

# Applying Physics and Nanotechnology for Making the Thermal Insulation Materials of Beyond Tomorrow

- From Concept to Experimental Investigations
- A Lecture in the Physics Motivation Series

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Originally presented as:

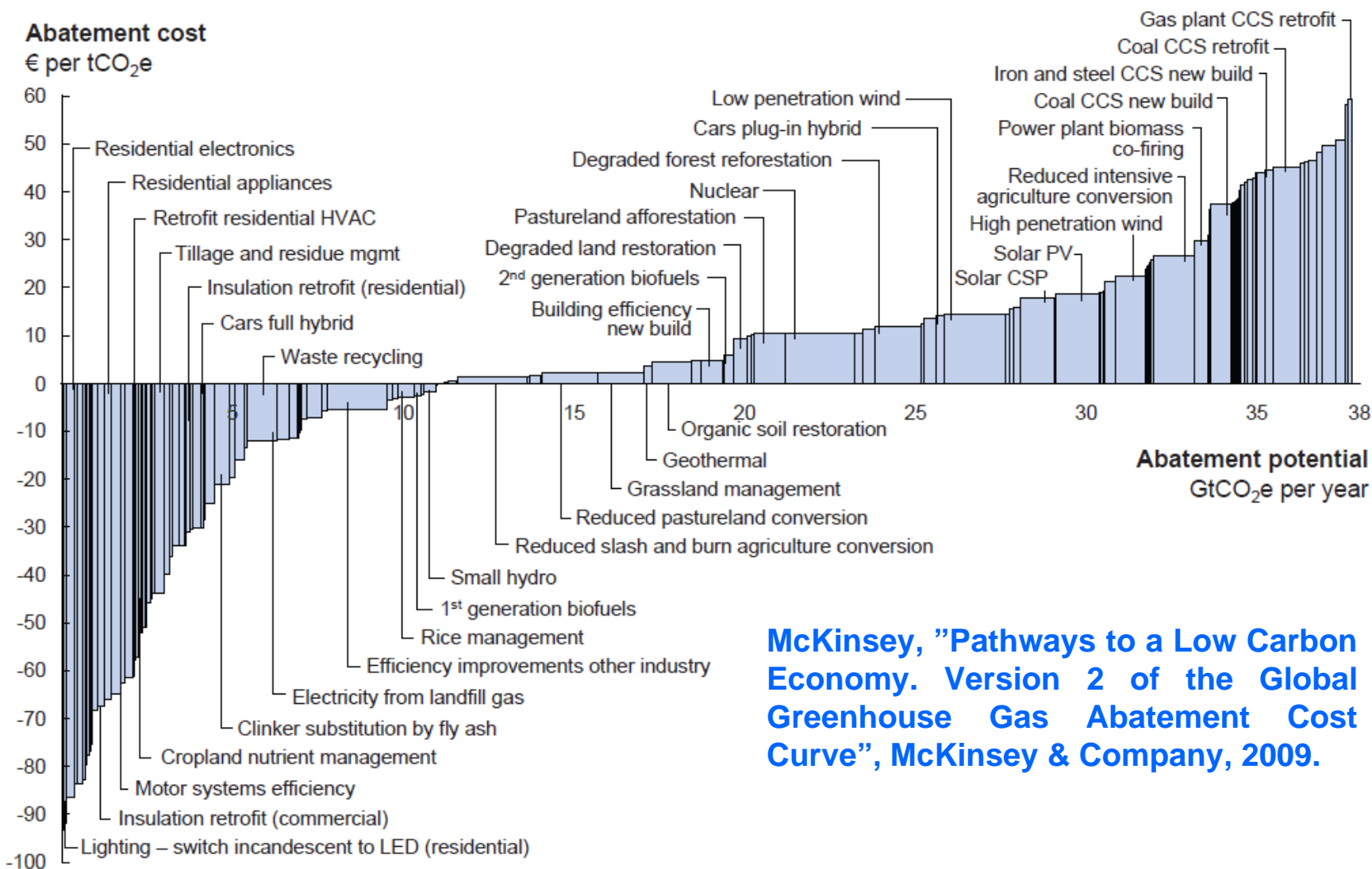
B. P. Jelle, B. G. Tilset, S. Jahren, T. Gao and A. Gustavsen, "Vacuum and Nanotechnologies for the Thermal Insulation Materials of Beyond Tomorrow - From Concept to Experimental Investigations", *10th International Vacuum Insulation Symposium (IVIS-X)*, Ottawa, Canada, 15-16 September, 2011.

*Lecture in the Physics Motivation Series, Trondheim, Norway, 5th of October, 2011.*

## - What Measures Amounts the Most ?



Global GHG abatement cost curve beyond business-as-usual – 2030

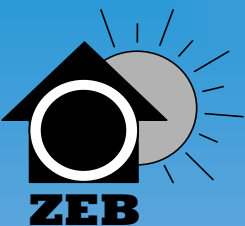


McKinsey, "Pathways to a Low Carbon Economy. Version 2 of the Global Greenhouse Gas Abatement Cost Curve", McKinsey & Company, 2009.

Note: The curve presents an estimate of the maximum potential of all technical GHG abatement measures below €60 per tCO<sub>2</sub>e if each lever was pursued aggressively. It is not a forecast of what role different abatement measures and technologies will play.  
 Source: Global GHG Abatement Cost Curve v2.0

# Thermal Background

## - Thermal Conductivity Contributions



$$\lambda_{\text{tot}} = \lambda_{\text{solid}} + \lambda_{\text{gas}} + \lambda_{\text{rad}} + \lambda_{\text{conv}} + \lambda_{\text{coupling}} + \lambda_{\text{leak}}$$

$\lambda_{\text{tot}}$  = total overall thermal conductivity

$\lambda_{\text{solid}}$  = solid state thermal conductivity

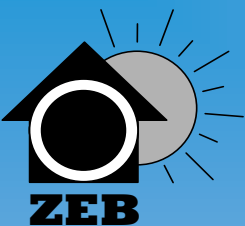
$\lambda_{\text{gas}}$  = gas thermal conductivity

$\lambda_{\text{rad}}$  = radiation thermal conductivity

$\lambda_{\text{conv}}$  = convection thermal conductivity

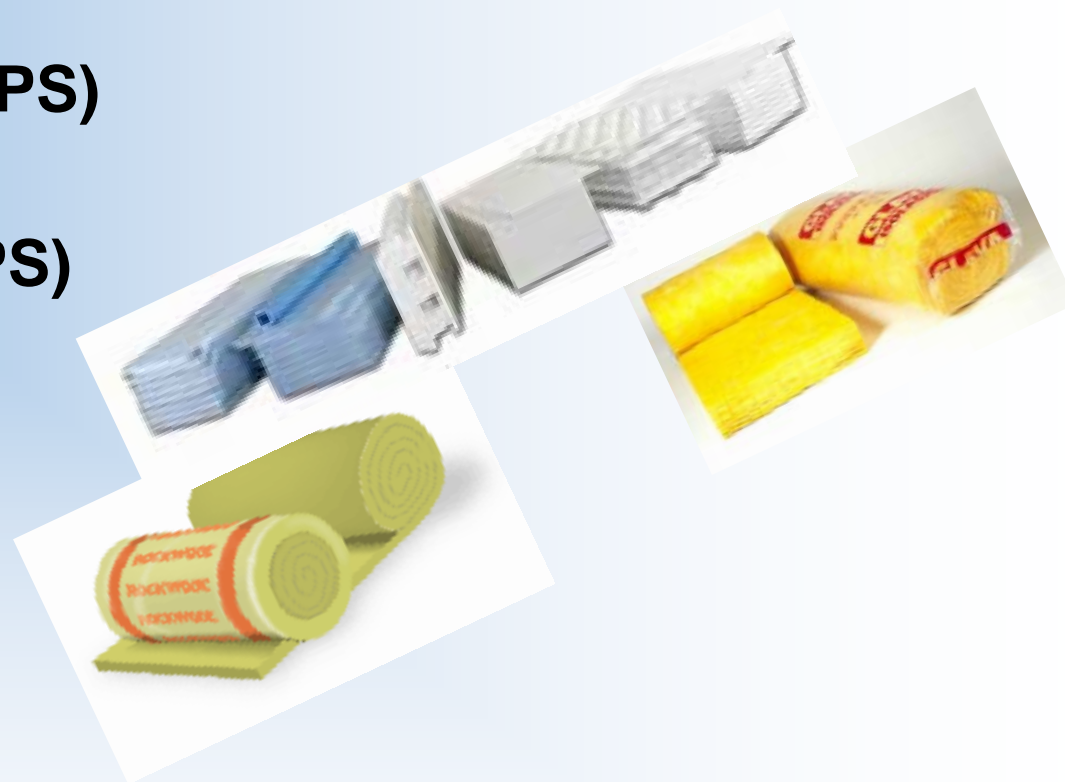
$\lambda_{\text{coupling}}$  = thermal conductivity term accounting for second order effects between the various thermal conductivities

$\lambda_{\text{leak}}$  = leakage thermal conductivity



## - What is Out There?

- **Mineral Wool**
  - Glass wool (fibre glass)
  - Rock wool
  - 30-40 mW/(mK)
  
- **Expanded Polystyrene (EPS)**
  - 30-40 mW/(mK)
  
- **Extruded Polystyrene (XPS)**
  - 30-40 mW/(mK)
  
- **Cellulose**
  - 40-50 mW/(mK)
  
- **Cork**
  - 40-50 mW/(mK)
  
- **Polyurethane (PUR)**
  - Toxic gases (e.g. HCN) released during fire
  - 20-30 mW/(mK)



# State-of-the-Art Thermal Insulation of Today

## - What is Out There?



### ■ Vacuum Insulation Panels (VIP)

*"An evacuated foil-encapsulated open porous material as a high performance thermal insulating material"*

- Core (silica, open porous, vacuum)
- Foil (envelope) - 4 - 8 - 20 mW/(mK)

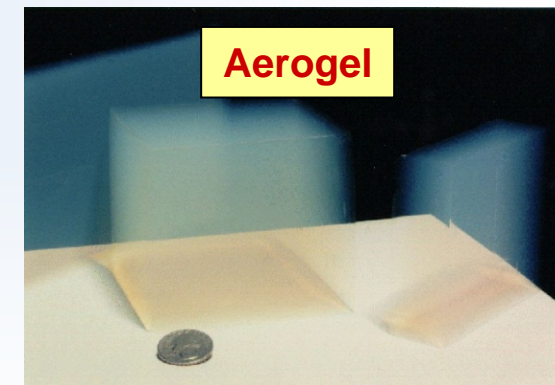
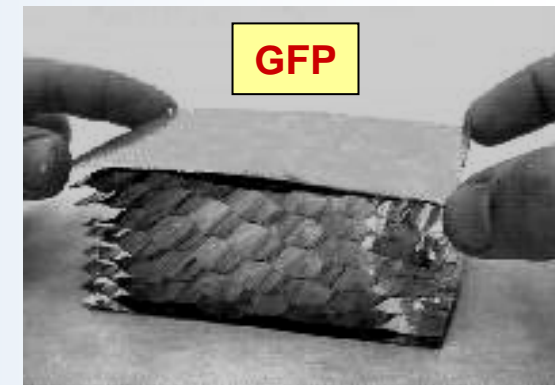
### ■ Gas-Filled Panels (GFP) - 40 mW/(mK)

### ■ Aerogels - 13 mW/(mK)

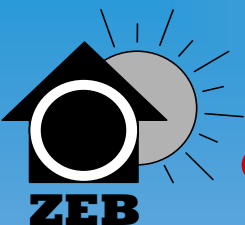
### ■ Phase Change Materials (PCM)

- Solid State  $\leftrightarrow$  Liquid
- Heat Storage and Release

### ■ Beyond State-of-the-Art High Performance Thermal Insulation Materials ?

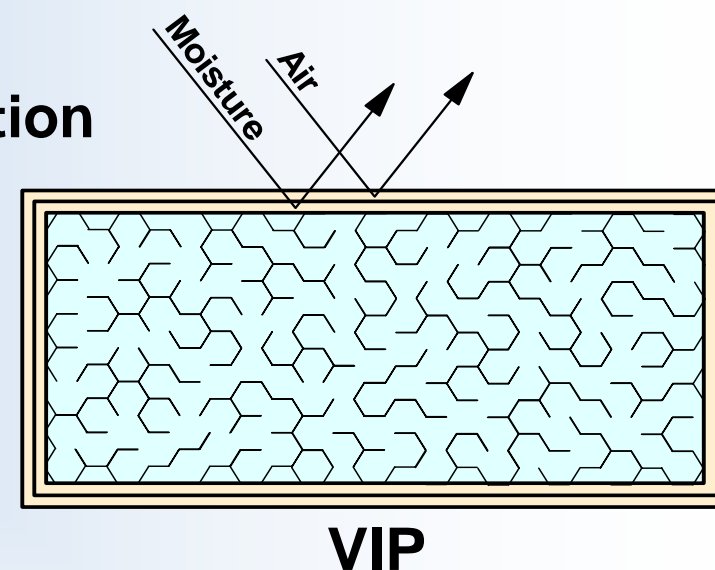


# Major Disadvantages of VIPs

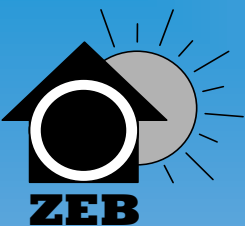


- Thermal bridges at panel edges
- Expensive at the moment, but calculations show that VIPs may be cost-effective even today
- Ageing effects - Air and moisture penetration
  - 4 mW/(mK) fresh
  - 8 mW/(mK) 25 years
  - 20 mW/(mK) perforated
- Vulnerable towards penetration, e.g nails
  - 20 mW/(mK)
- Can not be cut or adapted at building site
- Possible improvements?

- Vacuum Core  
- Air and Moisture Tight Envelope

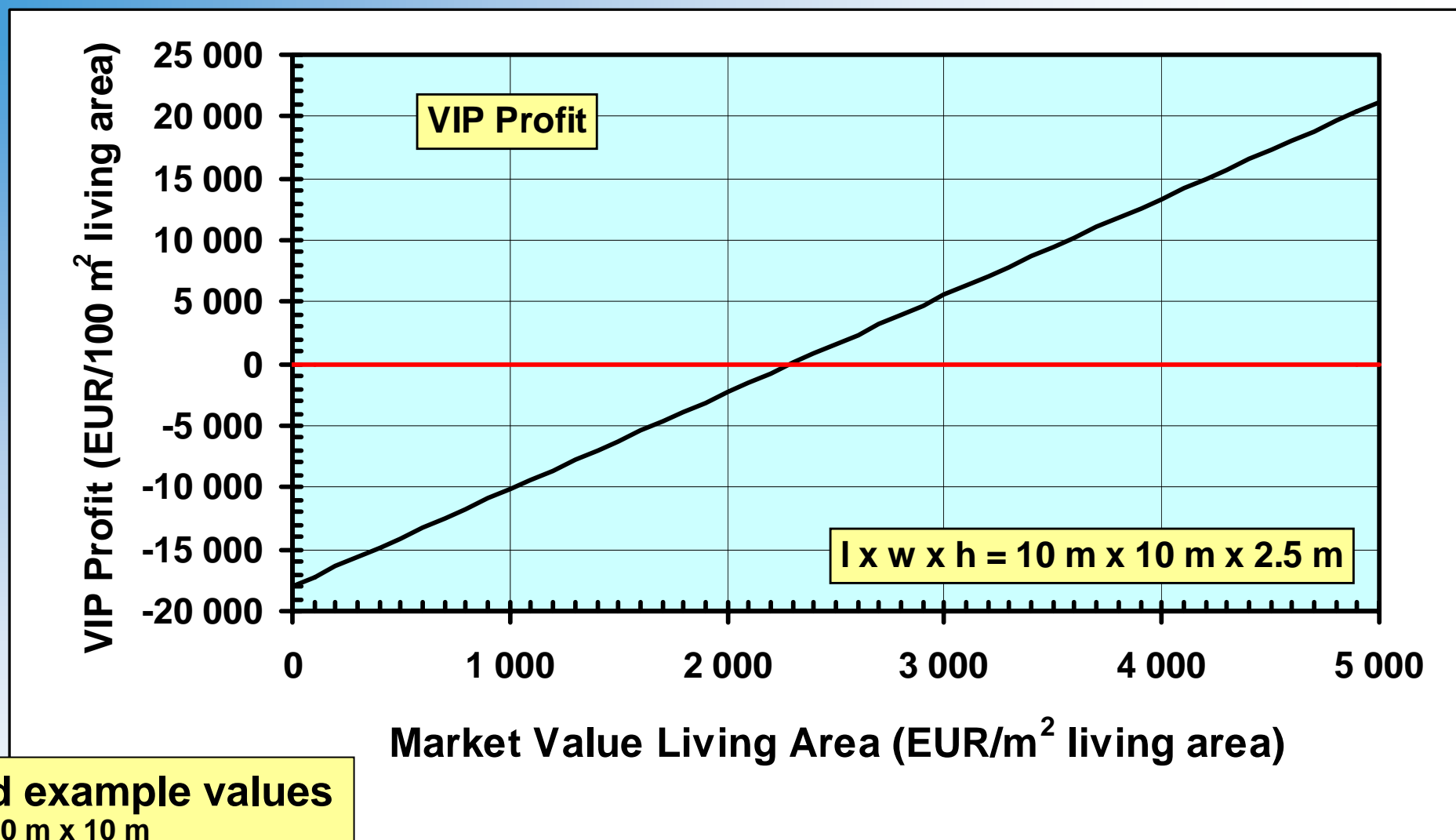
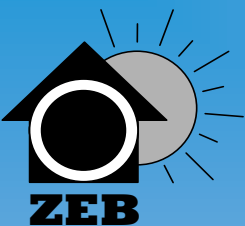


# VIPs – The Thermal Insulation of Today ?



- **VIPs - Despite large disadvantages - A large leap forward**
- **Thermal conductivities 5 to 10 times lower than traditional insulation**
  - 4 mW/(mK) fresh
  - 8 mW/(mK) 25 years
  - 20 mW/(mK) perforated
- **Wall and roof thicknesses up to 50 cm as with traditional insulation are not desired**
  - Require new construction techniques and skills
  - Transport of thick building elements leads to increased costs
- **Building restrictions during retrofitting of existing buildings**
  - Lawful authorities
  - Practical Restrictions
- **High living area market value per m<sup>2</sup> ⇒ Reduced wall thickness ⇒ Large area savings ⇒ Higher value of the real estate**
- **VIPs - The best solution today and in the near future?**
- **Beyond VIPs?**

# Potential Cost Savings by Applying VIPs



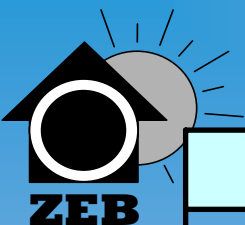
## Assumed example values

- Building of 10 m x 10 m
- Interior floor to ceiling height of 2.5 m
- 20 cm wall thickness reduction
- VIP costs 6 cm: 200 EUR/m<sup>2</sup>
- Mineral wool costs 35 cm: 20 EUR/m<sup>2</sup>

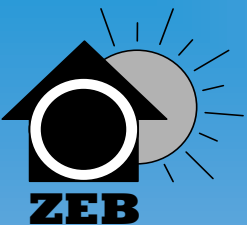
B. P. Jelle, "Traditional, State-of-the-Art and Future Thermal Building Insulation Materials and Solutions - Properties, Requirements and Possibilities", *Energy and Buildings*, 43, 2549-2563, 2011.



# Requirements of the Thermal Insulation of Tomorrow



Property	Requirements
Thermal conductivity – pristine	< 4 mW/(mK)
Thermal conductivity – after 100 years	< 5 mW/(mK)
Thermal conductivity – after modest perforation	< 4 mW/(mK)
Perforation vulnerability	not to be influenced significantly
Possible to cut for adaption at building site	yes
Mechanical strength (e.g. compression and tensile)	may vary
Fire protection	may vary, depends on other protection
Fume emission during fire	any toxic gases to be identified
Climate ageing durability	resistant
Freezing/thawing cycles	resistant
Water	resistant
Dynamic thermal insulation	desirable as an ultimate goal
Costs vs. other thermal insulation materials	competitive
Environmental impact (including energy and material use in production, emission of polluting agents and recycling issues)	low negative impact



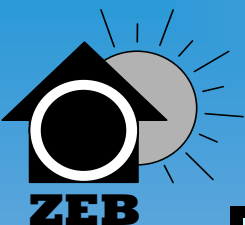
# Properties of Concrete – A Construction Material

- **Thermal Conductivity**
  - **Concrete**
    - 150 – 2500 mW/(mK)
  - **Traditional Thermal Insulation**
    - 36 mW/(mK)
  - **Vacuum Insulation Panels (VIPs)**
    - 4 mW/(mK)

*Possible to decrease the thermal conductivity of concrete?*

# Properties of Concrete

Some key properties of concrete (example values)



Property	With Rebars	Without Rebars
Mass density (kg/dm <sup>3</sup> )	2.4	2.2
Thermal conductivity (mW/mK)	2500	1700
Specific heat capacity (J/(kgK))	840	880
Linear thermal expansion coefficient (10 <sup>-6</sup> /K)	12	12
Compressive strength (MPa)	30	30
Tensile strength (MPa) <sup>a</sup>	500 <sup>b</sup>	3
Fire resistance	> 2 h	> 2 h
Environmental impact (incl. energy and material use in production, emission of polluting agents and recycling issues)	large CO <sub>2</sub> emissions	large CO <sub>2</sub> emissions

<sup>a</sup> As a comparison, note that carbon nanotubes have been manufactured with tensile strengths as high as 63 000 MPa and have a theoretical limit at 300 000 MPa. <sup>b</sup> Rebars.

