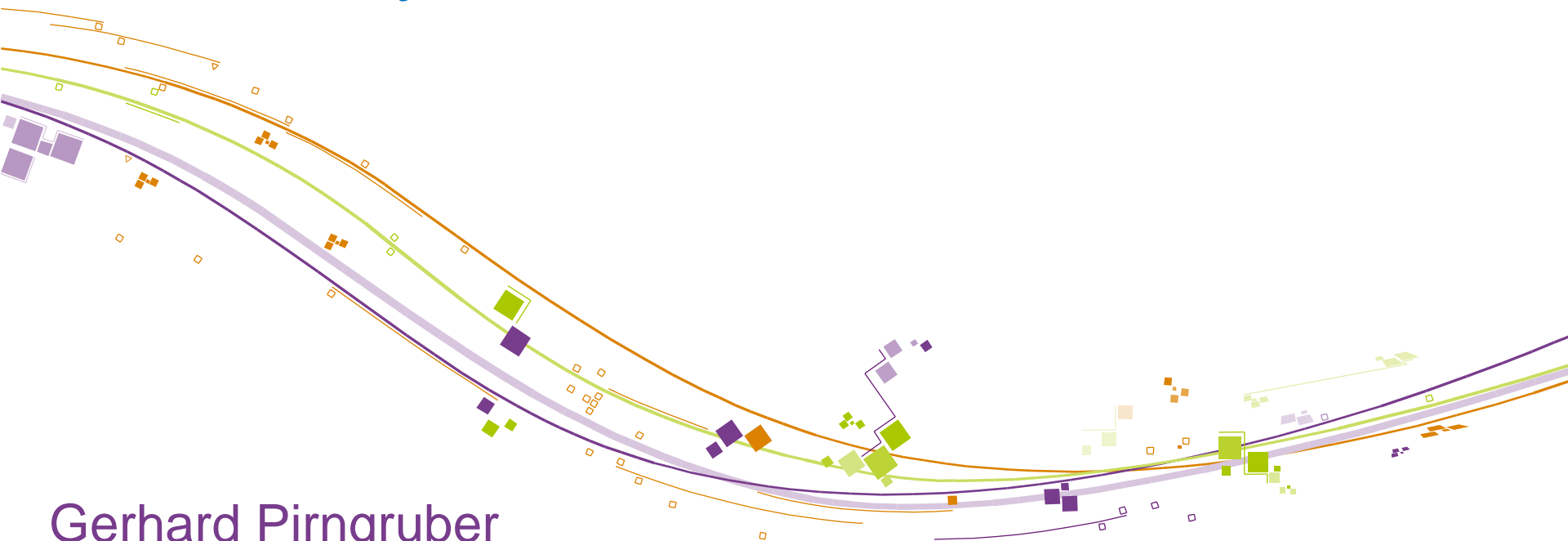# Physisorption and pore size analysis

Gerhard Pirngruber

Direction Catalyse et Séparation

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CV Gerhard Pirngruber

- **1995 – 1999   PhD in heterogeneous catalysis**
  - Universiteit Twente (NL)

- **2000 – 2005   Oberassistent**
  - ETH Zurich, Inst of Chemical and Bioengineering
  - Research activity
    - zeolites
    - mesoporous silica

- **2005 – now   R&D Scientist, project leader**
  - IFP Energies nouvelles, Catalysis and Separation Division
  - Research activity
    - 2005 – 2012 : CO2 capture, separation of hydrocarbons
    - 2012 – now: hydrotreating and hydrocracking catalysts

Porous solids in catalysis

- **Supported catalysts**
    - e.g. noble metals, transition metal sulfides
    - Porous support
        - provides surface for dispersing the catalyst
        - provides mechanical stability
        - has an influence on diffusion of reactants and products
        - has an influence on adsorption of reactants and products
        - determines reactor volume
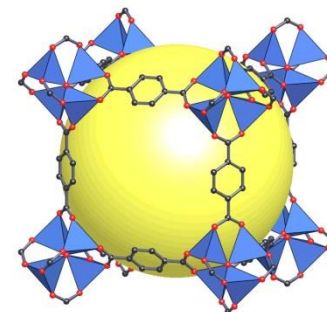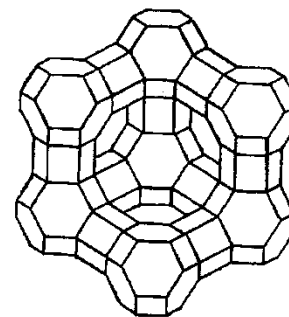
- **Porous catalysts**
    - Zeolites
    - Oxydes

Optimising porosity is often the key to improving catalytic performance.
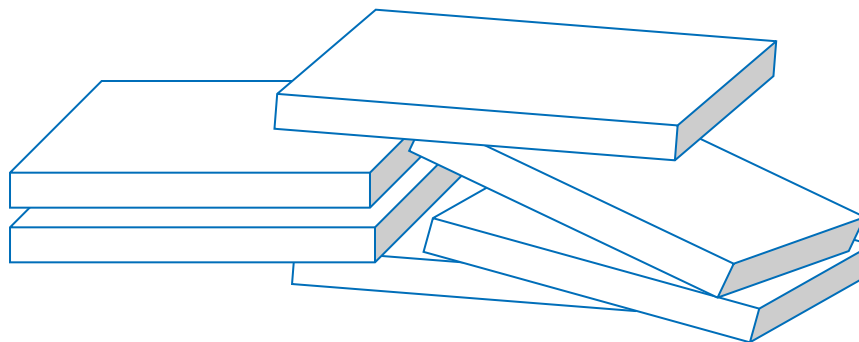
Types of porosity

- **Porous cristalline structures**
  - Zeolites,
  - Metal Organic Frameworks

- **Ordered or disordered stacking of small particles generates an interparticles porosity**
  - oxides (silica, alumina, etc.)
  - activated carbon

Characterisation of porosity

- **Physisorption (N_2, Ar, Kr)**
  - surface area
  - pore volume
  - pore size distribution

- **Hg intrusion**
  - pore volume
  - pore size distribution
  - surface area

- **Imaging methods**
  - Transmission Electron Microscopy
  - Secondary Electron Microscopy

Terminology

- Adsorption is a surface phenomenon.
- Adsorbent = solid that provides a surface for adsorption.
- Adsorbate = molecule adsorbed on the surface.
- Adsorptive = molecule susceptible of being adsorbed.

- Physisorption: no formation of chemical bonds, no transfer of electron density
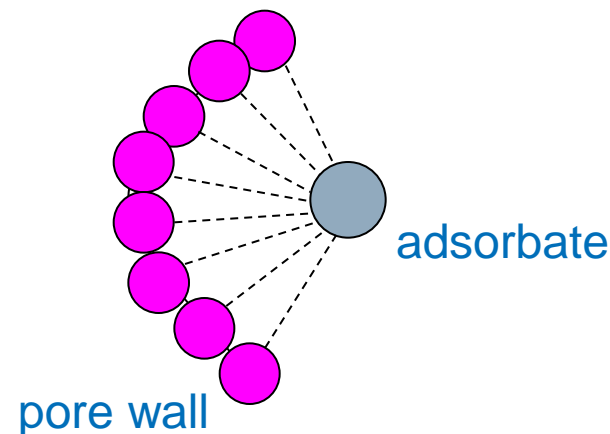- Chemisorption: formation of a chemical bond (exchange of electrons)
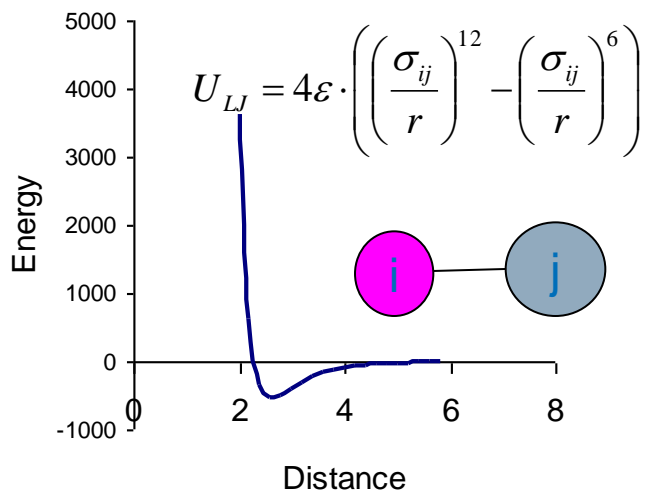
Terminology

- **IUPAC distinguishes 3 catagories of pore sizes**
  - Micropores   < 2 nm
  - Mesopores   2 – 50 nm
  - Macropores   > 50 nm

Forces involved in physisorption

- **van der Waals forces**

  - **amplified by multiple interactions with atoms or pore wall (i)**

$$U_{LJ} = 4\varepsilon \cdot \left(\left(\frac{\sigma_{ij}}{r} \right)^{12} - \left(\frac{\sigma_{ij}}{r} \right)^{6} \right)$$

adsorbate

pore wall

  - **maximal when size of adsobate (j) close to pore size**
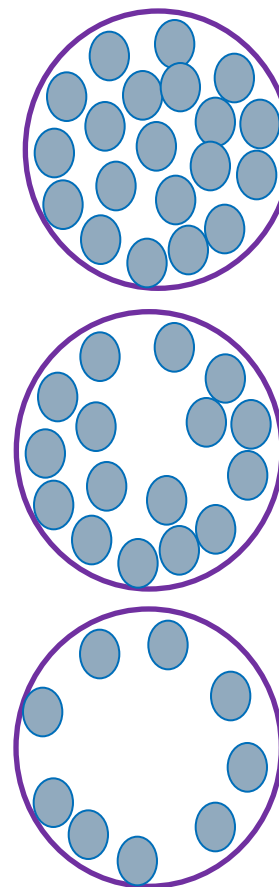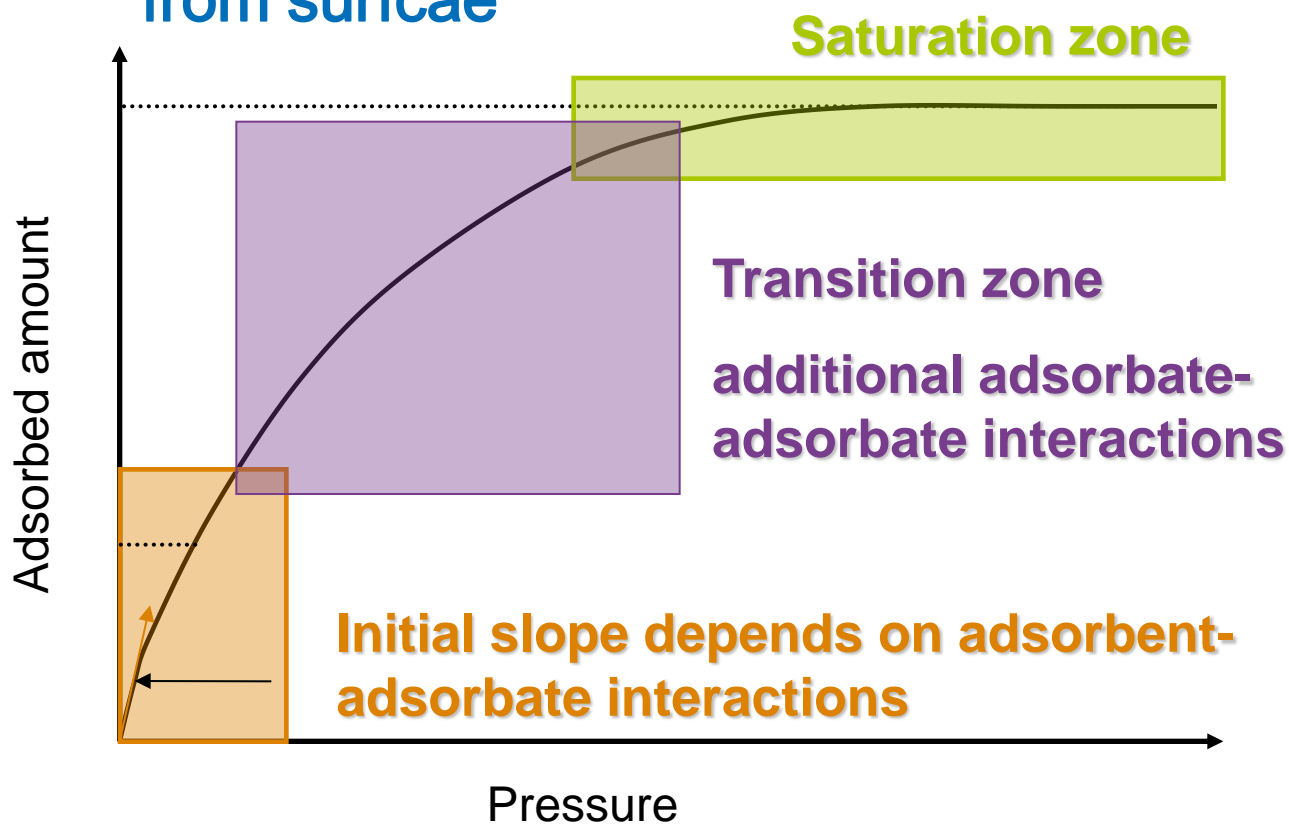

adsorbate

pore wall

Forces involved in physisorption

- **Electrostatic forces**
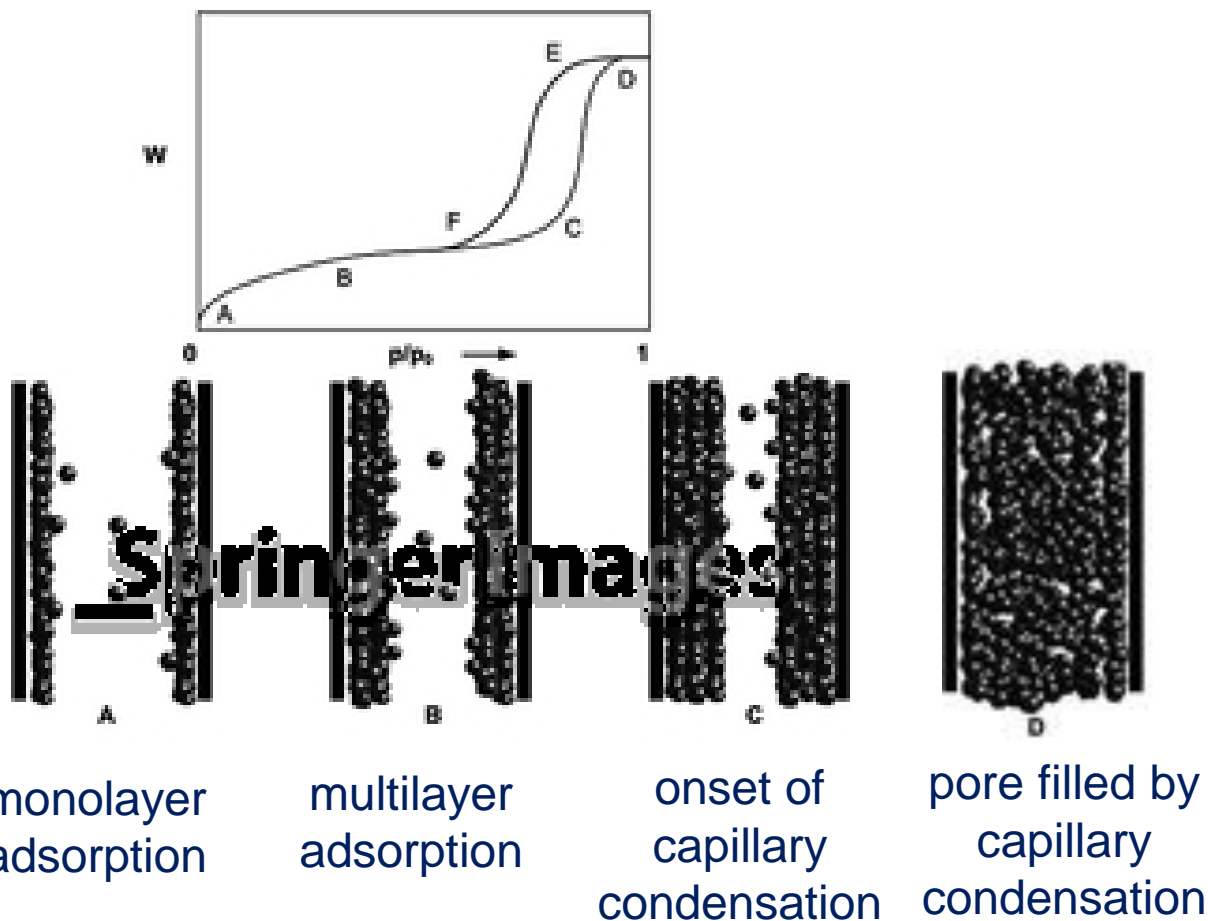 - Any non-symmetric charge distribution in the adsorbent generates an electric field
  - adsorbates with an electric moment (dipole, quadrupole) interact with the electric field
  - undesirable in analysis of porosity/pores size because surface chemistry/chemical composition enter into the game
  - N_2 has a small quadrupole moment → use of Ar, Kr is preferable for precise micropore size analysis

