Repetition: Physical Deposition Processes

PVD (Physical Vapour Deposition)

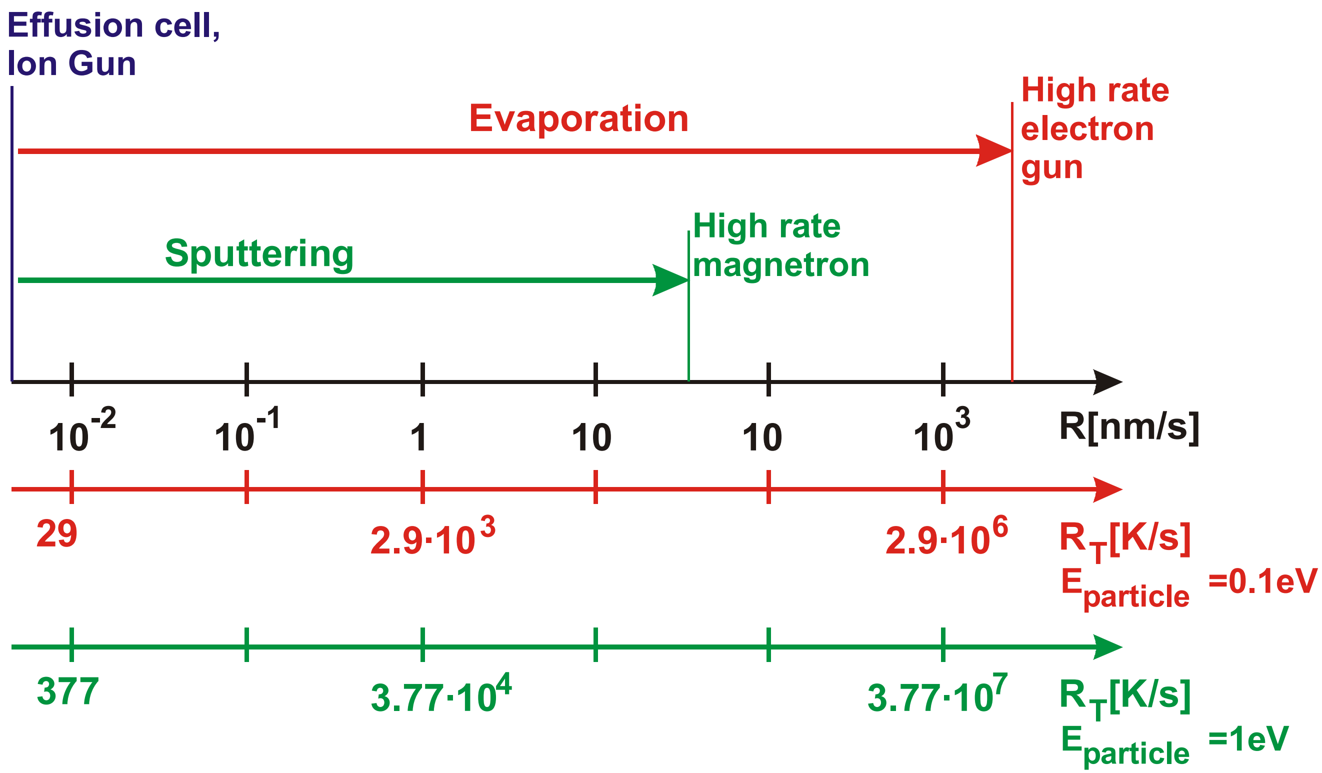
Evaporation

Sputtering
- **Diode-system**
- **Triode-system**
- **Magnetron-system ("balanced/unbalanced")**
- **Ion beam-system**

Ionplating
- **DC-glow-discharge**
- **RF-glow-discharge**
- **Magnetron- discharge**
- **Arc-discharge**
- **Ion-Cluster-beam**

Reactive versions of the above processes

Repetition: Rates and Cooling Rates PVD



These extremely high cooling rates show, that PVD processes (apart from being a direct transition from vapor → solid state) always have to be considered as non equilibrium processes.

Vacuum Physics

Central Termini:

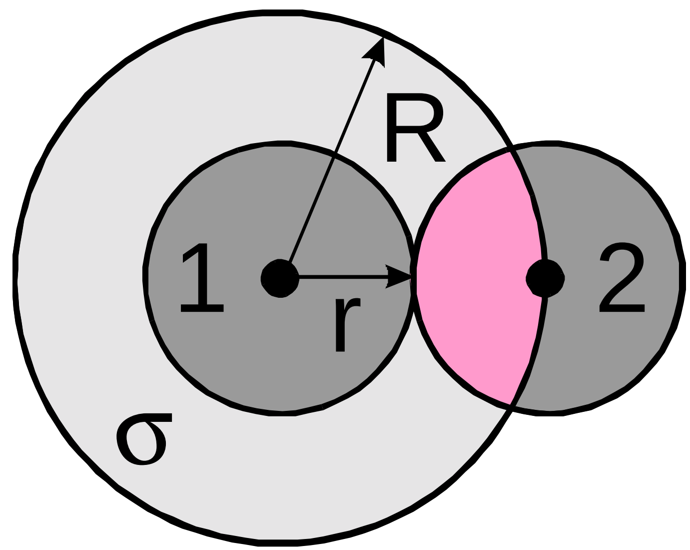
- **Mean free path:** the way a gas particle (or a film particle) can travel **without a collision with another particle.**

