Probe techniques for particulate detection

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Ministero dell'Università e della Ricerca
Italiadomani

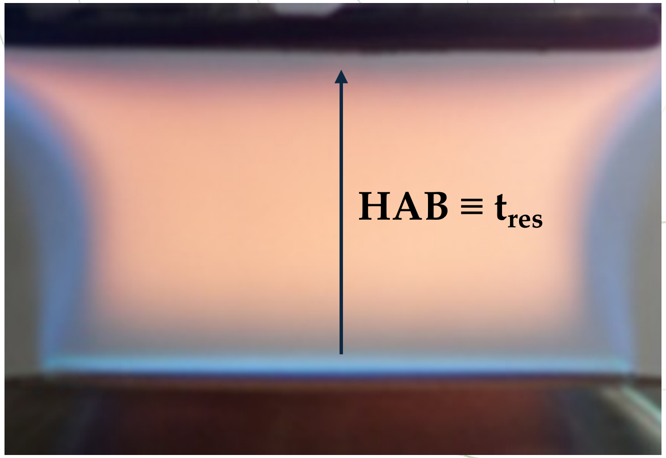
Combustion Systems - Lab Scale

Laminar Premixed Flame of Ethylene/Air at Atmospheric Pressure

The simplest lab-scale combustion system

Plug Flow Reactor

[HAB: Height Above the Burner surface]



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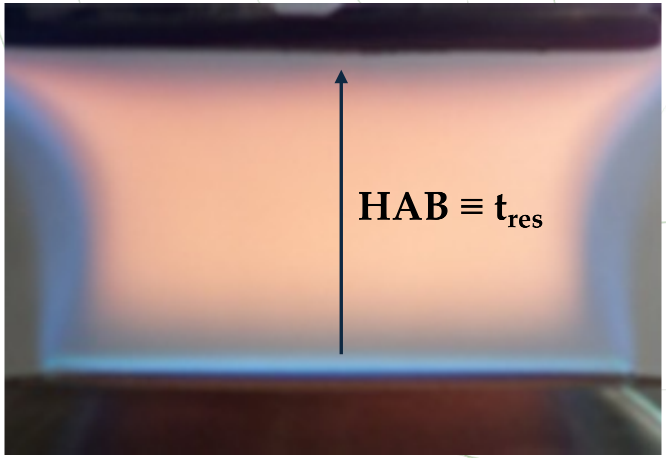


The simplest lab-scale combustion system

- Plug Flow Reactor

  [HAB: Height Above the Burner surface]

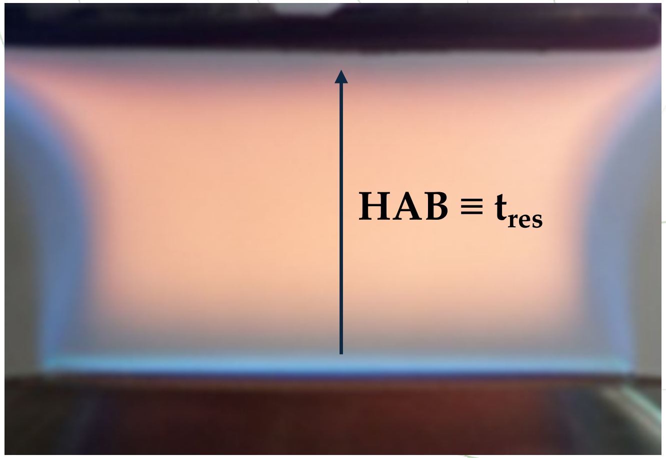
- Easy controlling and tuning

- Wide range of fuel-rich combustion conditions

  [Flame equivalence ratio Φ]

Combustion Systems - Lab Scale

Laminar Premixed Flame of Ethylene/Air at Atmospheric Pressure



Flame equivalent ratio Φ:

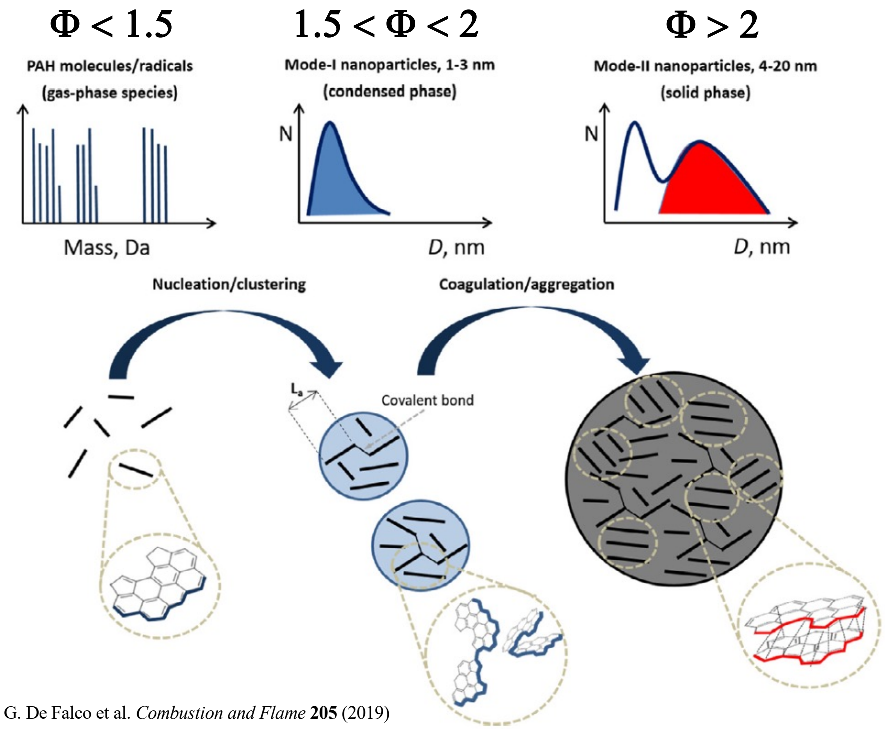
$$\boldsymbol{\Phi} = \frac{\textbf{actual fuel–to–oxidizer ratio}}{\textbf{stoichiometric fuel–to–oxidizer ratio}}$$

- $\Phi < 1$ → Fuel-lean Flame
- $\Phi = 1$ → Stochiometric Flame
- $\Phi > 1$ → Fuel-rich Flame → **Particulate Matter Formation**

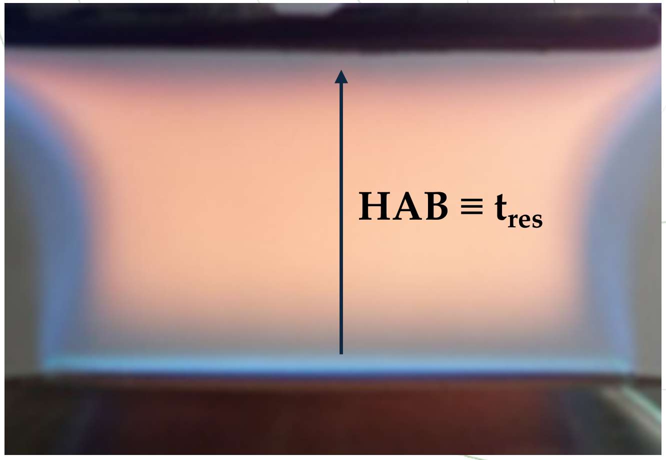
N.B.: $\lambda = \frac{1}{\Phi}$

Combustion Systems - Lab Scale

Laminar Premixed Flame of Ethylene/Air at Atmospheric Pressure



G. Vitiello, G. De Falco et al. *Combustion and Flame* **205** (2019)

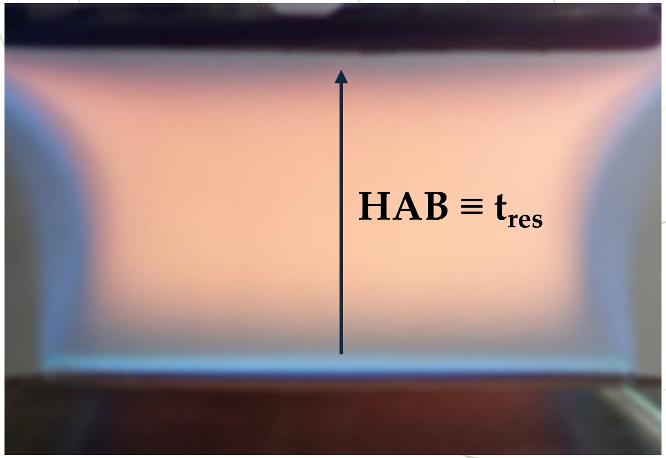


$\Phi > 1$ → Fuel-rich Flame → **Particulate Matter Formation**

Combustion Systems - Lab Scale

Characterization of the properties of nanoparticles produced in combustion systems

Ex-situ ***In-situ***



Combustion Systems - Lab Scale

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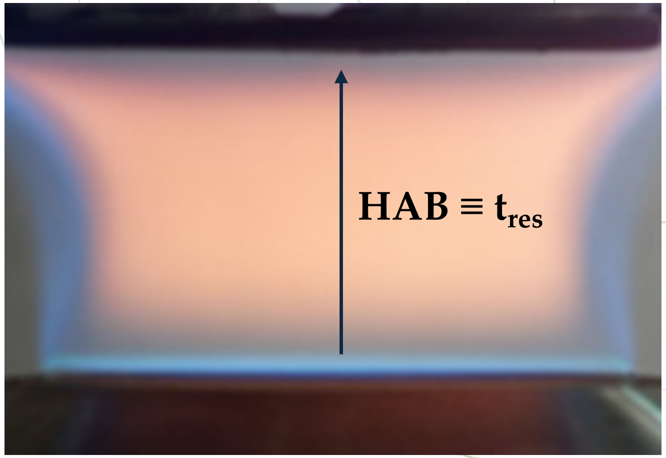
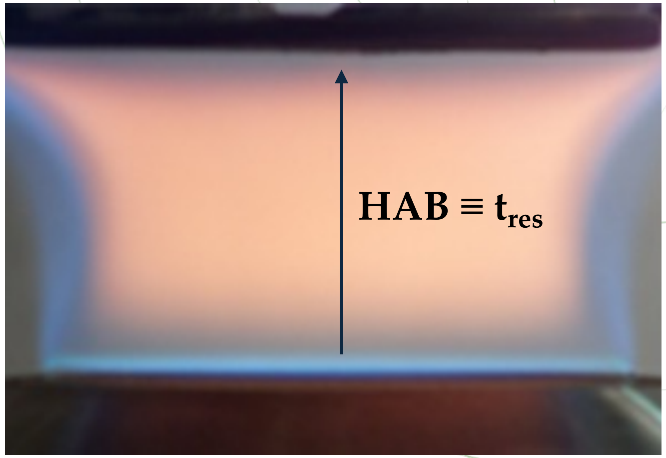


