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Measuring the thermal conductivity of aerogel thin films with time domain thermoreflectance

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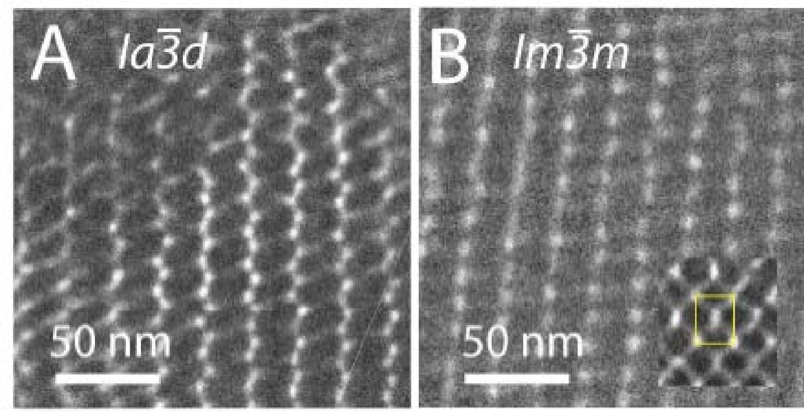
Thermal conductivity of porous nanofilms

- •Low thermal conductivities

- •Ideal for many applications (insulations, chemical sensors)

- •Measurement challenges
  - •Brittle
  - •Fragile
  - •Non conformal (i.e., not specular)
- •Porous silica (e.g., aerogels)
  - •Transparent
  - •Electrically insulative
  - •Can “collapse” with contact/pressure

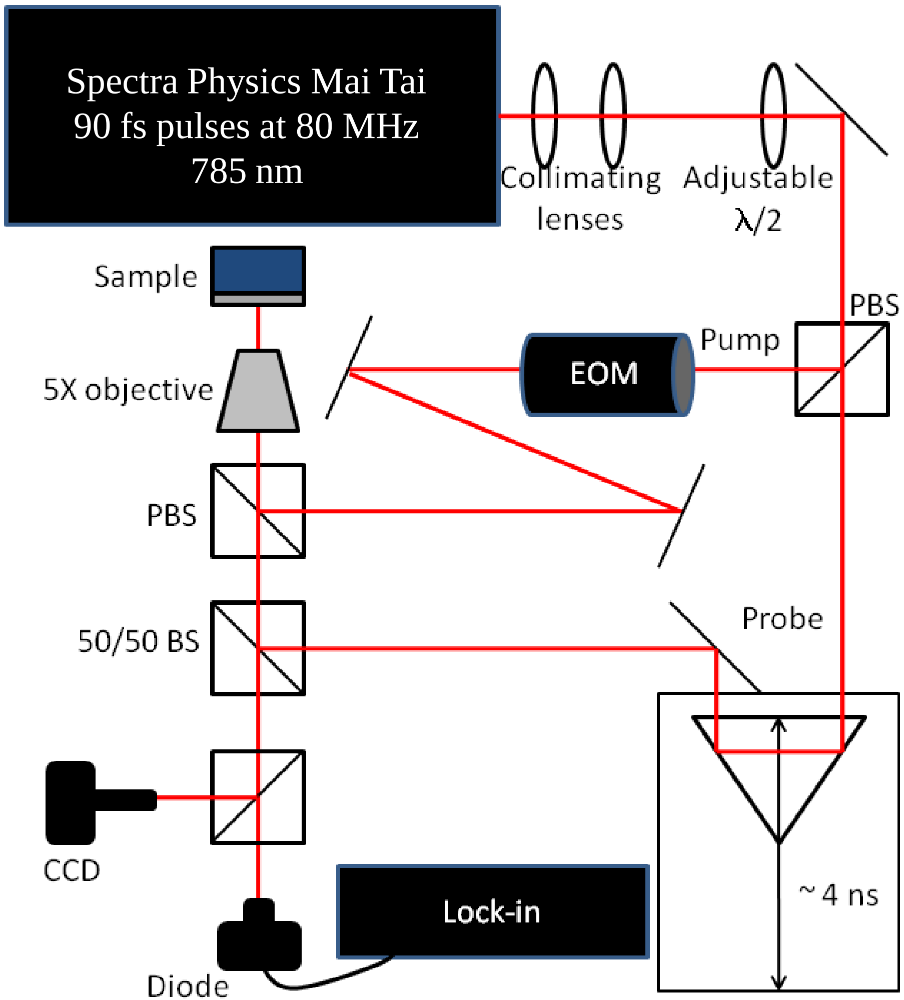


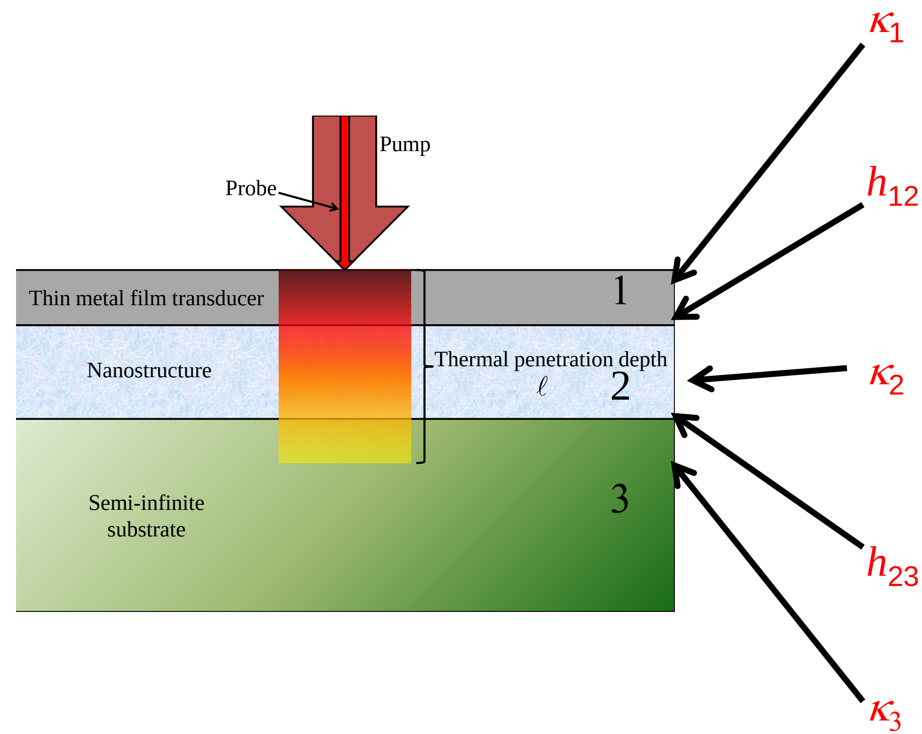
Dunphy *et al*. to appear in *Chemistry of Materials*

Outline

- Time domain thermoreflectance – measuring thermal properties of porous samples
- Sensitivities and measurements
- Thermal conductivity of aerogel thin films
- “Porous” minimum limit to thermal conductivity

Time domain thermoreflectance (TDTR)





