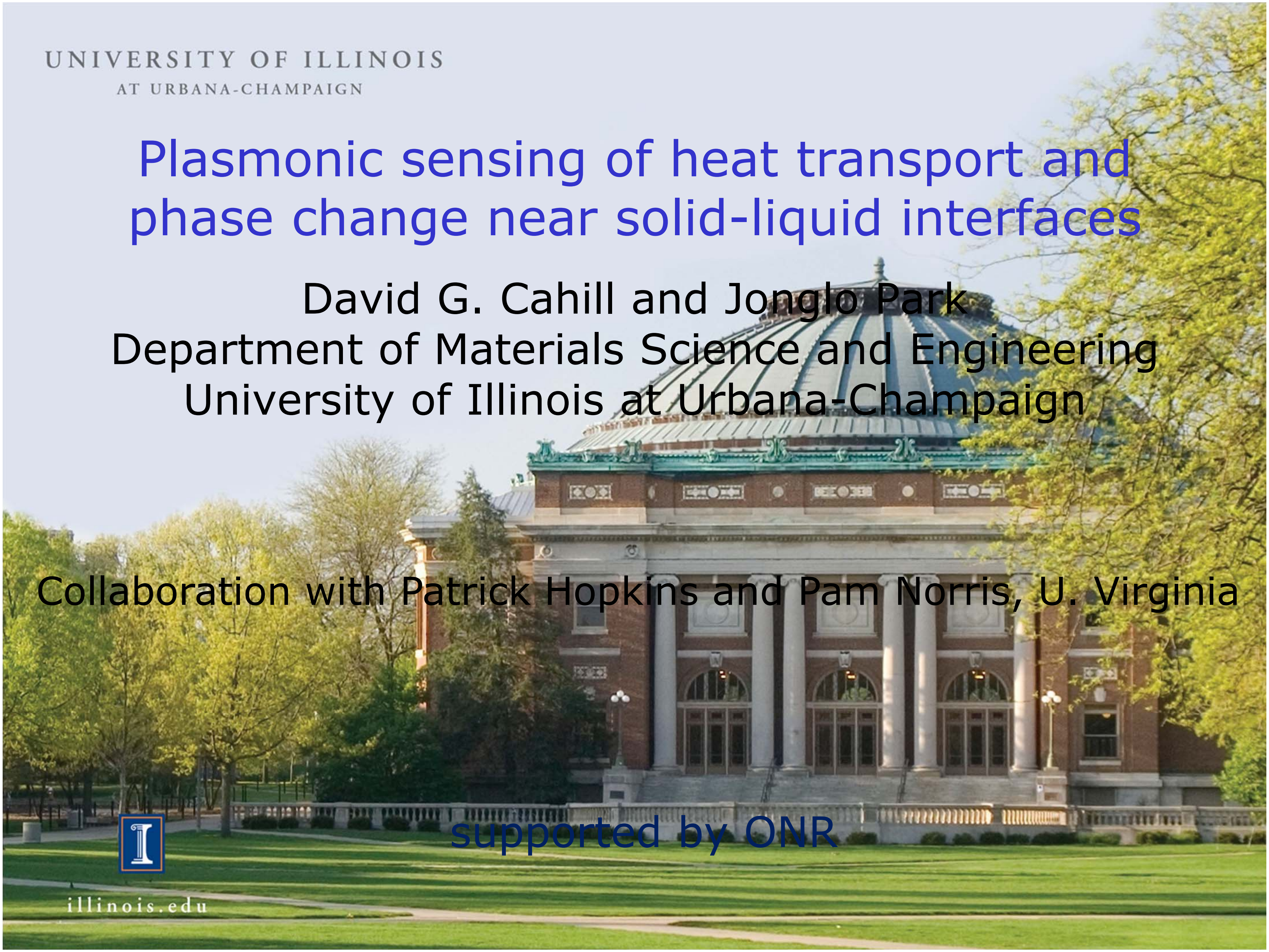

UNIVERSITY OF ILLINOIS
AT URBANA-CHAMPAIGN

Plasmonic sensing of heat transport and phase change near solid-liquid interfaces

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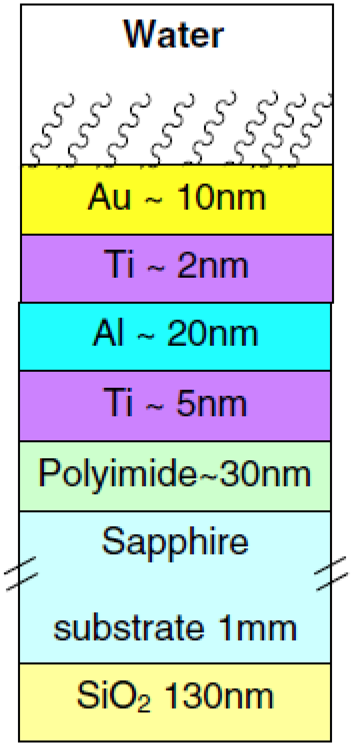
Collaboration with Patrick Hopkins and Pam Norris, U. Virginia

supported by ONR

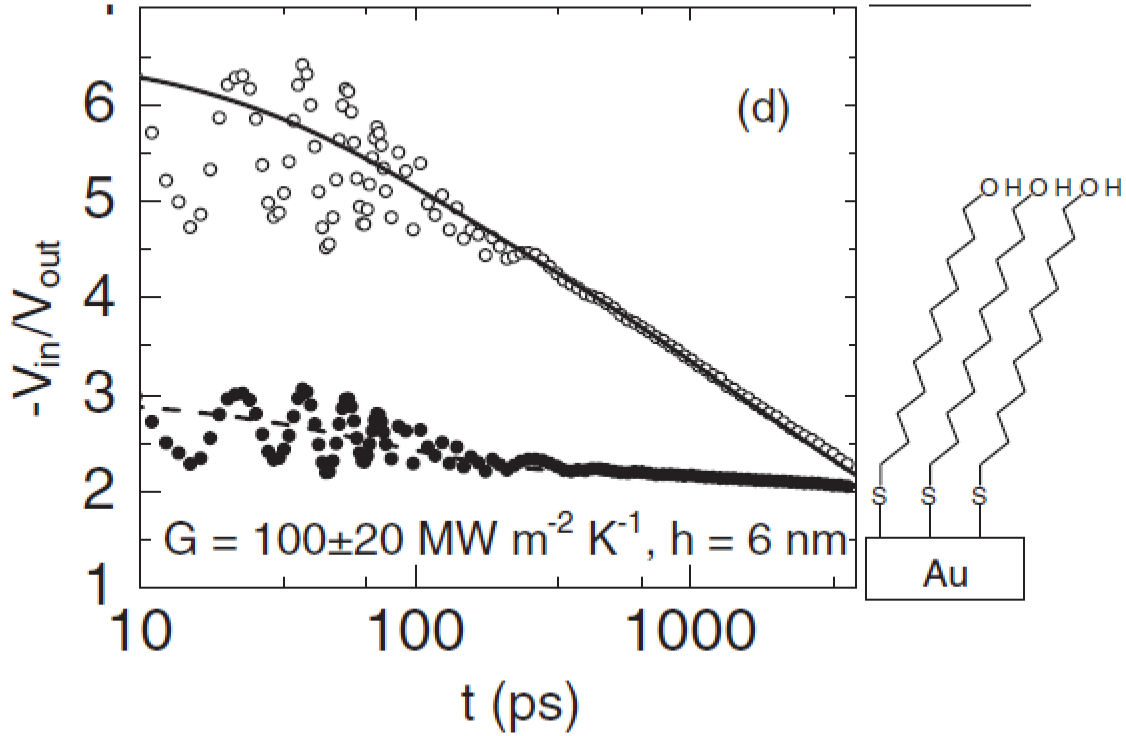
illinois.edu

Motivation (big picture): Improve experimental methods for probing heat transfer and phase transformations at solid/liquid and vapor/liquid interfaces

- Prior study of thermal conductance of hydrophobic and hydrophilic interfaces with water



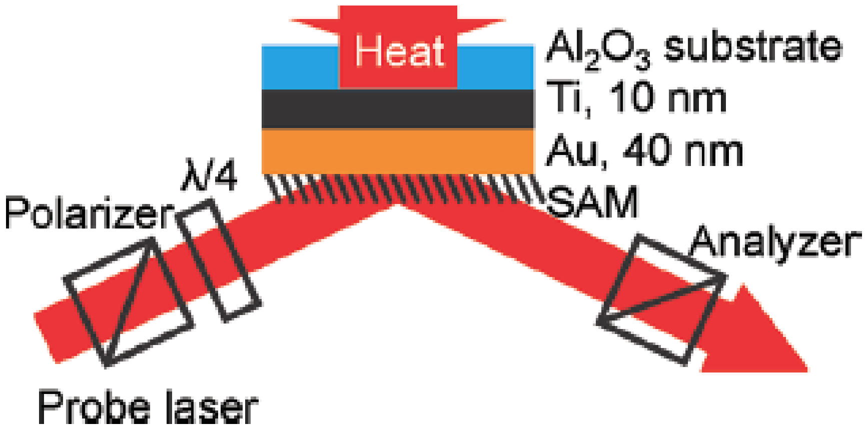
(b)

