

Fabrication of thin films

Magnetic materials in nanoelectronics

- **properties and fabrication**

Fabrication of thin films

1. Introduction
2. Physical vapor deposition
3. Basic techniques

Introduction

We will be concerned today only with a few out of the numerous deposition methods

Some of the deposition methods*:

- Evaporation methods:

1. Vacuum evaporation
2. Electron-beam evaporation
3. Molecular-beam epitaxy

plan for today

- Sputtering

1. Diode sputtering
2. Magnetron sputtering
3. Bias sputtering
4. Ion beam sputtering

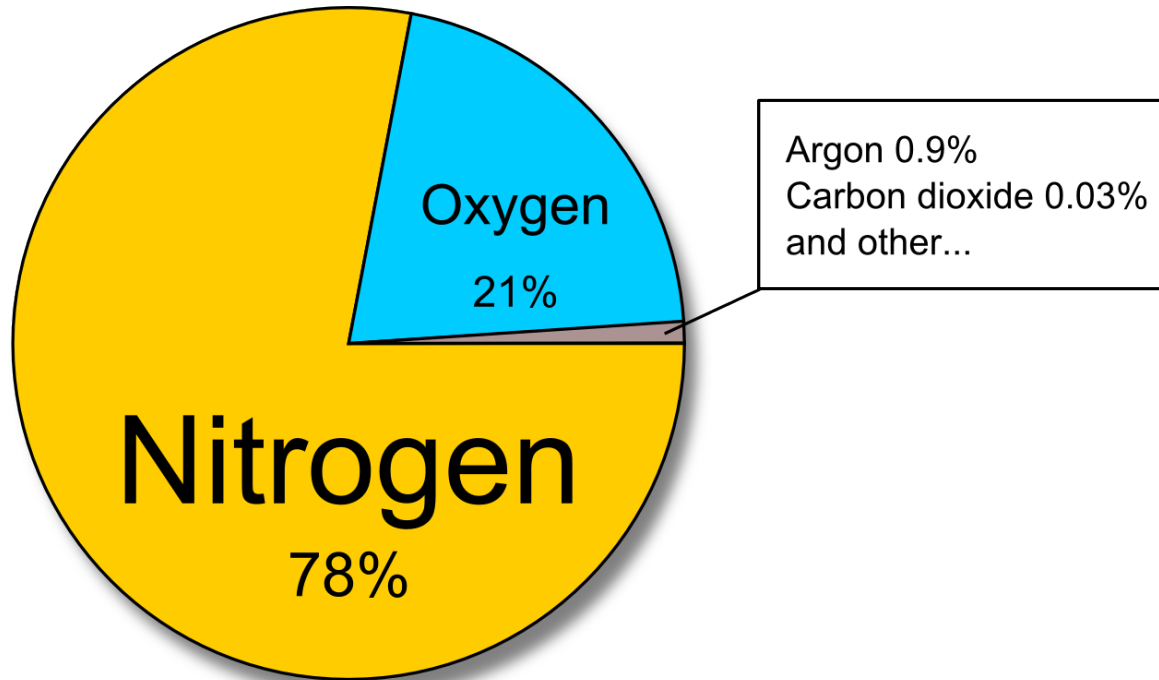
- Chemical vapor deposition

- Liquid phase chemical techniques

*for more methods see for example p.15 of Handbook of Thin-Film Deposition Processes and Techniques, edited by K. Seshan, 2002 Noyes Publications

Introduction

Earth atmosphere is composed mainly of two elements* (nitrogen and oxygen)



Water vapor constitutes about 0.25% of the mass of the atmosphere

The typical sea-level pressure is about 1000 hPa
 From Dalton's law we have for the atmospheric pressure:

$$P_{total} = \sum_i p_i = p_{Nitrogen} + p_{oxygen} + \dots$$

The mean mass of water vapor in atmosphere is estimated at 1.27×10^{16} kg [34] which corresponds to 12 700 km³ (cubic kilometers) of water liquid; which is roughly 55% of water in Baikal lake (23 000km³) [35].

*the graph shows the elements in a dry atmosphere – not including water vapor; data from spark.ucar.edu/shortcontent/earths-atmosphere

Introduction

For an ideal gas (non-interacting point-like particles) we have from Avogadro's law for the number of gas particles in a unit volume:

$$N = N_A \frac{P V}{R T}$$

$$R = k_B N_A$$

$$N = \frac{P V}{k_B T}$$

$$N_A \approx 6.022 \times 10^{23} \text{ mol}^{-1}$$

Avogadro constant

$$k_B \approx 1.38 \times 10^{-23} \text{ J K}^{-1}$$

Boltzmann constant

$$P V = n R T$$

For typical laboratory conditions (room temperature, sea level) it follows that there are about 2.47×10^{25} particles in cubic meter of air.

This corresponds to one particle in a cube of approx. 3.5 nm edges.

The same volume of a solid metal (eg. iron) contains approx. 3600 atoms.

Introduction

- In today's lecture we will use the kinetic theory of gases
- The theory is applicable if the thermal de Broglie wavelength λ_B of the gas particles is much less than the mean distance between particles d [4]

$$\lambda_B = \frac{h}{\sqrt{2\pi m k_B T}} \quad d \approx \left(\frac{V}{N}\right)^{1/3}$$

- For nitrogen molecules at RT we have:

$$\lambda_B \approx 20 \text{ pm}$$

$$d \approx 3.4 \text{ nm}$$

and

$$\frac{d}{\lambda_B} \approx 170$$

Introduction

Although the volume density of gas particles* is small their kinetic energy is significant

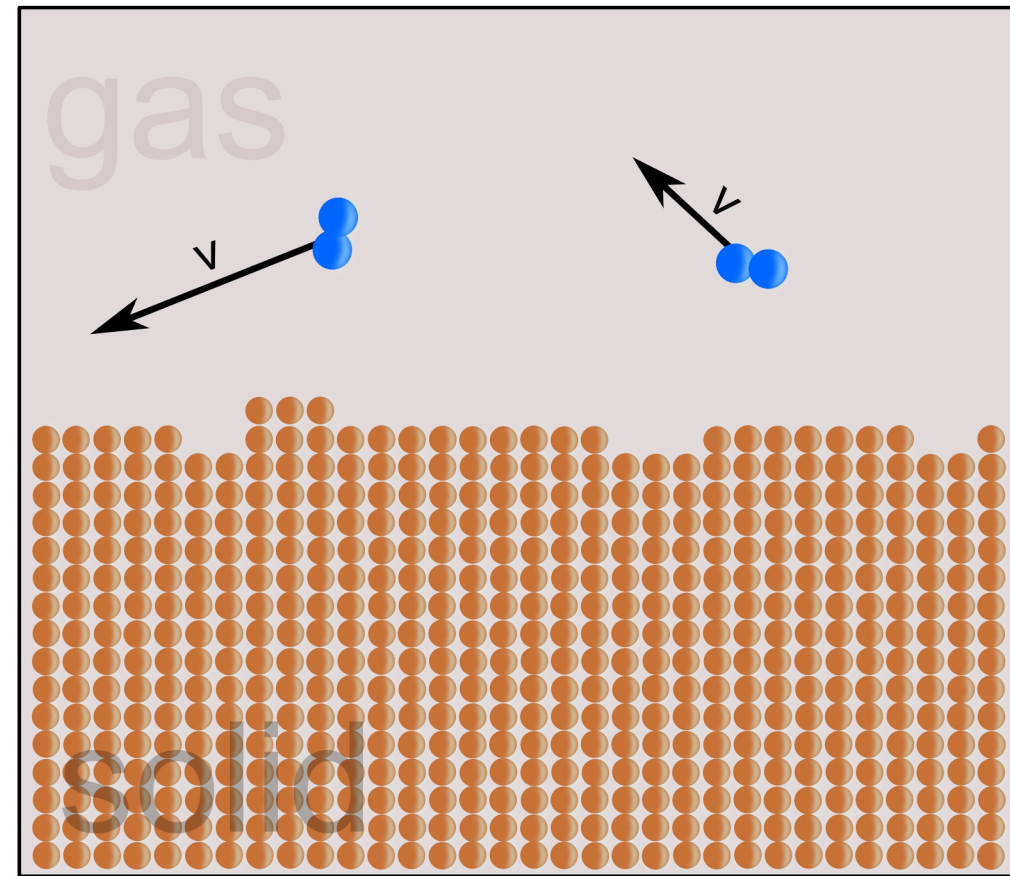
We start from Maxwell-Boltzmann distribution [2]:

$$dw = \frac{dN}{N} = \left(\frac{2\pi kT}{m} \right)^{-3/2} e^{-m \frac{v_x^2 + v_y^2 + v_z^2}{2kT}} dv_x dv_y dv_z$$

the probability that a given particle has velocity vector in the range $v_x \cdots v_x + dv_x, v_y \cdots v_y + dv_y, v_z \cdots v_z + dv_z$

We can express the above expression as a product [1]:

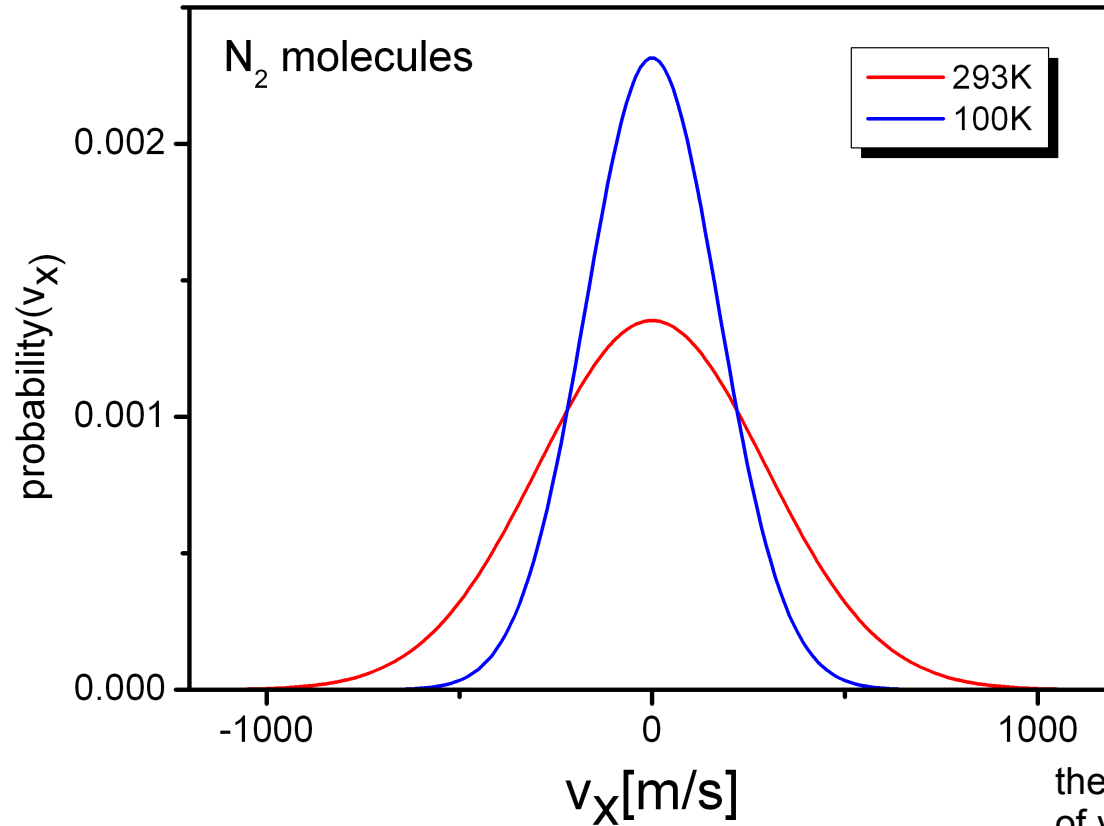
$$dw = \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-m \frac{v_x^2 + v_y^2 + v_z^2}{2kT}} dv_x dv_y dv_z = \left(\frac{m}{2\pi kT} \right)^{1/2} e^{-m \frac{v_x^2}{2kT}} dv_x \times \left(\frac{m}{2\pi kT} \right)^{1/2} e^{-m \frac{v_y^2}{2kT}} dv_y \times \left(\frac{m}{2\pi kT} \right)^{1/2} e^{-m \frac{v_z^2}{2kT}} dv_z$$



*number of molecules in a unit volume

Introduction

Let us take as an example the velocity distribution for Nitrogen at room temperature* (molar mass of N is $M=14.00674\text{g/mol}$, so the N_2 molecule has a mass of $2M/N_A \approx 4.652 \times 10^{-26} \text{ kg}$)



- velocity distribution is a normal distribution with mean value equal to zero
- room temperature velocities along given direction are of the order of several hundred m/s for typical atmospheric gases
- increasing the temperature broadens the distribution

the total distribution is a product of distributions of velocities along three Cartesian directions

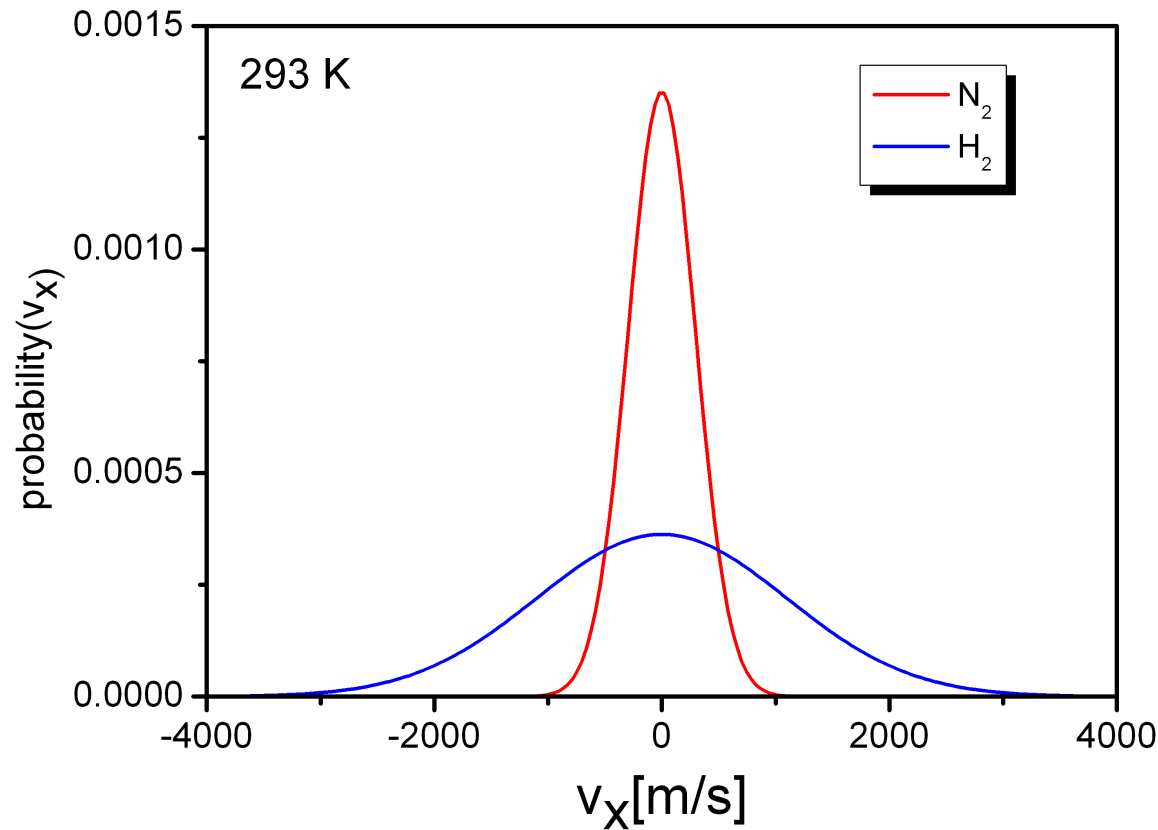
$$dw = \left(\frac{m}{2\pi kT} \right)^{1/2} e^{-m \frac{v_x^2}{2kT}} dv_x \times \left(\frac{m}{2\pi kT} \right)^{1/2} e^{-m \frac{v_y^2}{2kT}} dv_y \times \left(\frac{m}{2\pi kT} \right)^{1/2} e^{-m \frac{v_z^2}{2kT}} dv_z = f(v_x) f(v_y) f(v_z)$$

$dv_x dv_y dv_z$

* 293K

Introduction

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- velocity distribution depends strongly on molecular mass
- nitrogen molecules are roughly 14 times heavier than hydrogen ones

* 293K

Introduction

Very often one is more interested in magnitude of the velocity of the gas molecules rather than its components.

We start from Boltzmann distribution, but this time we are interested in $v = \sqrt{v_x^2 + v_y^2 + v_z^2}$.

$$dw = \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-m \frac{v_x^2 + v_y^2 + v_z^2}{2kT}} dv_x dv_y dv_z$$

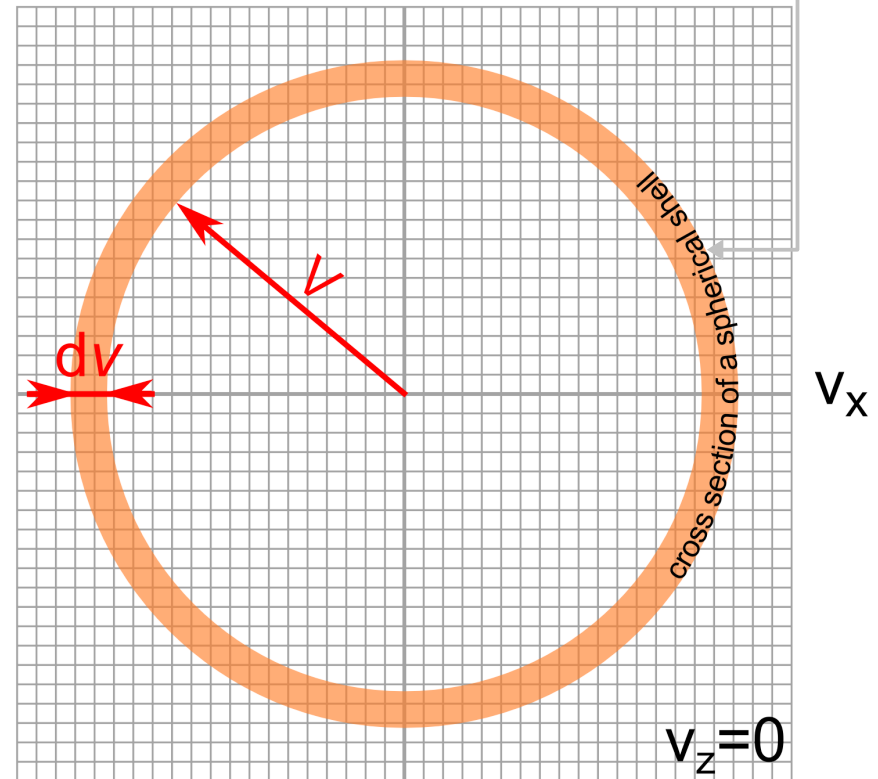
In velocity space the volume corresponding to velocities between v and $v+dv$ is given by

$$dw = \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-m \frac{v^2}{2kT}} 4\pi v^2 dv = \left(\frac{4v^2}{\sqrt{\pi}} \right) \left(\frac{m}{2kT} \right)^{3/2} e^{-m \frac{v^2}{2kT}} dv = f(v) dv$$

$d\Omega = 4\pi v^2 dv$
area of the spherical shell

$$f(v) = \frac{4v^2}{\sqrt{\pi}} \left(\frac{m}{2kT} \right)^{3/2} e^{-m \frac{v^2}{2kT}}$$

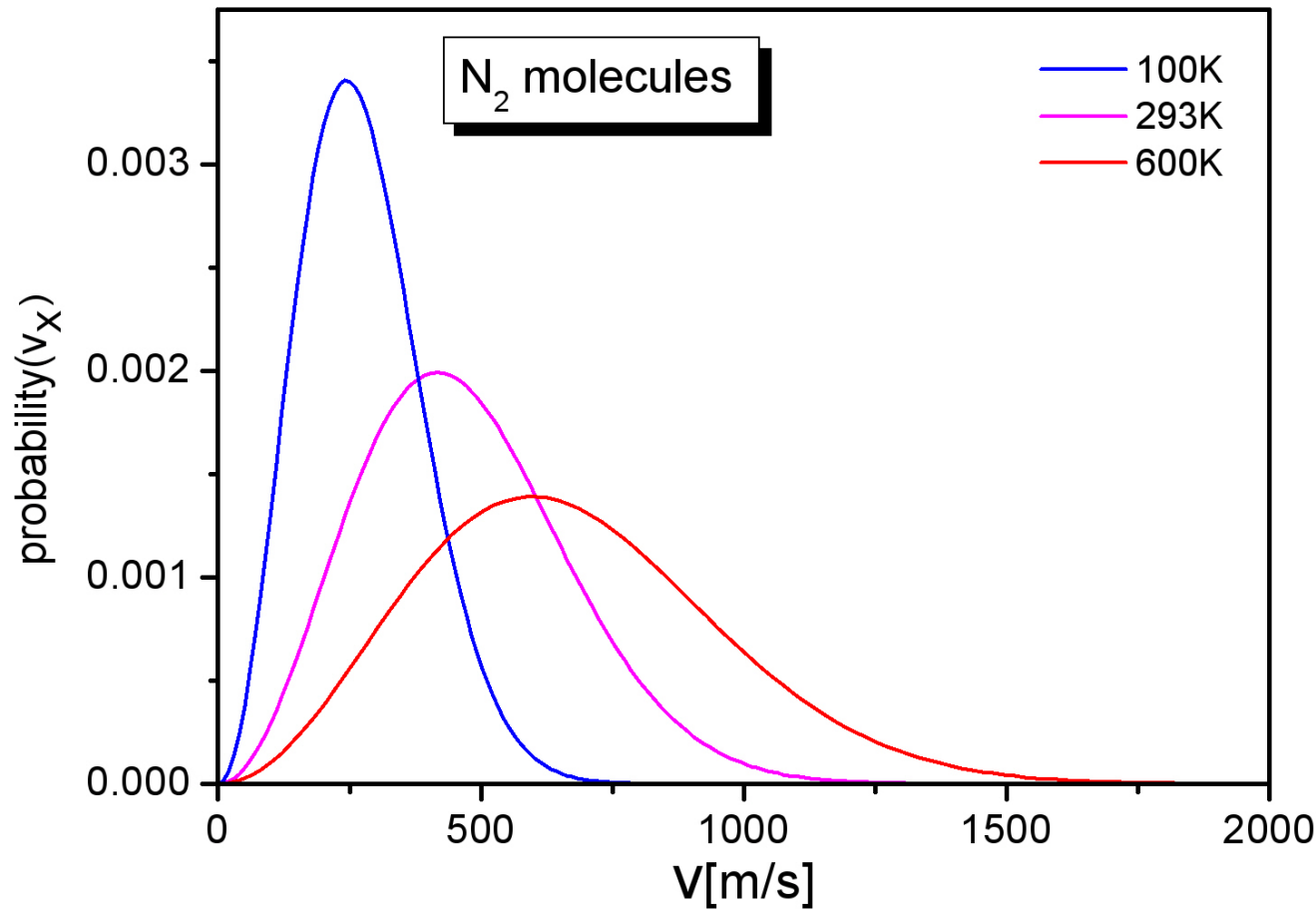
Boltzmann velocity distribution



Introduction

$$f(v) = \frac{4v^2}{\sqrt{\pi}} \left(\frac{m}{2kT} \right)^{3/2} e^{-m \frac{v^2}{2kT}}$$

Boltzmann velocity distribution

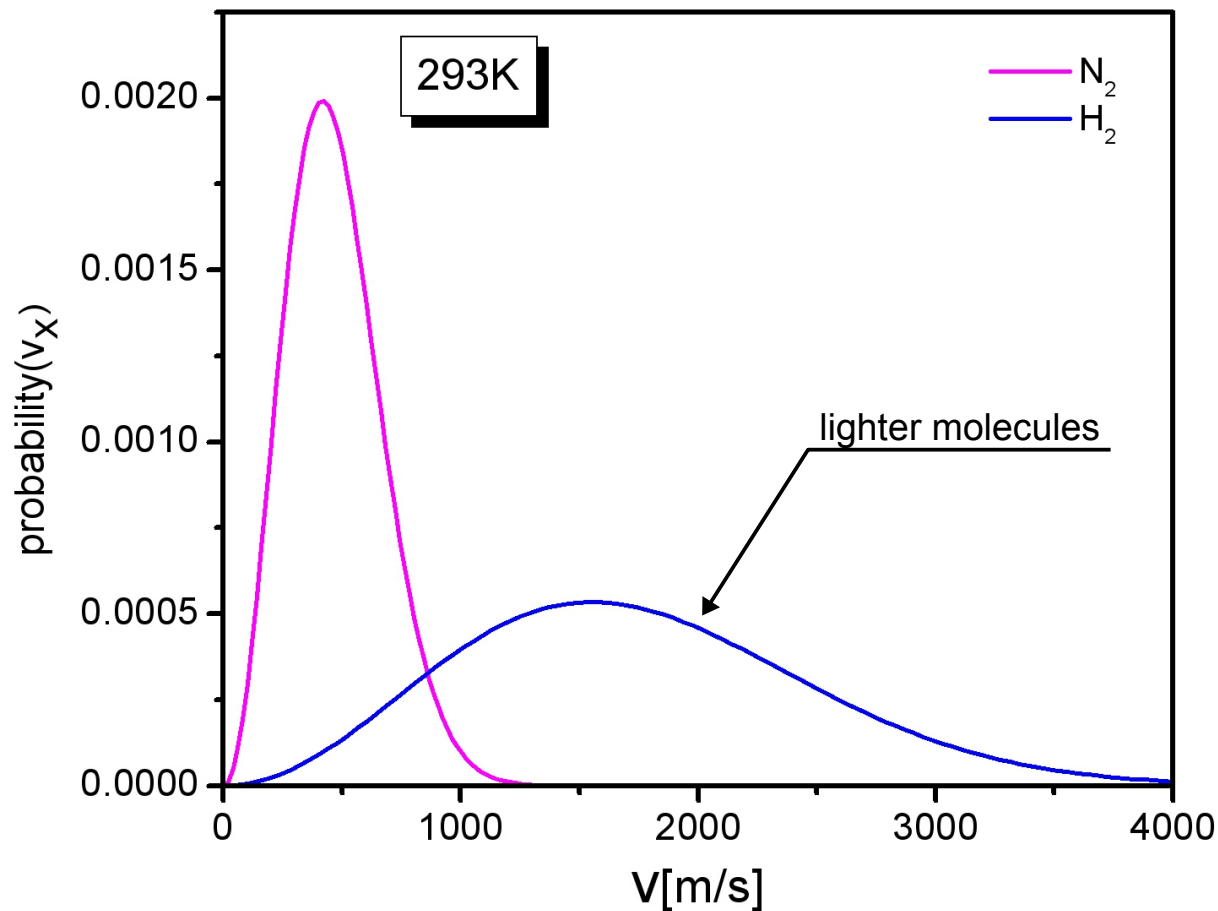


- With increasing temperature the velocity distribution spreads towards higher velocities

