
Practicing Molecular Simulations

**Lecture 2.
Physics & Chemistry of interfaces.
Physical adsorption.**



Lucyna Firlej

Notion of interface.

Interface: Separation between two (volume) phases.

Although words 'interface' and 'surface' mean practically the same, the word 'interface' is often used when :

- two condensed phases are in contact or
- two phases are explicitly considered

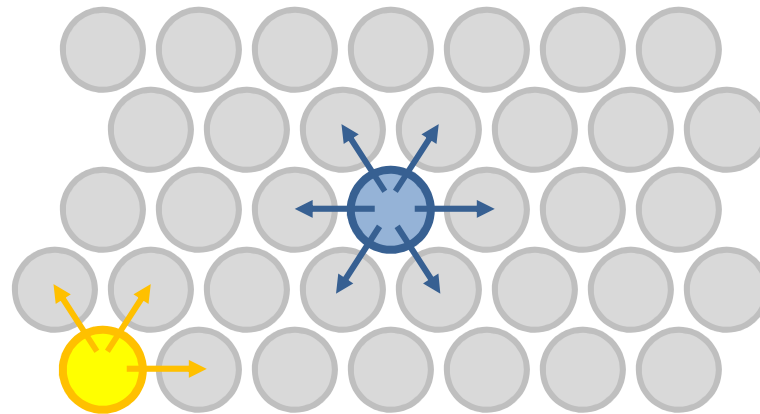
Exemple : interface solid/liquid; interface solid/gaz.

The word 'surface' mean is used to describe the interface of solid, no matter if it is (or it is not) in a contact with other phase.

Atoms at the interface.

For atoms
at the surface A_s

$$\sum_i f_i \neq 0$$



For atoms in a bulk A_v

$$\sum_i f_i = 0$$

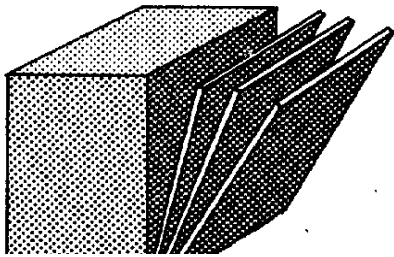
The energy of the atoms at the surface of the solid (experiencing surface tension) is larger than that of atoms in the bulk.

Consequences:

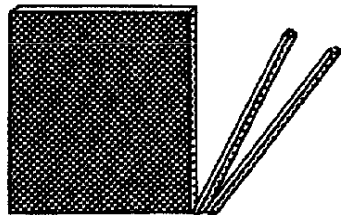
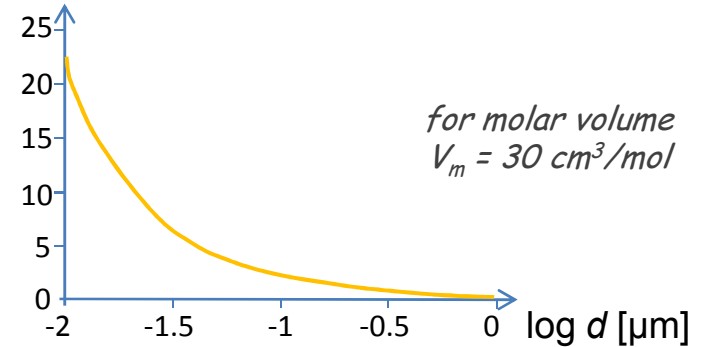
1. surface atoms can release energy \longrightarrow immersion
2. surface atoms can retain other atoms at the interface \longrightarrow **adsorption.**

Divided solids.

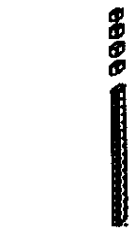
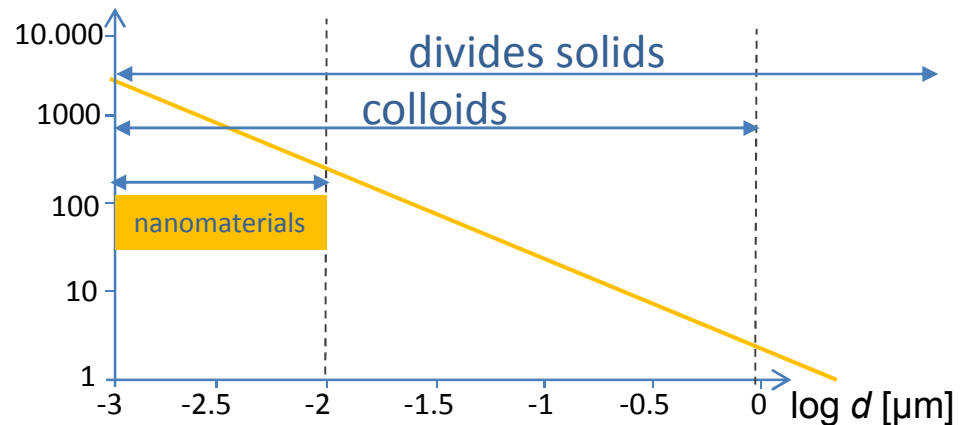
1,2 or 3 dimensions
are in the range of nanometers.



Fraction of surface atoms/molecules (in %)



Specific surface area (in m^2/g)

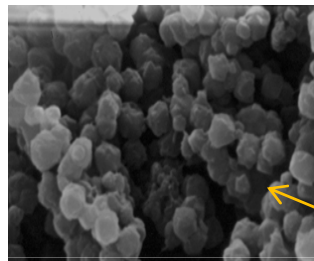


Buzagh, "Colloid systems", 1937
Londres, Technical Press

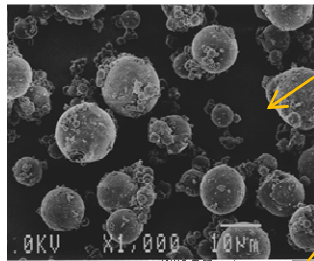
Divided solids.

divided materials: specific surface between 0.1 and 2600 m²g⁻¹

POWDERS (grains' size < 1 μm)



carbon blacks

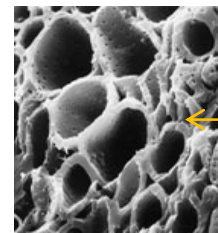


silicas

powdered sulfur

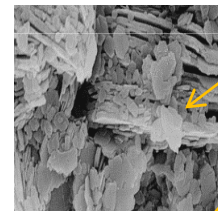


POROUS SOLIDS (pores' size < 50 nm)



activated carbons

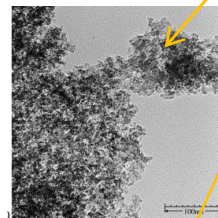
activated alumina



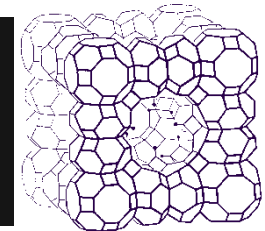
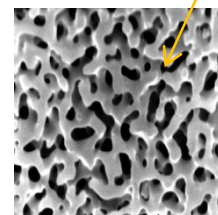
bridged clays

silica gels

porous glasses

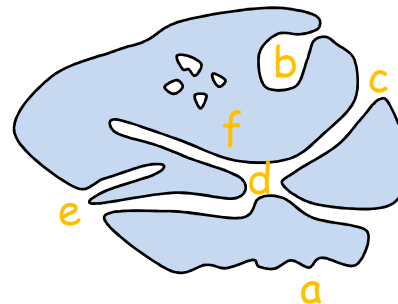


zeolites (natural or synthetic)