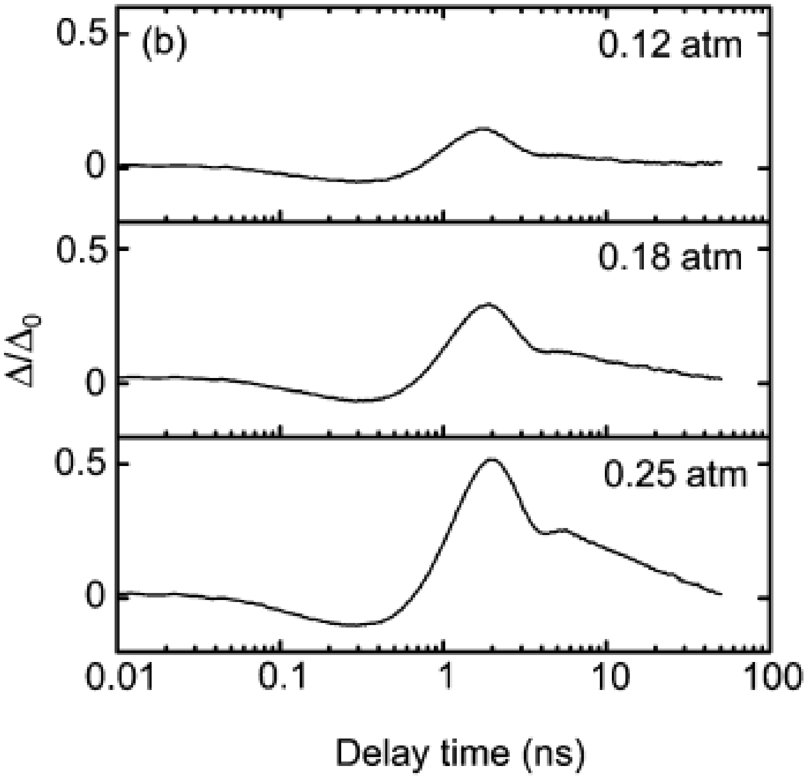


Ge *et al.*, *Phys. Rev. Lett.* (2006)

Motivation (big picture): Improve experimental methods for probing heat transfer and phase transformations at solid/liquid and vapor/liquid interfaces

- Prior study of fast water desorption from a hydrophilic surfaces by time-resolved ellipsometry





Min *et al.*, *J. Phys. Chem*. C (2012)

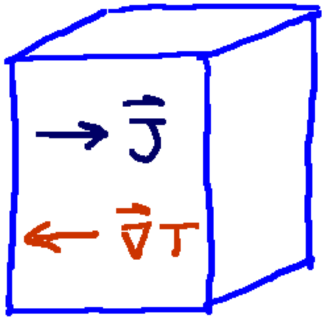
Outline

- Thermal conductance of interfaces
- Nanodisk sensors (prepared for us by Insplorion) and characterization of their sensitivity and depth resolution.
- Application to interface thermal conductance and thermal diffusivity of fluids by separating the response from the Au temperature and the index change in the adjacent fluid. (unpublished)
- Initial application to fast condensation and evaporation of a refrigerant (R124) from interfaces with controlled chemistry. (work in progress)

Thermal transport coefficients

- Thermal conductivity Λ is a property of the continuum

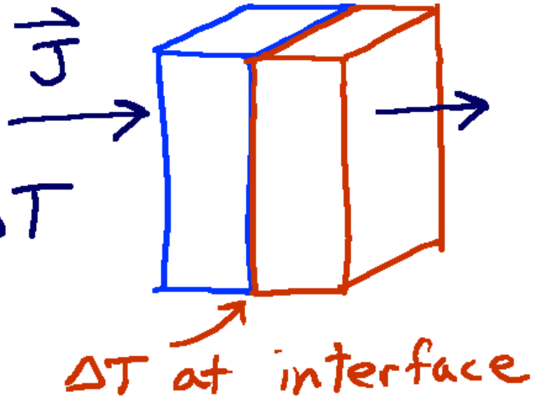
$$\vec{J} = -\Lambda \vec{\nabla} T$$



$$\Lambda = \frac{1}{3Vk_BT^2}\int_0^\infty \langle \vec{j}(t)\cdot\vec{j}(0)\rangle \, dt$$

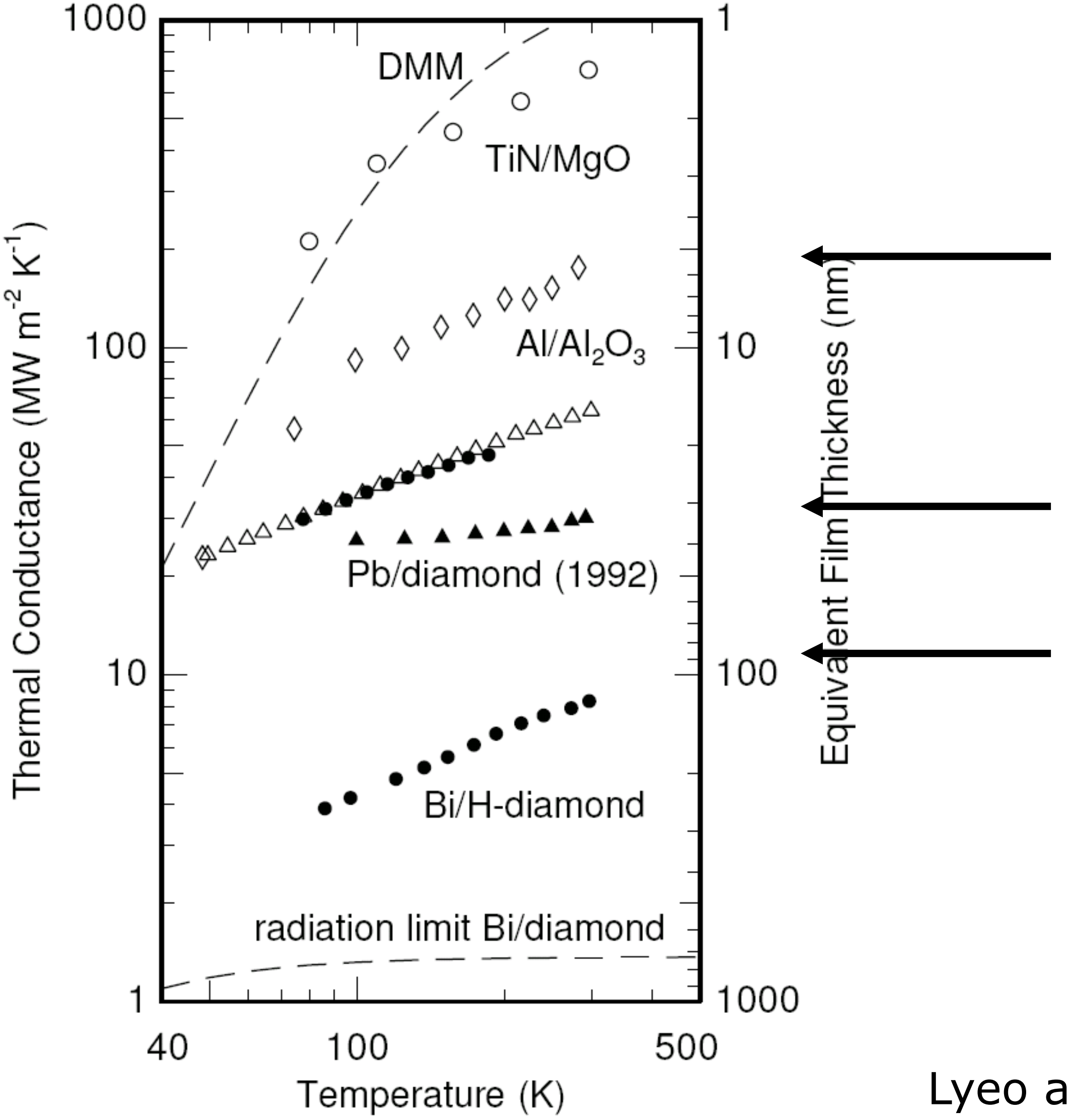
- Thermal conductance (per unit area) G is a property of an interface