Introduction

$$f(v) = \frac{4v^2}{\sqrt{\pi}} \left(\frac{m}{2kT} \right)^{3/2} e^{-m \frac{v^2}{2kT}}$$

Boltzmann velocity distribution



- At given temperature lighter molecules attain higher speed

Introduction

Basic parameters of Boltzmann velocity distribution [1,2]:

- Average speed:

$$\bar{v} = \int_0^{\infty} v f(v) dv = \sqrt{\frac{8kT}{\pi m}}$$

- Average kinetic energy of the molecule:

$$\bar{E} = \frac{m}{2} \bar{v}^2 = \int_0^{\infty} v^2 f(v) dv = \frac{3}{2} kT \quad \rightarrow \quad \bar{v}^2 = \frac{3kT}{m}$$

- Most probable speed (the maximum of probability):

$$v_{max} = \sqrt{\frac{2kT}{m}}$$

For Boltzmann distribution we have (general property):

$$v_{max} : \bar{v} : \sqrt{\bar{v}^2} = 1 : \frac{2}{\sqrt{\pi}} : \sqrt{\frac{3}{2}} \approx 1 : 1.128 : 1.225$$

$$f(v) = \frac{4v^2}{\sqrt{\pi}} \left(\frac{m}{2kT} \right)^{3/2} e^{-m \frac{v^2}{2kT}}$$

Boltzmann velocity distribution

Introduction

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$$f(v) = \frac{4v^2}{\sqrt{\pi}} \left(\frac{m}{2kT} \right)^{3/2} e^{-m \frac{v^2}{2kT}}$$

Boltzmann velocity distribution

The number of molecules in a cubic meter of the ideal gas is (from the idea-gas law):

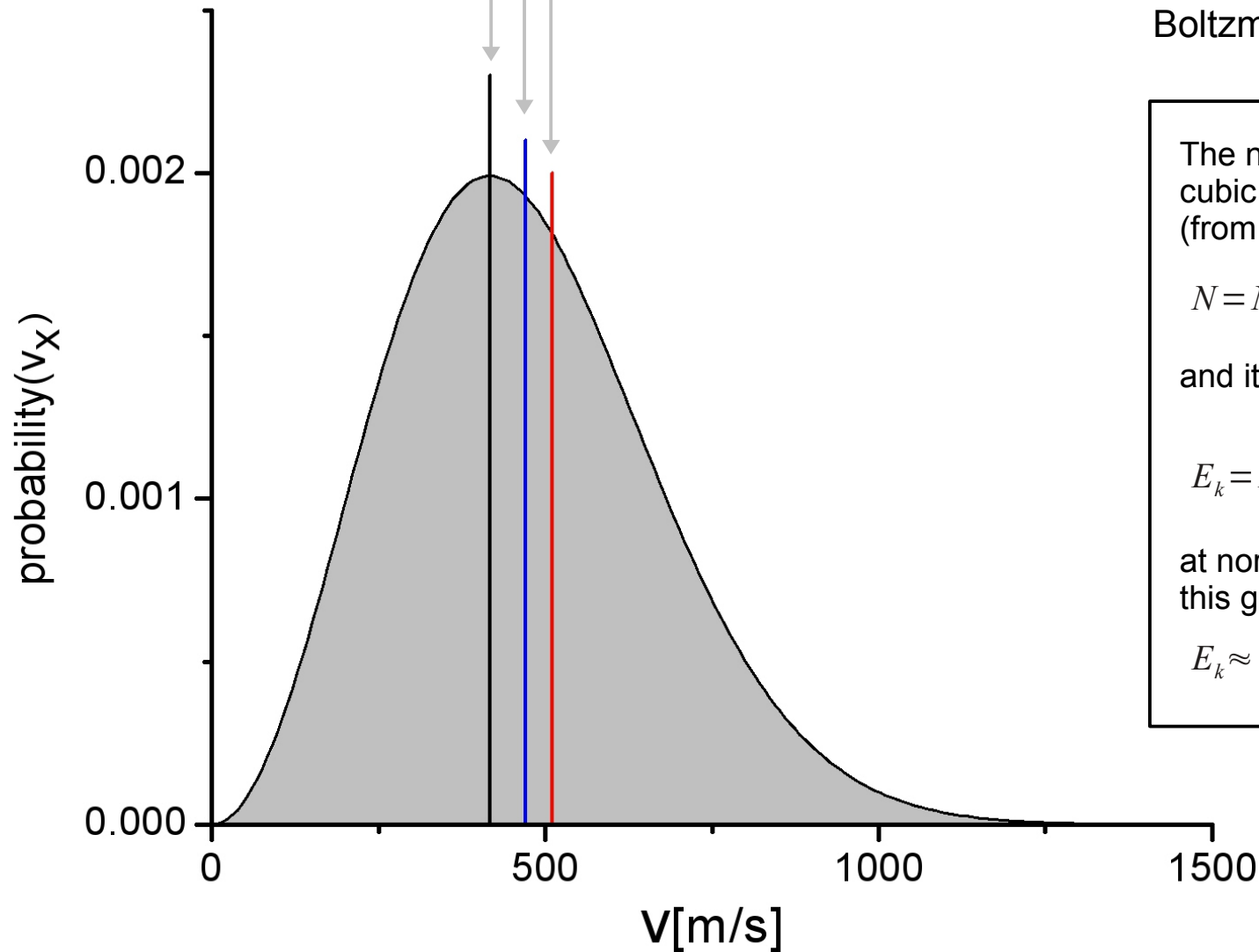
$$N = N_A \frac{pV}{RT} = N_A \frac{p}{RT}$$

and its kinetic energy is:

$$E_k = N \bar{E} = \frac{3N_A p k}{2R}$$

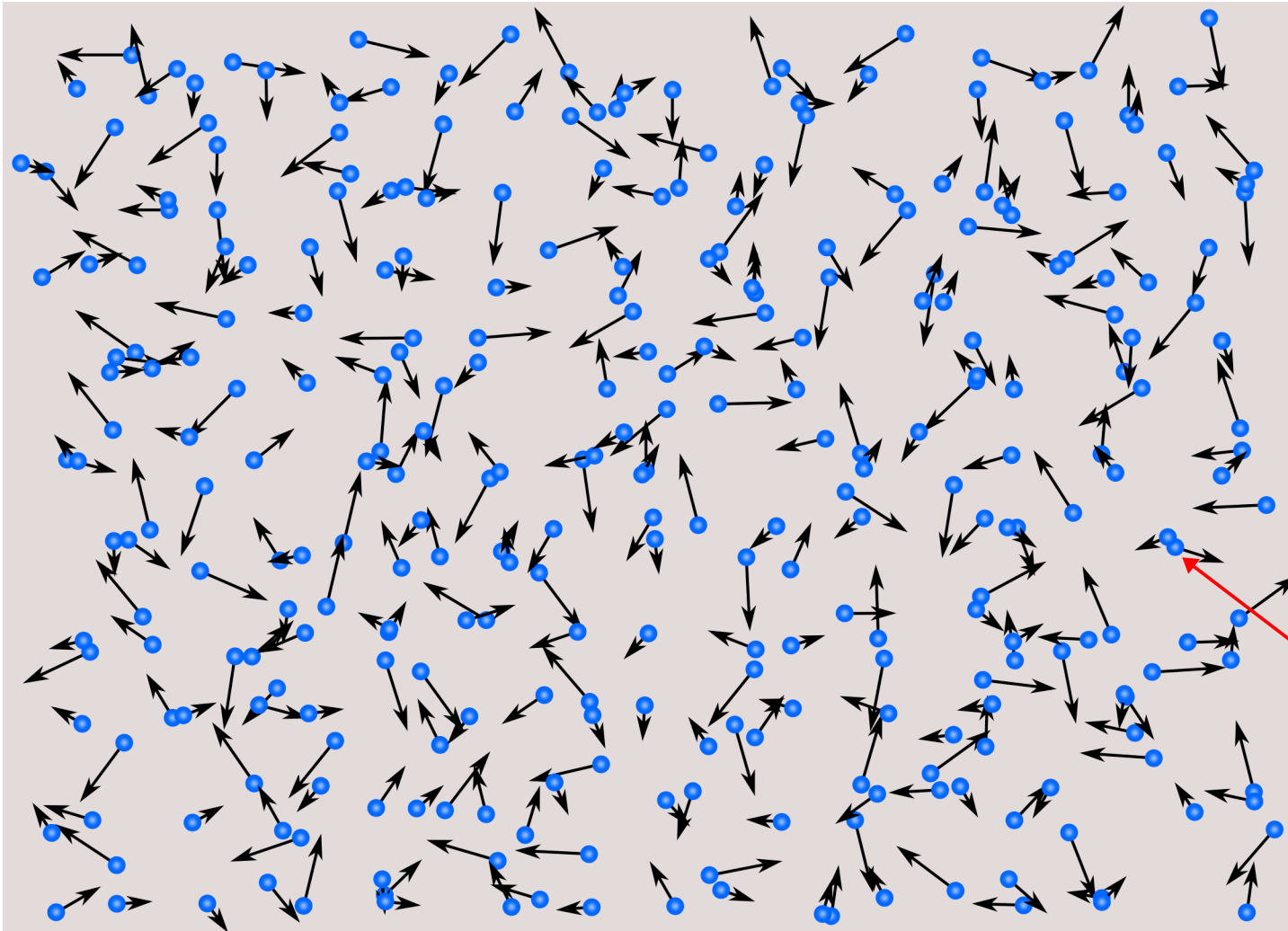
at normal pressure (1000 hPa)
this gives:

$$E_k \approx 150 \text{ kJ}$$



Introduction

- Till now we discussed the properties of the ideal gas
- In real gases the size of molecules and interactions between them introduce new phenomena and change properties



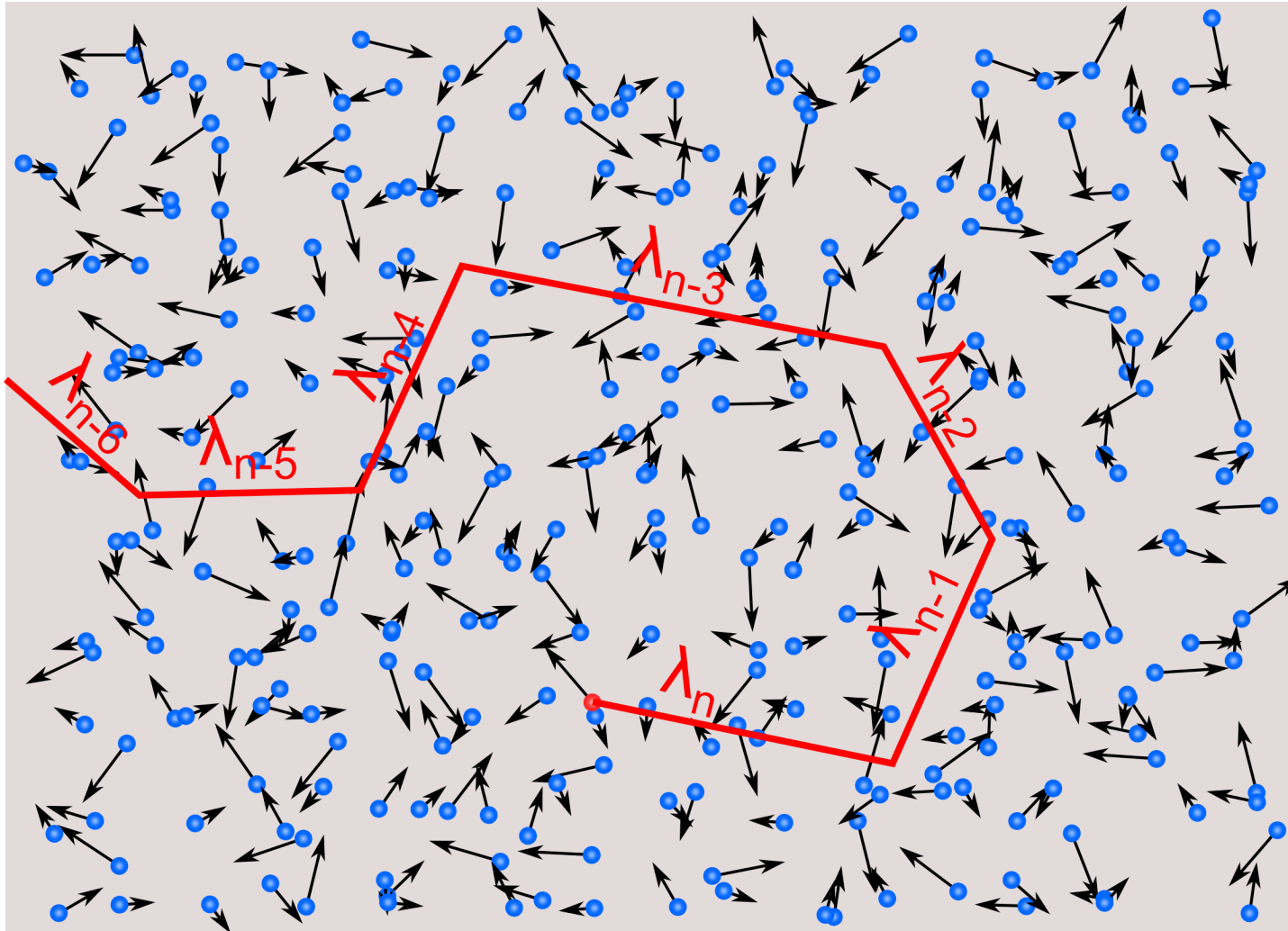
Ideal gas:

- the interactions between the molecules can be neglected
- the size of molecules is small in comparison to the average intermolecular distance

collision

Introduction

- If one follows the path of a single molecule in the real gas it turns out that it consists of a number of more or less straight sections*
- The abrupt changes of the direction of motion of the molecule are associated with collisions with other molecules



The average distance covered by a particle between consecutive collisions is called mean free path (mfp or λ_{mfp})

$$\lambda_{mfp} = \frac{1}{n} \sum_n \lambda_n$$

*the sections are not straight due to interactions of the molecule with the rest of gas through electromagnetic interactions

Introduction

- the probability of collision is higher the higher the concentration and/or sizes of the molecules [3]
- the effective diameter of the atom/molecule is larger than the atomic size (diameter of the electron valence orbits d_0); for qualitative analysis it can be assumed that the effective cross section is:

$$A = \pi d_0^2$$

- It can be shown that mfp can be expressed as [3]:

$$\lambda = \frac{1}{\sqrt{2} \pi d_0^2 N}$$

N – number of molecules in unit volume

- In practice one is often interested in pressure and temperature dependence of the mfp:

$$N = \frac{n N_A}{V} = \frac{N_A P}{RT} \quad \leftarrow \quad pV = nRT$$

$$\lambda = \frac{R}{\sqrt{2} \pi N_A d_0^2 p} \approx 3.11 \times 10^{-24} \frac{T}{d_0^2 p}$$

- For a nitrogen molecule ($d_0 \approx 0.11 \text{ nm}$) at normal pressure (1000 hPa) and room temperature the equation gives mfp of **750 nm**.

Introduction

$$\lambda = \frac{R}{\sqrt{2}\pi N_A} \frac{T}{d_0^2 p} \approx 3.11 \times 10^{-24} \frac{T}{d_0^2 p}$$

vacuum	pressure [Pa]	mfp [m]	collision frequency* [Hz]
low	10^5	7.5×10^{-7}	6×10^8
medium	10^2 10^{-1}	7.5×10^{-1}	6×10^2
high	$< 10^{-6}$	$> 7.5 \times 10^4$	6×10^{-3}

$$\leftarrow f_{collision} := \frac{\bar{v}}{\lambda}$$

vacuum terminology

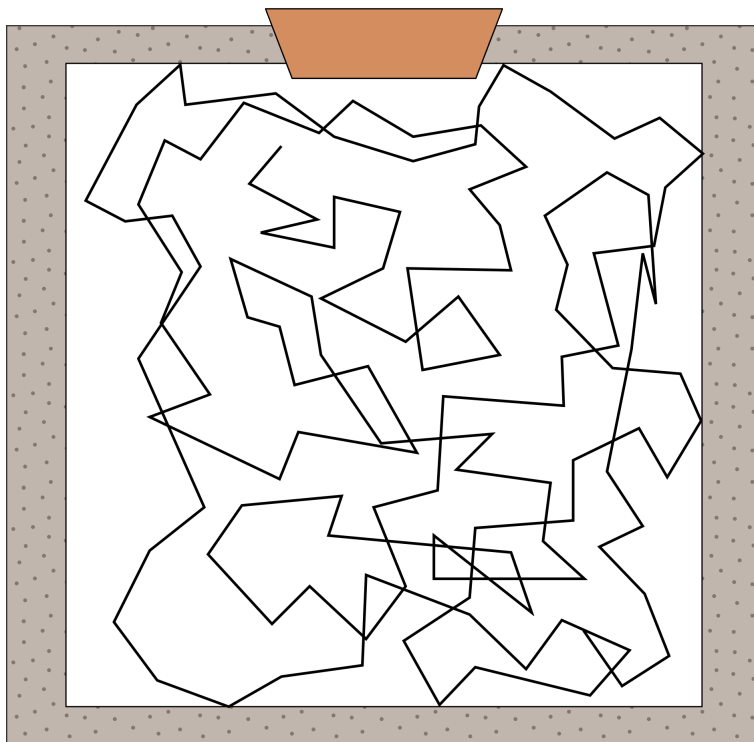
for nitrogen molecules at room temperature
 *for average speed of 470 m/s

- Note that in high vacuum the mfp exceeds ten kilometers.
- For other molecules present in air the values are of the same order.

Introduction

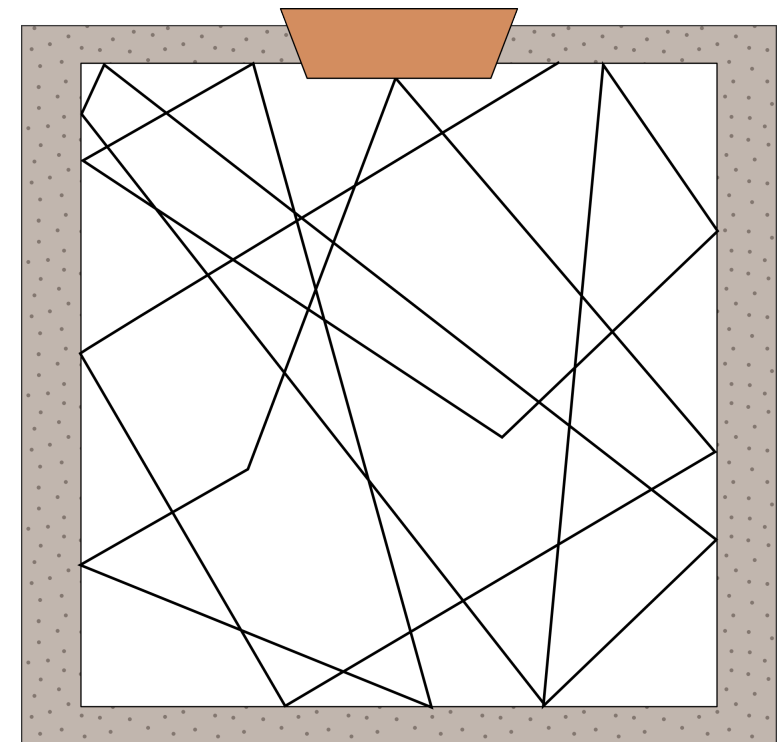
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- In low vacuum the molecules collide mainly with other gas molecules
- In high vacuum the molecules collide mainly with the walls of the vacuum chamber



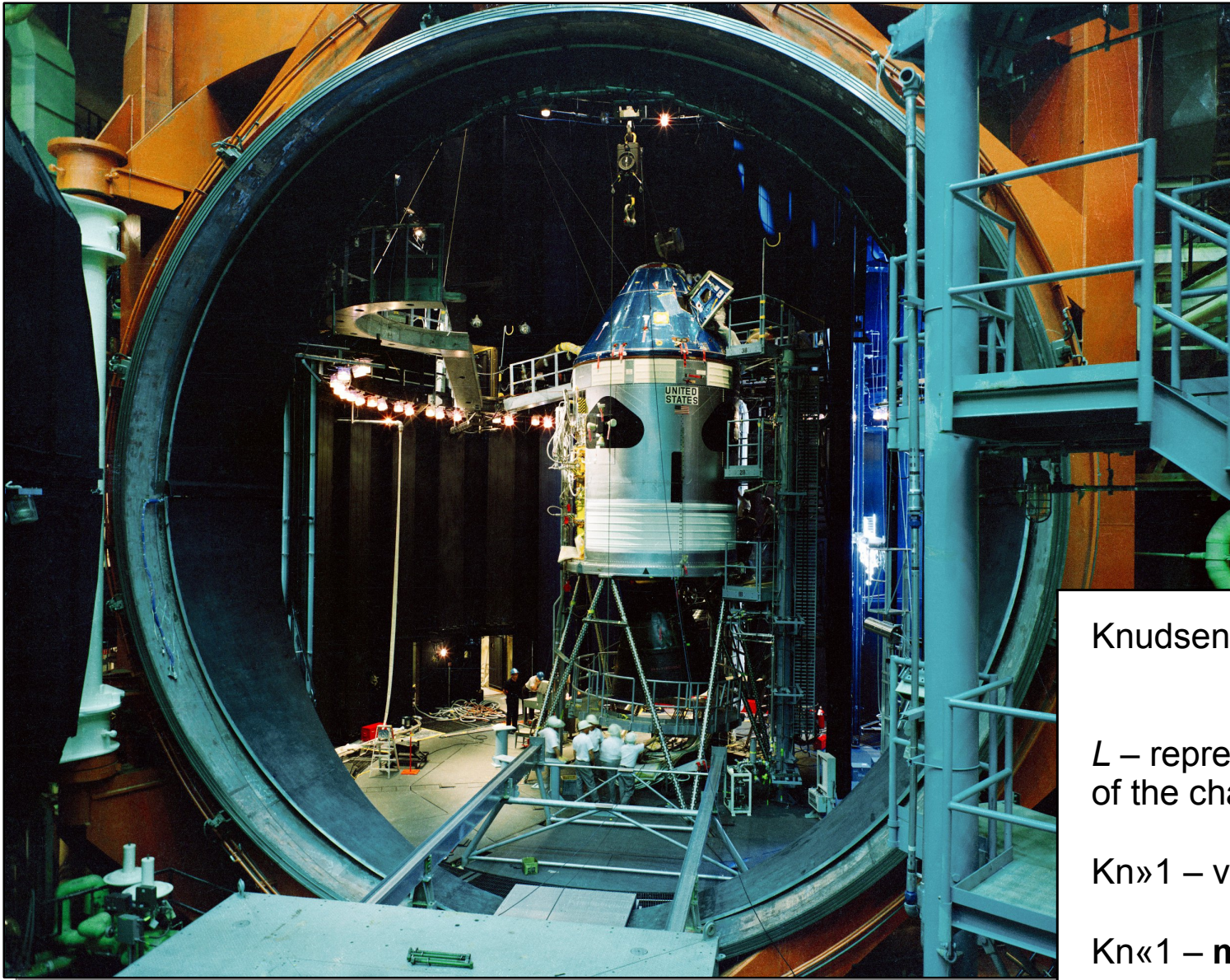
low vacuum

the line shows the trajectory of a single particle



high vacuum

Introduction



Vacuum chambers are usually less than 1m in diameter. The big ones are exceptions.

image source: NASA, USA

Knudsen number:

$$K_n = \frac{L}{\lambda_0}$$

L – representative length scale of the chamber, vessel, pipe etc.

$Kn \gg 1$ – viscous conditions

$Kn \ll 1$ – **molecular** conditions

Space Environment Simulation Laboratory at NASA's Johnson Space Center in Houston

Introduction

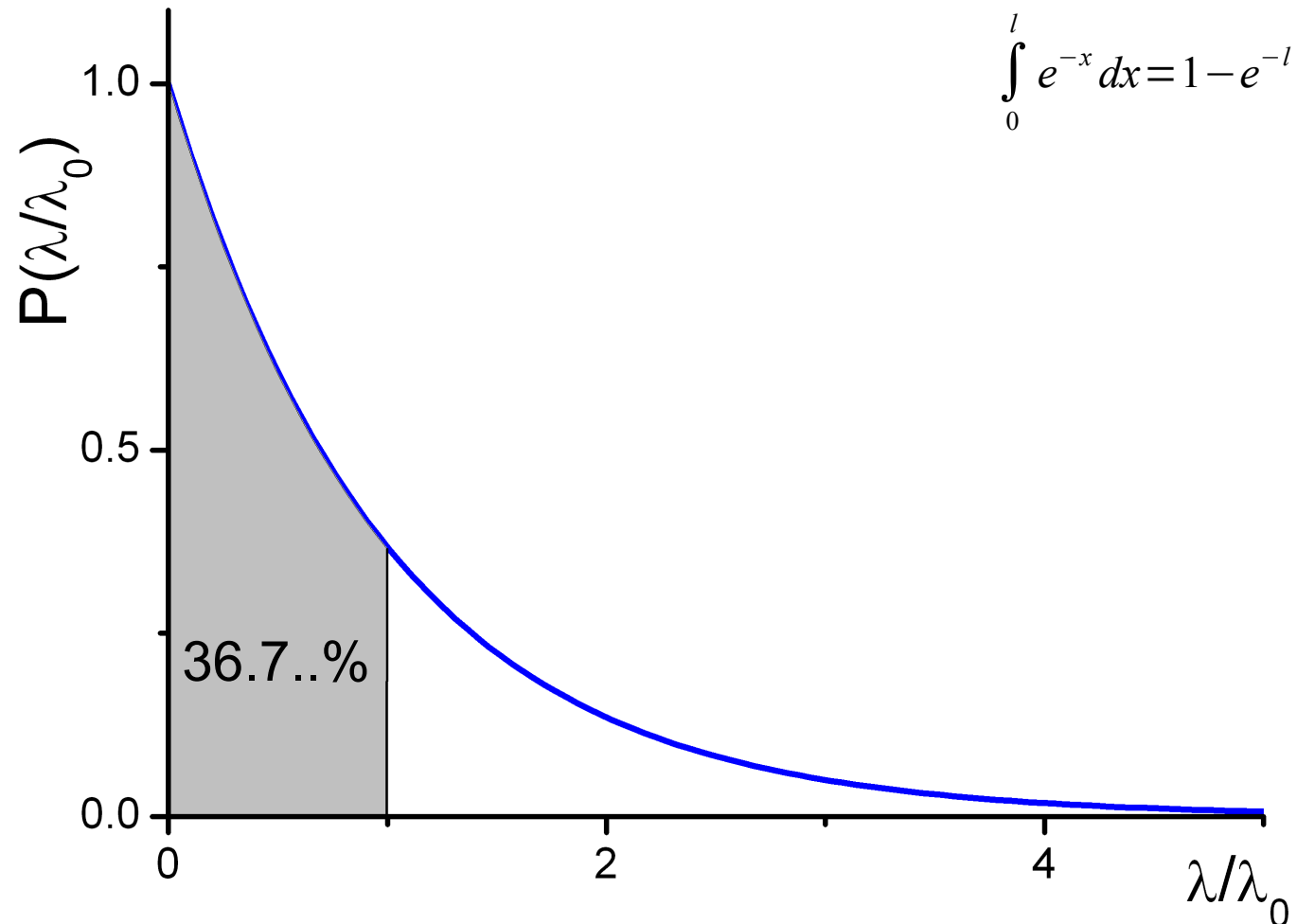
The mean free path is a statistical quantity – the actual distance traveled by a molecule between consecutive collisions is governed by probability too.