Adsorption in micropores

- **Gradual filling of pore volume starting from surfcae**

Saturation zone

Transition zone

additional adsorbate-adsorbate interactions

Initial slope depends on adsorbent-adsorbate interactions

Adsorbed amount

Pressure

Adsorption in mesopores

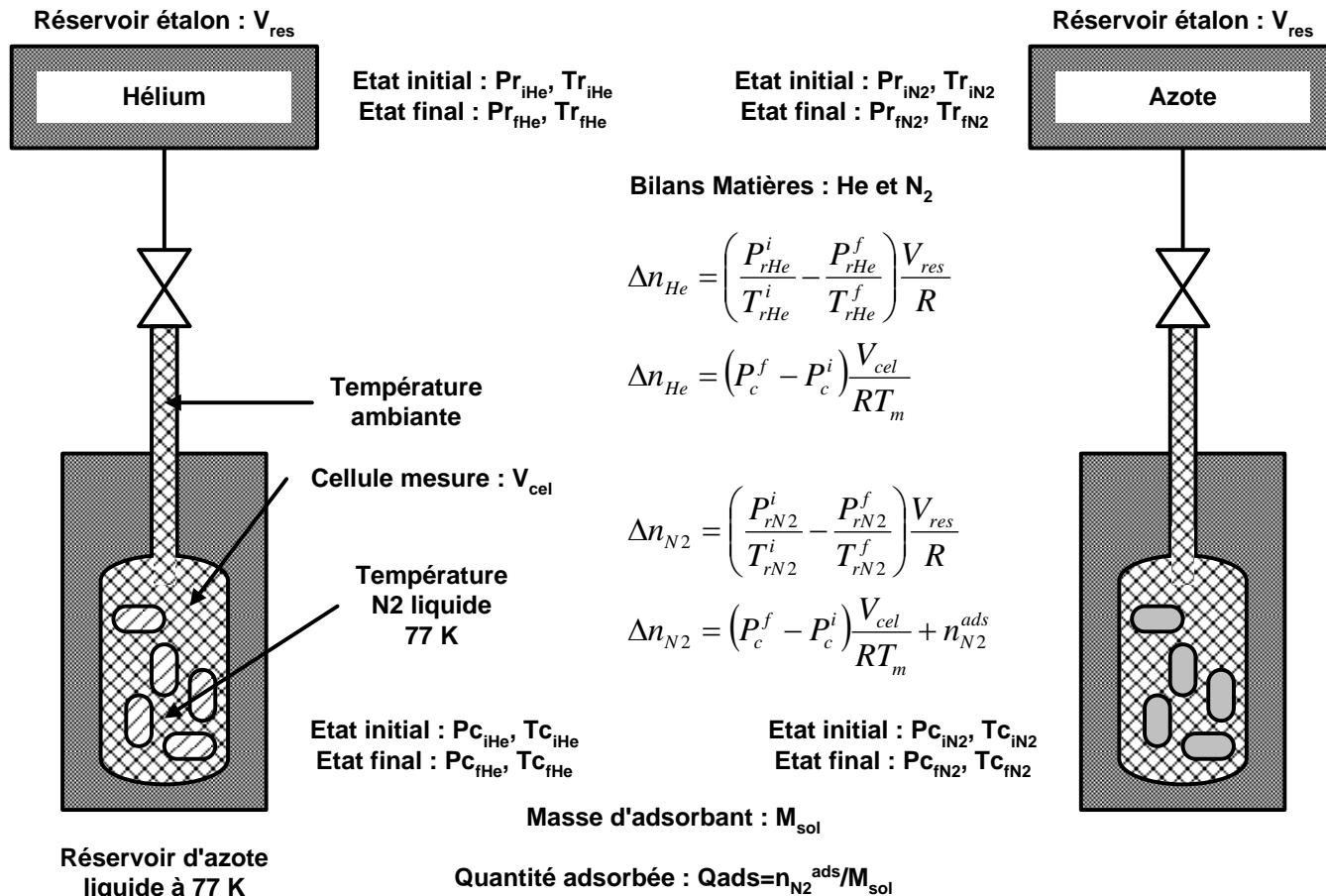| monolayer adsorption | multilayer adsorption | onset of capillary condensation | pore filled by capillary condensation |

Adsorption in macropores
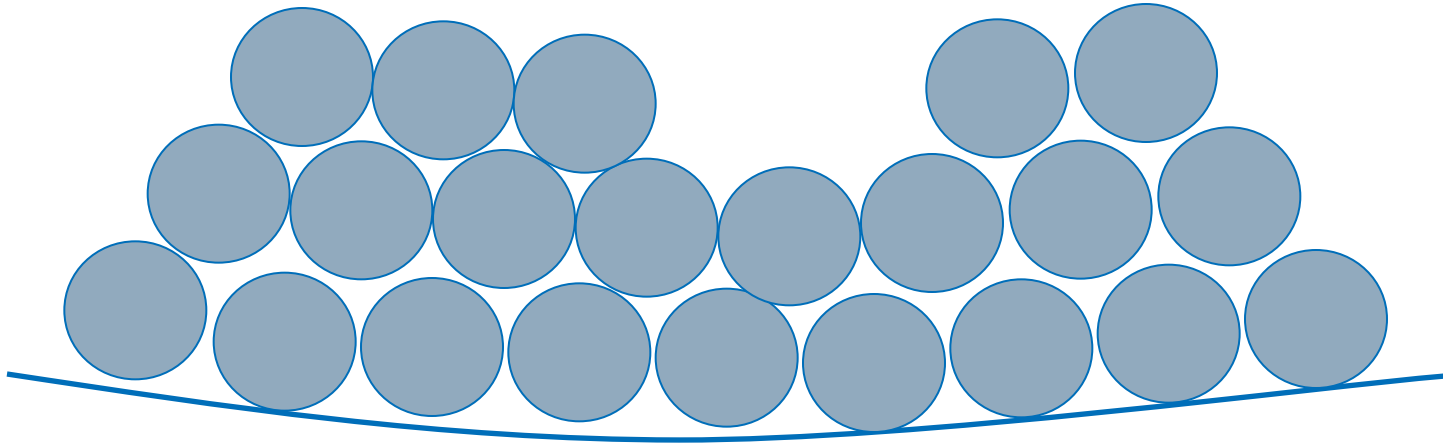
- **Opposite pore wall is too far away to influence adsorption and provoke capillary condensation**
- **First monolayer, then multilayer adsorption**

How to measure an adsorption isotherm?

- ## Volumetric method

Réservoir étalon : V$_{res}$

Hélium

Etat initial : Pr$_{iHe}$, Tr$_{iHe}$
Etat final : Pr$_{fHe}$, Tr$_{fHe}$

Etat initial : Pr$_{iN2}$, Tr$_{iN2}$
Etat final : Pr$_{fN2}$, Tr$_{fN2}$

Réservoir étalon : V$_{res}$

Azote

Bilans Matières : He et N$_2$

$$\Delta n_{He} = \left(\frac{P_{rHe}^i}{T_{rHe}^i} - \frac{P_{rHe}^f}{T_{rHe}^f} \right) \frac{V_{res}}{R}$$

$$\Delta n_{He} = \left(P_c^f - P_c^i \right) \frac{V_{cel}}{RT_m}$$

Température ambiante

Cellule mesure : V$_{cel}$

Température N2 liquide 77 K

$$\Delta n_{N2} = \left(\frac{P_{rN2}^i}{T_{rN2}^i} - \frac{P_{rN2}^f}{T_{rN2}^f} \right) \frac{V_{res}}{R}$$

$$\Delta n_{N2} = \left(P_c^f - P_c^i \right) \frac{V_{cel}}{RT_m} + n_{N2}^{ads}$$

Etat initial : Pc$_{iHe}$, Tc$_{iHe}$
Etat final : Pc$_{fHe}$, Tc$_{fHe}$

Etat initial : Pc$_{iN2}$, Tc$_{iN2}$
Etat final : Pc$_{fN2}$, Tc$_{fN2}$

Réservoir d'azote liquide à 77 K

Masse d'adsorbant : M$_{sol}$

Quantité adsorbée : Qads=n$_{N2}$^{ads}/M$_{sol}$

Material balance

- ## Reservoir : 1   Sample cell : 2

- ## without adsorption (He), sample cell initially under vacuum

$$\frac{p_{init}V_1}{RT_1} = \frac{p_{final}V_1}{RT_1} + \frac{p_{final}V_2}{RT_2}$$

$$\frac{V_2}{T_2} = \frac{V_1}{T_1} \cdot \frac{p_{init} - p_{final}}{p_{final}}$$

- ## with adsorption (N_2)

determined with He

quantity initially present in the reservoir

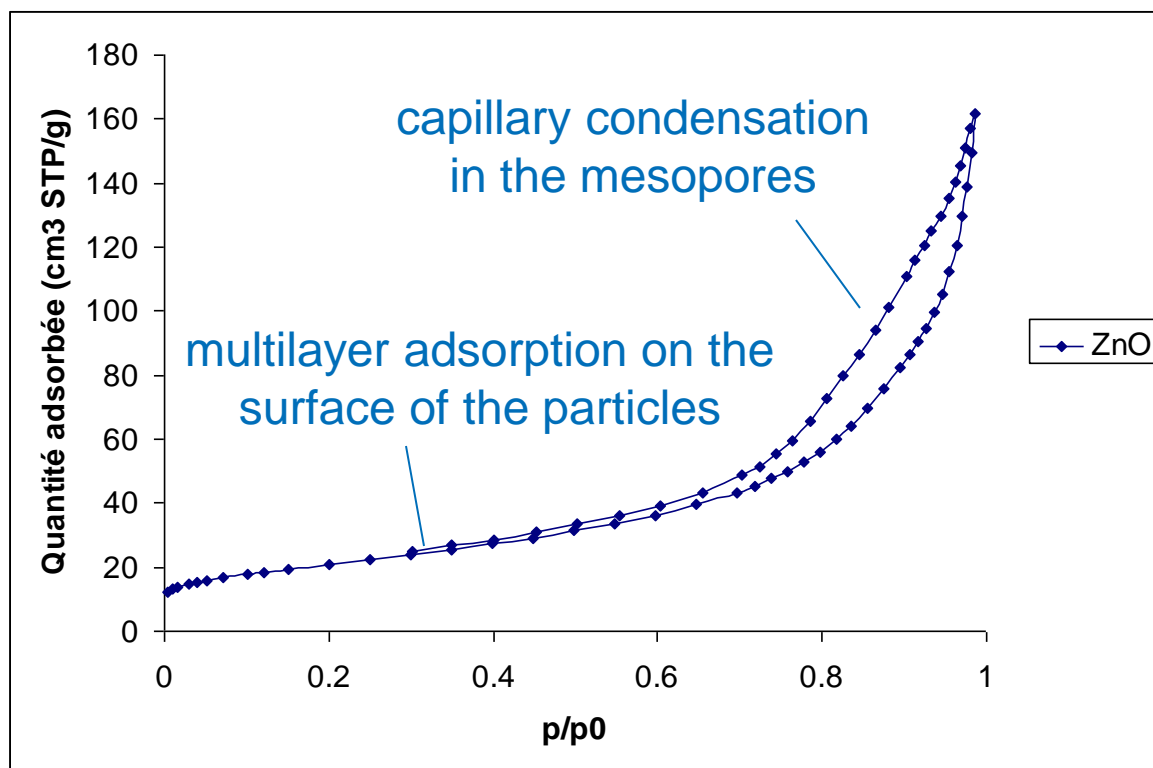$$n_{tot} = \frac{pV_1}{RT_1} + \frac{pV_2}{RT_2} + n_{ads}$$

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Experimental difficulties

- **Precise measurement of pressure required**
  - difficult at low pressure
  - difficult to measure a micropore distribution
- **Isotherm !!**
  - T_2 in principle 77 K (temperature of liquid N_2)
    - part of the cell is not plunged into liquid N2, but is at ambient temperature
    - temperature gradient must be the same as during the initial calibration of the volume with He
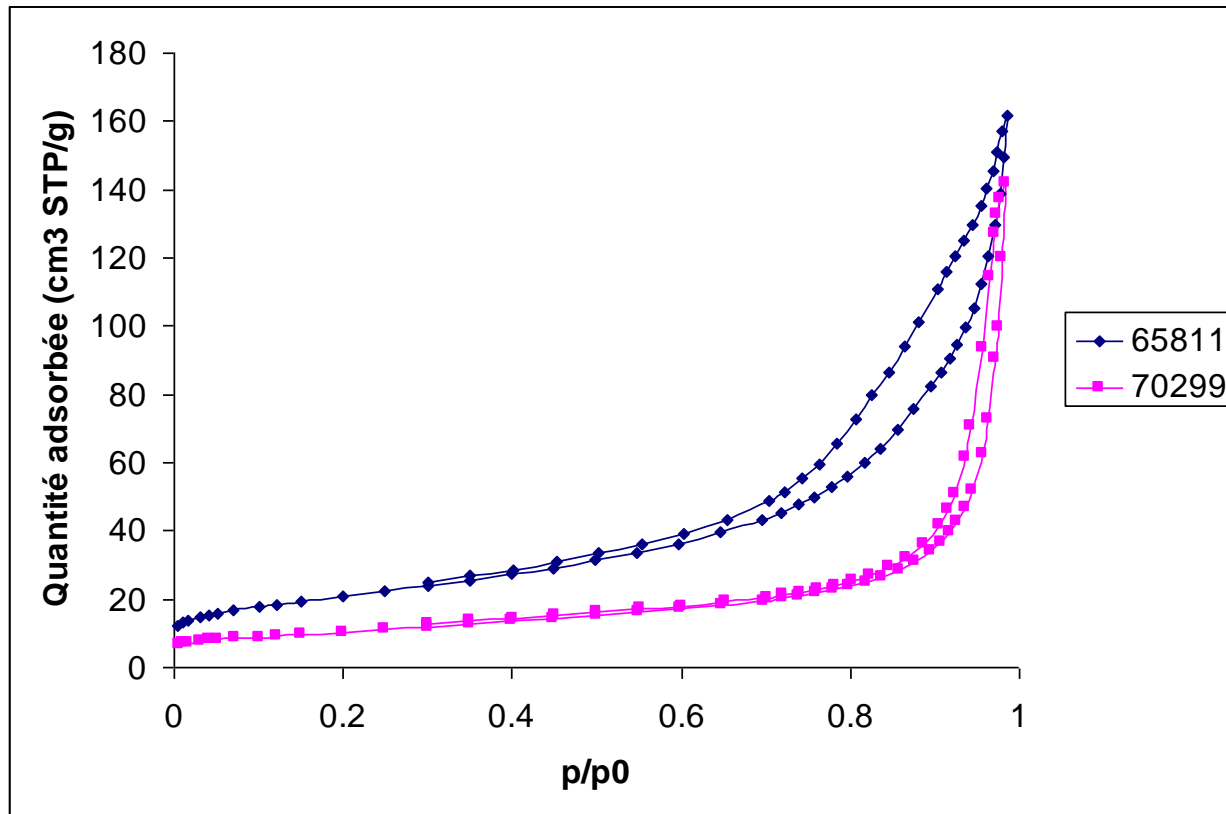 - pay attention to the level of liquid N_2

