)

4. Thermal Plasma Diagnostics

Probes

- Langmuir probes
- Enthalpy probes

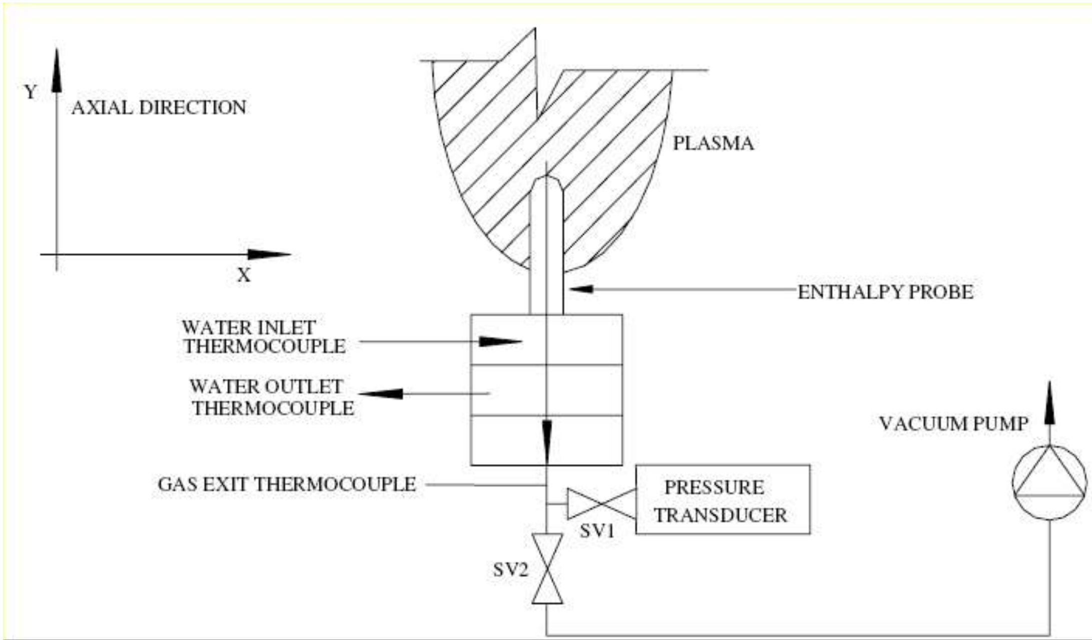
Spectroscopy

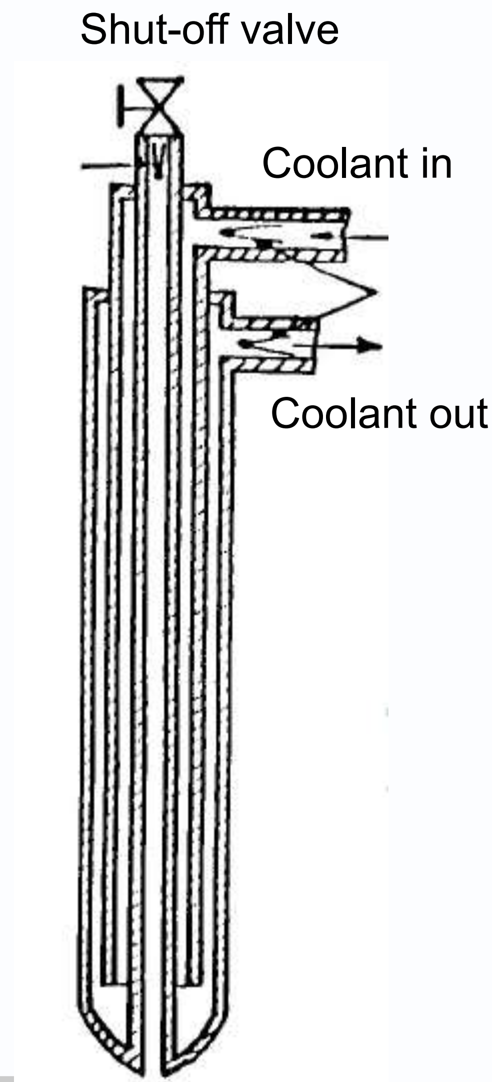
- Emission spectroscopy
- Absorption spectroscopy

Laser scattering

- Elastic scattering
  - Rayleigh scattering
  - Thomson scattering
  - Raman scattering
- Inelastic
  - LIF (laser-induced fluorescence)
  - Two-photon LIF
  - CARS (coherent anti-Stokes Raman scattering)

Enthalpy Probes





Enthalpy

$$h = \frac{\dot{m}_w}{\dot{m}_g} C_{p\ \text{water}} \left(\Delta T_{\text{gas flow}} - \Delta T_{\text{no gas flow}} \right)$$

