Physisorption and pore size analysis

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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

Characterization of porous solids - Characterization of Catalysts and Surfaces - G Pirngruber 17 October 2017
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 crystalline 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** (N₂, 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 categories 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)
  - Maximal when size of adsorbate (j) close to pore size

\[ U_{LJ} = 4 \varepsilon \left( \left( \frac{\sigma_{ij}}{r} \right)^{12} - \left( \frac{\sigma_{ij}}{r} \right)^{6} \right) \]
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
- $\text{N}_2$ 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 surfaces

Saturation zone

Transition zone
additional adsorbate-adsorbate interactions

Initial slope depends on adsorbent-adsorbate interactions
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 : $P_{iHe}$, $T_{iHe}$
    - Etat final : $P_{fHe}$, $T_{fHe}$
  - **Cellule mesure :** $V_{cel}$
    - Température ambiante
  - **Température N2 liquide 77 K**
    - **Réservoir d’azote liquide à 77 K**
  - **Azote**
    - Etat initial : $P_{iN2}$, $T_{iN2}$
    - Etat final : $P_{fN2}$, $T_{fN2}$

  **Bilans Matières : He et N2**

  \[
  \Delta n_{He} = \left(\frac{P_{fHe}}{T_{fHe}} - \frac{P_{iHe}}{T_{iHe}}\right) V_{res} \frac{1}{R}
  \]

  \[
  \Delta n_{N2} = \left(\frac{P_{fN2}}{T_{fN2}} - \frac{P_{iN2}}{T_{iN2}}\right) V_{res} \frac{1}{R}
  \]

  \[
  \Delta n_{N2} = \left(\frac{P_{fHe}}{T_{fHe}} - \frac{P_{iHe}}{T_{iHe}}\right) V_{res} \frac{1}{R} + n_{ads}^{N2}
  \]

  **Masse d’adsorbant :** $M_{sol}$
  
  **Quantité adsorbée :** $Q_{ads} = n_{N2}^{ads} / M_{sol}$
Material balance

- **Reservoir : 1**  
- **Sample cell : 2**

**without adsorption (He), sample cell initially under vacuum**

\[
\frac{p_{\text{init}} V_1}{RT_1} = \frac{p_{\text{final}} V_1}{RT_1} + \frac{p_{\text{final}} V_2}{RT_2}
\]

\[
\frac{V_2}{T_2} = \frac{V_1}{T_1} \cdot \frac{p_{\text{init}} - p_{\text{final}}}{p_{\text{final}}}
\]

**with adsorption (N\textsubscript{2})**

determined with He

\[
\text{quantity initially present in the reservoir}
\]

\[
n_{\text{tot}} = \frac{pV_1}{RT_1} + \frac{pV_2}{RT_2} + n_{\text{ads}}
\]
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**

After shaping with a binder.
Examples - ZnO

- no micropores
- mesopores generated by stacking of individual particles

- capillary condensation in the mesopores
- multilayer adsorption on the surface of the particles
Comparison of two ZnO samples

- Surface: 65811 > 70299
- Pore size: 70299 > 65811
Example – $\text{Al}_2\text{O}_3$

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

Capillary condensation in mesopores

Multilayer adsorption on surface of particles
Comparison Al$_2$O$_3$

- **Surface**: 79999 > 61399 > 47148
- **Pore size**: 47148 > 61399 > 79999
Quantitative treatment of N₂ isotherms

- **Pore volume:** $V_{\text{micro}}$, $V_{\text{meso}}$, $V_{\text{total}}$
  - 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

\[
\text{number of surface adsorption sites (monolayer)} = n_m
\]

\[
\text{total number of adsorbed molecules} = n_{\text{ads}}
\]
BET equation

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

\[ C = \frac{K_{surface}}{K_{condensation}} \]

- \( V_M \) = 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 Å²)

\[ S_{BET} = a \cdot \frac{P_0 V_M}{R \cdot 273 K} \cdot N_A \]

\[ S_{BET} \left( m^2 / g \right) = 4.355 \cdot V_m \left( cm^3 STP / g \right) \]

Recommended range of \( p/p_0 \): 0.05 - 0.35 max.
Exemple ZnO

Isothermes

BET plot

\[ S_{BET} = \frac{4.355}{\text{slope} + \text{int ercept}} \]

\[ C_{BET} = \frac{\text{slope}}{\text{int ercept}} + 1 \]