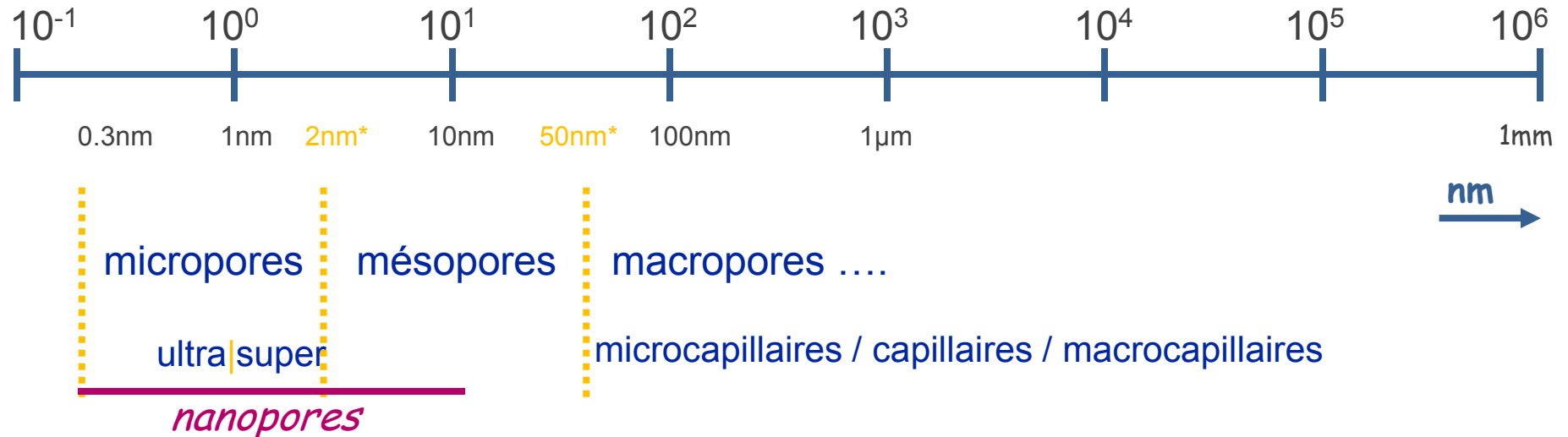


Porous solids.

porous materials: specific surface between 0.1 and 2600 m²g⁻¹

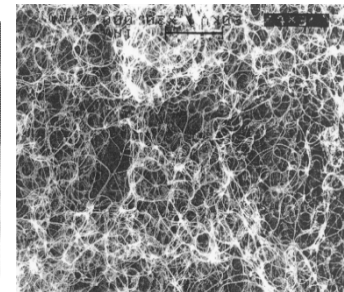
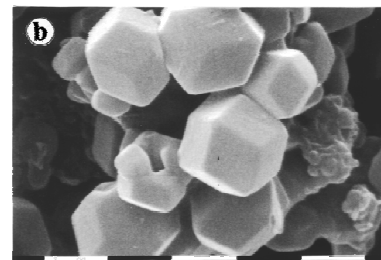
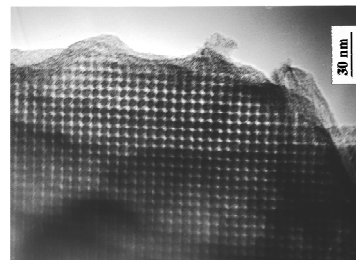
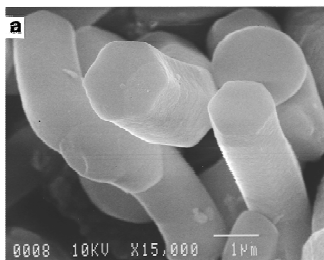
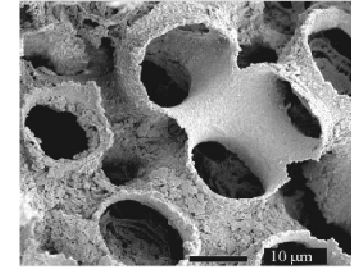
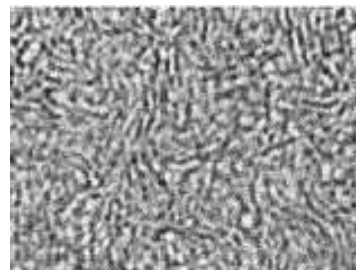
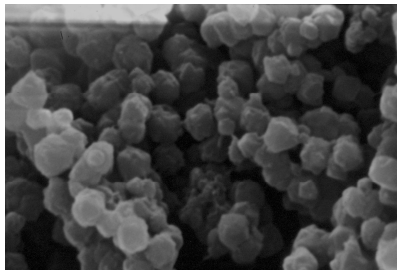
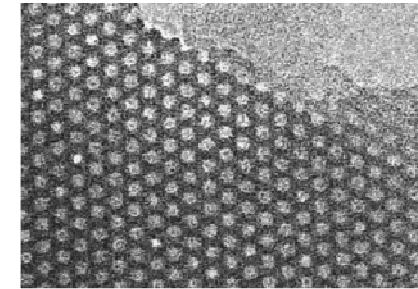
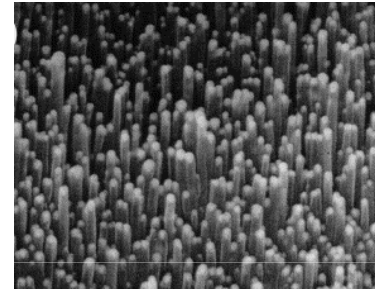
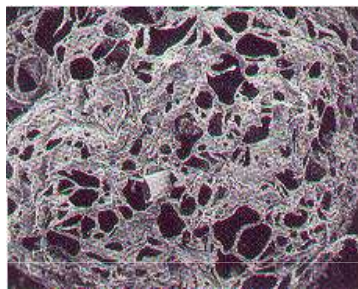
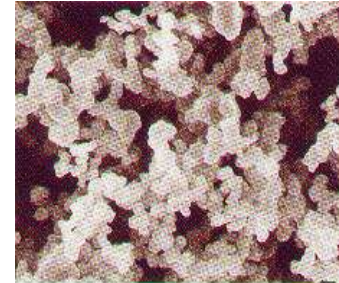
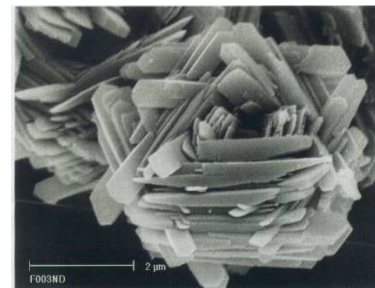
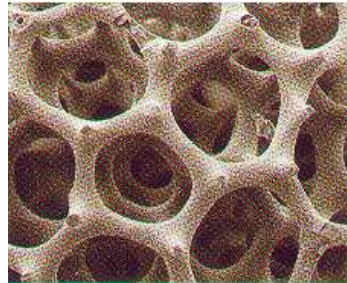
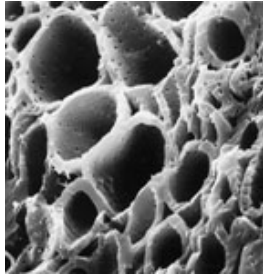


- a : corrugation
- b : bottle neck
- c : opening
- d : interconnection
- e : close-ended
- f : closed (isolated)



* normes IUPAC

More examples of porous solids.



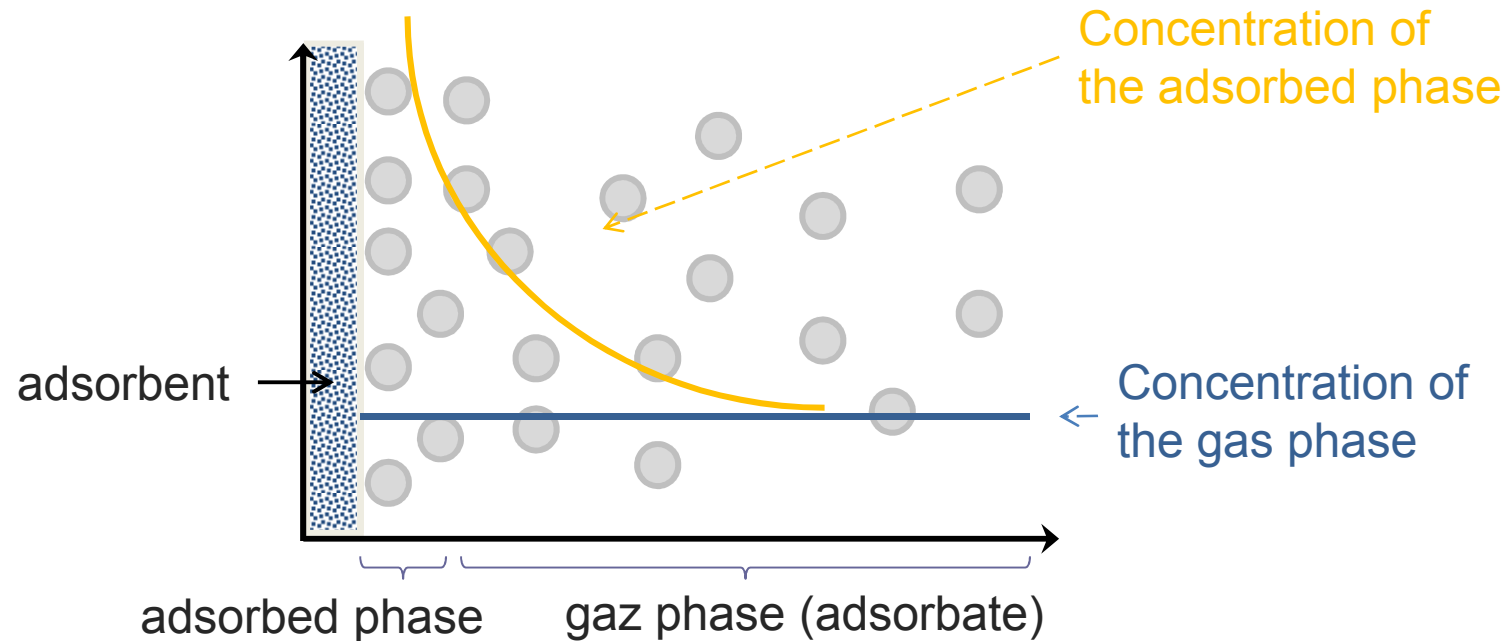
Some applications of porous solids.