- **Impingement rate:** number of particles which hit a surface per second and unit area at **constant pressure.**

- **Coverage time:** time needed for the formation of a full **monolayer.**

Mean Free Path I

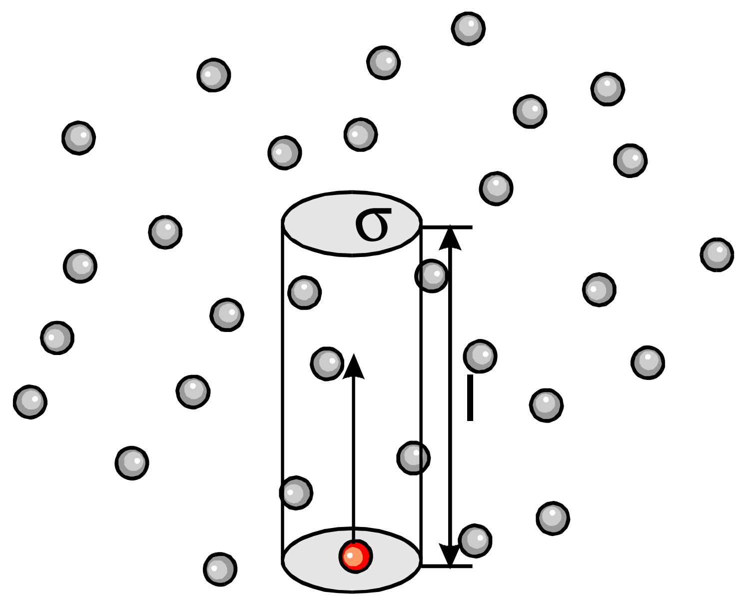
Collision of two particles, 1 and 2 with radius r = R/2:



If both particles are considered as points then a collision happens, if particle 1 is located within a disk of the area $\sigma = \pi \cdot R^2$. σ is called the collision cross section.

Mean Free Path II

Aparticle moves straight for a distance l through a gas. Within a cylinder of the volume V = l·σ it will collide with each particle located in V.



The cylinder contains $N = n \cdot V$ particles. For straight movement this is the collision number.

Mean Free Path III

One collision happens if N = 1. This yields the mean free path λ as:

$$N \equiv 1 \Rightarrow n \cdot V = n \cdot \lambda \cdot \sigma = 1$$

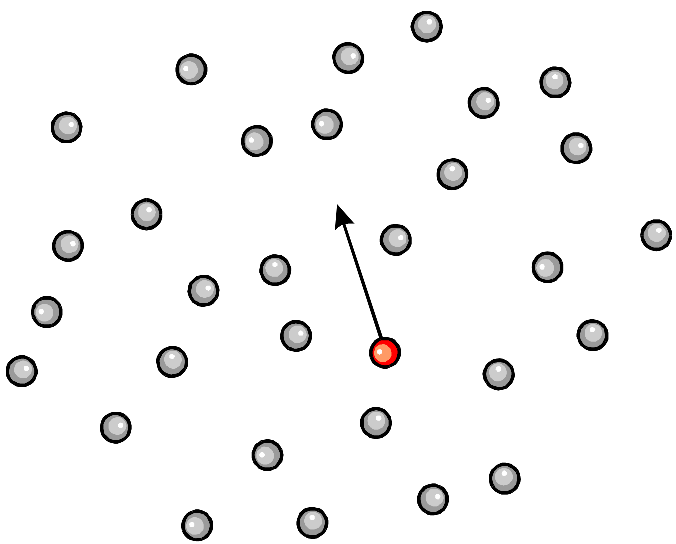
$$\lambda = \frac{1}{n \cdot \sigma} = \frac{1}{\pi \cdot n \cdot R^2} = \frac{1}{4 \cdot \pi \cdot n \cdot r^2}$$

- **Macroscopic information: Particle density n, from the ideal gas equation.**
- **Microscoic information: Collision cross section σ, contains energy dependent atom/molecule radii or the general interaction cross sections of the colliding particles.**