Example zeolite NaX
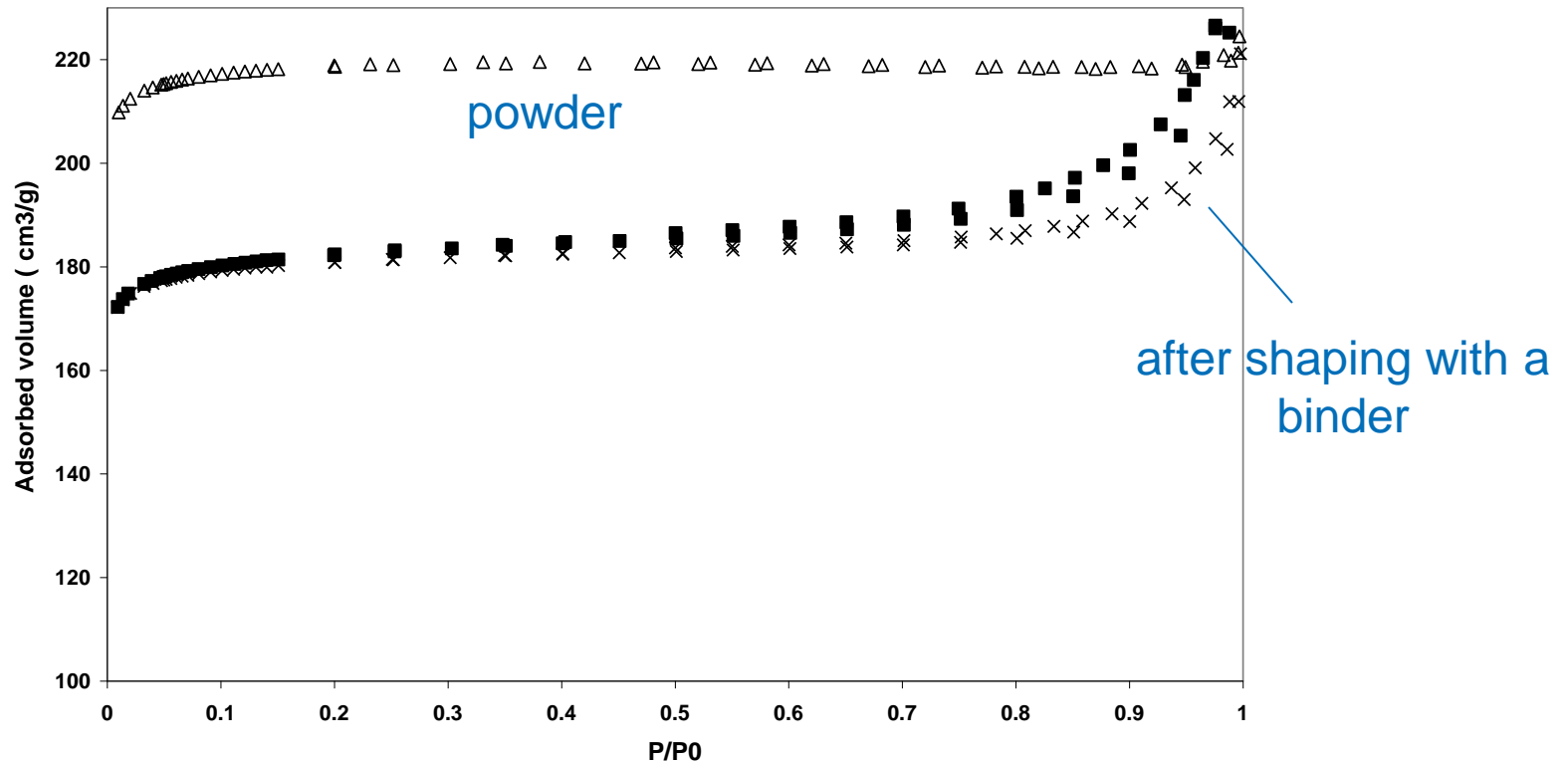
- **Micropores are entirely filled at very low pressure.**
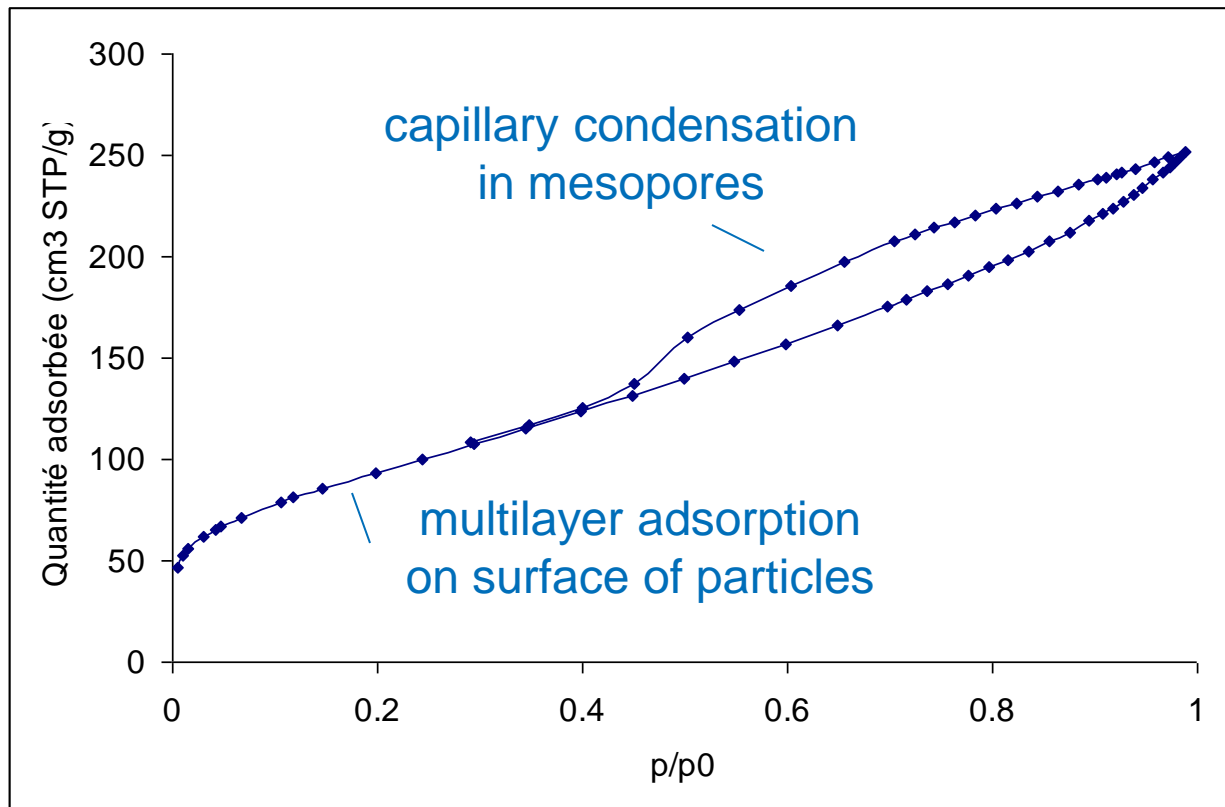- **Isotherm is totally flat once micropores are filled.**
  - **saturation zone**

Characterization of porous solids - Characterization of Catalysts and Surfaces - G Pirngruber 17 october 2017

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Examples - ZnO

- **no micropores**
- **mesopores generated by stacking of inidividual particles**
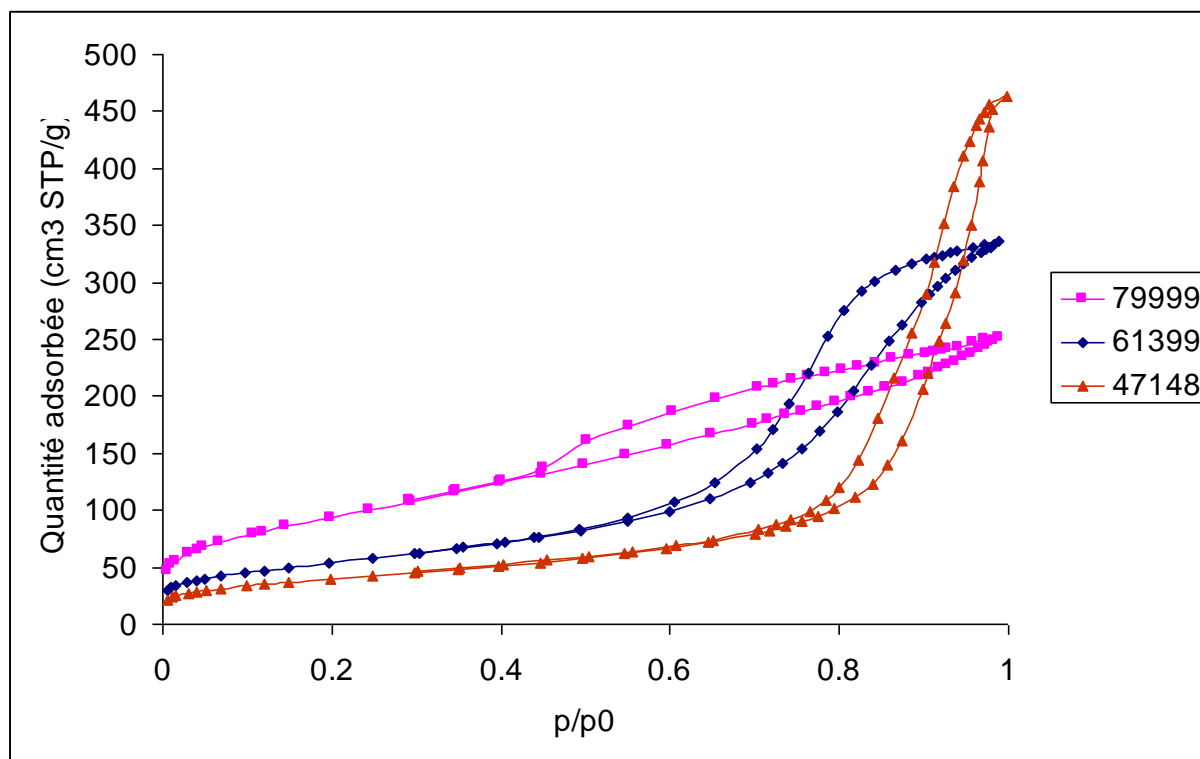
Comparison of two ZnO samples

- **Surface : 65811 > 70299**
- **Pore size : 70299 > 65811**

Example – Al$_2$O$_3$

capillary condensation
in mesopores

multilayer adsorption
on surface of particles

(Chart axes: Quantité adsorbée (cm3 STP/g) from 0 to 300; p/p0 from 0 to 1)

- **no micropores**
- **high surface area, broad pore size distribution**

Comparison Al$_2$O$_3$

- **Surface : 79999 > 61399 > 47148**

- **Pore size : 47148 > 61399 > 79999**

Quantitative treatment of N_2 isotherms

- **Pore volume: V_{micro}, V_{meso}, V_{total}**
  - t-plot

- **Surface area**
  - BET (Brunauer-Emerett-Teller)
  - Langmuir

- **Pore size distribution**
  - Micropores
    - Horwath-Kawazoe, Saito-Foley
  - Mesopores
    - BJH (Brunauer-Joyner-Halenda)
    - DFT (Density Functional Theory)

Determination of the surface area

- **BET (Brunauer Emmet Teller): multilayer adsorption**
  - first layer: adsorption on the surface
  - all the other layers are considered like a condensed liquid

$K_{condensation}$
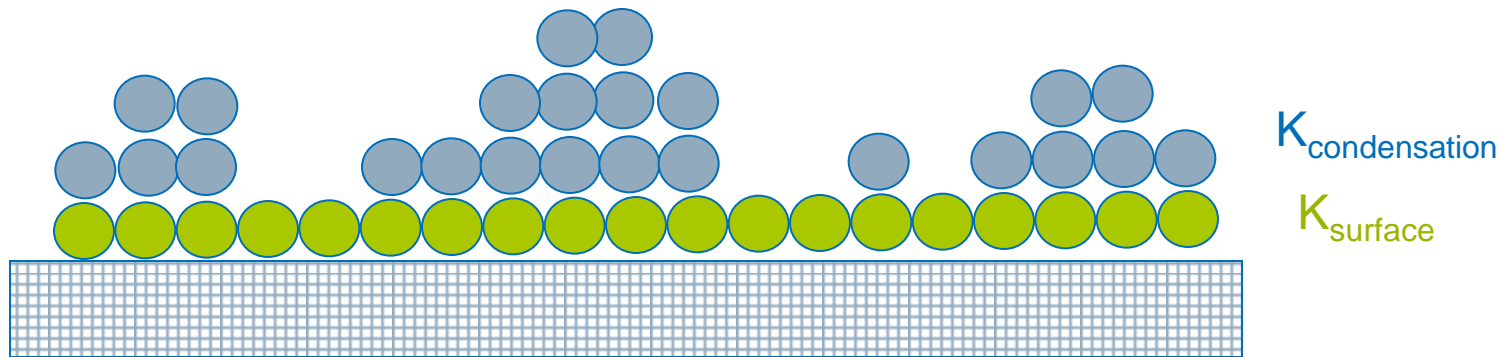
$K_{surface}$

n_m = number of surface adsorption sites (monolayer)
n_{ads} = total number of adsorbed molecules

BET equation

- **BET equation**

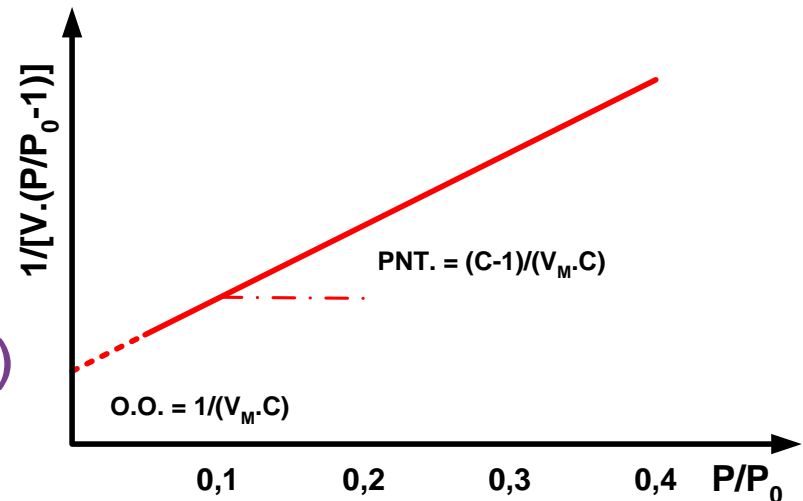$$\frac{P}{V_{ads}(P_0 - P)} = \frac{1}{V_M C} + \frac{C-1}{V_M C}\left(\frac{P}{P_0}\right)$$

$$C = \frac{K_{surface}}{K_{condensation}}$$

Recommended range of p/p$_0$: 0,05 - 0,35 max.

  - V_M = monolayer volume
  - V_{ads} = adsorbed volume

- **Plot p/V$_{ads}$(p$_0$-p) vs. p/p$_0$**

- **Calculation of surface area:**

  - N_{Av} : Avogadro number
  - a : area of N_2 molecule (16,2 Å^2)

PNT. = (C-1)/(V$_M$.C)

O.O. = 1/(V$_M$.C)

1/[V.(P/P$_0$-1)]

0,1   0,2   0,3   0,4   P/P$_0$

$$S_{BET} = a.\frac{p_0 V_M}{R \cdot 273K}.N_A$$

$$S_{BET}(m^2/g) = 4.355 \cdot V_m(cm^3 STP/g)$$

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Exemple ZnO

Isothermes

BET plot

$$S_{BET} = \frac{4.355}{slope + \text{int } ercept} \quad C_{BET} = \frac{slope}{\text{int } ercept} + 1$$

y = 0.1196x + 0.0005

y = 0.0594x + 0.0003
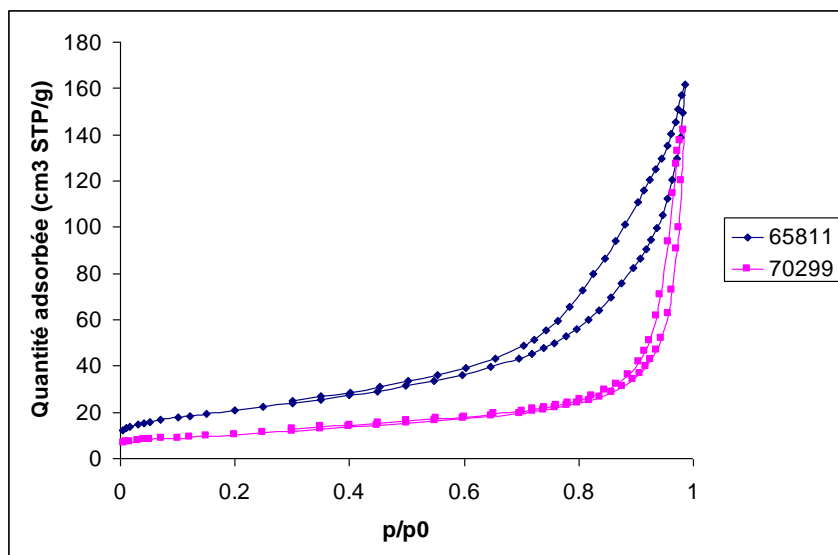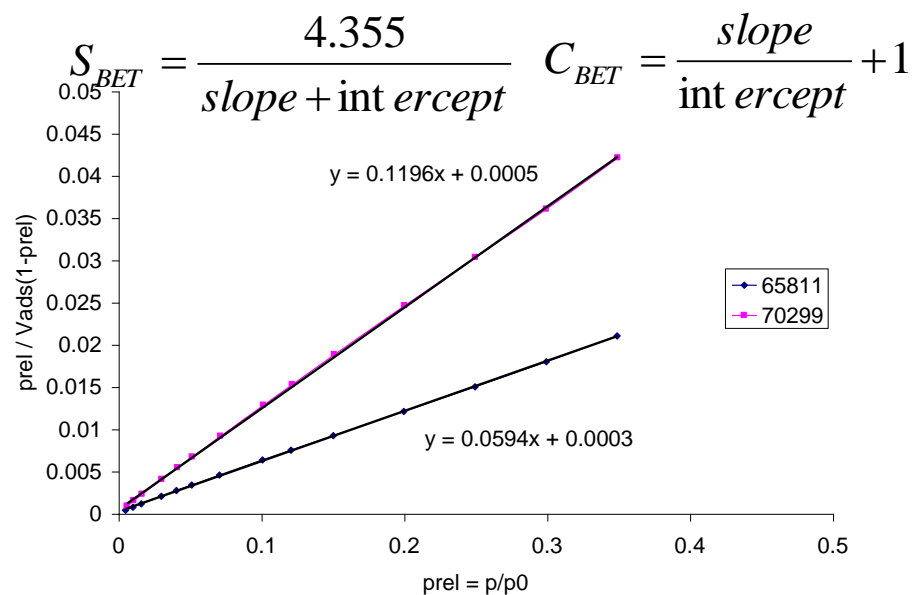
	S_{BET} (m^2/g)	C_{BET}
65811	74	136
70299	36	237