<table>
<thead>
<tr>
<th></th>
<th>( S_{BET} (m^2/g) )</th>
<th>( C_{BET} )</th>
</tr>
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<tbody>
<tr>
<td>65811</td>
<td>74</td>
<td>136</td>
</tr>
<tr>
<td>70299</td>
<td>36</td>
<td>237</td>
</tr>
</tbody>
</table>
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

\[
y = 0.0064x - 3 \times 10^{-5}
\]

\[
S_{BET} = \frac{4.355}{0.0064 - 0.0003} = 685 m^2 / g
\]
Langmuir Surface Area

- **Langmuir theory**
  - is a model of monolayer adsorption
  - this hypothesis is never fulfilled
- **Do not use Langmuir surface areas !!**
- $S_{\text{Langmuir}}$ is always $> S_{\text{BET}}$ because multilayer adsorption is treated like monolayer adsorption.
Determination of the pore volume

- In some cases possible without using any model.

\[ V_{\text{ads}} = 178 \text{ cm}^3 \text{ STP/g} \]

- \[ V_{\text{micro}} \]

\[ V_{\text{ads}} = 240 \text{ cm}^3 \text{ STP/g} \]

- \[ V_{\text{total}} \]

\[ V_{\text{meso}} = V_{\text{total}} - V_{\text{micro}} \]
Conversion gas volume – pore volume

- Volume of adsorbed gas corresponds to a certain number of moles
  - STP = Standard Temperature Pressure
    - $T = 273 \text{ K}, \ p = 1 \text{ bar} = 100 \text{ kPa}$
  - The adsorbed phase is considered like a liquid phase
  - Density of liquid $N_2$ at 77 K: 0.807 g/ml

\[
n_{ads} = \frac{V_{ads}P}{RT}
\]

\[
V_p = \frac{m_{N_2}}{\rho_{N_2,liq}} = \frac{n_{ads} \cdot M_{N_2}}{\rho_{N_2,liq}}
\]

\[
V_p (ml/g) = 1.5468 \cdot 10^{-3} \cdot V_{ads} (cm^3 STP / g)
\]
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 ($\text{SiO}_2$, $\text{Al}_2\text{O}_3$, $\text{ZrO}_2$, $\text{TiO}_2$, $\text{MgO}$) form a universal curve $t = f(p/p_0)$.

- Numerical description of that curve
  - valid for $t = 3.5 - 10$ Å
  - and $p/p_0 = 0.1 - 0.8$

**Harkins Jura**

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

**Halsey**

$$t = 3.54 \left( \frac{5}{\ln \left( \frac{P_0}{P} \right)} \right)^{1/3}$$

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 $p/p^o$. $n$ is the number of moles adsorbed per gram of adsorbent and $n_m$ is the monolayer capacity, expressed in the same units. Line A: $\bullet$ = silica; $\circ$ = 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

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

limit of validity
Interpretation of t-plots

- **Adsorption on a non-porous solid**
  
  - Adsorption on a non-porous solid
  
  - Adsorption on a microporous solid
    - Micropores rapidly filled
    - Then adsorption on external surface

\[
\frac{V_{\text{ads}}}{S} = \frac{V_{\text{ads}}}{t}
\]

\[
S = \frac{V_{\text{ads}}}{t}
\]
Example zeolite NaX

- $V_{\text{micro}} = 175 \text{ cm}^3 \text{ STP/g} = 0.271 \text{ ml/g}$
Surface BET vs. Surface t-plot

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

<table>
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Micro- and mesoporous solids

Solide non poreux : Adsorption sur Surface Externe - Courbe $t = t(P/P_0)$

Solide poreux : Adsorption sur Surfaces Internes & Externes

Pressions relatives $P/P_0$ croissantes

Solide poreux : Adsorption sur Surfaces Internes & Externes

Solide non poreux : Adsorption sur Surface Externe

$V_{µP} + V_{mP}$

$V_{µP}$

$V_{mP}$

$S_{B.E.T.}$
**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

![Graphs showing nitrogen adsorption isotherms for H-MCBeta and H-MCBeta steamed and leached](graph.png)

- \( N_2 \) ads cm\(^3\)/g STP
- \( p/p_0 \)
- \( V_{ads} \) cm\(^3\)/g STP
- Thickness - Halsey [Å]
Average pore size

- From geometrical rules
  - Cylindrical Pore:
    - \( V = \pi r^2 h \)
    - \( S = 2\pi rh \)
    - \( \frac{S}{V} = \frac{2}{r} \)
    - \( d = \frac{4V}{S} \)
  - Spherical pore:
    - \( V = \frac{4}{3} \pi r^3 \)
    - \( S = 4\pi r^2 \)
    - \( \frac{S}{V} = \frac{3}{r} \)
    - \( d = \frac{6V}{S} \)
  - Slit pore:
    - \( V = lhr \)
    - \( S = lh \)
    - \( \frac{S}{V} = \frac{1}{r} \)
    - \( d = \frac{2V}{S} \)
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

Input parameters

- pore geometry: slit-shaped, cylinder, sphere
- parameters of the Lennard-Jones potential well: $\varepsilon$ and $\sigma_{ij}$
  - not always well known for atypical solids

Input data

- high precision isotherm at very low pressure!