Flow velocity

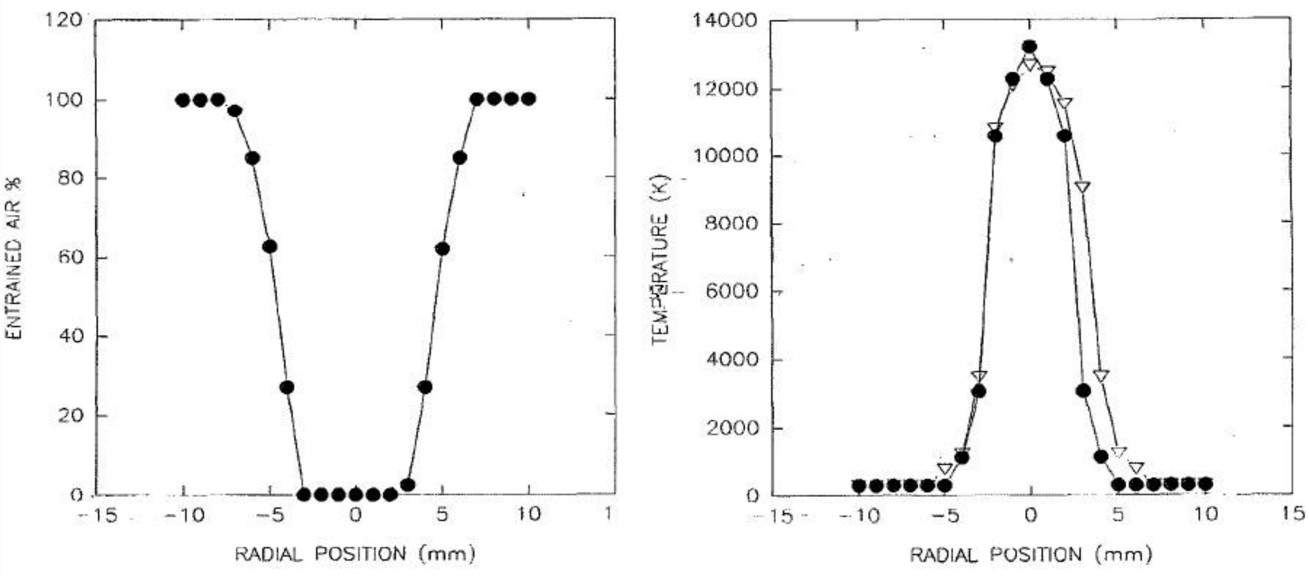
$$v = \sqrt{\frac{2\left(P_{\text{stagnation}} - P_{\text{atm}}\right)}{\rho(T)}}$$

$\dot{m}_w$ is cooling water mass flow rate

$\dot{m}_g$ is gas sampling mass flow rate

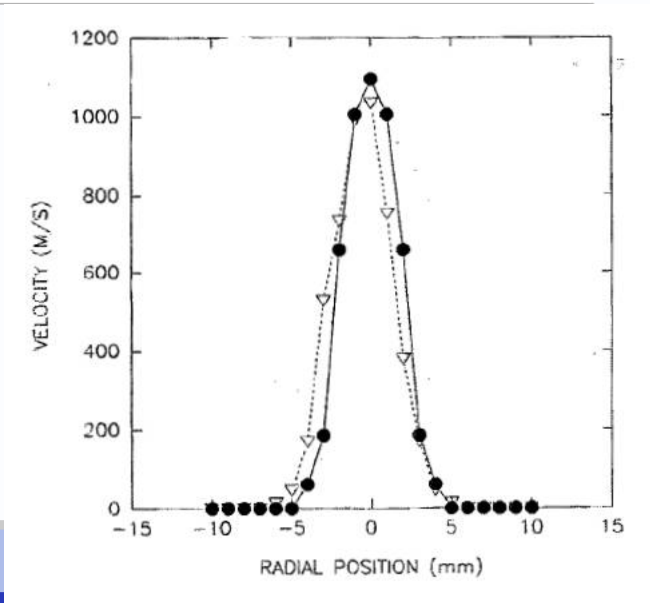
Can also measure composition using gas analyser

Enthalpy Probe Results



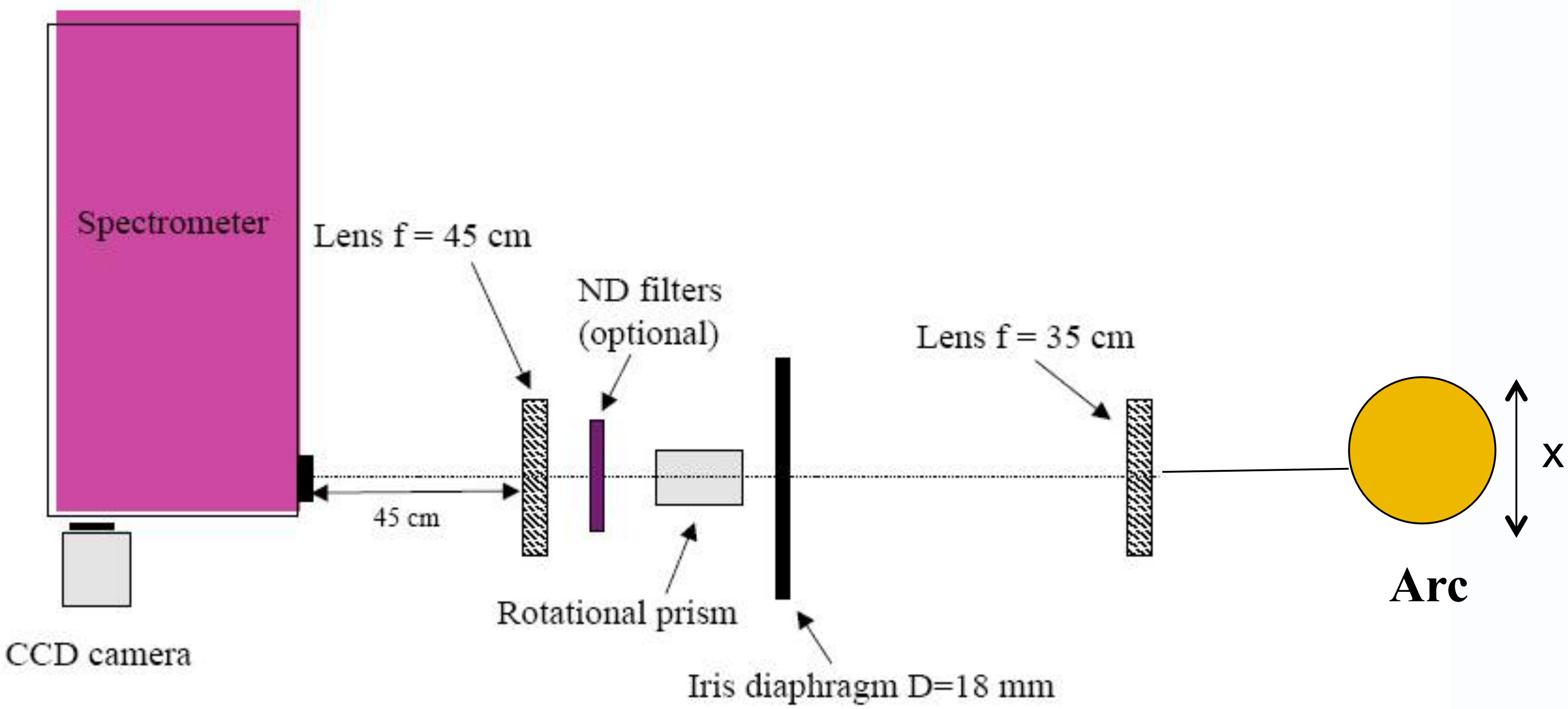
Entrained air %, temperature (K) and velocity (m/s) for enthalpy probe (●) and laser scattering (Δ)