Ex-situ **characterizations need <u>suitable sampling techniques:</u>**

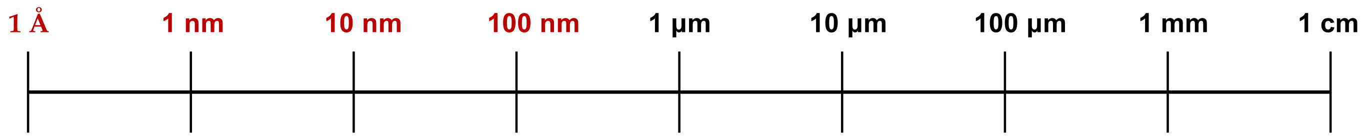
- **Particle samples are collected from flames in a proper way;**
- **The amount of particles is enough to perform the characterization analysis;**
- **No modification of particle status or properties during the sampling procedure.**

Combustion Systems - Lab Scale

The characterization analysis and the sampling techniques have to be effective in the <u>NANOSCALE</u>



1 nm = 10^{-9} m

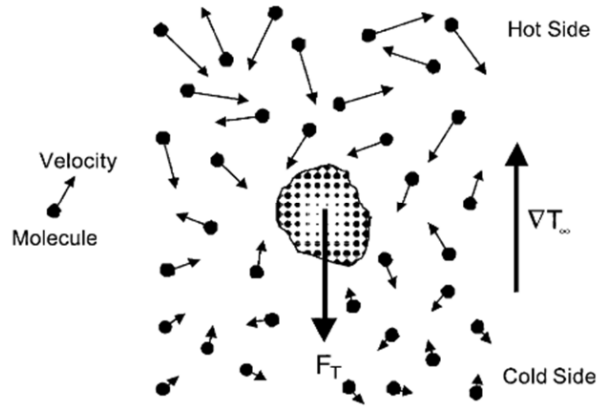


<u>Nanoscale</u>

Thermophoretic Sampling

Thermophoresis F_{th} is a net force acting on particles suspended in a gas (<u>Aerosol</u>) when subjected to a temperature gradient.

F_{th} results in the motion of particles from the high-temperature region towards the lower temperature zone, with a velocity V_{th}



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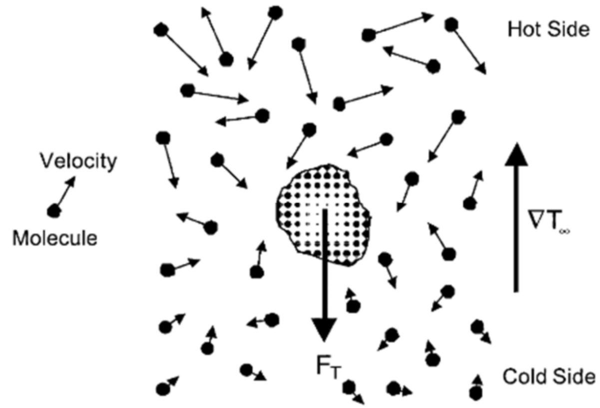

$$V_{th} = 0.55 \frac{\mu_{gas}}{\rho_{gas}} \frac{\nabla T}{T}$$

V_{th} does not depend on the particle size

Thermophoresis is the controlling deposition mechanism for particles in the nanoscale

Thermophoretic Sampling

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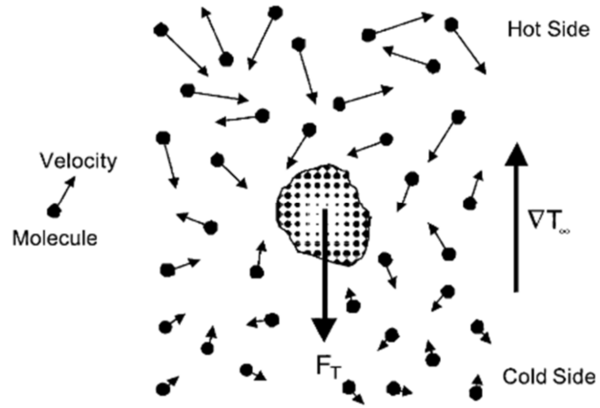
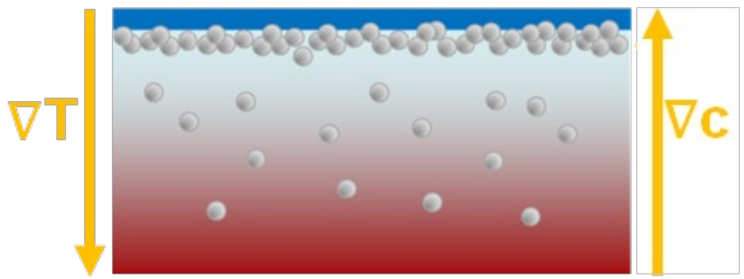
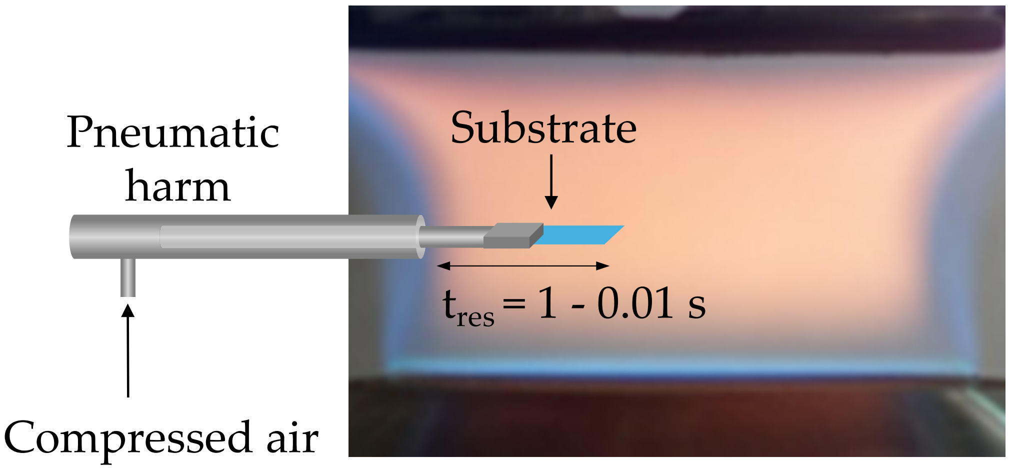


When a cold substrate is rapidly inserted in the hot flame environment, nanoparticles are moved by thermophoresis towards the substrate surface where they impact and deposit



Thermophoretic Sampling

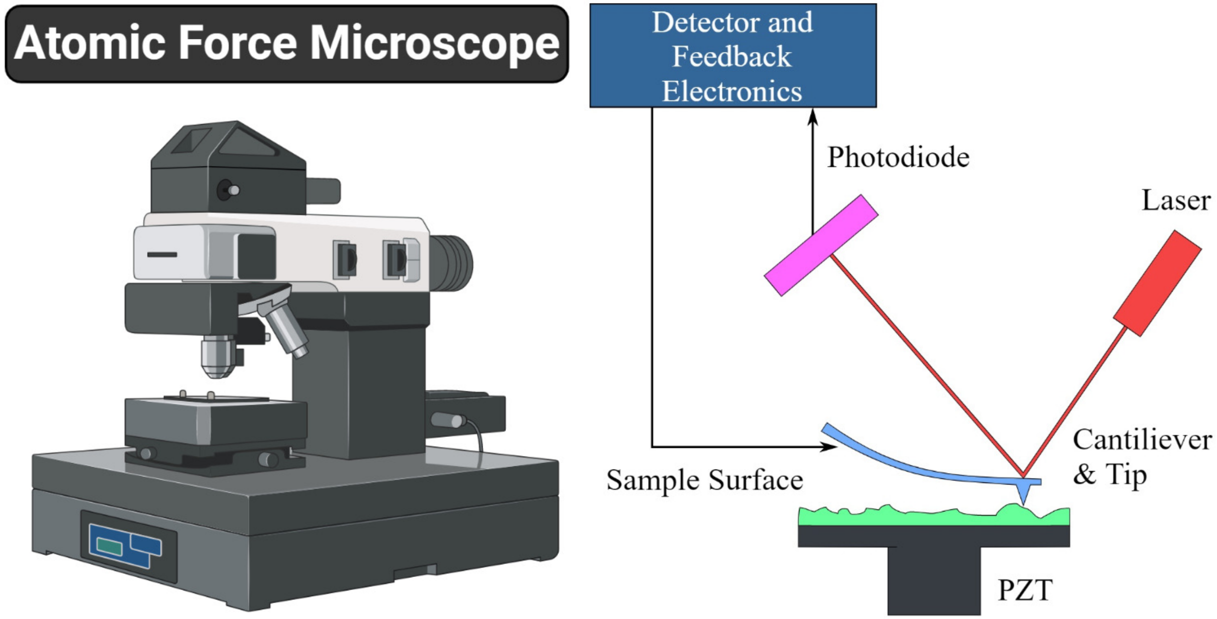
PNEUMATIC ACTUATOR



Thermophoretic sampling with short insertion times (10-30 ms) and a few numbers of insertions (1-3) allows to collect enough single and isolated particles representative of particles population in the aerosol