$$J = G\Delta T$$



$$G = \frac{1}{Ak_BT^2}\int_0^\infty \langle q(t)q(0)\rangle \, dt$$

Interface conductance spans a factor of 60 range at room temperature



W/Al$_2$O$_3$

Au/water

PMMA/Al$_2$O$_3$

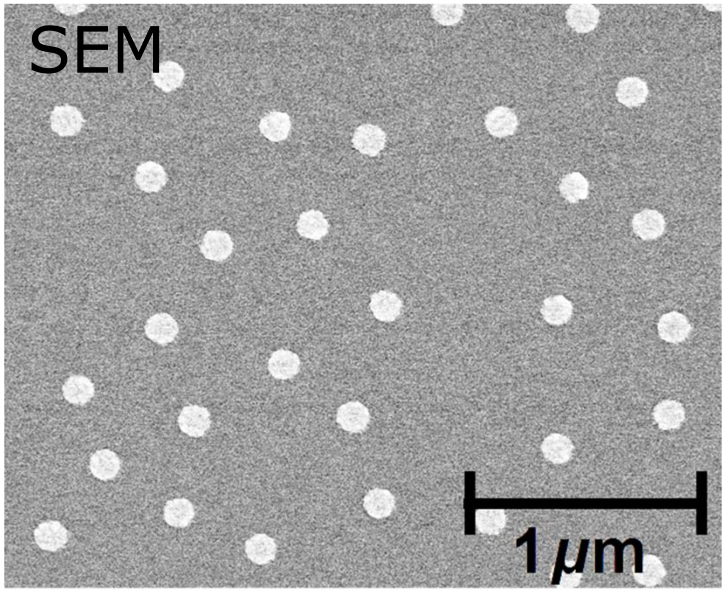
nanotube/alkane

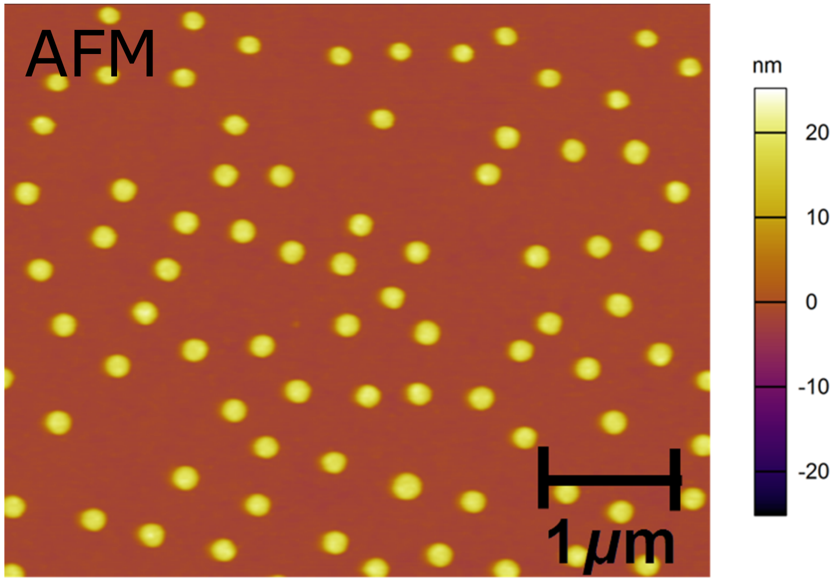
Lyeo and Cahill, PRB (2006)

Insplorion nanodisk plasmonic sensors

- Fabricated by “hole-mask colloidal lithography”
- Au adhesion to SiO_2 substrate is good even though they avoided the use of a conventional Cr or Ti adhesion layer (Cr or Ti would damp the plasmon)

Au disk diameter 120 ± 10 nm, height 20 ± 2 nm





Sensitivity *d(Tr)/dn* (change in transmission coefficient with respect to optical index) approaches unity

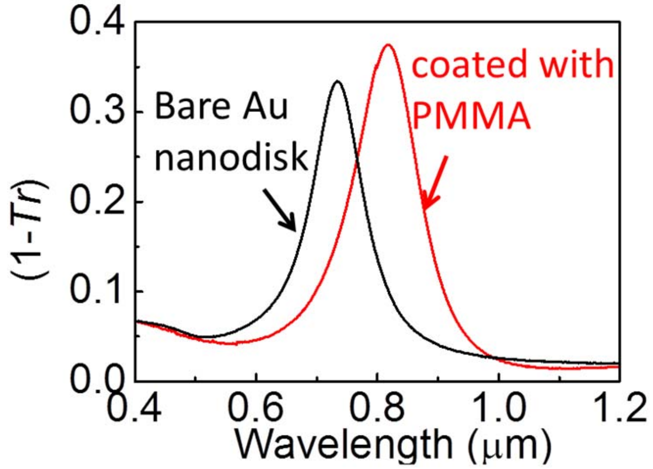
- Coat with PMMA and take difference spectra of the absorption.
- Noise floor of pump-probe measurements should be →

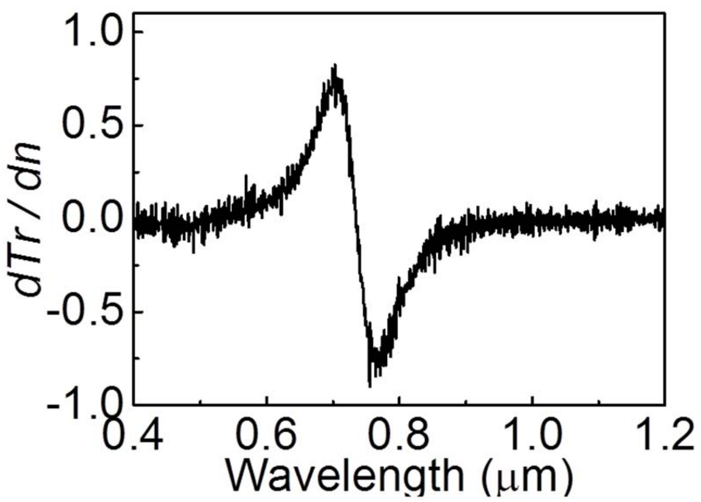
$$\Delta n \approx 0.3 \text{ ppm Hz}^{1/2}$$