(only those related to adsorption phenomenon)

- ➔ Purification of gases (closed atmosphere)
or liquids (eatable fluids (especially water), toxins elimination...)
or solids (cleaning of the soil: elimination of fertilizers, insecticides, radioactive waste)
- ➔ Detergency and cleaning in liquid medium (adsorption of surfactant, dissolution of stains and re-adsorption on porous powders, softening of water by adsorption)
- ➔ Catalysis (carried out in confined geometry)
- ➔ Separation of molecules (molecular sieves)
- ➔ Storage of gas (natural responsible for greenhouse effect, hydrogen)
- ➔ Storage of energy (adsorption is exothermic)

Adsorption.

Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of adsorbent, forming a molecular or atomic film.



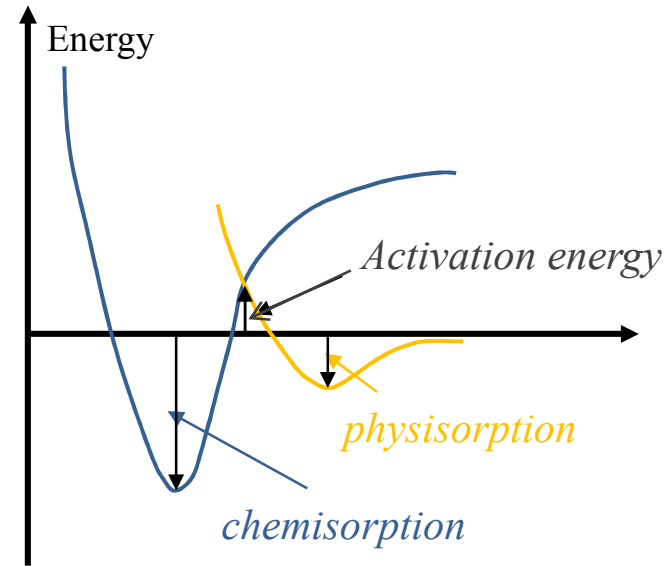
Physical adsorption is caused mainly by **van der Waals forces** and **electrostatic forces** between adsorbate molecules and the atoms which compose the adsorbent surface.

Chemical versus physical adsorption.

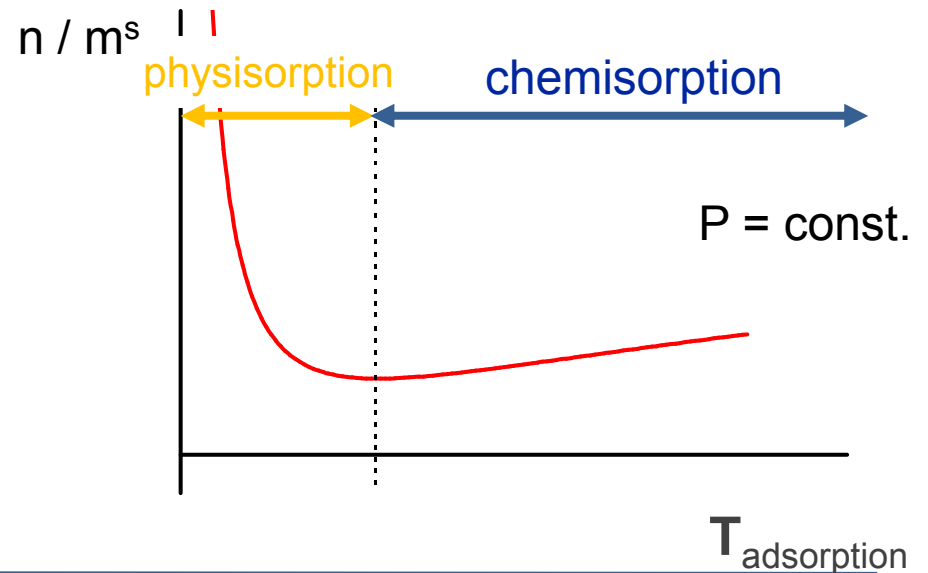
in chemisorption
there is an exchange of electrons
between the surface and the adsorbed molecules .



the energy of chemisorption is stronger. →

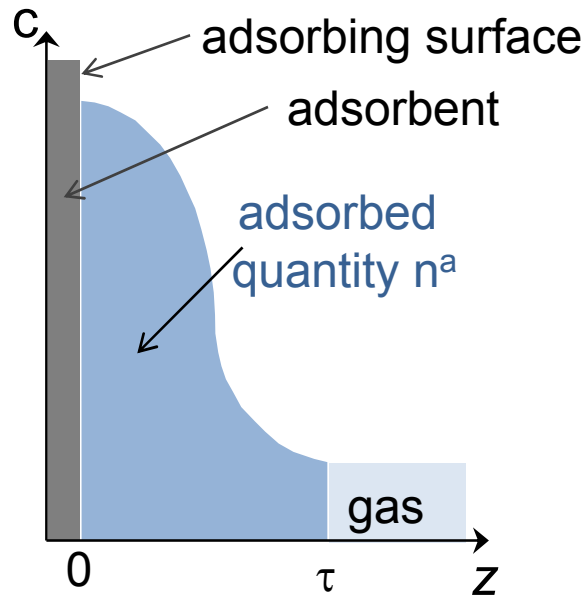


at constant pressure, chemisorption
occurs at higher temperature.



How to represent the adsorbed quantity?

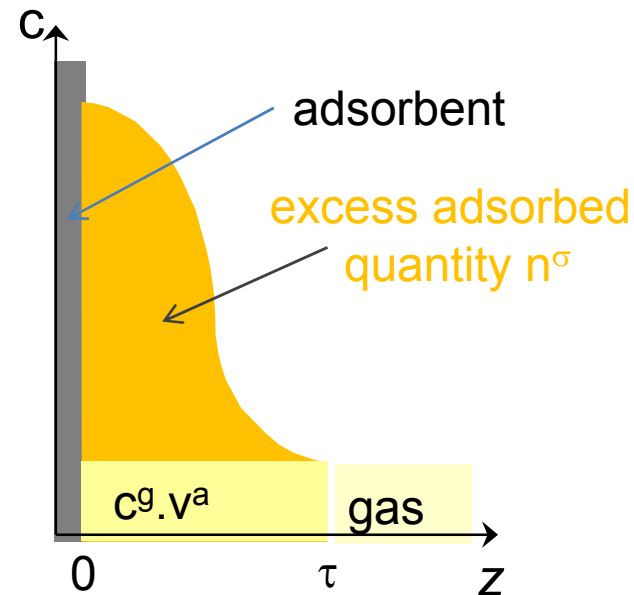
TOTAL amount adsorbed



(Total) adsorbed quantity n^a

$$n^a = A \int_0^{\tau} c \cdot dz$$

EXCESS amount adsorbed



Excess quantity on surface n^σ

$$n^\sigma = n_i^g - n_f^g$$

$$n^a = n^\sigma + c^g \cdot v^a$$

$$T \downarrow : n^a \approx n^\sigma$$

Isotherm of adsorption.