Example NaX

- **The multilayer adsorption model does not apply well to microporous solids when the pores are filled.**

- **Choose a lower pressure range for microporous solids.**
  - **$p/p_0 = 0.05 – 0.10$**

- **C constant may be negative. Does not make physical sense**
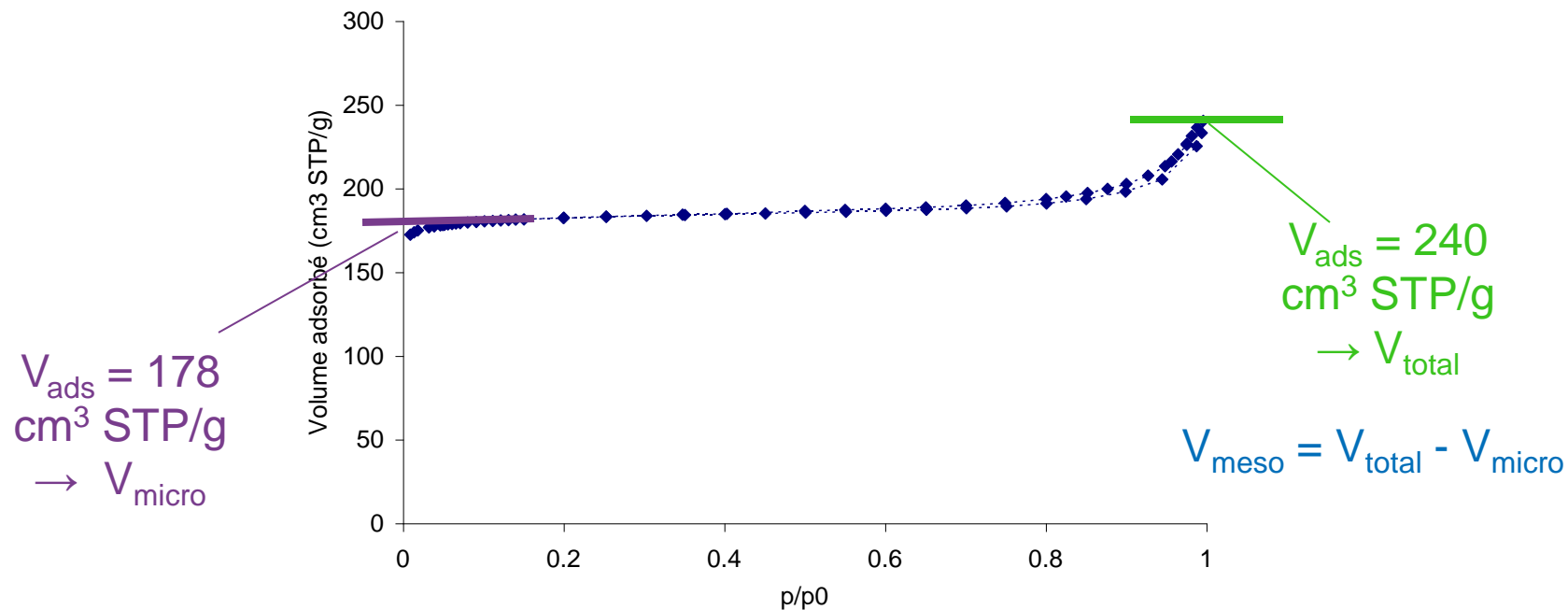 - **lower the pressure range further**

y = 0.0064x - 3E-05
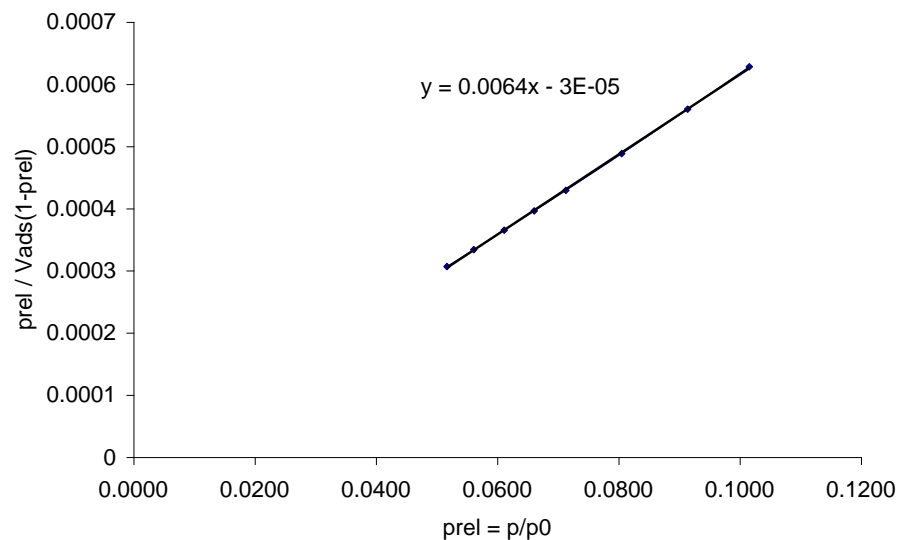
$$S_{BET} = \frac{4.355}{0.0064 - 0.00003} = 685 m^2 / g$$

Langmuir Surface Area

- **Langmuir theory**
  - is a model of monolayer adsorption
  - this hypothesis is never fulfilled

- **Do not use Langmuir surface areas !!**

- $S_{Langmuir}$ is always > S_{BET} because multilayer adsorption is treated like monolayer adsorption.

Determination of the pore volume

Graph: Volume adsorbé (cm3 STP/g) vs p/p0

$V_{ads} = 178$ cm^3 STP/g $\rightarrow V_{micro}$

$V_{ads} = 240$ cm^3 STP/g $\rightarrow V_{total}$

$V_{meso} = V_{total} - V_{micro}$

- **In some cases possible without using any model.**

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Conversion gas volume – pore volume

- **Volume of adsorbed gas correponds to a certain number of moles**
  - STP = Standard Temperature Pressure
    - T = 273 K, p = 1 bar = 100 kPa

$$n_{ads} = \frac{V_{ads} p}{RT}$$

- **The adsorbed phase is considered like a liquid phase**
  - Density of liquid N_2 at 77 K : 0.807 g/ml

$$V_p = \frac{m_{N2}}{\rho_{N2,liq}} = \frac{n_{ads} \cdot M_{N2}}{\rho_{N2,liq}}$$

$$V_p (ml/g) = 1.5468 \cdot 10^{-3} \cdot V_{ads}(cm^3 STP/g)$$

t-plot

- **Transform adsorbed amount in an average thickness (t) of the adsorbed layer**
- **For multilayer adsorption on a flat surface**

$$t = \frac{V_{ads}}{S}$$
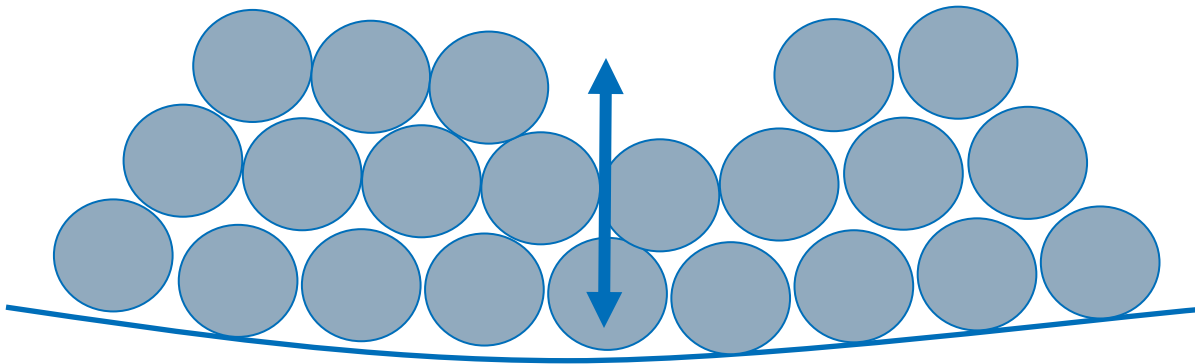
Universal curve t *vs.* p/p$_0$

- **The isotherms (V_{ads}/S_{BET}) of many low surface area oxides (SiO_2, Al_2O_3, ZrO_2, TiO_2, MgO) form a universal curve t = f(p/p$_0$).**

- **Numerical description of that curve**
  - valid for t = 3.5 – 10 Å
  - and p/p$_0$ = 0.1 – 0.8

$$t = \frac{V_{ads}}{S_{BET}}$$

Harkins Jura
$$t = \left(\frac{13.99}{-\log\dfrac{p}{p_0} + 0.034}\right)^{1/2}$$

Halsey
$$t = 3.54 \left[\frac{5}{\ln\left(\dfrac{P_0}{P}\right)}\right]^{1/3}$$
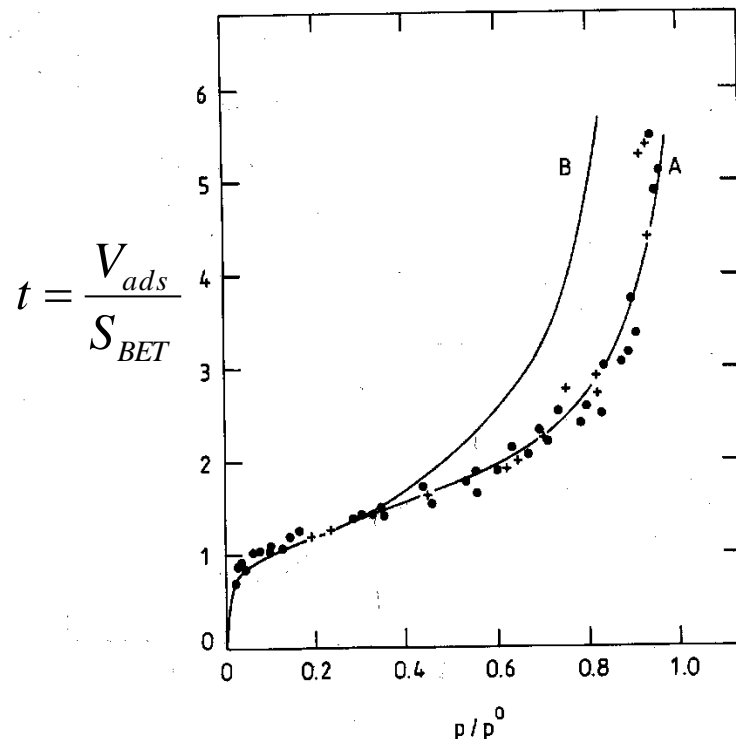
Fig. 12.3. The adsorption of nitrogen on nonporous samples of silica and alumina, the surface areas ranging from 2.6–11.5 m^2 g^{-1} for silica and from 58–153 m^2 g^{-1} for alumina. n/n_m is plotted against $p/p°$. n is the number of moles adsorbed per gram of adsorbent and n_m is the monolayer capacity, expressed in the same units. Line A: ● = silica; + = alumina. Line B: the BET isotherm (Eqn. 12.19) with c values of 100–200.
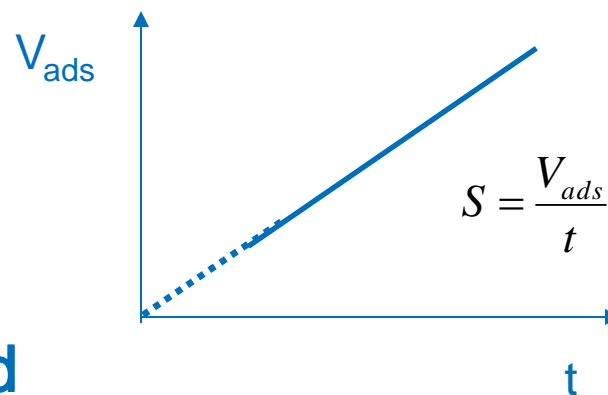
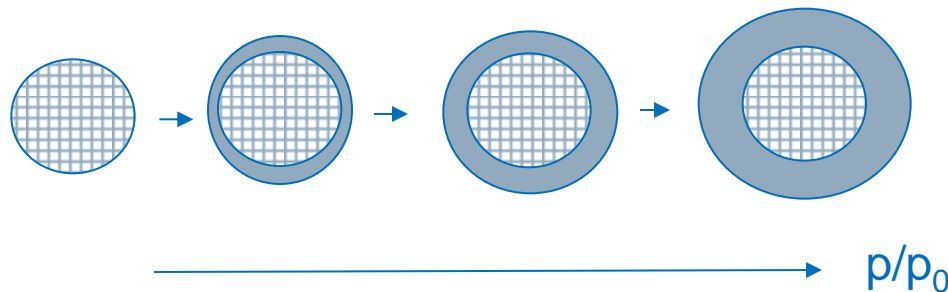# Isotherm expressed as $V_{ads} = f(t)$
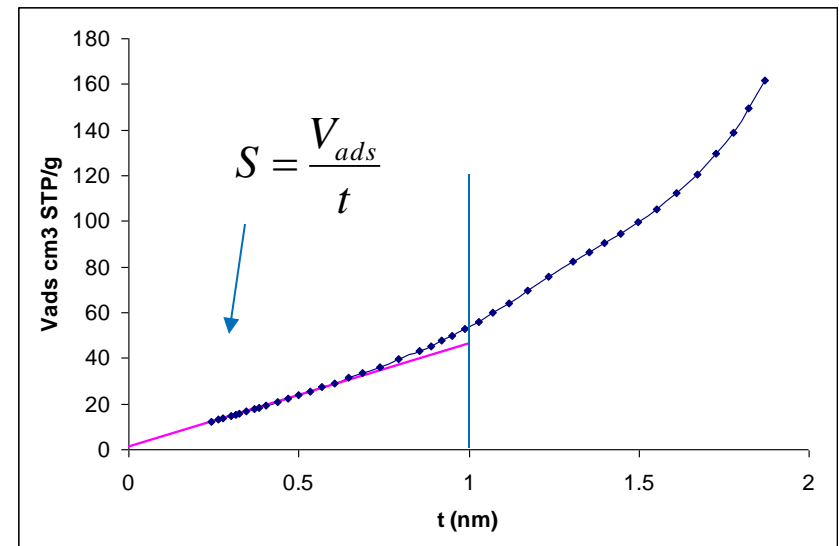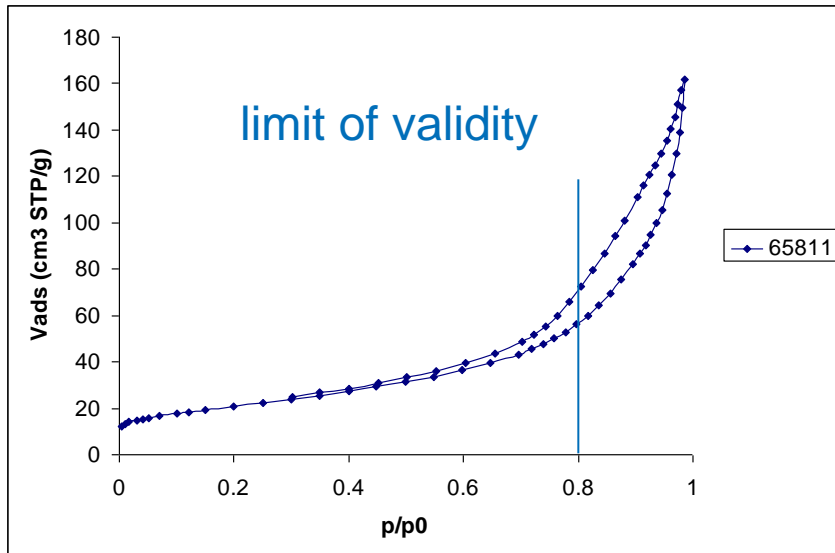
$$t = \left(\frac{13.99}{-\log\frac{p}{p_0} + 0.034}\right)^{1/2}$$

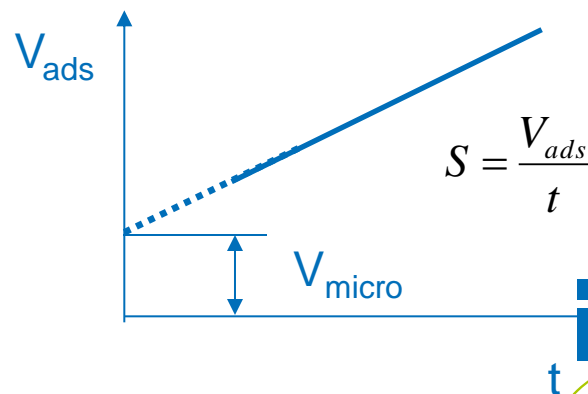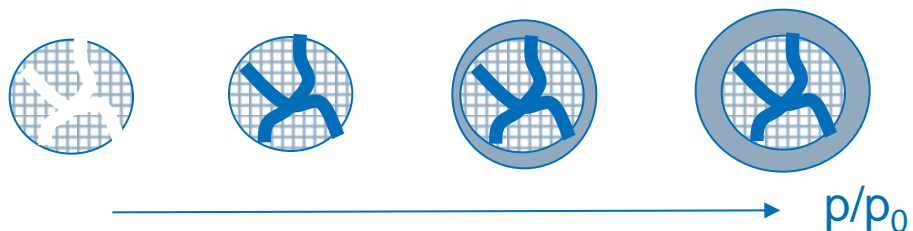t = thickness that the adsorbed phase would have on a non-porous material