Mean Free Path IV

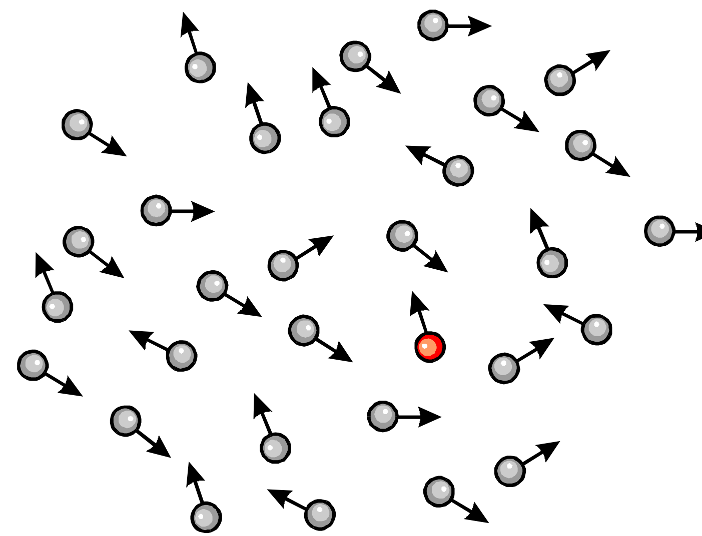
State of movement of the background gas:

Energetic coating particle: relative movement may be neglected



$$\lambda = \frac{1}{4 \cdot \pi \cdot n \cdot r^2}$$

Gas particle: relative movement may not be neglected



$$\lambda = \frac{1}{\sqrt{2} \cdot 4 \cdot \pi \cdot n \cdot r^2}$$

Mean Free Path - Example

$$\lambda = \frac{1}{4 \cdot \pi \cdot n \cdot r^2} \qquad p \cdot V = N \cdot k_B \cdot T \Rightarrow \frac{N}{V} = n = \frac{p}{k_B \cdot T}$$

p = 0.1 Pa

k_B=1,38·10^{-23}J/K

T = 300K

r = 1.5·10^{-10}m

$$\lambda = \frac{k_B \cdot T}{4 \cdot \pi \cdot p \cdot r^2} =$$

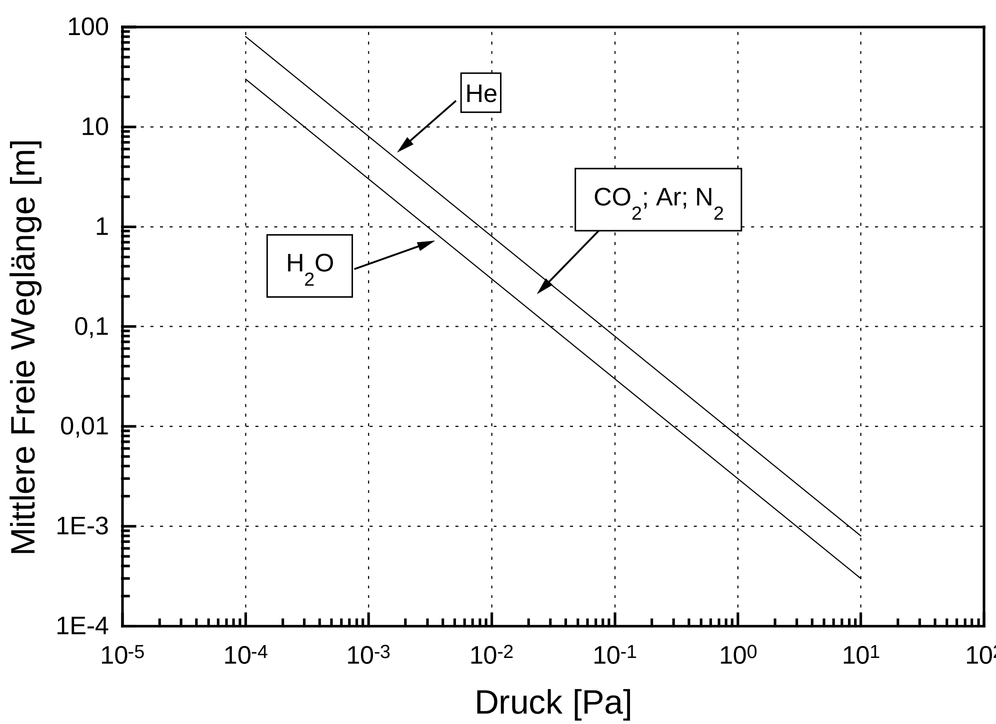
$$= \frac{1.38 \cdot 10^{-23} [J/K] \cdot 300 [K]}{4 \cdot \pi \cdot 0.1 [J \cdot m^{-3}] \cdot 1.5 \cdot 10^{-10} [m^2]} =$$

