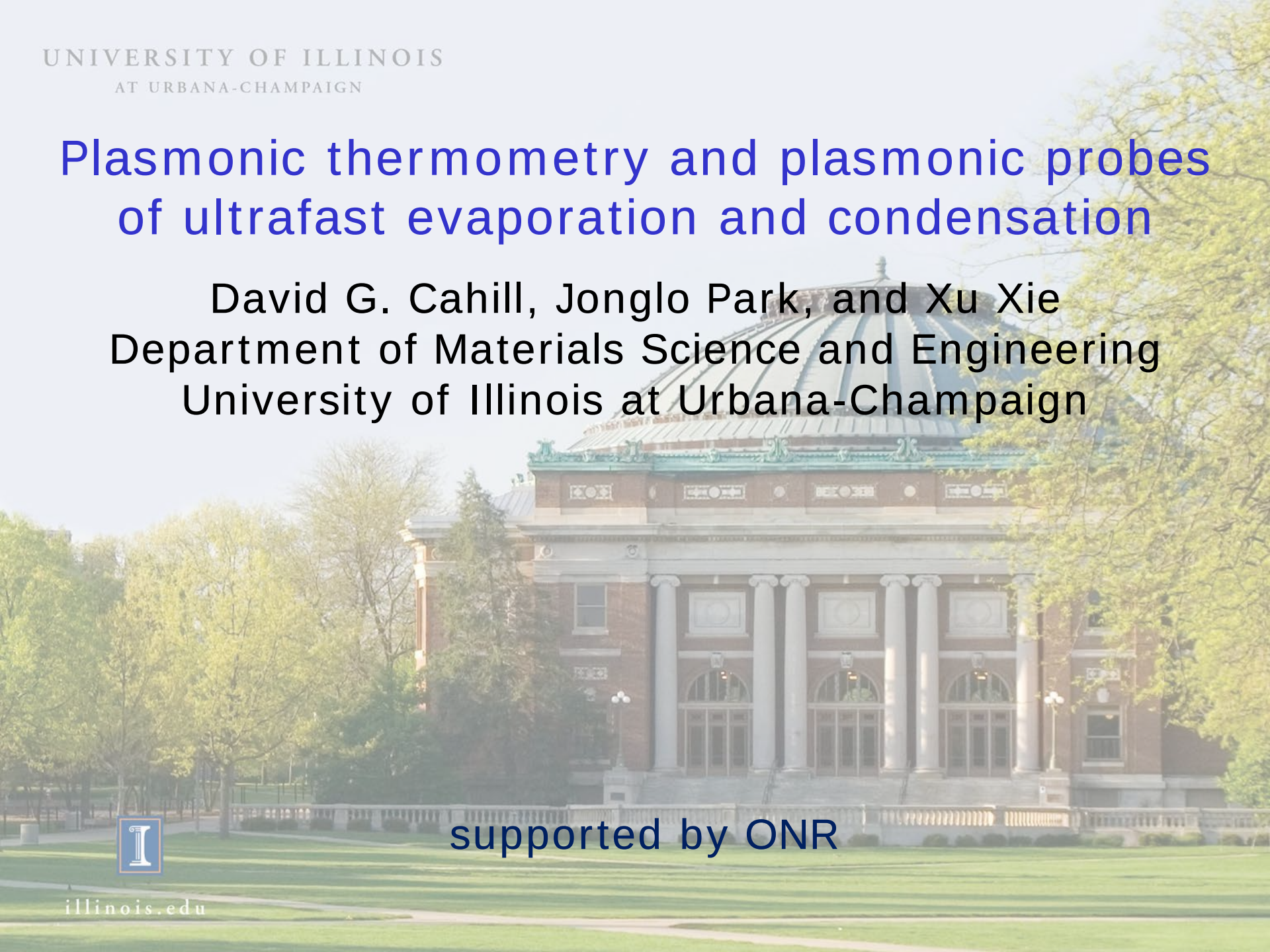

Plasmonic thermometry and plasmonic probes of ultrafast evaporation and condensation