$$\Delta T_{liquid} \approx 3 \text{ mK Hz}^{1/2}$$

$$\Delta h_{liquid} \approx 10^{-13} \text{ m Hz}^{1/2}$$

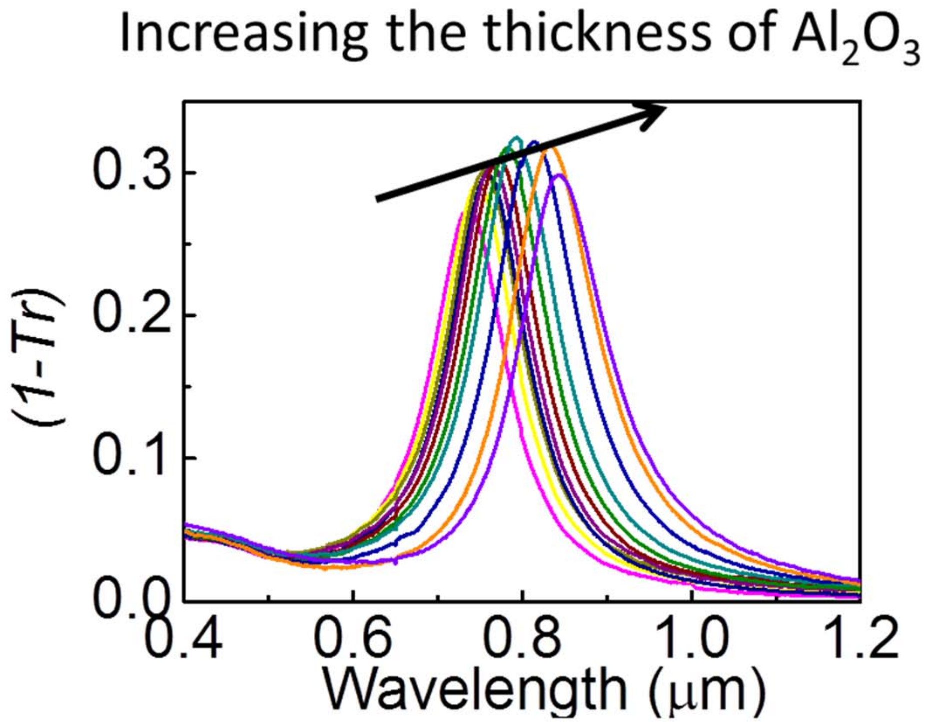
Tr=transmission

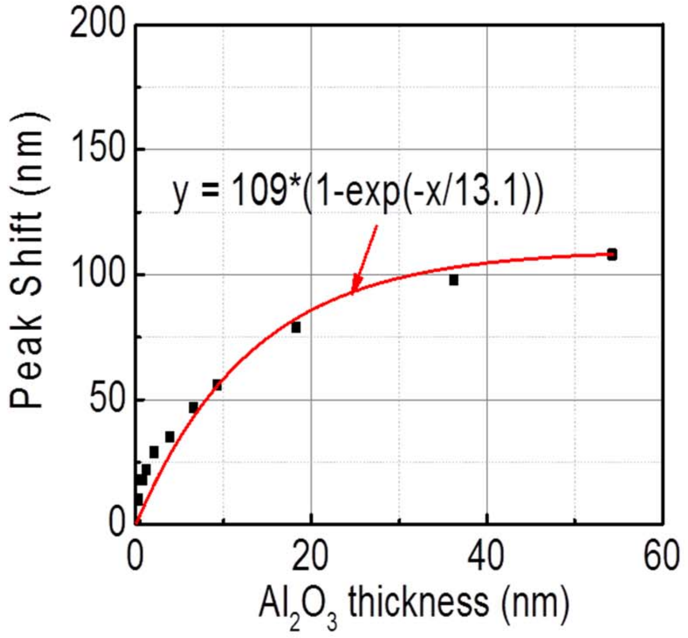




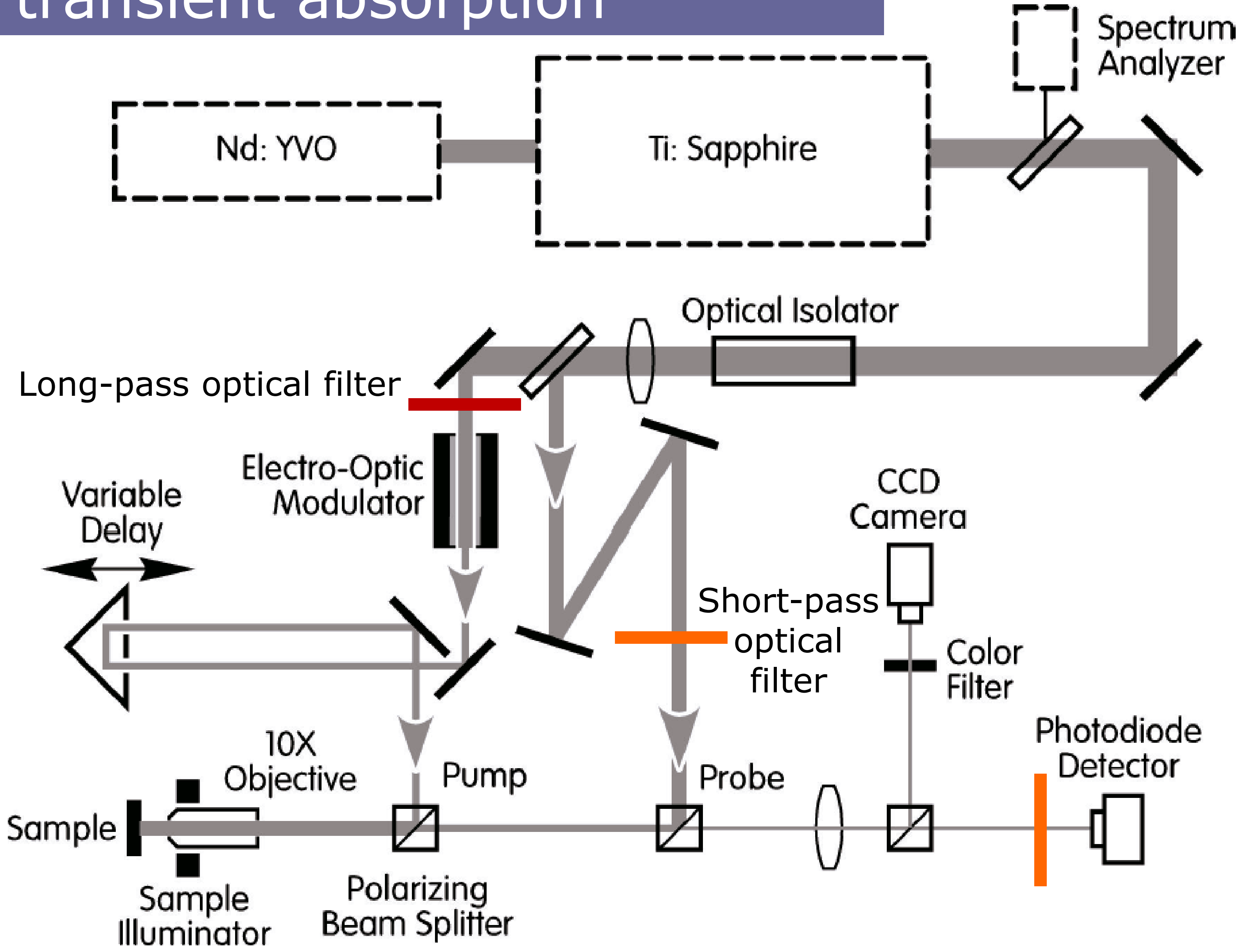
Sensitivity to dn is localized to within 13 nm of the Au surface

- Atomic-layer deposition of alumina
- Assuming constant deposition rate per cycle





Time-domain thermoreflectance and transient absorption



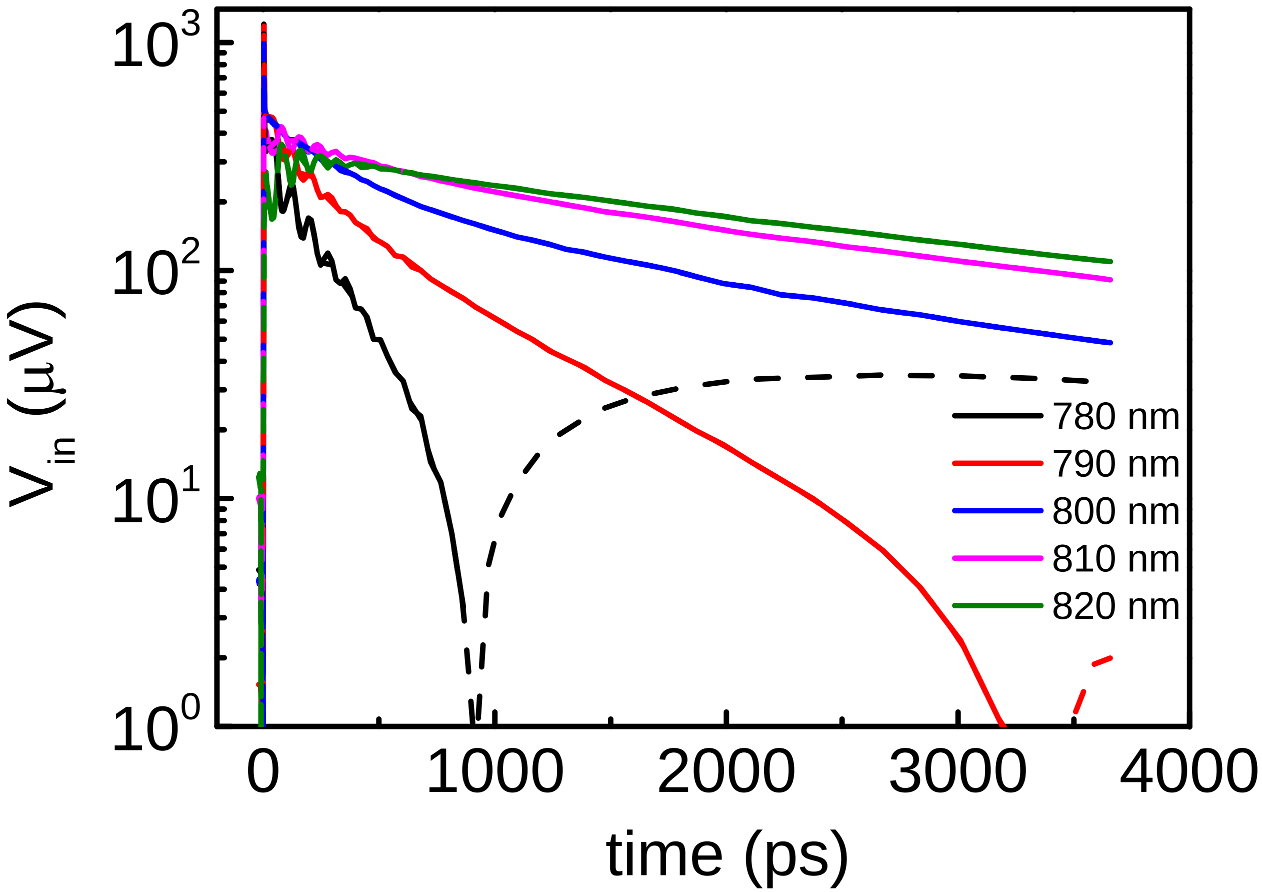
Kang *et al.*, RSI (2008)

Signal is a combination of the temperature change of the Au and the temperature (or pressure or density) change of the surroundings

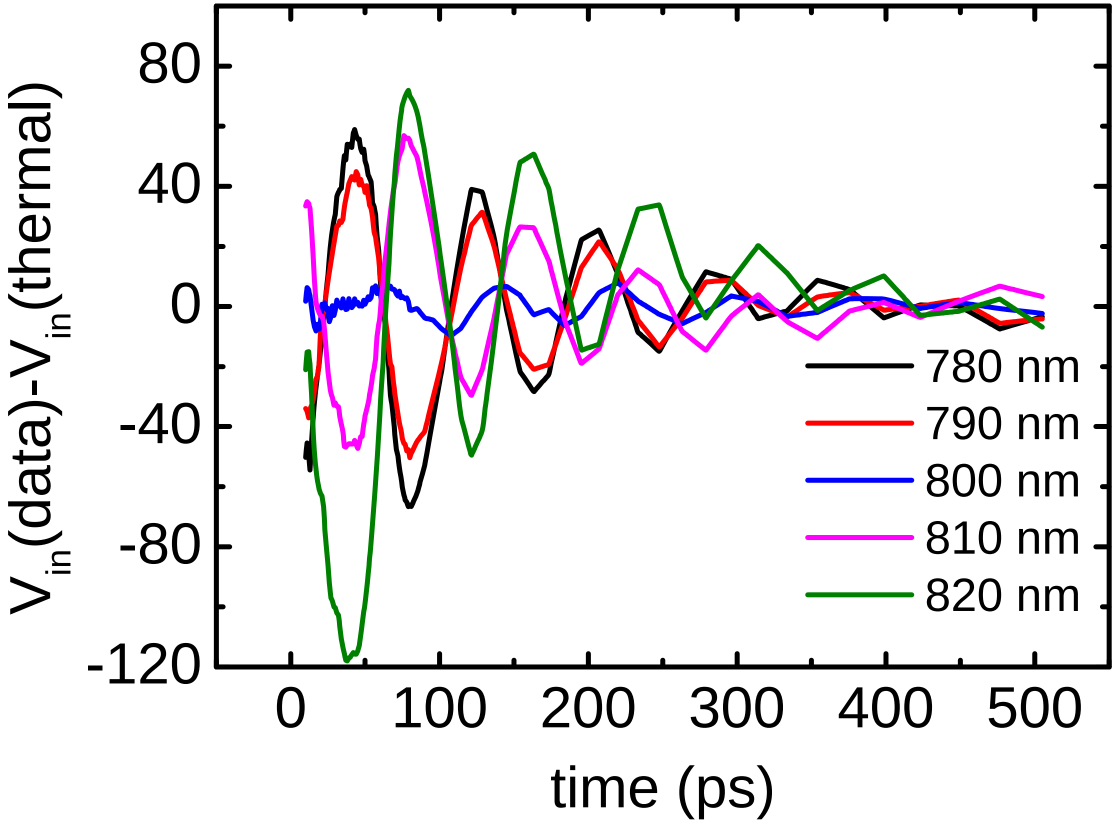
$$\Delta Tr = \frac{d(Tr)}{dT_{Au}} \Delta T_{Au} + \frac{d(Tr)}{dT_{fluid}} \Delta T_{fluid}$$

- Isolate the two terms using a linear combination of the response at two wavelengths.
- “breathing mode” acoustic oscillation is minimized at the same wavelength that minimizes the sensitivity to fluid temperature.