Plasma torch, 900 A, argon,
2 mm downstream from orifice



J. C. Fincke, S. C. Snyder, W. D. Swank, *Rev. Sci. Instrum.* **64** (1993) 711

Optical Emission Spectroscopy



Emission Spectroscopy: Determining the Temperature

$$\text{Intensity } S(T) = \frac{n(T)}{Z(T)} A_{mn} g_m h\nu_{mn} \exp\left(-\frac{E_m}{k_B T}\right)$$

E_m is energy of upper level

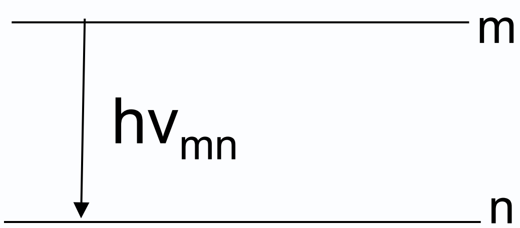
A_{mn} is transition probability

g_m is statistical weight of upper level

ν_{mn} is transition frequency

n is number density of species (e.g. atoms)

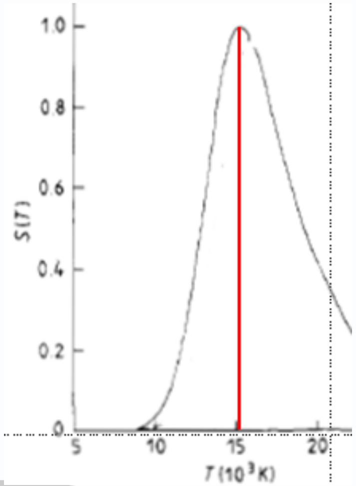
Z is partition function of species



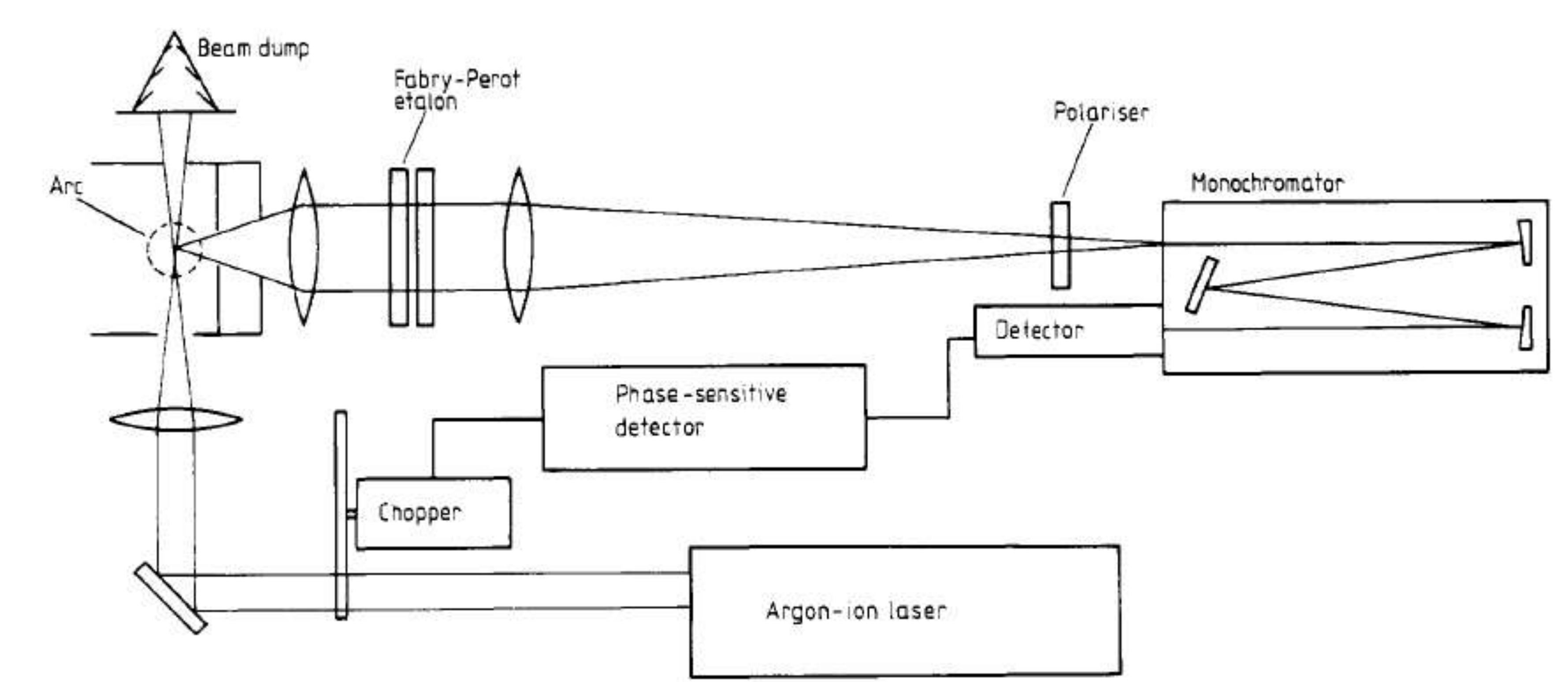
The measurement system has to be calibrated