$$= 14.6 \text{ cm}$$

Mean Free Path - Rough Estimate

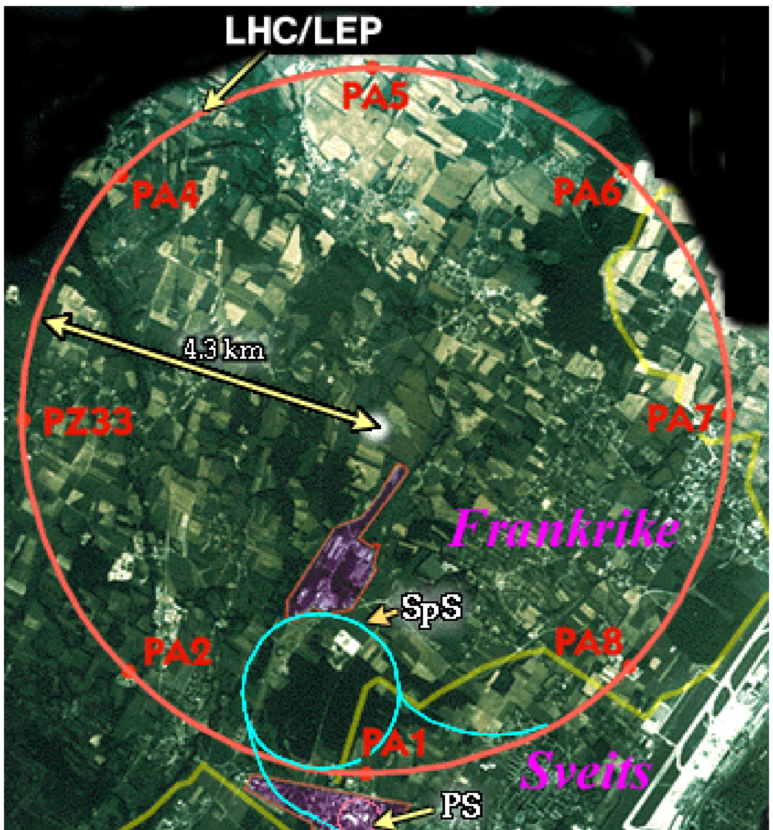
$\lambda p = 5 mmPa$

p = 1 Pa → λ = 5 mm
p = 10^{-4} Pa → λ = 50 m



Mean Free Path: Scale Consideration

CERN – LHC:
U = 2·4.3 ·π = 27 km



$\lambda p = 5 mmPa$

$$\lambda[mm] = \frac{5}{p[Pa]}$$

$$p[Pa] = \frac{5}{\lambda[mm]} = \frac{5}{2.7 \cdot 10^7} =$$

$$= 1.8 \cdot 10^{-7}\,Pa = 1.8 \cdot 10^{-9}\,mbar$$

Within LHC a pressure of approx. 10^{-9} mbar has to be maintained, to exclude interparticle collisions.

Gas Phase Transport

Clausius' law of distance:

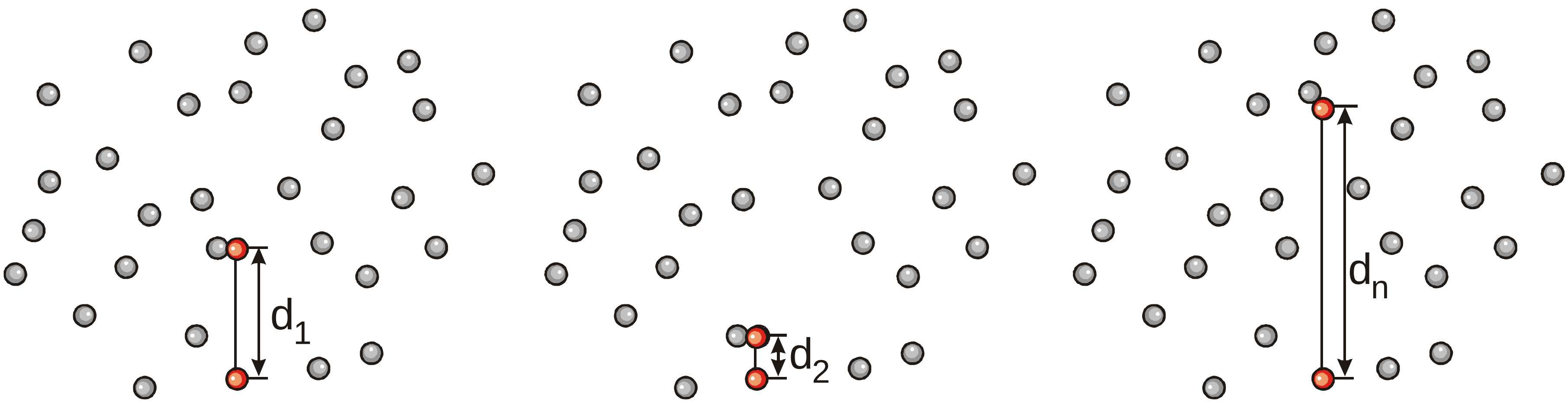
$$N(x) = N(0) \cdot \exp\left[-\frac{x}{\lambda}\right]$$