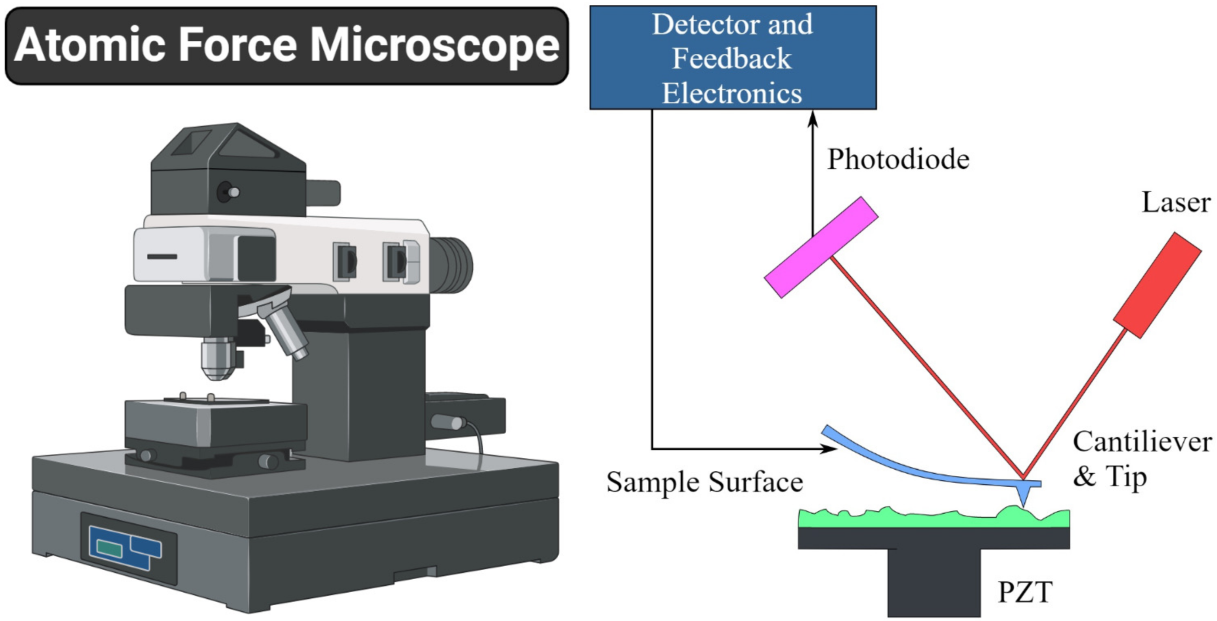
Thermophoretic sampling with longer insertion times (100 ms) and a very high number of insertions (> 100) produces a homogenous coating of particles on the whole substrate

Atomic Force Microscopy



- **Belongs to the series of SPM (Scanning Probe Microscopes);**
- **Can be easily operated in ambient condition, with a fast-imaging procedure;**
- **Furnishes 2-D and 3-D topological maps of the samples;**
- **The imaging resolution is down to the order of Angstrom**

Atomic Force Microscopy



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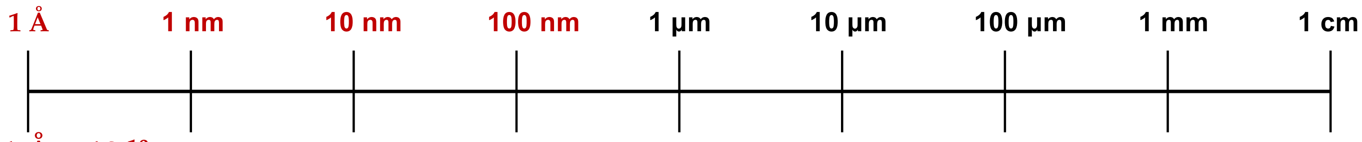
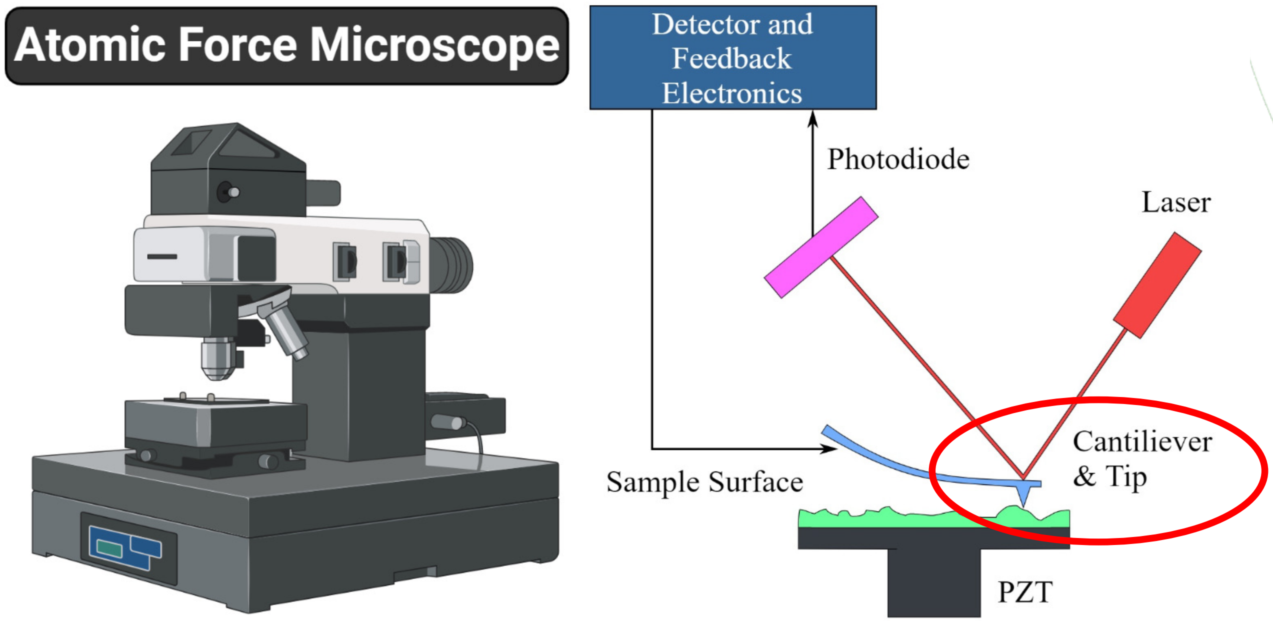


0.1 nm = 1 Å = 10^{-10} m

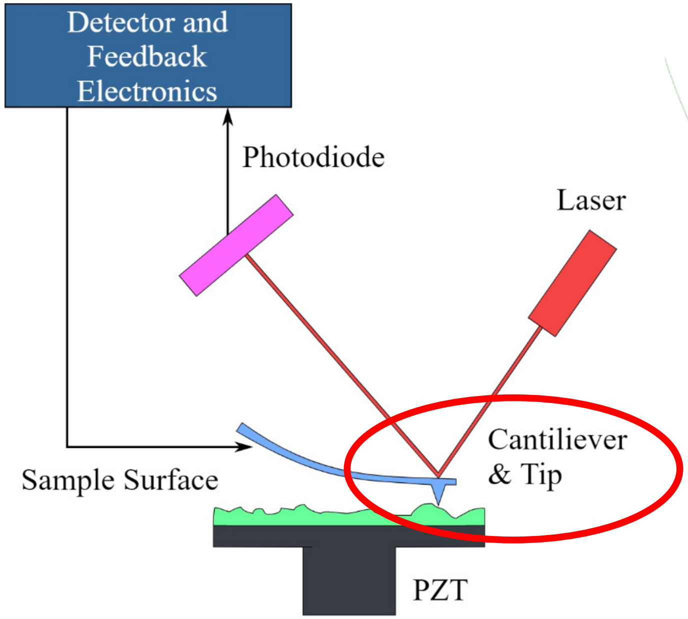
Nanoscale

Atomic Force Microscopy



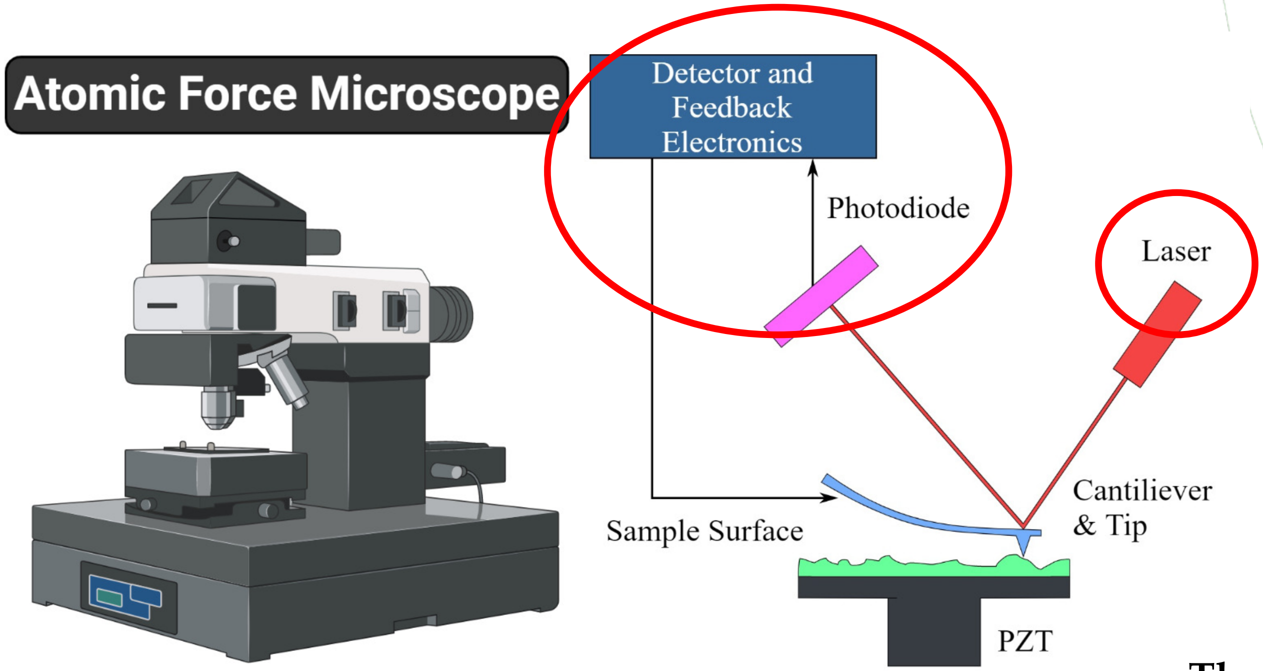
The AFM probe is characterized by a radius of curvature of the order of few nanometers and it is made of a cantilever and a sharp tip.
The sample is scanned by the tip, which is fixed to the free end of the cantilever.