# Large CO<sub>2</sub> Emissions from Cement Production

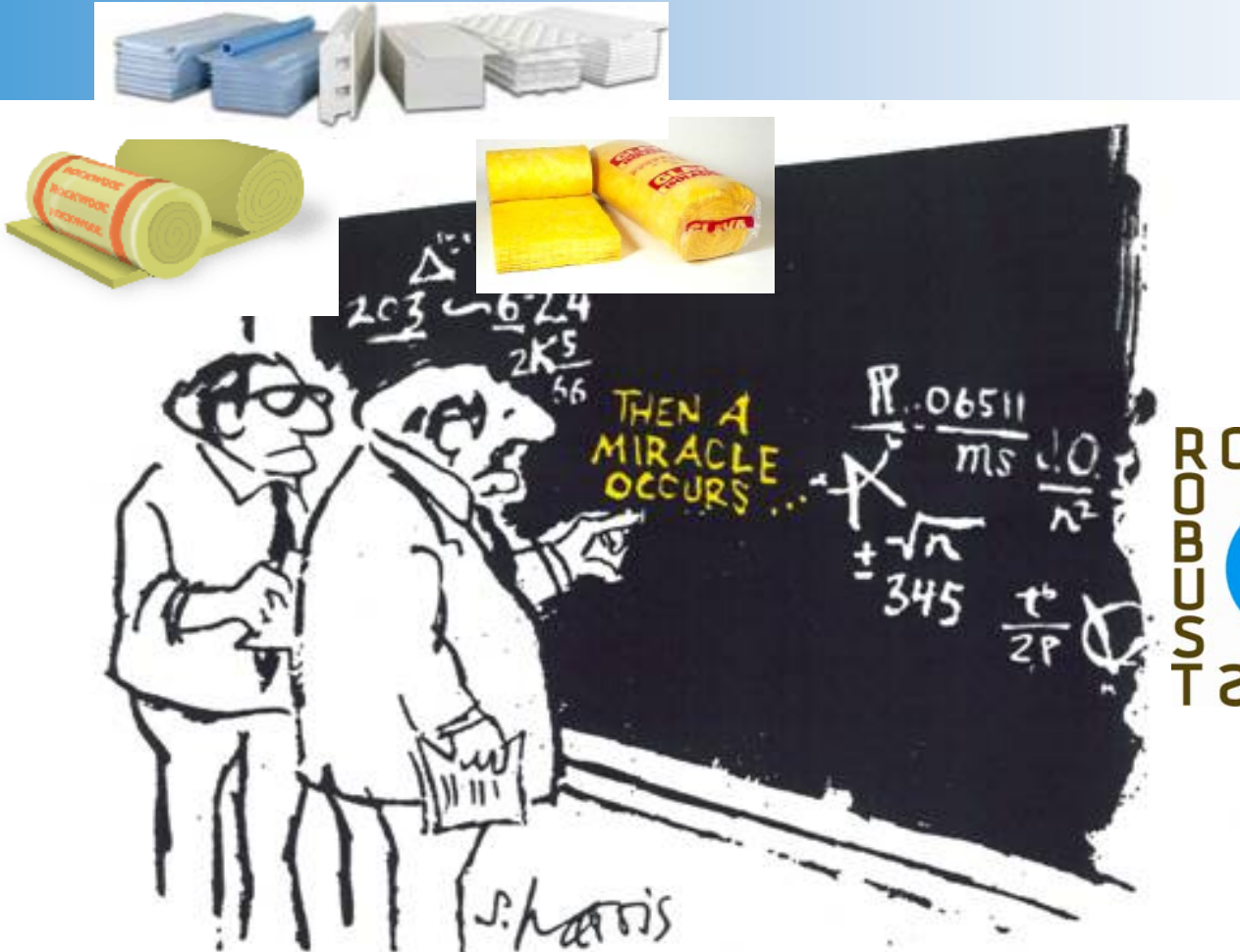


- The cement industry produces 5 % of the global man-made CO<sub>2</sub> emissions of which:
  - 50 % from the chemical process
    - e.g.:  $3\text{CaCO}_3 + \text{SiO}_2 \rightarrow \text{Ca}_3\text{SiO}_5 + 3\text{CO}_2$
    - $2\text{CaCO}_3 + \text{SiO}_2 \rightarrow \text{Ca}_2\text{SiO}_4 + 2\text{CO}_2$
  - 40 % from burning fossil fuels
    - e.g. coal and oil
  - 10 % split between electricity and transport uses

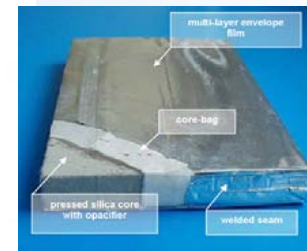
**And let us not forget the corrosion issues with reinforced concrete...**

World Business Council for Sustainable Development, "The cement sustainability initiative – Our agenda for action", July 2002.

# Beyond Traditional Thermal Insulation?



ROBUST

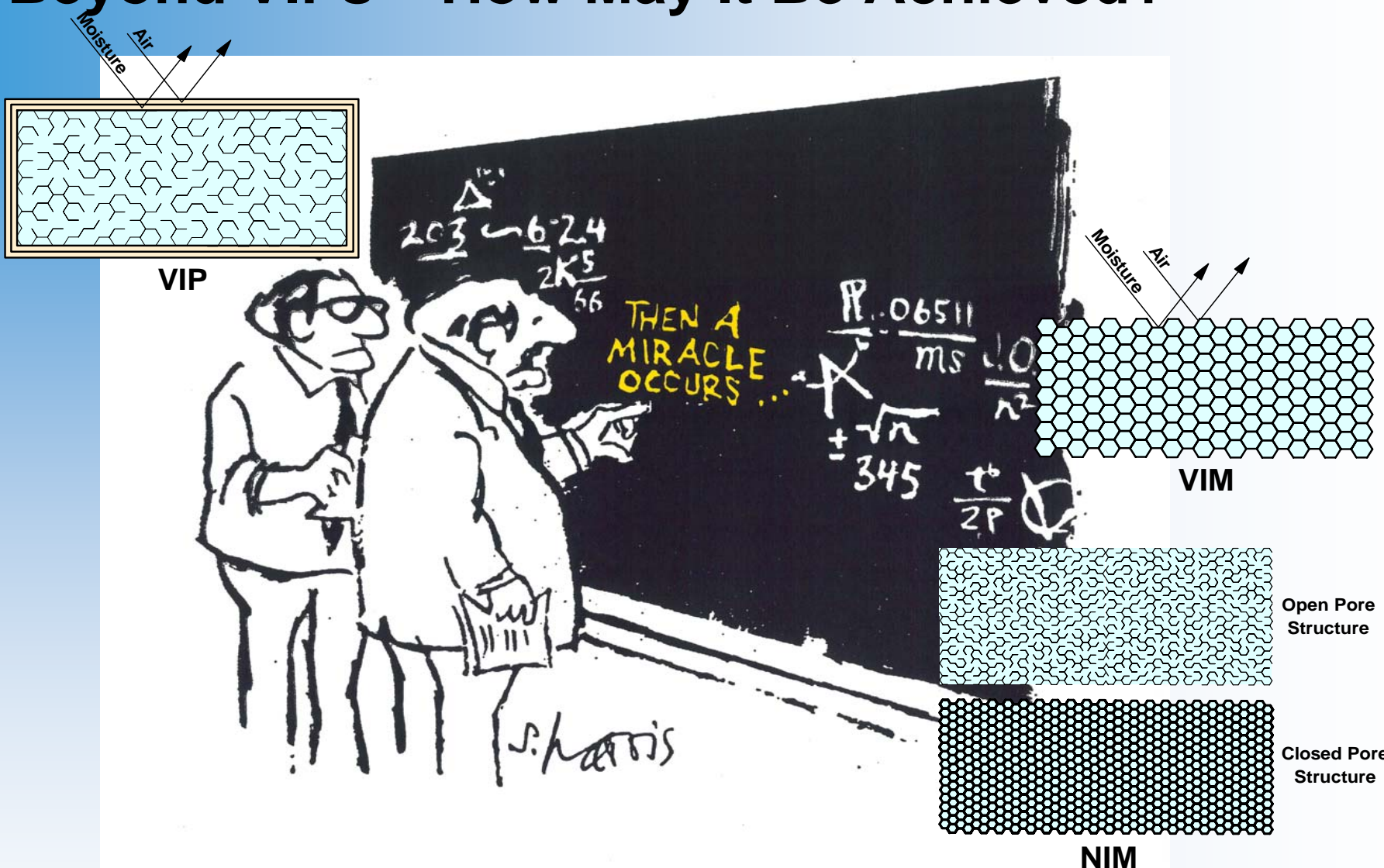
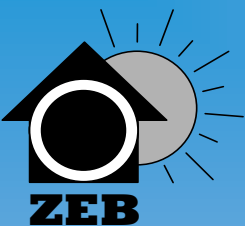


VIP  
GFP



"I think you should be more explicit here in step two"

# Beyond VIPs – How May It Be Achieved?

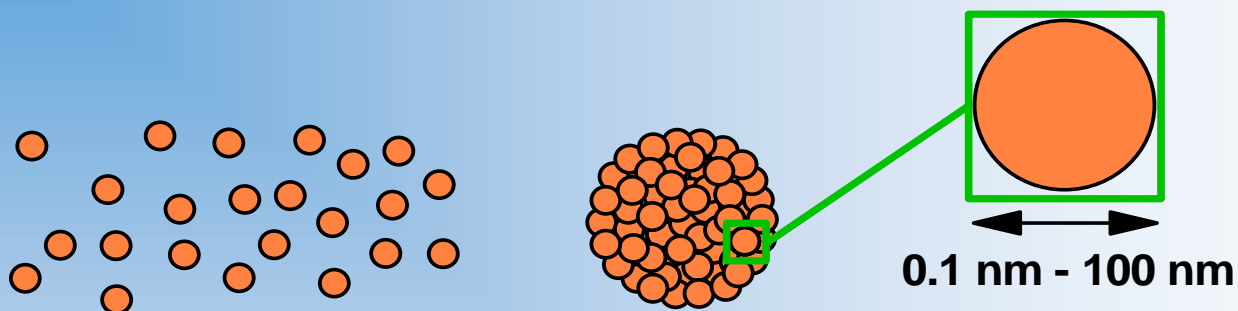


"I think you should be more explicit here in step two"



# Nano Technology

**Nanotechnology:**  
Technology for controlling matter of dimensions between 0.1 nm - 100 nm.

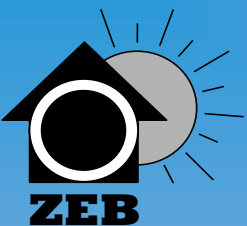


For comparison:

- Solar radiation: 300 nm - 3000 nm
- Atomic diameters: Hydrogen: 0.16 nm
- Carbon: 0.18 nm
- Gold: 0.36 nm
- Molecular length: Stearic Acid: 2.48 nm  
( $C_{17}H_{35}COOH$ )

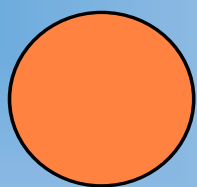
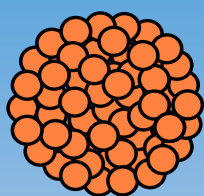


**Nanotechnology:**  
Technology for controlling matter at an atomic and molecular scale.



# Nano Technology and Thermal Insulation

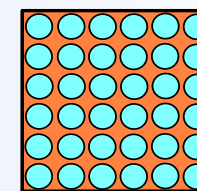
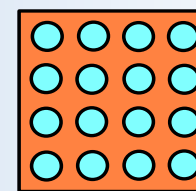
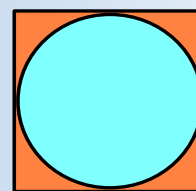
## Nano Particles



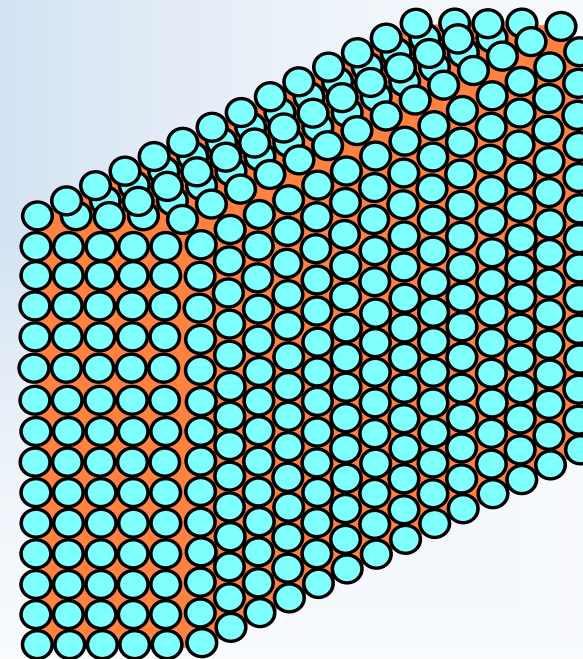
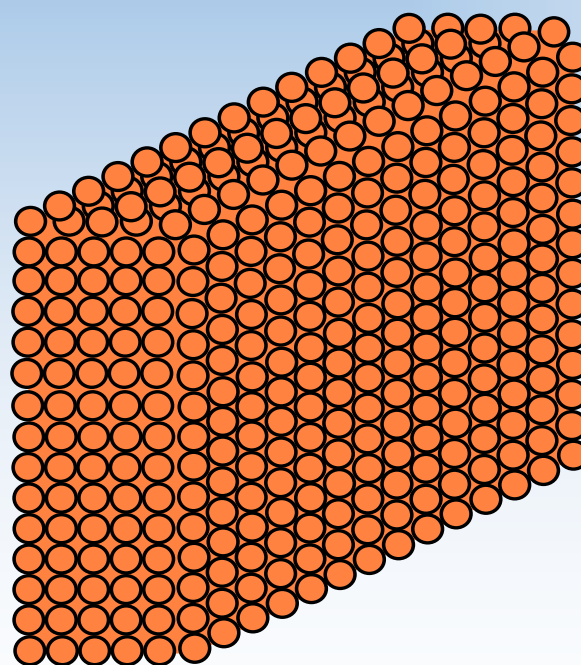
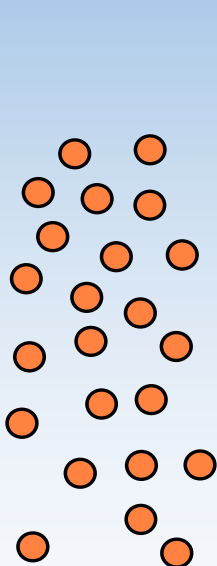
0.1 nm - 100 nm



## Nano Pores



0.1 nm - 100 nm

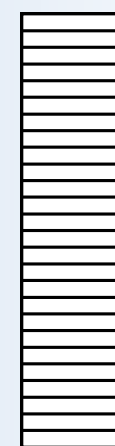
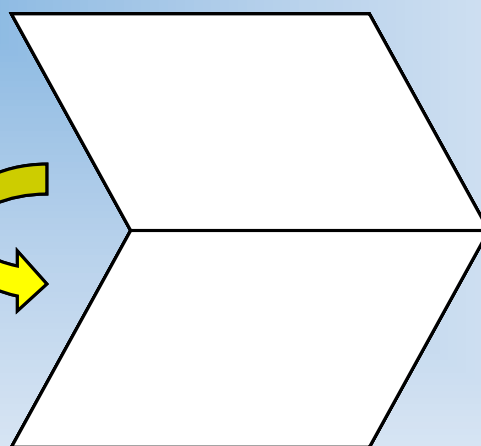
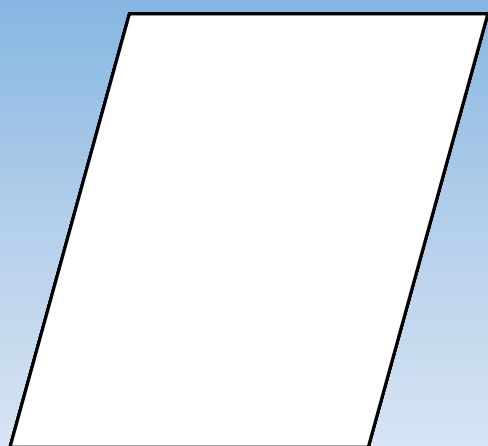






# How Good are You at Guessing?

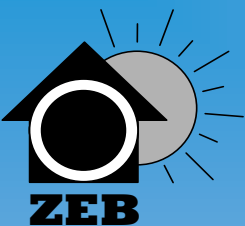
## The A4 Paper Folding



How high ?

- Fold an A4 paper 100 times.
- Press out all air between the paper sheets.
- Put the paper pile on the table in front of you.
- Guess how far above the table does the paper pile reach ?

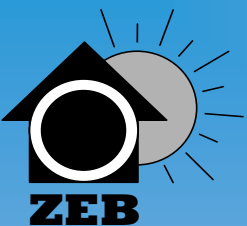
# Beyond VIPs – How May It Be Achieved?



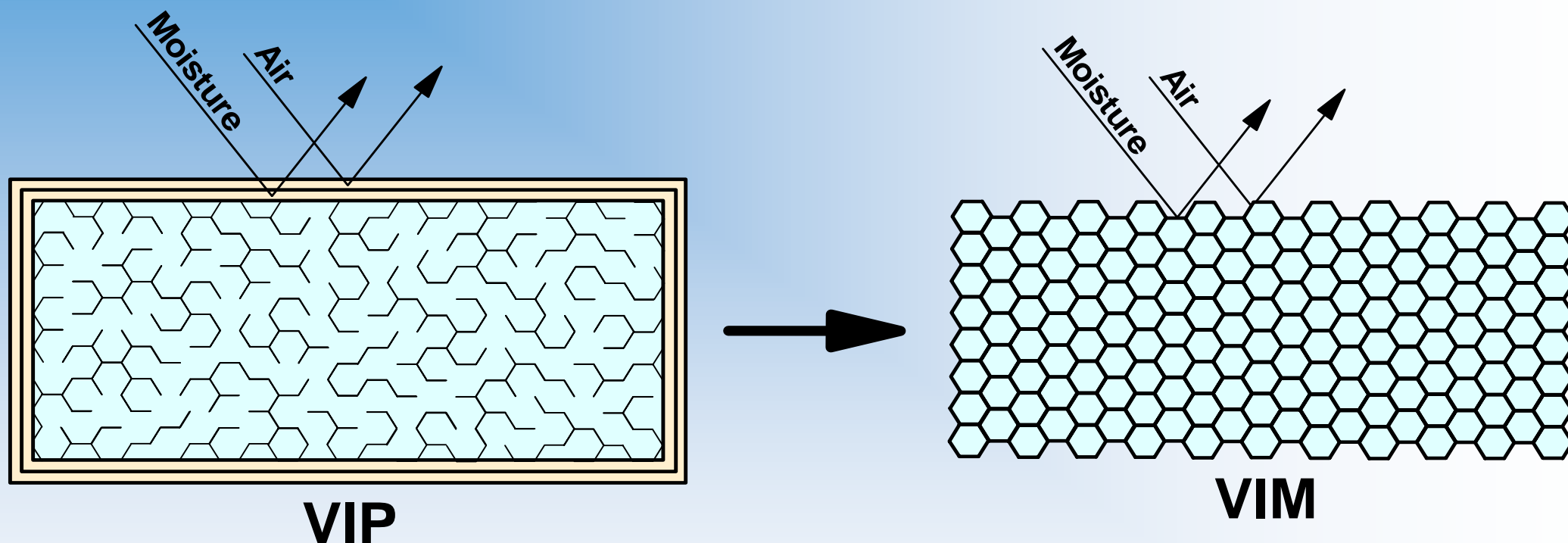
## Introducing New Concepts as

- **Advanced Insulation Materials (AIM):**
- **Vacuum Insulation Materials (VIM)**
- **Gas Insulation Materials (GIM)**
- **Nano Insulation Materials (NIM)**
- **Dynamic Insulation Materials (DIM)**

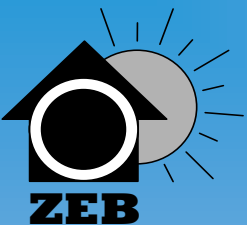
B. P. Jelle, A. Gustavsen and R. Baetens, "The Path to the High Performance Thermal Building Insulation Materials and Solutions of Tomorrow", *Journal of Building Physics*, **34**, 99-123, 2010.