This means:

- **A significant number of collisions happens before the mean free path is reached.**
- **Only approx. 37% of the particles reach λ without a collision.**
- **The mean free path is only a statistical measure.**

Gas Phase Transport - Statistics

Consider large ensemble of single situations:

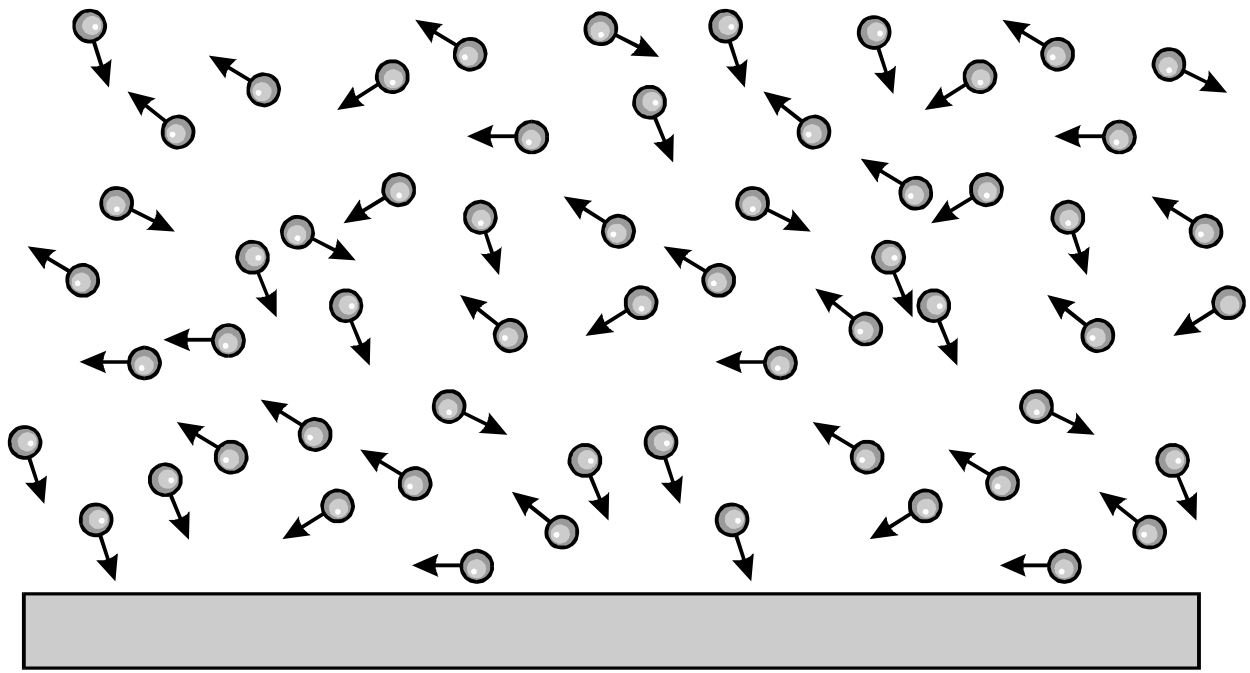


Calculate the expectation value of free throw distances:

$$\langle d \rangle = \frac{\int_0^\infty x \cdot \exp\left[-\frac{x}{\lambda}\right]}{\int_0^\infty \exp\left[-\frac{x}{\lambda}\right]} = \lambda$$