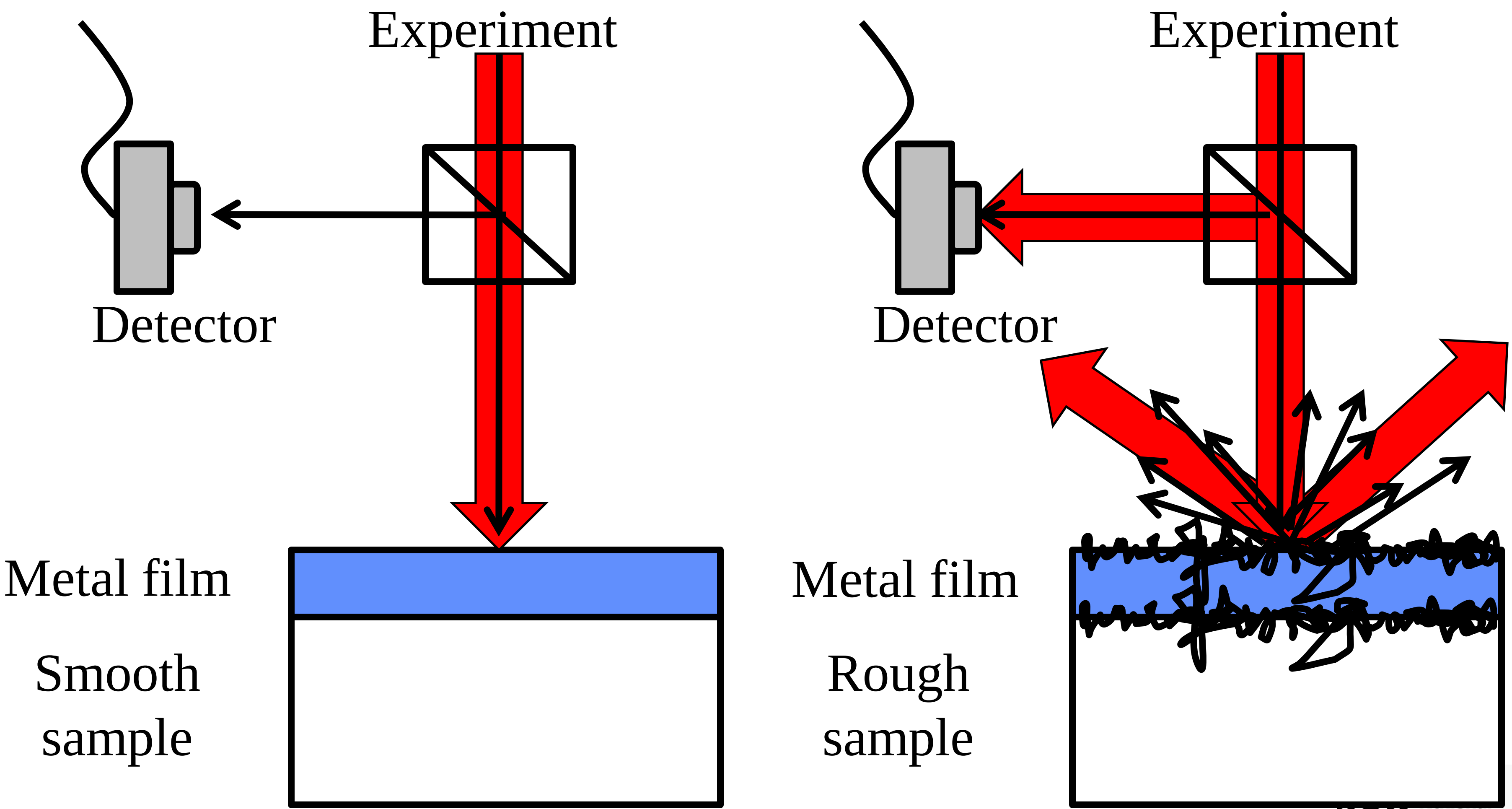
Hopkins, *et al. J. Heat Trans.* **132**, 081302 (2010)

- Can measure thermal conductivity of thin films and substrates (*k*) separately from thermal boundary conductance (*h*)
- Nanometer spatial resolution (~10's of nm)
- Femtosecond to nanosecond temporal resolution
- Noncontact