Atomic Force Microscopy



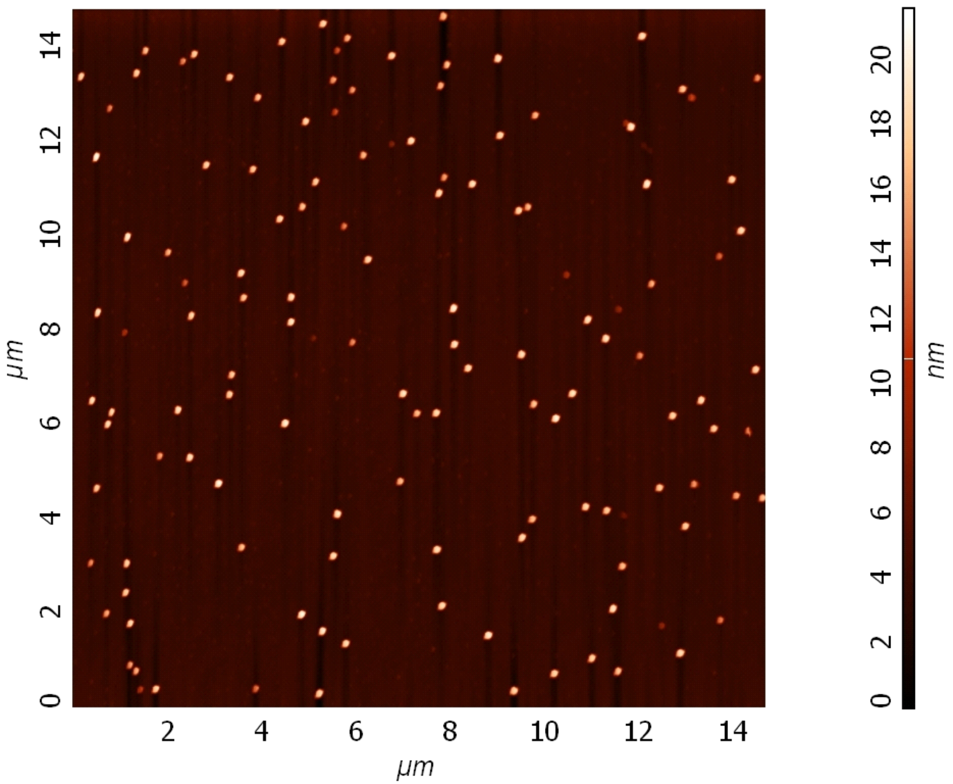
When the tip approaches the sample surface, the forces acting between the tip and the sample lead to a deflection of the cantilever (according to Hooke's law).

Atomic Force Microscopy



The probe scans the sample surface over a defined area. A laser beam deflection system is used to acquire the deflection of the probe during the scan and to control the position of the probe through a feedback loop.

Atomic Force Microscopy



AFM topographic image of MgO nanoparticles produced in a Flame Synthesis reactor

- **Height variations in the sample results in a change in the forces acting between the tip and the sample and so in the deflection of the cantilever.**
- **A topographic image is then obtained, and the height (z-axis) is visualized using a false color mapping.**

Atomic Force Microscopy

OPERATION MODES

CONTACT MODE

- **The tip is in touch with the sample surface and the cantilever deflection is due to repulsive Van der Waals forces;**
- **During the scanning, the force between the probe and the sample is kept constant by changing the probe height through the feedback circuit.**

SEMICONTACT MODE

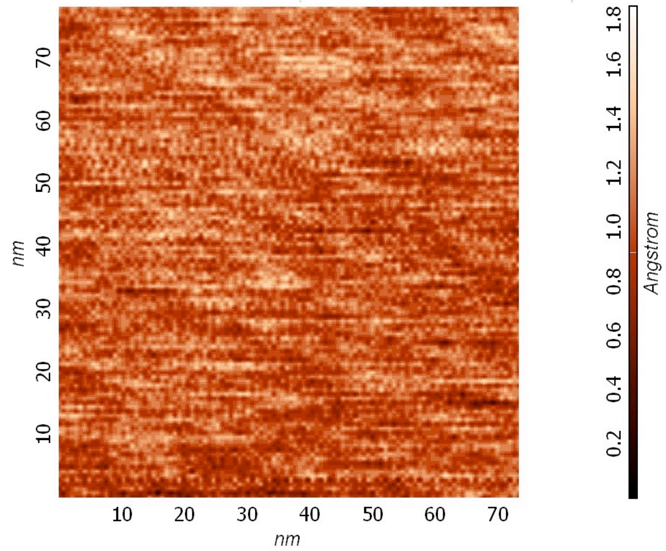
- **The tip is few nanometeres distant from the sample surface and the cantilever deflection is due to attractive Van der Waals forces;**
- **The cantilever is driven to oscillate up and down at or near its resonance frequency.**

Atomic Force Microscopy

AFM SUBSTRATES

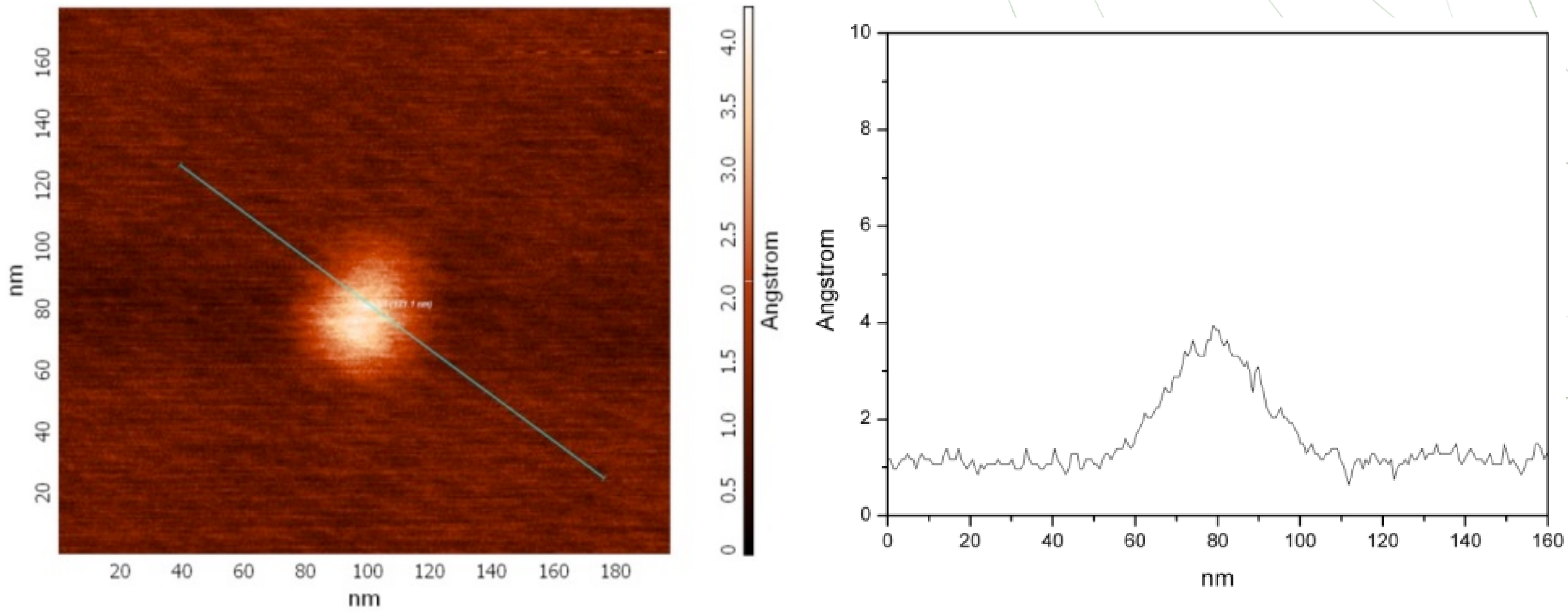
- **Very low roughness (< 0.2 nm) -> nanometric structure can be properly detected on the substrate;**
- **High mechanical and thermal resistance;**
- **Easy cleavage process -> a clean and atomically flat surface is obtained.**