Areal Impingement Rate I

Initial situation: Gas molecules hit surface

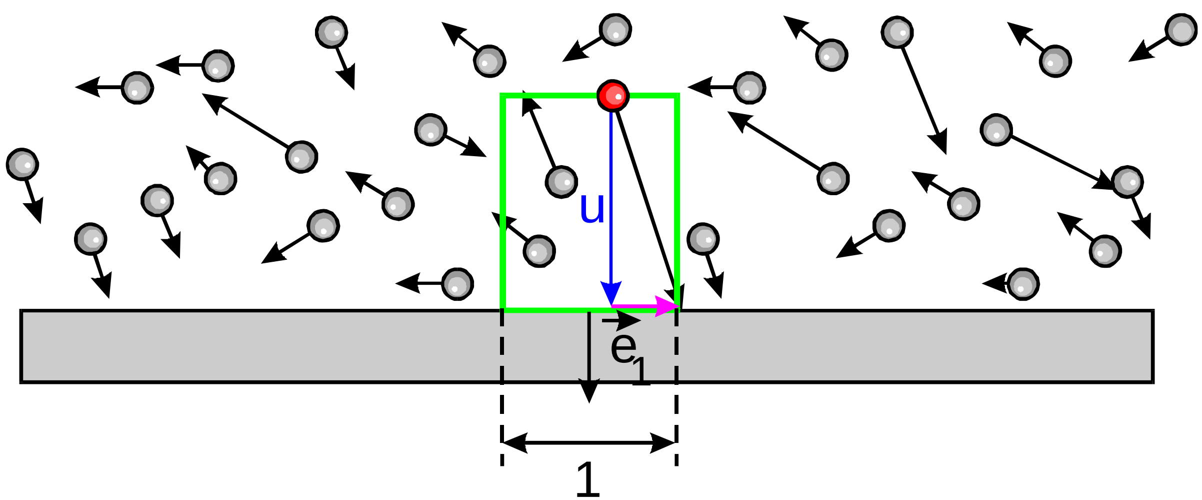


Wanted: number of gas molecules, which hit the unit surface within 1 second.

Areal Impingement Rate II

Approach: cylinder with unit top areas, heigth u.

Only particles with a velocity component u in the direction of $\vec{e}_1$, which trespass the top cylinder surface reach the surface within unit time.



Differential areal impingement rate:

$$dz_u = \underbrace{u \cdot 1}_{\text{cylinder-volume}} \cdot \underbrace{n}_{\text{particle-density}} \cdot \Phi(u) \cdot du$$

Areal Impingement Rate III

Differential areal impingement rate:

$$dz_u = \underbrace{u \cdot 1}_{\text{cylinder–volume}} \cdot \underbrace{n}_{\text{particle–density}} \cdot \Phi(u) \cdot du$$

Total areal impingement rate:

$$Z = \int_0^\infty dz_u = n \cdot \int_0^\infty u \cdot \Phi(u) \cdot du$$

Maxwell-distribution of one velocity-component:

$$\Phi(u) = \sqrt{\frac{m}{2 \cdot \pi \cdot m \cdot k_B \cdot T}} \cdot e^{-\frac{m \cdot u^2}{2 \cdot k_B \cdot T}}$$

Areal impingement rate IV

Calculation of the total areal impingement rate:

$$Z = \int_0^\infty dz_u = n \cdot \int_0^\infty u \cdot \Phi(u) \cdot du =$$

$$= n \cdot \sqrt{\frac{m}{2 \cdot \pi \cdot k_B \cdot T}} \cdot \underbrace{\int_0^\infty u \cdot e^{-\frac{m \cdot u^2}{2 \cdot k_B \cdot T}} du}_{\frac{k_B \cdot T}{m}} = n \cdot \sqrt{\frac{m}{2 \cdot \pi \cdot k_B \cdot T}} \frac{k_B \cdot T}{m} =$$

$$= \left| \frac{N}{V} = n = \frac{p}{k_B \cdot T} \right| = \frac{p}{m} \cdot \sqrt{\frac{m}{2 \cdot \pi \cdot k_B \cdot T}}$$

Areal Impingement Rate V

$$Z = Z(p,T,m) = \frac{p}{m} \cdot \sqrt{\frac{m}{2 \cdot \pi \cdot k_B \cdot T}}$$

$m = 5.3 \cdot 10^{-26}$ kg (O_2)