The probability that a molecule of a gas with mean free path λ_0 travels a distance λ between two consecutive collisions is approximately given by [3]:

$$P\left(\frac{\lambda}{\lambda_0}\right) = \exp\left(-\frac{\lambda}{\lambda_0}\right)$$

$$\int_0^l e^{-x} dx = 1 - e^{-l}$$

Some 37% of distances traveled by the gas molecules between consecutive collisions is less than mfp.



Introduction

Diffusion coefficient

Fick's law describes the number of particles v_D crossing the unit area of the surface which is perpendicular to the diffusion direction [3]

$$v_D = D \frac{dn}{dx}$$

$\frac{dn}{dx}$ -concentration gradient

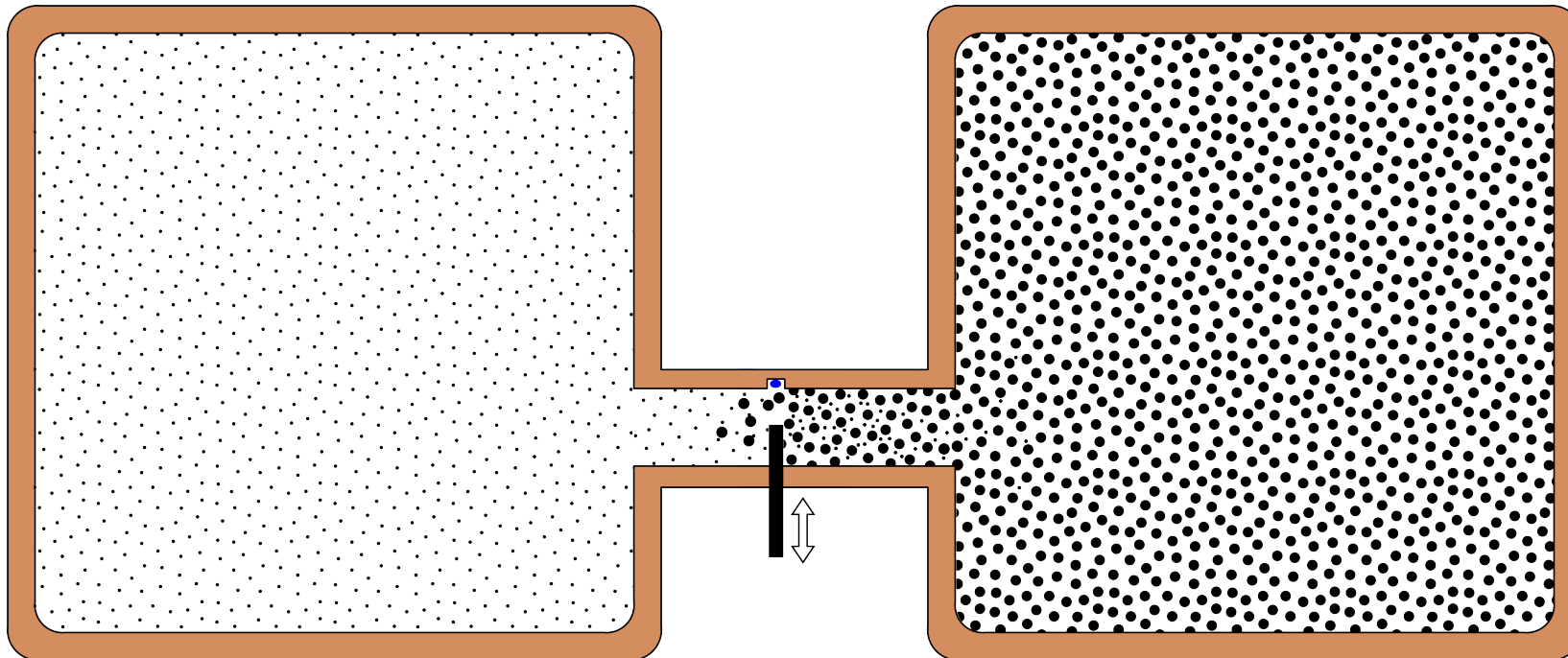
D -diffusion coefficient

It can be shown [3] that diffusion coefficient can be approximated by the expression:

$$D = \frac{1}{3} \lambda \bar{v}$$

\bar{v} -average speed of gas molecules

λ -mean free path



Introduction

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\bar{v} -average speed of gas molecules

λ -mean free path

which is valid for the mixture of two gases if the concentration of one of them is much lower than that of the other one. Substituting the expressions for mfp and the average velocity we obtain:

$$D \propto \frac{1}{d_0^2 \sqrt{m}} \frac{T^{3/2}}{p}$$

$$\lambda = \frac{R}{\sqrt{2} \pi N_A d_0^2 p} \frac{T}{d_0^2 p}$$

$$\bar{v} = \sqrt{\frac{8kT}{\pi m}}$$

- The diffusion is faster in higher temperature and lower pressure
- The diffusion is faster for smaller and/or lighter molecules

d_0 diameter of the electron valence orbits

Introduction

Diffusion coefficients for different gases in air [5] at $p=p_1+p_2=1013$ hPa at 273 K.

gas	H ₂	He	N ₂	O ₂	Ar
D [10 ⁻⁴ m ² /s]	0.661	0.57	0.18	0.1775	0.16

Because of high diffusion coefficient helium is utilized for leak detection (it diffuses relatively easily in metals too)

$$D \propto \frac{1}{d_0^2 \sqrt{m}} \frac{T^{3/2}}{p}$$

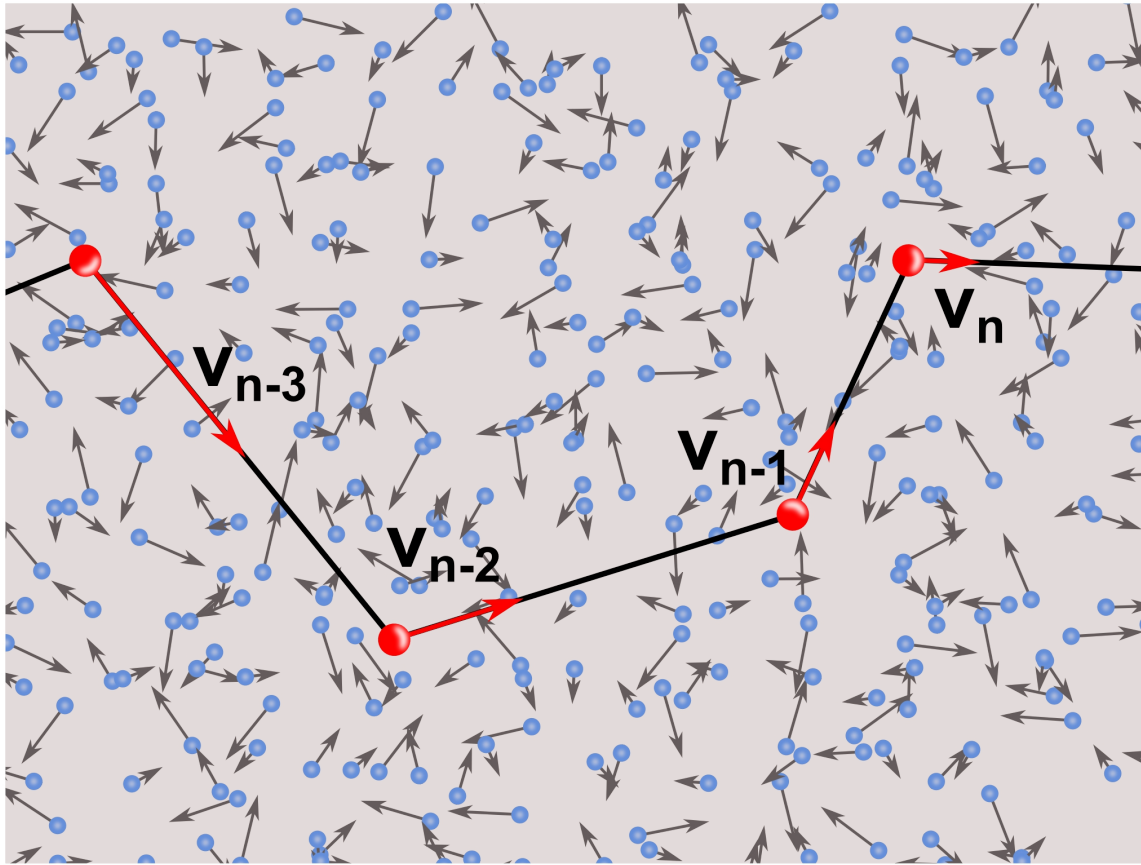
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Introduction

Thermalization “is defined as the process in which an energetic particle loses most of its initial energy through collisions with background thermal atoms” [6]



$$v_{n-3} > v_{n-2} > v_{n-2} > v_n \approx \bar{v}$$

Thermalization is important in thin film deposition methods involving the use of plasma – **sputtering**.

Introduction

Thermalization “is defined as the process in which an energetic particle loses most of its initial energy through collisions with background thermal atoms” [6]

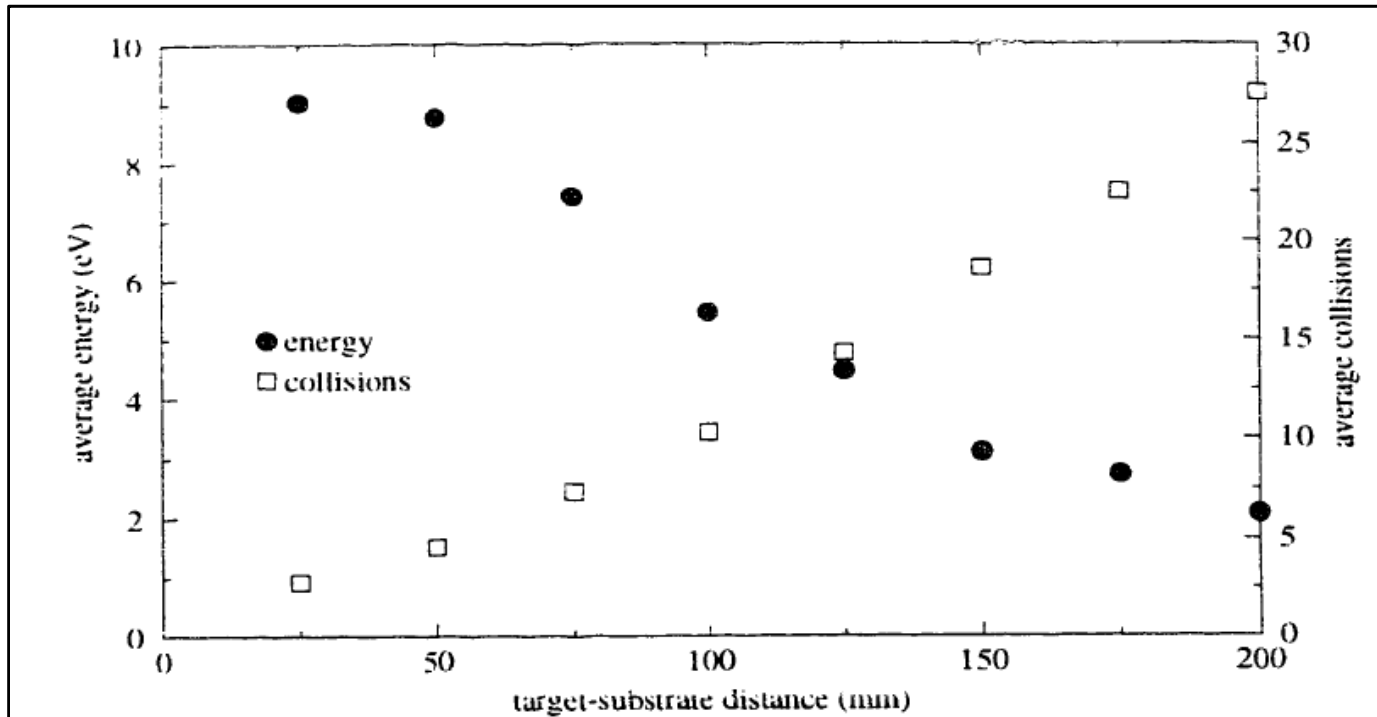


Figure 3.24: The effect of target-substrate distance on the average adatom energy (left axis) and average number of collisions with gas molecules (right axis).

molecules increases. The number of collisions is not linear with distance because, as the energy decreases, so does the mean free path between collisions due to the energy dependence of the collision cross-section.

image source: Processes and simulation for advanced integrated circuit metallization S.K. Dew, thesis Alberta 1992

Physical vapor deposition

Number of gas molecules impinging on unit area of the wall in 1s (**impingement rate**) is given by [5]*:

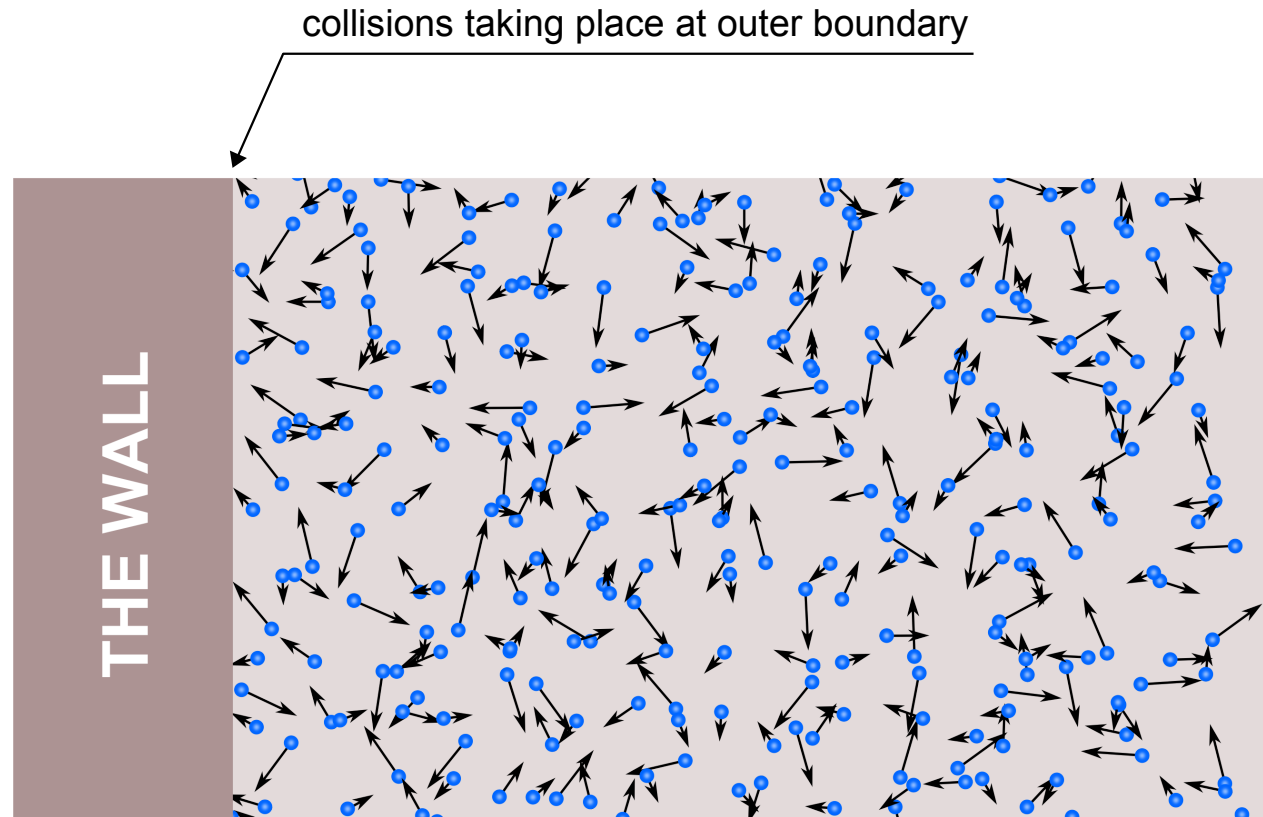
$$v = \frac{1}{4} n \sqrt{\frac{8 k_B T}{\pi m}}$$

$$v = p \sqrt{\frac{1}{2\pi m k_B T}}$$

- v - collision frequency
- n - number of molecules
- m - particle mass

For nitrogen molecules at RT and normal pressure we get:

$$v \approx 2.9 \times 10^{27} \text{ Hz/m}^2$$



*the equation is obtained from Boltzmann speed distribution and geometrical considerations

Physical vapor deposition

What time is needed to deposit one monolayer of adatoms on a clean surface*?

Let us assume that atoms spacing (nearest neighbor, regular grid) is 0.3nm (typical value for metal surfaces); than we have approx. 1.1×10^{19} sites per square meter (z).

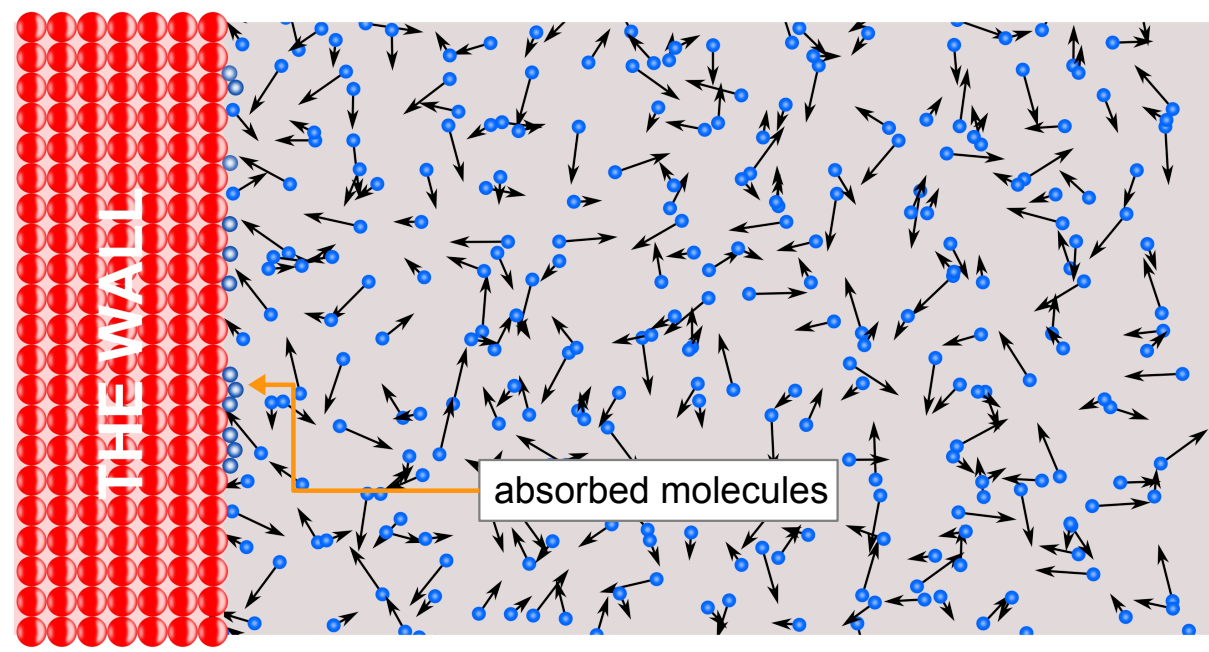
This would give the monolayer formation time (for nitrogen, at RT, and normal pressure):

$$t_{ML} = \frac{z}{v} \approx 4 \text{ ns} \quad !!!!!!!!!!!!!$$

In real systems only a fraction, usually small, of the impinging atoms sticks to the surface. The phenomenon is phenomenologically described by a **sticking coefficient s** which gives the fraction of molecules/atoms absorbed on the surface to the number of impingements.

Sticking coefficient depends on (among others):

- material and kind of surface (roughness, pollution, finish, texture)
- temperature of surface and of gas
- pressure
- coverage
- gas composition

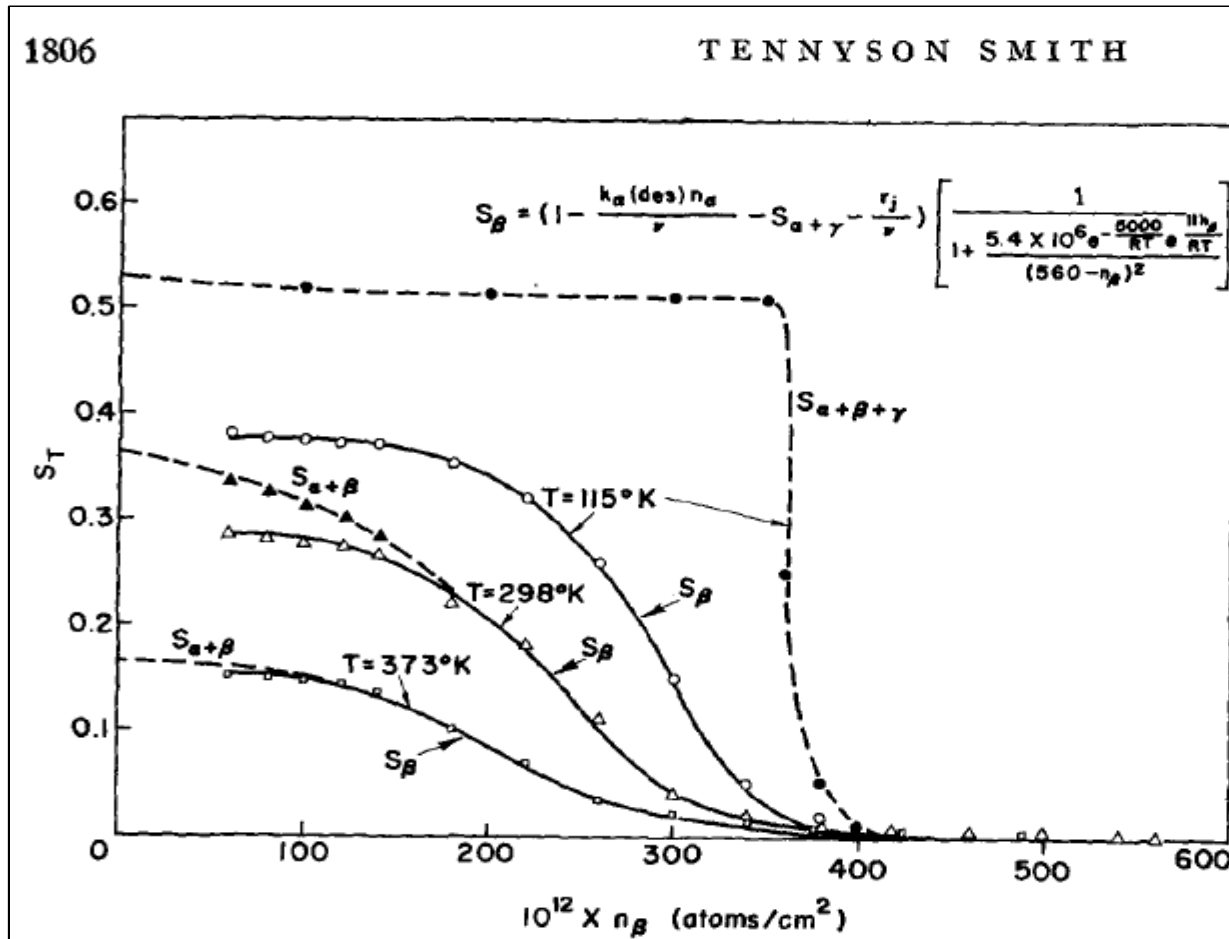


*this does not take into account the adsorption coefficient (not every molecule striking the surface sticks to it!)

Physical vapor deposition

Sticking coefficient tends to decrease, or goes to zero for some molecule/substrate pairs (see below), as the coverage (the number of already absorbed molecules) increases

For typical atmospheric gases the initial sticking coefficient (for zero coverage) is several tenths.



N on W
 $s \leq 1$

FIG. 1. Sticking coefficients for nitrogen on tungsten as a function of surface coverage of atomic nitrogen in the β state. The experimental points were taken from Ehrlich's⁷ Fig. 7, the solid lines are theoretical using Eq. (17).

Physical vapor deposition

From previous slides we have for the **monolayer formation time**:

$$t_{ML} = s z \frac{\sqrt{2 \pi m k_B T}}{p}$$

←

$$v = \frac{p}{\sqrt{2 \pi m k_B T}}, \quad t_{ML} = \frac{z}{v}$$

$$t_{ML} \propto \frac{1}{p}$$

vacuum	pressure [Pa]	t_{ML} [s]*
low	10^5	8×10^{-9}
medium	10^2 10^{-1}	8×10^{-3}
high	$< 10^{-6}$	$> 8 \times 10^2$

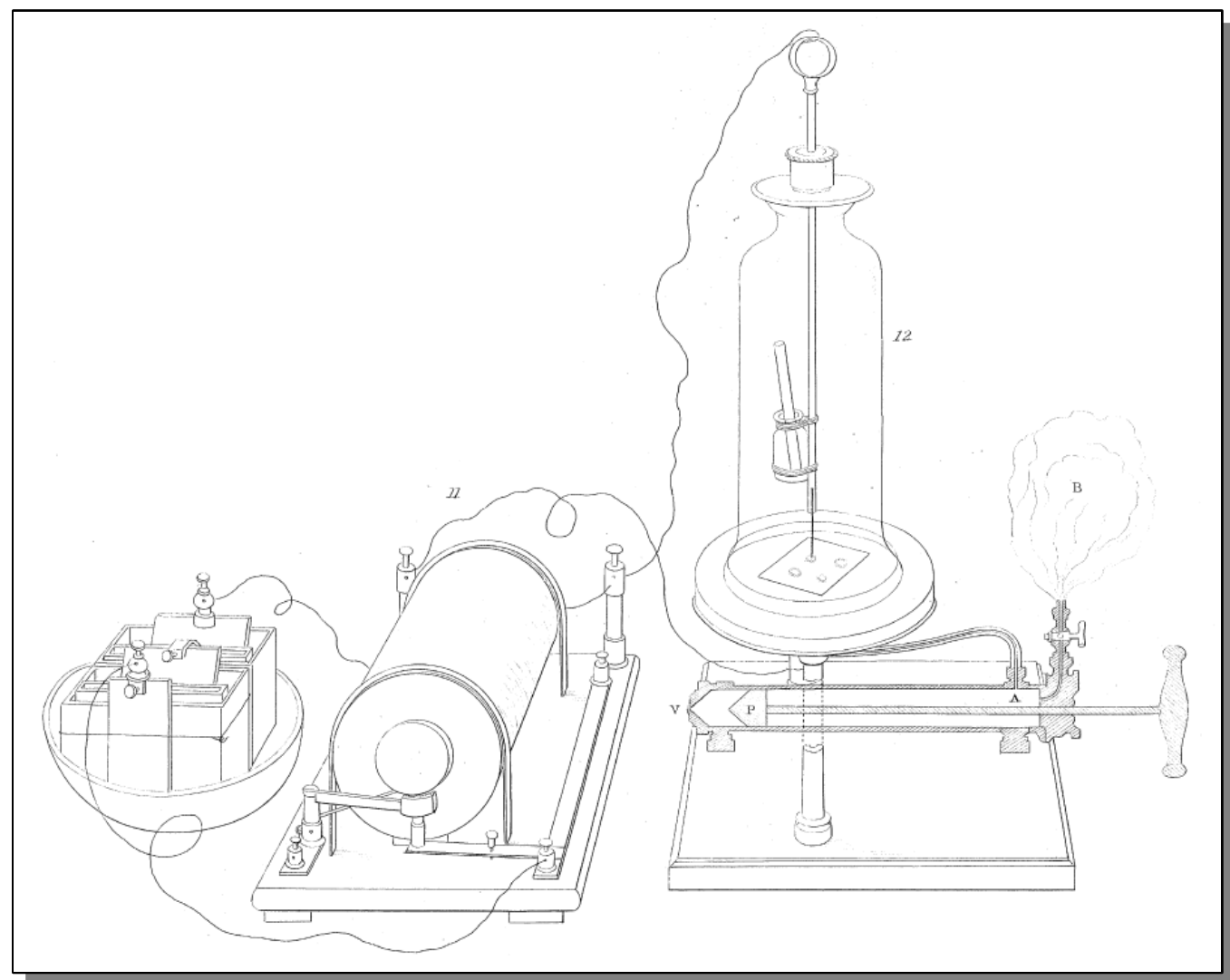
typical deposition processes have a duration of 100-1000s and one monolayer of material is deposited in some 1 -10s.
Monolayer of gas deposits in some 100s or more.

for nitrogen molecules at room temperature
*sticking coefficient 0.5

Only at sufficiently low pressure the contamination of the substrate/film by the rest gases can be reduced to acceptable levels.