TDTR for nonconformal/non-solid surfaces

TDTR requires a specular, partially reflecting surface

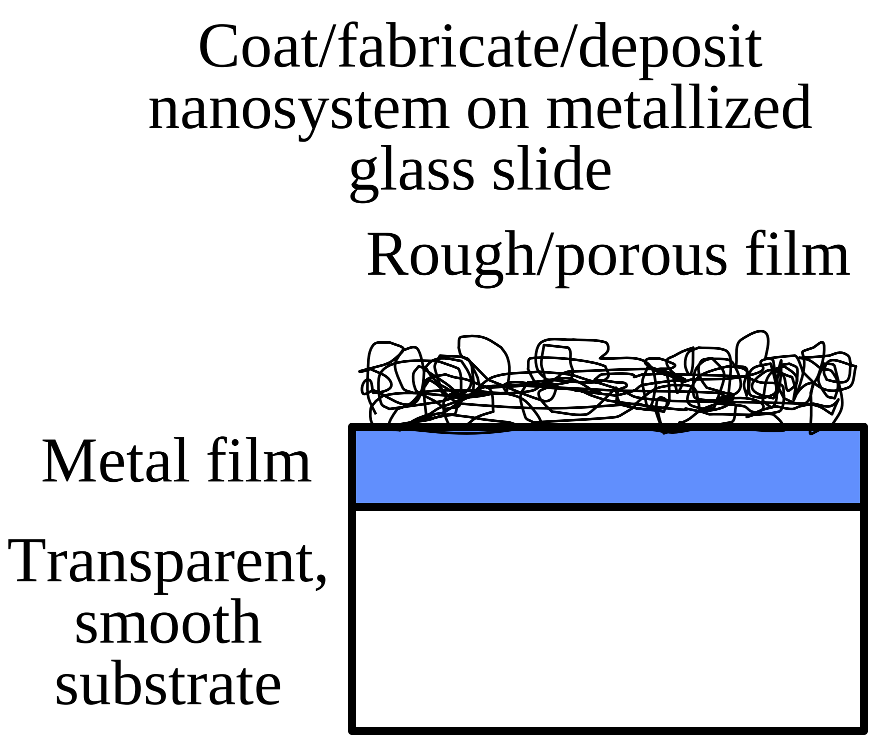
Typical geometry

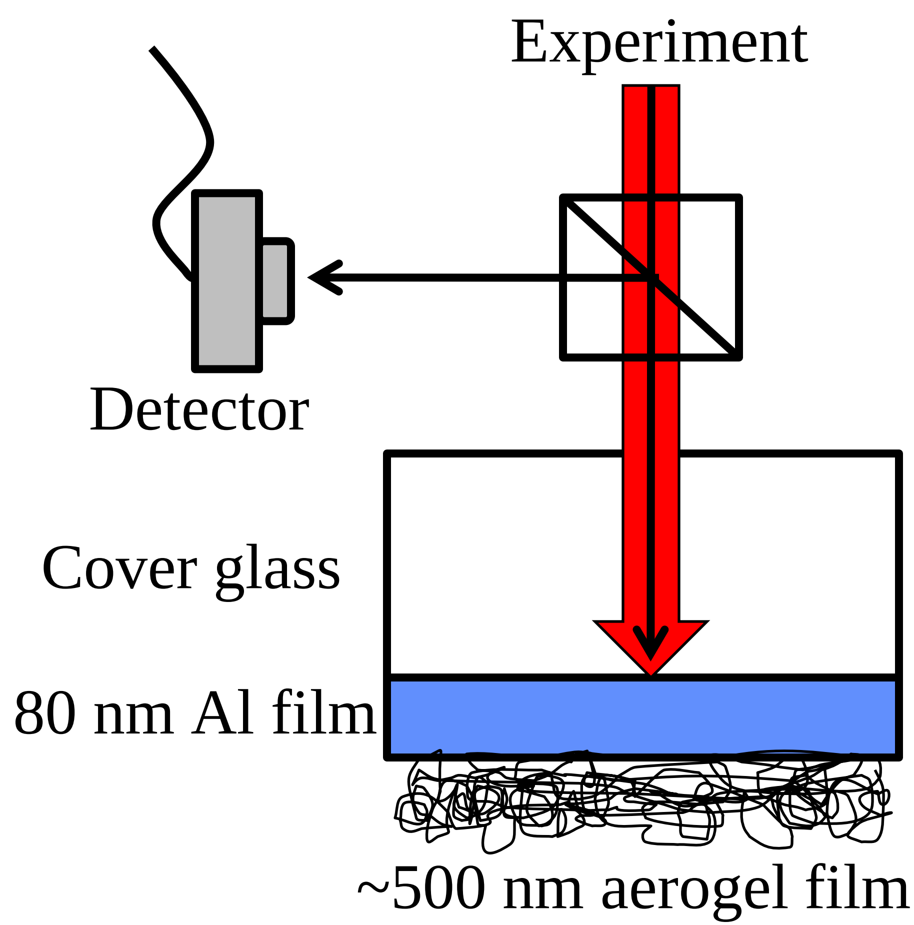


TDTR for nonconformal/non-solid surfaces

TDTR requires a specular, partially reflecting surface

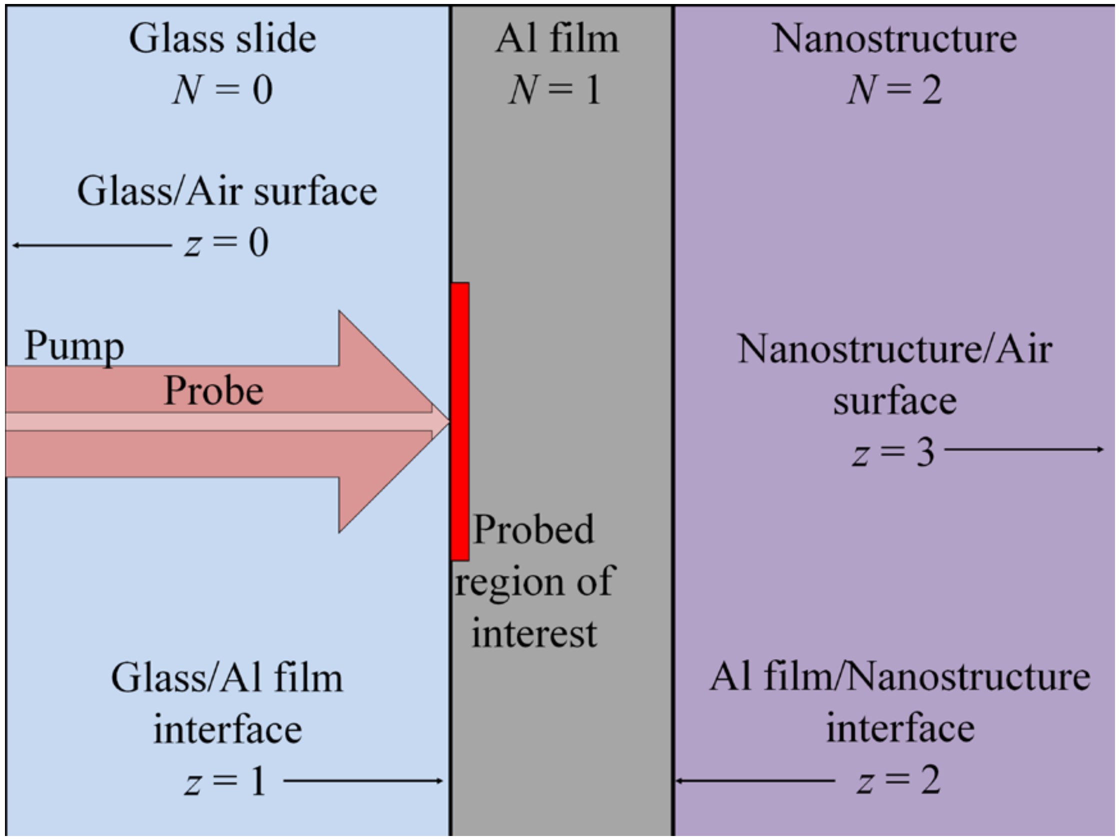
Geometry for rough nanosystem





TDTR for nonconformal/non-solid surfaces

For liquids: Ge *et al*., *Phys. Rev. Lett*. **96**, 186101 (2006)
For liquids: Schmidt *et al*., *Rev. Sci. Instrum.* **79**, 064902 (2008)
For porous composites: Hopkins, *et al*., *J. Heat Trans*. **133**, 061601 (2011)



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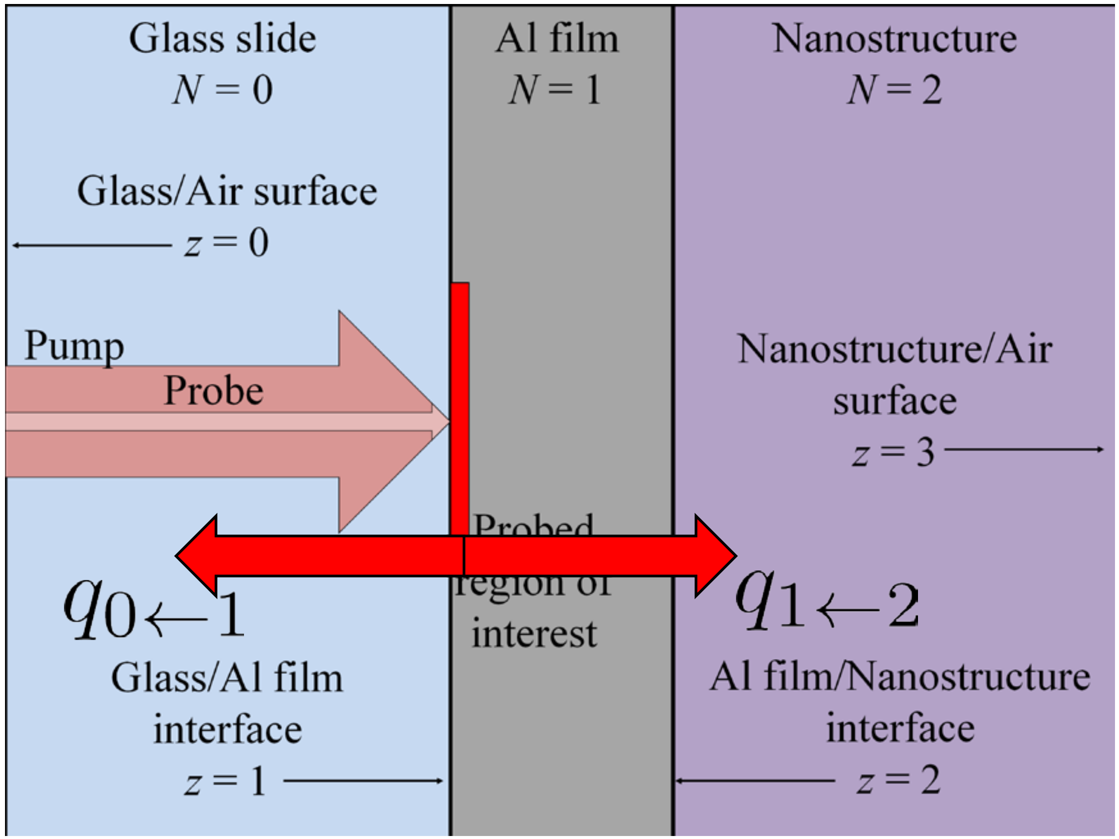
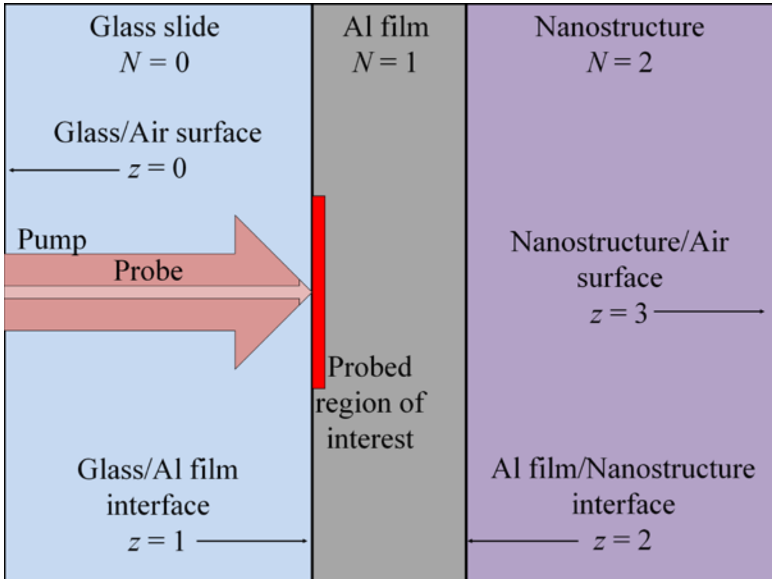