Interpretation of t-plots
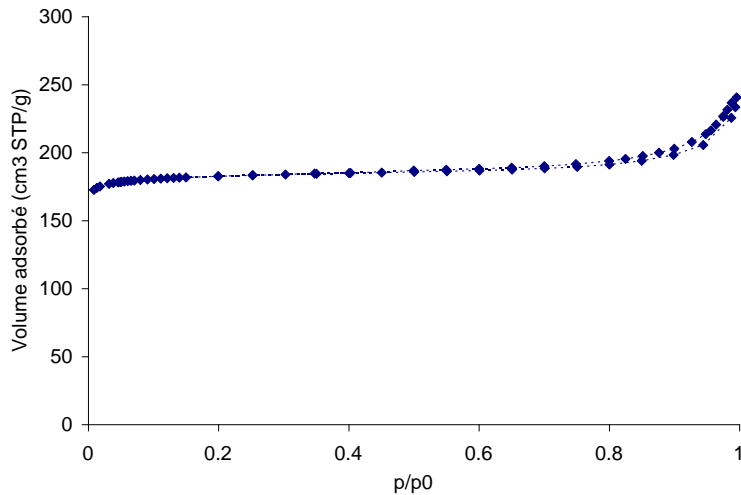
- ## Adsorption on a non-porous solid

$$S = \frac{V_{ads}}{t}$$

- ## Adsorption on a microporous solid

  - ### micropores rapidly filled

  - ### then adsorption on external surface

$$S = \frac{V_{ads}}{t}$$

Example zeolite NaX

Isotherm

t-plot
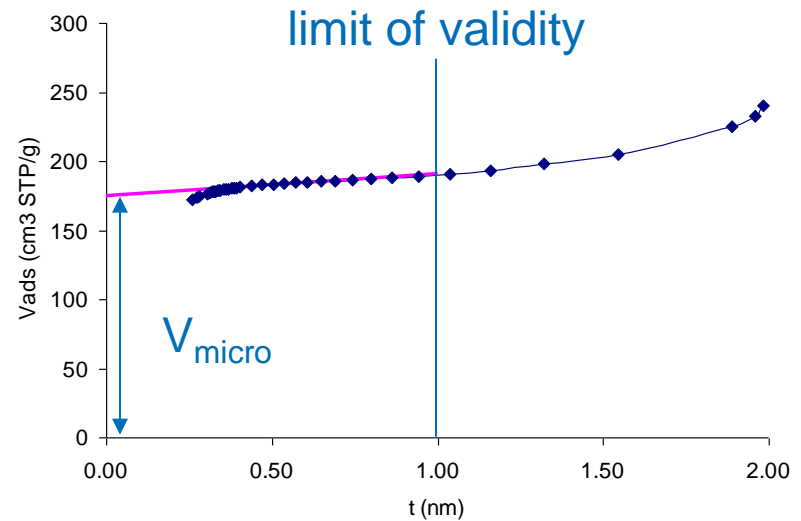
V_{micro} = 175 cm³ STP/g = 0.271 ml/g

Surface BET vs. Surface t-plot

$$S_{t-plot}(m^2 g^{-1}) = 1.5468 \cdot PNT(cm^3 g^{-1} nm^{-1})$$

y = 45.11x + 0.965

y = 21.83x + 0.685

Vads cm3 STP/g

t (nm)
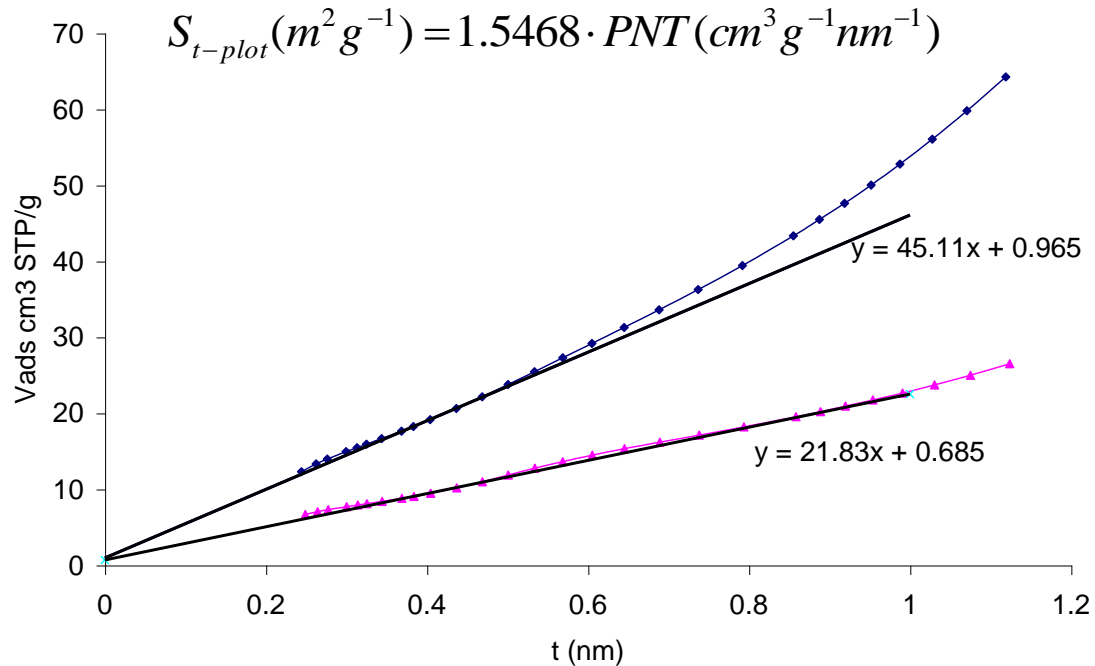
	S_{BET} (m^2/g)	S_{t-plot}
65811	74	70
70299	36	34

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Micro- and mesoporous solids

Solide non poreux : Adsorption sur Surface Externe   -   Courbe t = t(P/P$_0$)

←------------------   **Pressions relatives P/P$_0$ croissantes**   ------------------→

μP   **mP**
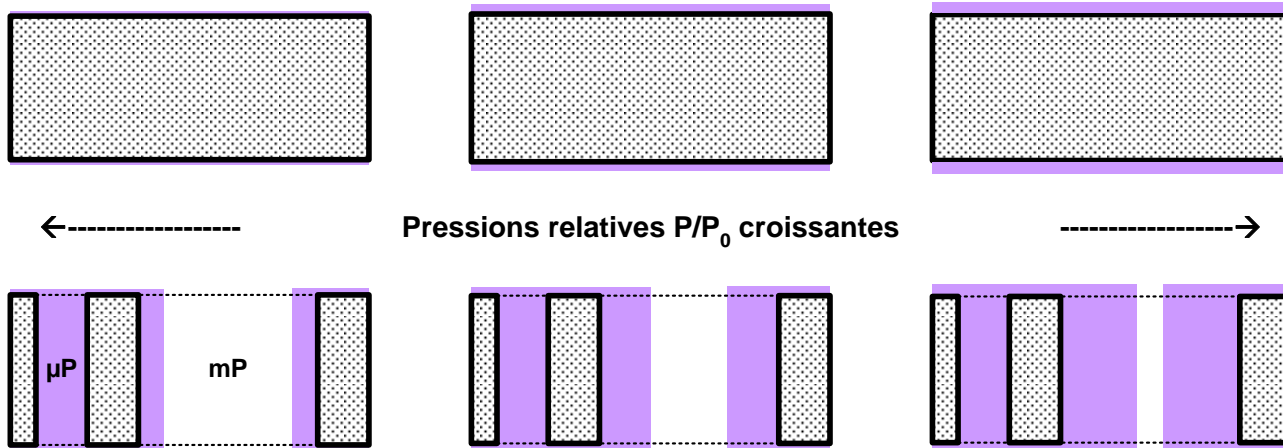
Solide poreux : Adsorption sur Surfaces Interne & Externe

Solide Non Poreux

Vol. Ads.

Adsorption sur Surface Externe

Epaisseur t

Solide μ et m-Poreux

Vol. Ads.

Adsorption sur Surface Externe

$V_{μP}+V_{mP}$

$V_{μP}$

Adsorption sur Surface Interne (mésopores) => S$_{B.E.T.}$

Epaisseur t
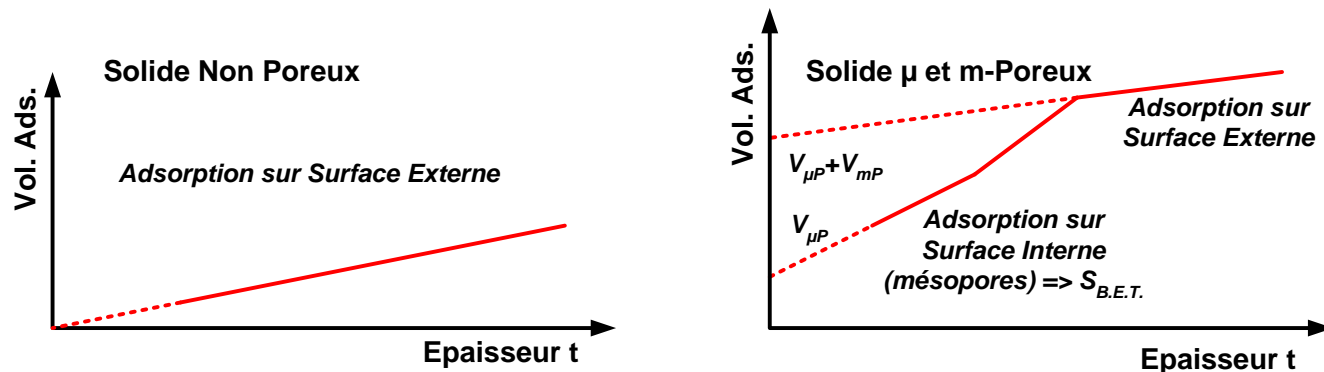
t-plot may be ambiguous

- **Zeolite beta with supermicropores**
  - no clear linear region in the t-plot
  - micropore volume depends on the interval chosen for extrapolation
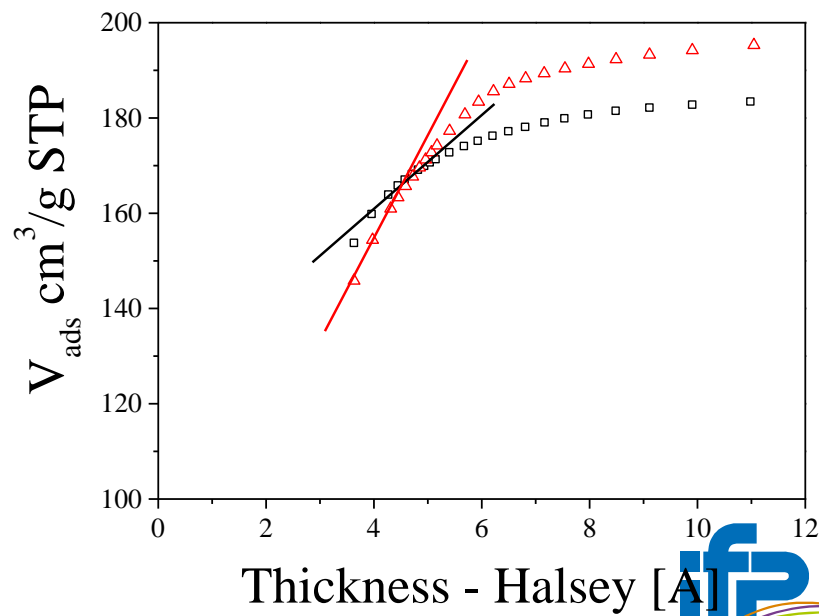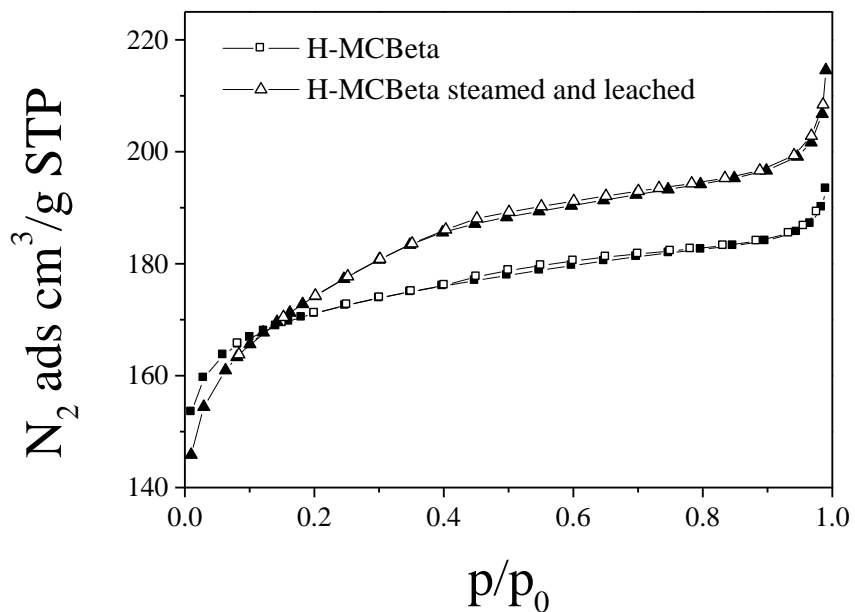
Average pore size

- **From geometrical rules**
  - **Cylindrical Pore:**
    - V = pore volume
    - S = surface

$$\begin{cases} V = \pi r^2 h \\ S = 2\pi r h \end{cases}$$

$$\frac{S}{V} = \frac{2}{r} \qquad d = \frac{4V}{S}$$

  - **Spherical pore :**

$$\begin{cases} V = \frac{4}{3}\pi r^3 \\ S = 4\pi r^2 \end{cases}$$

$$\frac{S}{V} = \frac{3}{r} \qquad d = \frac{6V}{S}$$

  - **Slit pore :**

$$\begin{cases} V = lhr \\ S = lh \end{cases}$$

$$\frac{S}{V} = \frac{1}{r} \qquad d = \frac{2V}{S}$$

Micropore size distribution

- **Based on the relation between adsorption strength and the ratio between adsorbate size and pore size**
  - condition: adsorption controled by van der Waals interactions only

- **Mathematical models**
  - Horvath-Kawazoe
  - Saito-Foley   *Saito, Foley, AICHE Journal 1991, 37, 429.*

- **Input parameters**
  - pore geometry: slit-shaped, cylinder, sphere
  - parameters of the Lennard-Jones potential well: ε and σ_{ij}
    - not always well known for atypical solids

- **Input data**
  - high precision isotherm at very low pressure !

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Mesopore size distribution

- **via the theory of capillary condensation**
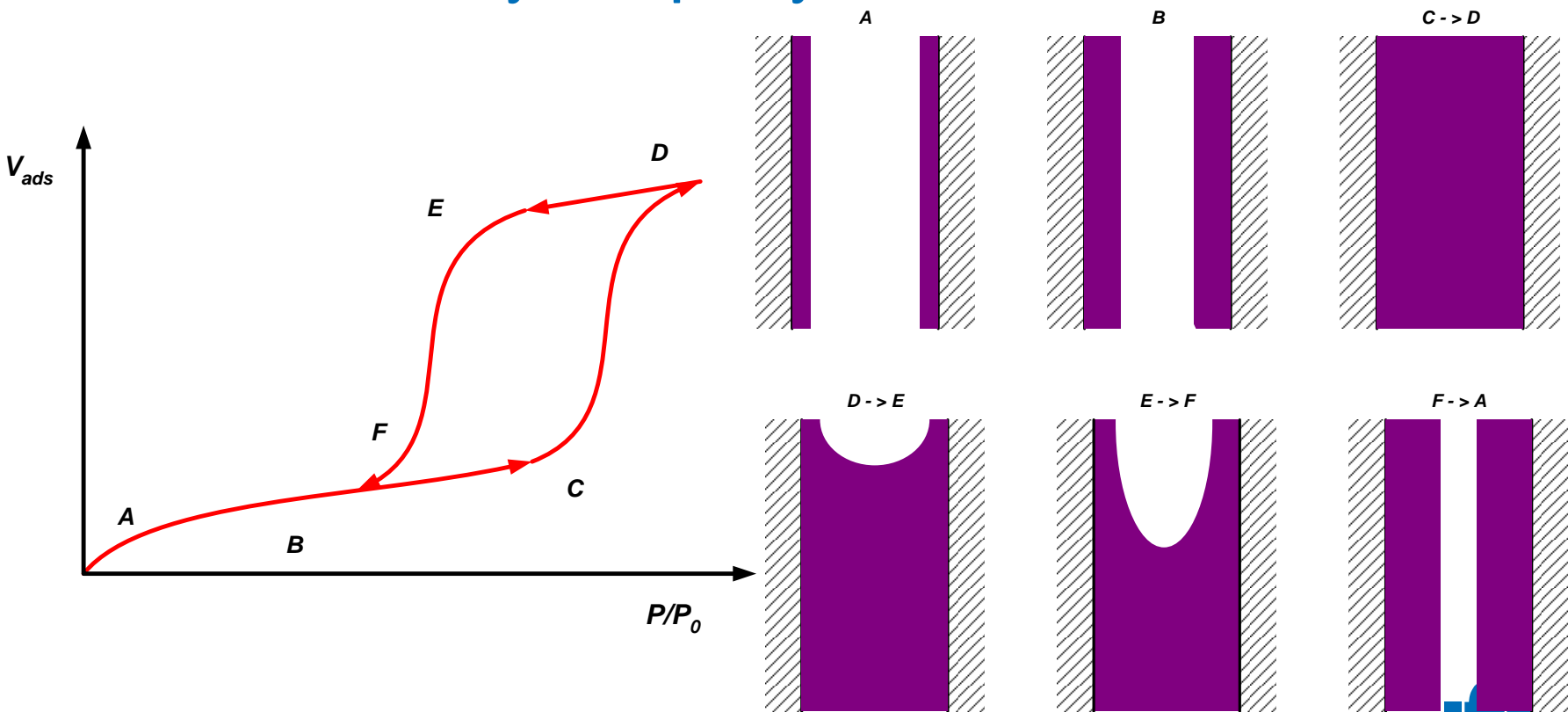
Kelvin equation

- **Capillary forces in the pore lower the vapor pressure of the condensed liquid**

  - Pressure at the concave side of an interface is higher than at the convex side.