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.
Kelvin equation

**Mathematical formalism**

- Work against interfacial tension = change in free enthalpy

\[
dA \cdot \gamma = dn_{\text{capliq}} \cdot \mu_{\text{capliq}} + dn_{\text{liq}} \cdot \mu_{\text{liq}}
\]

\[
dn_{\text{capliq}} = -dn_{\text{liq}} = \frac{dV_{\text{capliq}}}{V_m}
\]

\[
dA \cdot \gamma = \frac{dV_{\text{capliq}}}{V_m} \cdot \mu_{\text{capliq}} - \frac{dV_{\text{capliq}}}{V_m} \cdot \mu_{\text{liq}}
\]

\[
dA \cdot V_m \cdot \gamma = dV_{\text{capliq}} (\mu_{\text{capliq}} - \mu_{\text{liq}})
\]

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

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

\[
\mu_{\text{capliq}} = \mu_0 + RT \ln \frac{p_{\text{cap}}}{p_0}
\]

\[
\mu_{\text{liq}} = \mu_0 + RT \ln \frac{p_{\text{sat}}}{p_0}
\]
Generalized Kelvin equation

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

- \[ \frac{dV}{dA} = \text{change in volume per change in interface area} \]
- \[ V_m = \text{molar volume} \]

- \( \frac{dV}{dA} \) depends on the pore geometry
  - Sphere: \( \frac{dV}{dA} = \frac{r}{2} \)
  - Cylinder: \( \frac{dV}{dA} = r \)
  - Slit: \( \frac{dV}{dA} = d \) distance between slits

- Relation to curvature of the pore

\[ \ln \frac{p_{cap}}{p_{sat}} = - \frac{1}{r_{\text{curvature}}} \frac{V_m \gamma}{RT} \]
Capillary condensation

- Multilayer adsorption on the surface: layer thickness $t \uparrow$
- At a certain effective pore radius $r_p - t$, capillary condensation occurs
- Pore is filled. There is a step in the adsorption isotherm.

\[ p_c = p_0 \cdot \exp\left(-\frac{v_l \gamma}{RT \cdot (r_p - t)}\right) \]
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 2\textsuperscript{nd} largest pore, reduction of layer thickness in both pores
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 ($\Delta V_n$) 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 contribute $\Delta V_n$. 

\[
\Delta V = \frac{(r_k + \Delta t)^2}{r_p^2} \cdot V_p
\]
The BJH-equation

E.P. Barret, L.G. Joyner, P.P. Halenda, JACS 73 (1951) 373.

\[ V_{pn} = \frac{r_{pn}^2}{(r_{kn} + \Delta t_n)^2} \cdot \Delta V_n - \frac{r_{pn}^2}{(r_{kn} + \Delta t_n)^2} \cdot \Delta t_n \cdot \sum_{j=1}^{n-1} \frac{r_{pj} - t_j}{r_{pj}} A_{pj} \]

\[ A_p = \frac{2V_p}{r_p} \]

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: \( r_p = r_k + t \)

\[ \log \frac{p}{p_0} = 0.034 \cdot \frac{13.99}{t^2} \]

\[ \log \frac{p}{p_0} = -4.14 \cdot \frac{r_k}{r_k} \]

\( \Delta t \) is the change in layer thickness in each desorption step

\( \Delta V_n \) 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

Vol_{ads} (cm^3/g)

p/p_0

capillary condensation

capillary evaporation
Application of the Kelvin equation

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Harkins-Jura t-plot equation

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

Kelvin equation

\[ \log \frac{p}{p_0} = -\frac{4.14}{r_m} \]

<table>
<thead>
<tr>
<th></th>
<th>( \frac{p_c}{p_0} )</th>
<th>( t(p_c) )</th>
<th>( r_{\text{curvature}} )</th>
<th>( R_c )</th>
<th>( r_p = r_c + t )</th>
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</thead>
<tbody>
<tr>
<td>Ads</td>
<td>0.671</td>
<td>8.2</td>
<td>11.9</td>
<td>11.9</td>
<td>20.2</td>
</tr>
<tr>
<td>Des</td>
<td>0.565</td>
<td>7.0</td>
<td>8.35</td>
<td>16.7</td>
<td>23.7</td>
</tr>
</tbody>
</table>

Cylinder !!