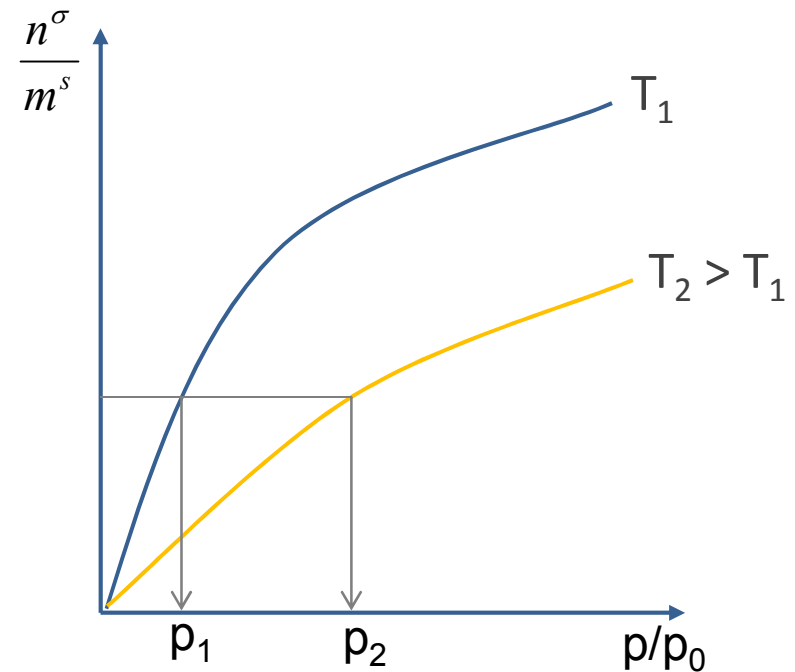
Isotherm of adsorption is an ensemble of equilibrium states, at temperature T , for all pressures p between 0 et p° (pressure of saturated vapor of adsorbate at temperature T).

p/p° is called
« relative equilibrium pressure ».

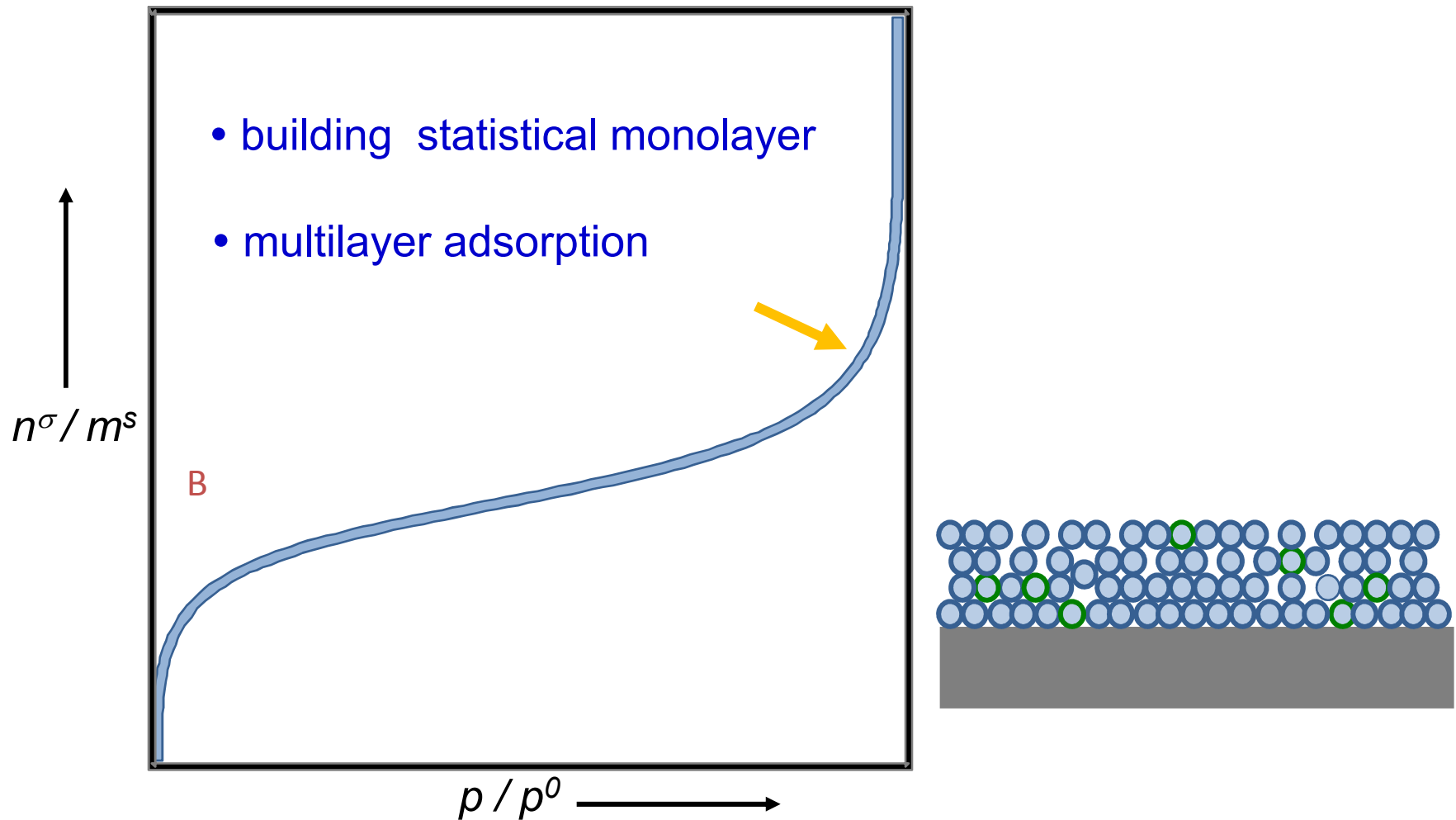
adsorption is exothermic!

isosteric enthalpies

$$\Delta_{ads} \dot{h} = -R \frac{T_1 T_2}{T_2 - T_1} \ln \left[\frac{p_2}{p_1} \right]_{n^\sigma / m^s}$$

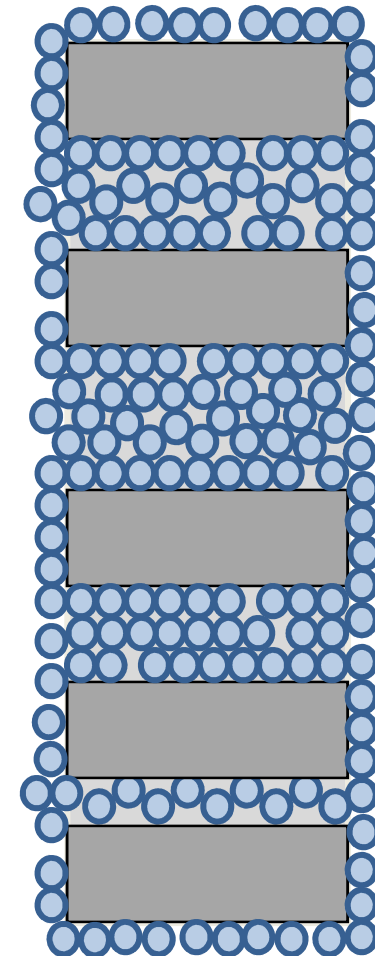
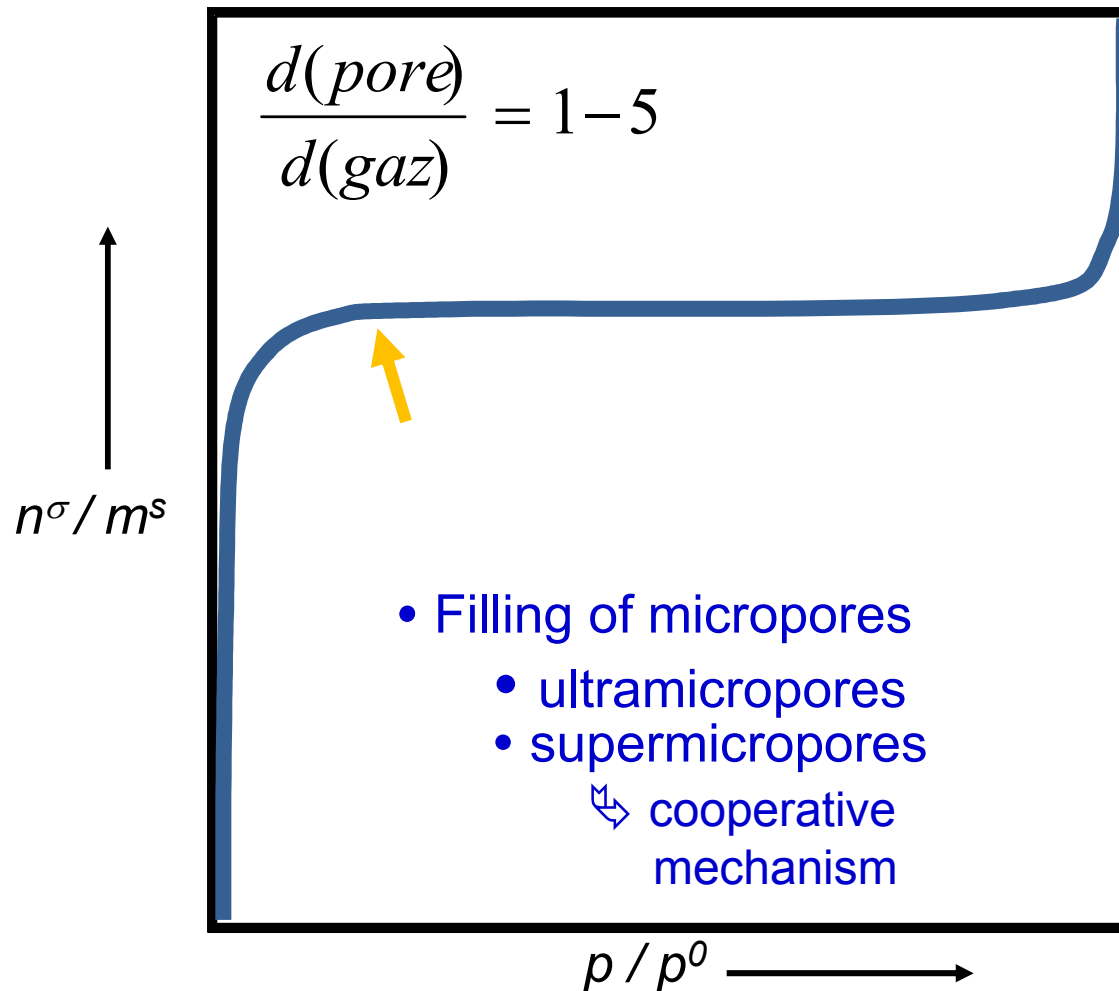