Physical vapor deposition

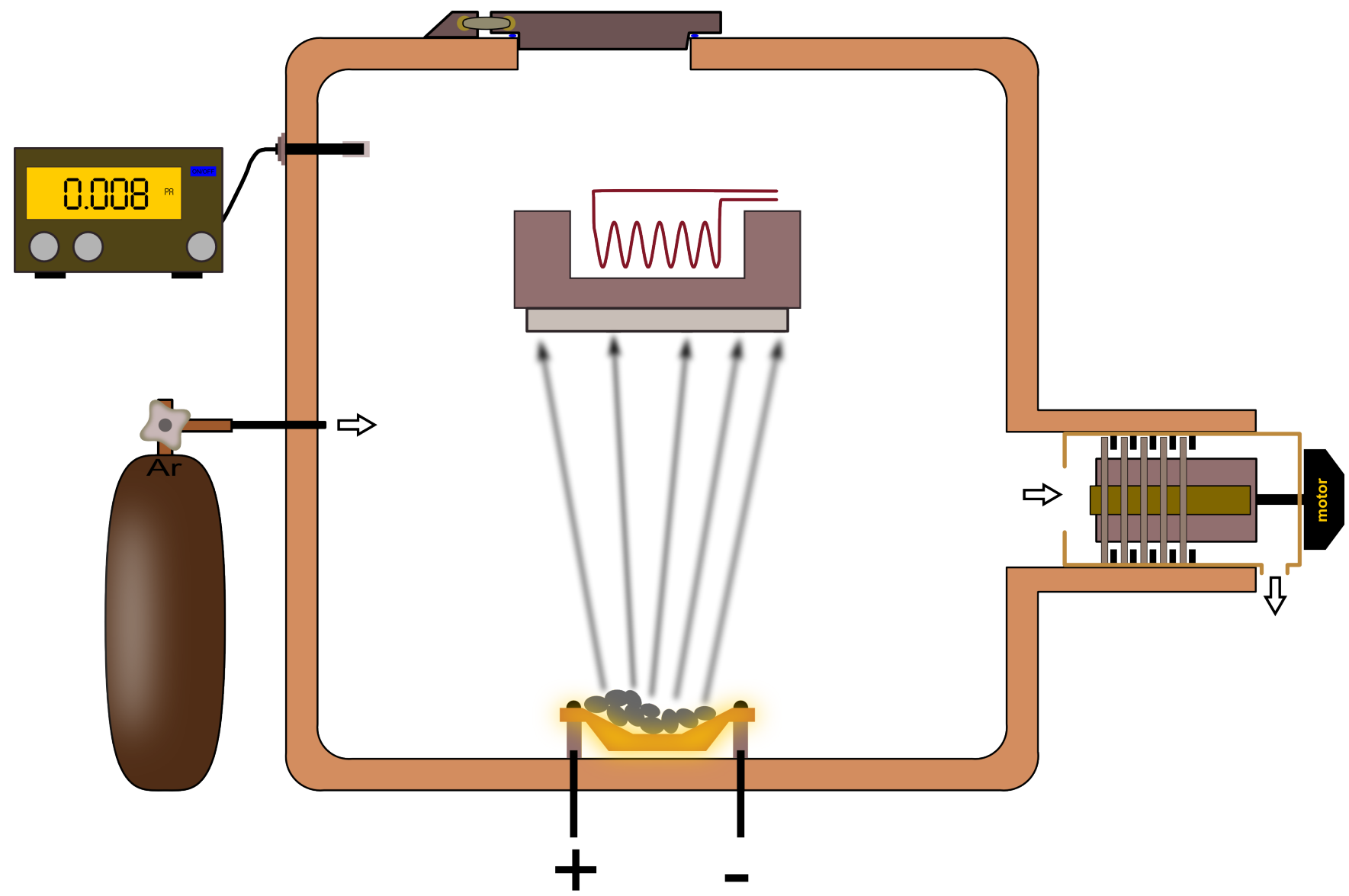
First observation of sputtering – Grove [7] - 1852



- $p \sim 1700 - 2500 \text{ Pa}$ [8]
- metallic needle close (0.5 to 2.5 mm) to metallic plate

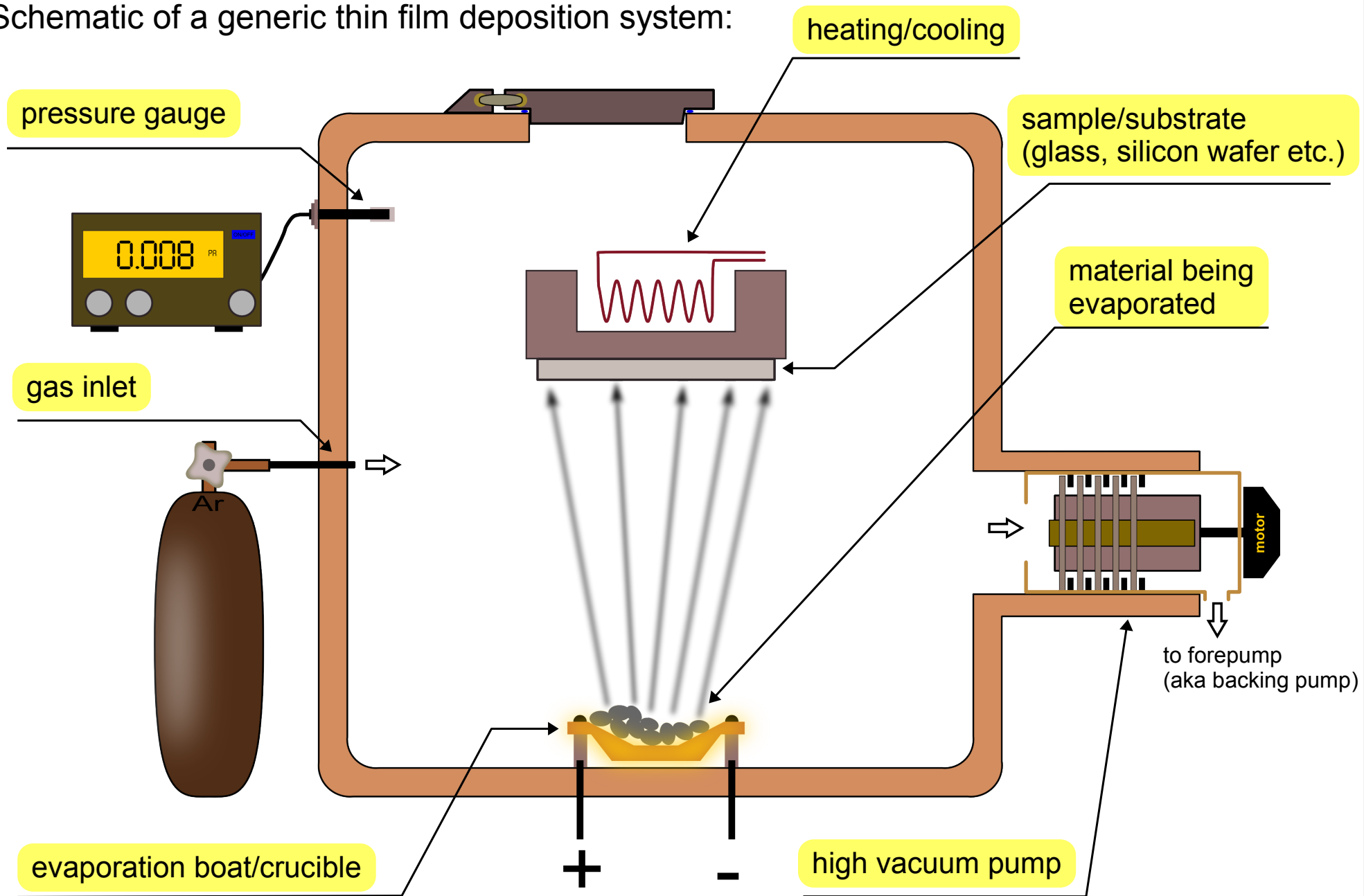
Physical vapor deposition

Schematic of a generic thin film deposition system:



Physical vapor deposition

Schematic of a generic thin film deposition system:

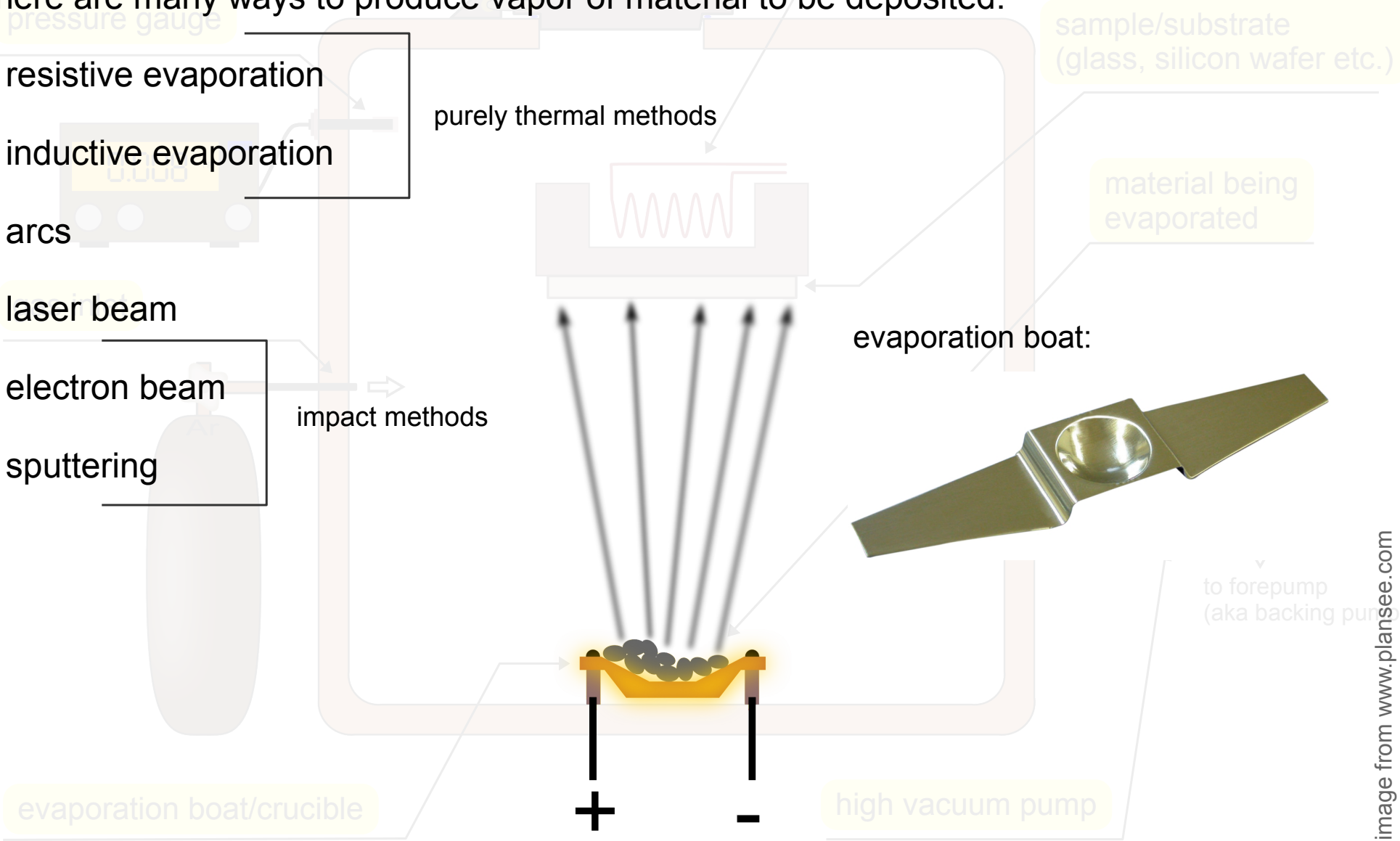


Physical vapor deposition

In today's talk we are interested only in the ways to produce the metallic/molecular vapor* in the process chamber - **vaporization**.

There are many ways to produce vapor of material to be deposited:

- resistive evaporation
- inductive evaporation
- arcs
- laser beam
- electron beam
- sputtering



* British spelling is vapour

Physical vapor deposition

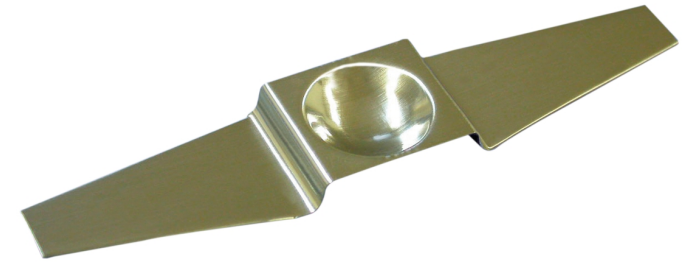
Thermal vaporization

Evaporation boats are usually manufactured from refractory metals (molybdenum, tungsten, tantalum):

- they have high melting temperature
- low reactivity with many materials used for deposition
- low vapor partial pressure

When choosing boat or crucible material both thermal and chemical compatibility with material to be vaporized.

Crucibles are useful when more material is to be vaporized or directional pattern of the evaporated atoms is desired.



Physical vapor deposition

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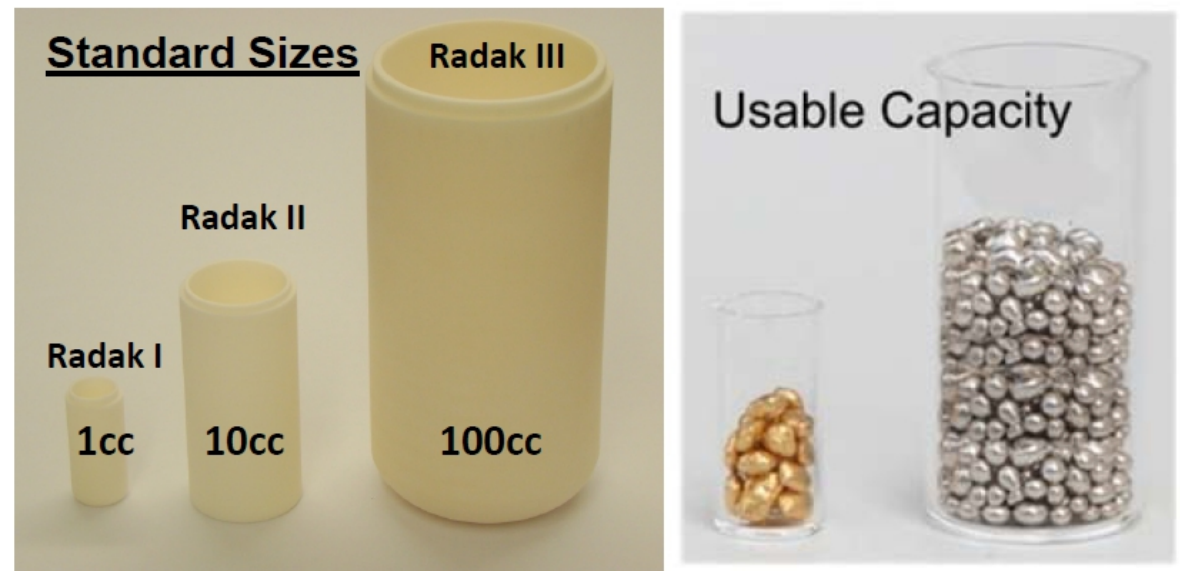


Figure 1 Left: Standard sizes with capacities of 1, 10, and 100cc respectively. Right: Recommended fill level is $\frac{3}{4}$ full.

Physical vapor deposition

Electron beam evaporation

- broad range of materials can be evaporated; $T > 3000\text{K}$
- reactive materials can be evaporated without heating the bulk of the evaporant and boats/crucibles – this reduces spurious chemical reactions
- path of electrons is controlled by magnetic field
- spot heating* prevents the chemical reactions between the ingot and the cooled holder

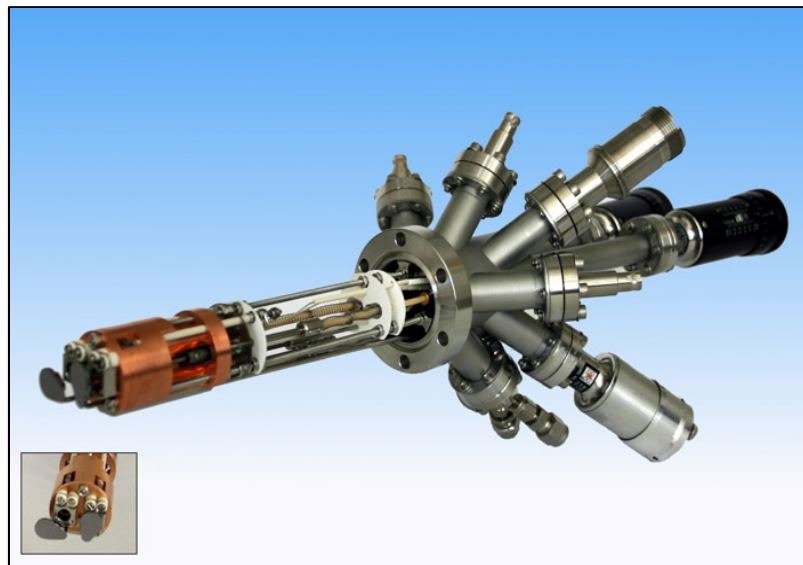
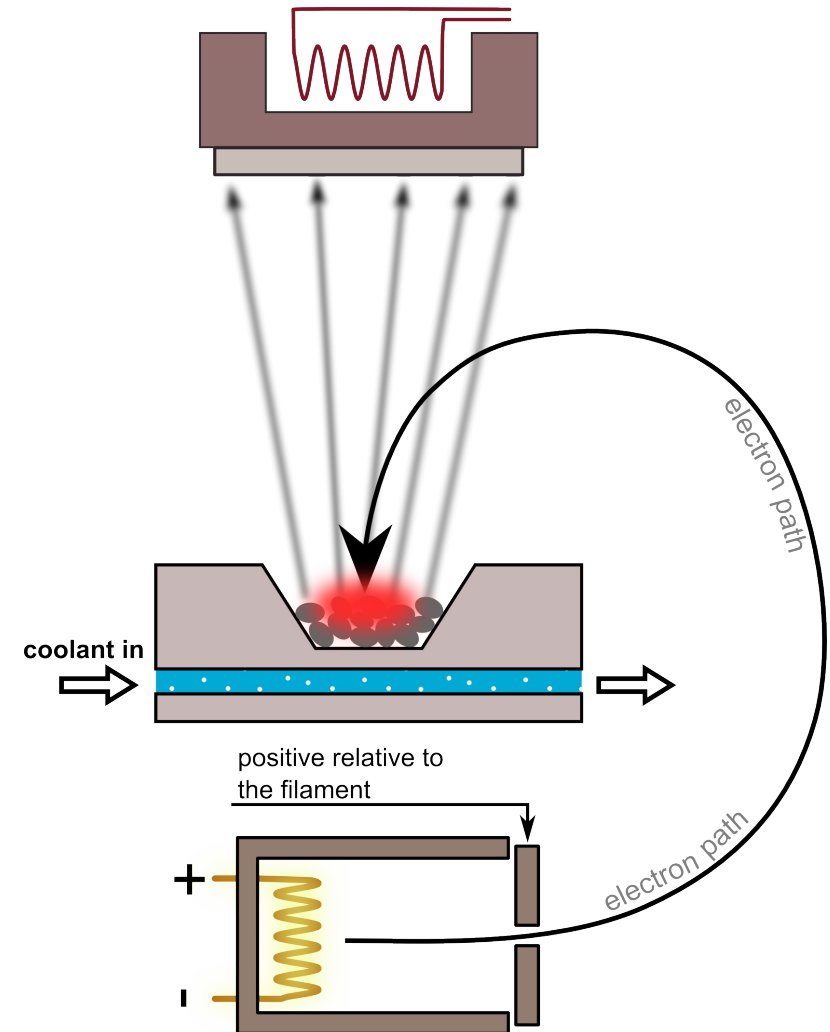


image from <http://www.tetra.de/e-flux4.htm>

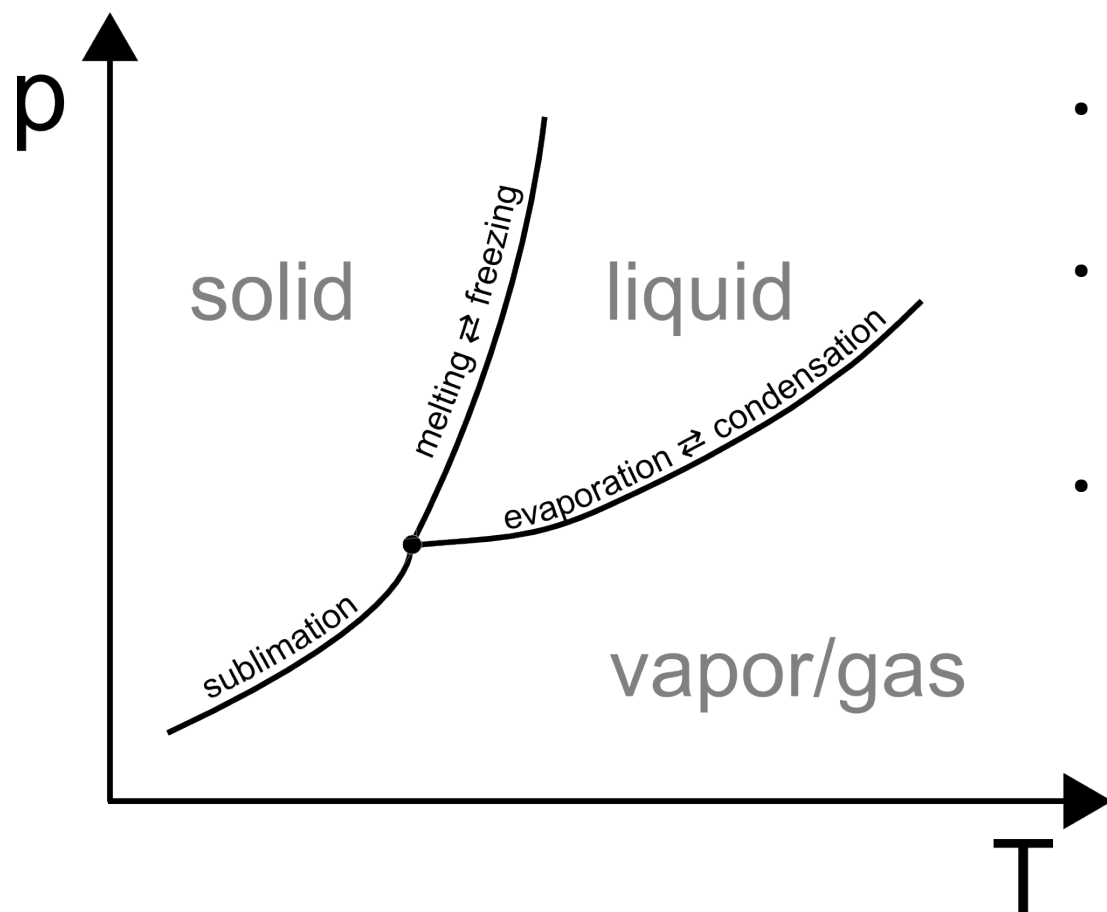


* only that spot is hot where the electrons fall

Physical vapor deposition

Vapor pressure

- a substance can exist in many phases (gas, liquid, solid phases) depending on pressure and temperature
- for every substance and temperature there is a vapor pressure at which the rate of sublimation/evaporation is equal to the rate of condensation



- Evaporation is a source of the condensate for thin films deposition
- Sublimation releases usually unwanted molecules to the process chamber
- Some films are manufactured by sublimation (Cr, Ti, Mo, Fe) [9]

Physical vapor deposition

Vapor pressure – **Clausius-Clapeyron equation** [10,11] describes the equilibrium curve in case of first order transition.