Bi-directional heat transfer

TDTR sensitivities



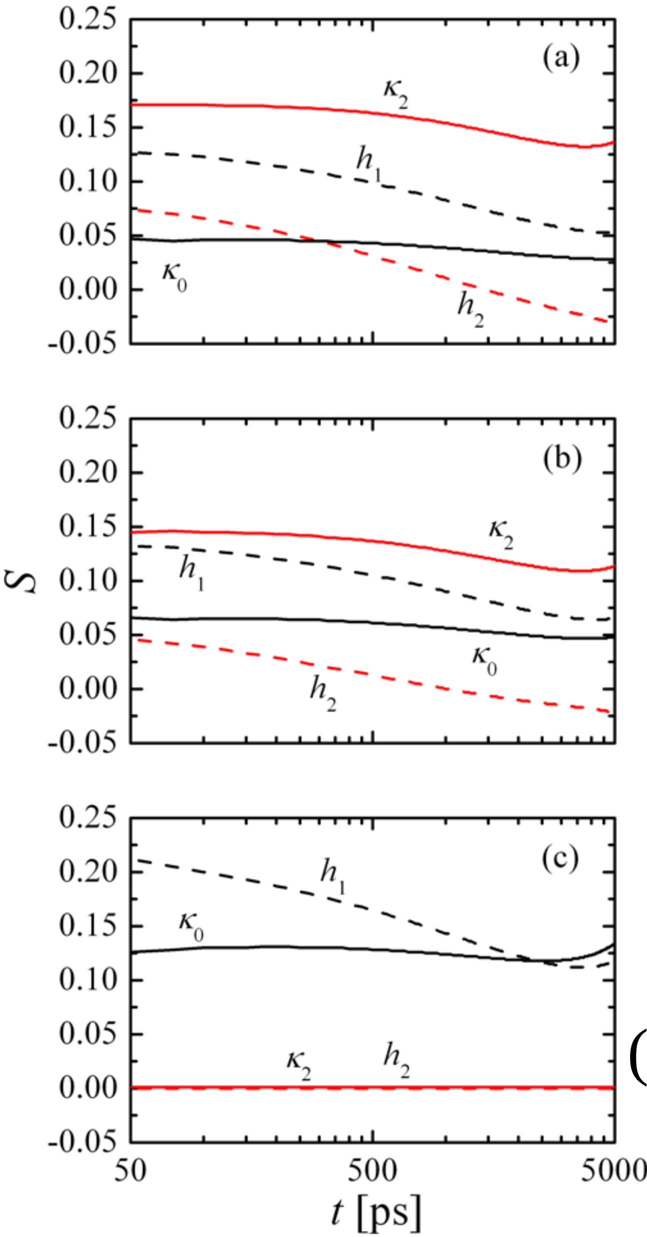
$$S_p = -\frac{\ln[X/Y]}{\ln[p]}$$

S_p - Sensitivity

X - Real component

Y - Imaginary component

p - property of interest



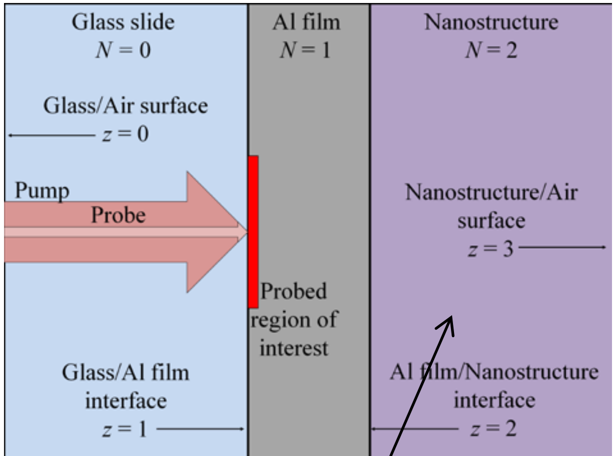
N=2 same as N=0

$\kappa_2 = \kappa_0/2$

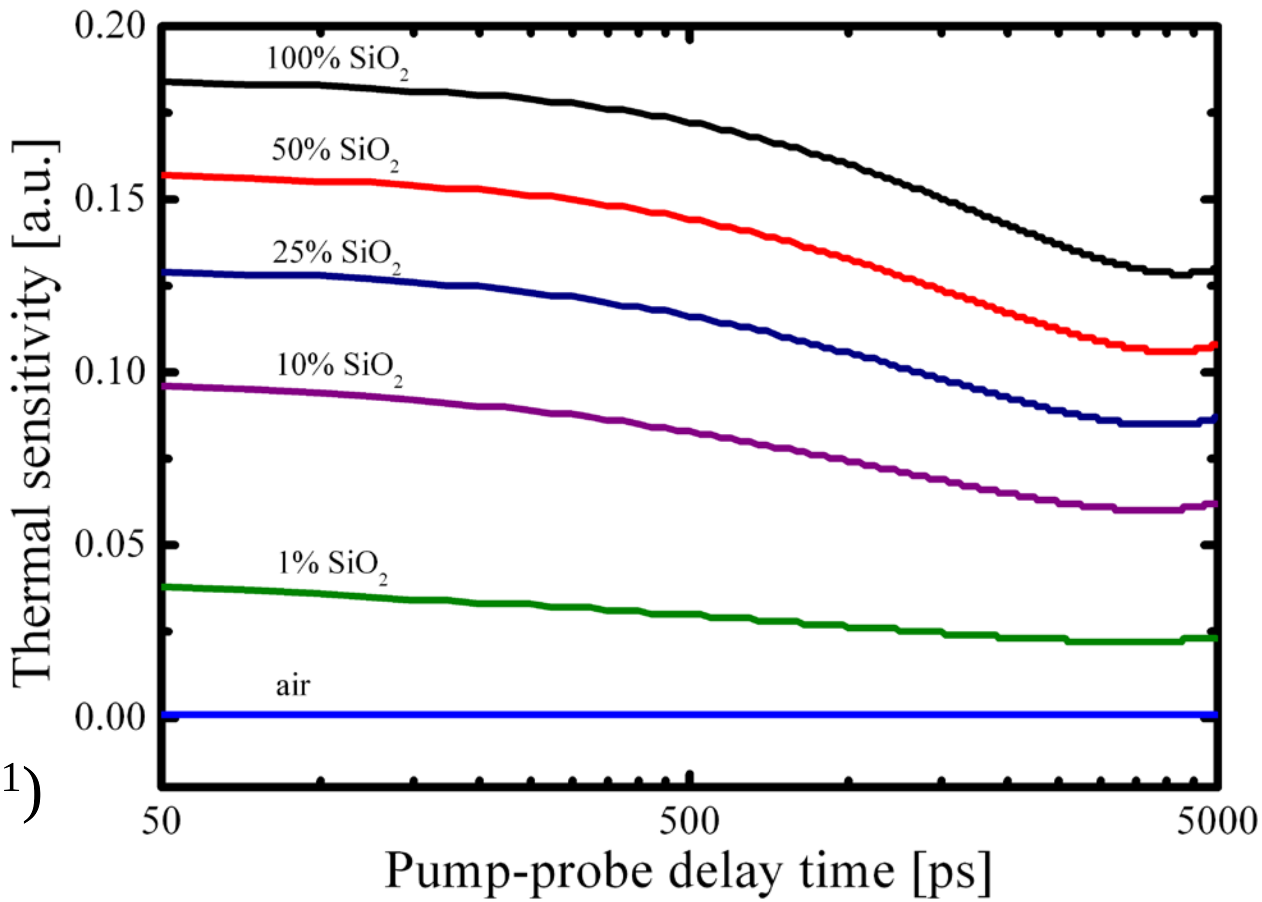
N=2 is air (insulated)