    - overpressure counteracts the surface tension, which tries to collapse the interface area

  - Application to interface between gas and adsorbed liquid film in a pore

    - Pressure in liquid is lower than gas pressure.

    - Means that chemical potential in liquid is lower, in other words that the equilibrium vapor pressure is lower.

    - Capillary condensation occurs at a lower pressure than condensation.

pressure difference Δp

surface tension
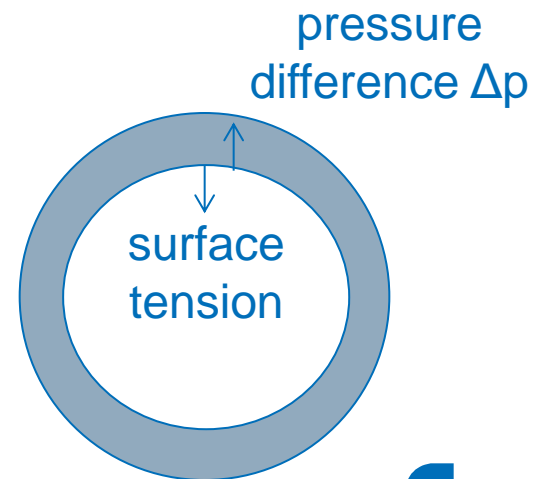
Kelvin equation

- ## Mathematic formalism
  - ### Work against interfacial tension = change in free enthalpy

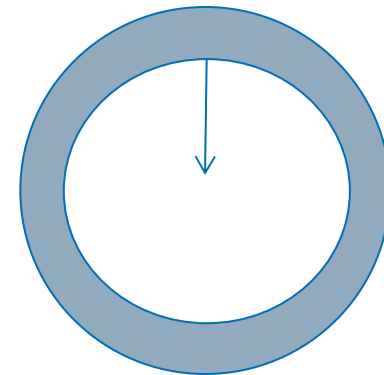$$dA \cdot \gamma = dn_{capliq} \cdot \mu_{capliq} + dn_{liq} \cdot \mu_{liq}$$

$$dn_{capliq} = -dn_{liq} = \frac{dV_{capliq}}{V_m}$$

$$dA \cdot \gamma = \frac{dV_{capliq}}{V_m} \cdot \mu_{capliq} - \frac{dV_{capliq}}{V_m} \cdot \mu_{liq}$$

$$dA \cdot V_m \cdot \gamma = dV_{capliq}(\mu_{capliq} - \mu_{liq})$$

$$(\mu_{capliq} - \mu_{liq}) = -\frac{dA}{dV_{cap,g}} \cdot V_m \cdot \gamma$$

$$RT \ln \frac{p_{cap}}{p_{sat}} = -\frac{dA}{dV_{cap,g}} V_m \gamma$$

$$\mu_{capliq} = \mu_0 + RT \ln \frac{p_{cap}}{p_0}$$

$$\mu_{liq} = \mu_0 + RT \ln \frac{p_{sat}}{p_0}$$

Generalized Kelvin equation

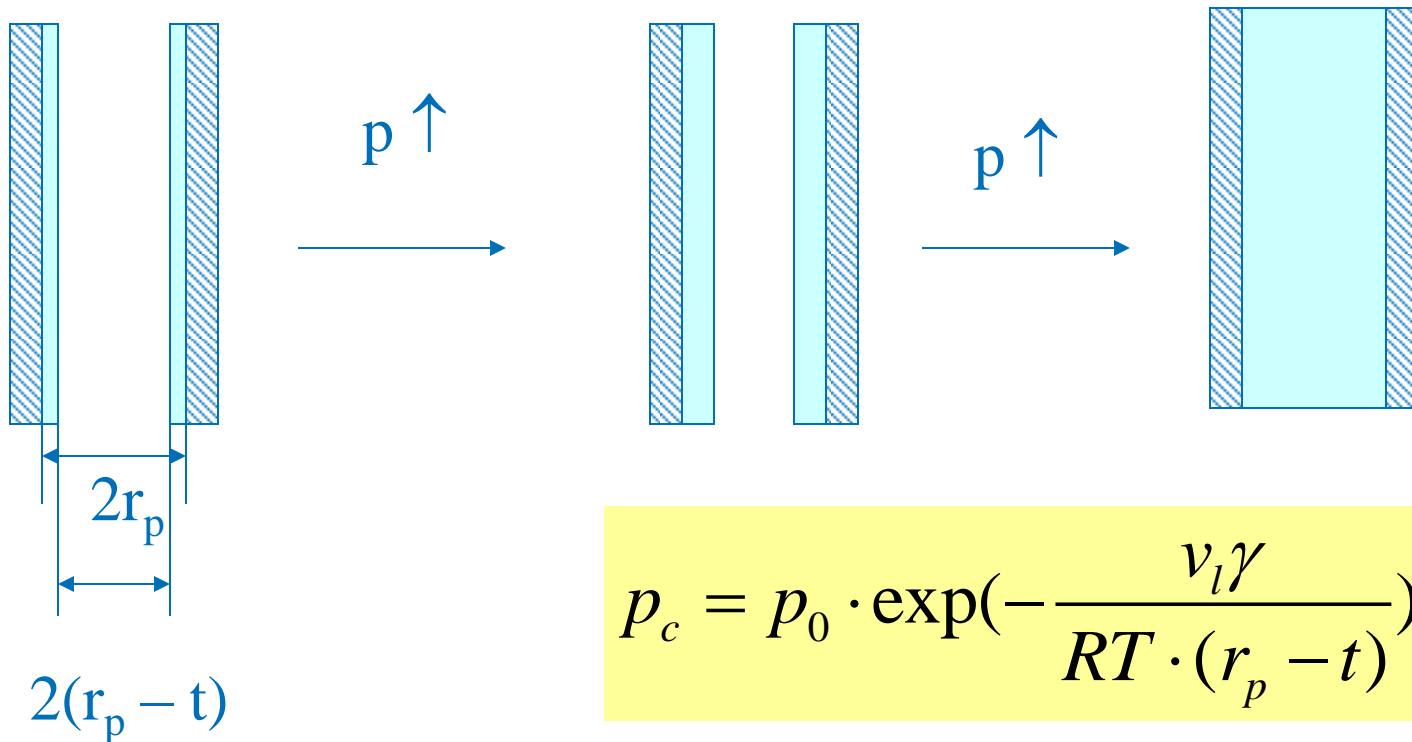$$\ln \frac{p_{cap}}{p_{sat}} = -\frac{V_m \gamma}{RT} \cdot \frac{dA}{dV}$$

dV/dA = change in volume per change in interface area

Vm = molar volume

- **dV/dA depends on the pore geometry**
  - Sphere: dV/dA = r/2
  - Cylinder dV/dA = r
  - Slit   dV/dA = d   distance between slits
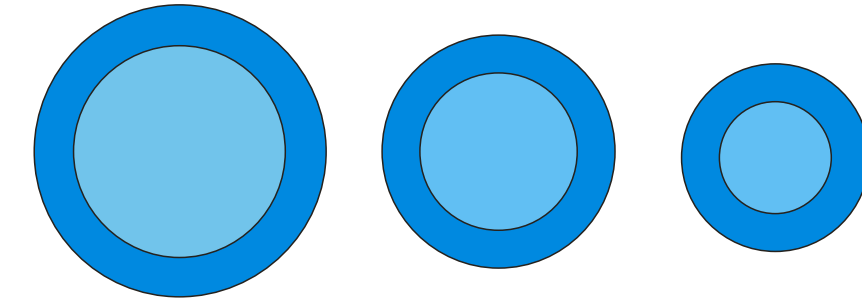
- **Relation to curvature of the pore**

$$\ln \frac{p_{cap}}{p_{sat}} = -\frac{1}{r_{curvature}} \frac{V_m \gamma}{RT}$$

Capillary condensation

$2r_p$

$2(r_p - t)$

p ↑

p ↑

$$p_c = p_0 \cdot \exp\left(-\frac{v_l \gamma}{RT \cdot (r_p - t)}\right)$$
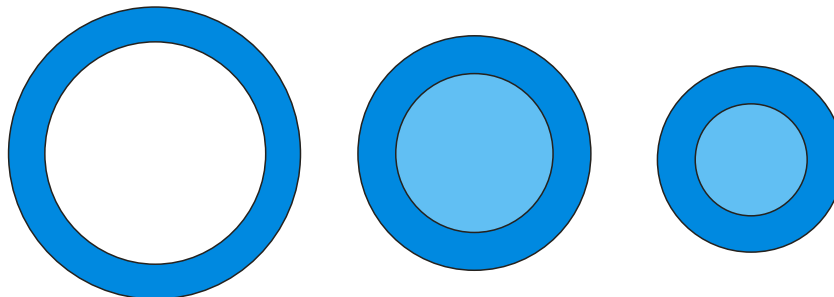
- Multilayer adsorption on the surface: layer thickness t ↑
- At a certain effective pore radius r_p-t, capillary condensation occurs
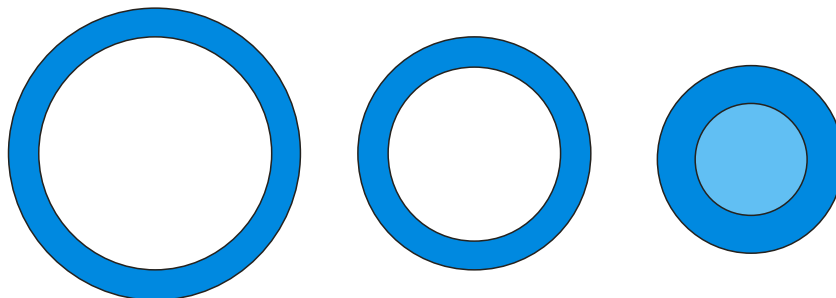- Pore is filled. There is a step in the adsorption isotherm.

Pore size distribution – BJH model
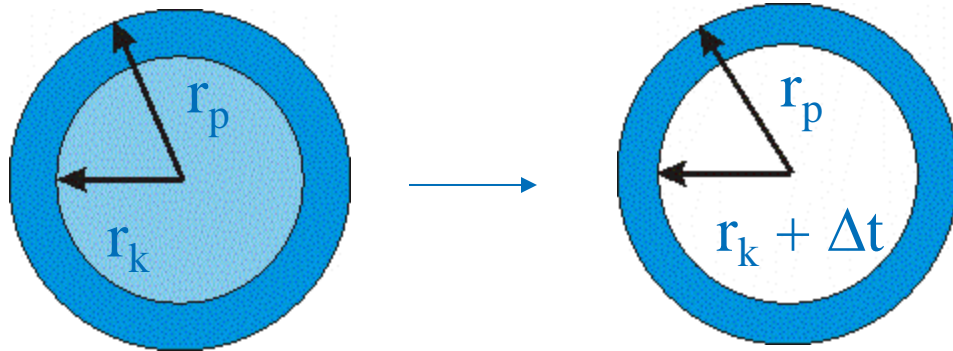
p_0 – all pores filled

p_1 – capillary evaporation in largest pore
reduction of layer thickness

p_2 – capillary evaporation in 2nd largest pore
reduction of layer thickness in both pores

Mathematic description - BJH

$$\Delta V = \frac{(r_k + \Delta t)^2}{r_p^2} \cdot V_p$$

- In each desorption step $p_{n-1} \rightarrow p_n$, capillary evaporation occurs from a pore of size r_{pn}

- The volume desorbed in that step (ΔV_n) can be related to the pore volume by the geometrical relation given above.

- Complication: Reduction in layer thickness in the pores, which were already emptied, also contributes ΔV_n

The BJH-equation

$$V_{pn} = \frac{r_{pn}^2}{(r_{kn} + \Delta t_n)^2} \cdot \Delta V_n - \frac{r_{pn}^2}{(r_{kn} + \Delta t_n)^2} \cdot \Delta t_n \cdot \sum_{j=1}^{n-1} \frac{r_{pj} - t_j}{r_{pj}} A_{pj} \qquad A_p = \frac{2V_p}{r_p}$$

capillary evaporation   correction term

- **For each desorption step the average diameter of the pore, which undergoes capillary evaporation is calculated from the Kelvin equation and the t-plot equation: $r_p = r_k + t$**

$$\log \frac{p}{p_0} = 0.034 - \frac{13.99}{t^2}$$

$$\log \frac{p}{p_0} = \frac{-4.14}{r_k}$$

- Δt is the change in layer thickness in each desorption step
- ΔV_n is the volume desorbed in each step

→ **A plot of pore volume vs. pore radius is obtained.**

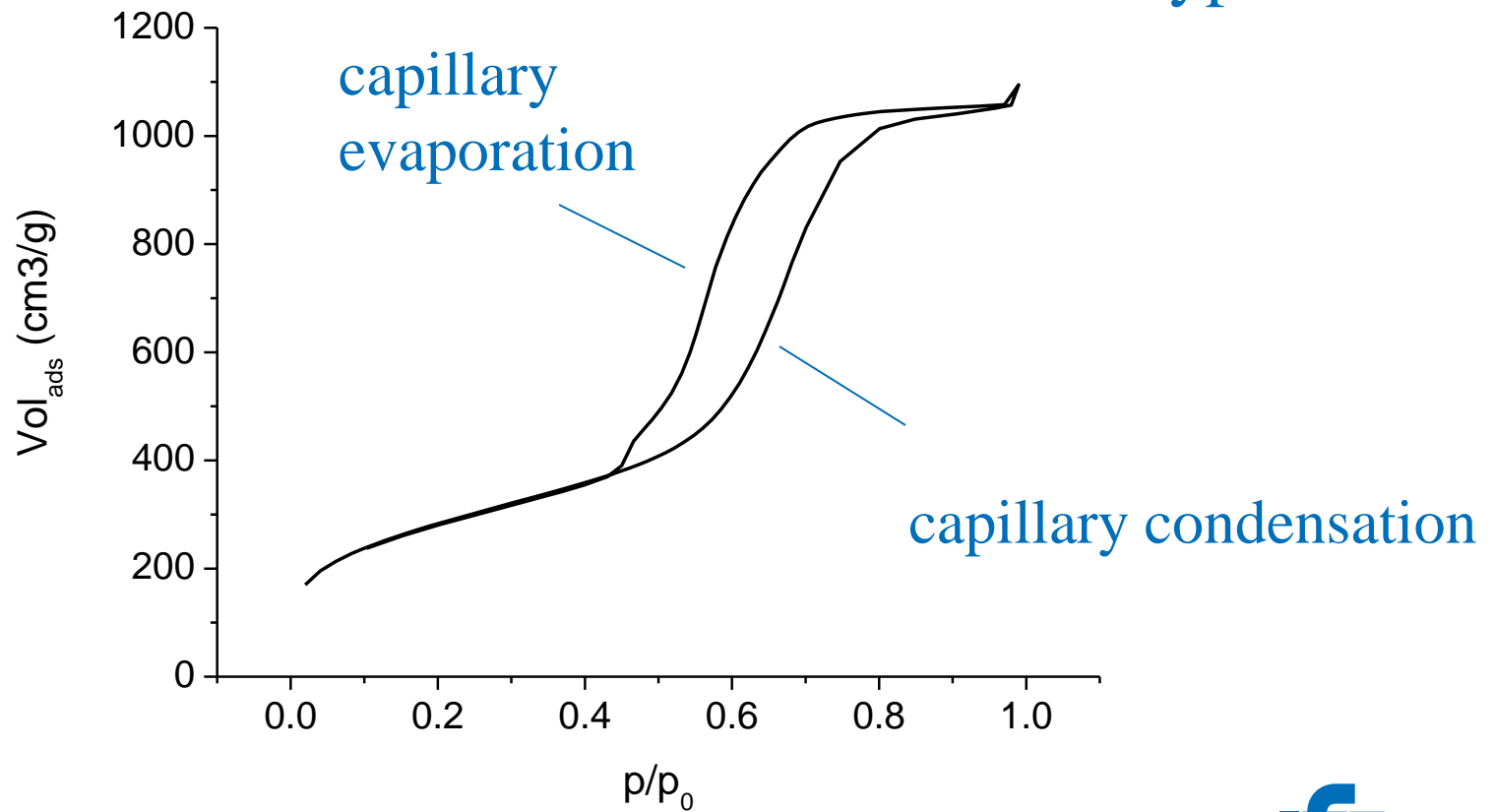# Limits of the BJH-model

- **BJH underestimates the pore size below 7.5 nm – WHY?**
  - Model separates the adsorbed film and the capillary condensate – not a realistic picture
  - Fluid-wall interactions are neglected
  - Kelvin equation may not be valid in very narrow pores
    - Surface tension might increase with curvature