$$\frac{dp}{dT} = \frac{Q}{(V_2 - V_1)T} \quad *$$

Q - molar heat of transition from phase 1 to phase 2

V_i - molar volume of phase i ; phase 2 - vapor

In case of the evaporation/sublimation the volume of liquid (or solid) is negligibly small compared to the volume of vapor and the above equation simplifies to [10]:

$$\frac{dp}{dT} = \frac{Q}{V_2 T} \quad pV_2 = RT$$

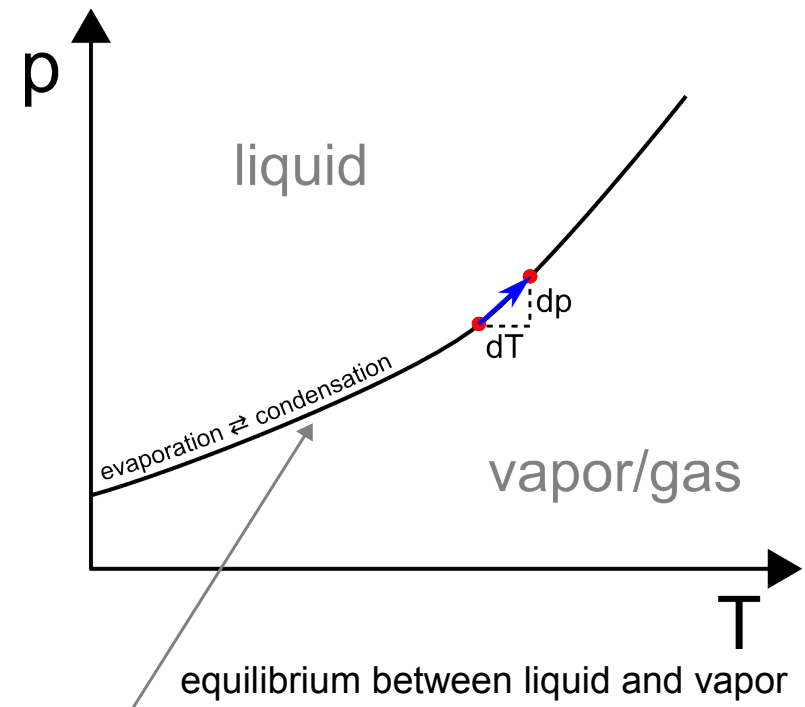
↑ assuming the vapor is the ideal gas

$$\frac{dp}{dT} = \frac{pQ}{RT^2} \quad \text{assuming } Q \text{ is constant}$$

$$\ln(p) = C_0 - \frac{Q}{RT}$$

$$p = p_0 e^{-\frac{Q}{RT}}$$

Vapor pressure is a very fast increasing function of temperature

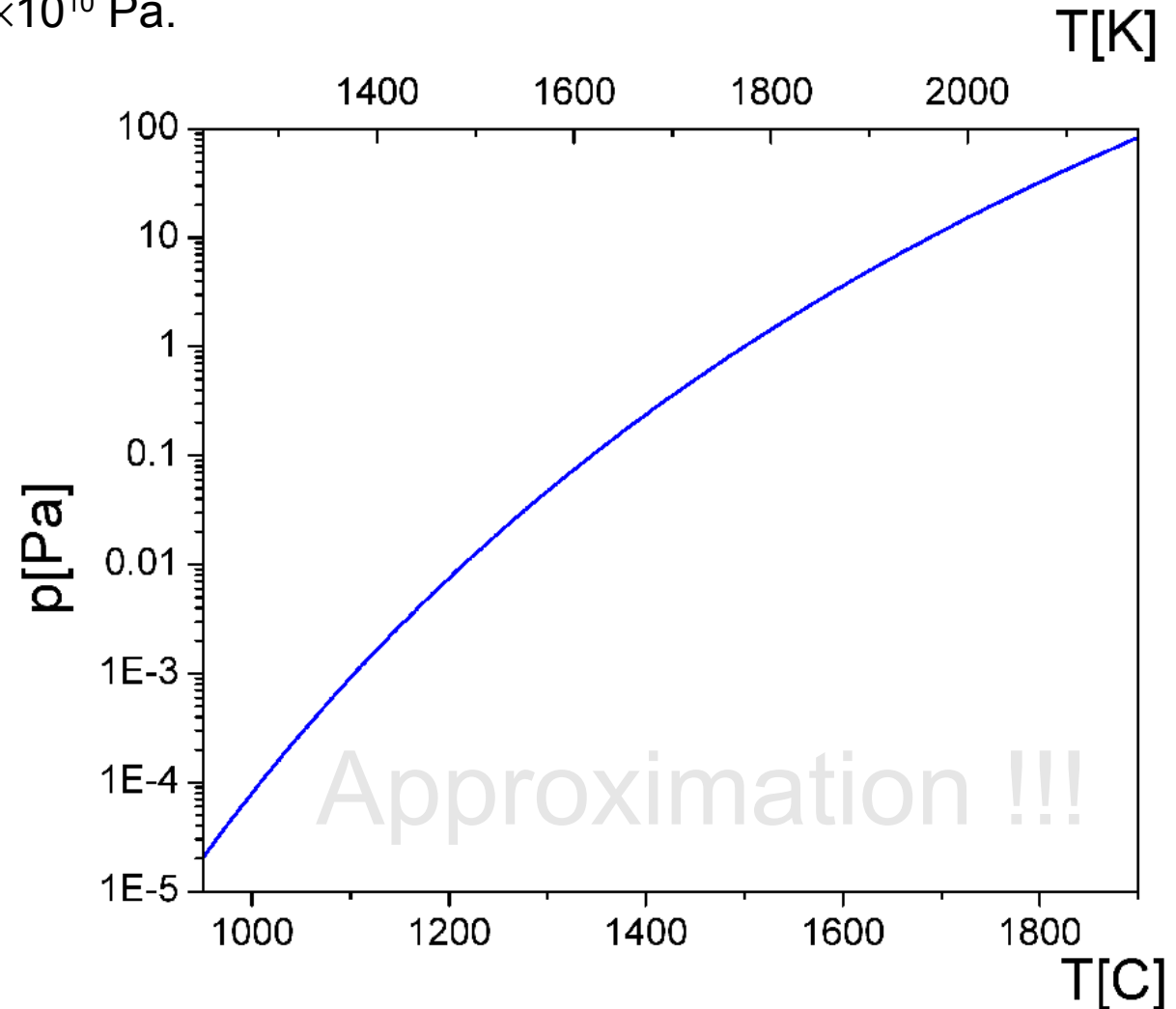


* to obtain the equilibrium curve from the equation the dependencies of molar volumes and Q on temperature must be known [10]

Physical vapor deposition

Vapor pressure of iron (molar heat of transition $Q=354$ kJ/mol [12]) calculated assuming constant Q with p_0 taken to be* 2.7×10^{10} Pa.

$$p = p_0 e^{-\frac{Q}{RT}}$$

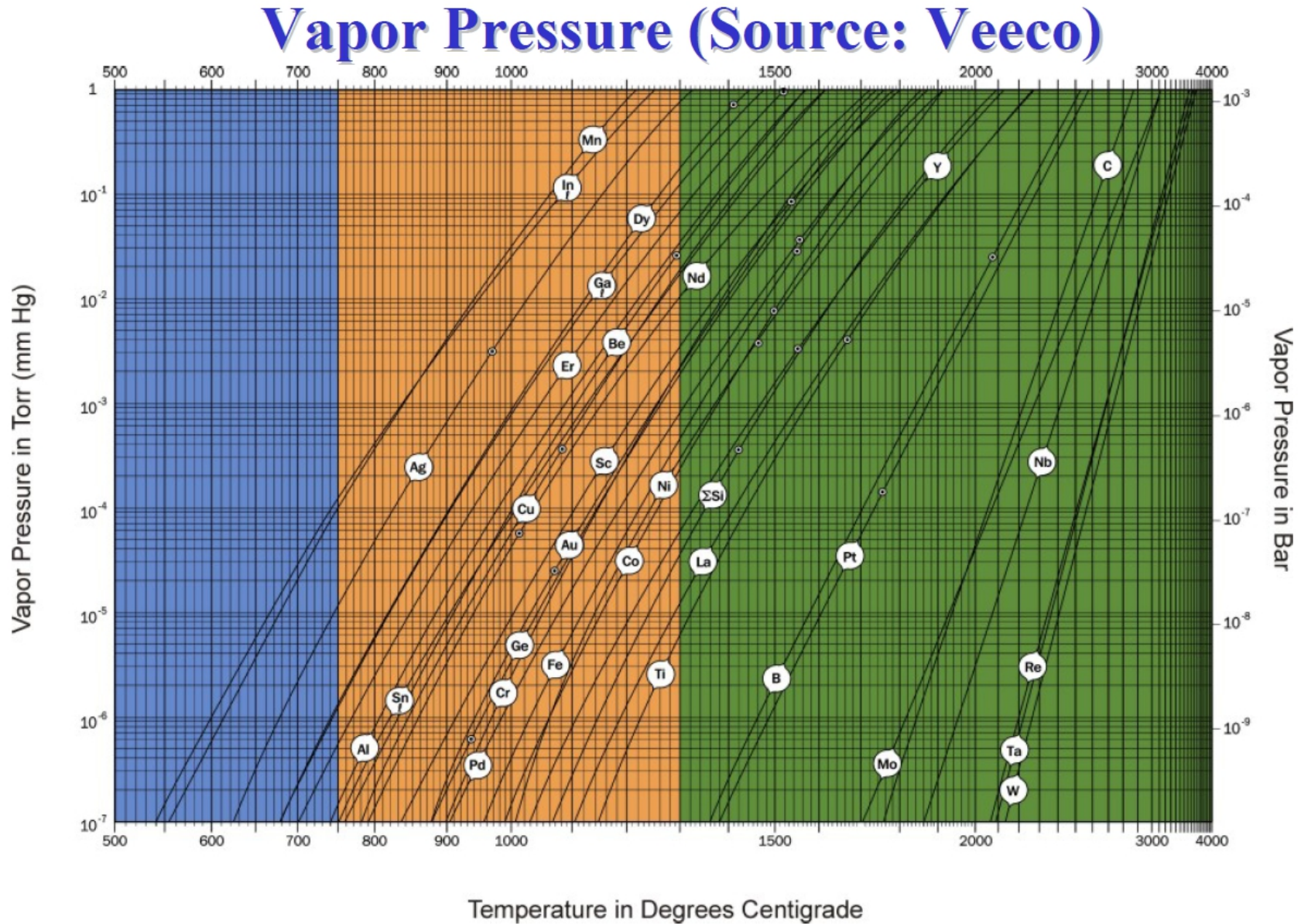


Vapor pressure is a very fast increasing function of temperature

* to get an agreement with experimental data

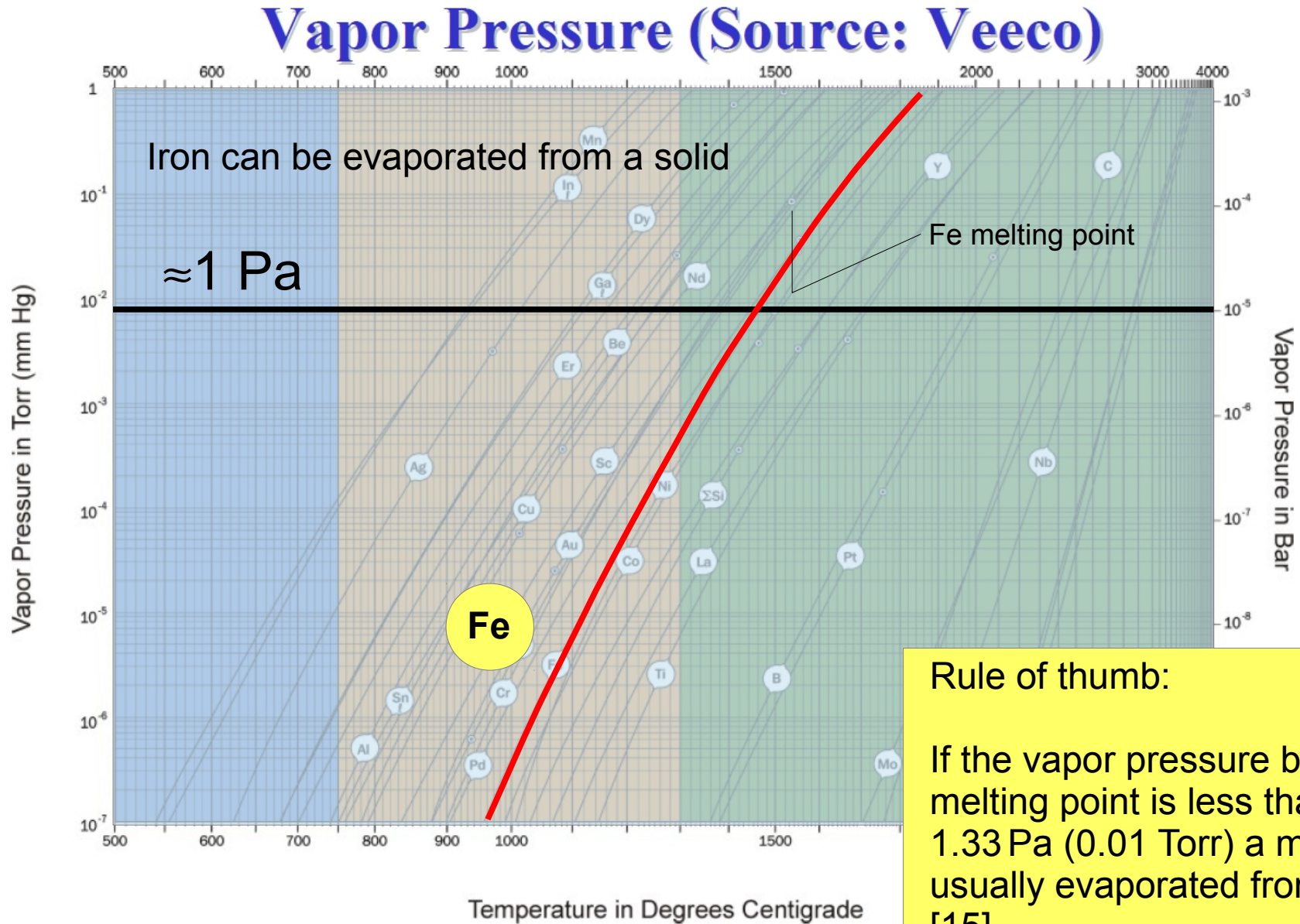
Physical vapor deposition

Vapor pressure of some elements.



Physical vapor deposition

Vapor pressure of some elements.



Rule of thumb:
 If the vapor pressure below melting point is less than 1.33 Pa (0.01 Torr) a material is usually evaporated from a melt [15]

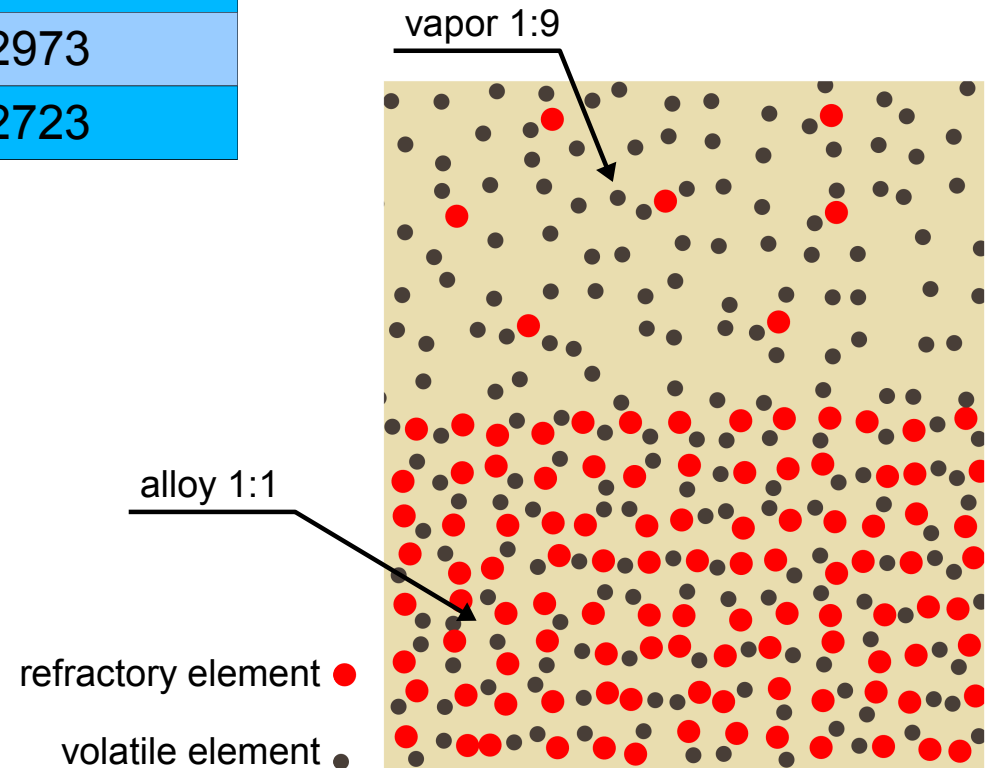
Physical vapor deposition

Melting and boiling temperatures of some metals [12,13]:

element	melting temperature [K]	boiling temperature* [K]
Fe	1808	3008
Co	1765	3153
Ni	1726	3073
Cu	1356	2863
Au	1336	2973
Al	933	2723

Zinc and cadmium, due to very high vapor pressure at low temperatures, **should be avoided** as a construction materials in vacuum systems (sample holders, manipulators etc.)

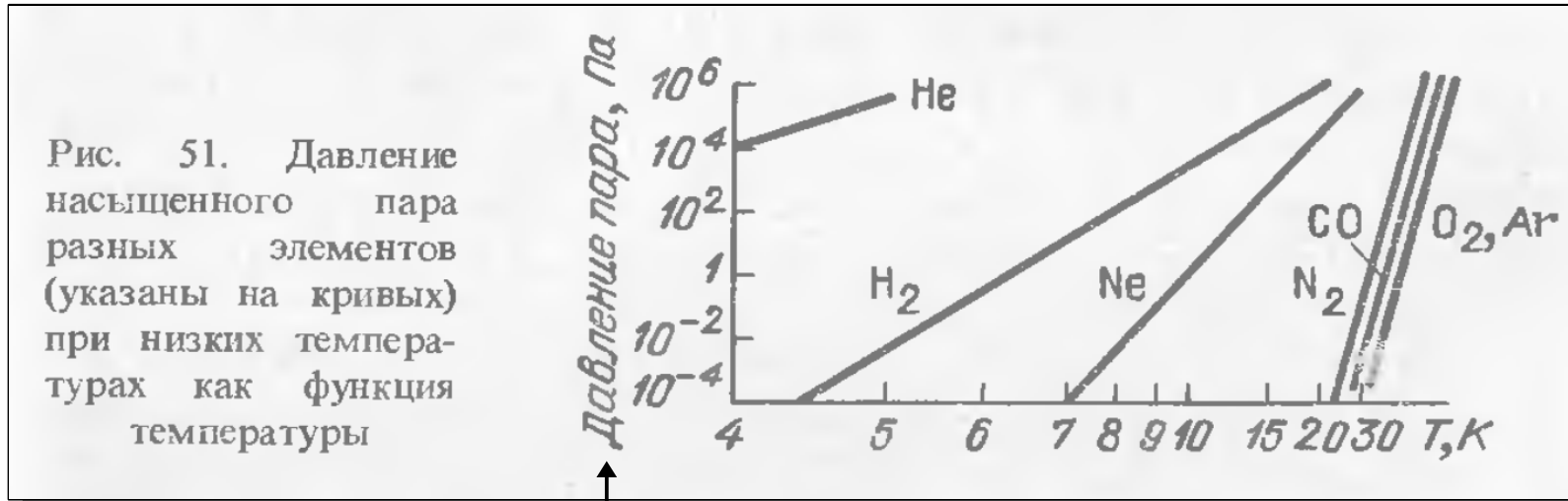
- evaporation of alloys usually results in different composition of vapor than that of the original alloy
- a solution is to use two or more evaporation sources to obtain desired composition of vapor (and the deposited film)



* at approx. 1013 hPa (760 Torr)

Physical vapor deposition

The other extreme – vapor pressure of atmospheric/vacuum gases:



graphics from [14]: Л.А. Ашкинази, Вакуум для науки и техники, Наука, Москва 1987
 vapor pressure [Pa]

- Cooling down the walls of the vacuum chamber to 20.4 K (liquid hydrogen) leads to condensation of nitrogen, oxygen etc.
- The effect is utilized in cryopumping

Physical vapor deposition

Evaporation rates – the Hertz-Knudsen equation [17]

- above certain vapor pressure the high vacuum cannot be maintained and condensation must be taken into consideration
- the net evaporation rate can be expressed as a difference between absolute rates of evaporation and condensation [18]

$$\frac{dN_e}{A_e dt} = a_v (2\pi mkT)^{-0.5} (p^* - p)$$

dN_e - number of molecules evaporated

A_e - evaporation area

a_v - evaporation coefficient*

p^* - vapor pressure of evaporated material at T

p - pressure in a vacuum chamber

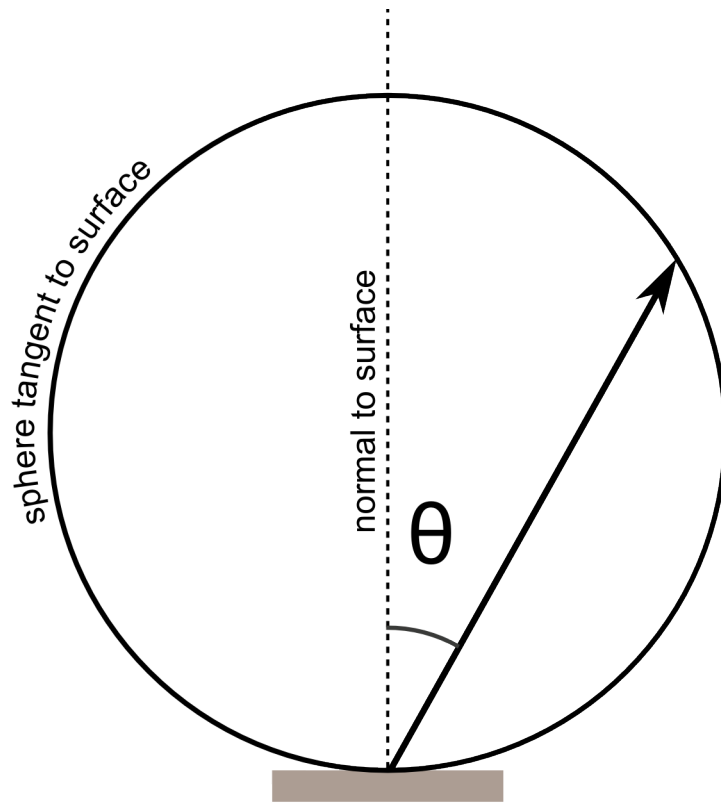
- maximum evaporation rate occurs in high vacuum: $p^* - p \rightarrow p^*$

* in general the evaporation and condensation coefficients are not necessarily equal [18]

Physical vapor deposition

Angular distribution of evaporation from a small source – Knudsen cosine law (1915) [3]:

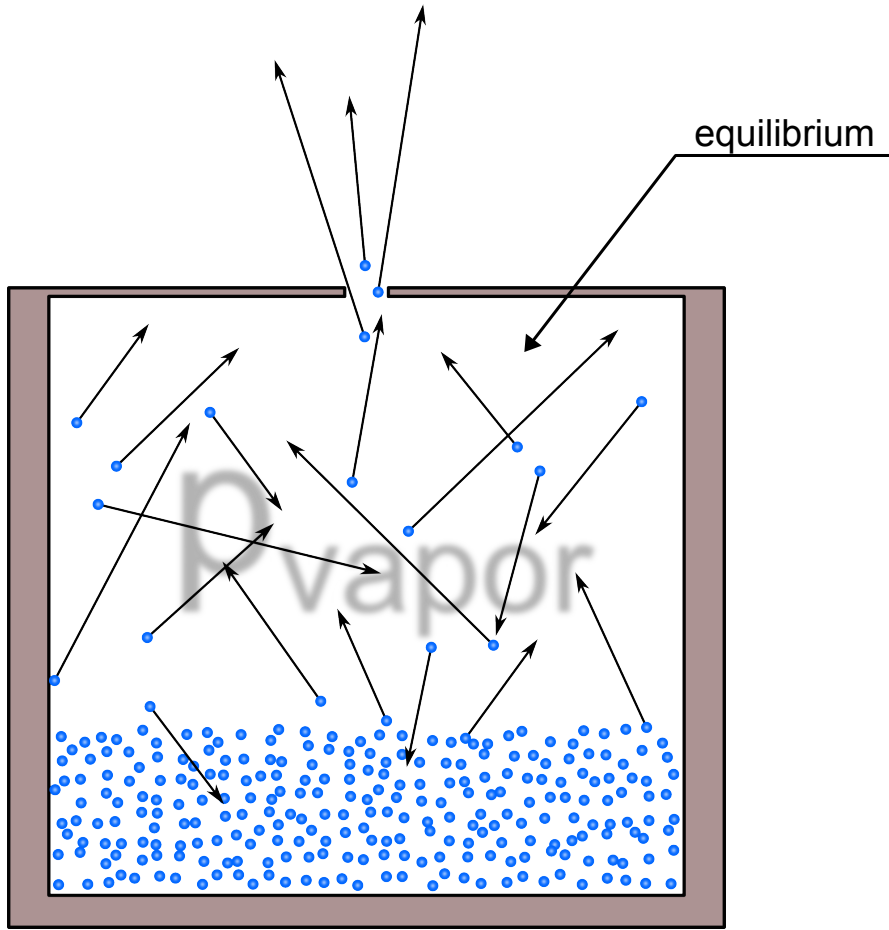
$$P(\theta) = P_o \cos(\theta) \quad \text{- probability of emission at angle } \Theta \text{ relative to surface normal}$$



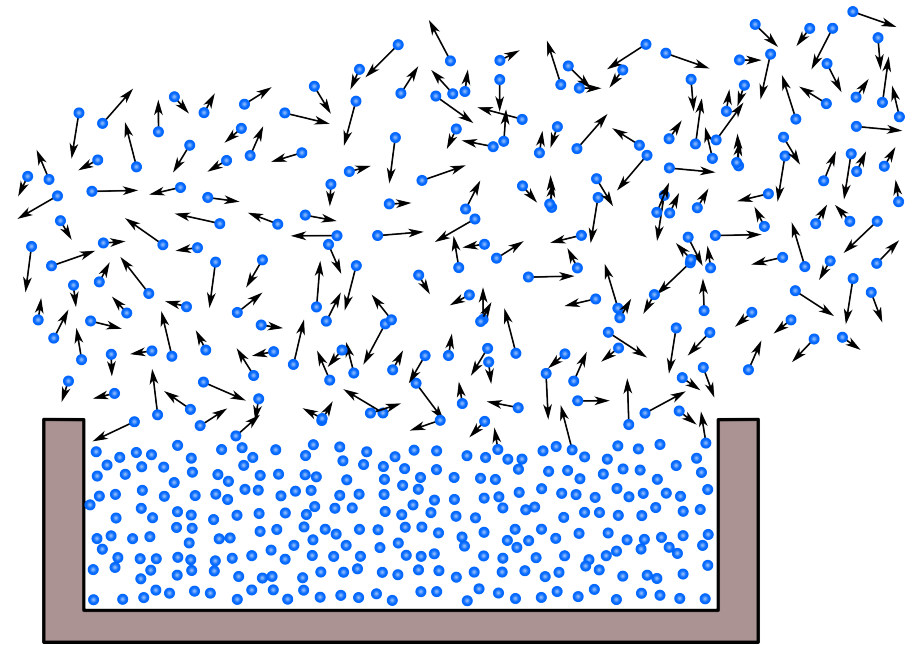
- Langmuir evaporation – evaporation from a free surface [17]
- Effusion - evaporation through an orifice by which the area of the orifice appears as an evaporation source of the same area