$k_B = 1,38.10^{-23}$ J/K

T = 300K

p = 0.1 Pa

$Z = 2.7 \cdot 10^{17}$ $s^{-1}cm^{-2}$

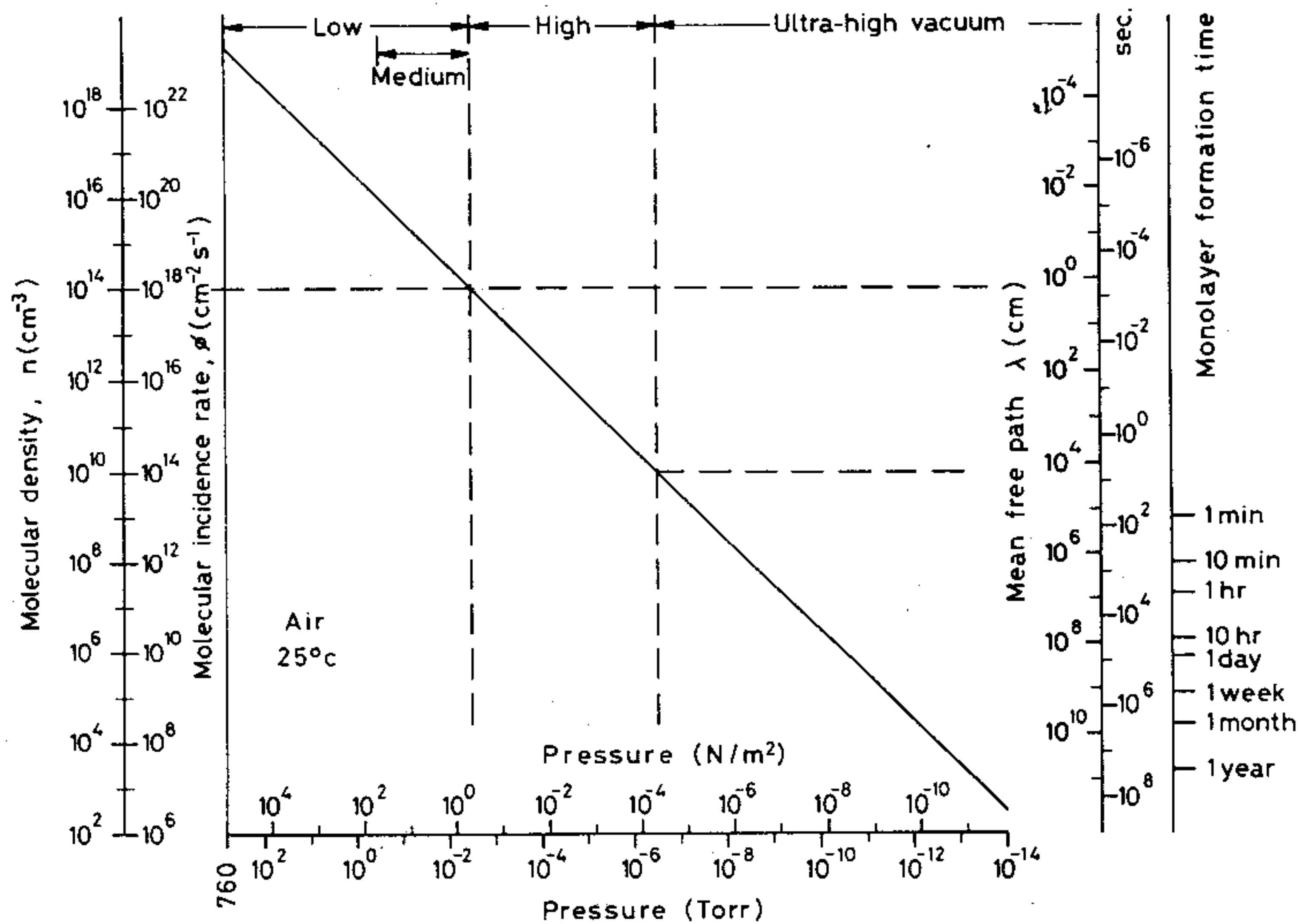
etwa 270 ML/s

$p = 10^{-4}$ Pa

$Z = 2.7 \cdot 10^{14}$ $s^{-1}cm^{-2}$

etwa 0.2 ML/s

Areal Impingement Rate - Graphic



Types of Vacuum

Name	Pressure [Pa]	Mean free path [mm]	Coverage time O_2, 300K [ML/s]
Rough vacuum	Atm→1	$5 \cdot 10^{-5}$→5	$2.7 \cdot 10^{5}$ → 2700
Fine vacuum	1 →0.1	5 →50	2700 → 270
High vacuum (HV)	0.1 →10^{-5}	50→$5 \cdot 10^{5}$	270 → 0.027
Ultra high vacuum (UHV)	10^{-5} →10^{-10}	$5 \cdot 10^{5}$→$5 \cdot 10^{10}$	0.027 → $2.7 \cdot 10^{-7}$
Extreme UHV (XHV)	<10^{-10}	$5 \cdot 10^{10}$→	$2.7 \cdot 10^{-7}$ →

$5 \cdot 10^{5}$ mm ≡ 500 m

$5 \cdot 10^{10}$ mm ≡ 50 000 km (!)

Types of Pumps

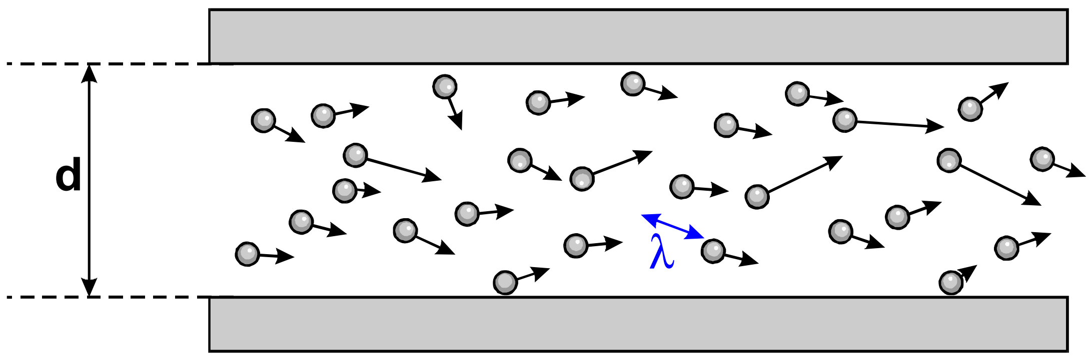
- **Gas transporting:**
  - + Rotary pump — Rough vacuum/fine vacuum
  - + Diffusion pump — High vacuum
  - + Turbomolecular pump — High vacuum