- **One should speak about a BJH-value rather than pore diameter.**

Example isotherm with hysteresis

Type H1

capillary evaporation

capillary condensation

Vol_{ads} (cm3/g)

1200
1000
800
600
400
200
0

0.0   0.2   0.4   0.6   0.8   1.0

p/p_0

Application of the Kelvin equation
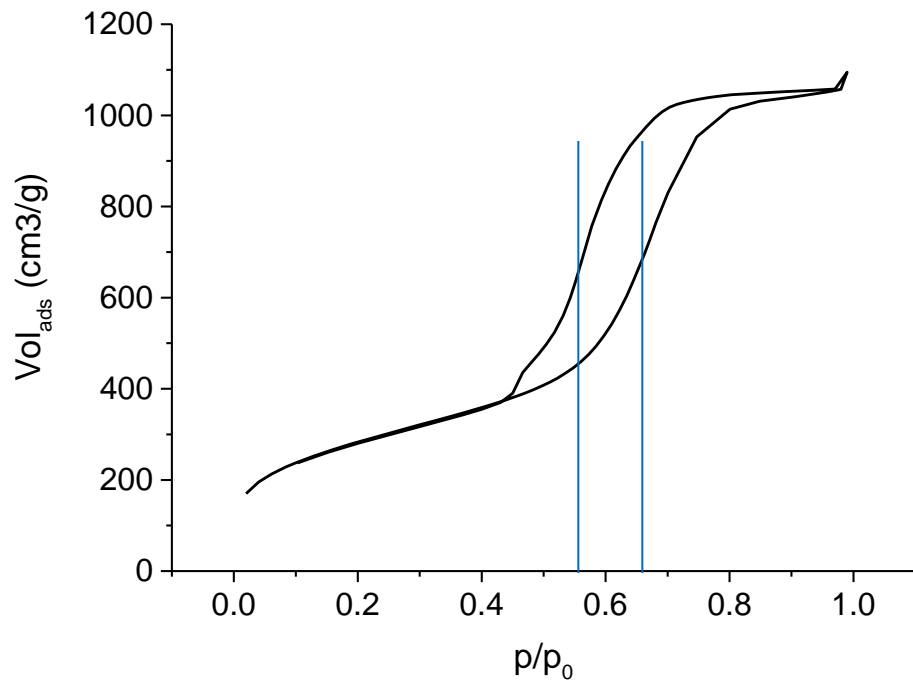
Harkins-Jura t-plot equation

$$\log \frac{p}{p_0} = 0.034 - \frac{13.99}{t^2}$$

$$\log \frac{p}{p_0} = \frac{-4.14}{r_m}$$
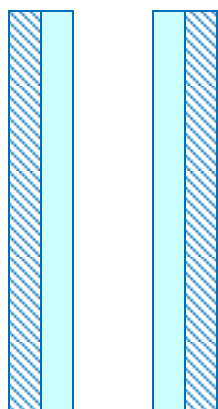
Kelvin equation

Cylinder !!

	p_c/p_0	$t(p_c)$	$r_{curvature}$	R_c	$r_p = r_c + t$
Ads	0.671	8.2	11.9	11.9	20.2
Des	0.565	7.0	8.35	16.7	23.7

Sphere !!

Origin of the hysteresis

Adsorption:
cylindrical meniscus
$r_m = 2r_{eff}$
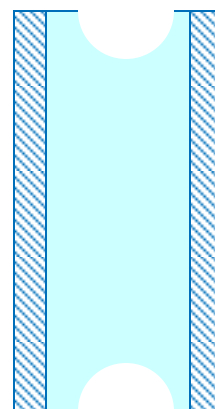
Desorption:
hemisperical meniscus
$r_m = r_{eff}$

- **The lower r_m, the lower is the pressure of capillary condensation/evaporation**

- **$r_{m,ads} = 2\ r_{m,des}$**

- **Capillary evaporation at a lower pressure than capillary condensation**

$\rightarrow$ **Hysteresis loop in isotherm**

L.H. Cohan, JACS 60 (1938)

Origin of the hysteresis

- **Truth seems to be complicated than in Cohan's theory.**

- **Cohan's theory, based on the shape of mensiscus, theory suggests that different vapor liquid equilibria exist in a spherical or cylindrical meniscus, which leads to hysteresis => is an equilibrium picture.**

- **Molecular simulations (DFT) suggest that adsorption branch is not in thermodynamic equilibrium, but is a metastable state.**

# Hysteresis and metastability

(a)

(b)

Monson, MMM, 2012.
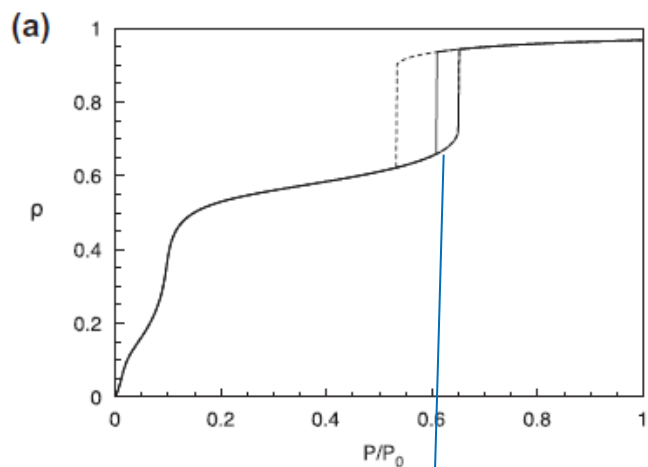
- Adsorption branch comprises metastable states.
  - grand free energy of filled pore is lower than that of the empty pore in the hysteresis
- Desorption branch is in thermodynamic equilibrium.
- Reason for metastability in adsorption branch
  - barrier of nucleation by formation of a liquid bridge across the pore
  - condensation occurs when limit of metastability is reached

limit of metastability

gas phase

liquid phase

Peterson, JCS Farad 2, 1986.
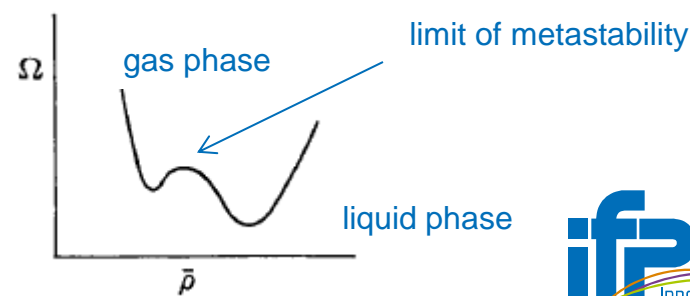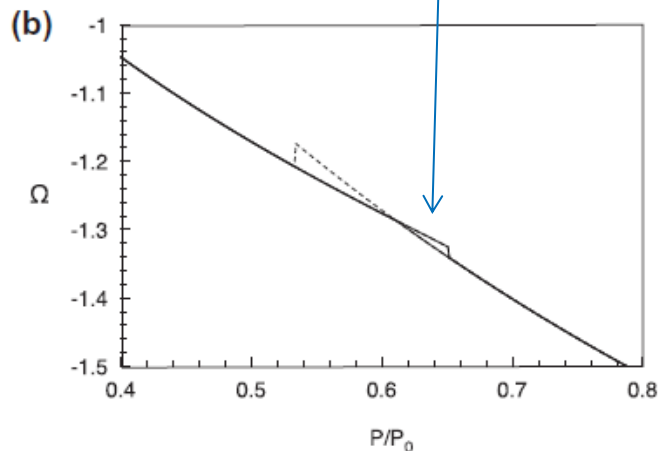
Ink-bottle pores
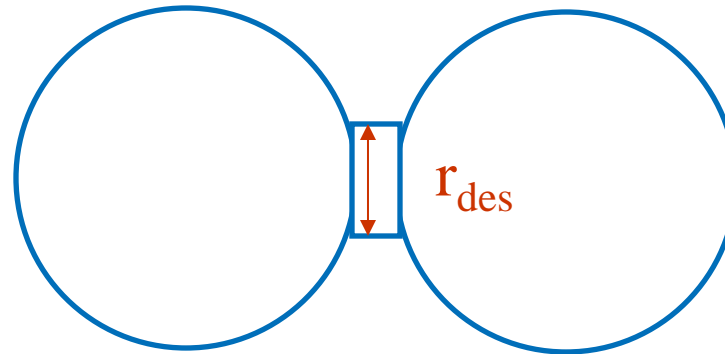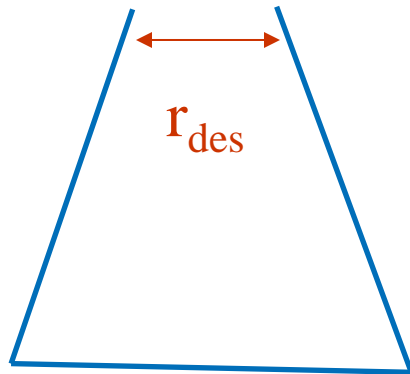
- **In desorption smallest pore openening is determining.**
- **When pressure of capillary evaporation is reached for the smallest pore opening, whole pore is suddenly emptied.**
- **Sudden drop in the desorption isotherm – type H2**

Pore network effects
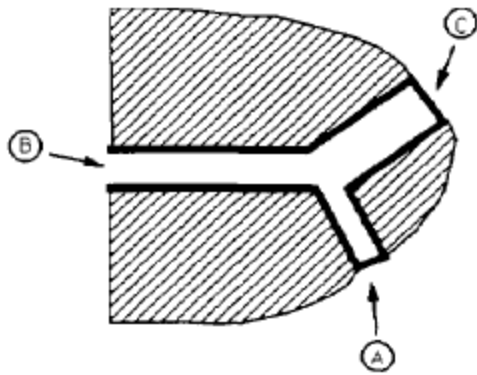
N_2 can only desorb from pore A and C if pore B has already been emptied.

Seaton, CES, 1991.

- **Desorption branch of isotherm not in thermodynamic equilibrium any more, due to pore blocking.**

- **Desorption is controlled by a percolation process.**
  - **probability that the pore is connected to the outer surface.**

Adsorption vs. desorption isotherm

- **Adsorption isotherm – Pros and cons**
  - Condensation can be delayed – not in thermodynamic equilibrium
  - Cylindrical meniscus not stable – not advisable to use adsorption branch for cylindrical pores

- **Desorption branch – Pros and cons**
  - Evaporation not delayed, in thermodynamic equilibrium – generally preferred
  - Ink-bottle type pores: smallest openening determines the desorption
  - In a network of interconnected pores: percolation (transport) effects determine the desorption

- **Conclusion: look at both and compare them**

Ink-bottle type hysteresis loop
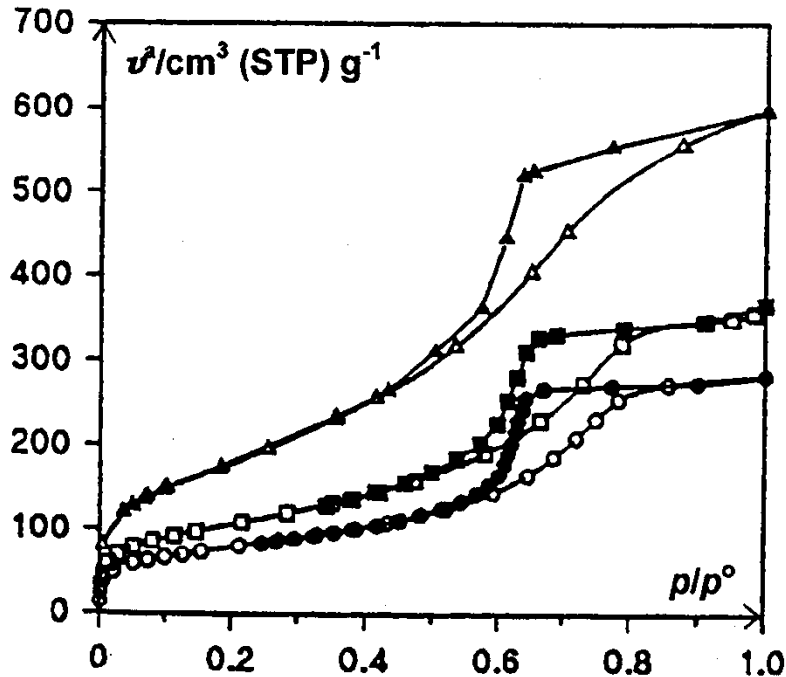
Type H2

Adsorbent: xerogel and alcogel

- If pore size distribution is calculated from desorption branch, an artificially narrow pore size distribution is obtained
- The adsorption branch has to be used to calculate the pore size distribution.

Ink-bottle type hysteresis loop

Isotherm
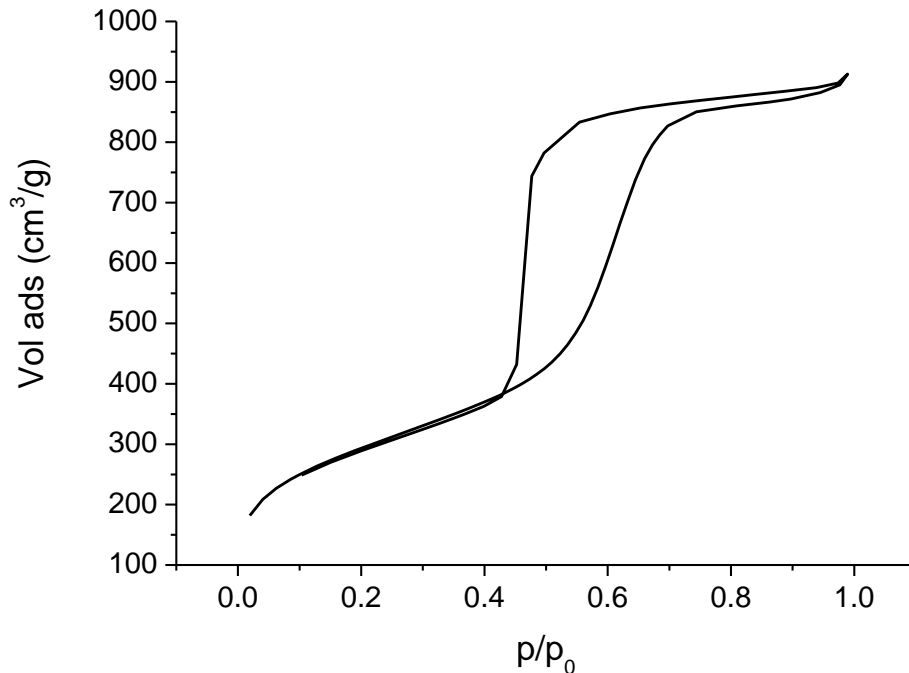
Pore size distribution
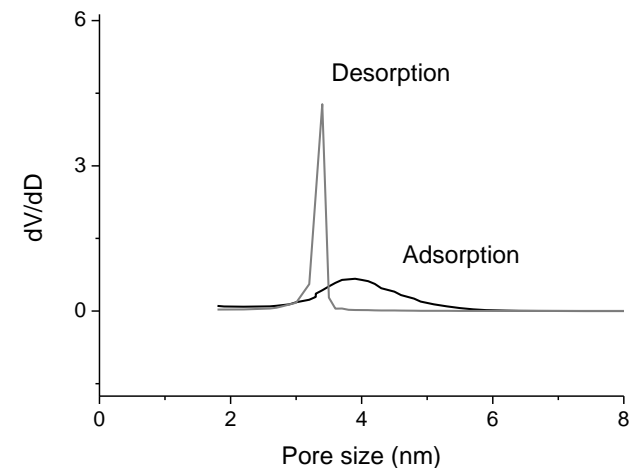
- **Narrow peak in the pore size distribution of the adsorption branch is an artefact caused by the forced closure of the isotherm at p/p_0 = 0.43**