# Vacuum Insulation Material (VIM)

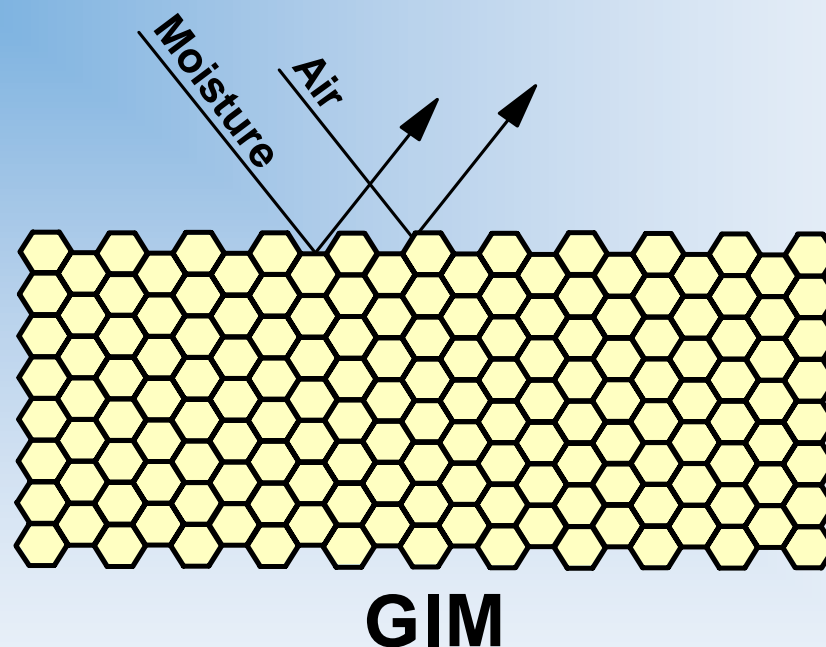


**VIM - A basically homogeneous material with a closed small pore structure filled with vacuum with an overall thermal conductivity of less than 4 mW/(mK) in the pristine condition**

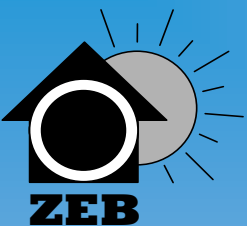


# Gas Insulation Material (GIM)

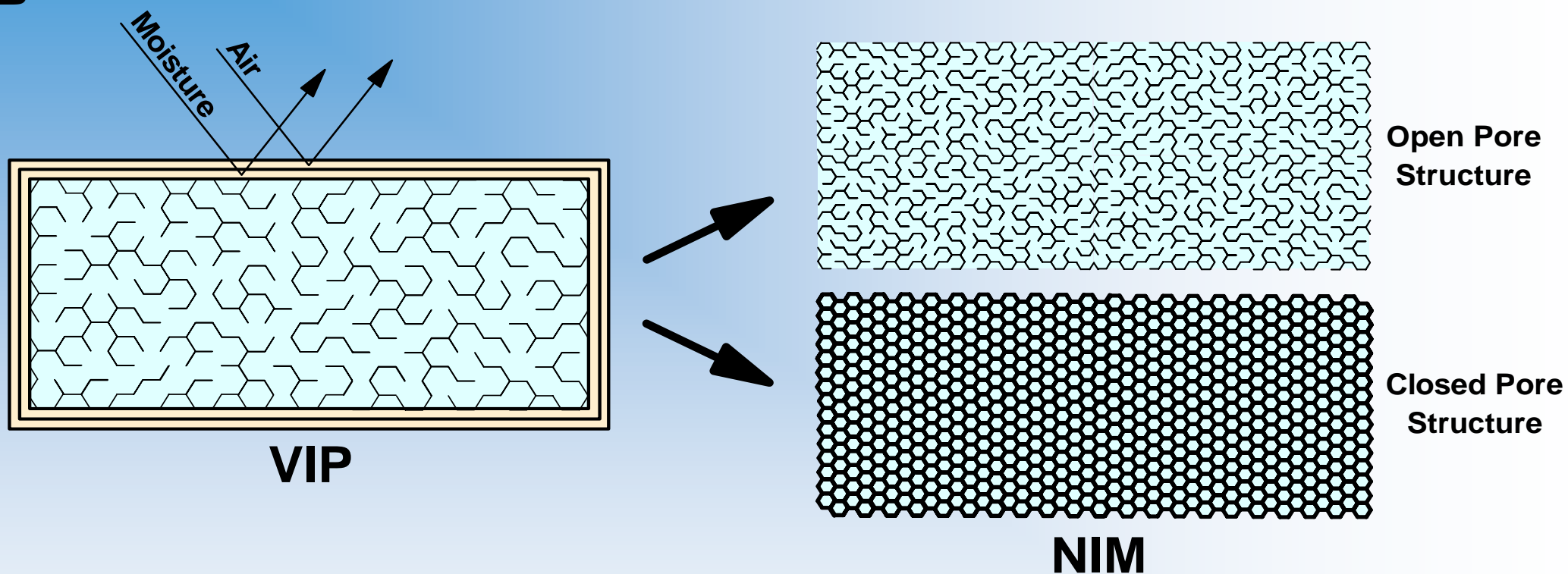
... and analogously with VIM we may define GIM as follows:



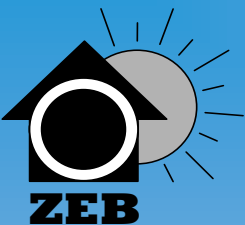
**GIM - A basically homogeneous material with a closed small pore structure filled with a low-conductance gas with an overall thermal conductivity of less than 4 mW/(mK) in the pristine condition**



# Nano Insulation Material (NIM)



**NIM - A basically homogeneous material with a closed or open small nano pore structure with an overall thermal conductivity of less than 4 mW/(mK) in the pristine condition**



# The Knudsen Effect – Nano Pores

Gas Thermal Conductivity  $\lambda_{\text{gas}}$

$$\lambda_{\text{gas}} = \frac{\lambda_{\text{gas},0}}{1 + 2\beta\text{Kn}} = \frac{\lambda_{\text{gas},0}}{1 + \frac{\sqrt{2\beta k_B T}}{\pi d^2 p \delta}}$$

$\sigma_{\text{mean}} > \delta$   
 $\Rightarrow$  LOW  $\lambda_{\text{gas}}$

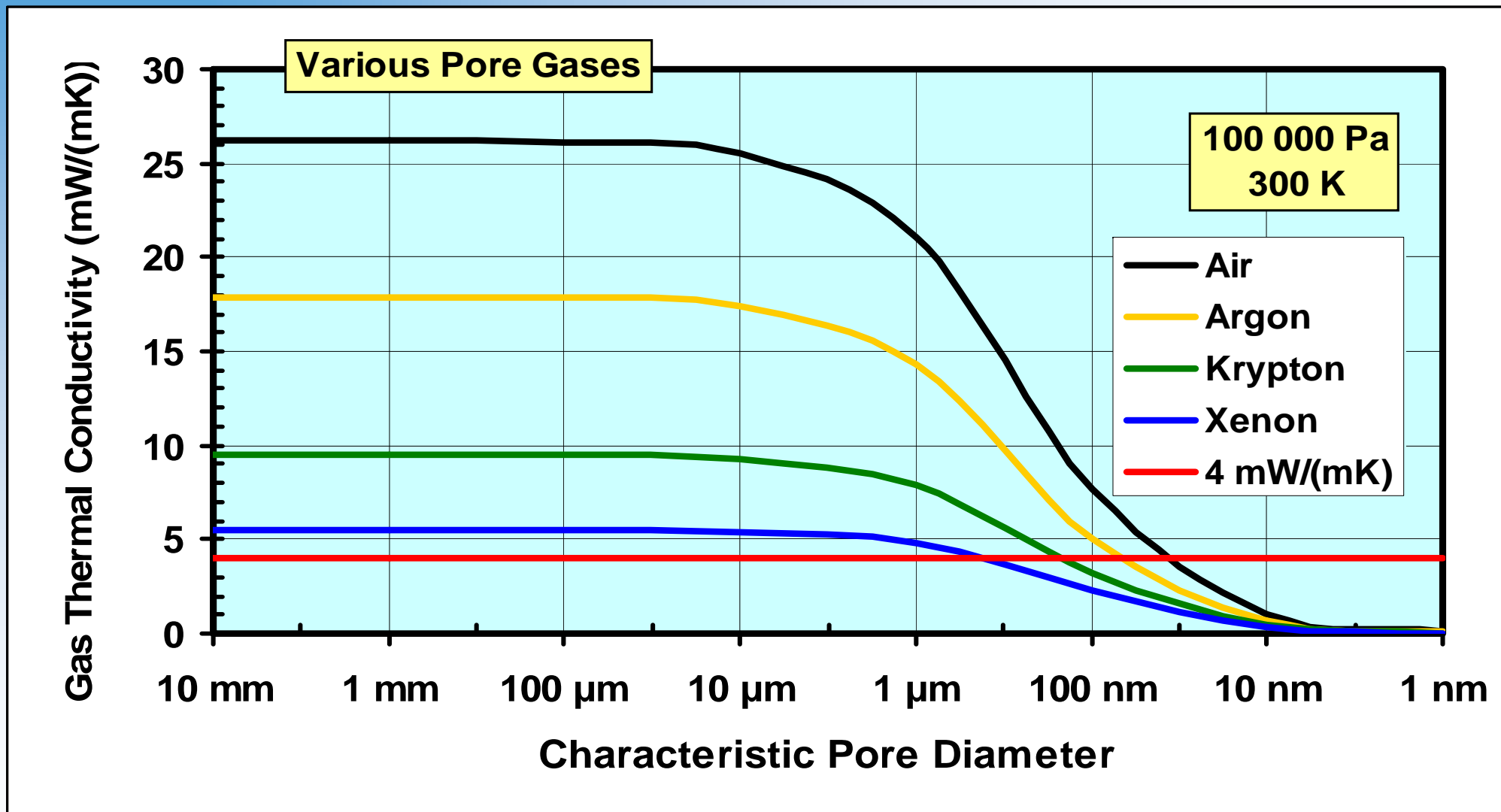
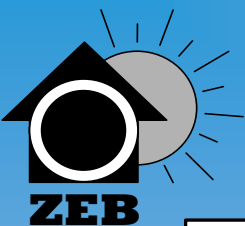
where

$$\text{Kn} = \frac{\sigma_{\text{mean}}}{\delta} = \frac{k_B T}{\sqrt{2} \pi d^2 p \delta}$$

$\lambda_{\text{gas}}$  = gas thermal conductivity in the pores (W/(mK))  
 $\lambda_{\text{gas},0}$  = gas thermal conductivity in the pores at STP (standard temperature and pressure) (W/(mK))  
 $\beta$  = coefficient characterizing the molecule - wall collision energy transfer efficiency (between 1.5 - 2.0)  
 $\text{Kn} = \sigma_{\text{mean}}/\delta = k_B T / (\sqrt{2} \pi d^2 p \delta)$  = the Knudsen number  
 $k_B$  = Boltzmann's constant  $\approx 1.38 \cdot 10^{-23}$  J/K  
 $T$  = temperature (K)  
 $d$  = gas molecule collision diameter (m)  
 $p$  = gas pressure in pores (Pa)  
 $\delta$  = characteristic pore diameter (m)  
 $\sigma_{\text{mean}}$  = mean free path of gas molecules (m)

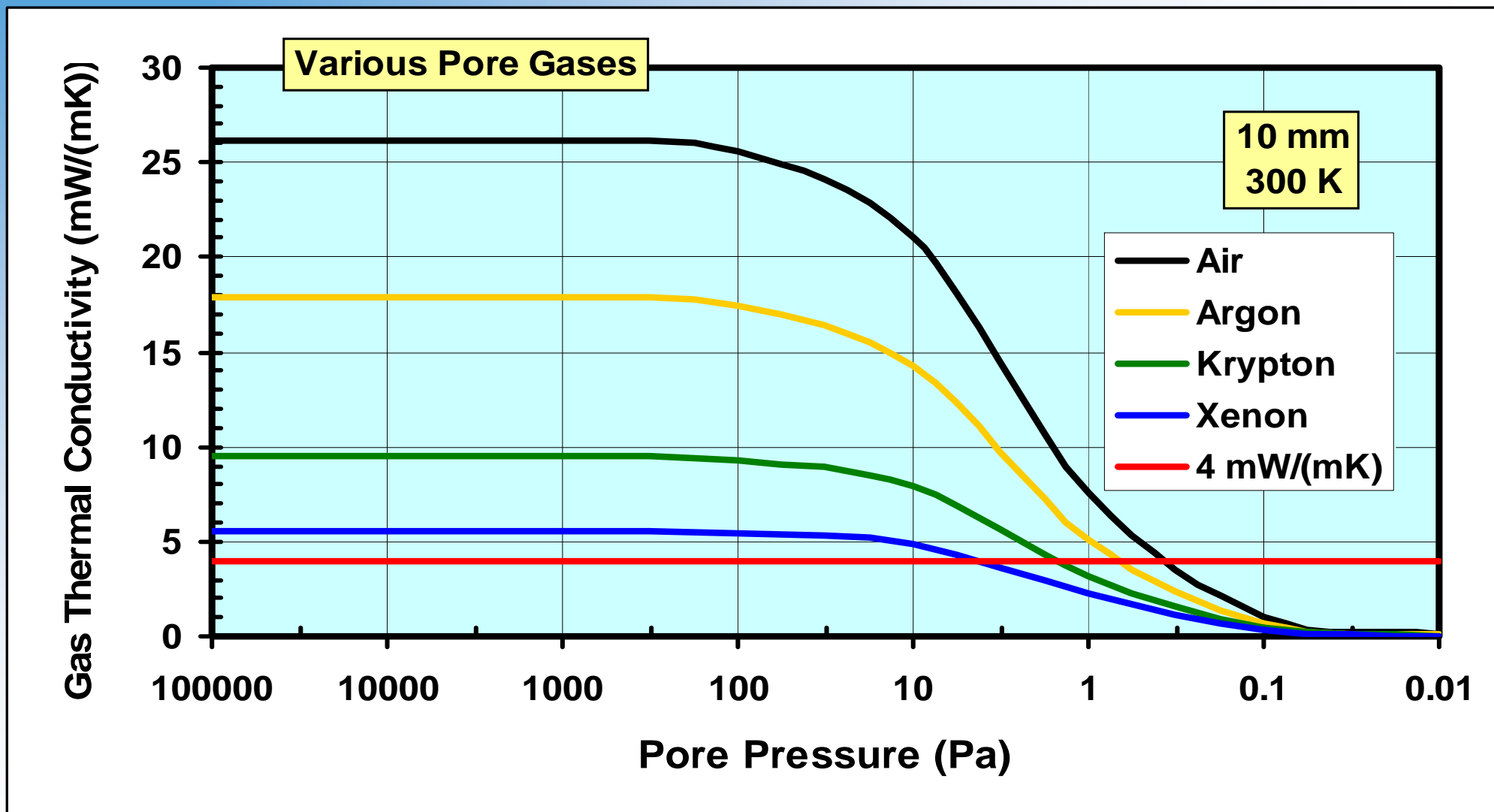
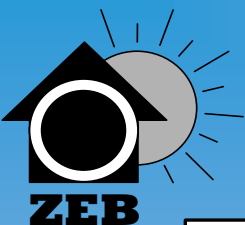
# Gas Thermal Conductivity

## Conductivity vs. Pore Diameter



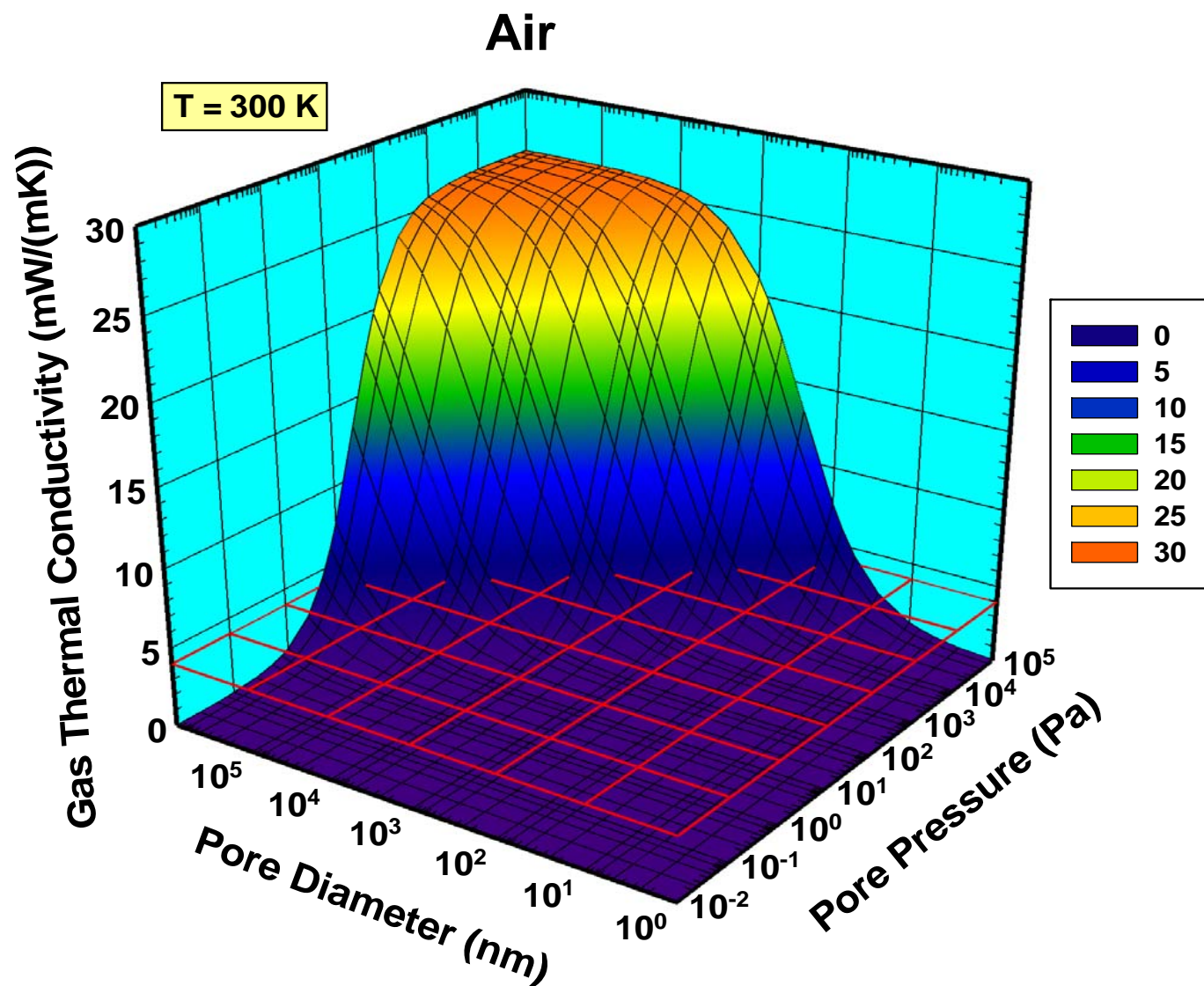
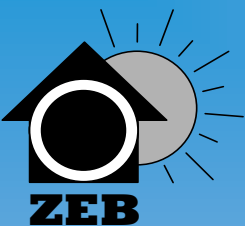
# Gas Thermal Conductivity