Hopkins, *et al.*, *J. Heat Trans.* 133, 061601 (2011)

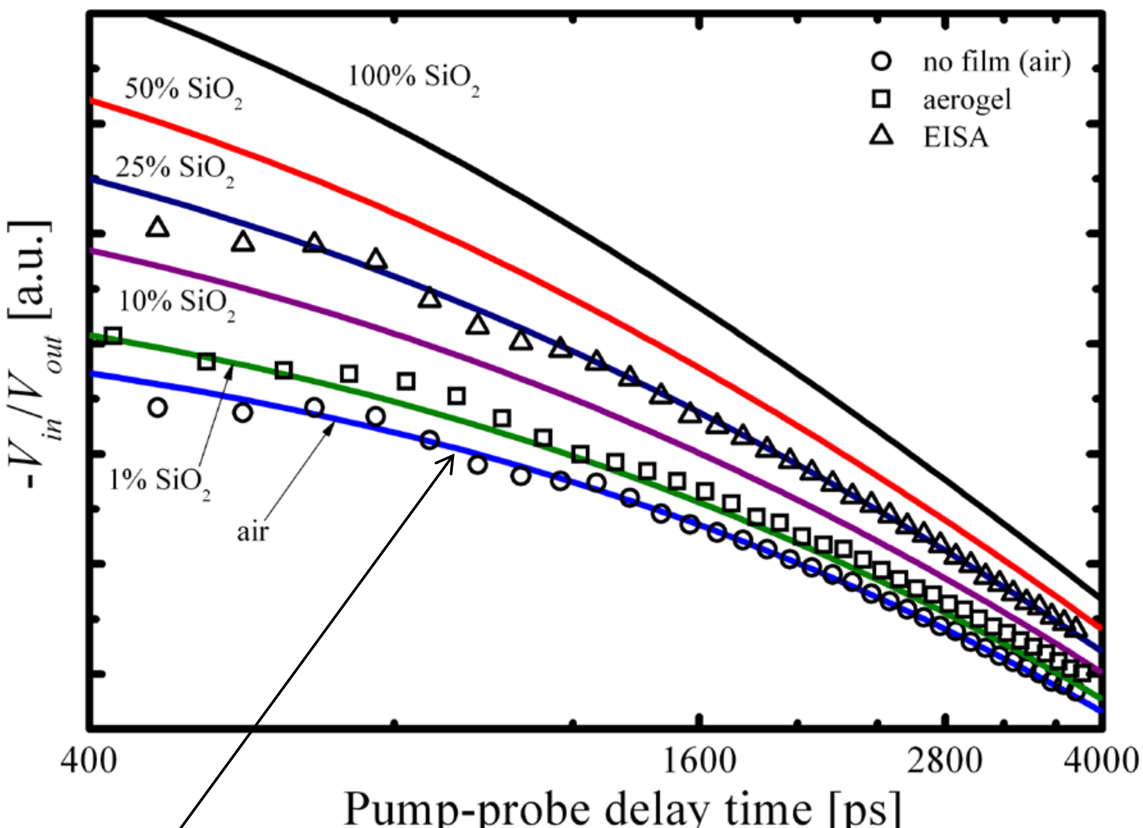
TDTR sensitivity to κ_2



Take κ_2 as some % of bulk κ_{SiO2} (1.2 W m^{-1} K^{-1})

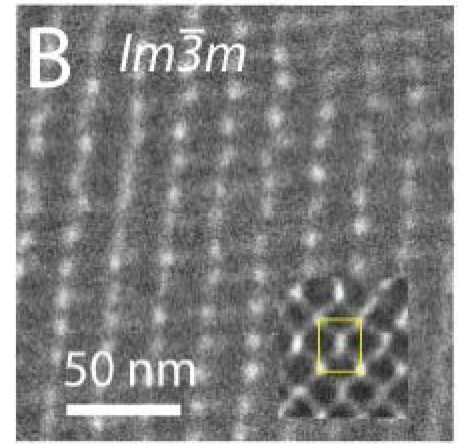


TDTR measurements of nanoporous silica films



glass - $\kappa_0 = 1.09\ \mathrm{W\ m^{-1}\ K^{-1}}$

Al/glass - $h_1 = 40\ \mathrm{MW\ m^{-2}\ K^{-1}}$



EISA: Dunphy *et al*. to appear in *Chemistry of Materials*

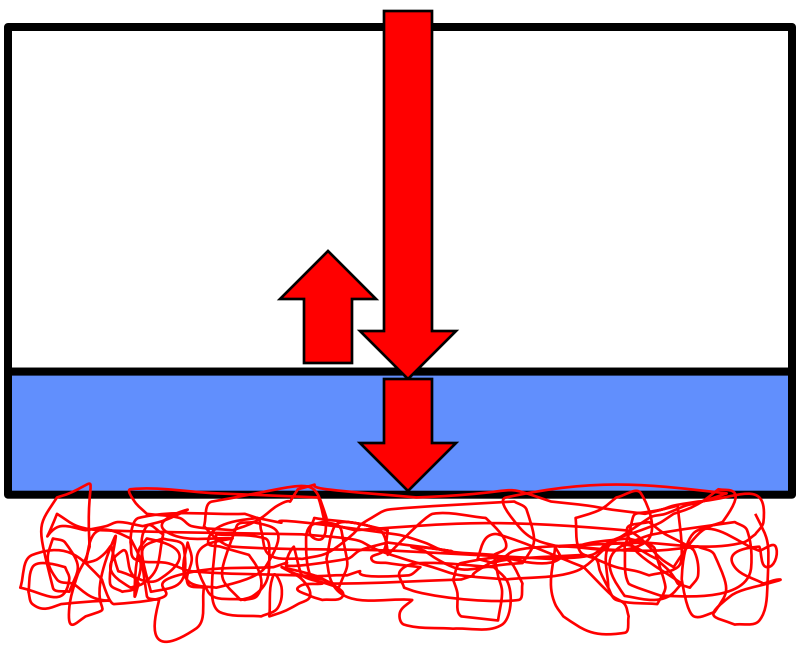
Effusivity measurements of nanoporous films

$$E_2 = \sqrt{C_2 \kappa_2}$$

Heat capacity of the sample during TDTR

$$E_2 = \sqrt{C_2 \kappa_2}$$

If no energy is transferred to air in pores,
assume $C_2 = C_2$ of bulk solid



- Measurement only ~4-5 ns in duration
- Not enough time for energy transfer to air
- All energy absorbed in Al film then transferred to solid in nanoporous film

$$h_{solid \to solid} \gg h_{solid \to air}$$

Validate bulk heat capacity assumption mathematically

C_2 of porous SiO_2 = C_2 of bulk SiO_2
in TDTR measurements

"Two fluid" model for conduction in porous media (Kaviany,1991)

Heat conduction in solid part

$$(1-\phi)C_s\frac{\partial T_s}{\partial t} = (1-\phi)\kappa_s\nabla^2 T_s - h_{s\rightarrow g}(T_s - T_g) + (1-\phi)q_{abs,s}$$

Heat conduction in gas part

$$(\phi)C_g\frac{\partial T_g}{\partial t} = (\phi)\kappa_g\nabla^2 T_g + h_{s\rightarrow g}(T_s - T_g) + (\phi)q_{abs,g}$$

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- **No heat transfer from solid to gas**

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- **No heat transfer from solid to gas**
- **No energy absorbed in gas from pulse**

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Heat conduction in gas part

$$(\phi)C_g\frac{\partial T_g}{\partial t} = (\phi)\kappa_g\nabla^2 T_g + h_{s\rightarrow g}(T_s - T_g) + (\phi)q_{abs,g}$$

- **No heat transfer from solid to gas**
- **No energy absorbed in gas from pulse**
- **Therefore, no heat transfer in gas**