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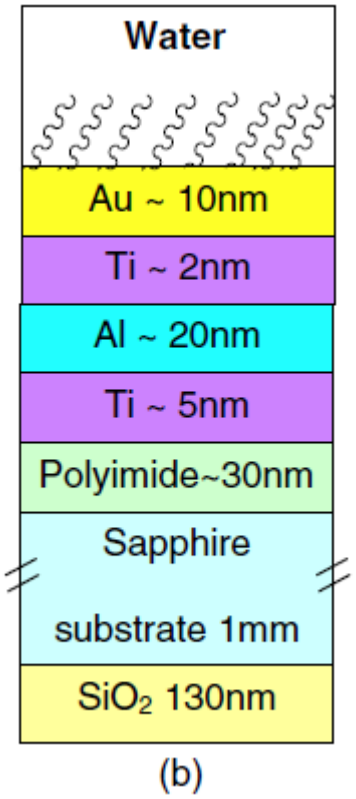
Department of Materials Science and Engineering
University of Illinois at Urbana-Champaign

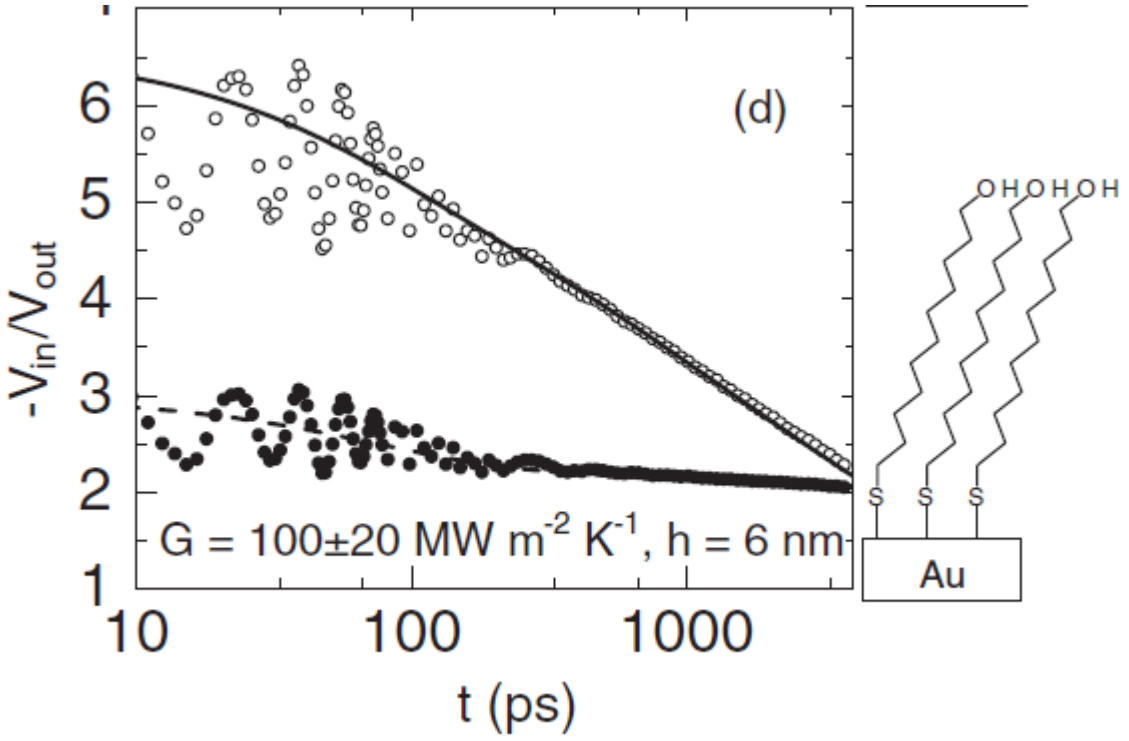
supported by ONR

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

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



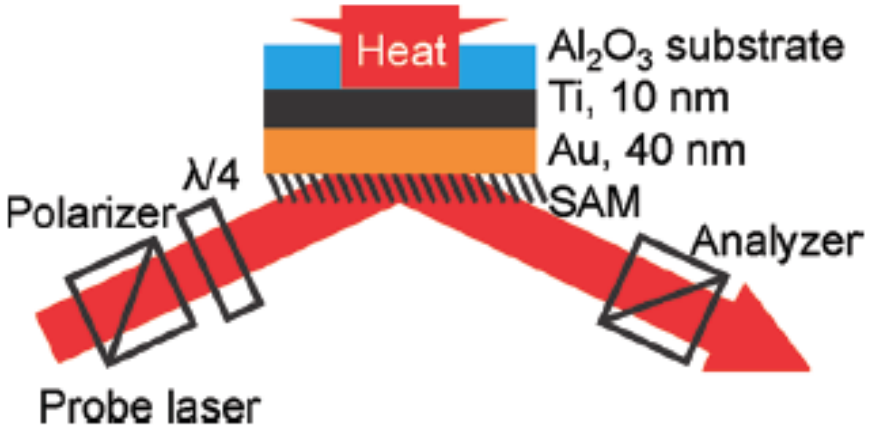
(b)