Adsorption on surface: purely non-porous sample.



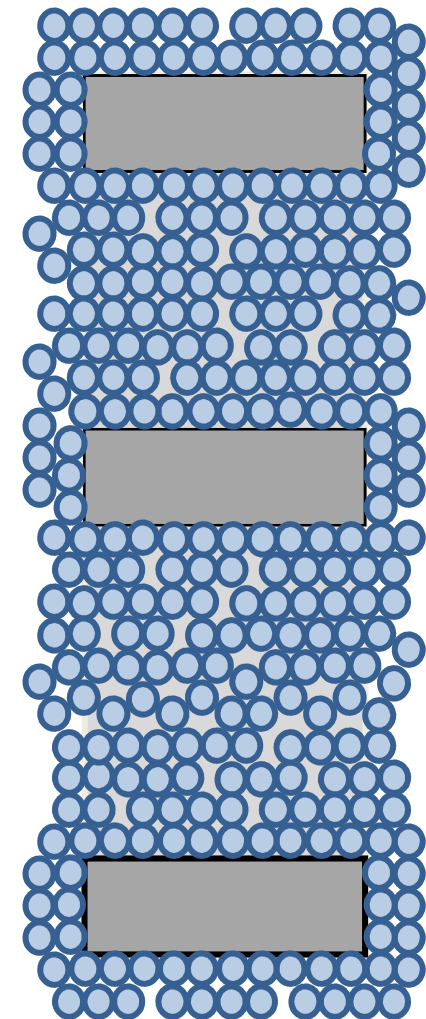
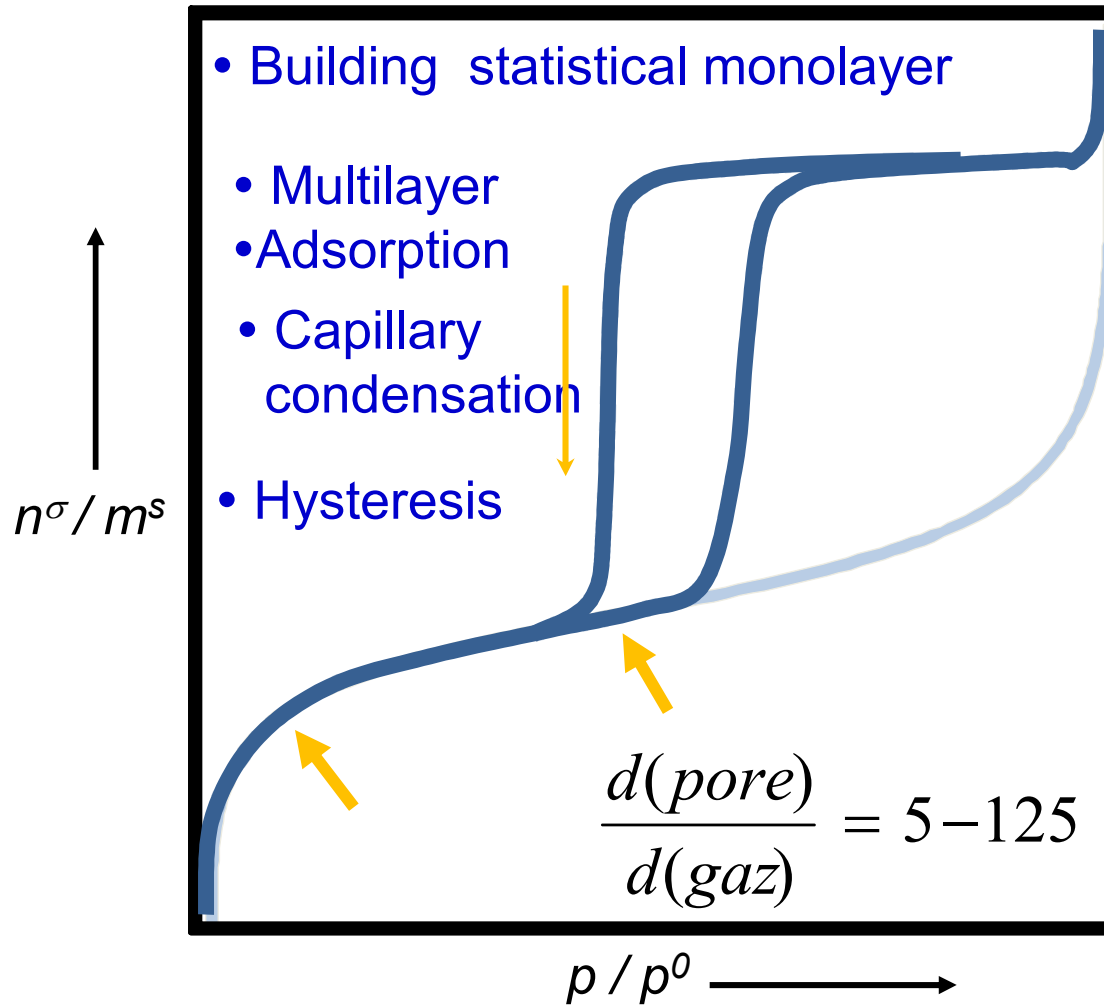
Adsorption: purely microporous samples.