MICA MUSCOVITE DISKS



Atomic Force Microscopy

PROFILING

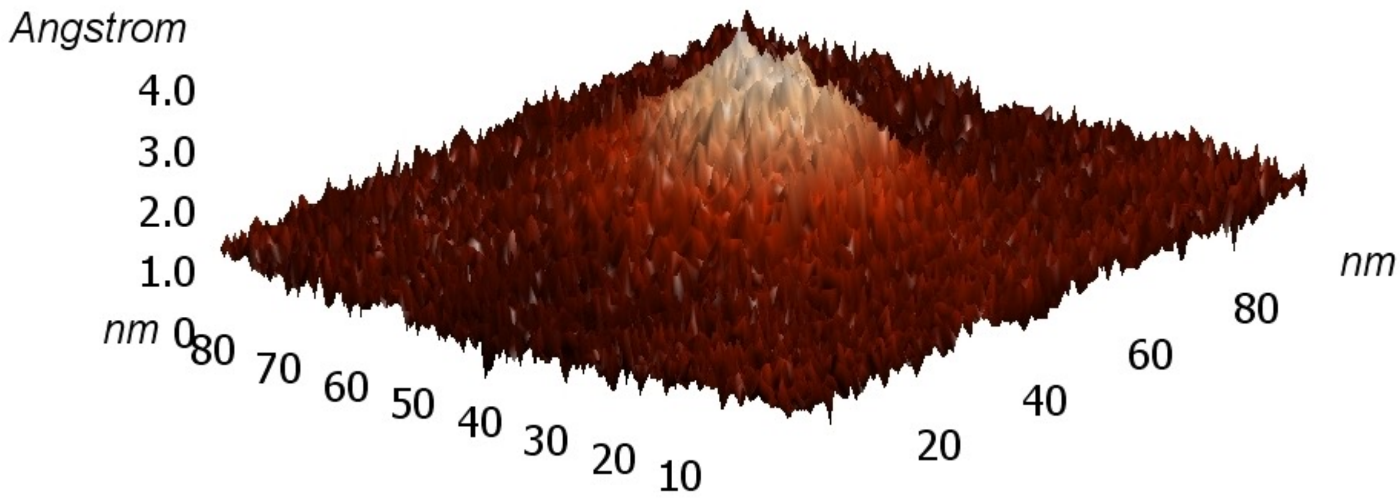


AFM topographic image (left) and height profile (right) of a carbon nanoparticle produced in a premixed ethylene/air flame

P. Minutolo et al. *Carbon* **68** (2014)

Atomic Force Microscopy

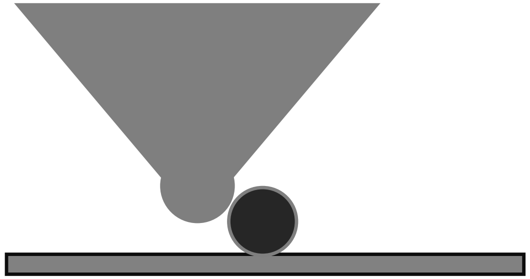
3D MAPS



AFM 3D topographic image of a carbon nanoparticle produced in a premixed ethylene/air flame

Atomic Force Microscopy

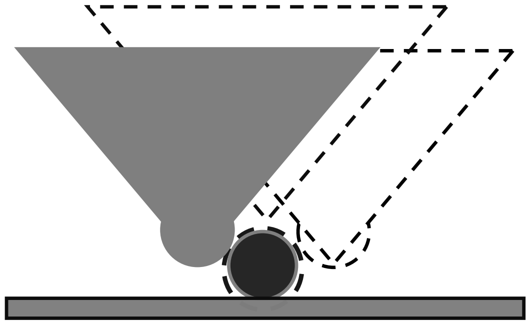
POST-PROCESSING: DECONVOLUTION OF AFM TOPOGRAPHIC IMAGES



- **Tip effects can distort AFM images if the sample features are similar in size to the tip radius;**
- **Typical AFM tip radius = 2-50 nm;**

Atomic Force Microscopy

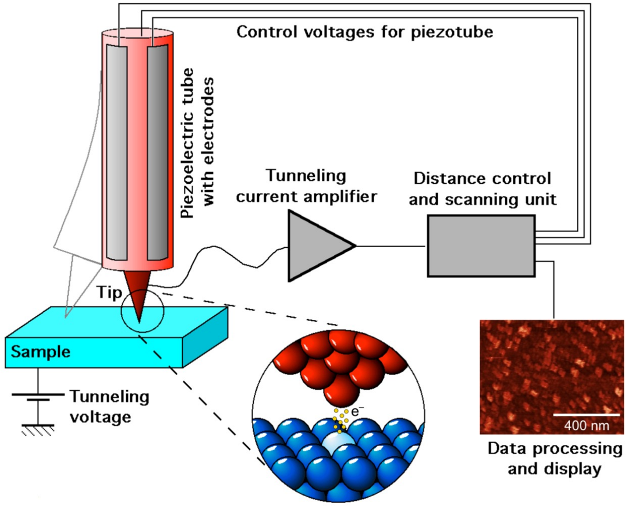
POST-PROCESSING: DECONVOLUTION OF AFM TOPOGRAPHIC IMAGES



- **Tip effects can distort AFM images if the sample features are similar in size to the tip radius;**
- **Typical AFM tip radius = 2-50 nm;**
- **The lateral dimensions of the sample can be overestimated by the probe (the height is not affected) when the underside of the particle cannot be properly captured;**
- **Tip artifacts are corrected by a deconvolution process of the images.**

Atomic Force Microscopy

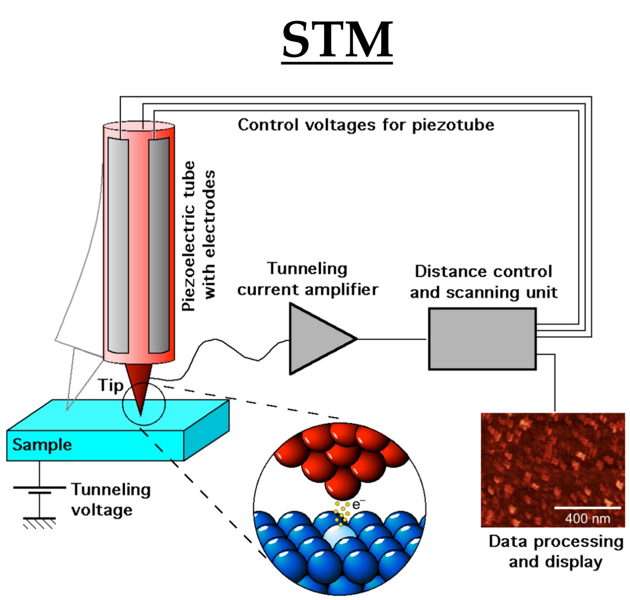
STM



R.M. Feenstra *Phys. Rev. B* **50** (1994)
H.J.W Zandvliet and A. van Houselt *Annu. Rev. Anal. Chem.* **2** (2009)
K.W. Hipps *Handbook of Applied Solid State Spectroscopy* (2006)

- **The working principle of STM is based on electron tunneling through a narrow potential energy barrier between a probe tip and a sample in an external electric field.**

Atomic Force Microscopy



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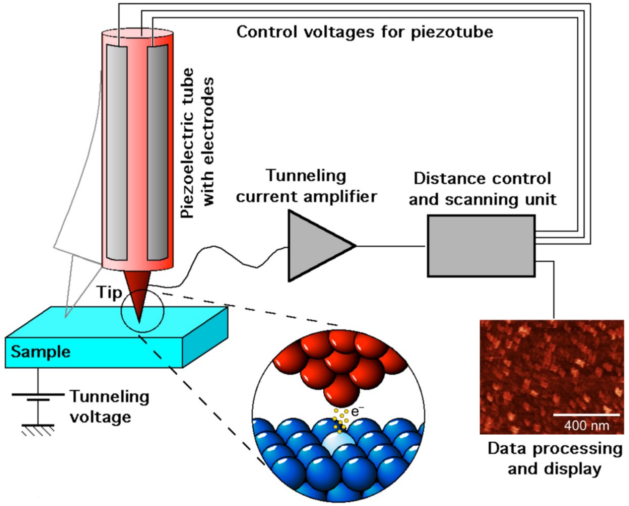
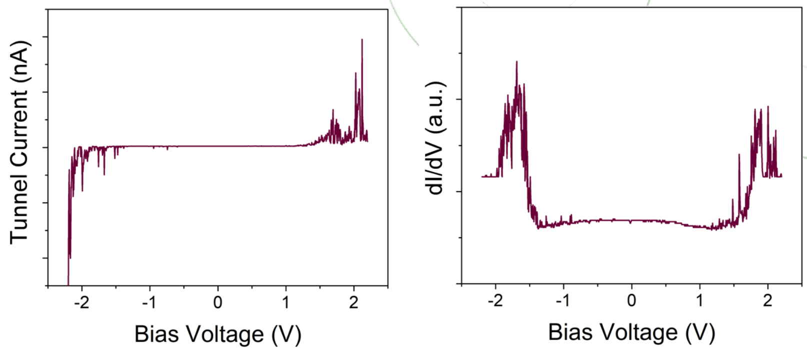
- **The working principle of STM is based on electron tunneling through a narrow potential energy barrier between a probe tip and a sample in an external electric field.**
- **STM can be operated in the STS mode, which measures the current-voltage (I-V) curve as well as the differential conductance (dI/dV-V) spectrum of an investigated sample**