Three standard methods:

1. Use a calibrated radiation source
2. Use ratio of intensity of two or more lines
3. Fowler-Milne method – use maximum in *S*(*T*)



Laser Scattering



Local (point) data is obtained

Scattering of Laser Light Occurs from Electrons – Both Bound (to Atoms or Ions) and Free

Elastic scattering: $\lambda_{laser} \neq \lambda_{transition}$

$$\lambda_{scattered} = \lambda_{laser}$$

Thomson scattering: elastic scattering from free electrons
Rayleigh scattering: elastic scattering from bound electrons

$$\lambda_{scattered} \neq \lambda_{laser}$$

Raman scattering: elastic scattering from bound electrons

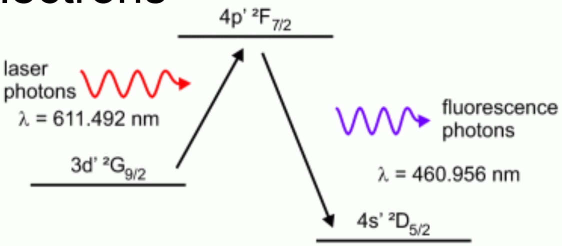
Inelastic scattering: $\lambda_{laser} = \lambda_{transition}$

$$\lambda_{scattered} = \lambda_{laser}$$

Resonance scattering: inelastic scattering from bound electrons

$$\lambda_{scattered} \neq \lambda_{laser}$$

Laser-induced fluorescence: inelastic scattering from bound electrons

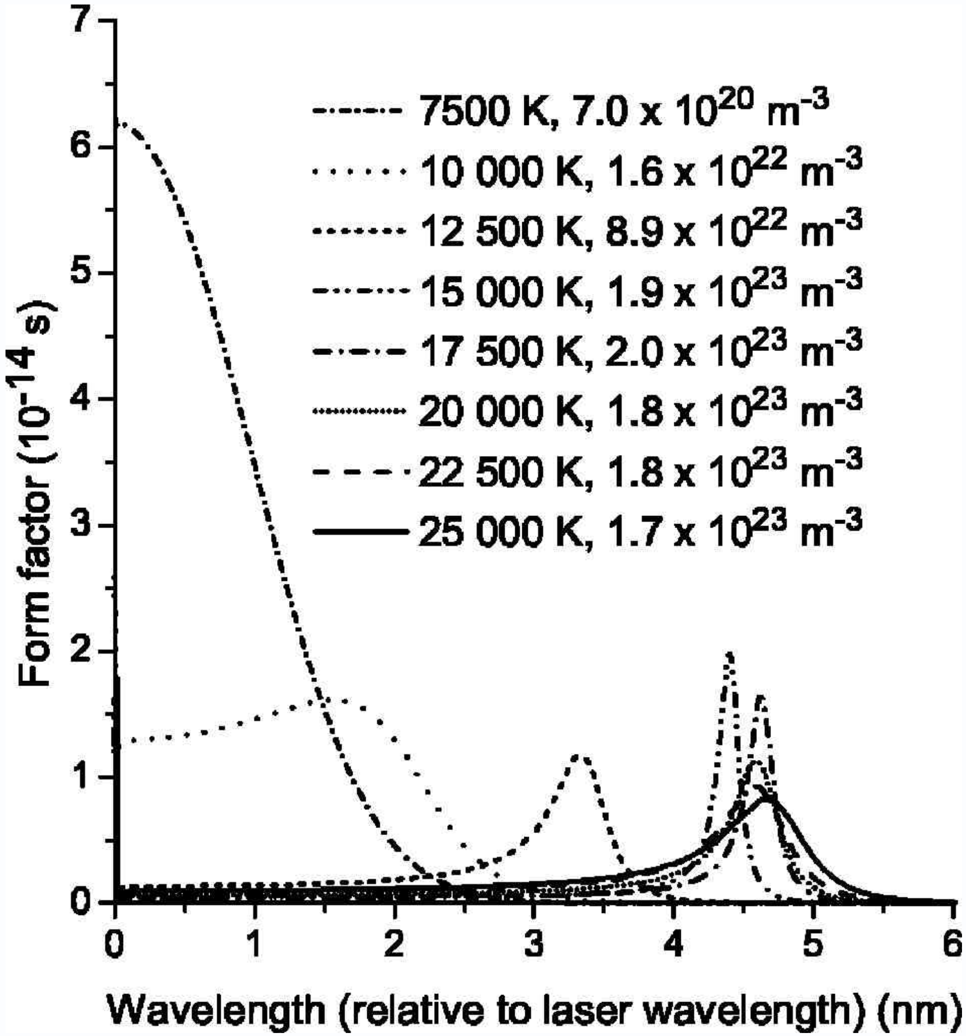


Thomson Scattering

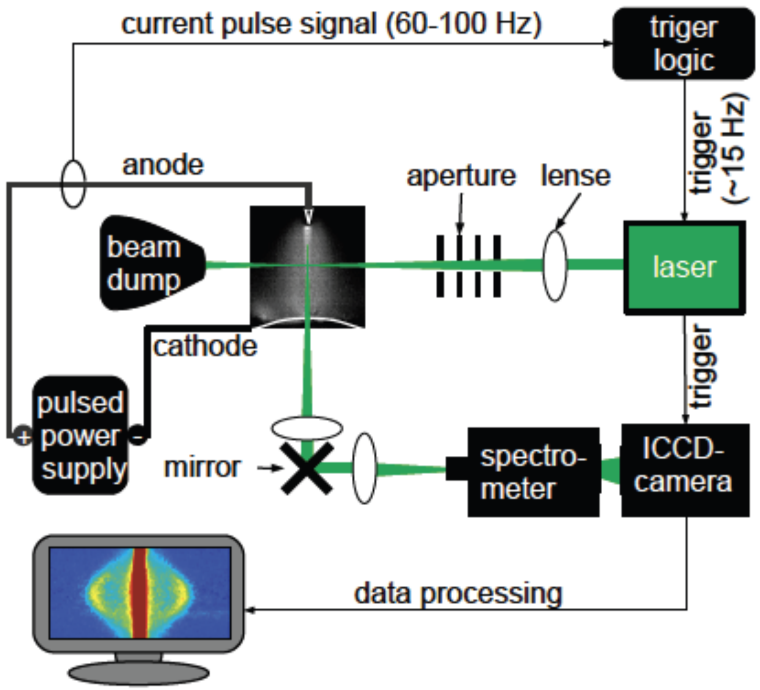
Spectrum of scattered light depends on T and n_e

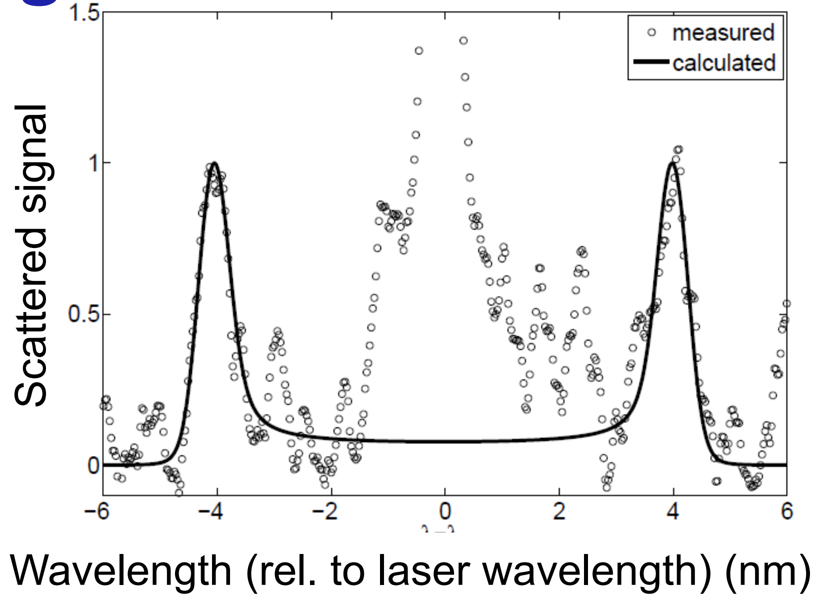
Approach 1. Wavelength-resolved scattering:
Measure scattered light as a function of wavelength – need to be careful of heating the plasma!

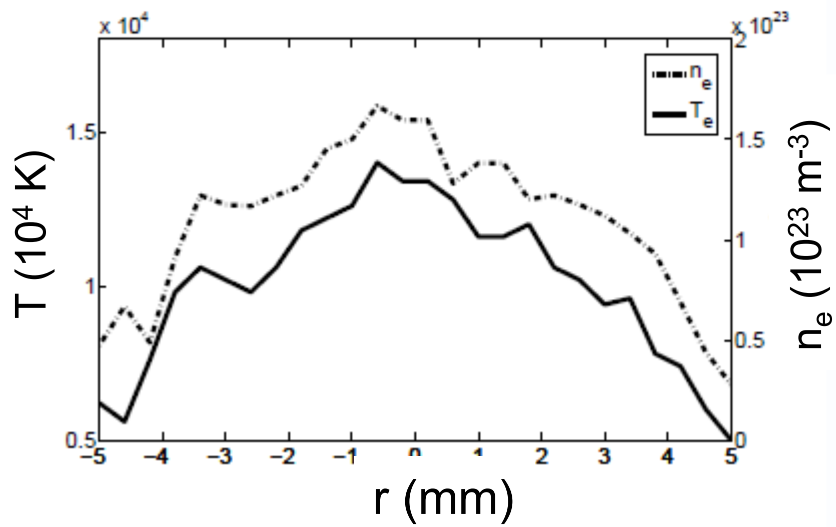
Approach 2. Integrated scattering:
No wavelength resolution
Accept all light in a given range of wavelengths around laser wavelength