$d \approx 0.4 - 2 \text{ nm}$

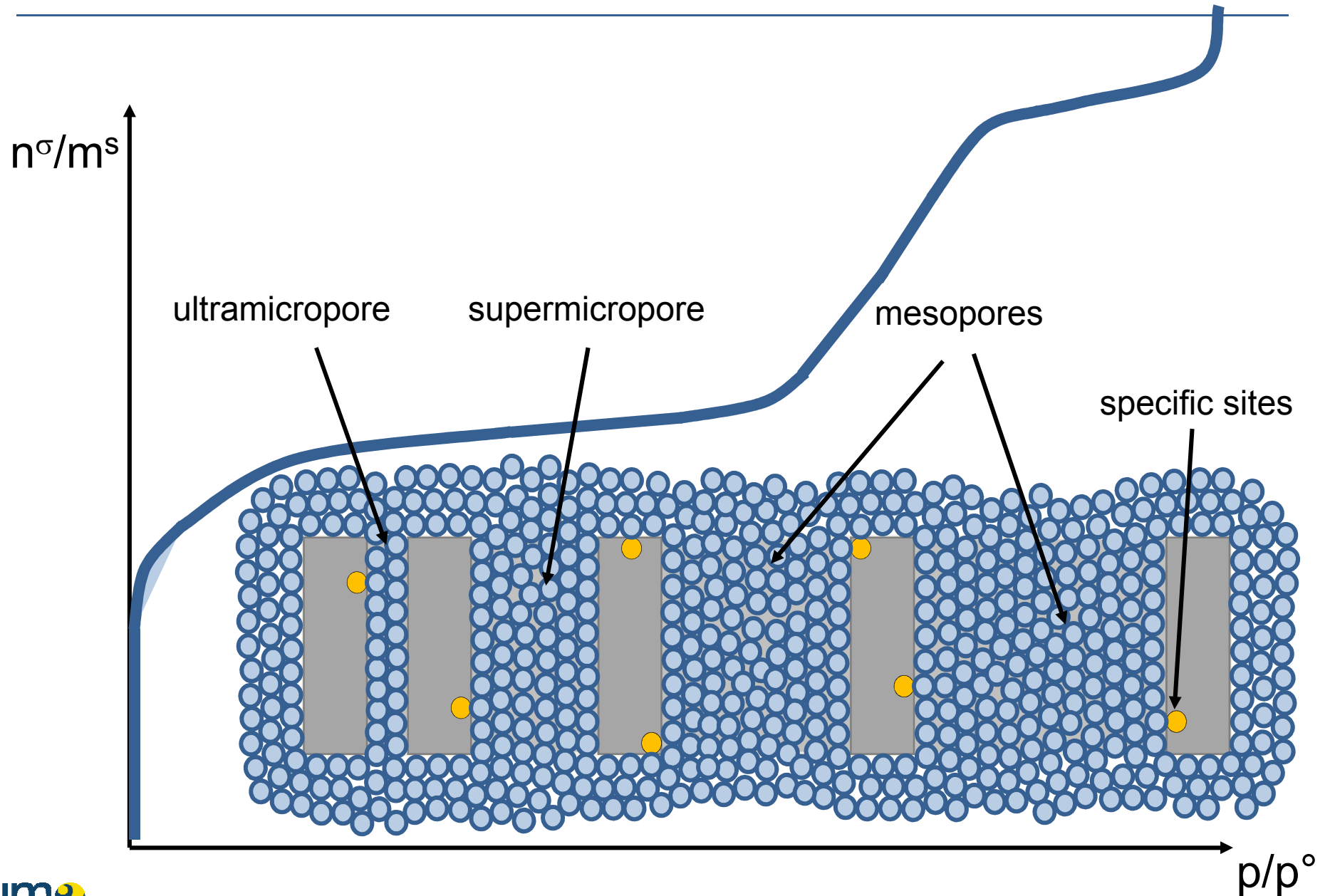


Adsorption on purely mesoporous samples.

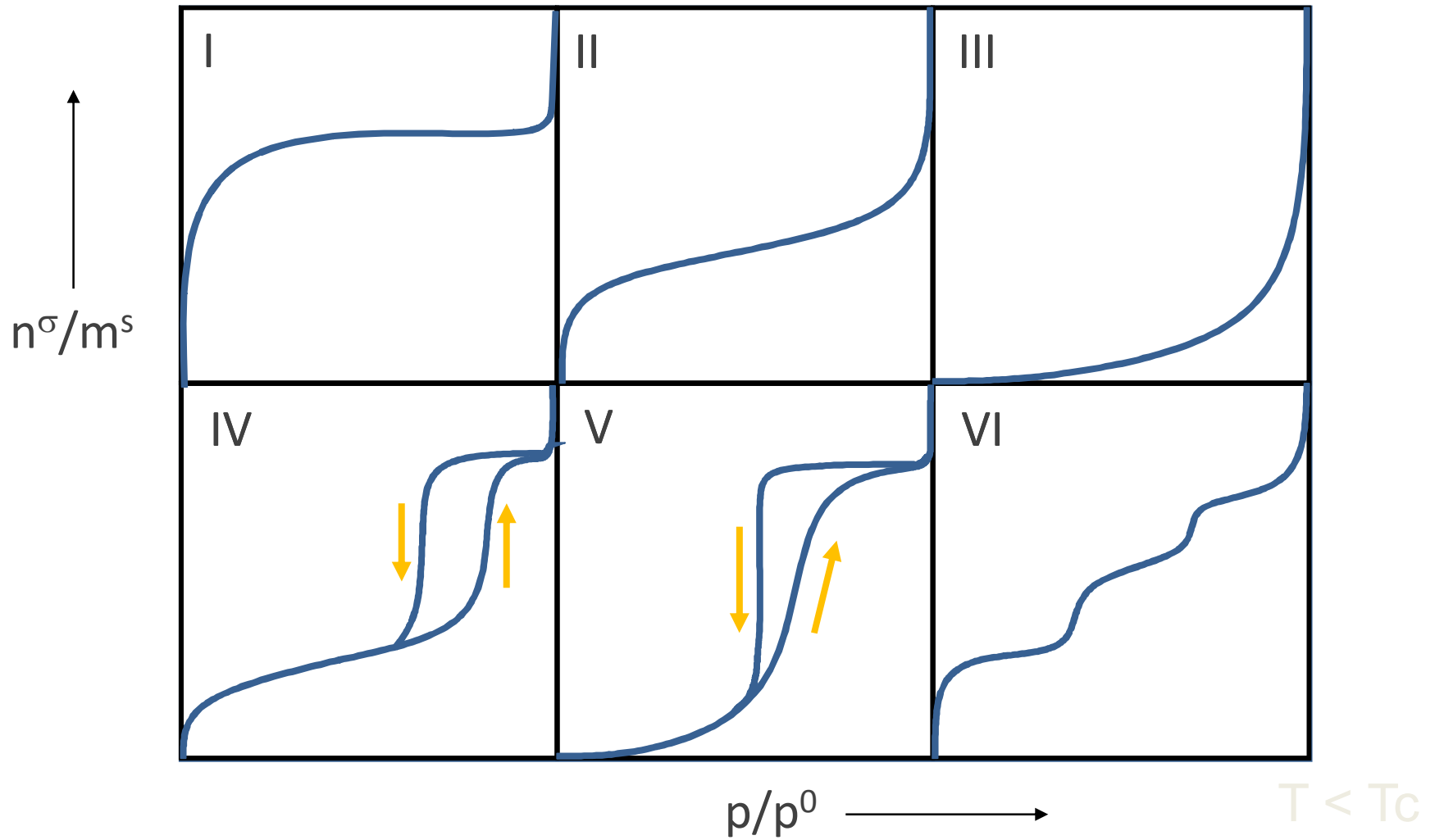
$d \approx 2 - 50 \text{ nm}$



Adsorption on heterogeneous samples.