Physical vapor deposition

Knudsen effusion cell



Free surface evaporation

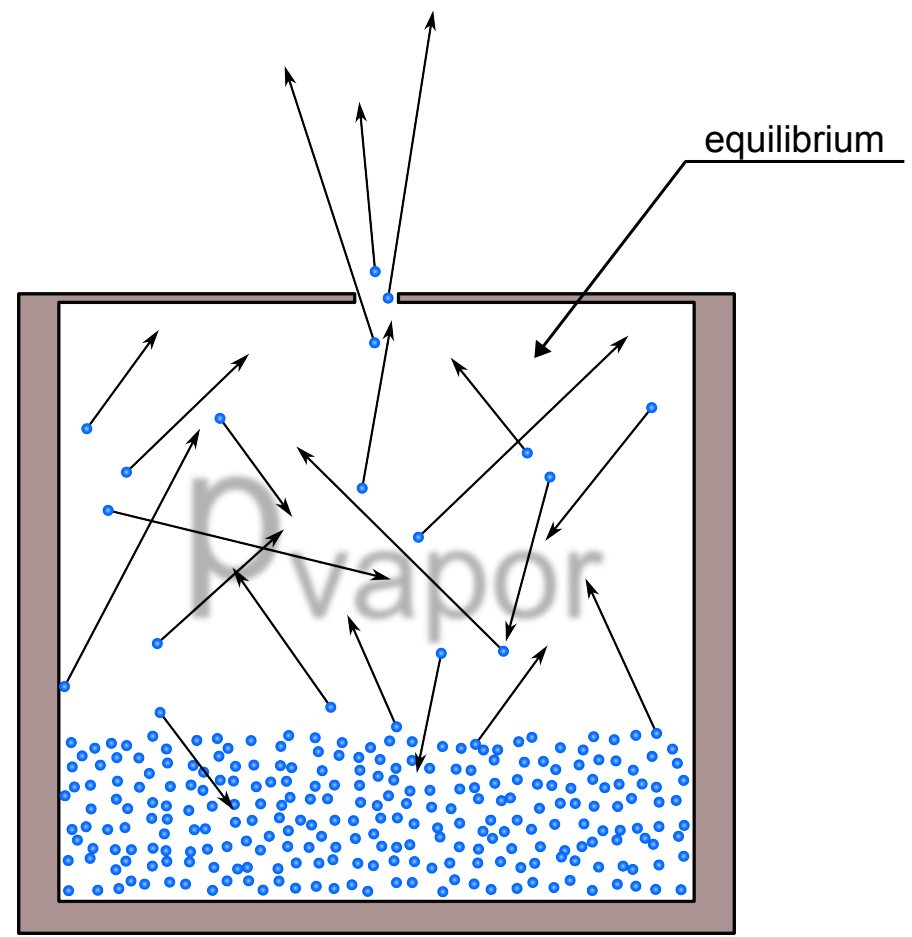


- defined, by the temperature, vapor pressure over the material
- possible regulation of yield (amount of evaporated material)

- pressure over the material influenced strongly by pumping and other vapors present in a chamber
- difficult regulation of yield

Physical vapor deposition

Knudsen effusion cell



- defined, by the temperature, vapor pressure over the material
- possible regulation of yield (amount of evaporated material)

Note an ambiguous nomenclature:
In Knudsen effusion cell the orifice should be small so that the vaporizing surface is more than approx. 100 times larger than the orifice surface.
In molecular beam epitaxy one often uses sources with large openings and calls them Knudsen cells too – they do not guarantee stable flow as a function of time [19]

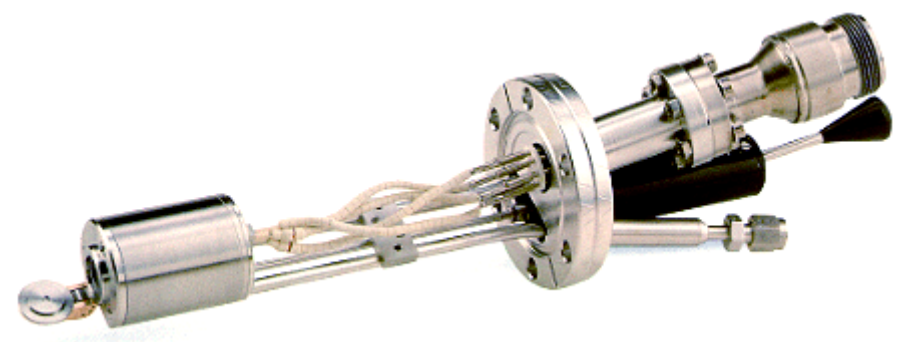
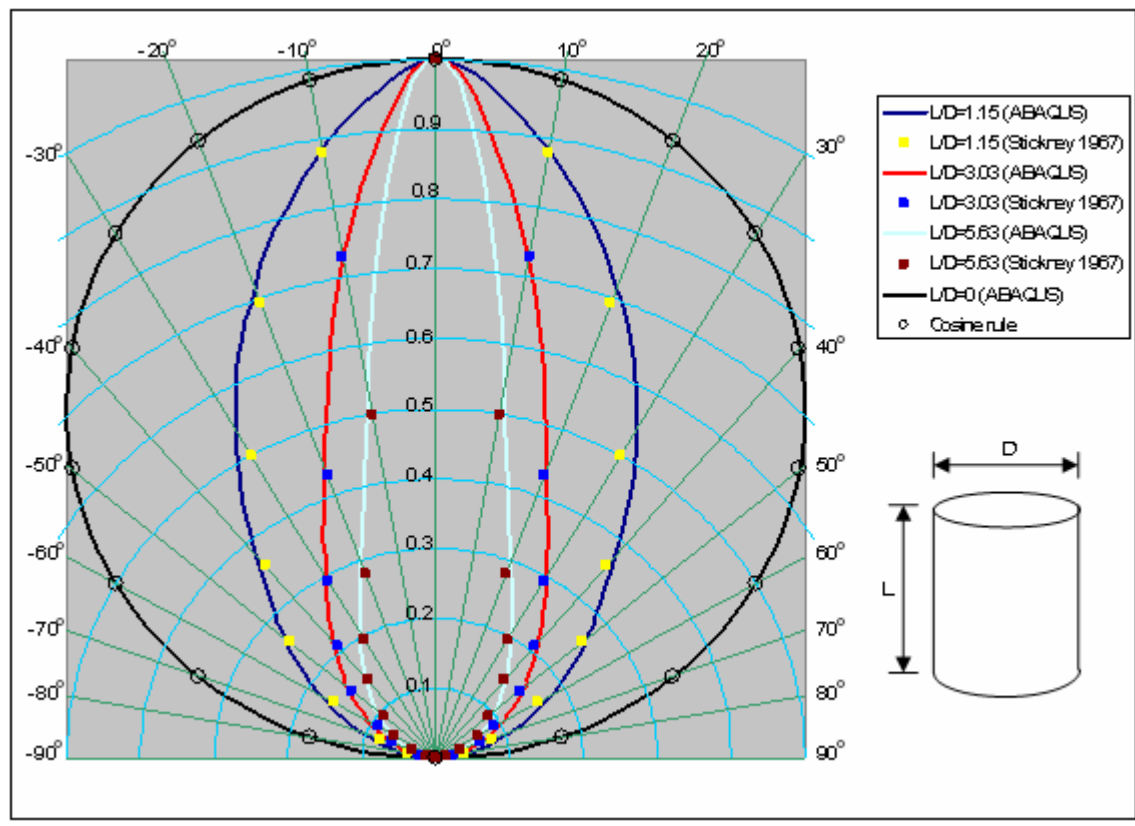


image source: <http://www.topac.com/kcel.html>

Physical vapor deposition

Knudsen effusion cell – profile of a particle beam

- angular profile of the molecular beam depends on the exact shape of the effusion cell and the orifice
- for simple geometry analytical approximations were obtained [17]: emission patterns from effusion cells tend to be more directional than the cosine emission pattern



The profile of molecular beam of real sources can often be approximated by [23]:

$$P(\theta) = P_o [\cos(\theta)]^n$$

image from:
C.P. Malhotra, R.L. Mahajan,
J. Heat. Transfer **129**, 1546 (2006)

Fig 5: Comparison of normalized angular distribution of radiation flux from short tubes with aspect ratios 1.15, 3.03 and 5.63 from ABAQUS (continuous lines) with experimental measurements of Stickney et al [28] (solid dots). **The open dots represent the Cosine Law which corresponds to L=0.**

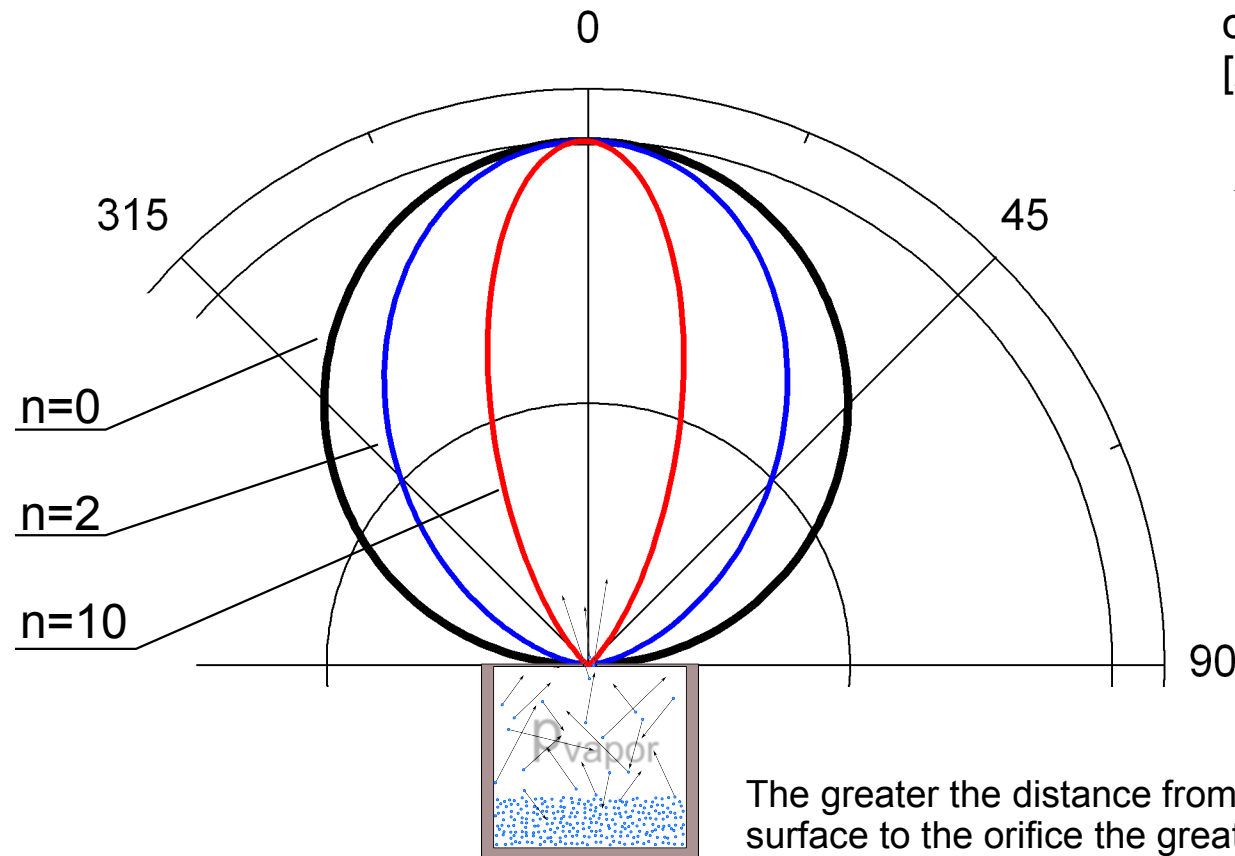
Physical vapor deposition

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The profile of molecular beam of real sources can often be **approximated** by [23]:

$$P(\theta) = P_o [\cos(\theta)]^n$$



The greater the distance from the vaporizing surface to the orifice the greater the n [9]

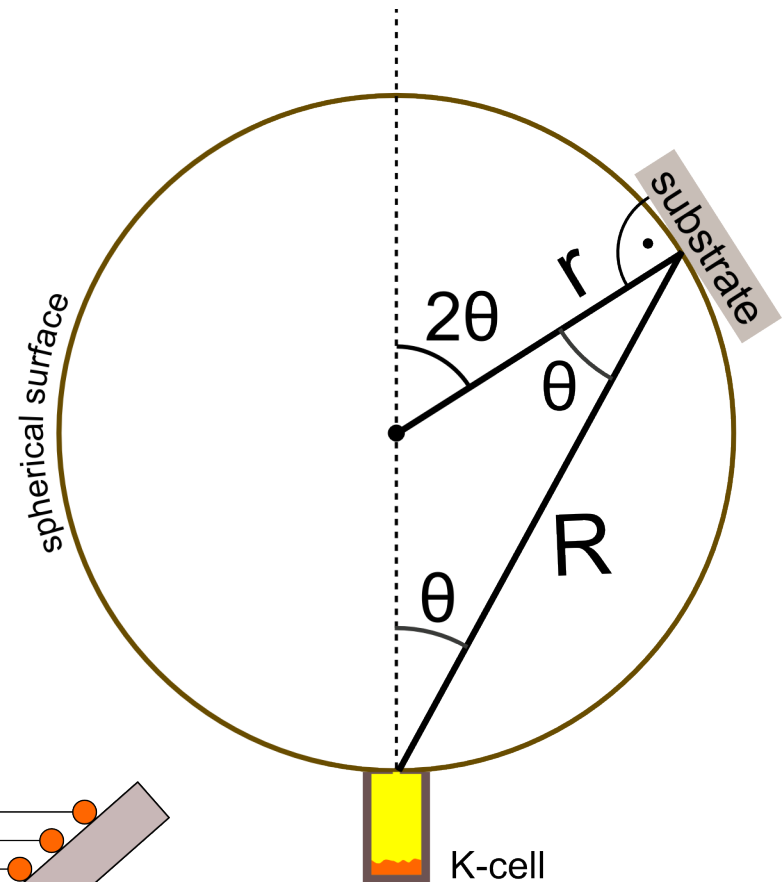
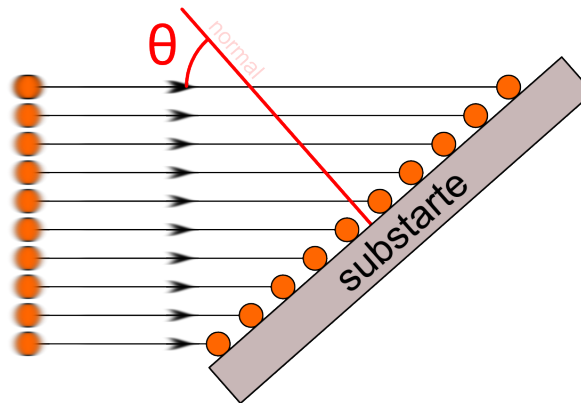
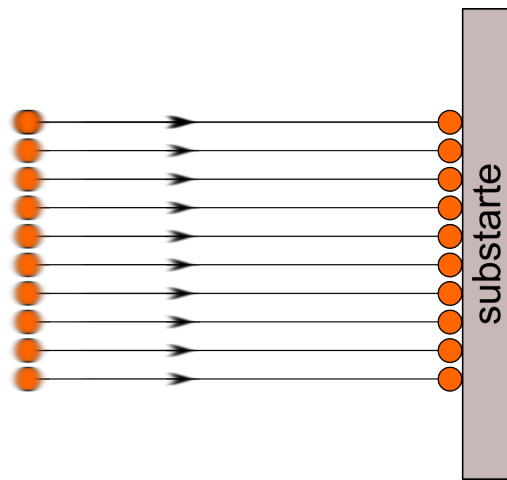
Physical vapor deposition

Knudsen effusion cell – uniform thickness profile

We assume cosine emission profile from Knudsen cell (or whatever source)

$$P(\theta) = P_o \cos(\theta)$$

- If the substrates are placed tangentially to the surface of the sphere* the incidence angle of the molecular beam on the substrate is θ (provided the orifice is small).
- The amount of the material deposited on unit area of the substrate is diminished, relative to the case of perpendicular impingement, by a factor $\cos(\theta)$.



* the derivation is strictly true only for the case of sphere; if the sizes of individual substrates are small it is a good approximation

Physical vapor deposition

Knudsen effusion cell – uniform thickness profile

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- If the substrates are placed tangentially to the surface of the sphere* the incidence angle of the molecular beam on the substrate is θ (provided the orifice is small).
- The amount of the material deposited on a unit area of the substrate is diminished, relative to the case of perpendicular impingement, by a factor $\cos(\theta)$.
- The amount of deposited material is inversely proportional to R^2 (the area corresponding to a given solid angle on a sphere). The amount of the material deposited on a unit area can be expressed as (C is a constant proportional to the yield of the source – number of emitted molecules in a second):

$$m = C \frac{\cos(\theta) \cos(\theta)}{R^2}$$

$$m = \frac{C}{4r^2} = C_2$$

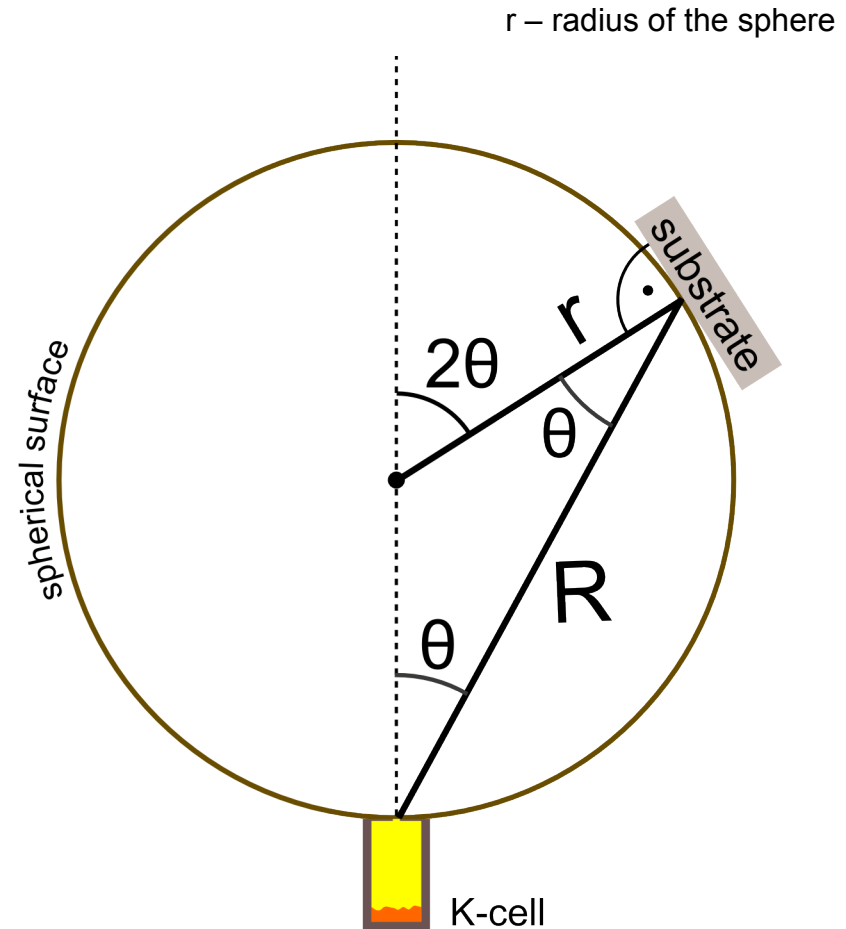
$$R^2 = [r + r \cos(2\theta)]^2 + r^2 \sin^2(2\theta) = r^2 + 2r^2 \cos(2\theta) + r^2 \cos^2(2\theta) + r^2 \sin^2(2\theta) = 2r^2(1 + \cos(2\theta))$$

$$\exp(i2\theta) = \cos(2\theta) + i \sin(2\theta)$$

$$\exp(i2\theta) = \exp(i\theta) \exp(i\theta) = [\cos(\theta) + i \sin(\theta)][\cos(\theta) + i \sin(\theta)] = \cos^2(\theta) - \sin^2(\theta) + i 2 \cos(\theta) \sin(\theta)$$

$$\cos(2\theta) = \cos^2(\theta) - \sin^2(\theta)$$

$$R^2 = 2r^2(1 + \cos(2\theta)) = 2r^2(1 - \sin^2(\theta) + \cos^2(\theta)) = 2r^2 2 \cos^2(\theta)$$



r – radius of the sphere

* the derivation is strictly true only for the case of sphere; if the sizes of individual substrates are small it is a good approximation

Physical vapor deposition

Knudsen effusion cell – uniform thickness profile

Knudsen apparatus used to establish cosine law

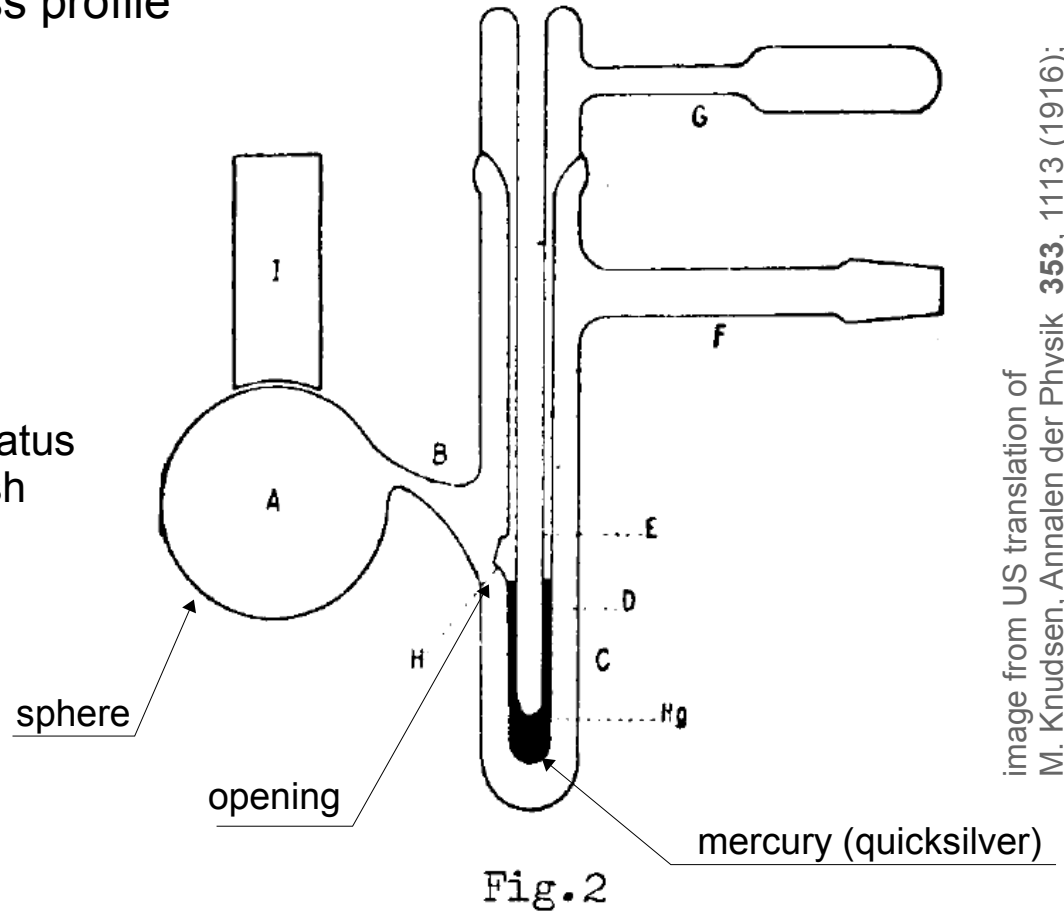


image from US translation of M. Knudsen, Annalen der Physik 353, 1113 (1916); NASA publication: NASA TT F-486

$$m = C \frac{\cos(\theta) \cos(\theta)}{R^2}$$

$$m = \frac{C}{4r^2} = C_2$$

Thickness of the film deposited from Knudsen source (with n=1) is the same all over the inner surface of the sphere

Physical vapor deposition

Thickness profile from small surface and point source [17]

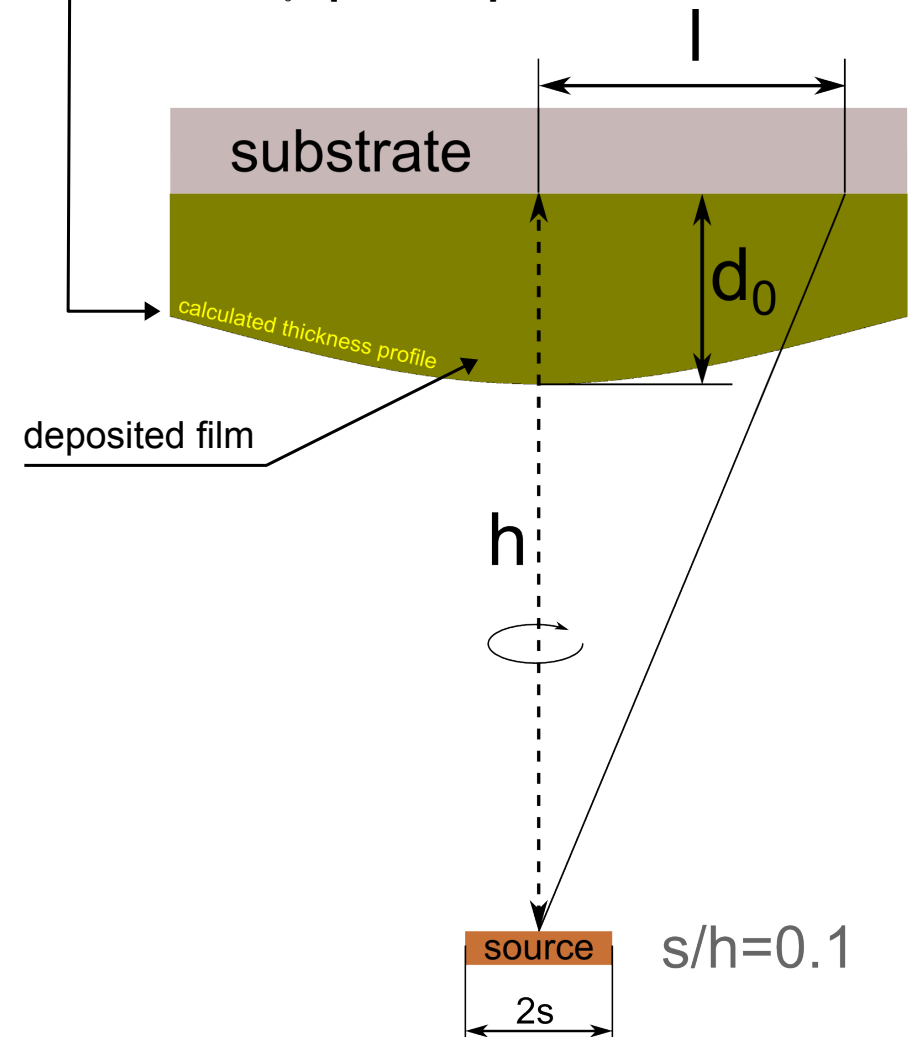
small area source (cosine emission law):

$$d/d_0 = \left(\frac{1+(s/h)^2}{2(s/h)^2} \right) \left(1 - \frac{1+(l/h)^2 - (s/h)^2}{\sqrt{[1-1-(l/h)^2+(s/h)^2]^2 + 4(l/h)^2}} \right)$$

point source (isotropic emission):

$$d/d_0 = [1+(l/h)^2]^{-3/2}$$

- the substrate area which can be covered uniformly is a significant figure of merit for vapor sources [17]
- the analytical expressions above are obtained from geometrical consideration not including the collisions between gas molecules
- in practice the source behavior is variable [20]: intrinsic differences between materials, conditioning or depletion of material during a run etc.