Vary the contributions from ΔT_{Au} and ΔT_{fluid} by varying wavelength of the probe light



Signal from the lateral “breathing mode” acoustic oscillation is minimized at the same wavelength that minimizes the sensitivity to fluid temperature

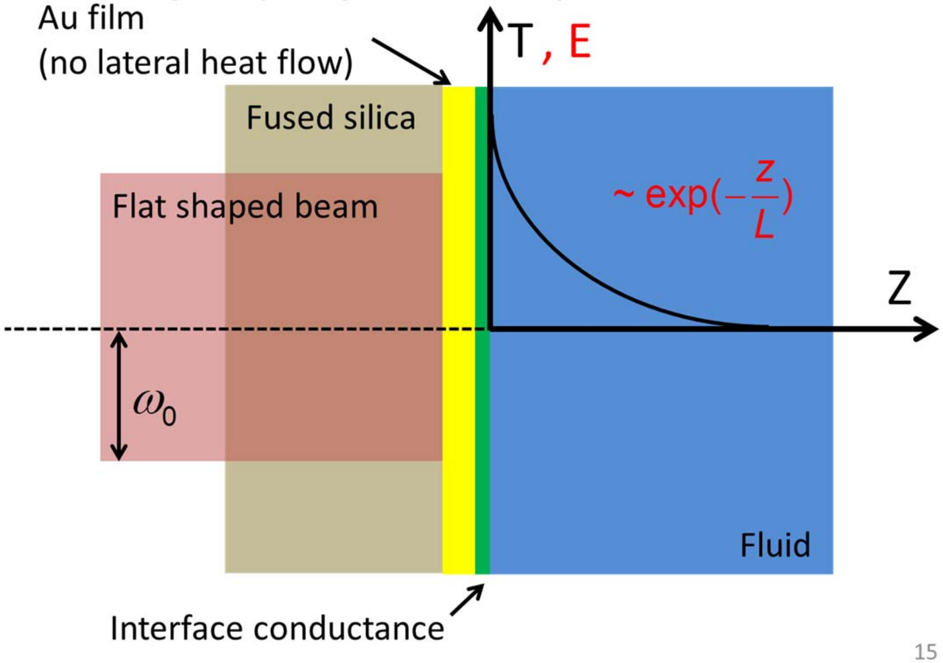


Data after subtracting thermal response

Modeling of heat transfer builds on our standard methods of analyzing TDTR data.

- Model the 120 nm diameter, 20 nm thick heat source as a 120 nm diameter uniform intensity laser beam heating a blanket 20 nm Au film that has zero in-plane thermal conductivity.
- dn/dT of the fluid dominates over dn/dT of the glass substrate so model the signal as a weighted average of the temperature of the fluid within 13 nm of the Au

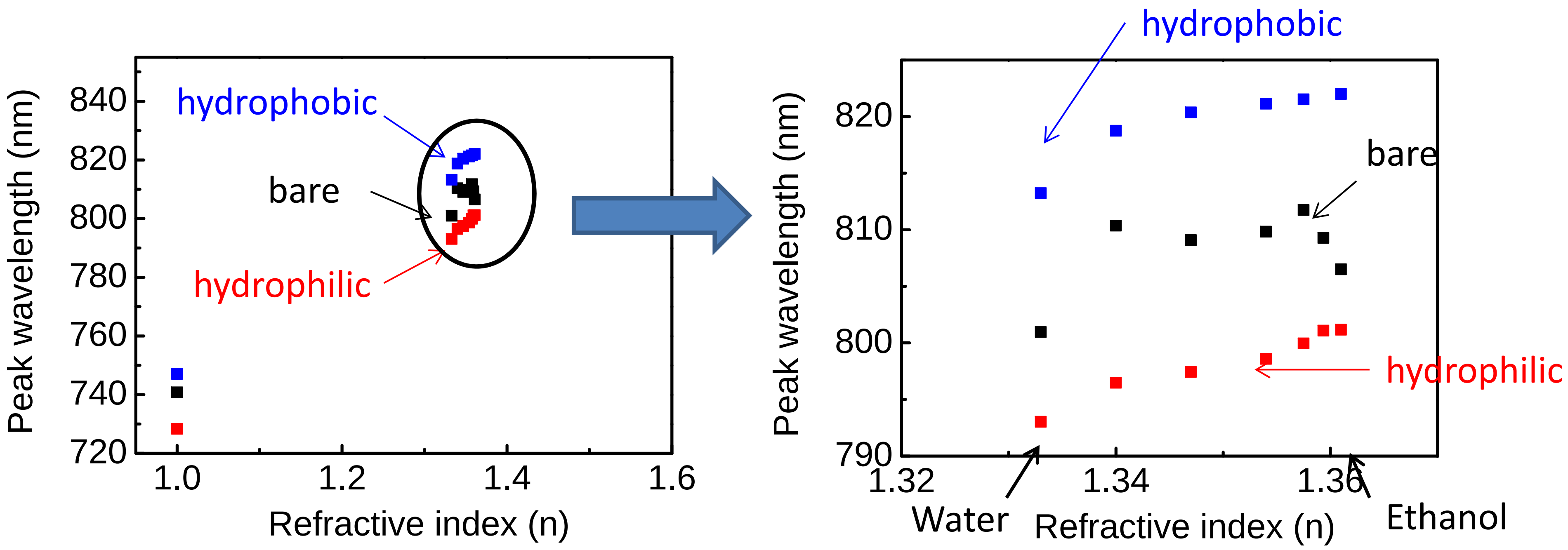
Data analysis (analytical model)



Control the surface chemistry using self-assembled monolayers (thiol bond to Au surface)

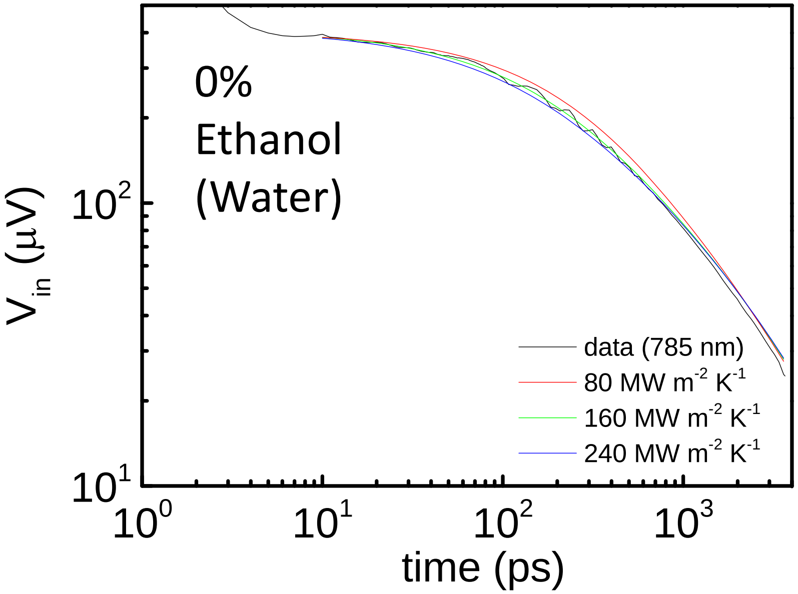
- Plasmon resonance is a built-in diagnostic for what is happening near the interface.