Sphere !!
Origin of the hysteresis

- The lower \( r_m \), the lower is the pressure of capillary condensation/evaporation
- \( r_{m,\text{ads}} = 2 r_{m,\text{des}} \)
- Capillary evaporation at a lower pressure than capillary condensation

→ 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 meniscus, 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

- 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

Monson, MMM, 2012.
Peterson, JCS Farad 2, 1986.
Ink-bottle pores

- In desorption smallest pore opening 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

- 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.

\[ \text{N}_2 \text{ can only desorb from pore A and C if pore B has already been emptied.} \]

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 opening 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.
Narrow peak in the pore size distribution of the adsorption branch is an artefact caused by the forced closure of the isotherm at $p/p_0 = 0.43$. 
Isotherm without hysteresis loop
Closure point of the isotherm

- Critical temperature inside a pore lower than in bulk:
  \[ T_{c, \text{pore}} < T_{c, \text{bulk}} \]
- \( T_{c, \text{pore}} \) 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
- \( T_{c, \text{pore}} < 77 \) K for pores, which show capillary condensation at \( p/p_0 = 0.4 \) → closure point of isotherm
- \( T_c(\text{Ar}) > T_c(\text{N}_2) \) → Ar isotherms show hysteresis when \( \text{N}_2 \) isotherms don‘t\(^2\)

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

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

- \(\rho(r)\) = fluid density at position \(r\)
- \(F(\rho)\) = Helmholtz energy of the system due to fluid-fluid interactions, in the absence of an external field
- \(V(r)\) = external potential at position \(r\)
- \(\mu\) = chemical potential
More recent DFT equation

\[ \Omega[\rho(r)] = k_B T \int \rho(r) \left[ \ln \left( \Lambda^3(r) \right) - 1 \right] dr + k_B T \int dr \Phi(\{\bar{\rho}_\alpha\}(r)) + \frac{1}{2} \int dr \int \rho(r)\rho(r')\phi_{att}(|r-r'|)dr' - \int \rho(r)[\mu - \phi_{ext}(r)] dr \]

- Ideal gas
- Excess energy (non-ideality)
- Fluid-fluid interaction
- External potential

- Everything is in the expression of \( \Phi_{ext} \)
  - Solid-fluid interaction
  - Effect of pore size and pore geometry (confinement)
    - Similar to the HK, SF models of micropore size analysis
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 integrated 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
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

Alternative explanations of the Kelvin equation
Physical principles of capillary condensation

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

**External pressure**

- **Equilibrium gas-liquid** $\mu_g = \mu_l$
- **Vapour pressure** $p_{g,0}$
- **Equilibrium disturbed by external pressure**

\[ \text{External pressure on liquid (H}_2\text{O), which induces the change in vapour pressure} \]

\[ \text{d}\mu_g = \text{d}\mu_l \rightarrow \nu_l \text{d}p_l = \nu_g \text{d}p_g \]

\[ \nu_l \Delta p_l = \frac{RT}{p_g} * \text{d}p_g \]

\[ \nu_l \Delta p_l = RT \ln \left( \frac{p_g}{p_{g,0}} \right) \]

\[ p_g = p_{g,0} \cdot \exp\left( \frac{\nu_l}{RT} \Delta p_l \right) \]

\[ p_g = \text{new vapour pressure of H}_2\text{O} \]

\[ p_{g,0} = \text{original vapour pressure of H}_2\text{O} \]

\[ \Delta p_l = \text{external pressure on liquid (H}_2\text{O), which induces the change in vapour pressure} \]

\[ \nu_l = \text{molar volume of liquid (H}_2\text{O)} \]
Vapour pressure of a drop of liquid

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

\( \gamma \) = surface tension
\( r \) = radius of curvature

\[ p_{l} - p_{out} = \frac{2\gamma}{r} \]

\[ p_{l} = p + \frac{2\gamma}{r} \]
Vapour pressure of a liquid void

\[ p_{\text{in}} - p_{\text{out}} = \frac{2\gamma}{r} \]

\[ p_{\text{in}} - p_{l} = \frac{2\gamma}{r} \]

\[ p_{l} = p - \frac{2\gamma}{r} \]

Kelvin equation: vapour pressure inside a void is lowered

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

### Capillary forces in the pore lower the vapor pressure of the condensed liquid

\[ \mu_{\text{cap}} = \mu_0 + RT \ln \frac{p_{\text{cap}}}{p_0} \]

\[ \mu_{\text{liq}} = \mu_0 + RT \ln \frac{p_{\text{sat}}}{p_0} \]

Evaporate \( n \) moles from capillary and condense on a flat surface. You have to work against the surface tension \( \gamma \).

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

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

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

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