Laser Scattering: Wavelength-Resolved Scattering







M. Kuhn-Kauffeldt, J.-L. Marques, J. Schein,
Proc. 20th Int. Conf. Gas Discharges & Applications, Orleans, 2014, p. 730

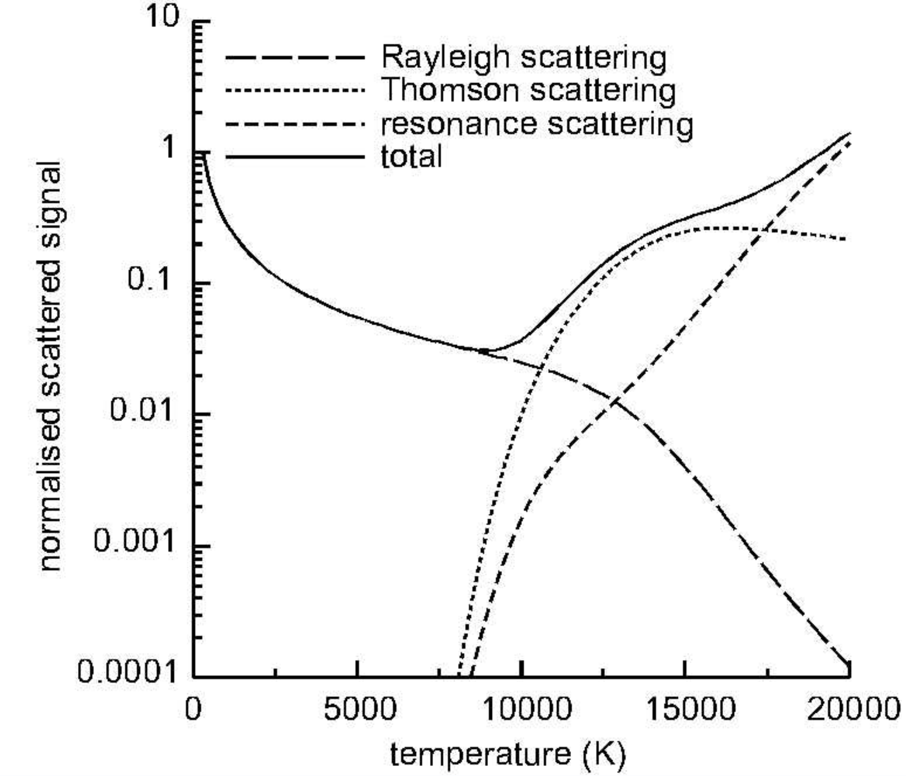
Laser Scattering: Integrated Scattering

Rayleigh scattering (elastic scattering from atoms/ions)

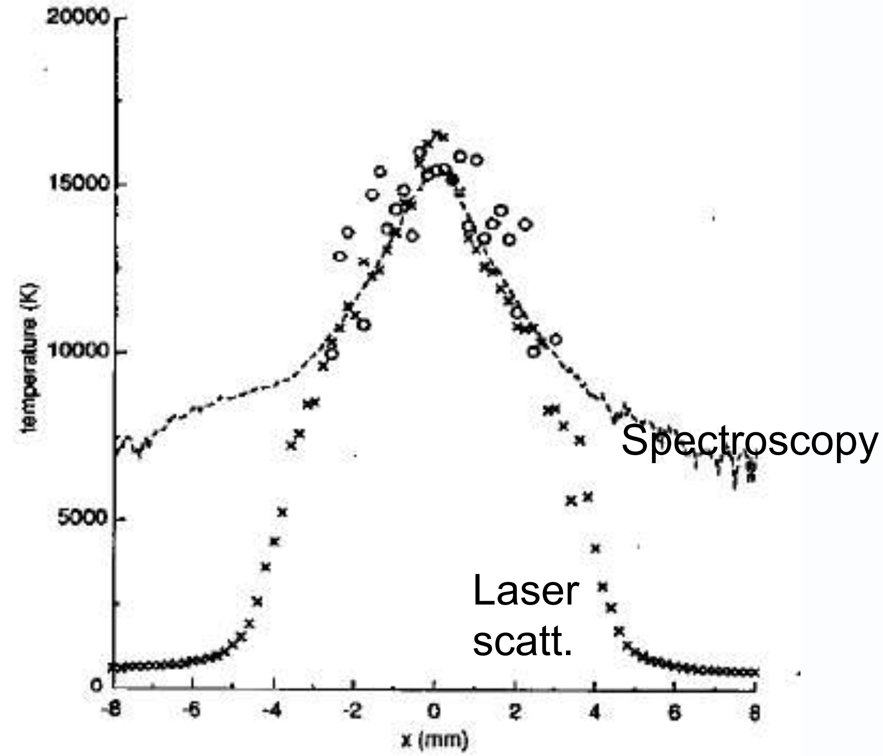
Thomson scattering (elastic scattering from free electrons)

Resonance scattering (inelastic scattering from atoms/ions)

Ar ion laser – 514.5 nm



100 A argon arc: T vs r



5. Thermal Plasma Applications

Arc welding

Plasma spraying

Plasma cutting

Mineral processing

- Arc furnaces
- Plasma remelting
- Plasma spheroidisation

Arc lighting

Circuit interruption

Chemical synthesis

Production of nanostructured materials

- Nanoparticles
- Bulk nanostructured materials
- Carbon nanomaterials (nanotubes, graphene, etc.)