- **Gas adsorbing:**
  - + Cold traps — Fine vacuum
  - + Cryo pumps — High vacuum/UHV
  - + Sublimation pumps — UHV
  - + Getter pumps — UHV
    - reactive gases
  - + Ione getter pumps — UHV
    - inert molecules (activation)

Flow Types

Flow through a pipe, diameter d:

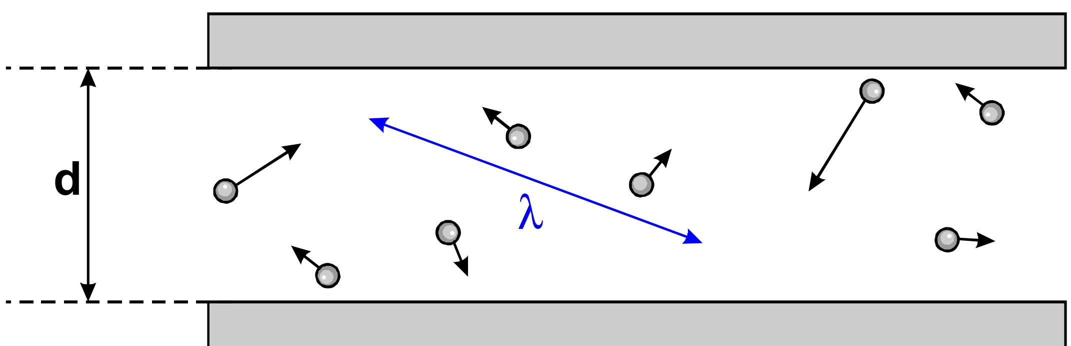
- **Laminar/turbulent: Rough vacuum/fine vacuum**



$\lambda << d$

Particle collisions probable, global flow

- **Molecular: High vacuum, UHV**



$\lambda >> d$

Wall collisions probable, no flow

Flow Types and Pumping Systems

- **Efficient in the laminar region:**
  + Gas transporting pumps:
  Rotary pump
  Ejector pump
  + Rotary pumps, except Turbomolecular pumps

- **Efficient in the molecular region :**
  + Gas transporting pumps:
  Diffusion pump
  Turbomolecular pump
  + Gas adsorbing pumps

Design Criteria for Vacuum Systems

- **Mean free path λ:**
  - + Choice of pump type
  - + Pump velocity
  - + Dimension of pipe diameters

- **Areal impingement rate Z:**
  - + Coverage times (e. g. surface analytics)
  - + Impurity content in coatings (ratio of impingement rate of the coating particles and of the background gas particles)

Impurities

Sticking coefficient α:

$$\alpha = 1 - \frac{Z_{Des}}{Z}$$

Z ... Ipingement rate
Z_{Des}... Desorption rate

- **High sticking coefficient $\alpha \approx 1$ ($Z_{Des} \approx 0$):**
  - **Reactive gases:**
    - **O_2**
    - **$H_2 0$**
    - **Complex carbohydrates (pump oil)**
- **Low sticking coefficient $\alpha \ll 1$ ($Z_{Des} \approx Z$):**
  - **Inert gases:**
    - **Noble gases**
    - **N_2**
    - **CH_4**
    - **Carbohydrates without reactive groups**

Impurities: Example

Coating material: **Al, $m = 4.5 \cdot 10^{-26}$ kg**
Rate Al: **10 nm/s = $3 \cdot 10^{19}$ At/($m^2 s^{-1}$)**
Impurity: **O_2, $m = 5.3 \cdot 10^{-26}$ kg**
Sticking coefficient α: **approx. 1 für Al und O_2**
Temperture: **300K**

Wanted: Background gas pressure, at which 1% Oxygen is incorporated unto the coating

$$\frac{Z_{O_2}}{Z_{Al}} = 10^{-2} = \frac{1}{3 \cdot 10^{19}} \cdot \frac{p}{m_{O_2}} \cdot \sqrt{\frac{m_{O_2}}{2 \cdot \pi \cdot k_B \cdot T}}$$

$$p = 10^{-2} \cdot 3 \cdot 10^{19} \cdot m_{O_2} \cdot \sqrt{\frac{2 \cdot \pi \cdot k_B \cdot T}{m_{O_2}}} = 1.11 \cdot 10^{-5}\,\mathrm{Pa}$$

Design Criteria: Summary

- **Mean free path λ:**
  Influences gas dynamics. Even at rather high pressures (10^{-2} Pa) the mean free path reaches the dimensions of average deposition chambers .

- **Areal impingement rate Z:**
  Crucial for coating purity. The pressure of the background gas has to be at least in the medium high vacuum to guarantee sufficient film purity.