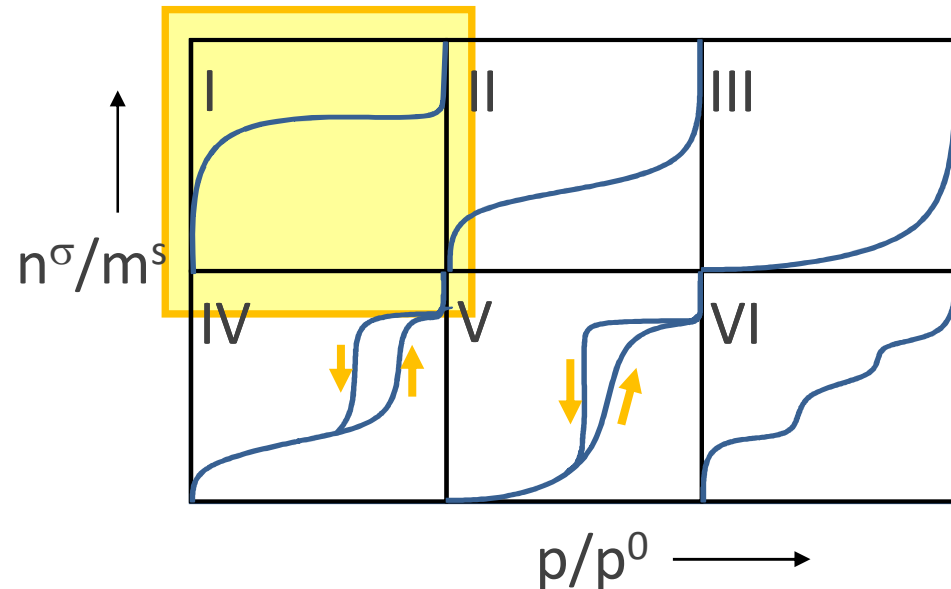


IUPAC classification of adsorption isotherms



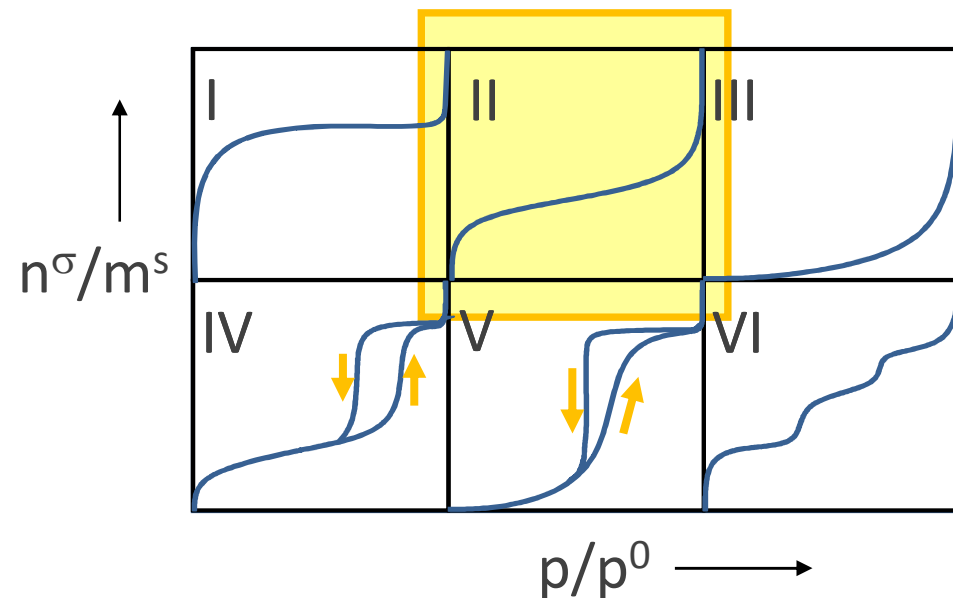
Type I isotherms.

The **type I** isotherms are characterized by a horizontal line which indicates saturation of the adsorbent. This isotherm is observed in adsorbents having only **micropores** that are filled at low pressures. Lower pressure of filling, smaller the size of the pores.



Type II isotherms.

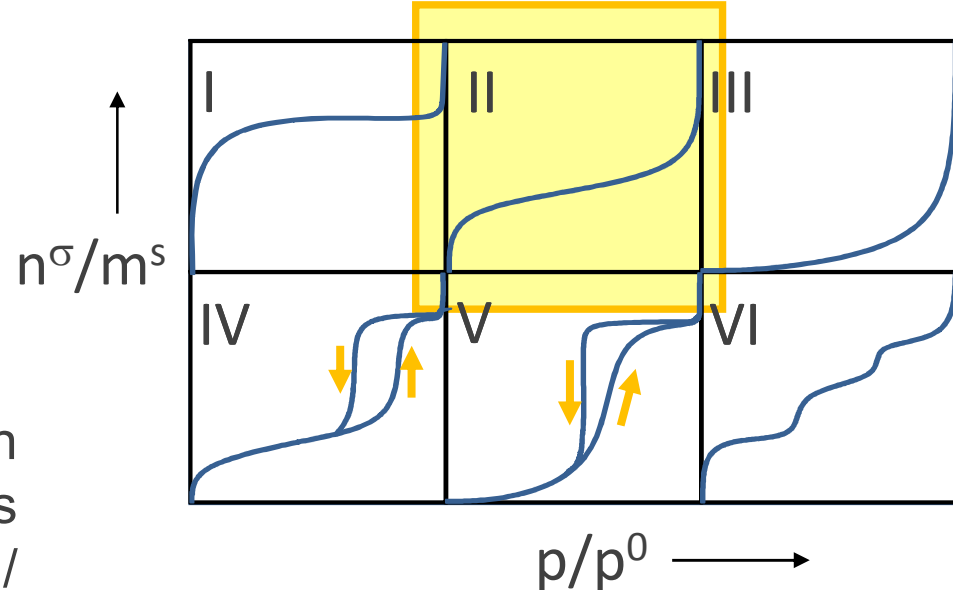
The **type II** isotherms are characterized par increase of the adsorbed quantity, in a continuous way, as a function of the equilibrium pressure. This type of isotherms is observed in **non-porous adsorbents** or in **macropores**. It indicates the multilayer adsorption.



Type IV isotherms.

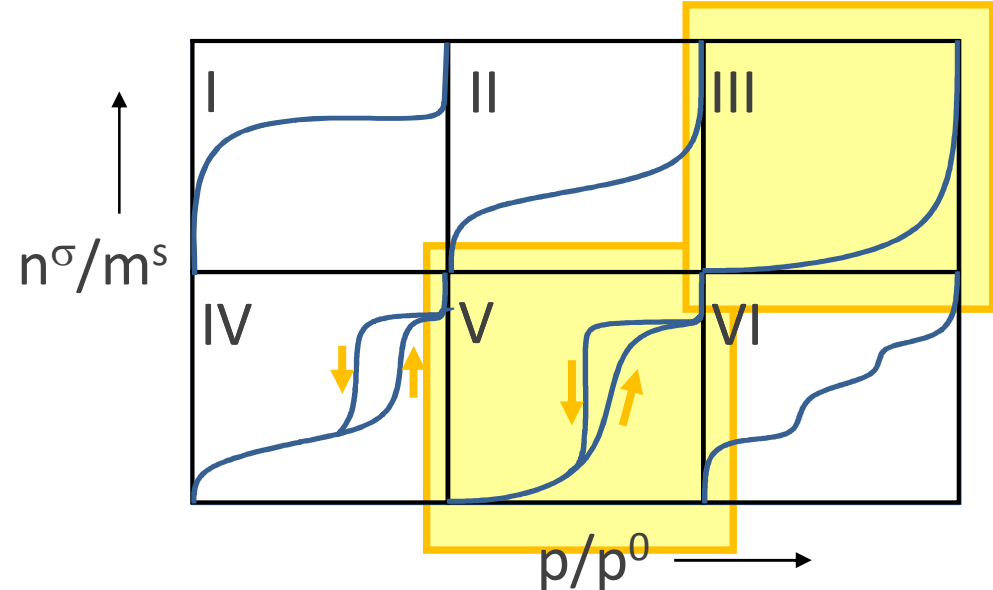
The **type IV** isotherms have the same shape as the type II isotherms at low pressures (below $p/p^0 \approx 0.4$). At higher pressure they are characterized par saturation of adsorption. This type of isotherms is observed in mesoporous materials where the capillary condensation is observed.

Desorption is very often nonreversible; a hysteresis is observes between desorption/ /adsorption branches.



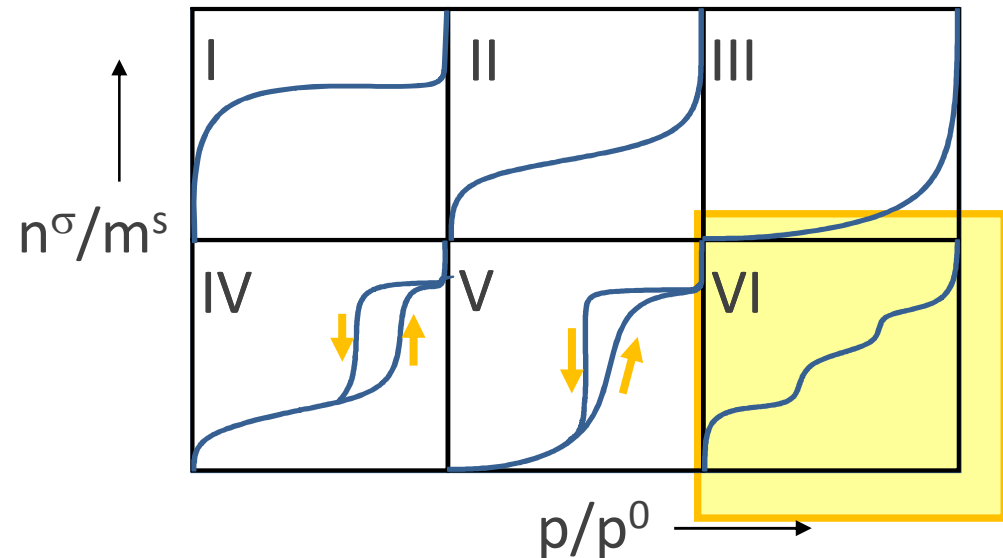
Type III and V isotherms.