Plasma waste treatment

Plasma Waste Treatment

Compared to high-temperature incineration, plasma gives:

Higher temperature and energy densities

- Shorter residence times
- More compact systems

Heat source is independent of waste

- Exhaust gas flow decreased
- Rapid shut-off possible

No lower limit on size

- Easy integration into processes
- On-site destruction possible

BUT:

High cost

Component lifetimes can be limited

High power plasma source difficult to make

Trend from Niche to Mainstream Applications

Highly-concentrated wastes or wastes requiring high temperatures:

Asbestos-containing wastes

Incinerator fly-ash and grate-ash

Ozone-depleting substances

Other concentrated chemicals

→

General wastes:

Municipal solid wastes

Medical wastes

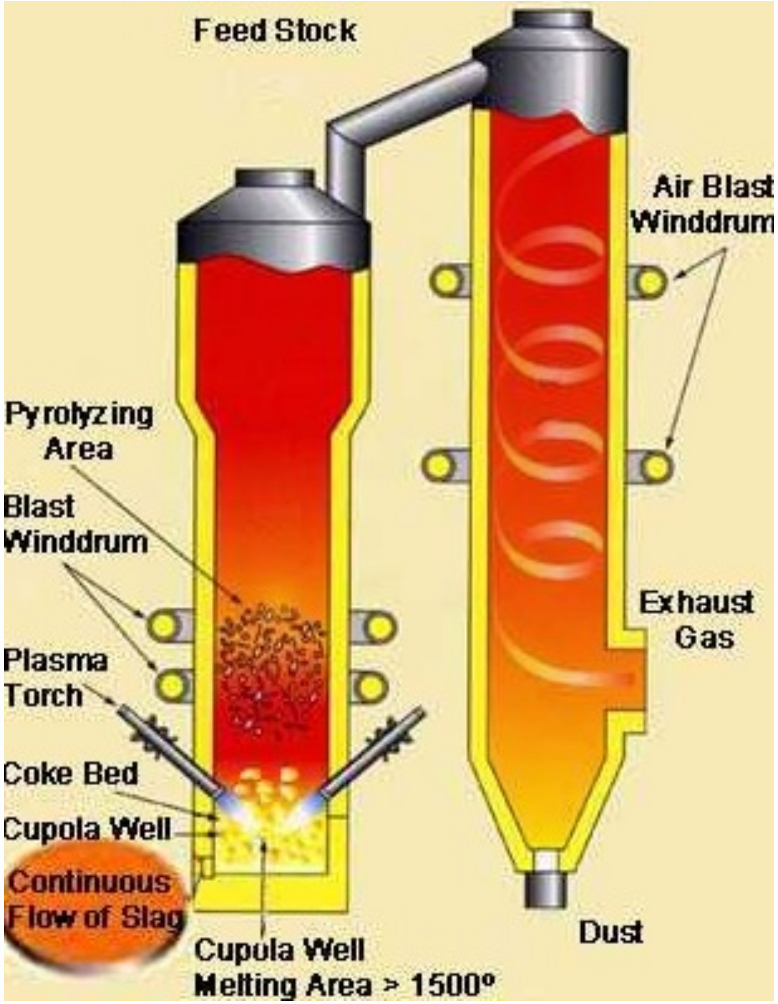
Auto-shredder residues

Tyres

Sewage sludge

Westinghouse Plasma: Waste Treatment & Fuel Production

- DC plasma torch, up to 2.5 MW
- Treat MSW, auto-shredder residue, industrial liquid and solid wastes
- Plants capacities from 25 to 300 tonnes per day
- E.g., Eco Valley Utashinai, Japan: 165 t auto-shredder waste per day, 8 MW electrical power from burning syngas (CO + H2) produced