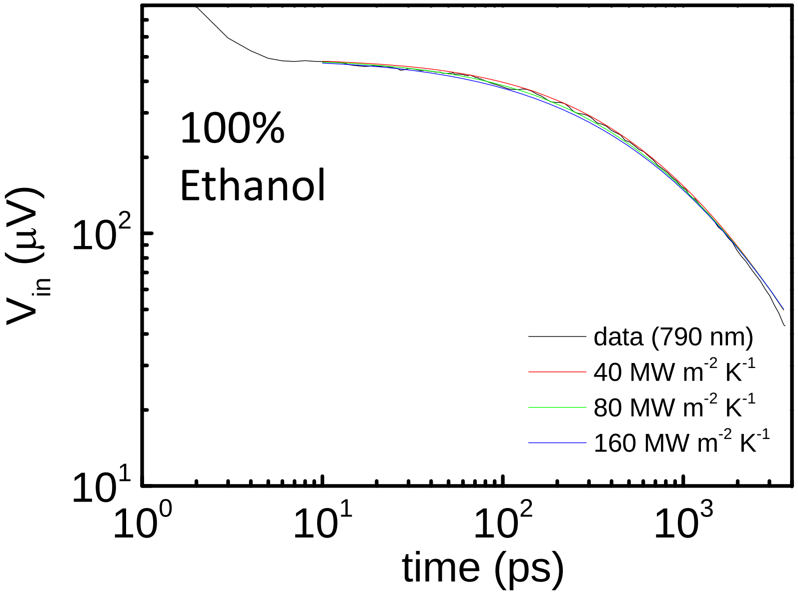
Hydrophilic $HS(CH_2)_3SO_3$ and hydrophobic $HS(CH_2)_9CH_3$



Data acquisition and analysis for interfaces with fluid mixtures

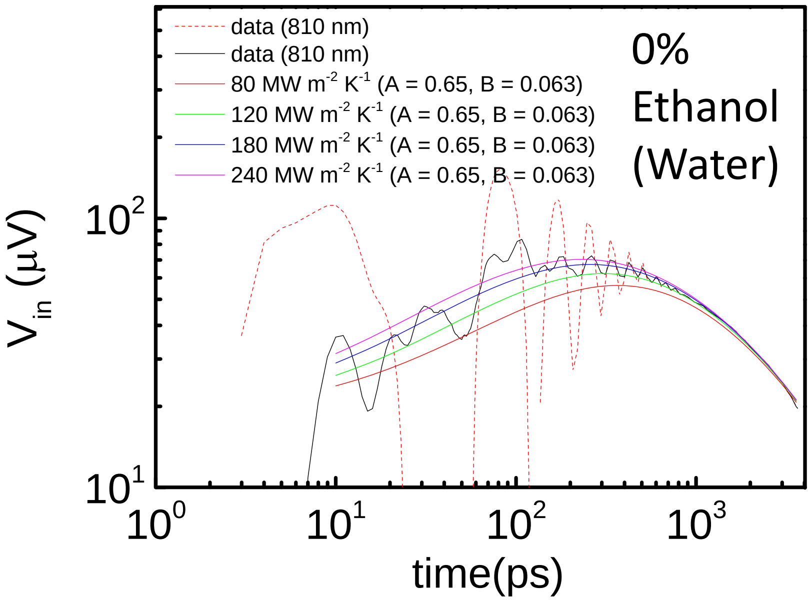
- First step: select wavelength that minimizes contribution from fluid temperature
- Compare to thermal model with interface conductance as a free parameter using literature values for fluid thermophysical properties

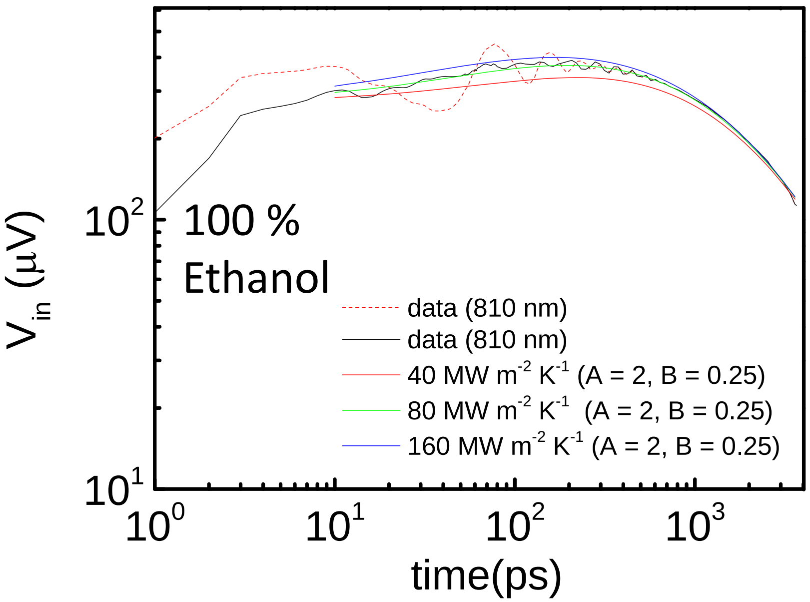




Data acquisition and analysis for interfaces with fluid mixtures

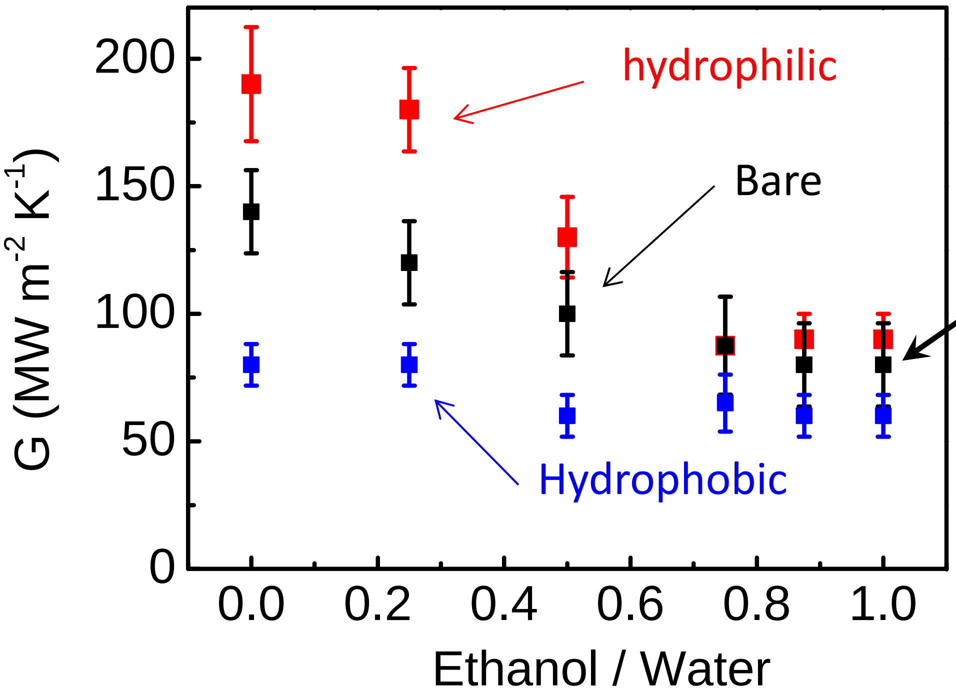
- Next step: shift wavelength to provide greater sensitivity to fluid temperature near the interface.
- Subtract breathing mode acoustic signal by fitting to a damped oscillator
- Compare to thermal model with interface conductance as a free parameter





Vary liquid composition between pure ethanol and pure water for hydrophobic SAM, hydrophilic SAM, and “bare” Au.

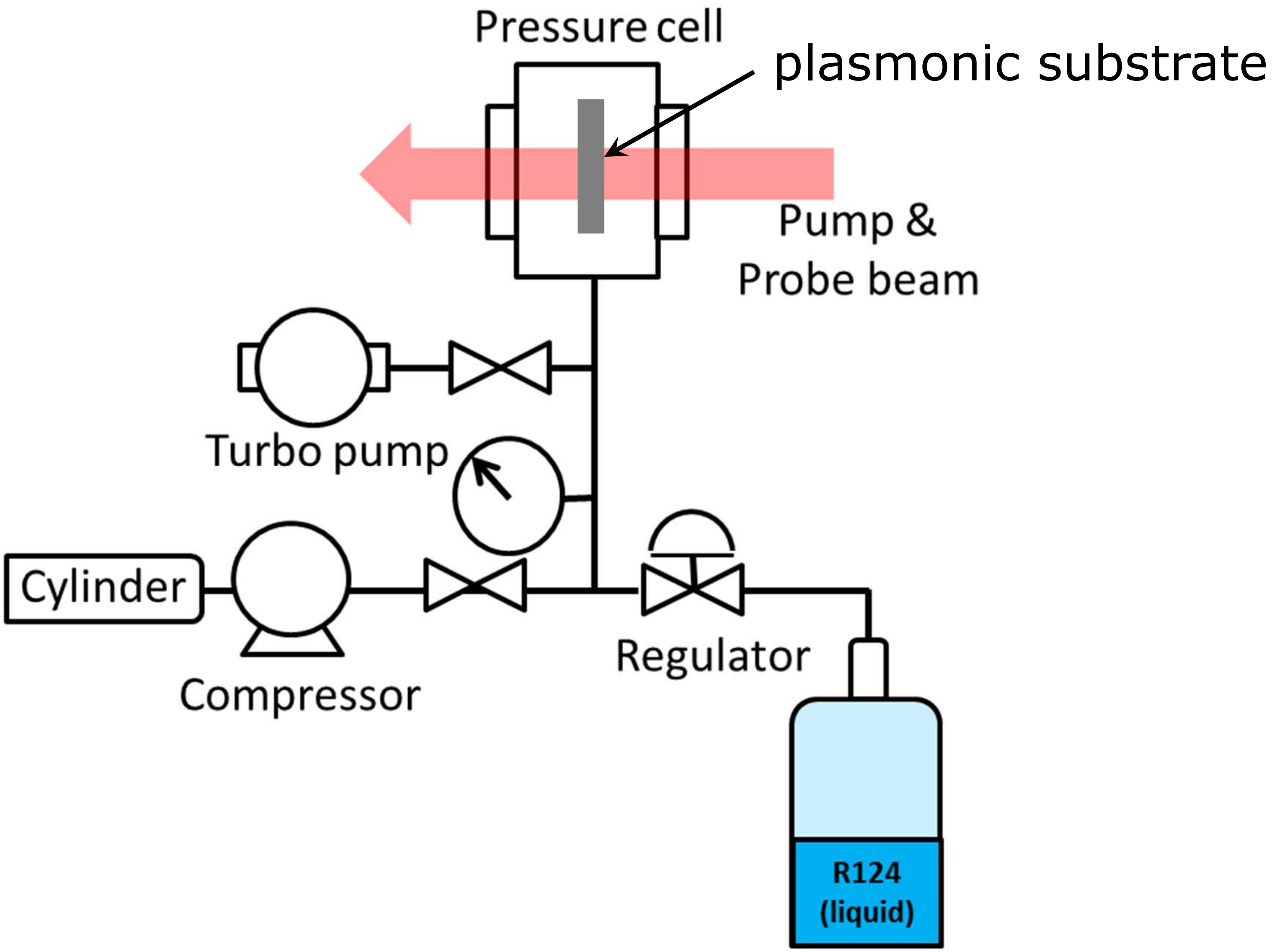
- Data for pure water and pure ethanol are in agreement with prior work for planar interfaces and supported nanoparticles.
- Data for pure ethanol are relatively insensitive to the interface chemistry.
- Competitive adsorption of water at the hydrophilic interface (?)