## Conductivity vs. Pore Pressure

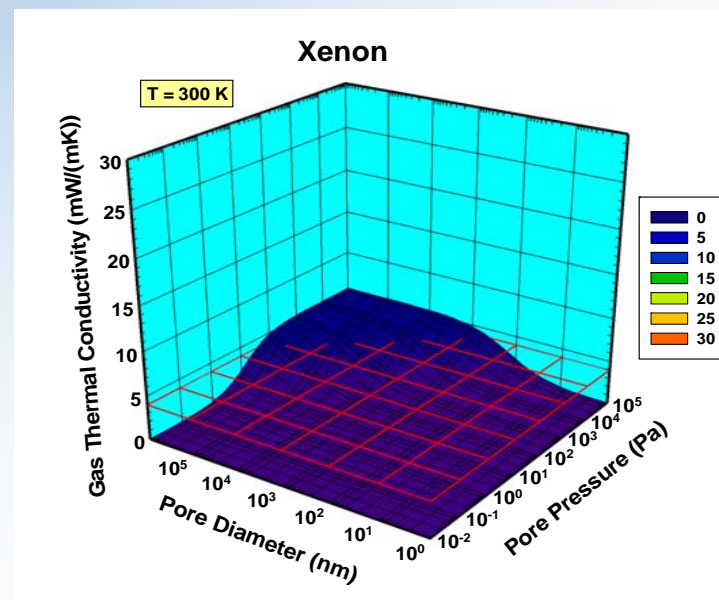
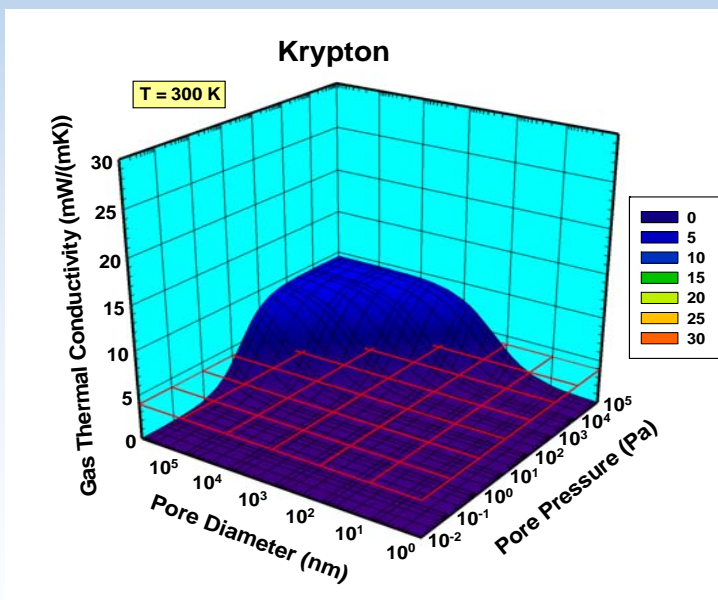
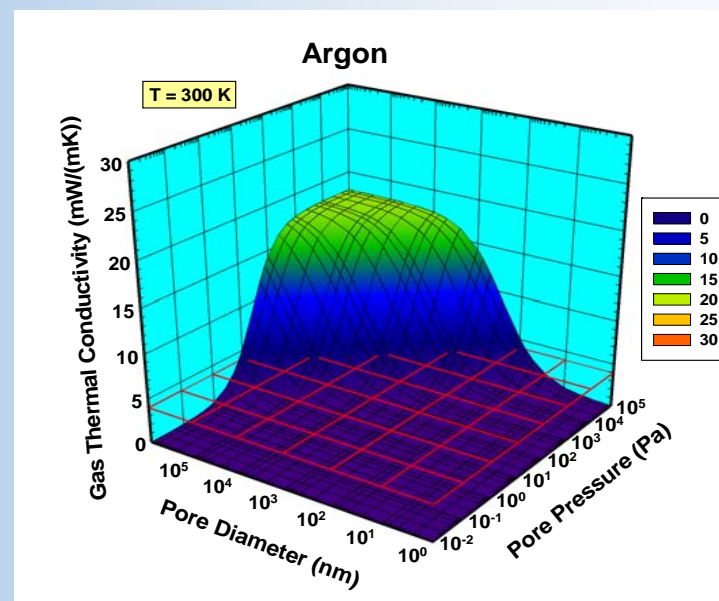
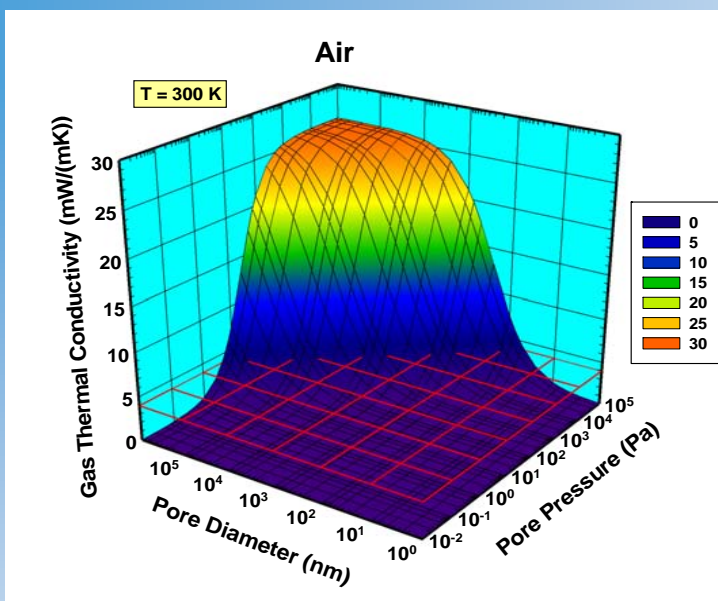
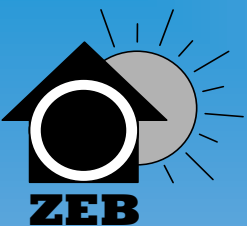


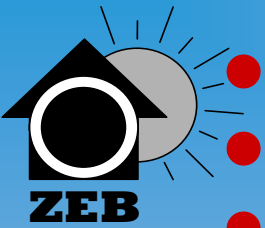


# Gas Thermal Conductivity



# Gas Thermal Conductivity





- Knudsen effect  $\Rightarrow \sigma_{\text{mean}} > \delta \Rightarrow$  low gas thermal conductivity  $\lambda_{\text{gas}}$
- What about the thermal radiation in the pores?
- "Classical" – from Stefan-Boltzmann's law (Linear  $\lambda_{\text{rad}}$  vs.  $\delta$  relationship):

$$\lambda_{\text{rad}} = \frac{\pi^2 k_B^4 \delta}{60 \hbar^3 c^2 \left[ \frac{2}{\varepsilon} - 1 \right]} \frac{(T_i^4 - T_e^4)}{(T_i - T_e)}$$

$\lambda_{\text{rad}}$  = radiation thermal conductivity in the pores (W/(mK))

$\sigma = \pi^2 k_B^4 / (60 \hbar^3 c^2)$  = Stefan-Boltzmann's constant  $\approx 5.67 \cdot 10^{-8}$  W/(m<sup>2</sup>K<sup>4</sup>)

$k_B$  = Boltzmann's constant  $\approx 1.38 \cdot 10^{-23}$  J/K

$\hbar = h/(2\pi) \approx 1.05 \cdot 10^{-34}$  Js = reduced Planck's constant ( $h$  = Planck's constant)

$c$  = velocity of light  $\approx 3.00 \cdot 10^8$  m/s

$\delta$  = pore diameter (m)

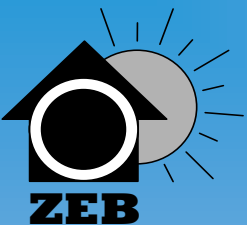
$\varepsilon$  = emissivity of inner pore walls (assumed all identical)

$T_i$  = interior (indoor) temperature (K)

$T_e$  = exterior (outdoor) temperature (K)

$\xi_{\text{ir}}$  = infrared radiation wavelength (m)

- Pore diameter  $\delta$  small  $\Rightarrow$  low thermal radiation conductivity  $\lambda_{\text{rad}}$
- But what happens when  $\xi_{\text{ir}} > \delta$  ? (IR wavelength  $>$  pore diameter)
- $\xi_{\text{ir}} > \delta \Rightarrow$  high thermal radiation conductivity  $\lambda_{\text{rad}}$  ?
- Tunneling of evanescent waves
- Indications that the large thermal radiation is only centered around a specific wavelength (or a few)  $\Rightarrow$
- The total thermal radiation integrated over all wavelengths is not that large (?)
- Currently looking into these matters...



# Thermal Radiation in Nano Pores

## Stefan-Boltzmann's Law

### Total Radiation Heat Flux $J_{\text{rad,tot}}$

$$J_{\text{rad,tot}} = \frac{\sigma}{n \left[ \frac{2}{\varepsilon} - 1 \right]} (T_i^4 - T_e^4)$$

### Radiation Thermal Conductivity $\lambda_{\text{rad}}$

$$\lambda_{\text{rad}} = \frac{\sigma \delta}{\left[ \frac{2}{\varepsilon} - 1 \right]} \frac{(T_i^4 - T_e^4)}{(T_i - T_e)} = \frac{\pi^2 k_B^4 \delta}{60 \hbar^3 c^2 \left[ \frac{2}{\varepsilon} - 1 \right]} \frac{(T_i^4 - T_e^4)}{(T_i - T_e)}$$

$\lambda_{\text{rad}} = J_{\text{rad,tot}} \delta / (T_{k-1} - T_k)$  is found by applying the approximation  $(T_{k-1} - T_k) = (T_i - T_e)/n$

$\lambda_{\text{rad}}$  = radiation thermal conductivity in the pores (W/(mK))

$\sigma = \pi^2 k_B^4 / (60 \hbar^3 c^2)$  = Stefan-Boltzmann's constant  $\approx 5.67 \cdot 10^{-8}$  W/(m<sup>2</sup>K<sup>4</sup>)

$k_B$  = Boltzmann's constant  $\approx 1.38 \cdot 10^{-23}$  J/K

$\hbar = h / (2\pi) \approx 1.05 \cdot 10^{-34}$  Js = reduced Planck's constant (h = Planck's constant)

c = velocity of light  $\approx 3.00 \cdot 10^8$  m/s

$\delta$  = pore diameter (m)

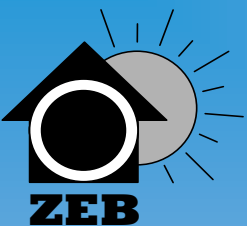
$\varepsilon$  = emissivity of inner pore walls (assumed all identical)

$T_i$  = interior (indoor) temperature (K)

$T_e$  = exterior (outdoor) temperature (K)

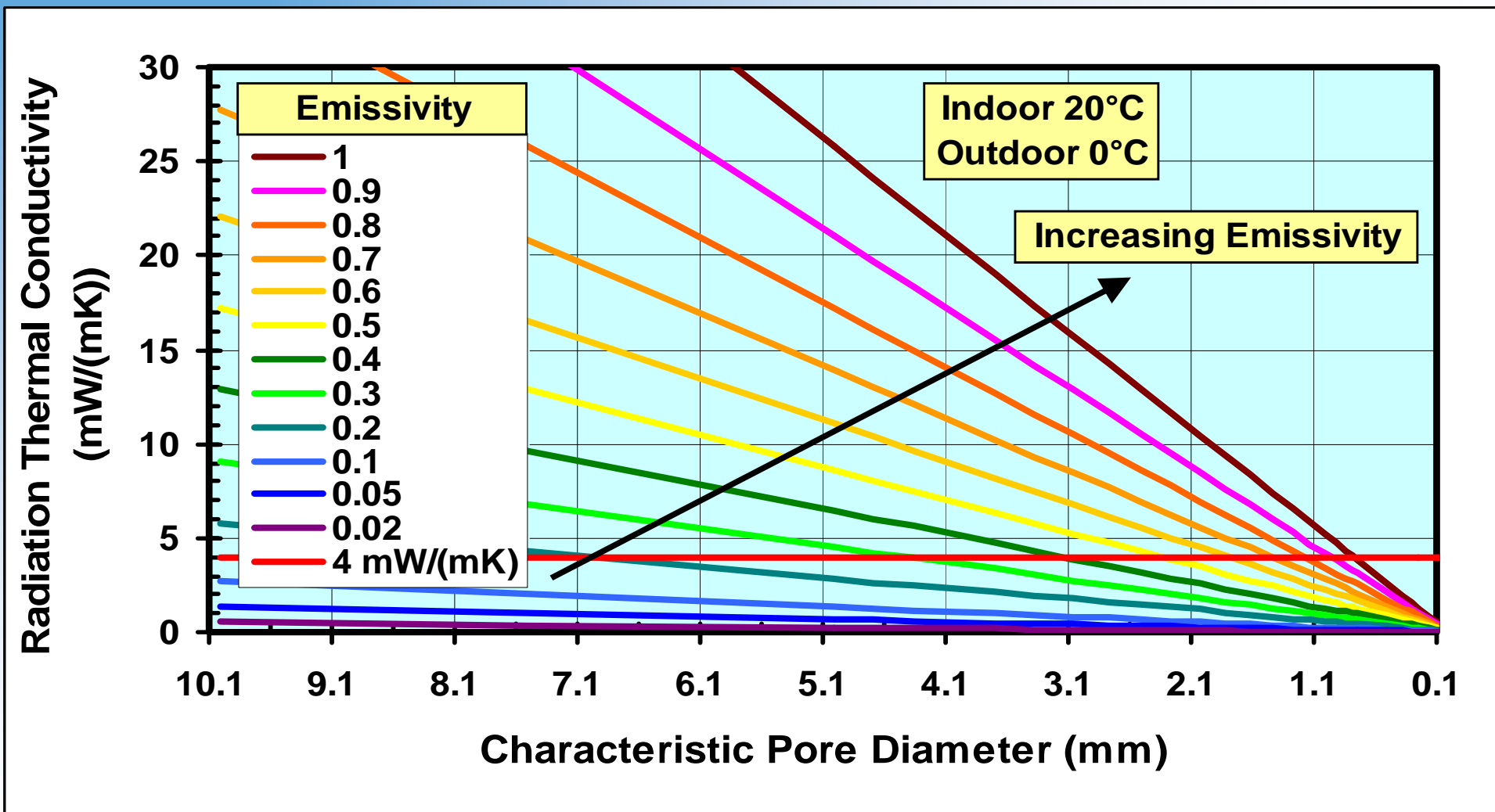
$J_{\text{rad,tot}}$  = total radiation heat flux (W/m<sup>2</sup>)

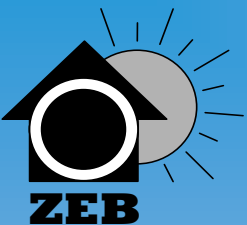
n = number of pores along a given horizontal line in the material



# Radiation Thermal Conductivity

**Conductivity vs. Pore Diameter**





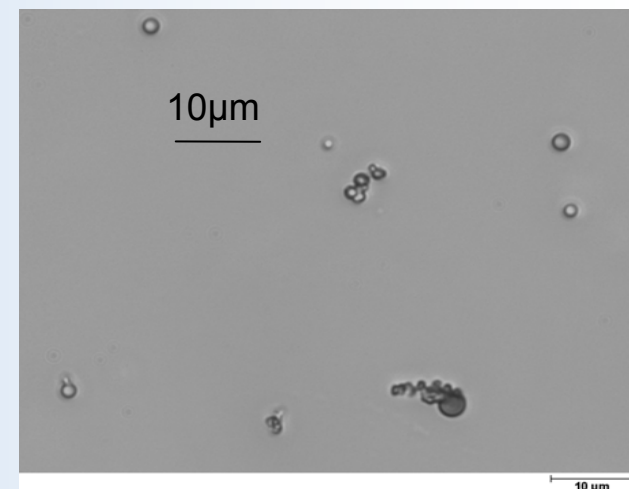
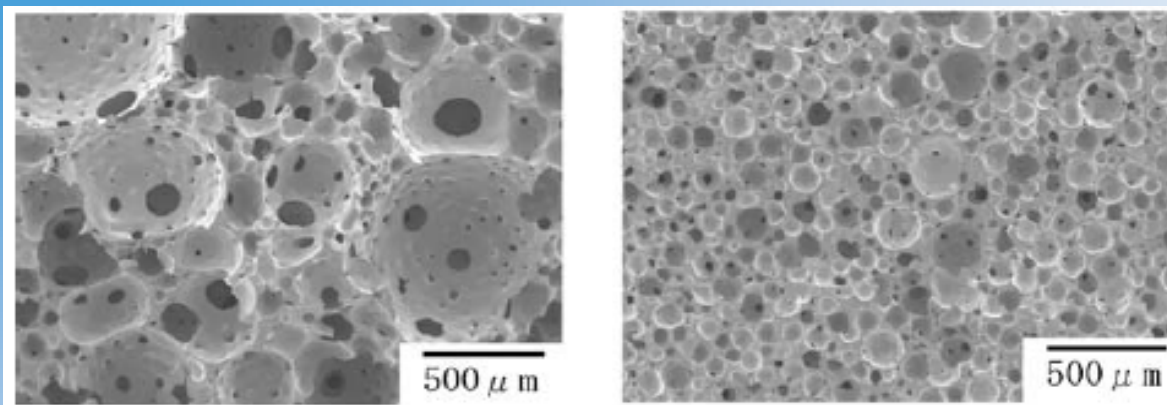
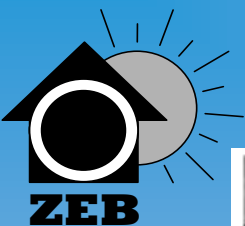
## First Experimental Attempts towards NIMs:

### *Hollow Nanospheres*

## Three Main Preparation Methods:

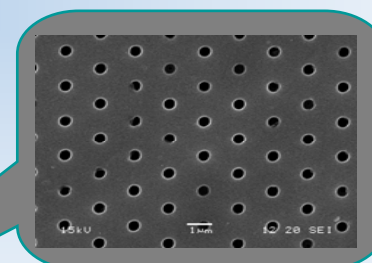
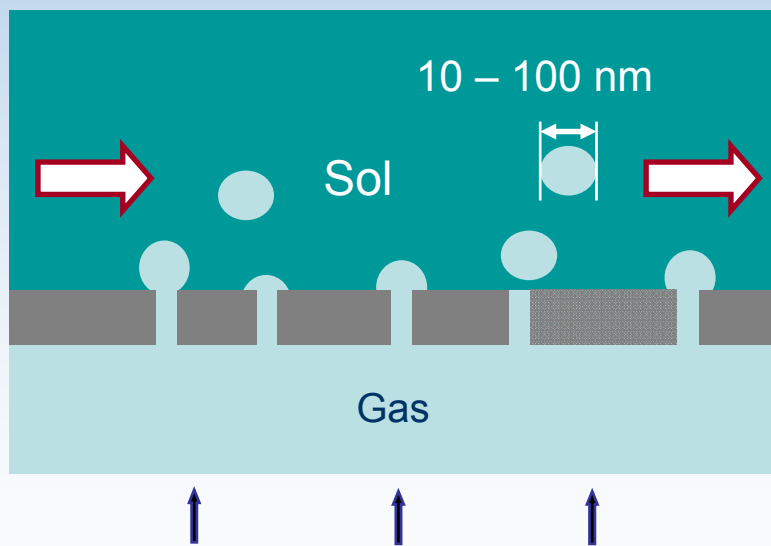
- 1. Membrane Foaming:** Use a membrane to prepare foam with nanoscale bubbles, followed by hydrolysis and condensation of a precursor within bubble walls to make a solid structure.
- 2. Internal Gas Release:** Controlled decomposition or evaporation of a component to form nanobubbles in a liquid system, followed by formation of a solid shell at the bubble perimeter.
- 3. Templating:** Formation of a nanoscale liquid or solid structure, followed by reactions to form a solid shell at the perimeter. Finally, the core is removed to make a hollow sphere.

# Membrane Foaming

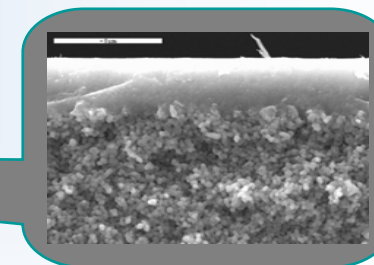


Silica sol stir foamed at 1000 (left) and 2500 (right) mPas  
 T. Tomita et al. *J. Porous Mater.* **12** (2005) 123.

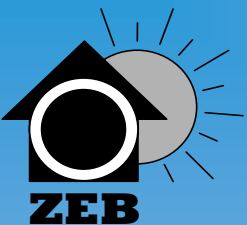
Gas capsules by membrane emulsification. J. Yang et al. SINTEF.



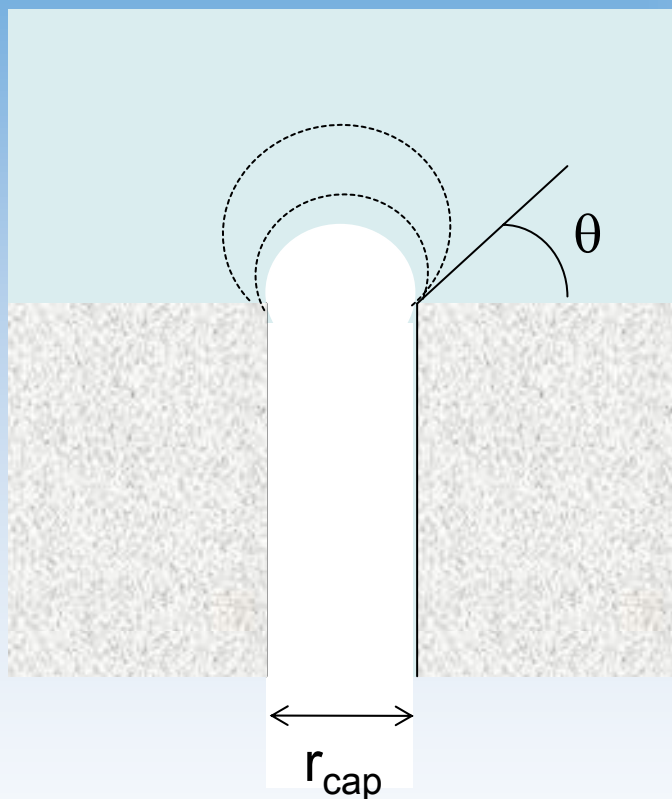
Microconstructed Membrane.