PLASCON

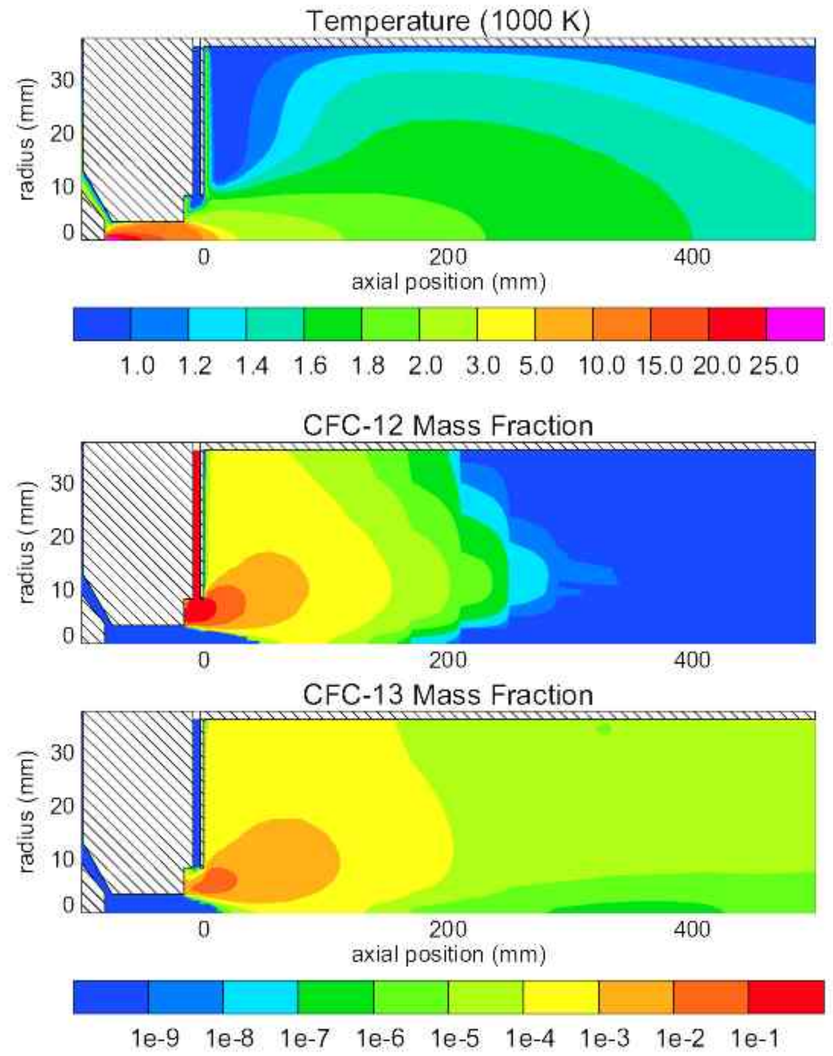
Treats liquid and gaseous waste streams

150 kW non-transferred arc

10 plants in Australia, Japan, USA, Mexico

Treats

- Ozone-depleting substances
- PCB-contaminated oils
- Greenhouse gases
- Liquid organic wastes



A. B. Murphy, T. McAllister, *Appl. Phys. Lett.* **73** (1998) 459

Fluorocarbon Greenhouse Gases are Formed as a By-product of HCFC Production

HFC-23 = CHF_3 = trifluoromethane

Global warming potential of 11 700

Byproduct of $CHClF_2$ (HCFC-22) production (2.4% by mass)

$$6HF + 2CHCl_3 \rightarrow CHCl_2F + CHClF_2 + CHF_3 + 6HCl$$

185 tonne/year produced at Quimobasicos SA d CV, Monterrey, Mexico

185 tonnes per year of HFC 23

is equivalent to 2.2 million tonnes per year CO_2

i.e., the annual emissions from

a 300 MW coal-fired power station

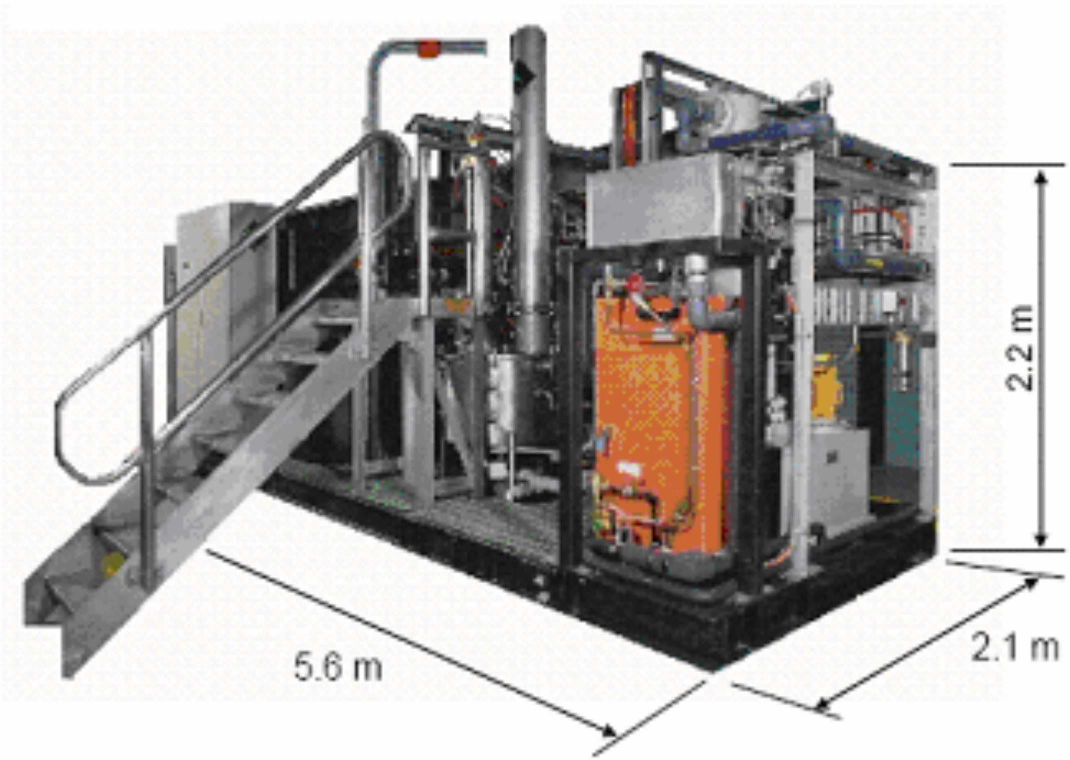
a 600 MW gas-fired power station

or 500 000 cars

CSIRO

Trifluoromethane is Successfully Destroyed By PLASCON

$$CHF_3 + H_2O + \tfrac{1}{2}O_2 \rightarrow CO_2 + 3HF$$



PLASCON Destruction of HCF 23 is Very Profitable

Carbon accounting:

Destroying 1 t HFC 23

Destroys equivalent of 11 700 t CO_2

Produces direct emissions of 0.6 t

and indirect emissions of 6 t CO_2

Economics (under Kyoto Protocol Clean Development Mechanism):

Destruction of 1 t HCF 23

- Equivalent to destruction of 11 663 t CO_2
- Carbon credits (@ \$10/t CO_2) have value of \$120 000
- Cost of destruction < \$10 000

185 t/year gives a profit of ~\$20M/year

Thank you

CSIRO Manufacturing Flagship
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