Kapitza length

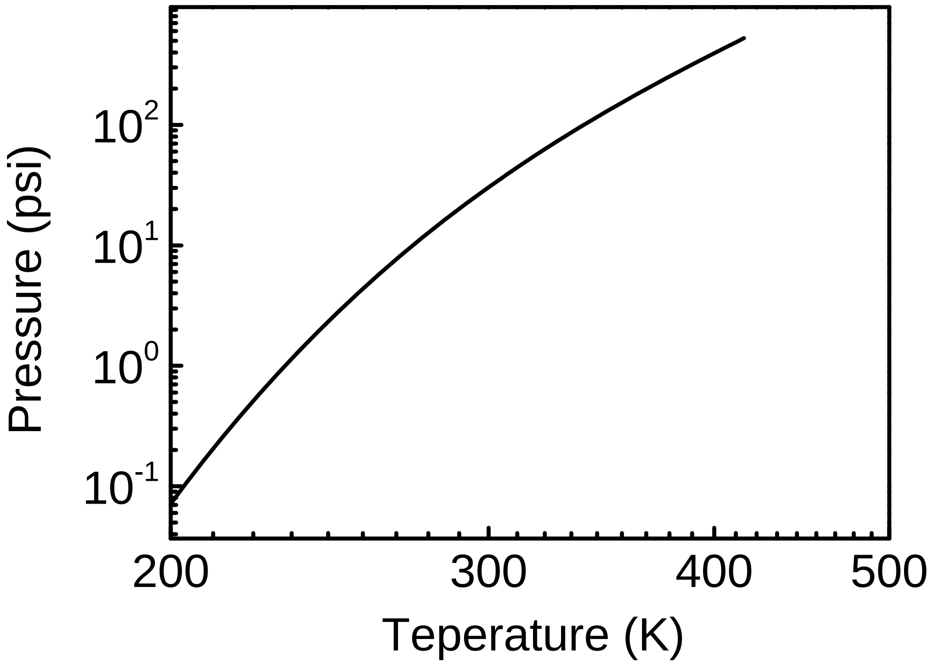
$L_K = \Lambda/G \approx 3$ nm

Initial experiments on a refrigerant as a function of pressure

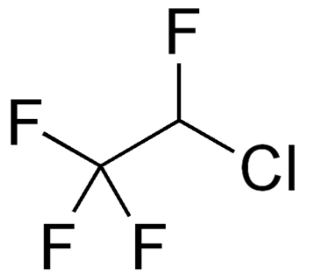


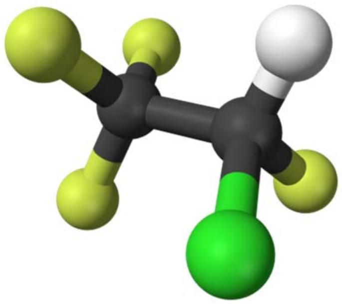
R124 gas chromatograph analysis
1-chloro-1,2,2,2-tetrafluoroethane (99.79%)
1,1,1,2,2 – pentafluoropropane (0.21 %)

- Vapor pressure is ≈40 psi at lab temperature



Data from NIST webbook
(http://webbook.nist.gov/chemistry/)

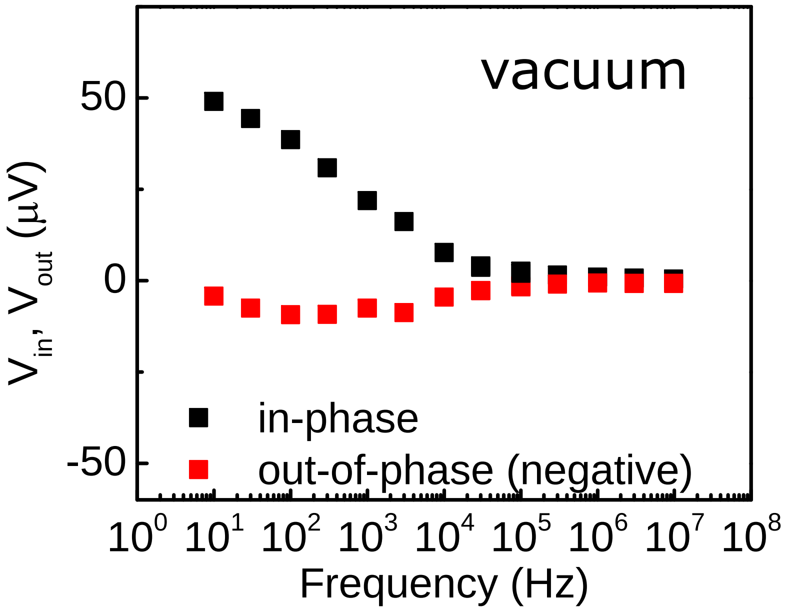


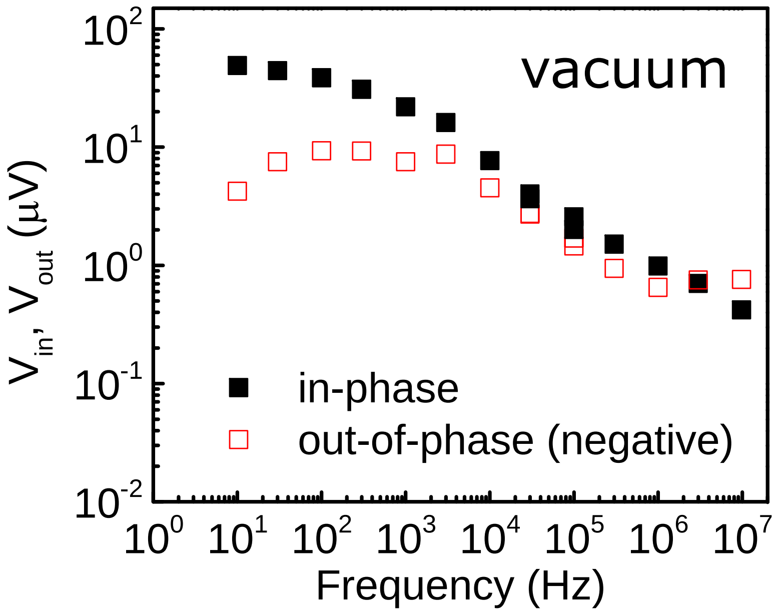


wikipedia.org

Initial experiments are “frequency domain” (not “time-domain”) to access longer time scales

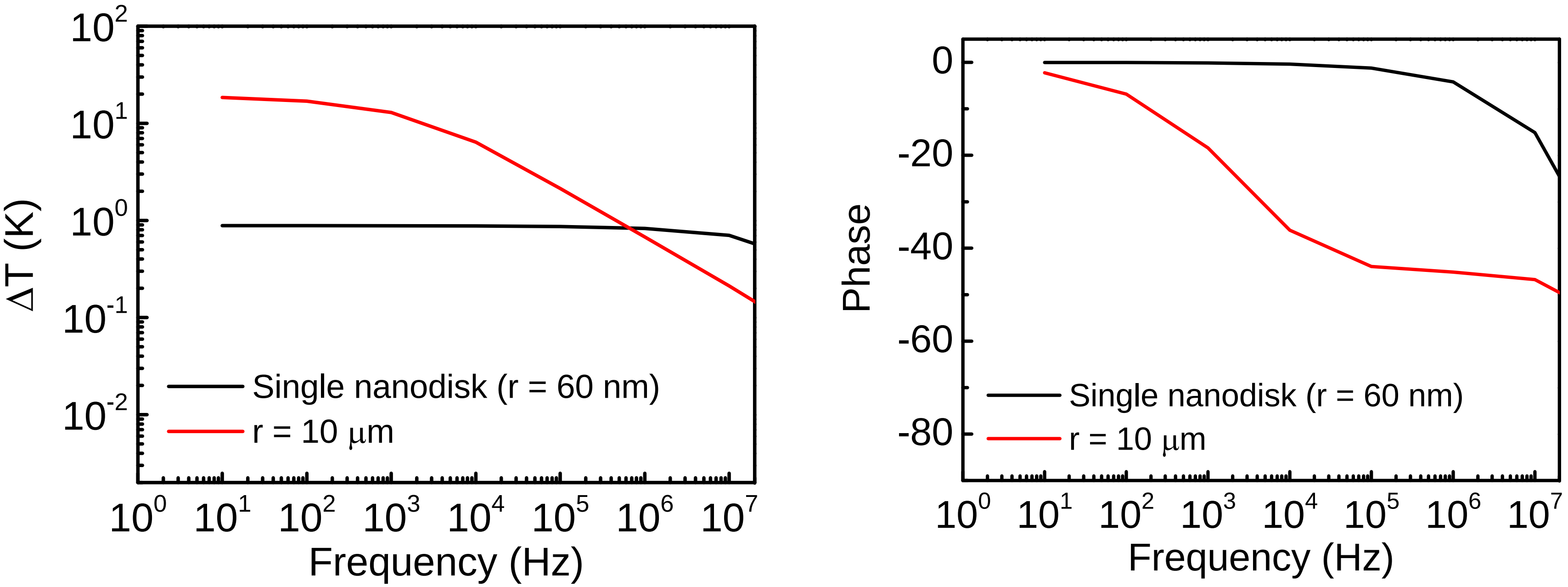
- Fixed negative delay time (probe pulse arrives 20 ps before pump pulse)
- Vary frequency of pump over a wide range (10 Hz to 10 MHz)
- Correct for the phase and amplitude of the system response using pump beam directly incident on the fast photodiode.
- In vacuum, the signal is due to the Au temperature