Physical vapor deposition

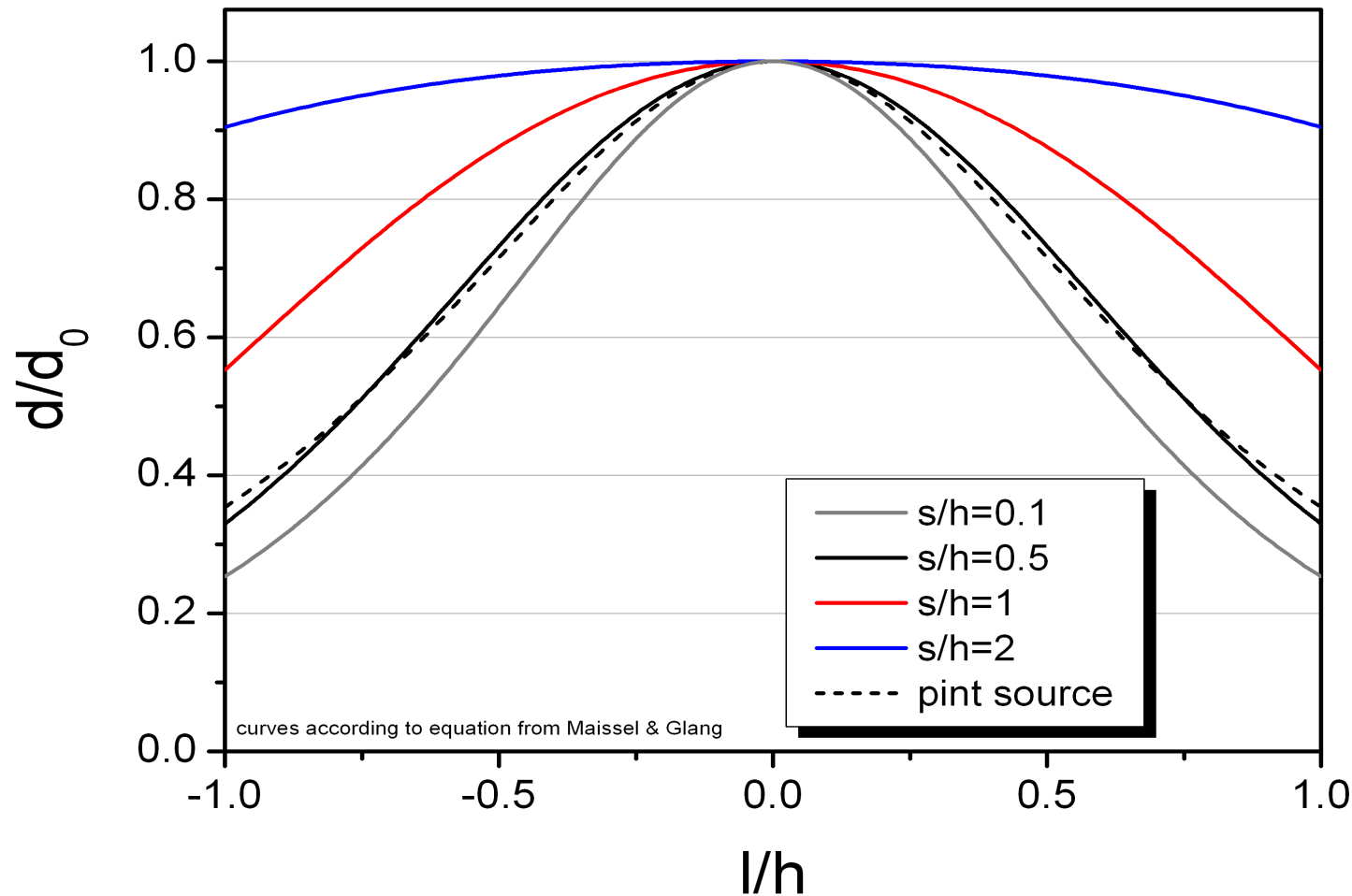
Thickness profile from small surface and point source [17]

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point source (isotropic emission):

$$d/d_0 = [1+(l/h)^2]^{-3/2}$$



Note:
The incidence angle of molecules relative to the substrate changes with l and sticking coefficient is in general dependent on that angle [22]

Physical vapor deposition

- In many optical applications as well as in microelectronics there is a need for high thickness uniformity of the films
- Evaporation from large area sources is technologically challenging so the alternative techniques to achieve uniformity were developed [20]

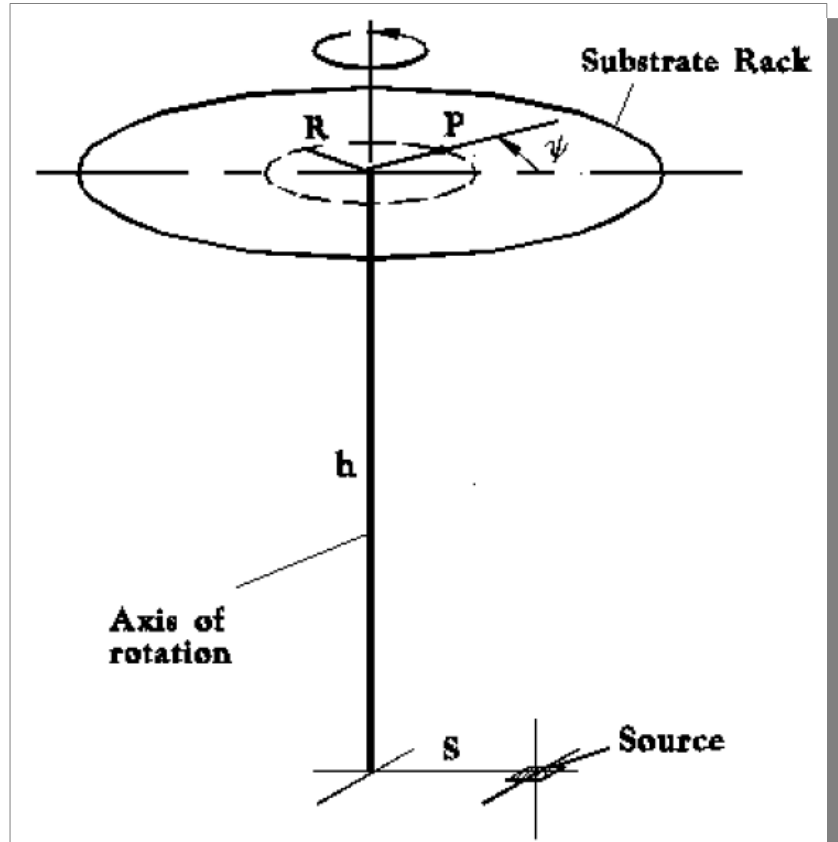


Figure 2: Geometry for an Offset Source

Substrate rotating on a flat workholder can be coated more uniformly if the source is properly placed off axis of rack rotation

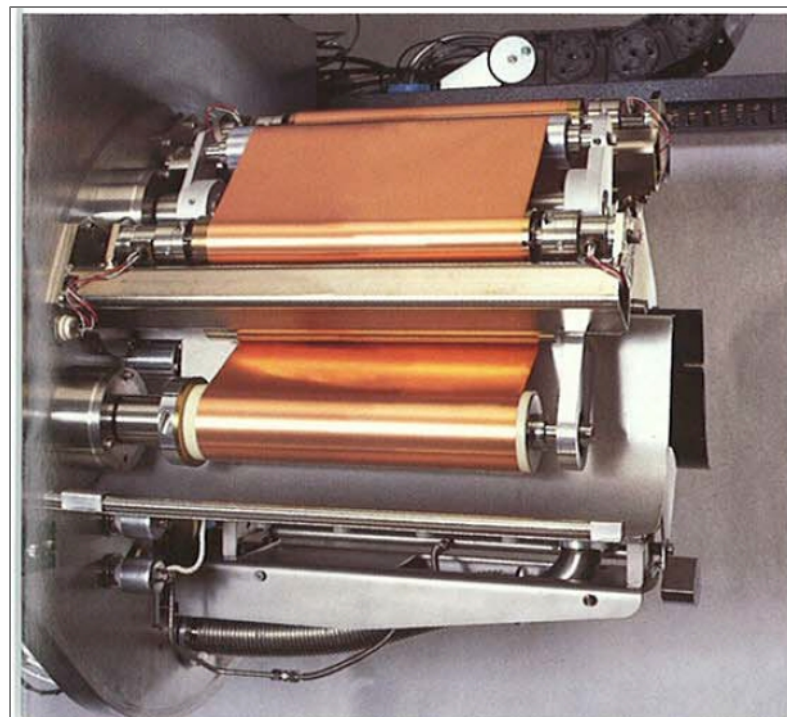
Rotating masks may be used to block some of the molecular flux to obtain better uniformity (the mask effectiveness depends on the source characteristics and its stability – value of n power in cosine law etc.)

graphics from:
 I.C. Stevenson, Denton Vacuum, LLC
 Optimizing Source Location For Control of Thickness Uniformity

Physical vapor deposition

In industrial applications there is often the need to deposit films on a very large areas or on continuous substrates – deposition on foils in package industry etc., or emerging **flexible electronics**.

The films may be deposited in roll-to-roll technology (web coater).



Web/Roll Fixture, which mounts on the rear door of the process chamber, is shown with a roll of copper foil installed. Sputtering cathode and shielding are mounted on the door immediately below the fixture.

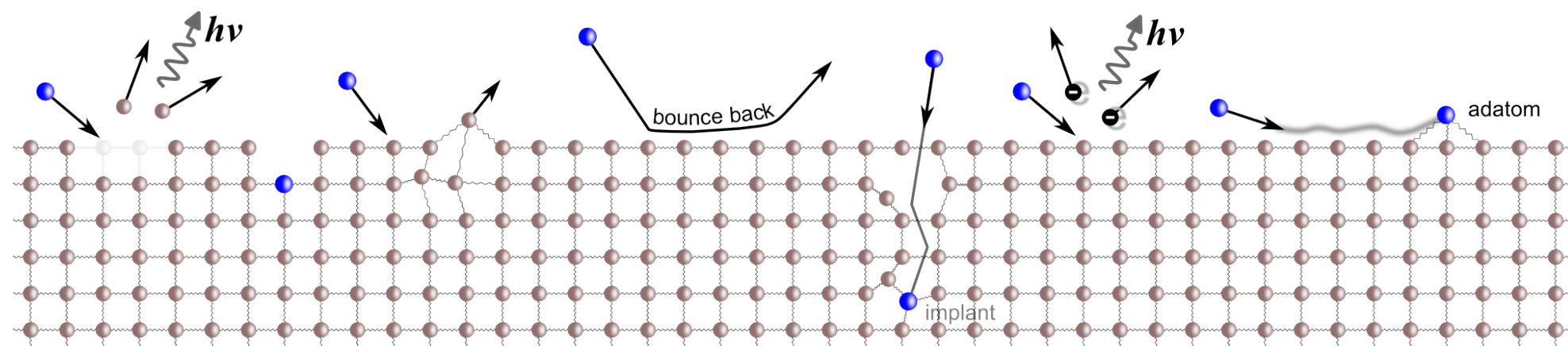
image source: company A-Tech System, from www.gtrade.or.kr/buyer/product/Evaporation-System-for-Continuous-Al-Deposition.do?productId=0000109285&categoryId=

Physical vapor deposition - sputtering

Sputtering, physical - the physical ejection (vaporization) of a surface atom **by momentum transfer** in the near-surface region by means of a collision cascade resulting from bombardment by an energetic atomic-sized particle [24].

Bombardment by atoms/ions can lead to various processes:

- sputtering
- thermal agitation of the lattice
- emission of radiation
- emission of electrons
- implantation of impinging atom/ion
- bounce back of atom/ion
- deposition of material, etc.



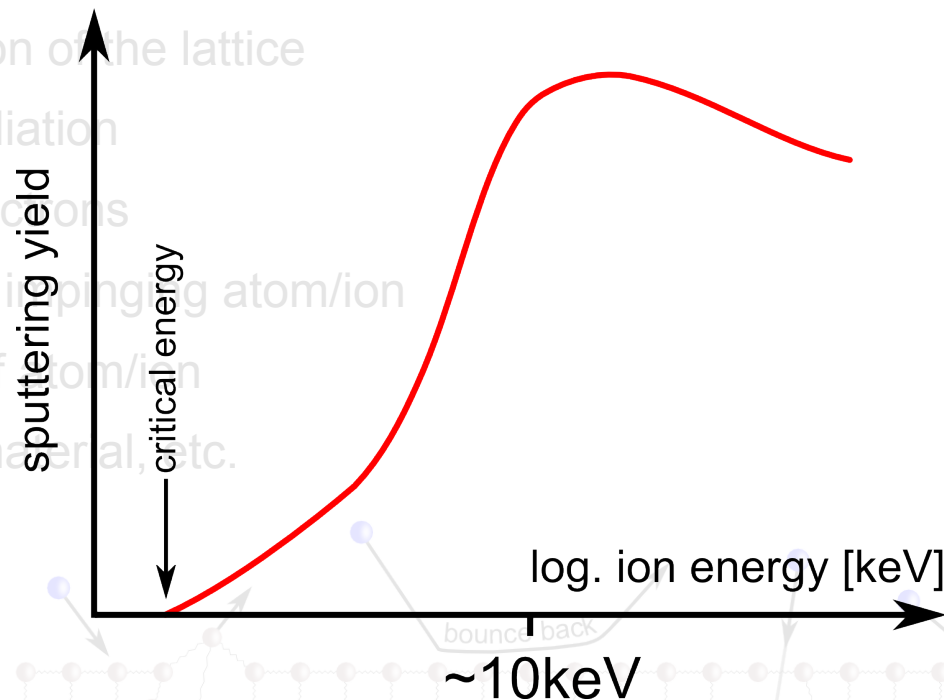
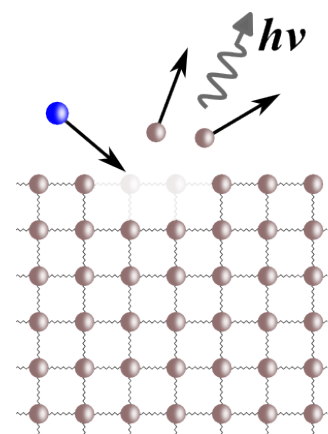
Physical vapor deposition - sputtering

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Bombardment by atoms/ions can lead to various processes:

- sputtering – vaporized atoms can be deposited on a substrate to form a layer

- thermal agitation of the lattice
- emission of radiation
- emission of electrons
- implantation of impinging atom/ion
- bounce back of atom/ion
- deposition of material, etc.



In sputtering technology we usually express ion energies in eV because the ions of working gases (argon, neon etc.) are accelerated by constant voltages. The first ionization energy is lower than the second ionization energy – more ions are in first ionization state (lacking one electron)

Argon:
 first ionization energy 15.7eV [25]
 second ionization energy 27.6eV

- sputtering yield* depends on the energy of bombarding ions/atoms
- only the ions with the energy exceeding certain value will sputter **the target** [25] (it is not the case in a potential sputtering [29]**)

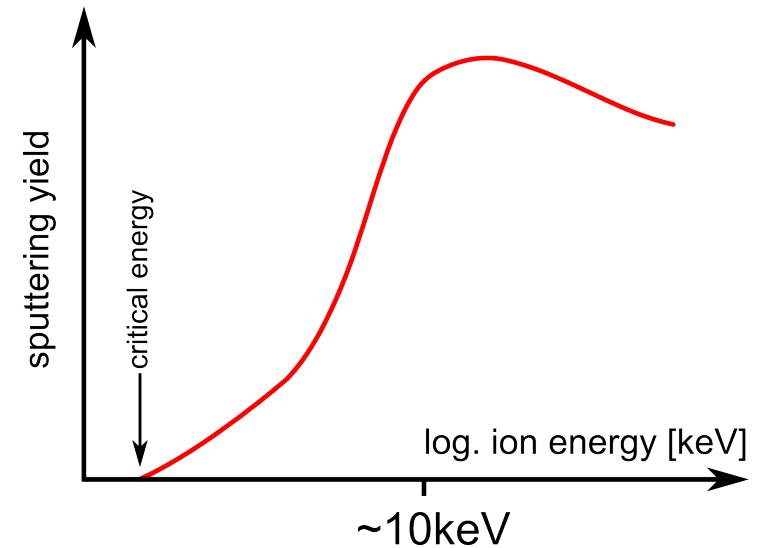
* number of ejected atoms per one impinging ion

**see later in the lecture

Physical vapor deposition - sputtering

Sputtering – critical energies for some ion-target pairs expressed in eV [25].

	Ne	Ar
Al	13	13
Ti	22	20
Fe	22	20
Co	20	25
Ni	23	21
Cu	17	17
Ag	12	15
Au	20	20



The threshold value of ions kinetic energy is roughly proportional to the heat of sublimation [25 p.65,26] and can be approximated with the expression:

$$E_{threshold} = \frac{(M_g + M_m)^2}{4 M_g M_m} \phi$$

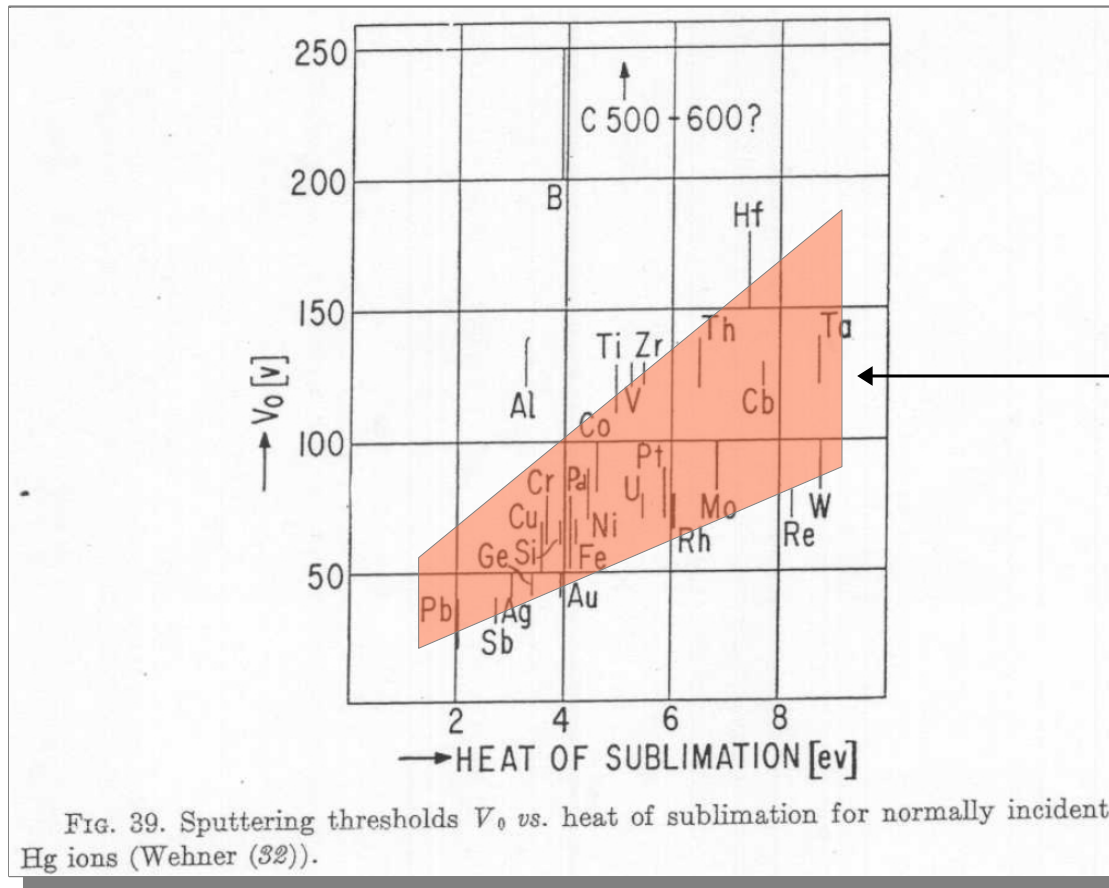
- M_g - ion mass
- M_m - mass of target atoms
- ϕ - the heat of sublimation

Physical vapor deposition - sputtering

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graphics from [26]: G.H. Wehner, Sputtering by ion bombardment, in Advances in Electronics and Electron Physics, edited by I. Marton, vol. VII, Academic Press, New York 1955

Physical vapor deposition - sputtering

The yield of the sputtering process depends on many factors; some of them are [9,25]:

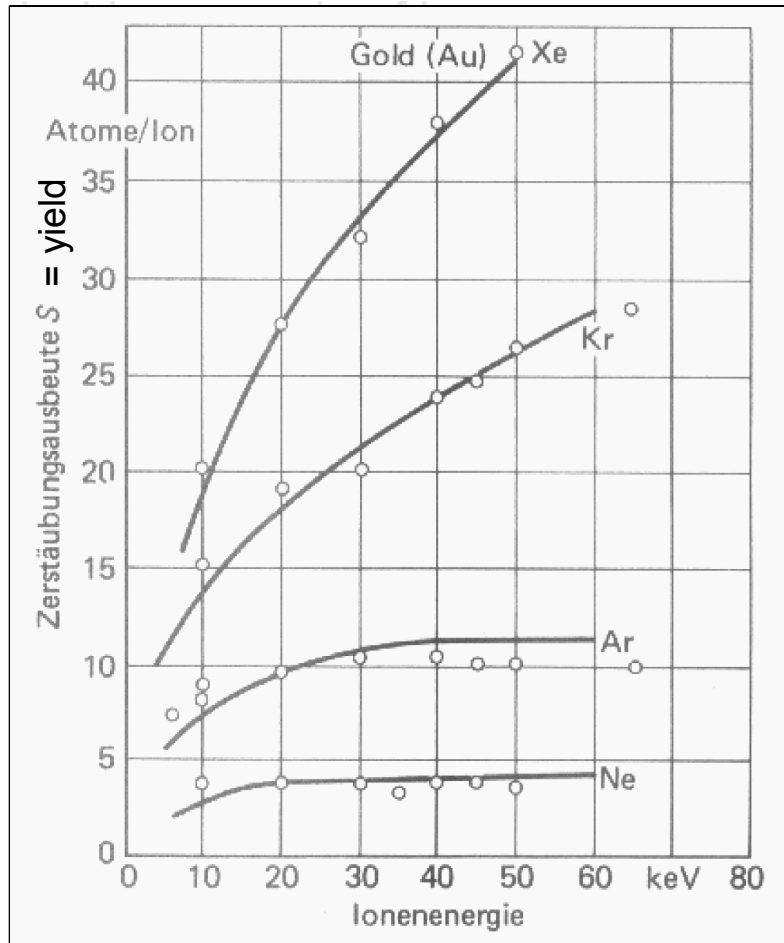
- ion*/target pairing - for example Ar sputters Au better than lighter Ne
- ion energy – the dependence is not monotonous as for higher energies the penetration depth of ions is high and displaced atoms do not reach the surface
- incidence angle of ions
- crystal orientation of the surface (or a texture in a case of polycrystalline targets used in sputtering) – polycrystalline Ag target is sputtered more effectively by Ar^+ ions than the one with (100) or (110) textures; the (111) texture ensures the highest yield [25]
- chemical reactions taking place on the surface
- temperature of the target – not significant below approx. 0.8 of the melting temperature [25]

* the word ion can be interchanged with the word atom; beams of neutral atoms can be produced too.