Atomic Force Microscopy

STM



STS



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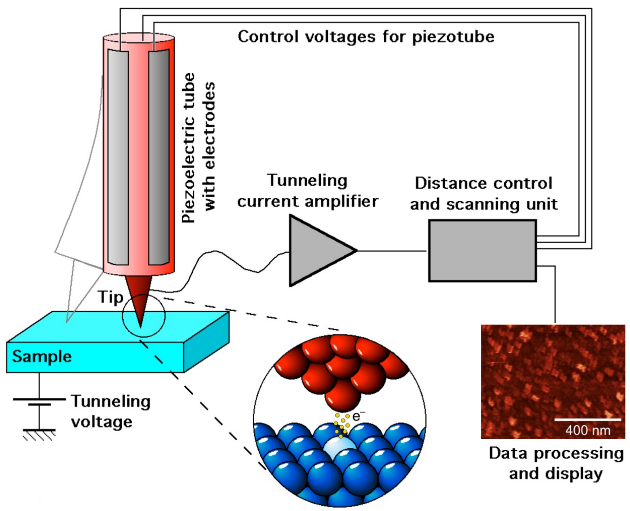
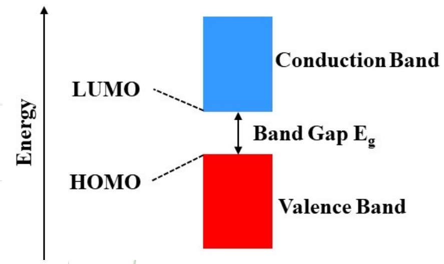
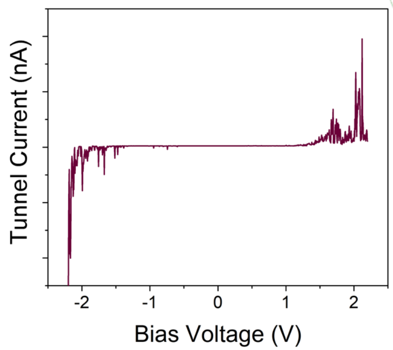
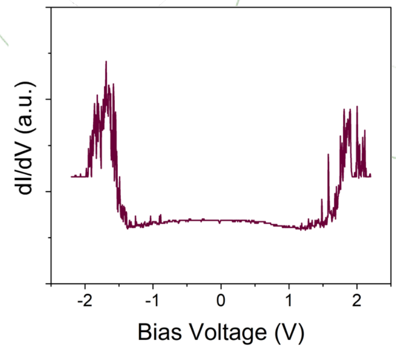


STS

Band Gap *Eg*







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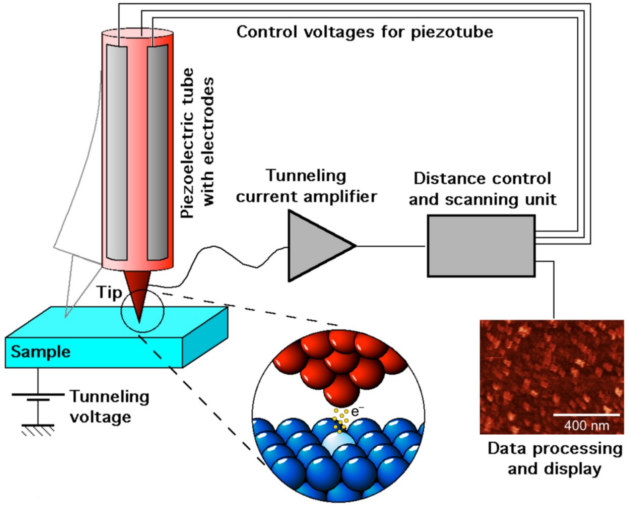

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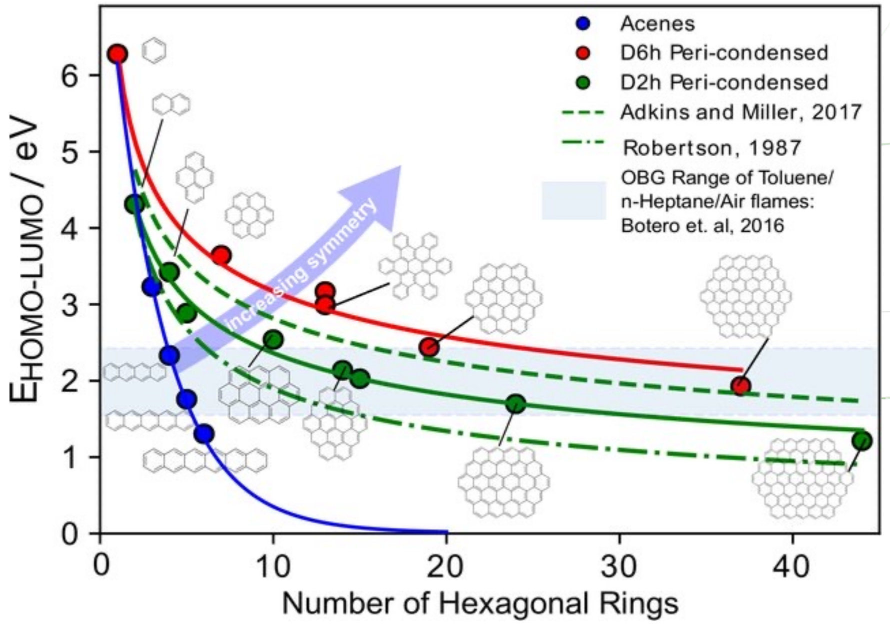
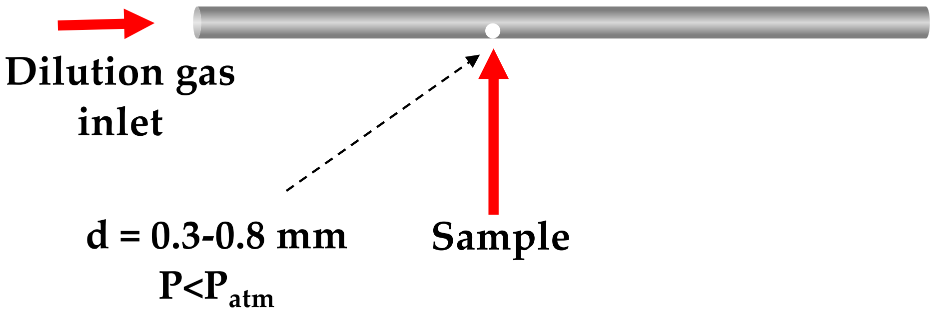


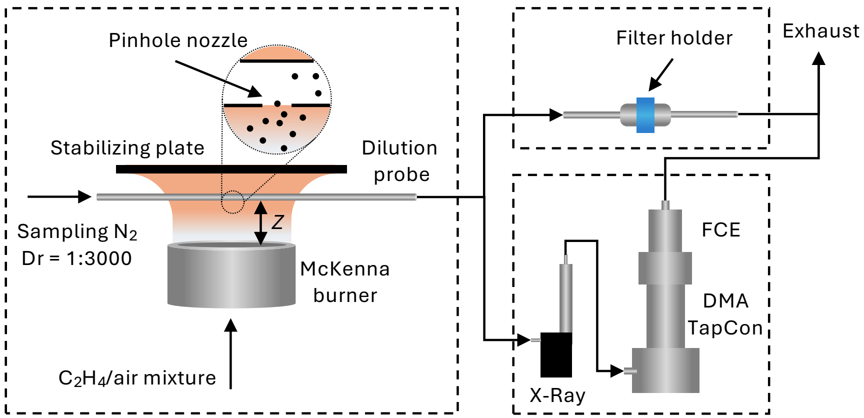
A. Menon *PCCP* **21** (2019)

Dilution Probe Sampling



- **The dilution probe is a sampling device used to dilute, quench and transport the aerosol collected from the flame to a Scanning Mobility Particle Sizer for the characterization of Particle Size Distributions (PSDs);**
- **It is made of a straight stainless tube with a small orifice for sample intake.**

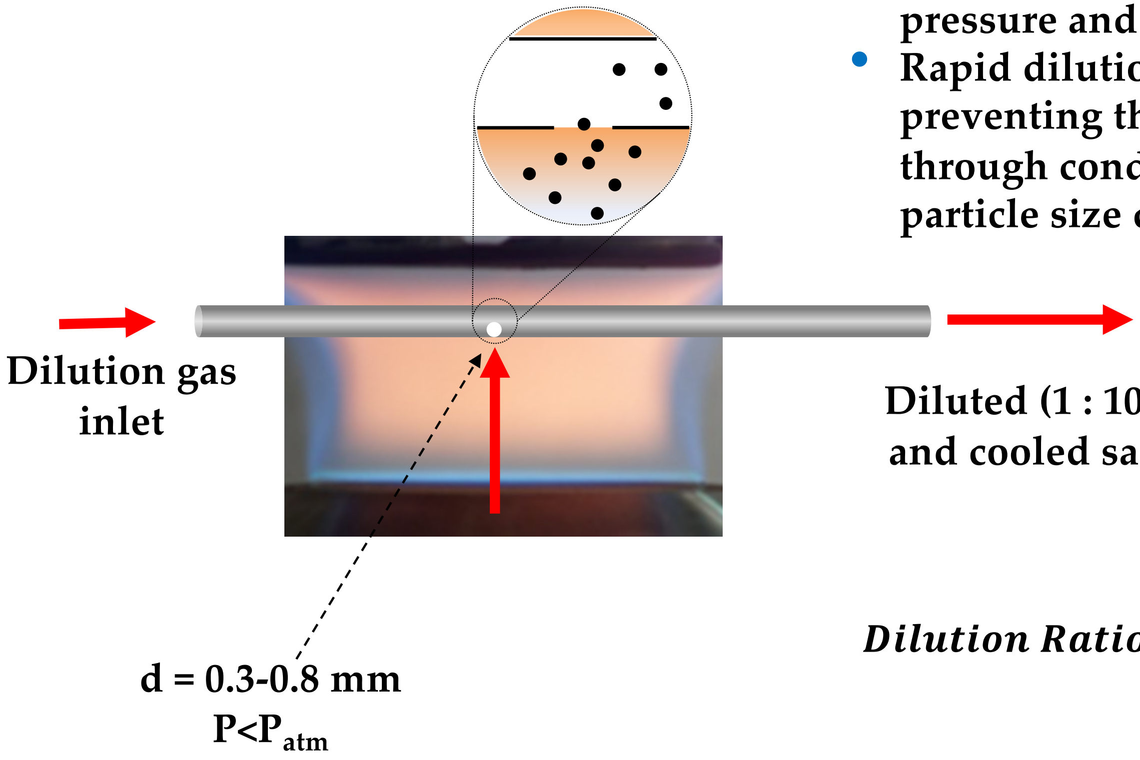
Particle generation and collection:



Particle characterization:

- DMA/SMPS – Particle size distributions;
- Raman spectroscopy – Structural/chemical characterization;
- XPS/UPS – Structural/chemical characterization (sp3/sp2; oxygen ..);
- HR-AFM – Molecular visualization;
- LS-MS – Chemical characterization;
- EPR spectroscopy – Radical monitoring and analysis