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Validate bulk heat capacity assumption mathematically

C_2 of porous SiO_2 = C_2 of bulk SiO_2
in TDTR measurements

"Two fluid" model for conduction in porous media (Kaviany,1991)

Heat conduction in solid part

$$(1-\phi)C\frac{\partial T}{\partial t} = (1-\phi)\kappa_s\nabla^2 T + (1-\phi)q_{abs}$$

$$C_s\frac{\partial T_s}{\partial t} = \kappa_s\nabla^2 T_s + q_{abs,s}$$

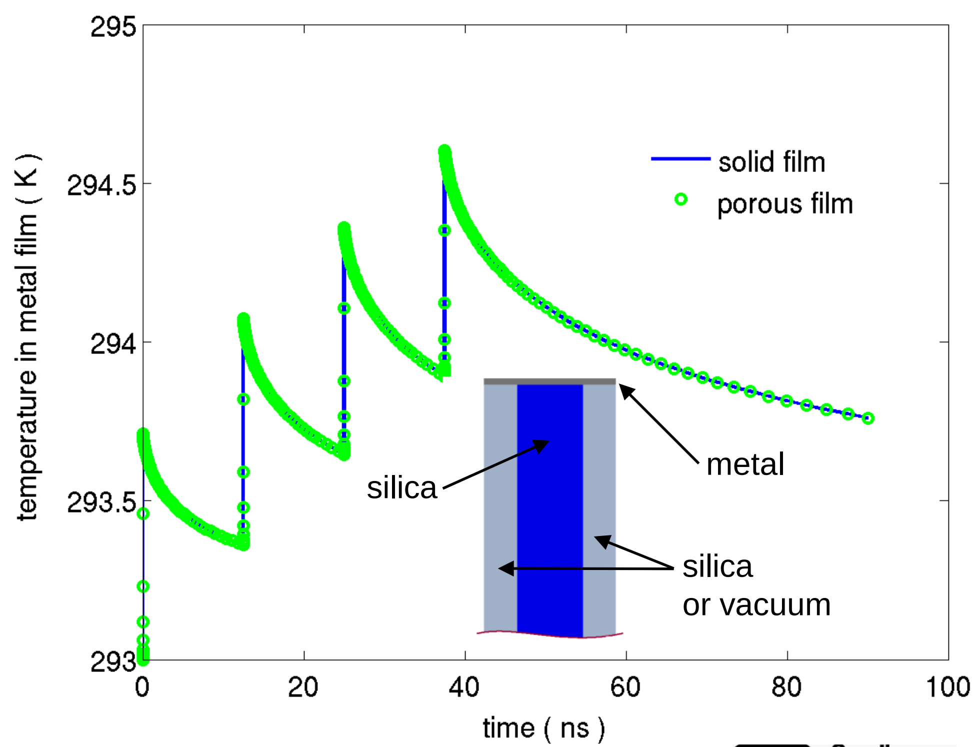
If no energy is transferred to or absorbed by air in nanoporous samples, effective medium does not have to be assumed for C_s to determine κ_s

Validate bulk heat capacity assumption numerically

C_2 of porous SiO_2 = C_2 of bulk SiO_2
in TDTR measurements

If we assume bulk properties in a reduced volume system with insulating pores, does the surface temperature change?

- **FEM simulations of experiment performed**
  - **one with solid silica film**
  - **one with half of silica removed**
- **In half-silica cases, all fluxes from metal were superposed on remaining silica**
- **Temperature measured in metal film**
- **No discernable difference observed in results**



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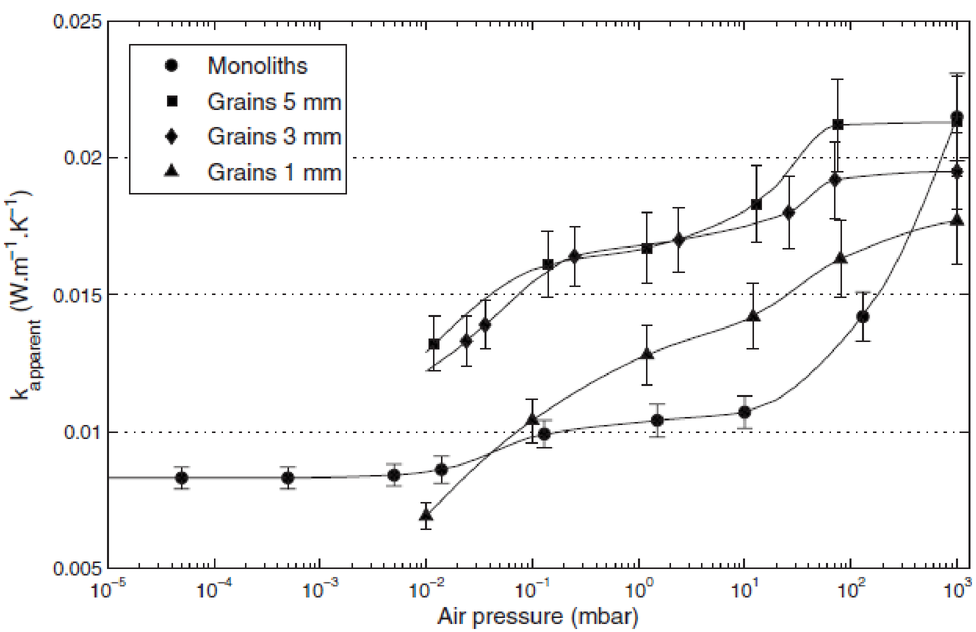
Validate bulk heat capacity assumption experimentally

Measure effusivity of aerogel films in ambient and under vacuum

Aerogel films: Prakash, Brinker, Hurd, *J. Non-Crystalline Solids* **190**, 264 (1995)

$$E_{\mathrm{aerogel,P}<10^{-3}\mathrm{mbar}} = \sqrt{C\kappa} = 223 \pm 95\ \mathrm{W\ m^{-2}\ K^{-1}}\ \sqrt{s}$$

$$E_{\mathrm{aerogel,P=ambient}} = \sqrt{C\kappa} = 233 \pm 121\ \mathrm{W\ m^{-2}\ K^{-1}}\ \sqrt{s}$$



Spagnol *et al.*, *J. Heat Trans.* **131** 074501 (2009)

Time scale of measurement too short to allow any thermal diffusion into air in pores **(~4 – 5 ns)**