© IFP

Isotherm without hysteresis loop
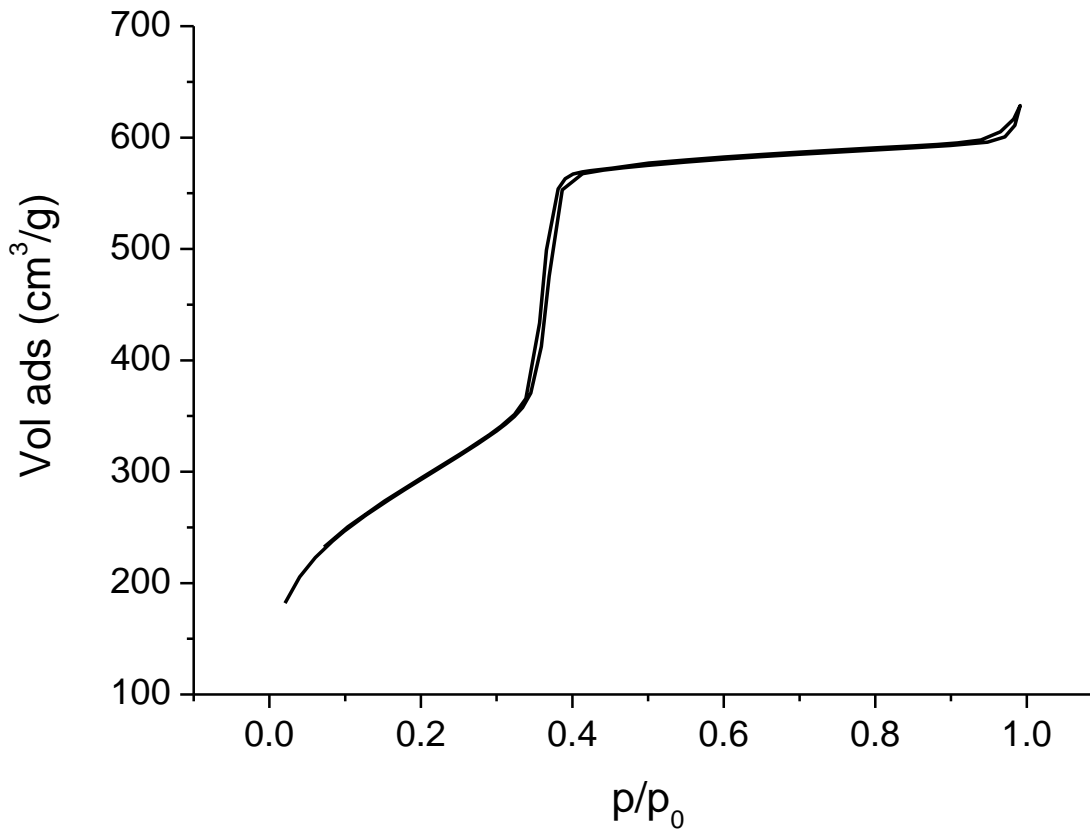
Closure point of the isotherm

- **Critical temperature inside a pore lower than in bulk: $T_{c,pore} < T_{c, bulk}$**

- **$T_{c,pore}$ decreases with decreasing pore diameter[1]**

- **Above T_c no condensate-vapour meniscus**

- **For narrow pores $T_c < 77$ K**

- **No hysteresis for filling and emptying of these pores**

- **$T_{c,pore} < 77$ K for pores, which show capillary condensation at $p/p_0 = 0.4 \rightarrow$ closure point of isotherm**

- **$T_c(Ar) > T_c(N_2) \rightarrow$ Ar isotherms show hysteresis when N_2 isotherms don't[2]**

[1] R. Evans, J. Phys. Condensed Matter 2 (1990) 8989.
[2] M. Thommes, R. Köhn, M. Fröba, J.Phys.Chem. B 104 (2000) 7932.

Summary – Pore size analysis

- **BJH relies on Kelvin equation and the universal t-curve for determining pore size distribution**
  - **both concepts have weaknesses**
- **Alternative methods exist**
  - **Density Functional Theory**
  - **Broekhoff de Boer – improvement of BJH**
  - **Derjaguin – concept of disjoining pressure**
    - **surface tension concept that takes interaction with solid into account**
- **Every model assumes a certain pore geometry (cylindrical, spherical, slit-shaped) – influences the results!!**
- **The adsorption and the desorption branch contain different information – look at both.**

DFT is becoming state of the art

- **Express the Grand Potential as a function of the fluid density distribution in space**

$$\Omega[\rho] = F[\rho] + \int \rho(\boldsymbol{r})V(r)dr - \mu \int \rho(\boldsymbol{r})dr$$

  - $\rho(\boldsymbol{r})$ = fluid density at position $\boldsymbol{r}$
  - $F(\rho)$ = Helmholtz energy of the system due to fluid-fluid interactions, in the absence of an external field
  - $V(r)$ = external potential at position $\boldsymbol{r}$
  - μ = chemical potential

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More recent DFT equation

Ideal gas   Excess energy (non-ideality)

$$\Omega\left[\rho(\boldsymbol{r})\right] = k_B T \int \rho(\boldsymbol{r}) \left[ln\left(\Lambda^3(\boldsymbol{r})\right) - 1 \right] d\boldsymbol{r} + k_B T \int d\boldsymbol{r}\, \Phi\left(\{\bar{n}_\alpha\}(\boldsymbol{r})\right)$$

$$+ \frac{1}{2} \int d\boldsymbol{r} \int \rho(\boldsymbol{r})\rho(\boldsymbol{r}')\phi_{att}(|\boldsymbol{r} - \boldsymbol{r}'|) d\boldsymbol{r}' - \int \rho(\boldsymbol{r})\left[\mu - \phi_{ext}(\boldsymbol{r})\right] d\boldsymbol{r}$$

Fluid-fluid interaction   External potential

- **Everything is in the experssion of Φ_{ext}**
  - Solid-fluid interaction
  - Effet of pore size and pore geometry (confinement)
    - Similar to the HK, SF models of micropore size analysis

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Pore size analysis with DFT

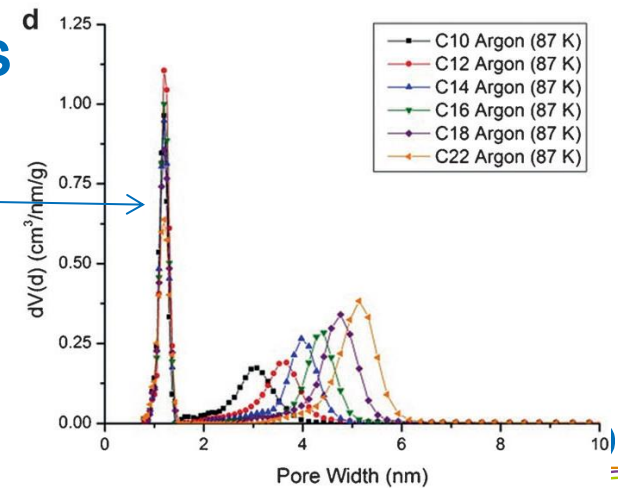- **Kernel of adsorption isotherms (= integrated fluid density) is calculated as function of pore size**

- **Experimental adsorption isotherm is fitted by a weighted sum of the kernel isotherms**

- **The weights give the pore size distribution.**

- **Recommended method :**
  - Use DFT to extract pore size distribution from adsorption branch.
  - Use desorption branch to analyze percolation phenomena

Be careful when using DFT

- **Modern commercial equipment has DFT analysis intergrated in the software**
  - **Is a press-button, black-box method**
  - **Depending on the solid-fluid interaction parameters and the pore geometry that the DFT method relies on you will get different results**
    - **You should know what you are doing**

- **Like BJH analysis, DFT produces an artifact : peak in pore size distribution at 1 nm**
  - **Due to formation of an ordered layer on the surface**

Legend:
- C10 Argon (87 K)
- C12 Argon (87 K)
- C14 Argon (87 K)
- C16 Argon (87 K)
- C18 Argon (87 K)
- C22 Argon (87 K)

x-axis: Pore Width (nm)
y-axis: dV(d) (cm³/nm/g)

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Literature

- **Textbooks on adsorption**
  - D.A. Ruthven, Principles of Adsorption and Adsorption Processes, Wiley
  - D.D. Do, Adsorption Analysis: Equilibria and Kinetics, Imperial College Press

- **Review articles discussing a more moderne view of hysteresis effects and pore size analysis**
  - P.A. Monson, Understanding adsorption/desorption hysteresis for fluids in mesoporous materials using simple molecular models and classical density functional theory, Microporous Mesoporous Materials 160 (2012) 47.
  - B. Coasne et al., Adsorption, intrusion and freezing in porous silica: the view from the nanoscale, Chem. Soc. Rev. 42 (2013) 4141.
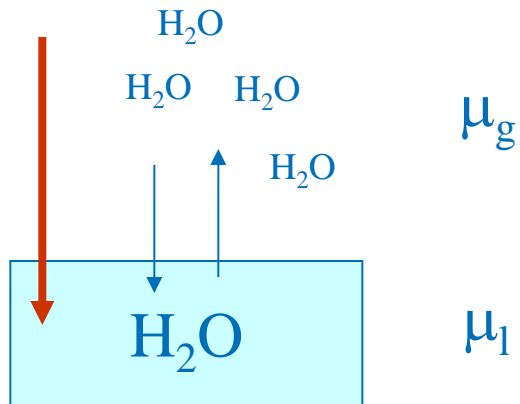
Alternative explanations of the Kelvin equation

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Physical principles of capillary condensation

- **Vapour pressure of a liquid under external pressure**

External pressure

H_2O

H_2O H_2O

μ_g

H_2O

H_2O μ_l

p_g = new vapour pressure of H_2O
p_{g0} = orignial vapour pressure of H_2O
Δp_l = external pressure on liquid (H_2O), which induces the change in vapour pressure
v_l = molar volume of liquid (H_2O)

- **Equlibrium gas-liquid $\mu_g = \mu_l$ vapour pressure $p_{g,0}$**

- **Equilibrium disturbed by external pressure**

$$d\mu_g = d\mu_l \rightarrow v_l\, dp_l = v_g\, dp_g$$

$$v_l\, dp_l = RT/p_g * dp_g$$

$$v_l \Delta p_l = RT \ln (p_g/p_{g0})$$

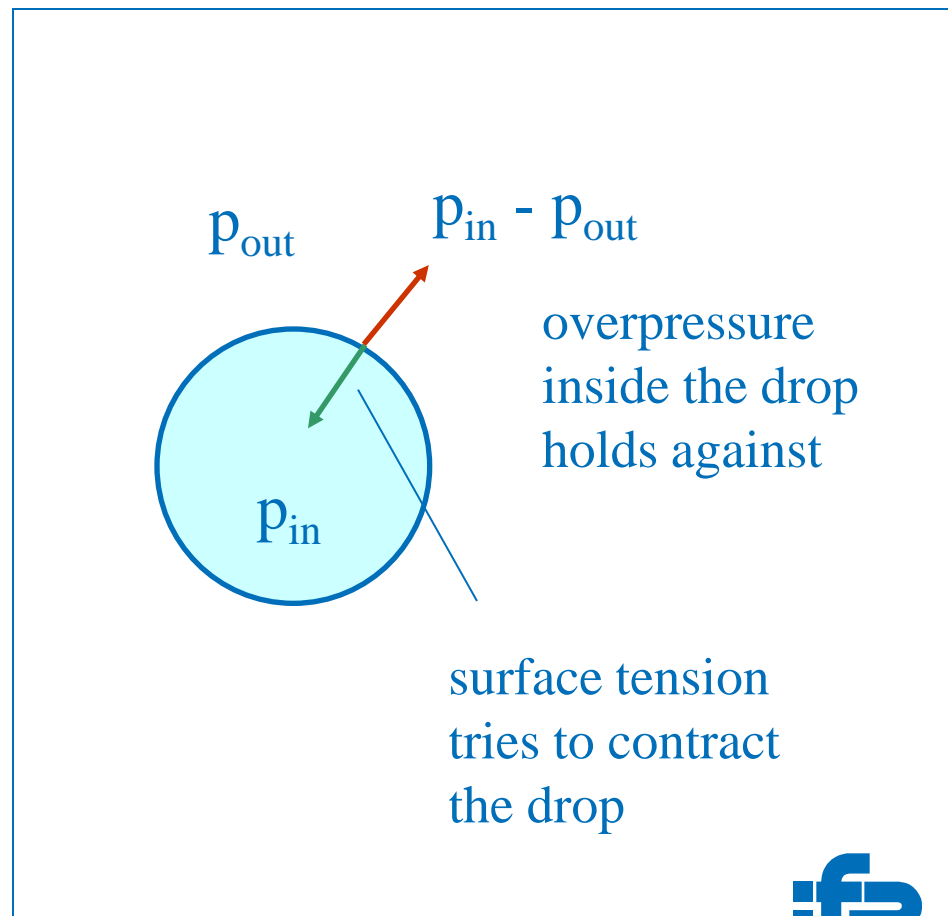$$p_g = p_{g,0} \cdot \exp\left(\frac{v_l}{RT}\Delta p_l\right)$$

Vapour pressure of a drop of liquid

$$p_{in} - p_{out} = \frac{2\gamma}{r}$$

γ = surface tension
r = radius of curvature

$$p_l - p_{out} = \frac{2\gamma}{r}$$

$$p_l = p + \frac{2\gamma}{r}$$

p_{out} p_{in} - p_{out}

p_{in}

overpressure inside the drop holds against

surface tension tries to contract the drop
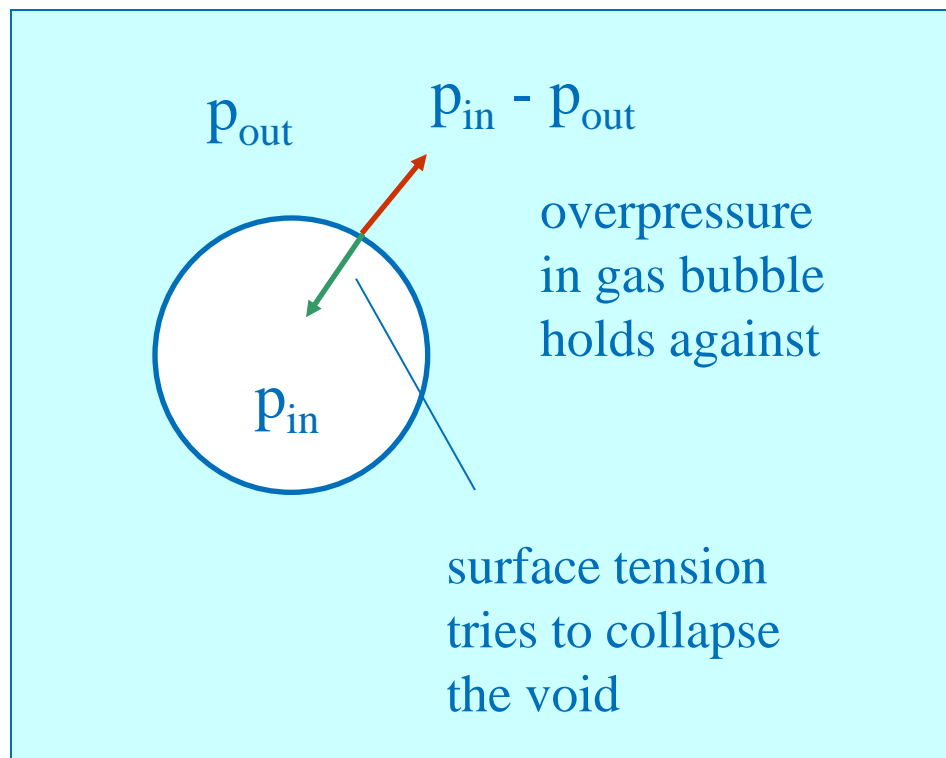
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Vapour pressure of a liquid void

$$p_{in} - p_{out} = \frac{2\gamma}{r}$$

$$p_{in} - p_l = \frac{2\gamma}{r}$$

$$p_l = p - \frac{2\gamma}{r}$$

p_{out}

p_{in} - p_{out}

overpressure
in gas bubble
holds against

p_{in}

surface tension
tries to collapse
the void

$$p_g = p_{g,0} \cdot \exp\left(-\frac{2v_l\gamma}{RT \cdot r}\right)$$

Kelvin equation: vapour pressure
inside a void is lowered

Kelvin equation

■ **Capillary forces in the pore lower the vapor pressure of the condensed liquid**

$$\mu_{cap} = \mu_0 + RT \ln \frac{p_{cap}}{p_0}$$

$$\mu_{liq} = \mu_0 + RT \ln \frac{p_{sat}}{p_0}$$

θ

Δl

n

capillary   unconfined liquid

Evaporate n moles from capillary and condense on a flat surface. You have to work against the surface tension γ.

$$W = \Delta A \gamma cos\theta = 2\pi r \Delta l \gamma cos\theta$$

The work done to overcome the surface tension is equal to change in chemical potential.

$$n \cdot \Delta \mu = \frac{\Delta V}{V_m} RT \ln \frac{p_{sat}}{p_{cap}}$$

Explains why vapor pressure of the unconfined liquid is higher than in the capillary.