The **type III and V** isotherms are less frequently observed: they are similar to isotherm of type II and IV but they differ at low pressures. This difference is attributed to **weak interaction between adsorbent and the adsorbed molecules**. For example, they are observed when water adsorbs on hydrophobic surfaces.



Type VI isotherms.

Step-wise isotherms of adsorption (type VI) are observed in adsorption on homogeneous surfaces when the interaction between adsorbent and the adsorbed molecules is strong. In consequence the layers are formed one after another.

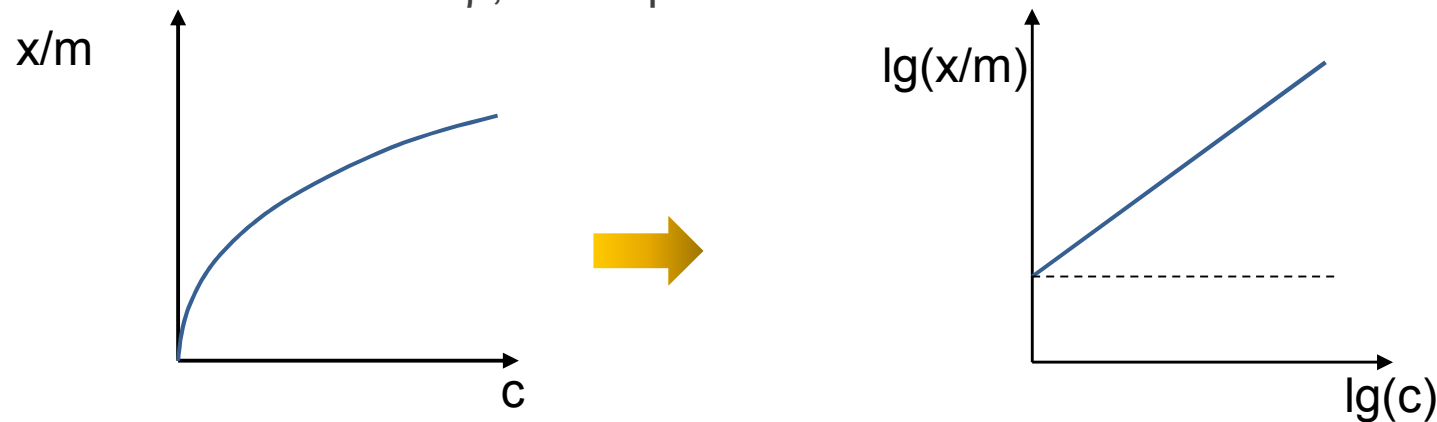


Modeling of adsorption: Freundlich equation.

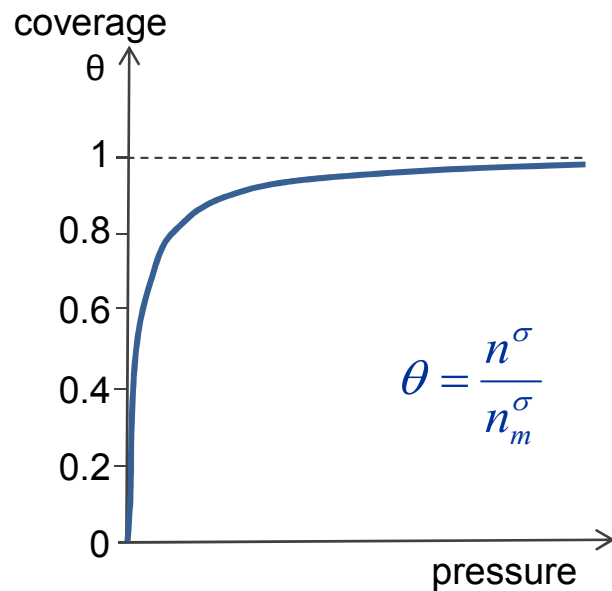
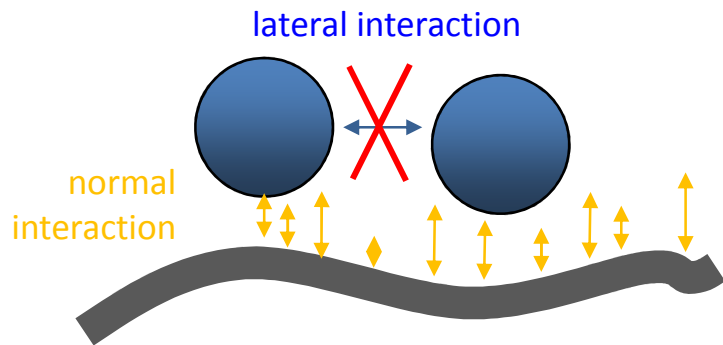
In 1909, Freundlich gave an empirical expression representing the isothermal variation of a quantity of gas adsorbed by unit mass of solid adsorbent with pressure (or, the concentration of a solute on the surface of an adsorbent to the concentration of the solute in the liquid with which it is in contact):

$$x/m = \beta p^{1/n} \quad \text{or} \quad x/m = \beta c^{1/n}$$

where: x – adsorbed mass
 m – mass of adsorbent
 p (c) – equilibrium pressure (concentration) of adsorbate (solute)
 β , n – experimental constants



Langmuir theory (1916).



- derived from statistical mechanics -

Basic assumptions:

- one type of adsorption sites
- one site allows the adsorption of one molecule (atom) of fluid
- no lateral interactions between fluid molecules (atoms) $b = K \exp^{E/RT}$

← **adsorption is limited to one layer**

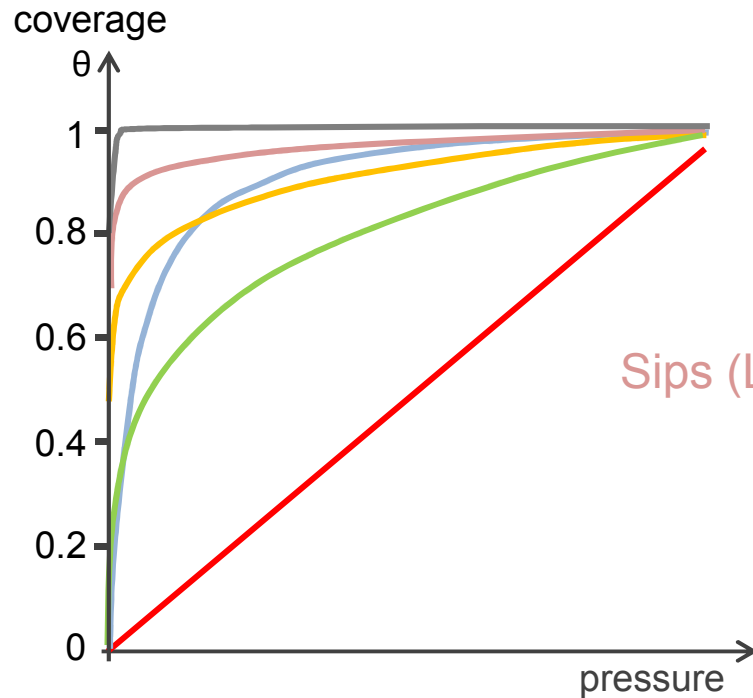
$$n^{\sigma} = n_m^{\sigma} \frac{bp}{1 + bp}$$

n_m^{σ}, K – constants
 $b = K \exp(E/RT)$

at low pressure $bp \ll 1$, so $1 + bp \approx 1$

$$n^{\sigma} = n_m^{\sigma} bp \quad \leftarrow \quad \text{Henry's law}$$

Variations of Langmuir theory.



Freundlich $n = k_H p^{1/m}$

Henry $n = k_H p$

Langmuir $\frac{n}{n_L} = \frac{bp}{1 + bp}$

Sips (Langmuir-Freundlich) $\frac{n}{n_L} = \frac{(k_H p)^{1/m}}{1 + (k_H p)^{1/m}}$

Toth $\frac{n}{n_L} = \frac{p}{(b + p^m)^{1/m}}$

Jensen & Seaton $n = k_H p \left[1 + \left(\frac{k_H p}{a(1 + \kappa p)} \right)^m \right]^{-1/m}$