Titania  
 6 nm pores.



# Foam Formation



## Requirement for nanosized bubbles:

Controlled pressure to avoid continuous gas stream.

$\Delta\rho$ : Density difference between gas and liquid, should be large.

$r_{cap}$ : Pore radius, should be small.

$\sigma_l$ : Surface tension of liquid, should be small.

$\theta$ : Contact angle, should be large.

## Foam walls should be thin and stable:

$\eta$ : Liquid viscosity, should be low.

$\sigma_l$ : Surface tension of liquid, should be small.

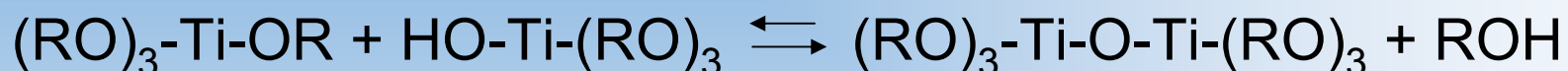
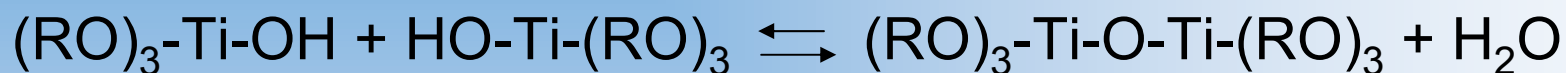
Stability: Requires surfactant bilayers.





## Membrane Foaming – Attempted the Following:

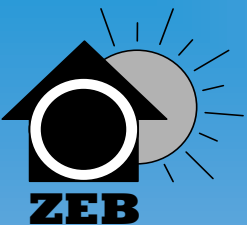
### Rapid Hydrolysis and Condensation:



**Should proceed upon exposure to  $\text{H}_2\text{O} + \text{CO}_2$   
to form a gel shell around bubbles**

### Not successful

- Reaction too slow; bubbles broke (with smoke).
- No suitable surfactant systems found to stabilize alcohol-based foams!



# Internal Gas Release

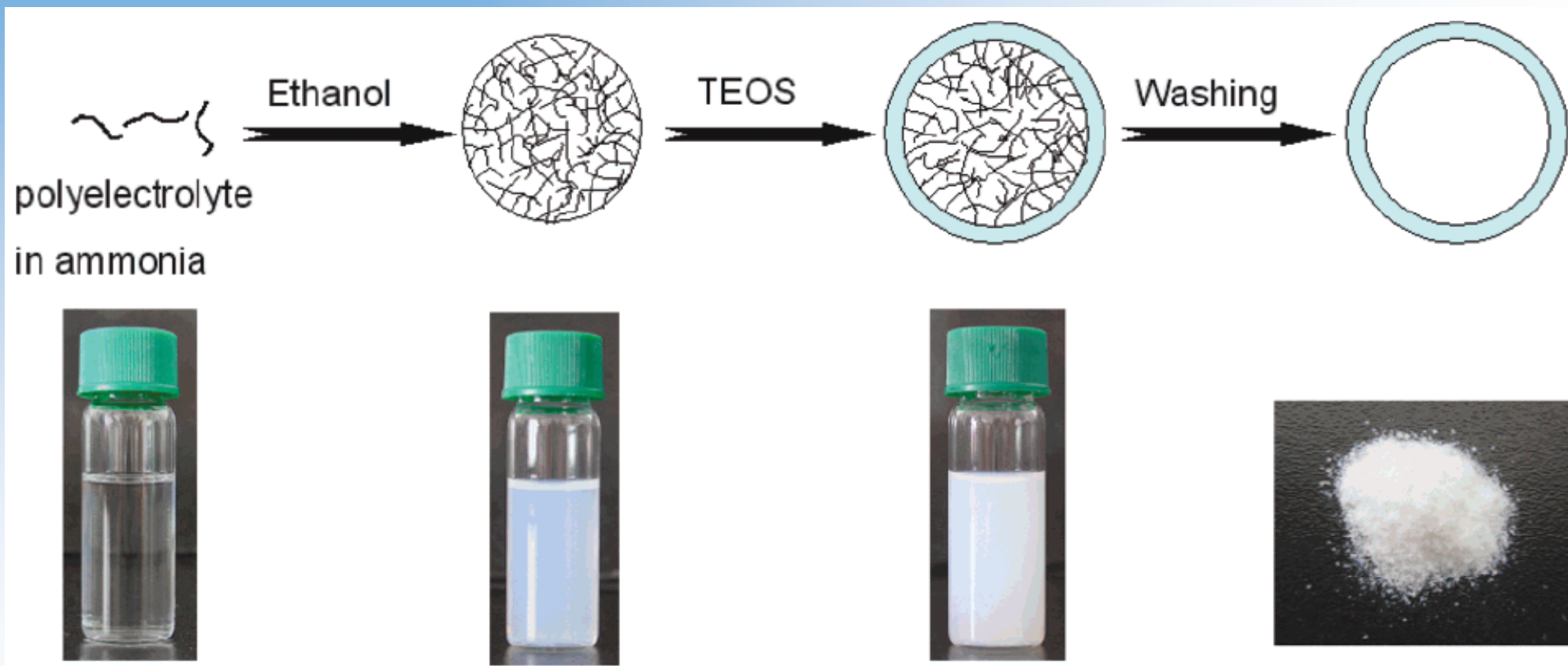
## Would Require:

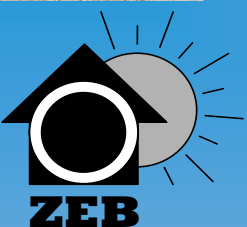
- Simultaneous formation of gas bubbles throughout reaction system.
- Narrow bubble size distribution.
- Very homogeneous system temperature.
- Rapid shell formation (before Ostwald ripening process).
- Extremely reactive chemicals, requiring strict humidity control.
- **Very demanding experimental conditions, work terminated.**



# Template-Assisted Systems

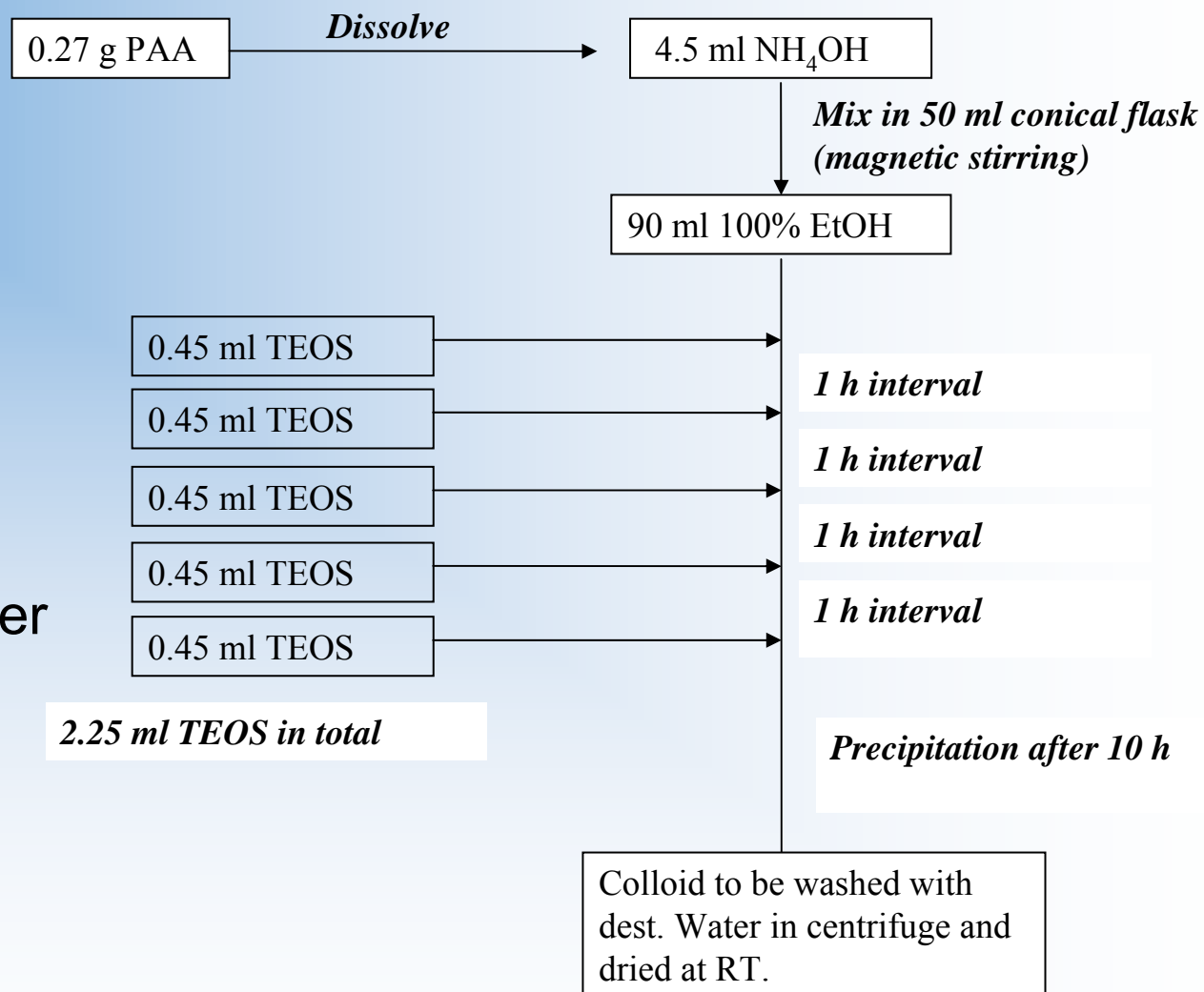
**Schematic diagram of the formation mechanism of hollow silica spheres, from (Wan and Yu 2008)**

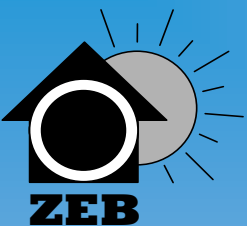




# Stöber Method for Synthesis of Hollow SiO<sub>2</sub> Nanoparticles (ex.)

- Polyacrylic acid (PAA, MW  $\approx$  5 000)
- Ammonium hydroxide (25 wt%)
- 100% ethanol
- Tetraethoxysilane (TEOS)
- Ion exchanged distilled water



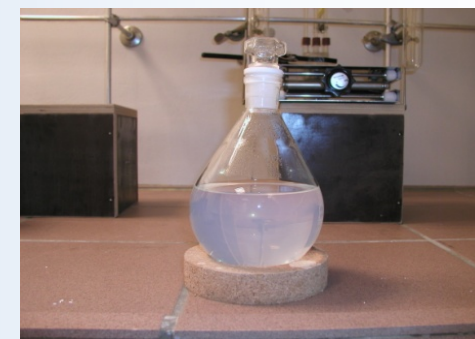
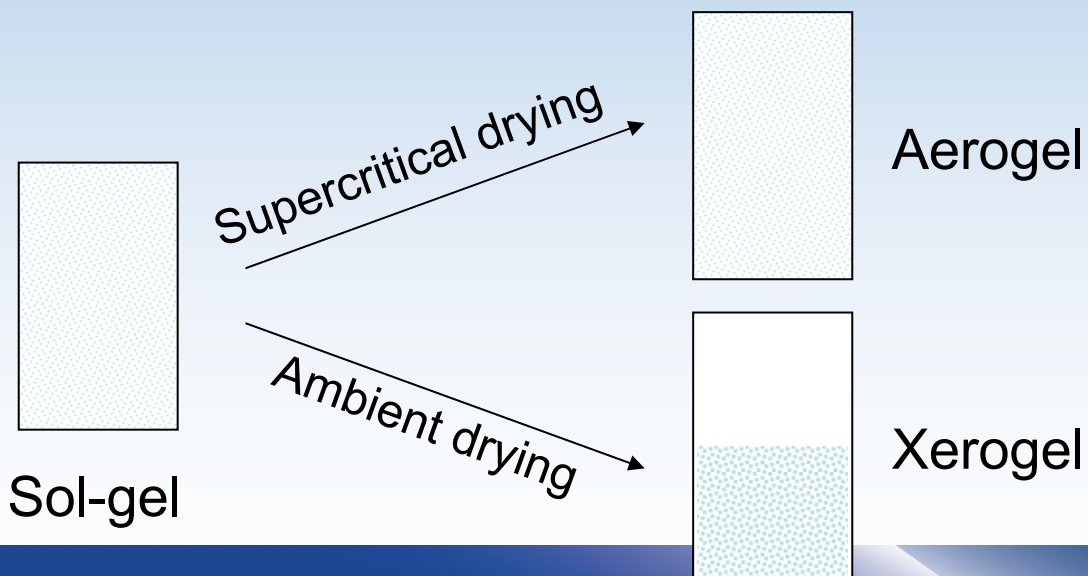
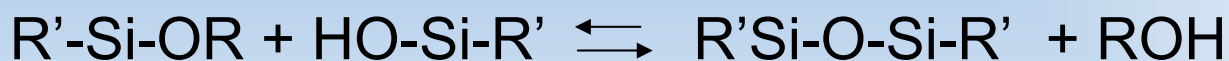
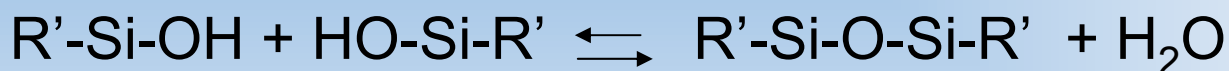


# Same Chemical Reaction as for Aerogel Production:

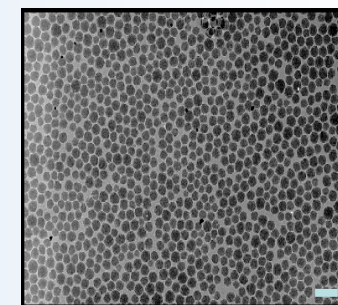
## Hydrolysis



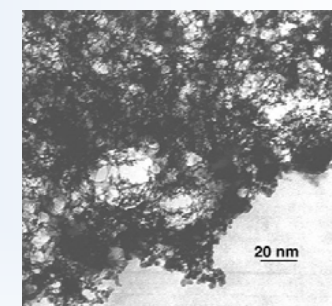
## Condensation



Sol



TEM of a basic silica sol.  
Scale bar 20 nm



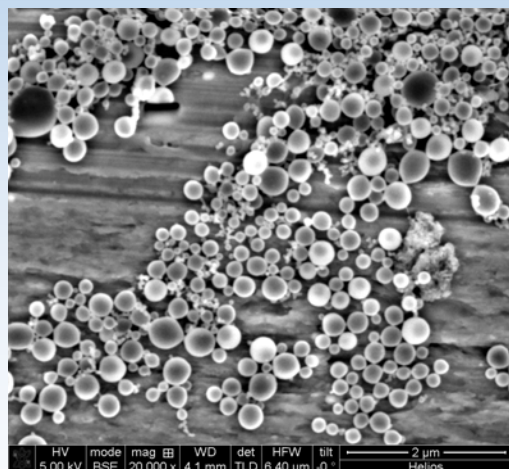
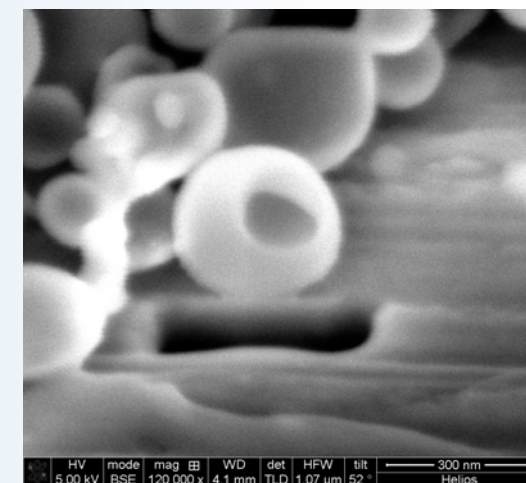
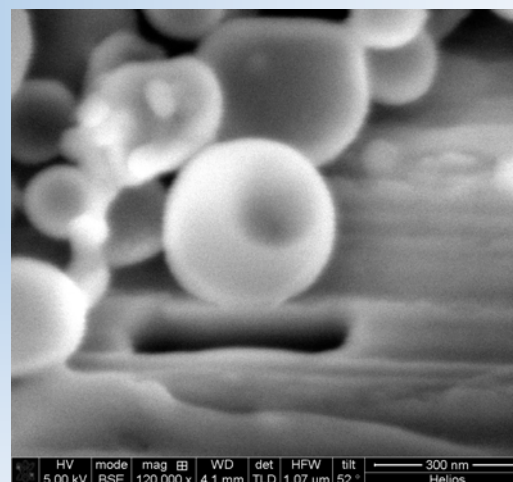
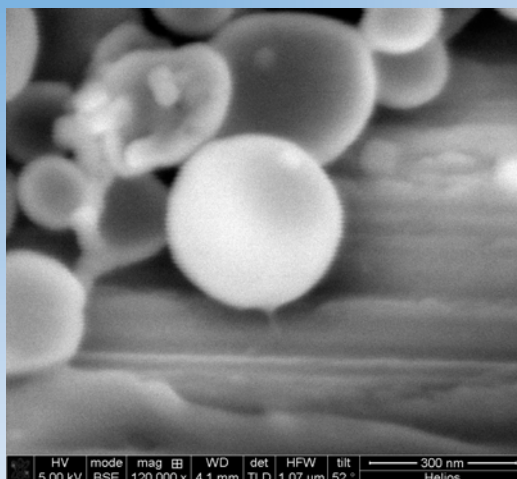
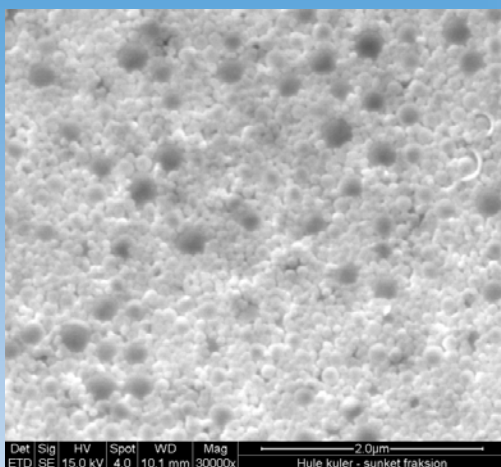
TEM of a base-catalysed silica aerogel  
Scale bar 20 nm  
Lawrence Berkeley National Laboratory



# First Attempts to Make the NIMs

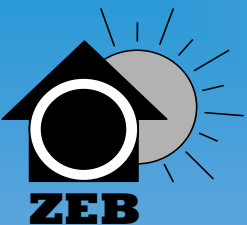
SEM Photos

- wish us good luck...!



FIB burning... confirming the nanospheres are hollow...

... are we getting the first glimpse at the Holy Grail here...?