Dilution Probe Sampling

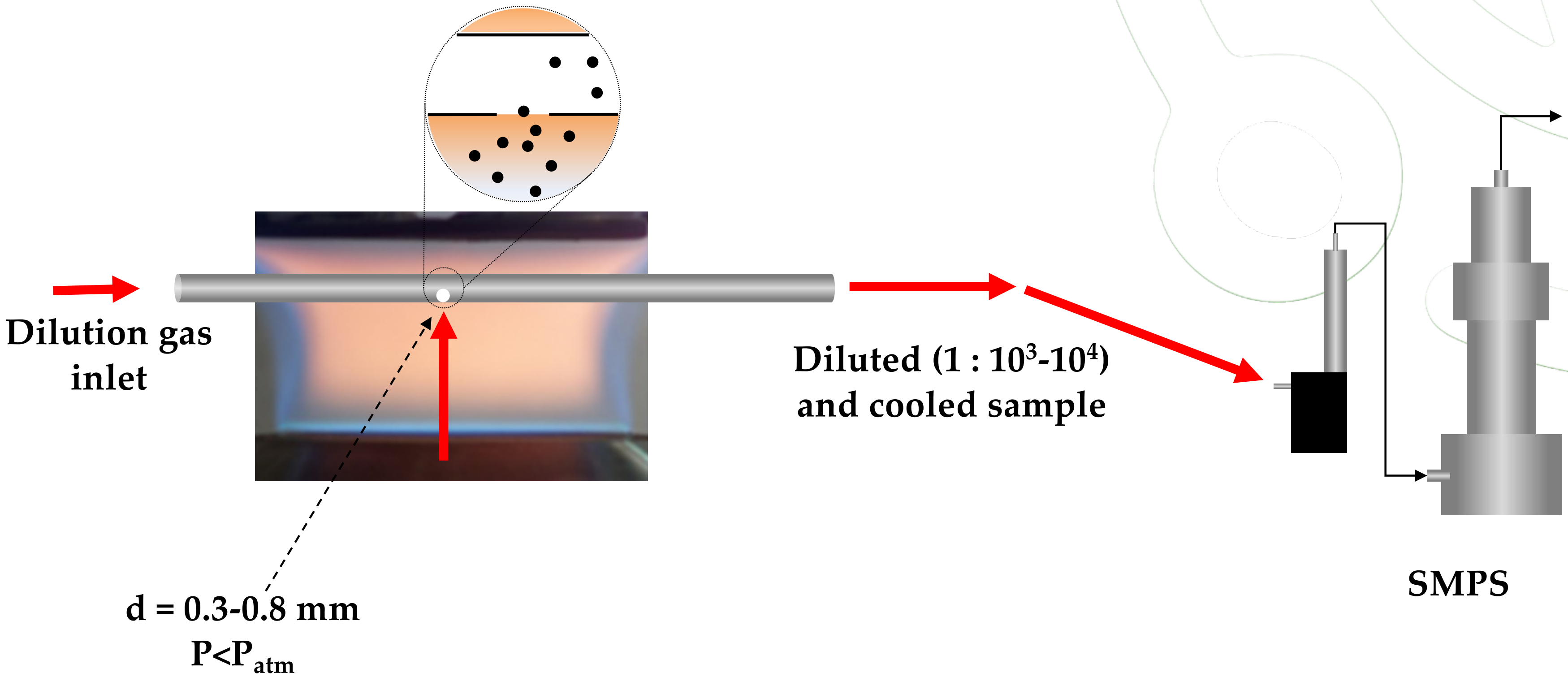


- **When inserted in the combustion system, the flame aerosol is sampled through the orifice due to a slight under-pressure and immediately diluted by nitrogen in the probe**
- **Rapid dilution allows to quench any chemical reaction, preventing the particles from coagulating or growing through condensation and therefore avoiding alteration of particle size distribution during the sampling process.**

$$\boldsymbol{Dilution\ Ratio\ DR} = \frac{\boldsymbol{Volume\ of\ dilution\ gas}}{\boldsymbol{Volume\ of\ flame\ gas\ sampled}}$$

Scanning Mobility Particle Sizer

- **The diluted sample is then sent to the SMPS system**



Scanning Mobility Particle Sizer

Electrical Mobility Z

$$\vec{u} = Z \cdot \vec{E}$$

u is the velocity of the charged particle in a gas induced by the electric field E

- **The SMPS is an on-line real time detection system used to determine the size distribution of charged particles, classified according to their electrical mobility**

SMPS

Scanning Mobility Particle Sizer

Electrical Mobility Z

$$\vec{u} = Z \cdot \vec{E}$$

$$Z = \frac{q \cdot e \cdot C_c}{3 \cdot \pi \cdot \mu \cdot d_M}$$

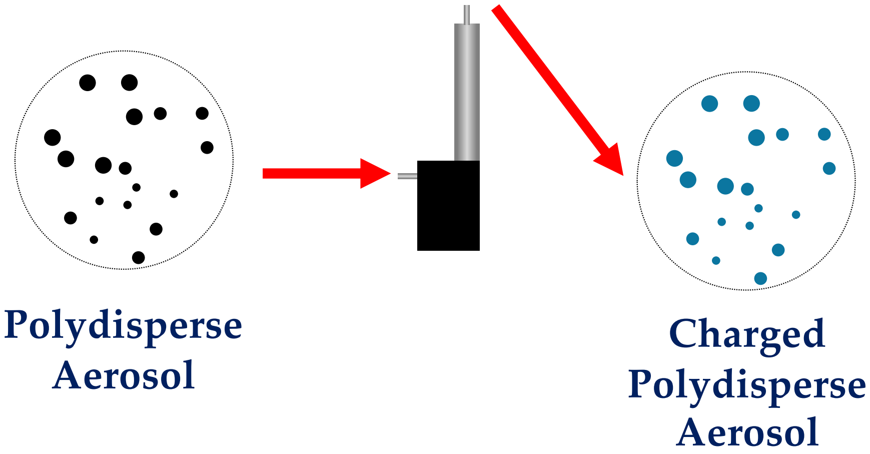
- **The SMPS is an on-line real time detection system used to determine the size distribution of charged particles, classified according to their <u>electrical mobility</u>**

Neutralizer
Electrostatic Classifier
Detector

SMPS

Scanning Mobility Particle Sizer

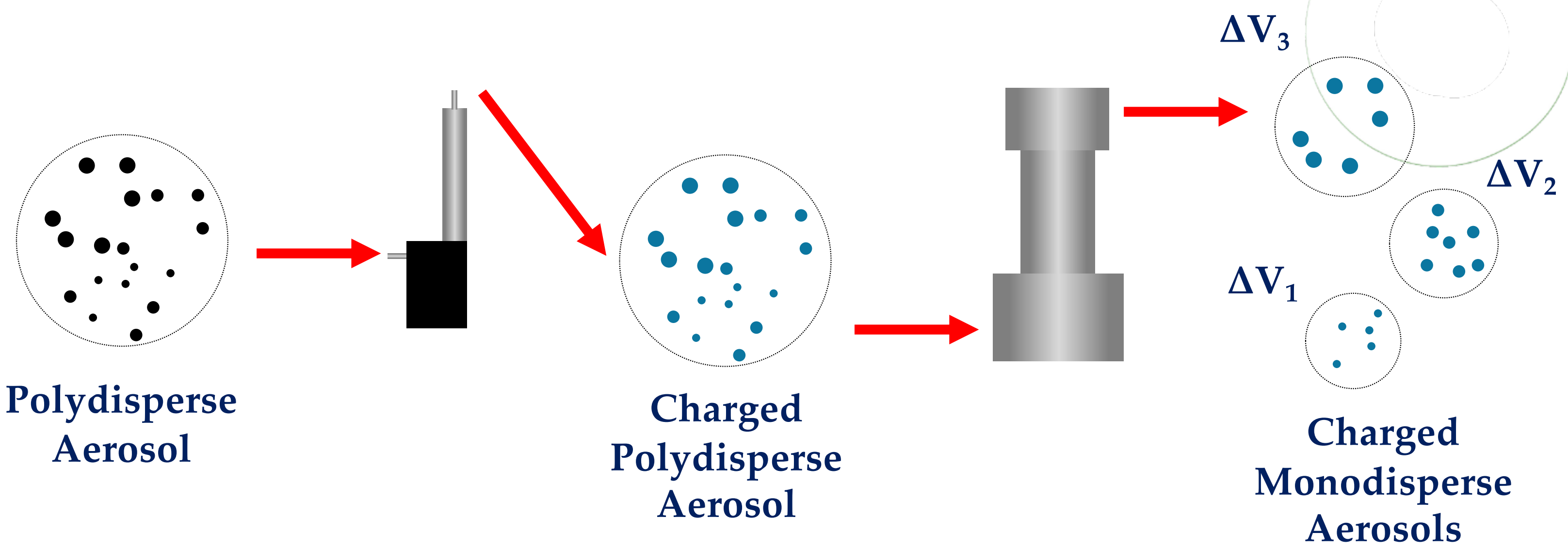
The NEUTRALIZER is used to charge particles with a known steady state charge distribution;



Scanning Mobility Particle Sizer

The NEUTRALIZER is used to charge particles with a known steady state charge distribution;

The ELECTROSTATIC CLASSIFIER classifies charged particles with respect to their electrical mobility and divide the charged polydisperse aerosol into different monodisperse aerosols;