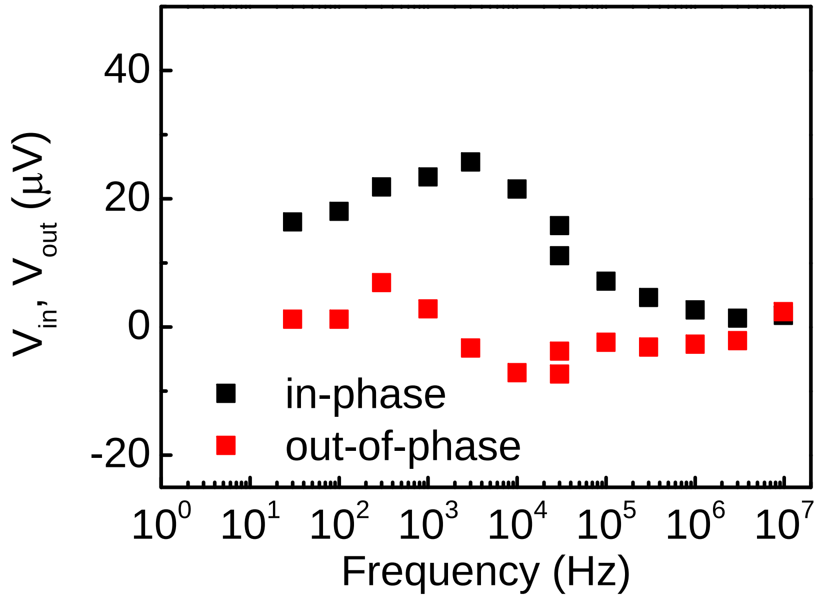
Only at the highest frequencies (>1 MHz) is the temperature not laterally homogeneous on the length scale of the separation between Au nanodisks (200 nm)

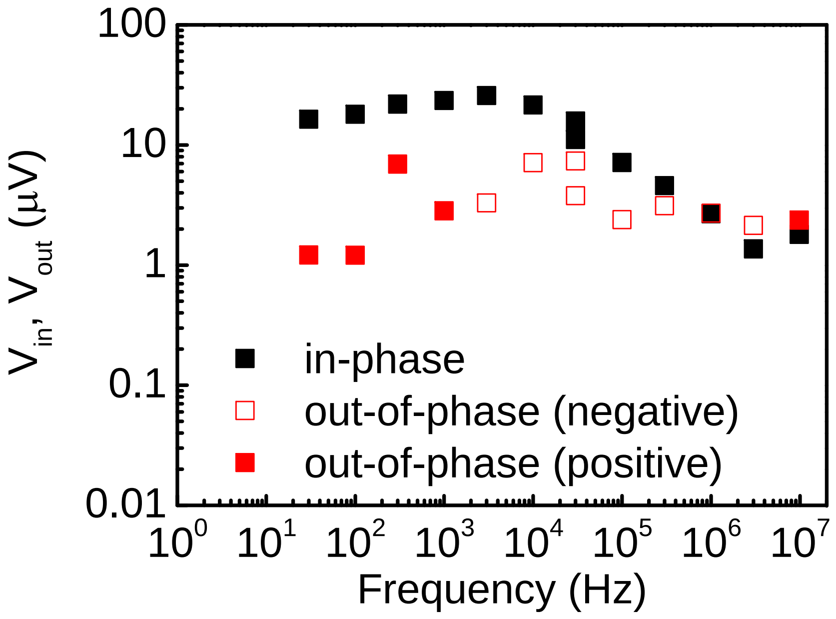
Calculated thermal response, 3 mW pump



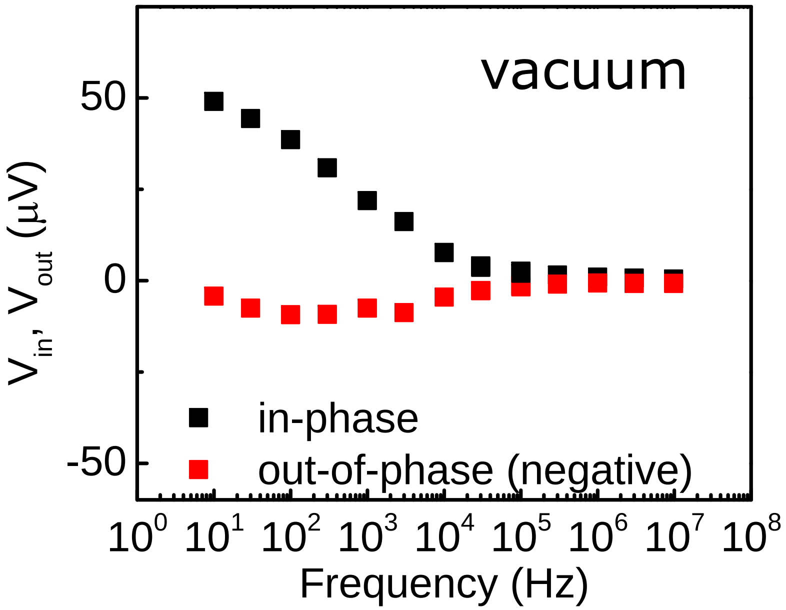
Now add R124 at 17 psi (approximately ½ of the vapor pressure)

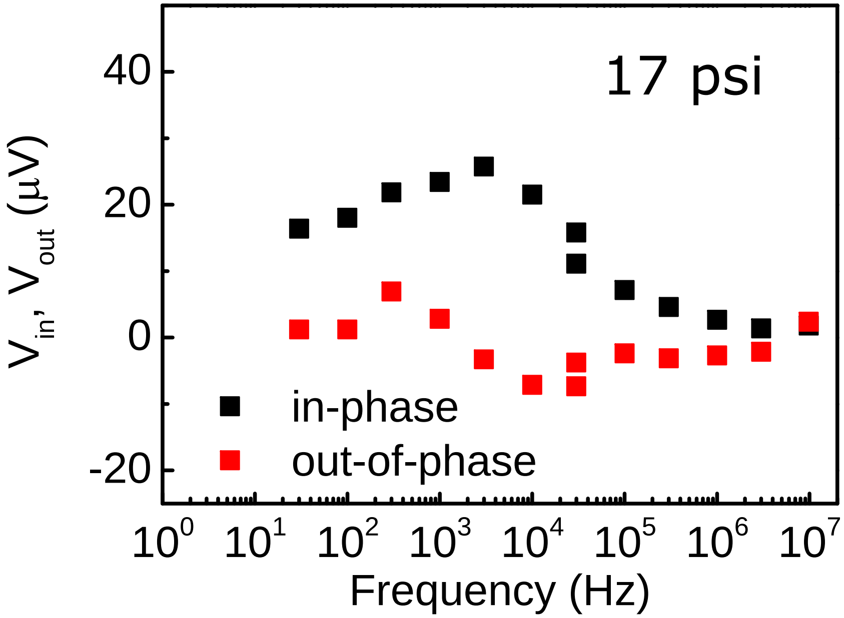
- Difference between vacuum and 17 psi only appears at f<10 kHz.
- Work in progress. Results are not what we were expecting. (Much smaller and much slower).
- Au surface is coated by hydrophobic SAM. Maybe not completely stable in contact with refrigerant vapor
- Will need to consider Maragoni effects (fluid flow) in addition to evaporation/condensation





Comparison of vacuum and 17 psi of R124





Summary

- Plasmonic nanodisks are powerful platform for probing small changes in index of refraction due to temperature excursions in liquids or evaporation/condensation of thin layers (or changes in density/pressure) near an interface.
- Signal due to the index of refraction of the fluid provides greater sensitivity to interface conductance (needed when the thermal effusivity of the fluid is small).
- Kaptiza length for ethanol in contact with hydrophilic and hydrophobic SAMs is ≈3 nm.
- Experiments on refrigerant (R124) as a function of pressure, temperature, and surface chemistry are in progress.