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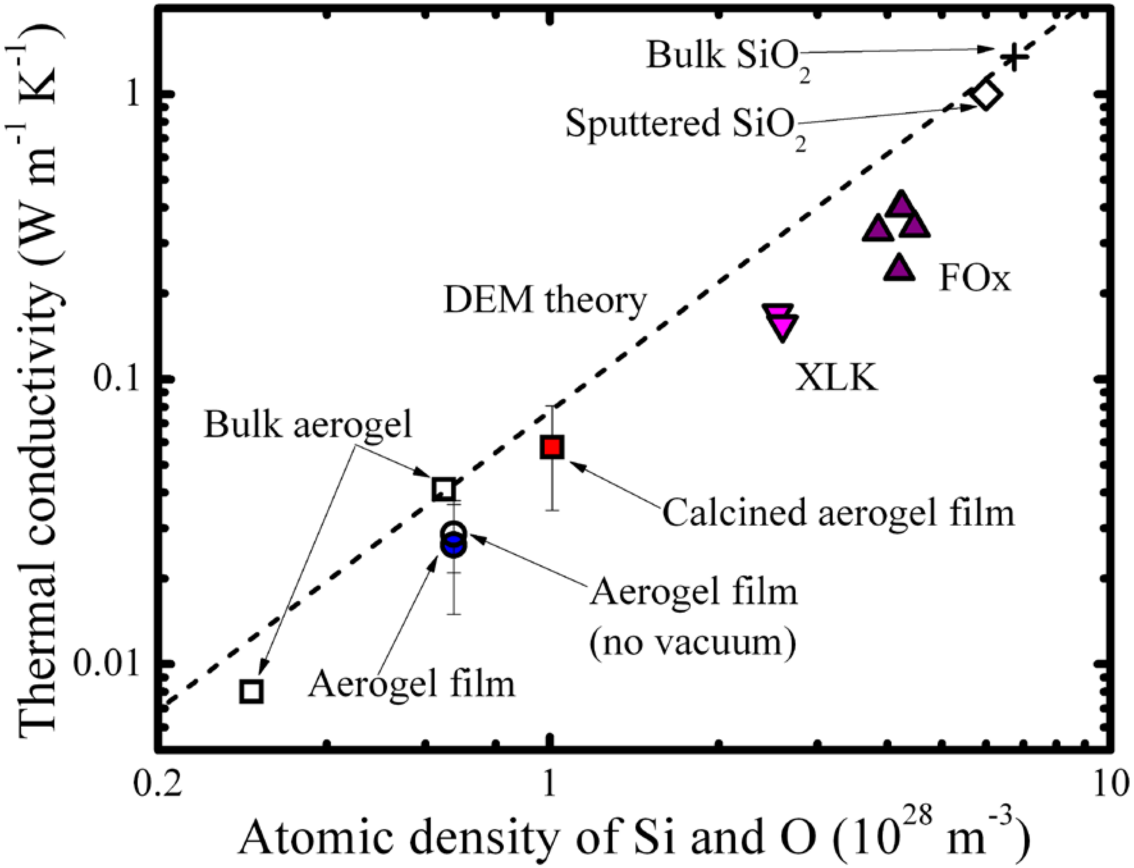
Thermal conductivity of aerogel thin films

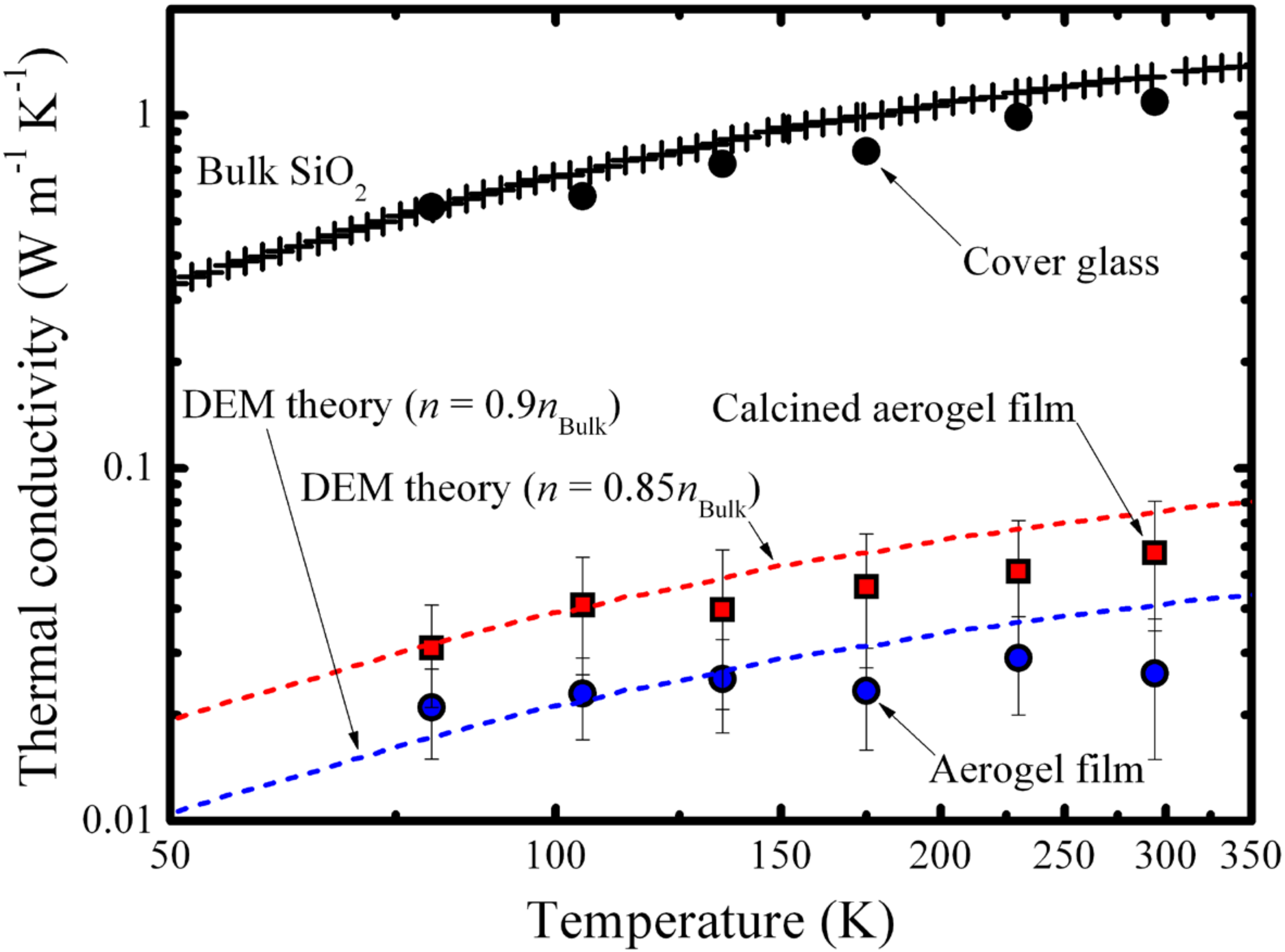


Differential Effective Medium (DEM) theory

$$\kappa_{\text{porous}} = \kappa_{\text{solid}} \left(\frac{n_{\text{porous}}}{n_{\text{solid}}} \right)^{\frac{3}{2}}$$

SiO_2, Fox, and XLK data: Costescu *et al.*, *Phys Rev. B* **65**, 094205 (2002)
Bulk aerogel data: Spagnol *et al.*, *J. Heat Trans.* **131**, 074501 (2009)
& Wei *et al.*, *J. Phys. Chem. C.* **113**, 7424 (2009)
DEM: Bruggeman, *Ann. Phys.* **416**, 636 (1935)

Thermal conductivity of aerogel thin films



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Lower limit to thermal conductivity

Thermal conductivity

$$\kappa = \frac{1}{3} C v \lambda = \frac{1}{3} C v_g v_p \tau$$

Scattering time is half period of oscillation (i.e. atomic spacing limited)

Einstein, *Annalen der Physik* **35**, 679 (1911) and Cahill *et al*., *Phys. Rev. B* **46**, 6131 (1992).

$$\tau = \frac{\pi}{\omega} \rightarrow \kappa = \frac{1}{3} C v_g v_p \frac{\pi}{\omega}$$

Scattering destroys “phase” of oscillation (“diffusive” scattering)

Hopkins and Beechem, *Nano. Micro. Thermophys. Eng*. **14**, 51 (2010).

$$v_g \neq v_p = \frac{\pi}{n^{1/3}\omega} \rightarrow \kappa = \frac{n^{-1/3}}{3} C v_g \frac{\pi^2}{\omega^2}$$

Assume Debye solid

$$\kappa = \left(\frac{\pi^2}{36}\right)^{1/3} n^{2/3} k_{\mathrm{B}} \sum_j \frac{T}{\Theta_j} v_{g,j} \int_0^{\Theta_j/T} \frac{x^2 \exp[x]}{(\exp[x]-1)^2} \mathrm{d}x$$

For porous media $v_g \propto n^{1.4}$

Costescu *et al*., *Phys Rev B* **65**, 094205 (2002).