Physical vapor deposition - sputtering

The yield of the sputtering process depends on many factors; some of them are [9,25]:

- ion*/target pairing - for example Ar sputters Au better than lighter Ne
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texture in a case of polycrystalline targets used in is sputtered more effectively by Ar⁺ ions than the (111) texture ensures the highest yield [25] the surface

cant below approx. 0.8 of the melting temperature

graphics from: Vakuumbeschichtung, edited by H. Frey, VDI-Verlag, Düsseldorf 1995

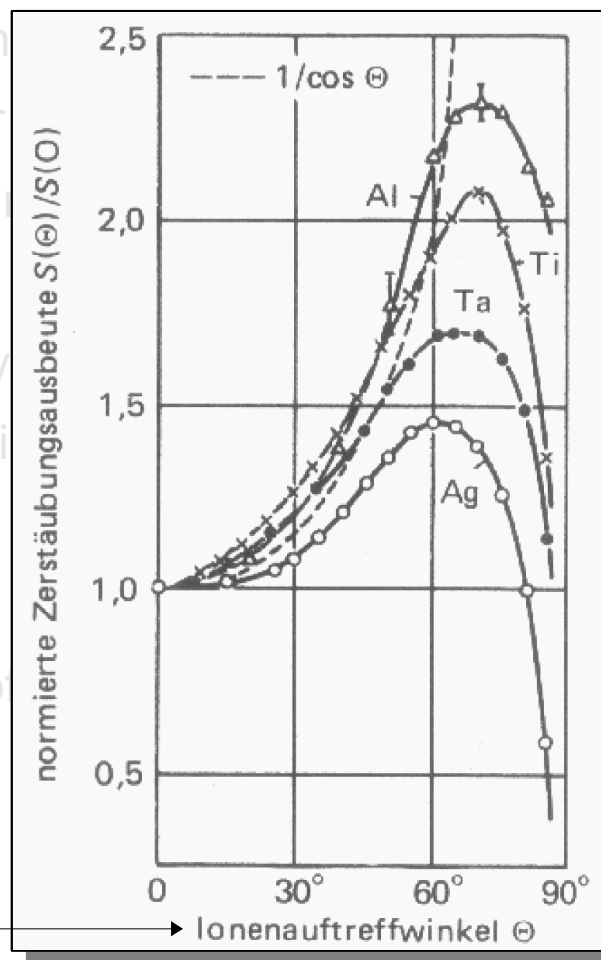
Physical vapor deposition - sputtering

The yield of the sputtering process depends on many factors; some of them are [9,25]:

- ion*/target pairing - for example Ar sputters Au better than light ions
- ion energy – the dependence is not monotonous as for higher energy the penetration depth of ions is high and displaced atoms do not reach the surface
- incidence angle of ions

The yield of the sputtering depends on the angle α between the direction of ions and the normal to the target [17,25]. For not too high α the dependence can be approximated by:

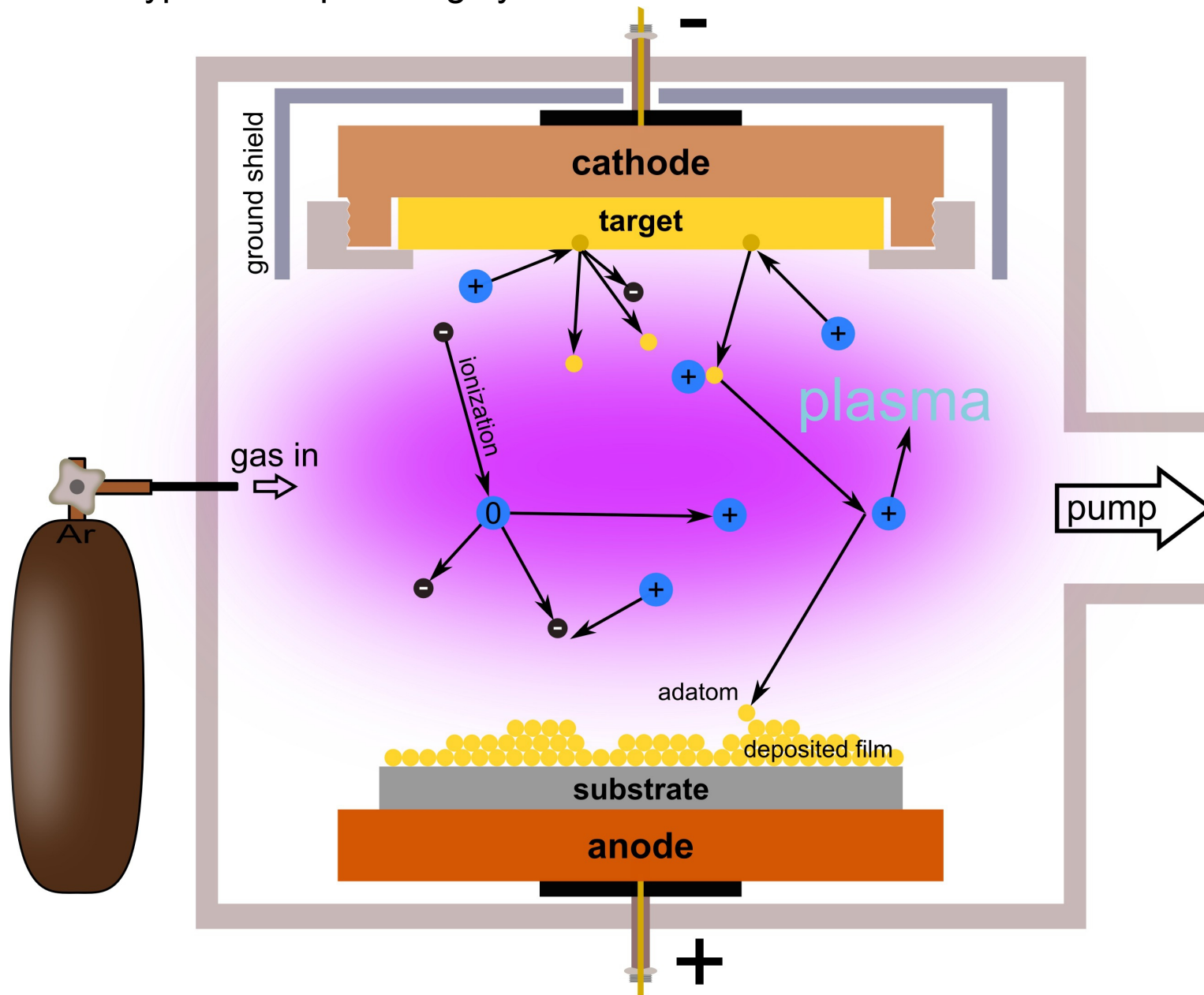
- $Y = Y_0 / \cos(\alpha)$
- temperature of the target – not significant below approx. 0.8 of melting point
- the yield increases because for higher α more energy is released in the near-surface region of the target
- the angle corresponding to the maximum yield increases with ion energy and decreases with mass of ions and target atoms [25, p.63].
- above some critical value of α the yield decreases as more ions get reflected



graphics from: Vakuumbeschichtung, edited by H. Frey, VDI-Verlag, Düsseldorf 1995

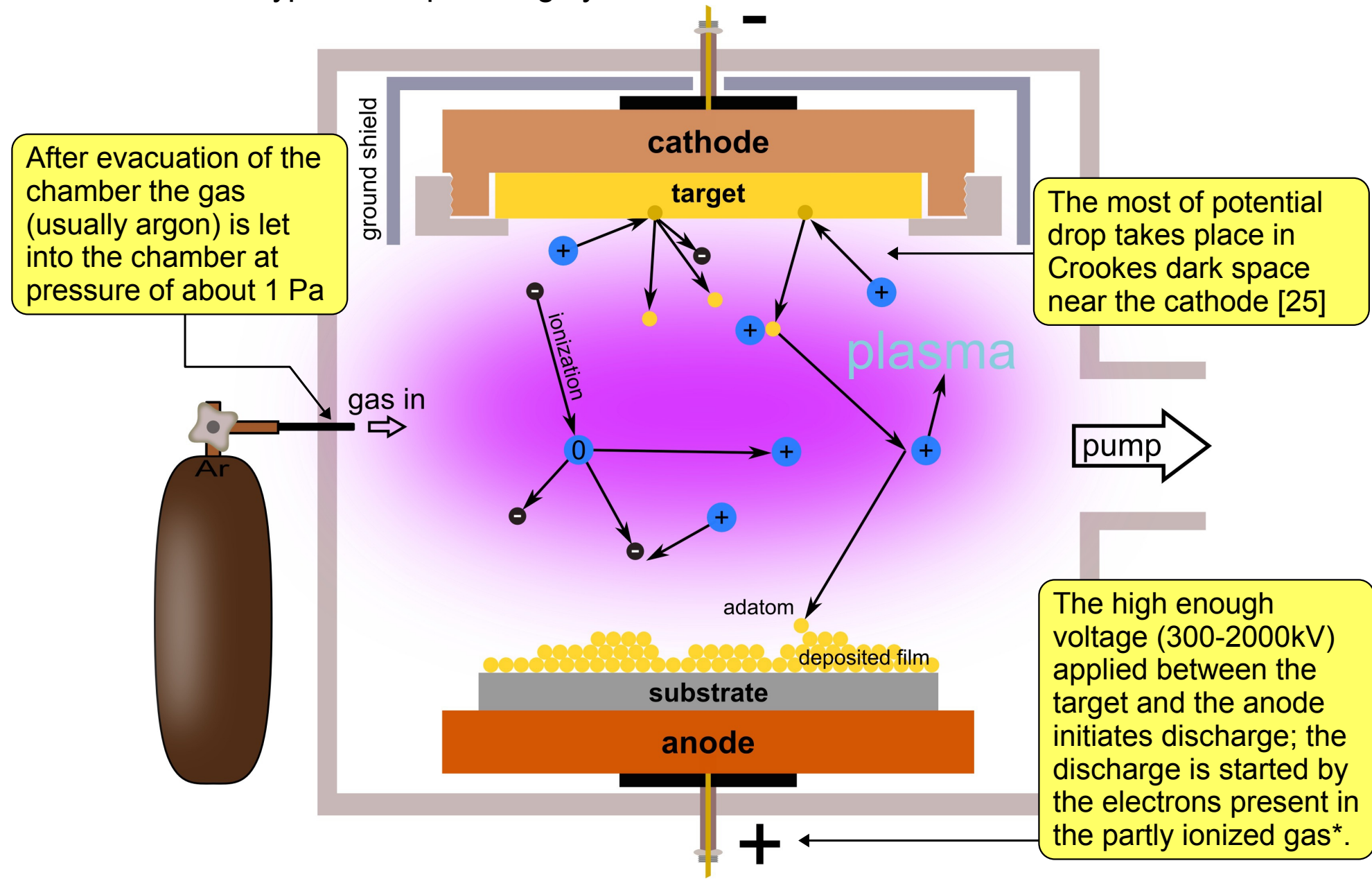
Physical vapor deposition - sputtering

A schematic of a typical dc sputtering system



Physical vapor deposition - sputtering

A schematic of a typical dc sputtering system



After evacuation of the chamber the gas (usually argon) is let into the chamber at pressure of about 1 Pa

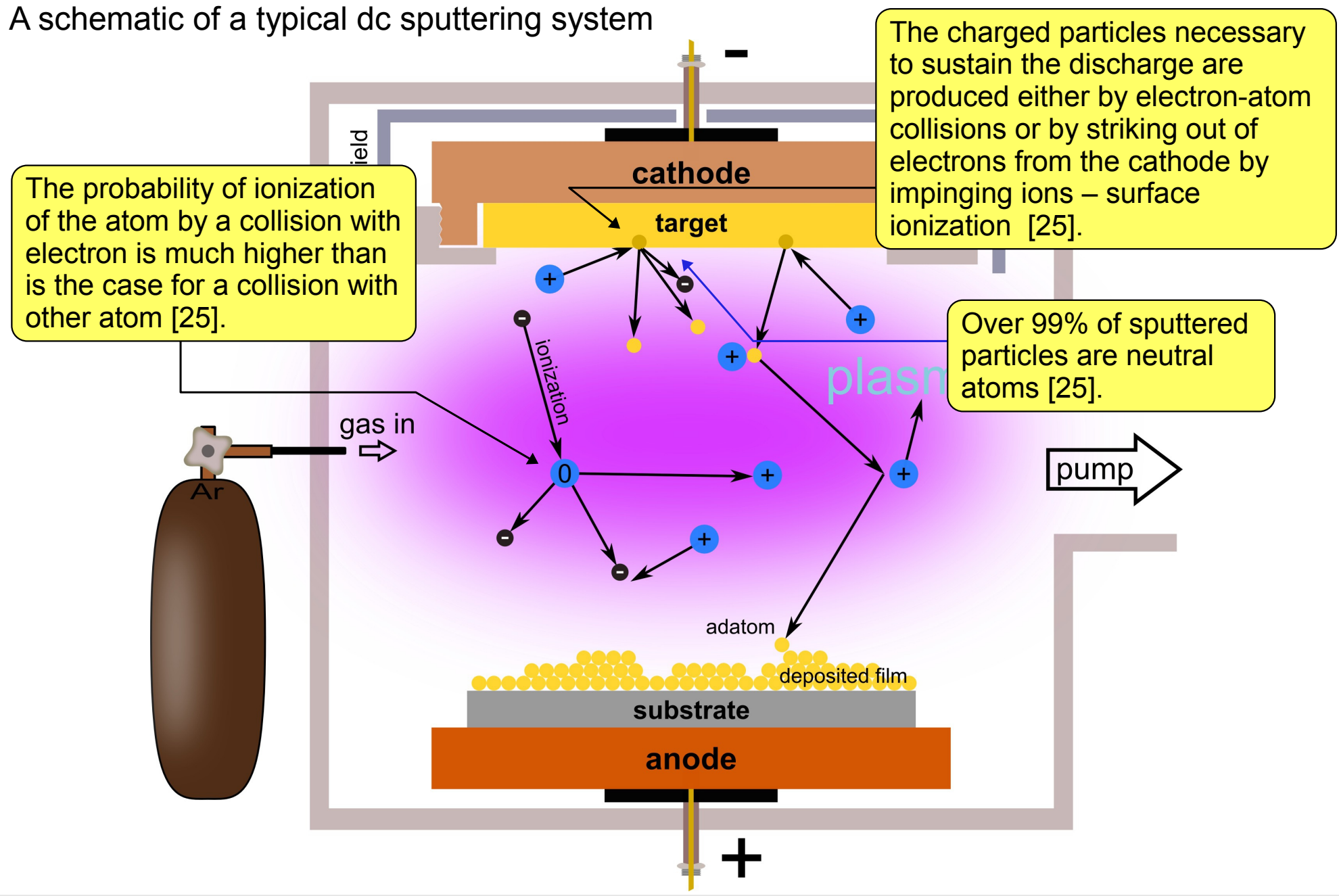
The most of potential drop takes place in Crookes dark space near the cathode [25]

The high enough voltage (300-2000kV) applied between the target and the anode initiates discharge; the discharge is started by the electrons present in the partly ionized gas*.

*ionization sources may be used to help start the discharge too.

Physical vapor deposition - sputtering

A schematic of a typical dc sputtering system



The probability of ionization of the atom by a collision with electron is much higher than is the case for a collision with other atom [25].

The charged particles necessary to sustain the discharge are produced either by electron-atom collisions or by striking out of electrons from the cathode by impinging ions – surface ionization [25].

Over 99% of sputtered particles are neutral atoms [25].

Physical vapor deposition - sputtering

Energy distribution of sputtered atoms [17,27]

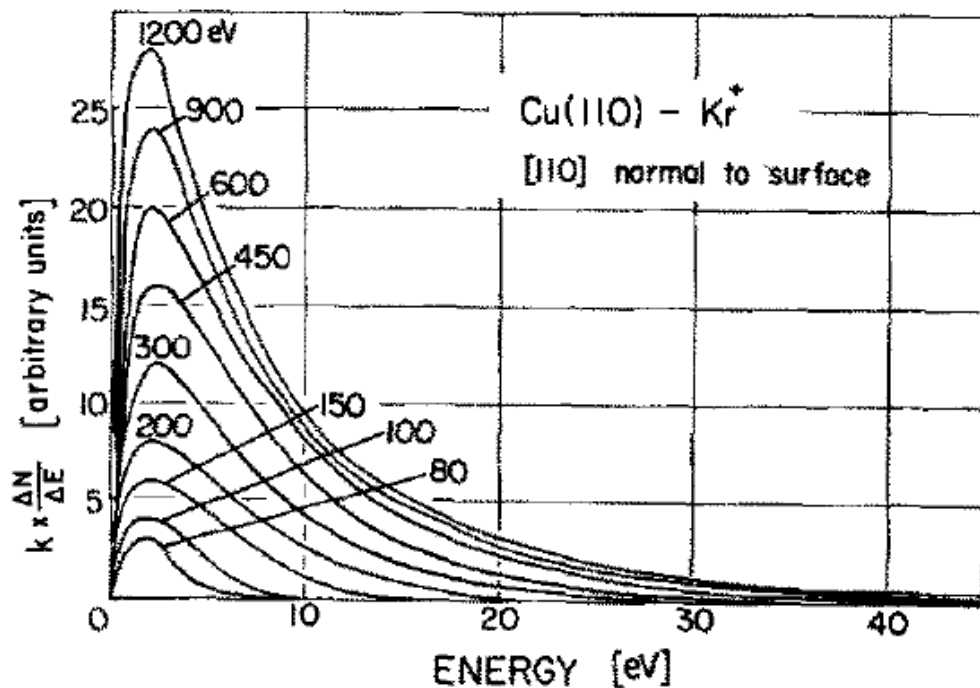


FIG. 4. Energy distributions of atoms ejected in the $[110]$ direction from the (110) surface for bombarding ion energies from 80–1200 eV.

graphics from:
R.V. Stuart, G.K. Wehner, J. Appl. Phys. **35**, 1819 (1964)

- ejection energies **decrease for lighter ions** in the order Kr^+ , Ar^+ , Ne^+ , He^+ [27]
- more oblique* ejection results in higher energies E_k of sputtered atoms/ions [17,27]
[$E_k(60 \text{ Deg}) > E_k(0 \text{ Deg}), E_k(75 \text{ Deg})$]

*neither parallel nor perpendicular to the normal.

Physical vapor deposition - sputtering

Energy distribution of sputtered atoms [17,27]

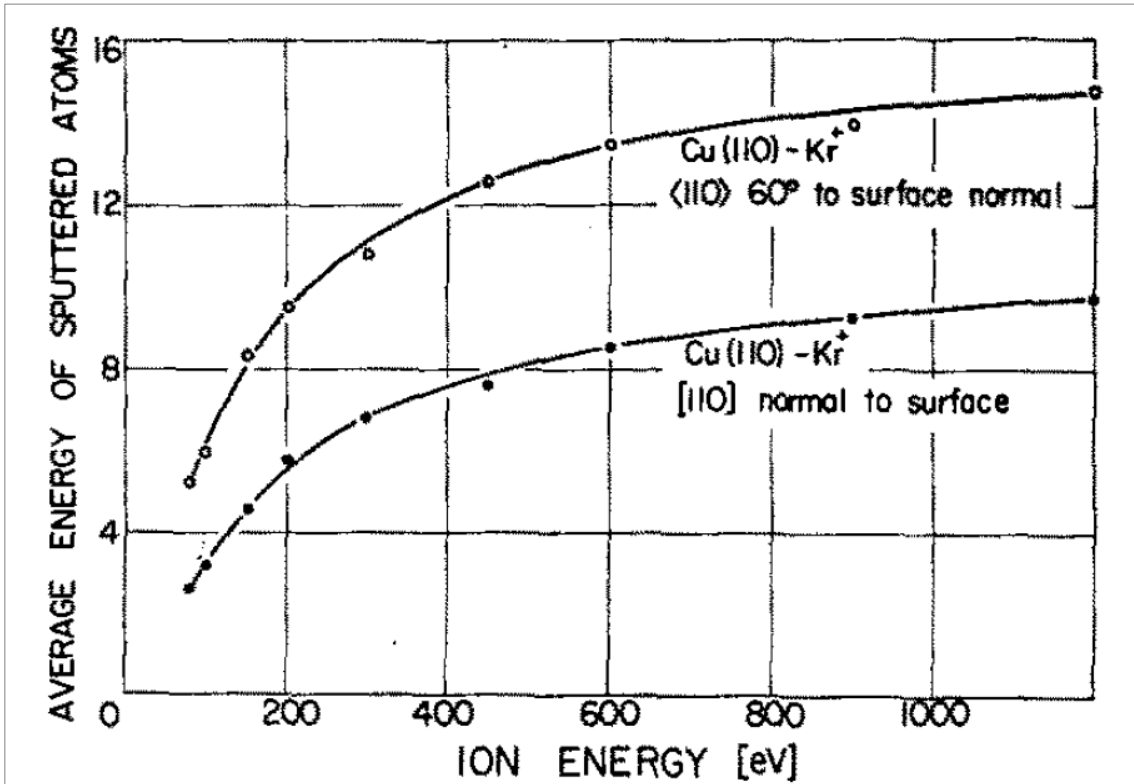


FIG. 5. Average ejection energies of sputtered atoms.

graphics from: R.V. Stuart, G.K. Wehner, J. Appl. Phys. 35, 1819 (1964)

Energies of the sputtered atoms are in the range of several eV.

For Cu atoms (atomic weight 63.546...) and 10eV this corresponds roughly to 170 m/s.

- ejection energies **decrease for lighter ions** in the order Kr^+ , Ar^+ , Ne^+ , He^+ [27]
- dependence on bombarding ion energy is very weak above 1000 eV where average energies of sputtered atoms are found to be **in the range 5-15 eV**

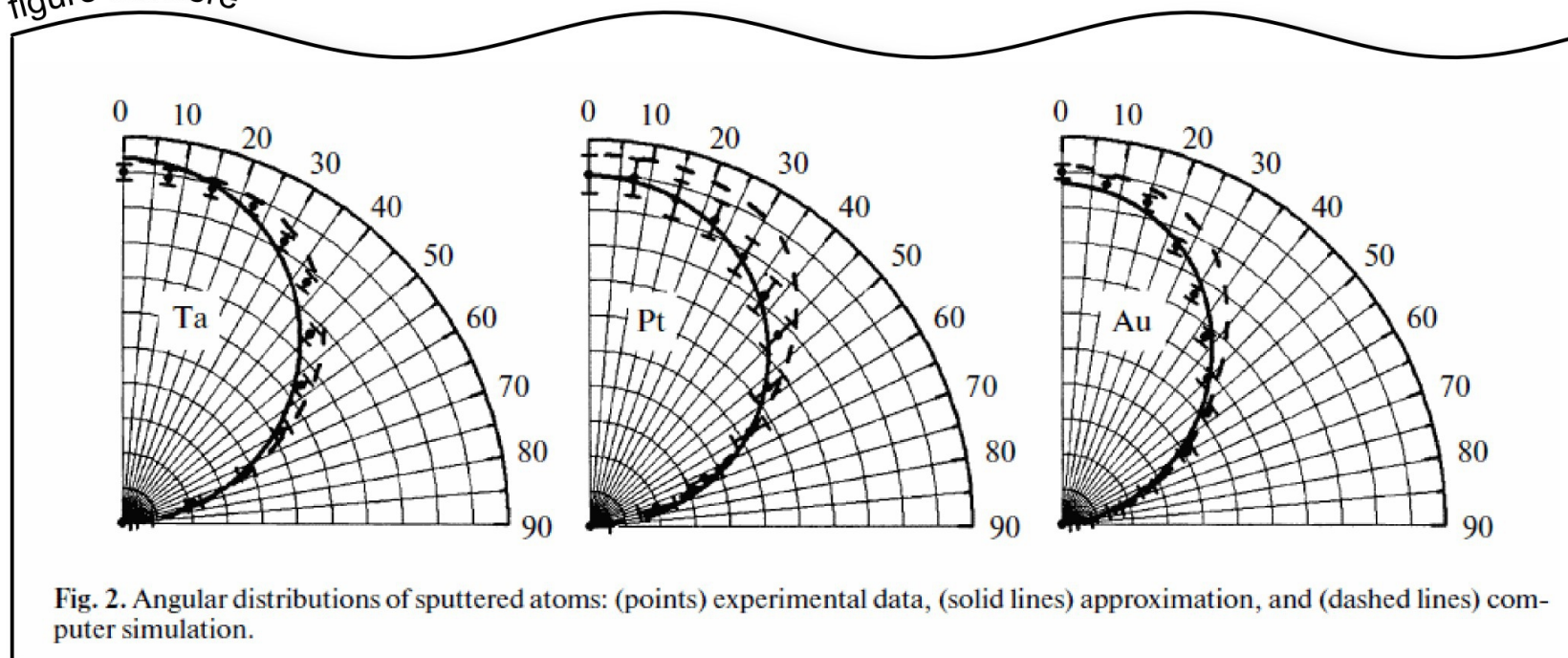
Physical vapor deposition - sputtering

Angular distribution of sputtered atoms [17,28]

$$P(\theta) = P_o [\cos(\theta)]^n$$

- sputtering is done almost exclusively with polycrystalline targets
- for such targets the angular distribution of sputtered material can be approximated by a cosine law (like in the case of evaporation)
- in general the distribution depends on multitude of factors; for lower energies of impinging ions the distribution differs considerably from cosine law [28]
- in case of sputtering from mono-crystals the distribution is related to the relative angle between the direction of ejection and crystallographic directions; in general the most preferred are nearest neighbor (nn) and second-nn directions [17]

figure cut here



Physical vapor deposition – potential sputtering

- there is a strong dependence of the sputtering yield from insulating targets on the charge state of the impinging ion [29]
- the significant sputtering can take place even if the ion energy is below kinetic sputtering threshold

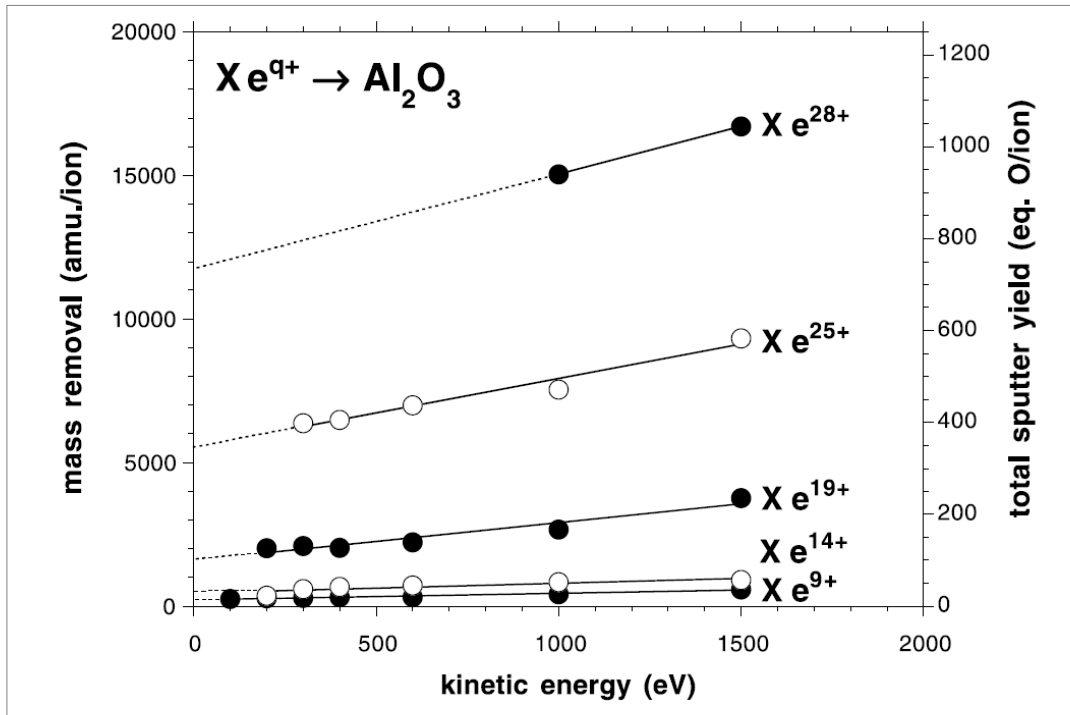


Fig. 2. Mass removal for sputtering of Al_2O_3 by highly charged Xe^{q+} ($q = 9, 14, 19, 25$ and 28) ions as a function of ion impact energy. Left ordinate: in atomic mass units per incident projectile (as measured by the quartz crystal microbalance). Right ordinate: corresponding sputter yield (in O atoms per incident ion) under the assumption that only O atoms are sputtered. Lines for guidance only.

- note the huge mass removal due to sputtering with low kinetic energy ions
- potential energy released during a capture of electrons by highly charged ions (HCI) leads to the sputtering
- there are numerous ways to produce HCI-s (plasma, laser heating, beam-foil method, electron beam ion trap*); even bare U^{92+} can be produced and “stored”.

* for the details see for example “The Heidelberg Electron Beam Ion Trap” (<http://www.mpi-hd.mpg.de/ullrich/page.php?id=89>, retrieved on 2014.03.25)

Physical vapor deposition – evaporation vs. sputtering*

Evaporation	Sputtering
<p>low kinetic energy of evaporant atoms (about 0.1 eV at 1200k)</p> <p>directional evaporation according to cosine law</p>	<p>high kinetic energy of sputtered atoms (1-100 eV)</p> <p>directional evaporation according to cosine law at high sputtering rates</p>
<p>high vacuum in the chamber – no collisions between evaporated particles</p> <p>thermal velocity of evaporant (a few hundred m/s)</p>	<p>low vacuum in the chamber – collisions with working gas particles</p>
<p>evaporant composition may differ much from the composition of the base material</p>	<p>generally good maintenance of target stoichiometry</p> <p>any material can be sputtered</p>
<p>deposition rates from thousandths of nm/s [36] up to several $\mu\text{m/s}$ [33] (electron beam evaporation)</p> <p>grains generally larger than in sputtered films with few orientations (texture)</p>	<p>up to tens of nm/s</p> <p>working gases (Ar, Kr, Xe) are usually not incorporated into the film; contamination from the end vacuum (before admitting working gas)</p> <p>generally many grain orientations</p>

* based on table 3-7 from M. Ohring, The materials science of thin films, Academic Press Inc., 1992 [32] and on [33]

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- POV-Ray www.povray.org
- Blender www.blender.org
- SketchUp sketchup.com.pl

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