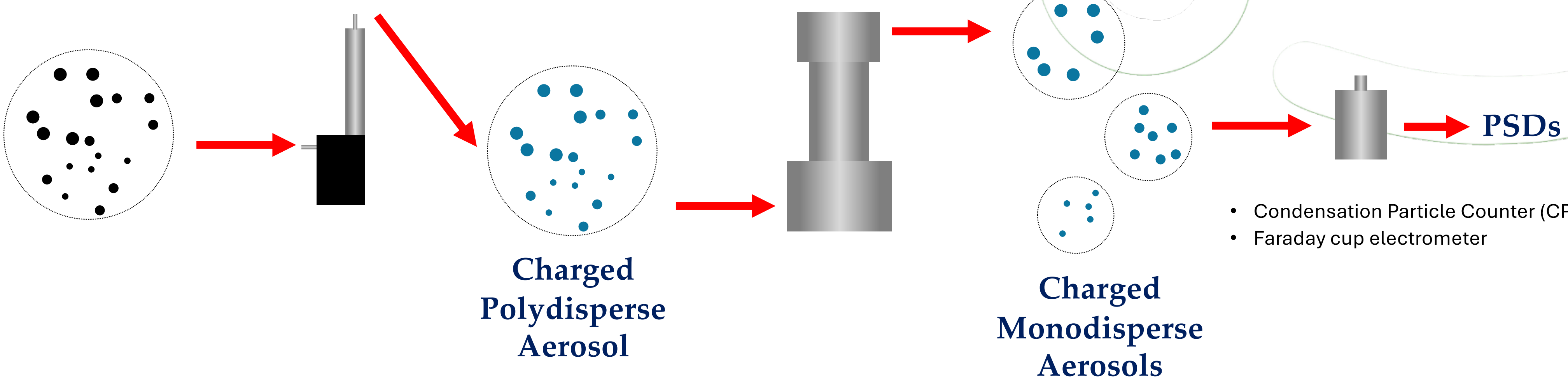


Scanning Mobility Particle Sizer

The NEUTRALIZER is used to charge particles with a known steady state charge distribution;

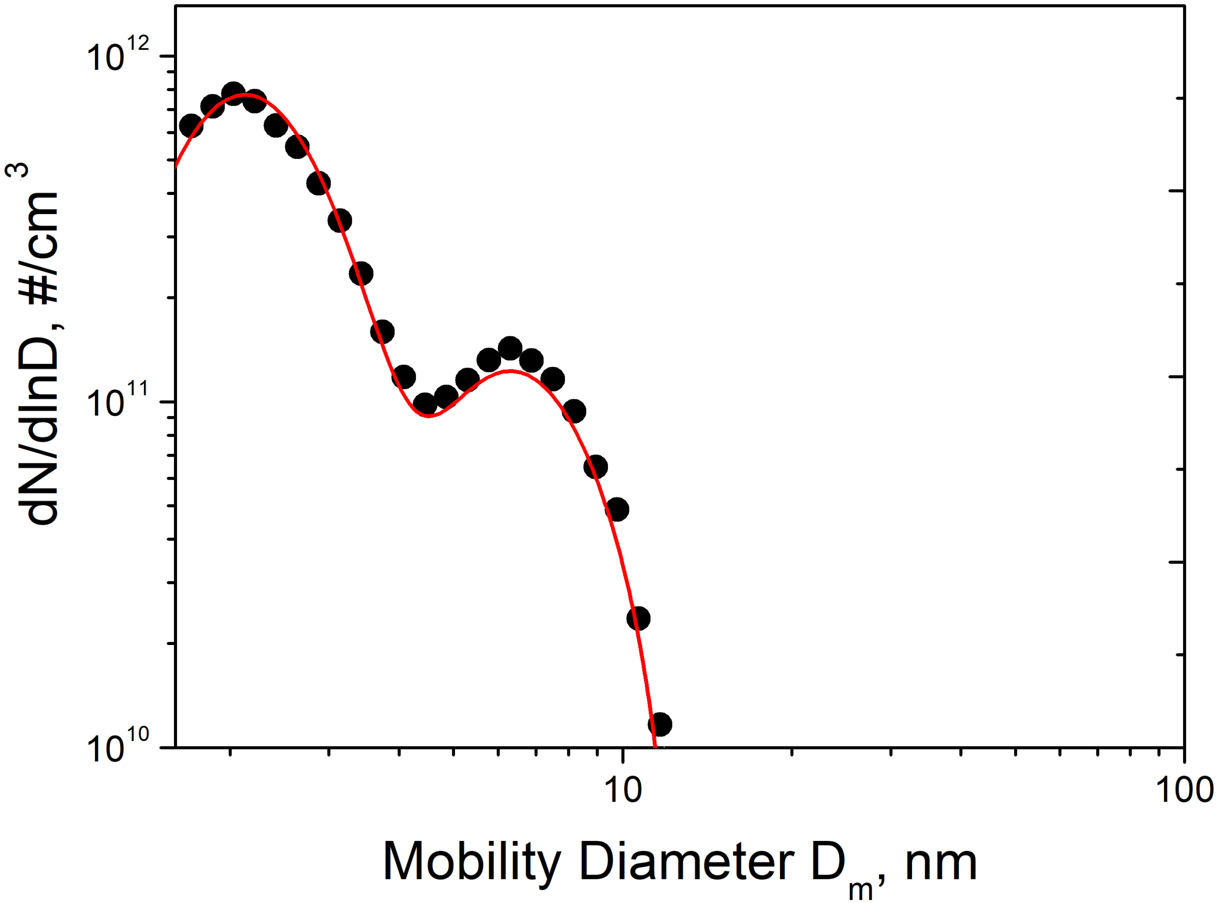
The ELECTROSTATIC CLASSIFIER classifies charged particles with respect to their electrical mobility and divide the charged polydisperse aerosol into different monodisperse aerosols;

The DETECTOR is able to count the number of particles per unit volume of each monodisperse aerosol.



- Condensation Particle Counter (CPC)
- Faraday cup electrometer

Scanning Mobility Particle Sizer



Number PSD:

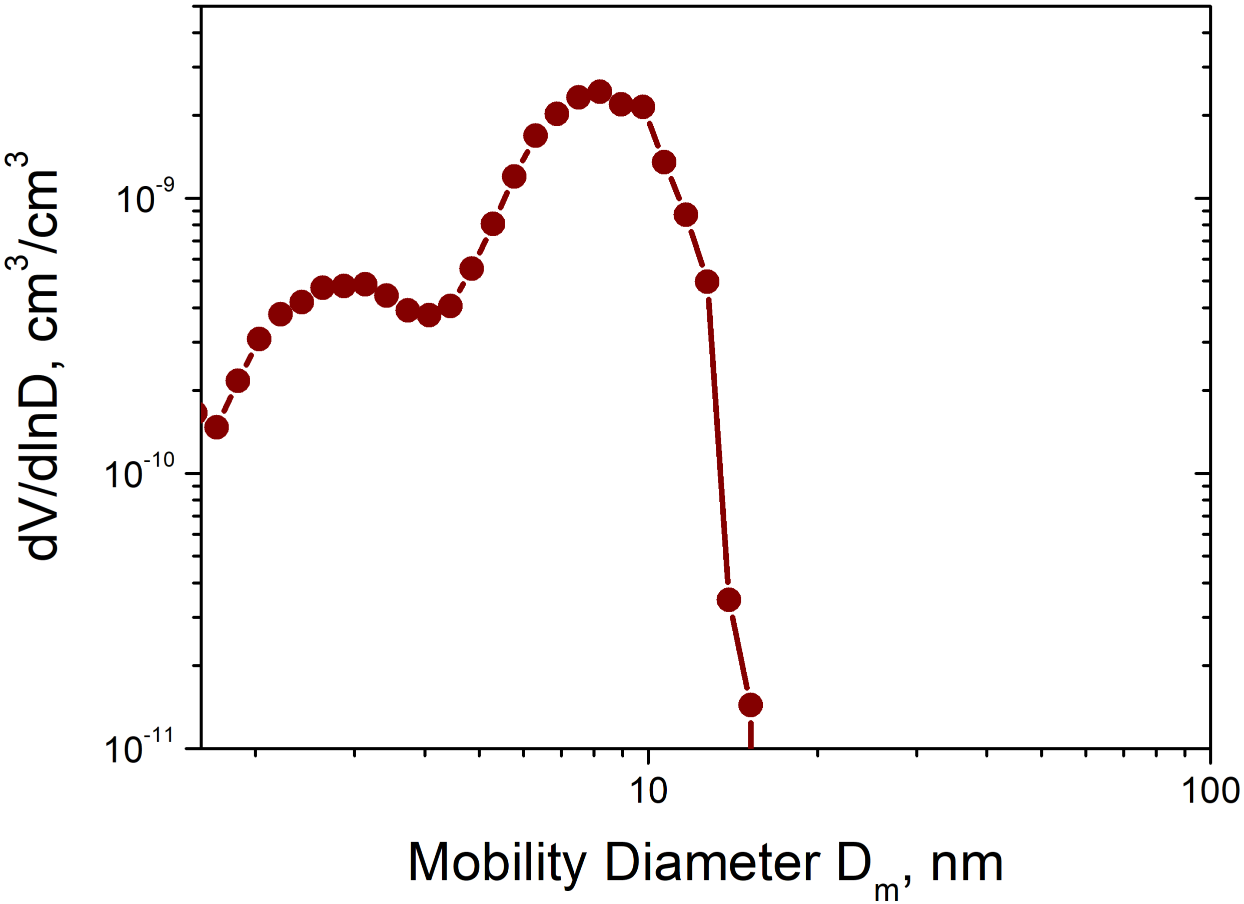
Particle number per unit volume of gas

Correction for the DILUTION:

$$DR = \frac{Volume\ of\ dilution\ gas}{Volume\ of\ flame\ gas\ sampled}$$

$$[dN\_SMPS] * DR = [dN\_Flame]$$

Scanning Mobility Particle Sizer



Volume PSD:

Particle volume per unit volume of gas

$$dV = dN * \pi \frac{D^3}{6}$$

Mass PSD:

Particle mass per unit volume of gas

$$dm = \rho_p * dN * \pi \frac{D^3}{6}$$

THANKS!

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