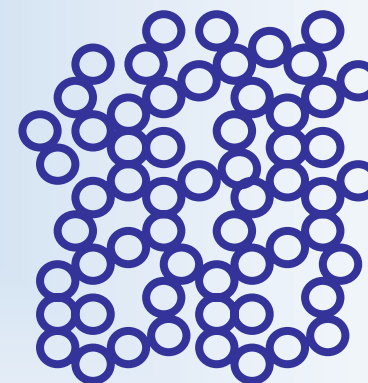


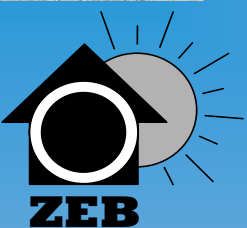
# Achieved particle size:

**90 – 400 nm, most: ~ 200 nm**

## Next:

- Control droplet size
  - Stirring rate
  - Membrane emulsification
  - Ultrasonic treatment
- Control shell thickness
- Drying to obtain powder
- Surface modification: hydrophobic
- Sintering to make NIMs

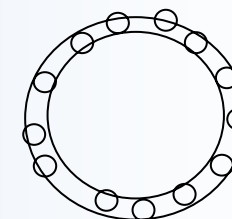
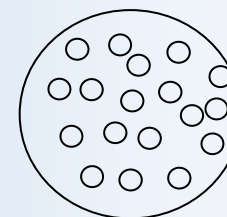
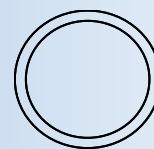




# Further Ahead

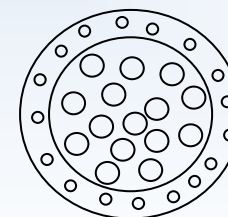
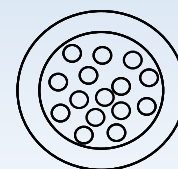
- **Vary particle morphology**

- Hollow  $\text{SiO}_2$  particles
- Mesoporous  $\text{SiO}_2$  particles
- Hollow particles with mesoporous shells



- **Particle synthesis – Optimization**

- Particle size
- Bulk mesoporosity
- Shell thickness
- Shell mesoporosity

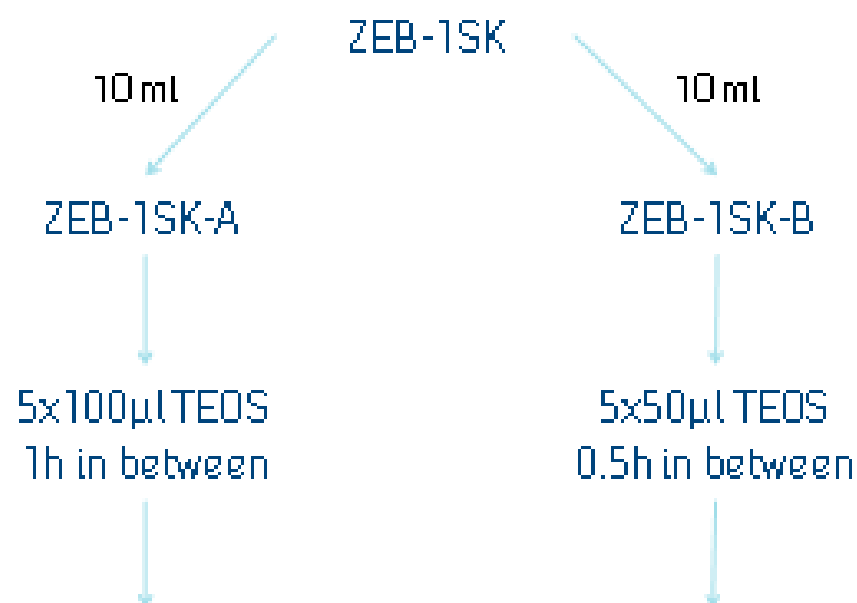






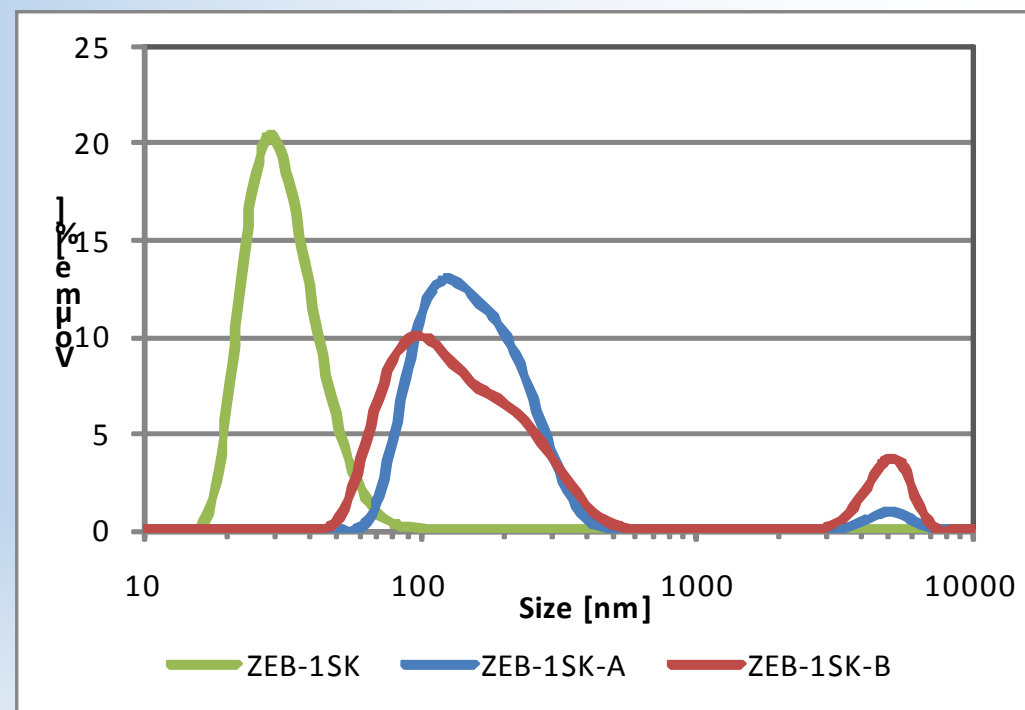
# ZEB-1SK (60 mg PAA, 2 ml NH<sub>4</sub>OH (28%), 20 ml EtOH)

## Preparation of Silica Capsules



- Partly precipitation
- Washed with water
- single capsules difficult to sediment in EtOH

- Less precipitation
- EtOH evaporated first
- Washed with water
- Capsules sediment a bit better w/o EtOH

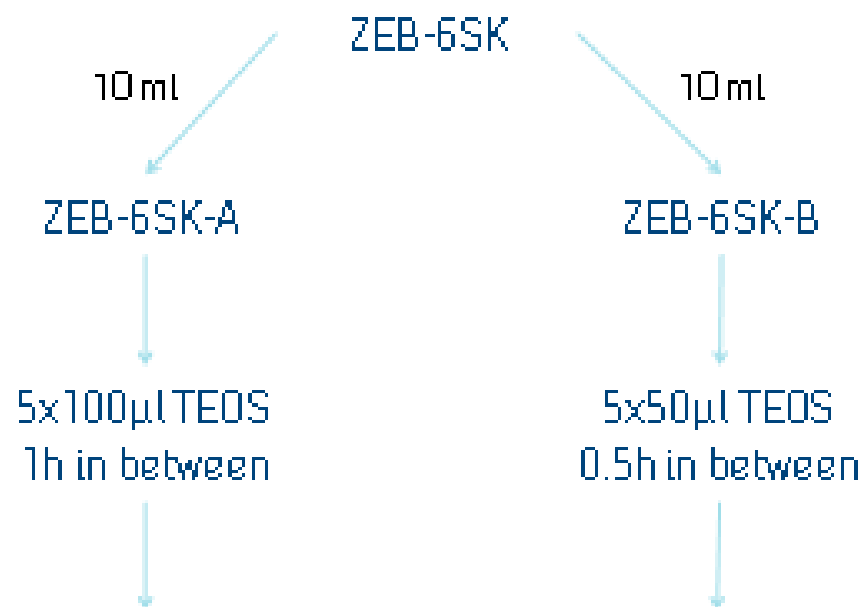


Sample	$d_z$ [nm]	PDI
ZEB-1SK	38.2	0.11
ZEB-1SK-A	155.5	0.16
ZEB-1SK-B	144.5	0.18



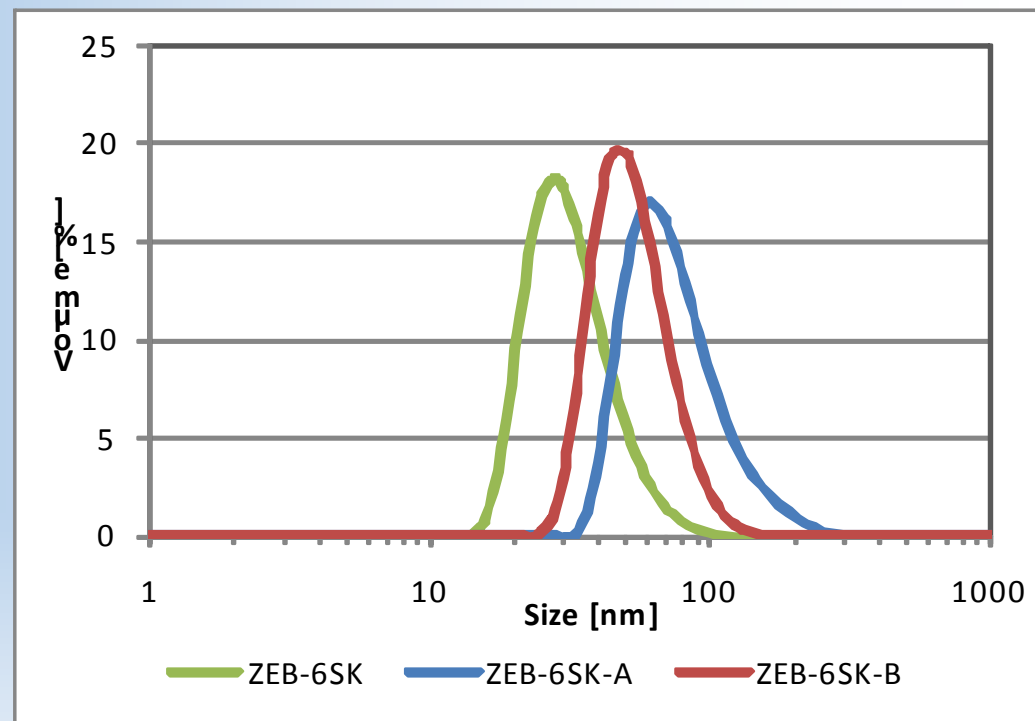
# ZEB-6SK (60 mg PAA, 2 ml NH<sub>4</sub>OH (14%), 20 ml EtOH)

## Preparation of Silica Capsules



- Slight precipitation
- Washed with water
- single capsules difficult to sediment in EtOH

- No precipitation
- EtOH evaporated first
- Washed with water
- Capsules sediment a bit better w/o EtOH

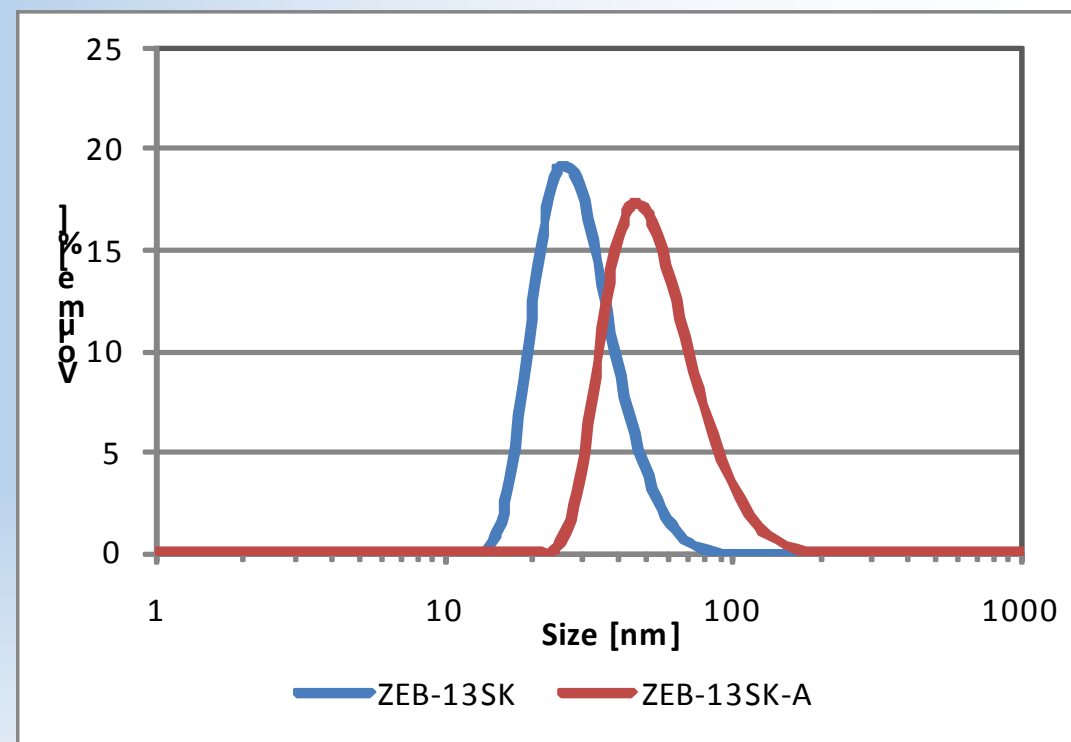
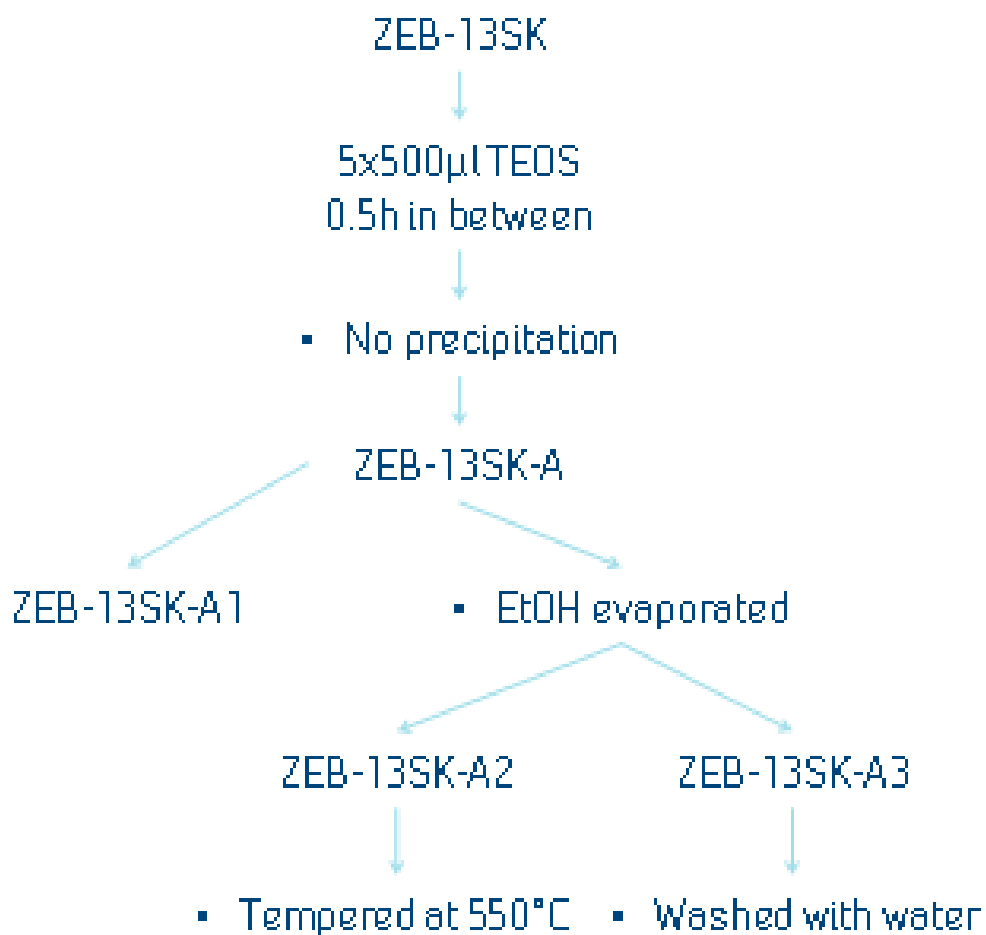