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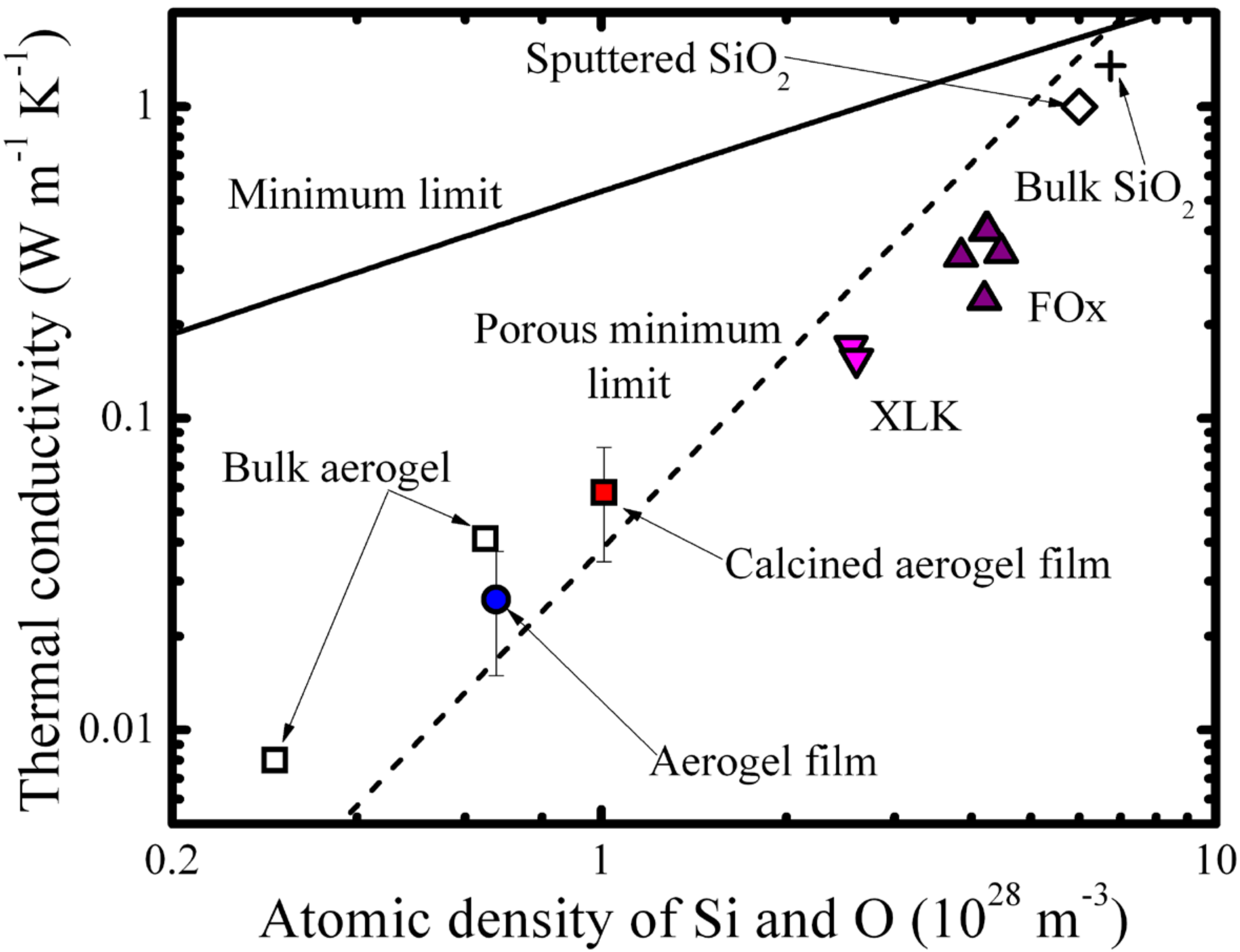
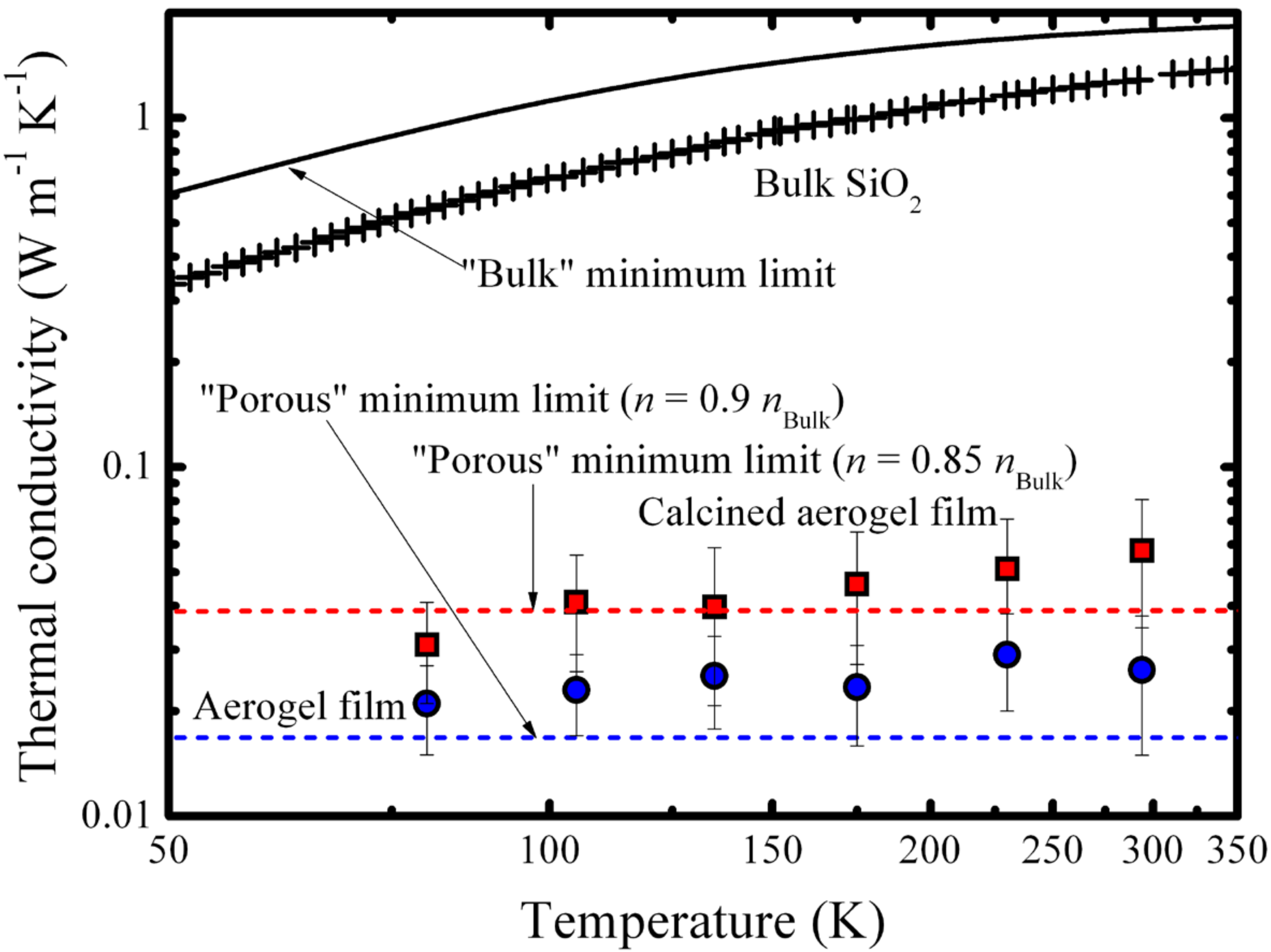
“Porous” minimum limt



“Porous” minimum limit



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Summary

- **TDTR can be used to measure thermal conductivity of porous materials with minimal losses from air in pores**
- **TDTR measurement is dominated by heat flow in the solid matrix due to time scale of measurements**
- **Thermal conductivity of aerogel thin films agrees with bulk aerogels with similar densities**
- **Porous minimum limit gives better estimate of thermal conductivity than traditional minimum**

- Thanks to: Harry S. Truman Fellowship program at Sandia (Hopkins and Kaehr), LDRD program at Sandia (Piekos and Brinker)

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