Sample	$d_z$ [nm]	PDI
ZEB-6SK	41.2	0.12
ZEB-6SK-A	89.9	0.12
ZEB-6SK-B	61.6	0.08

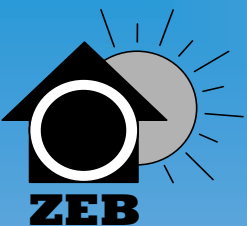


# ZEB-13SK (300 mg PAA, 10 ml NH<sub>4</sub>OH (14%), 100 ml EtOH)

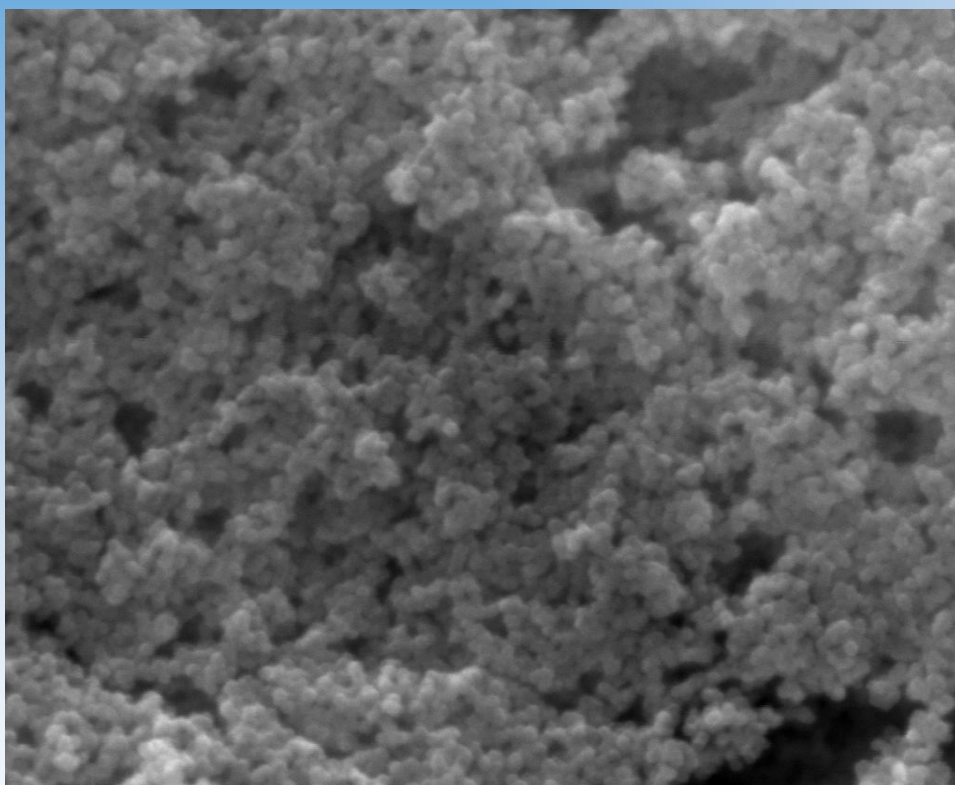
## Preparation of Silica Capsules



Sample	$d_z$ [nm]	PDI
ZEB-13SK	36.1	0.10
ZEB-13SK-A	67.1	0.10



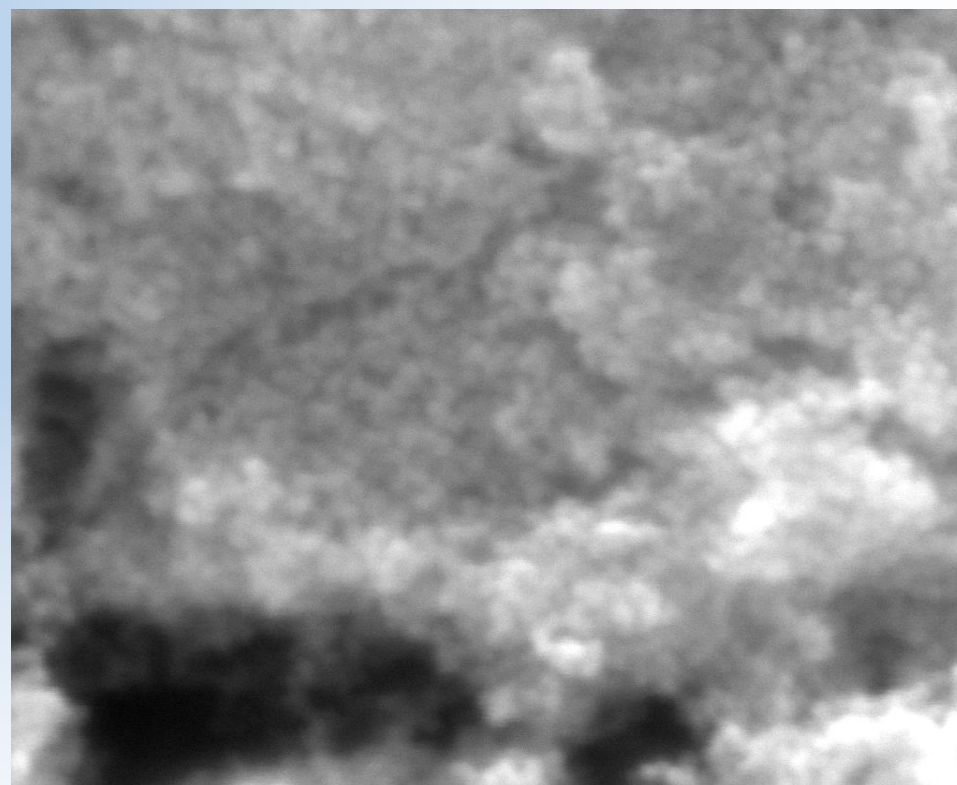
# SEM Photos



Det	HV	WD	Mag	Spot
ETD	20.0 kV	11.1 mm	23515x	4.0

2.0μm

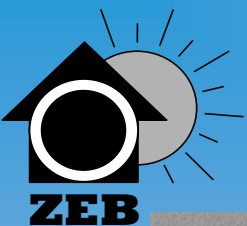
**ZEB-1SK-A**



Det	HV	WD	Mag	Spot
ETD	20.0 kV	11.0 mm	53316x	4.0

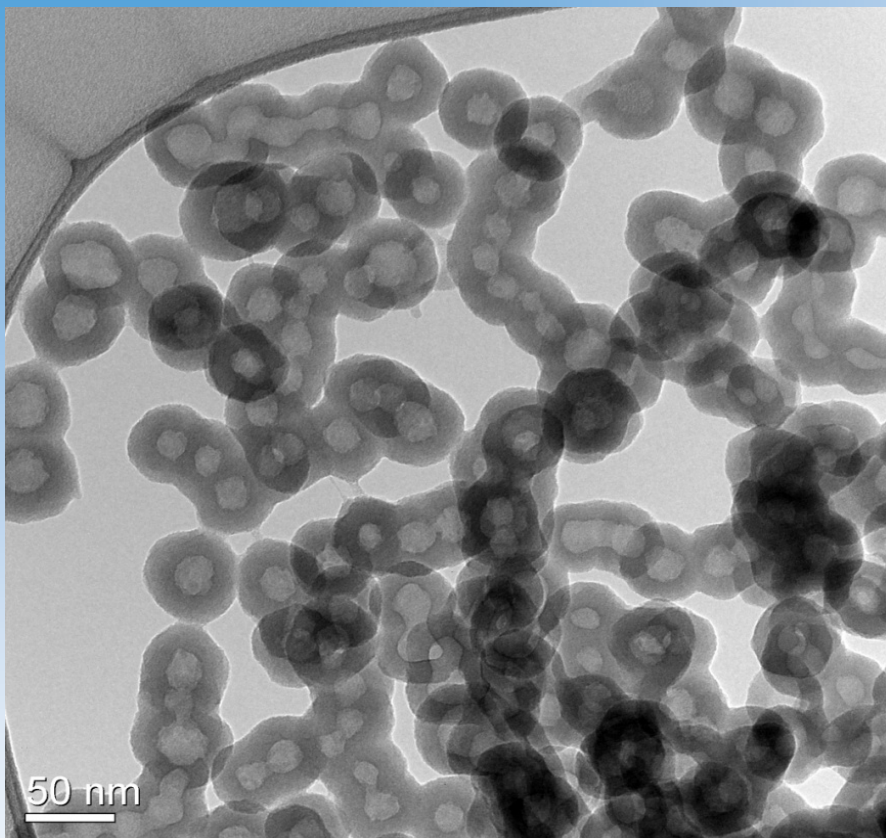
1.0μm

**ZEB-6SK-A**



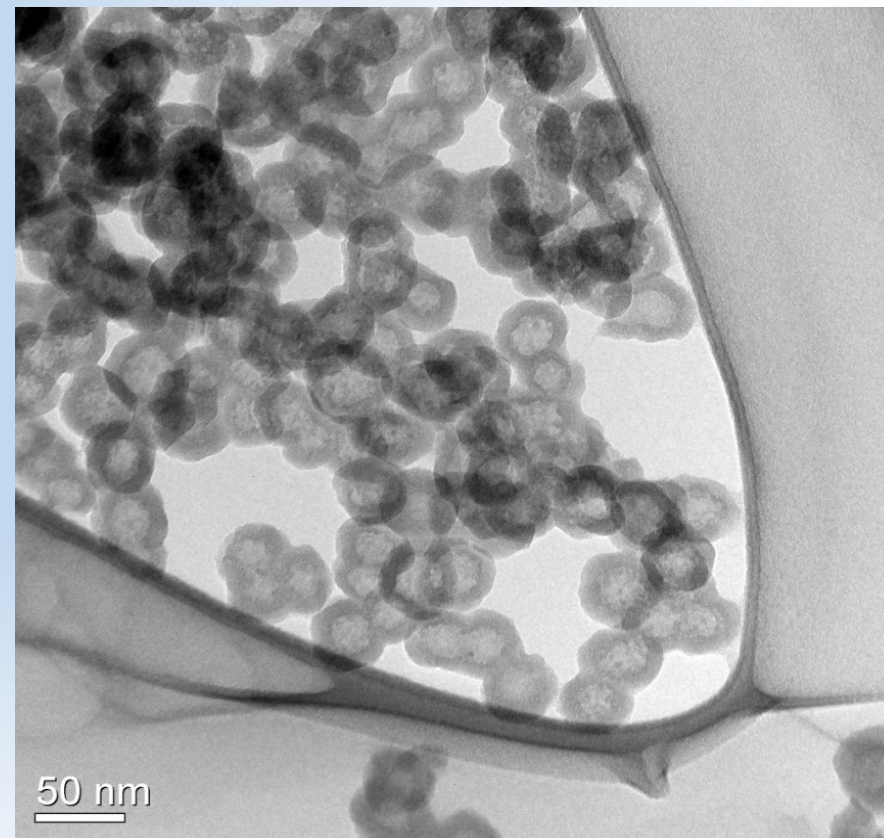
# TEM Photos

## Different amount of silicon



**ZEB-1SK-A**  
5x100 $\mu$ l TEOS  
1h in between  
2ml NH<sub>4</sub>OH (28%)

**Size: 50-60 nm**  
**Cavity: 20-25 nm**  
**Wall: 30-35 nm**

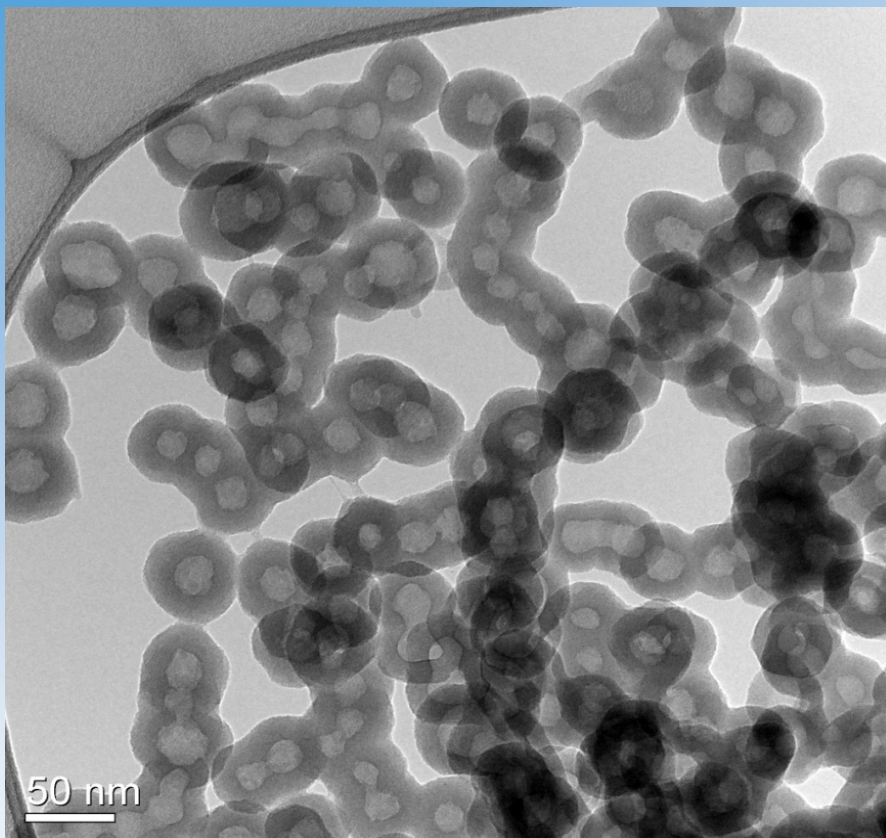


**ZEB-1SK-B**  
5x50 $\mu$ l TEOS  
0.5h in between  
2ml NH<sub>4</sub>OH (28%)

**Size: 40-45 nm**  
**Cavity: 20-25 nm**  
**Wall: 20-25 nm**

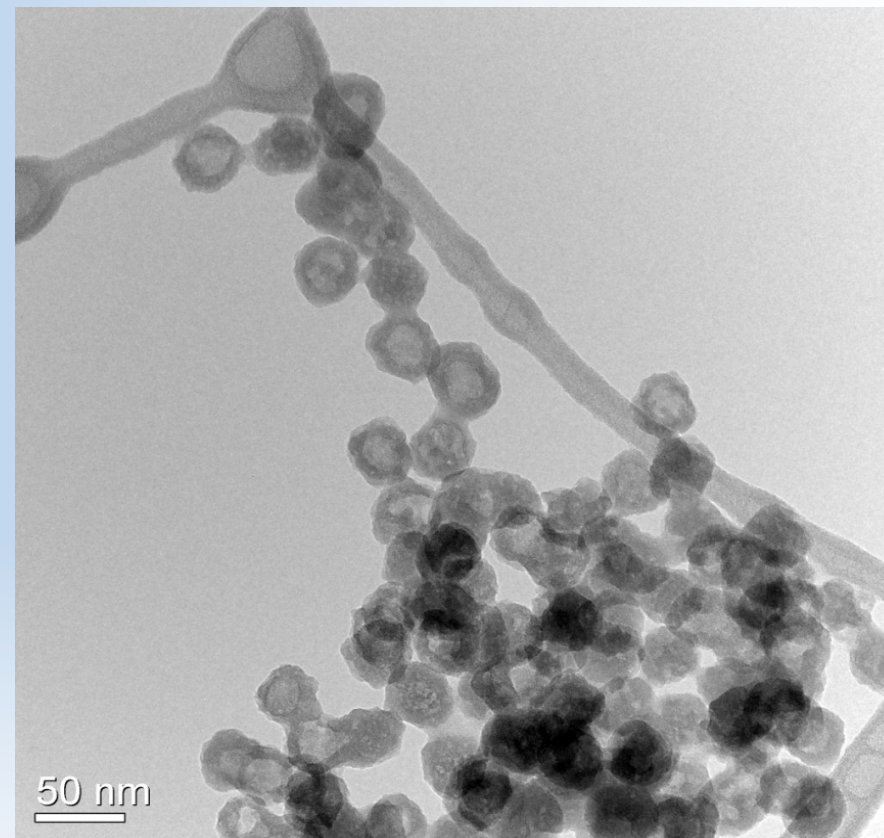


# TEM Photos **Different amount of $\text{NH}_4\text{OH}$**



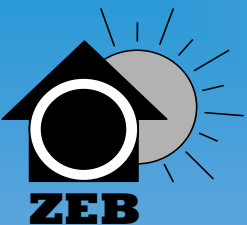
**ZEB-1SK-A**  
5x100 $\mu\text{l}$  TEOS  
1h in between  
2ml  $\text{NH}_4\text{OH}$  (28%)

**Size: 50-60 nm**  
**Cavity: 20-25 nm**  
**Wall: 30-35 nm**

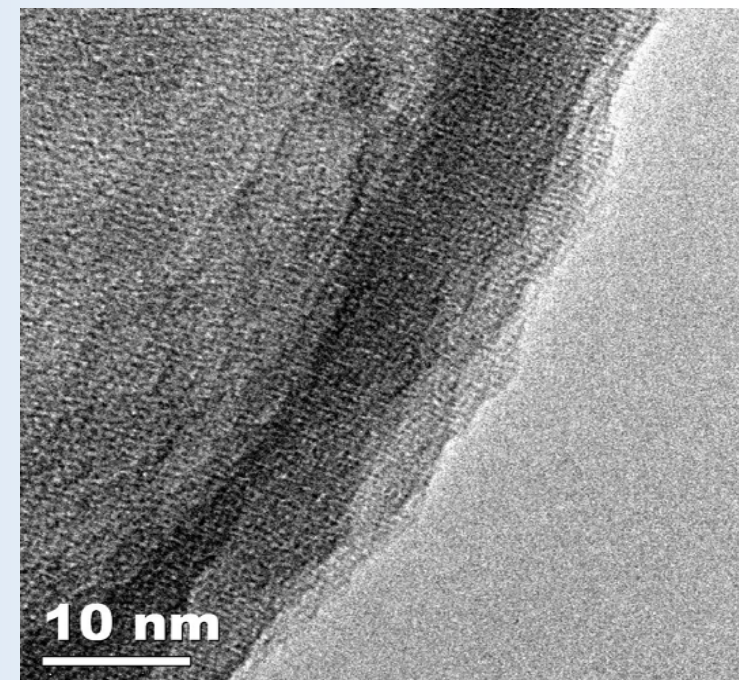
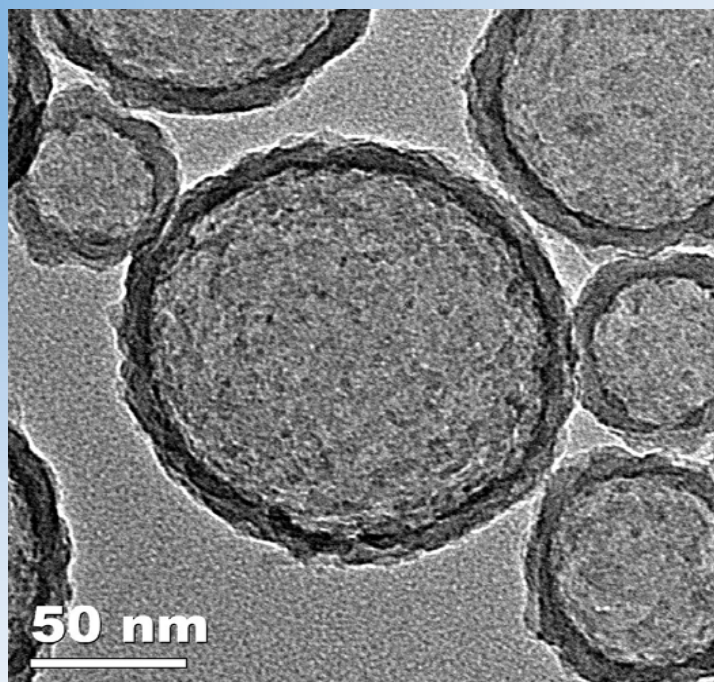
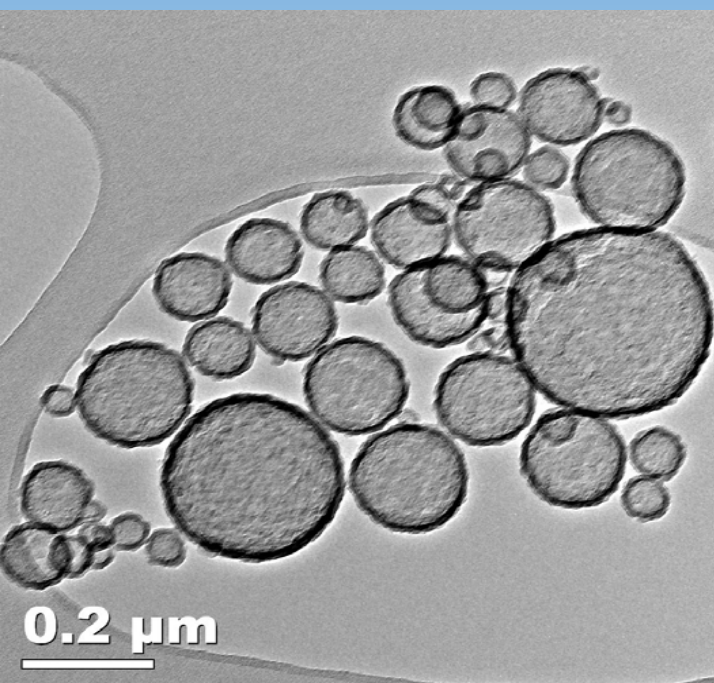


**ZEB-6SK-A**  
5x100 $\mu\text{l}$  TEOS  
1h in between  
2ml  $\text{NH}_4\text{OH}$  (14%)

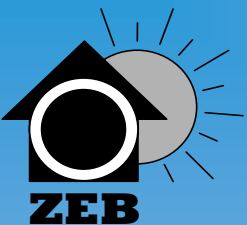
**Size: 40-45 nm**  
**Cavity: 18-22 nm**  
**Wall: 20-25 nm**



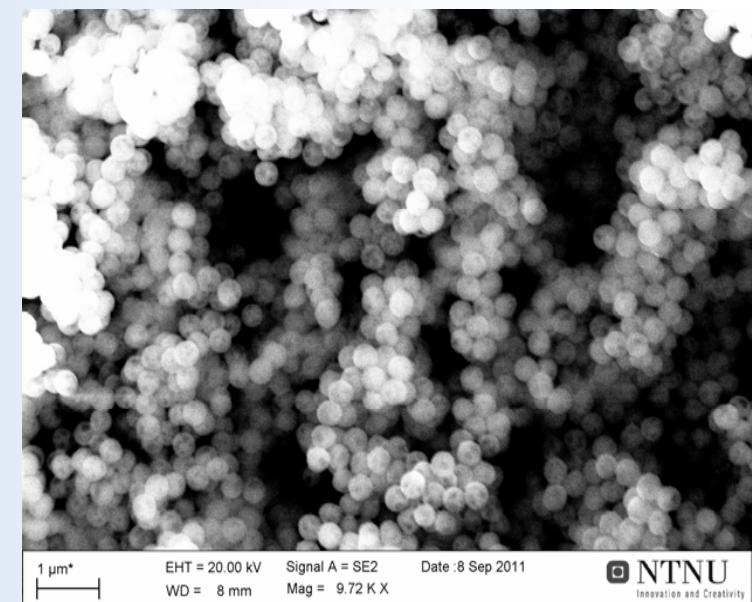
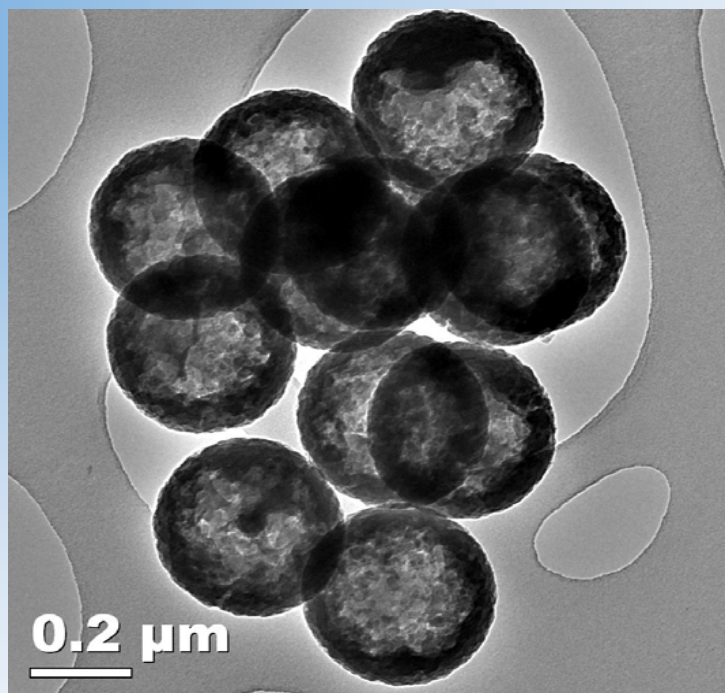
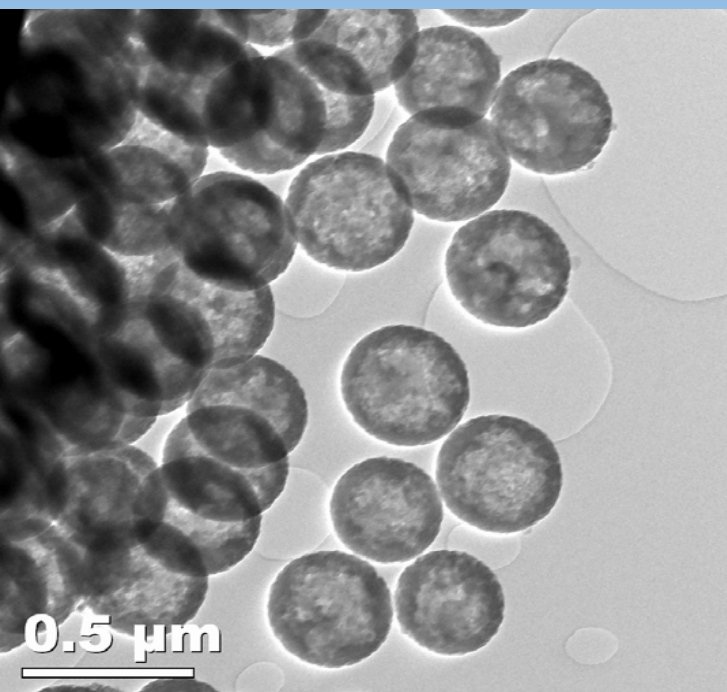
## Hollow silica nanospheres by templating



Sizes of the hollow silica nanospheres range from 50 to 250 nm; while the thickness is fairly uniform, about 10 nm, which can be tuned by varying the silica source materials.



## Hollow silica nanospheres by etching



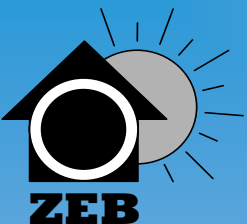
Sizes of the hollow silica nanospheres are fairly uniform, about 300 nm in diameter; the thickness of the shell is about 20 nm, which can be tuned by varying the etching time.





# The Path Ahead

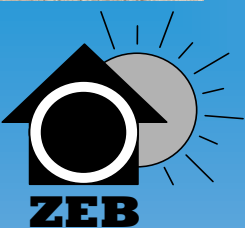
- At the moment following various paths to make hollow nanospheres
- First thermal conductivity measurements on the powder ... no optimization yet... measured yesterday...
- $\sim 37 \text{ mW}/(\text{mK})$  ... we intend to go further down yes...
- ... then to piece the nanospheres together to form a bulk insulation material...



# Dynamic Insulation Material (DIM)

**DIM – A material where the thermal conductivity can be controlled within a desirable range**

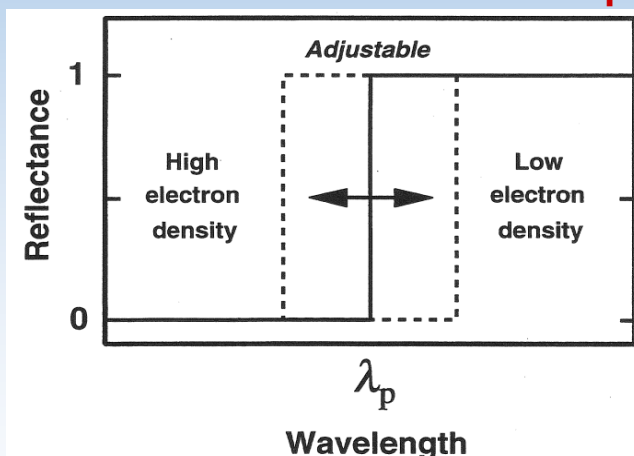
- Thermal conductivity control may be achieved by:
  - Inner pore gas content or concentration including the mean free path of the gas molecules and the gas-surface interaction
  - The emissivity of the inner surfaces of the pores
  - The solid state thermal conductivity of the lattice
- What is really solid state thermal conductivity? Two models:
  - Phonon thermal conductivity - atom lattice vibrations
  - Free electron thermal conductivity
- *What kind of physical model could describe and explain thermal conductivity?*
- *Could it be possible to dynamically change the thermal conductivity from very low to very high, i.e. making a DIM?*



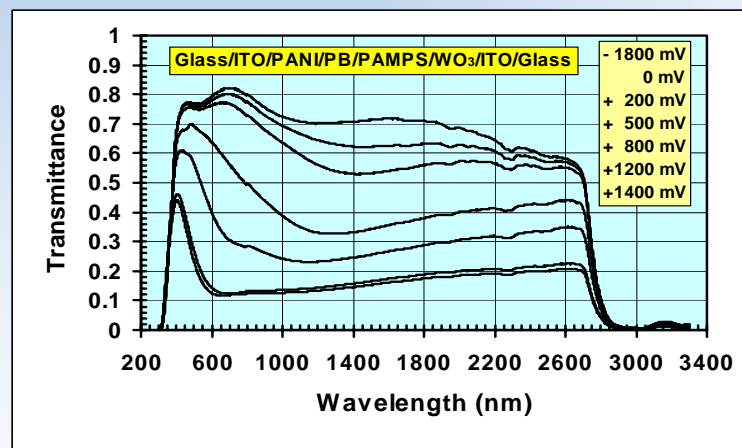
# Dynamic Insulation Material (DIM)

- Dynamic Vacuum
- Dynamic Emissivity of Inner Pore Surfaces
- Dynamic Solid Core Thermal Conductivity
  - Is it possible?
  - Fundamental understanding of the thermal conductance?
- Other?      Learning from Electrochromic Materials?:

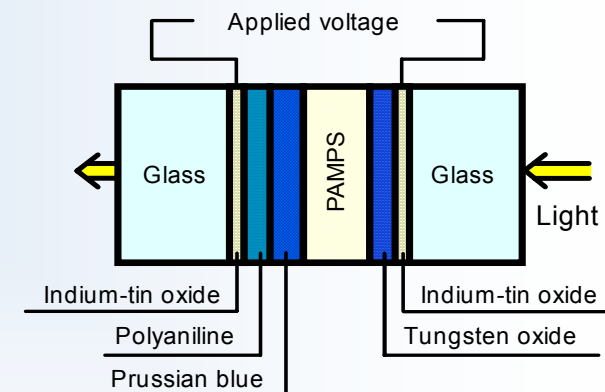
$$\lambda_p = (2\pi c/q_e)(m_e \epsilon_0/n_e)^{1/2}$$

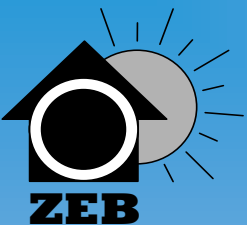


B. P. Jelle, "Electrochemical and Spectroscopic Studies of Electrochromic Materials", *Ph.D. thesis*, 1993:131, Department of Applied Electrochemistry, The Norwegian Institute of Technology, Trondheim, Norway, 1993.



B. P. Jelle, A. Gustavsen, T.-N. Nilsen and T. Jacobsen, "Solar Material Protection Factor (SMPF) and Solar Skin Protection Factor (SSPF) for Window Panes and other Glass Structures in Buildings", *Solar Energy Materials & Solar Cells*, 91, 342-354 (2007).





# Inspiration and Ideas

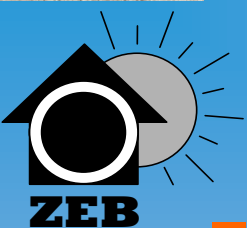
**Could other fields of science and technology inspire and give ideas about how to be able to make DIMs, e.g. from the fields?:**

- **Electrochromic Materials**
- **Quantum Mechanics**
- **Electrical Superconductivity**
- **Other?**



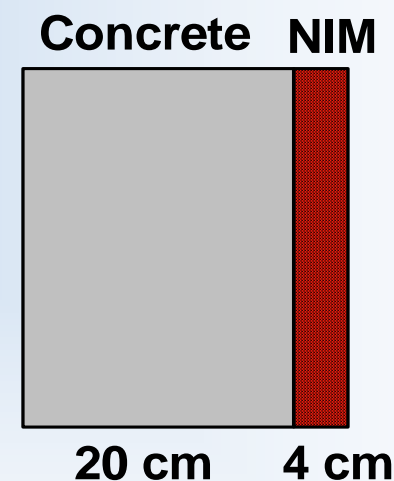
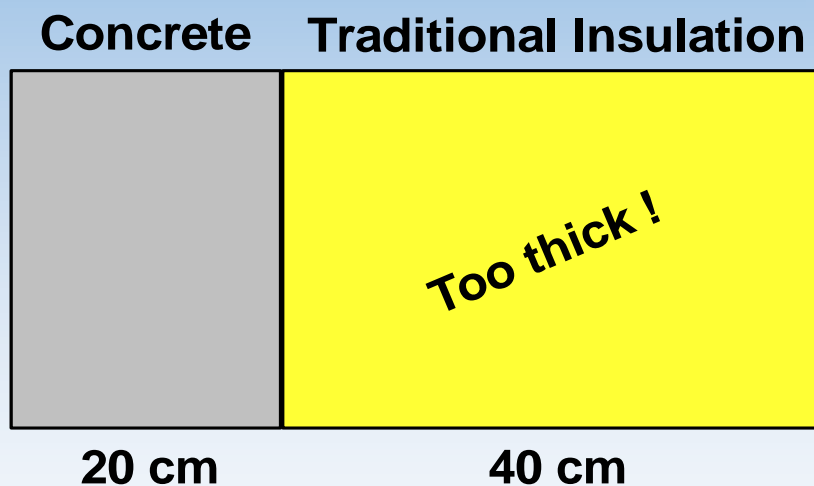
# Aerogels – Approaching the NIMs

- Aerogels – At the moment the closest commercial approach to NIMs
- 12 – 14 mW/(mK)
- Aspen Aerogels
  - Spaceloft
- Cabot Aerogel
  - Nanogel
- Production costs still high
- Relatively high compression strength
- Very fragile due to very low tensile strength
- Tensile strength may be increased by incorporation of a carbon fibre matrix
- May be produced as either opaque, translucent or transparent materials
  - ➔ Thus enabling a wide range of possible building applications



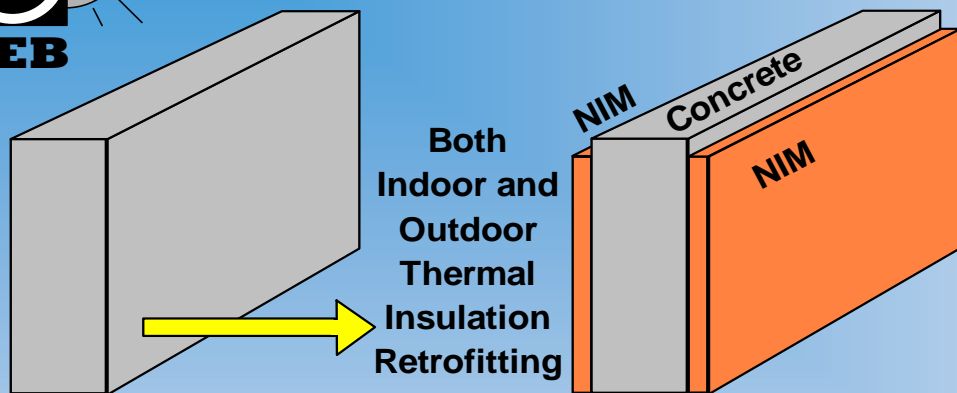
# Thinner Concrete Buildings with NIMs

- Mineral Wool or Polystyrene
- 36 mW/(mK)
- 40 cm traditional thermal insulation retrofitting
- NIM
- 3.6 mW/(mK)
- 4 cm NIM thermal insulation retrofitting

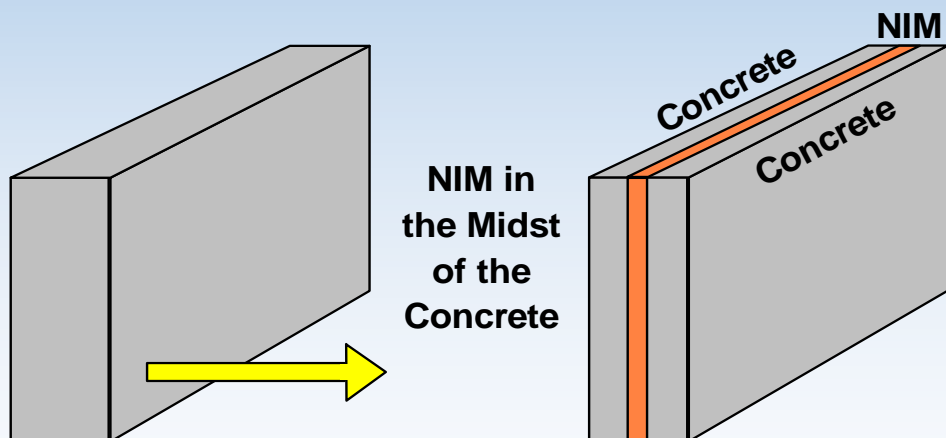


- A vast reduction – factor 10 – of the thermal insulation layer and thereby the total building envelope thickness.

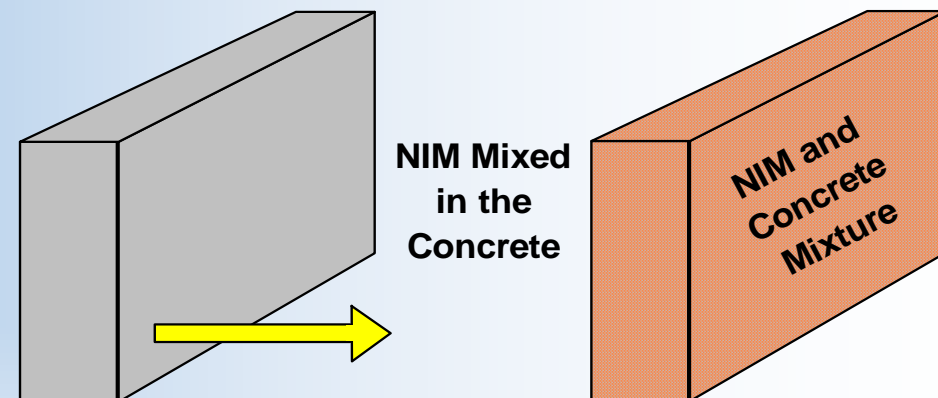
# Concrete with NIMs



**Concrete with NIM Indoor and Outdoor - Retrofitting**



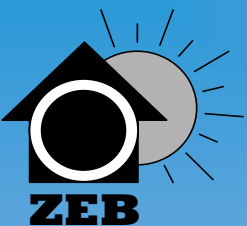
**NIM in the Midst of Concrete**



**NIM and Concrete Mixture**

**... or going beyond these...?**

# To Envision Beyond Concrete ?



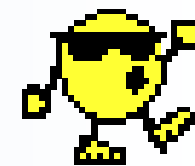
- *In the community of concrete it might be compared to using profane language in the church and close to blasphemy to suggest that maybe the answer is not concrete after all... 👍😊*

## ■ Concrete:

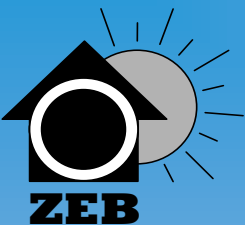
- High thermal conductivity.
- Total thickness of the building envelope will often become unnecessary large (passive house, zero energy building or zero emission building).
- Large CO<sub>2</sub> emissions connected to the production of cement.
- Prone to cracking induced by corrosion of the reinforcement steel.
- Easy accessible and workable, low cost and local production.
- High fire resistance.

**Emphasis on Properties and Functional Requirements**

- Is it possible to envision a building and infrastructure industry without an extensive usage of concrete?

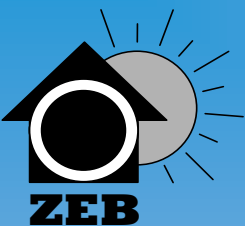




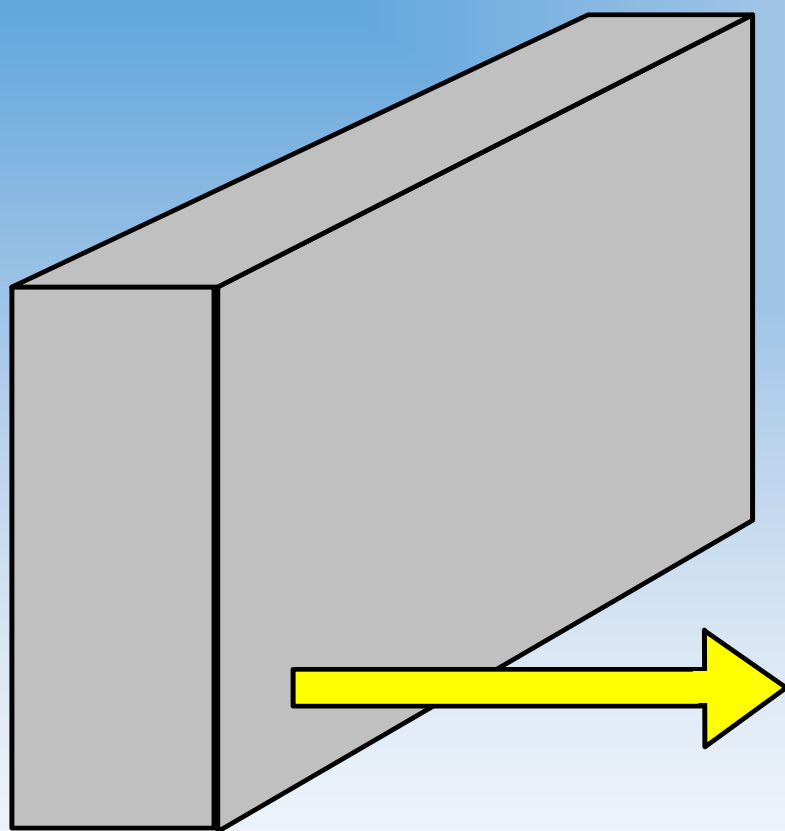


# Emphasis on Functional Requirements

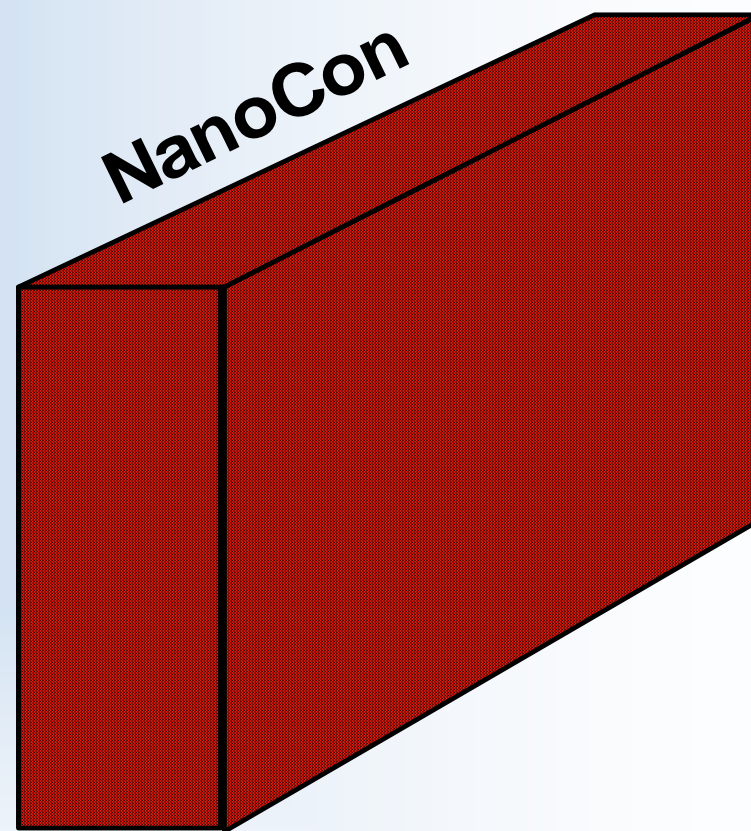
- Not the building material itself which is important.
- Property or functional requirements are crucial.
- Possible to invent and manufacture a material with the essential structural or construction properties of concrete intact or better, but with substantially lower thermal conductivity?
- Beneficial with a much lower negative environmental impact than concrete with respect to CO<sub>2</sub> emissions.
- Envisioned with or without reinforcement or rebars.



# NanoCon – Introducing a New Material



Making  
a New  
Material:  
NanoCon

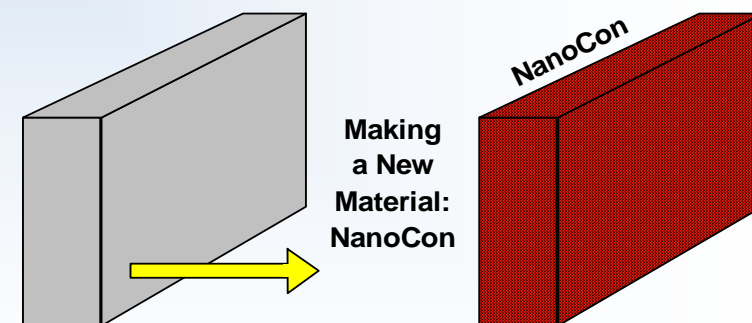


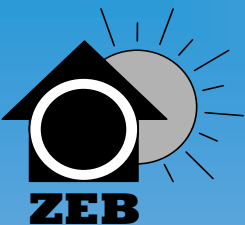
B. P. Jelle, A. Gustavsen and R. Baetens, "The High Performance Thermal Building Insulation Materials and Solutions of Tomorrow", *Proceedings of the Thermal Performance of the Exterior Envelopes of Whole Buildings XI International Conference (Buildings XI)*, Clearwater Beach, Florida, U.S.A., 5-9 December, 2010.



# NanoCon – Introducing a New Material

- NanoCon
- Basically a homogeneous material
- Closed or open small nano pore structure
- Overall thermal conductivity  $< 4 \text{ mW}/(\text{mK})$  (or another low value to be determined)
- Exhibits the crucial construction properties that are as good as or better than concrete.
  - Utilize carbon nanotubes (CNT)? Tensile strengths of 63 GPa (measured) and 300 GPa (theoretical). (Steel rebars 500 MPa and concrete 3 MPa.)
- Essentially, NanoCon is a NIM with construction properties matching or surpassing those of concrete.





## Materials and Solutions Not Yet Thought Of ?

- ***The more we know the more we know we don't know...!***
  - *... and the more we want to know...!*
  - *... and that's the whole fun of it...!*
- ***Think thoughts not yet thought of...!***



# Conclusions

- The Thermal Insulation Materials of Beyond Tomorrow ? :
- Theoretical concepts established – Others?
- Nano Insulation Materials (NIM)
- Dynamic Insulation Materials (DIM)
- NanoCon
- Others?
- First experimental attempts towards NIMs

Sunrise...  
and the Phoenix rises again...!