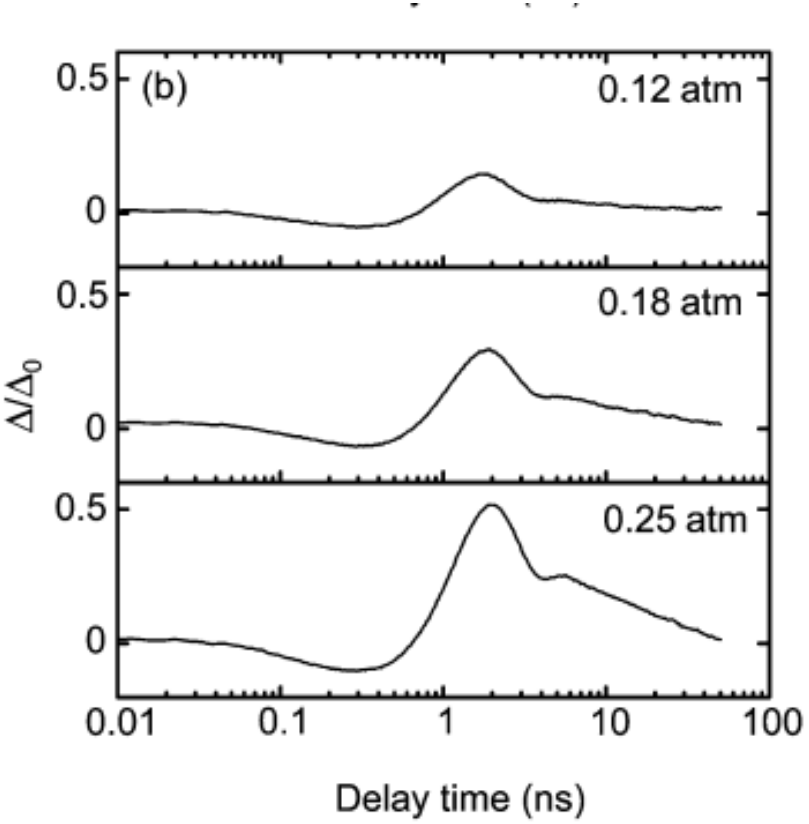


Ge *et al.*, *Phys. Rev. Lett.* (2006)

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

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





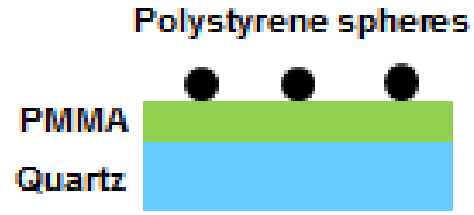
Min *et al.*, *J. Phys. Chem*. C (2012)

Outline

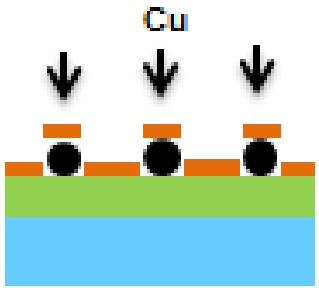
- Nanodisk sensors (prepared for us on silica by Insplorion and fabricated by us on quartz crystals) and characterization of their sensitivity and depth resolution.
- Application to interface thermal conductance and thermal diffusivity of fluids.
- Application to fast condensation and evaporation of a refrigerant (R124) from interfaces with controlled chemistry.

Nanodisk plasmonic sensors

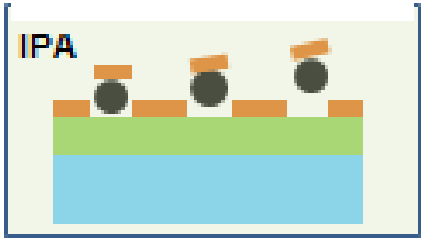
- Fabricated by “hole-mask colloidal lithography”



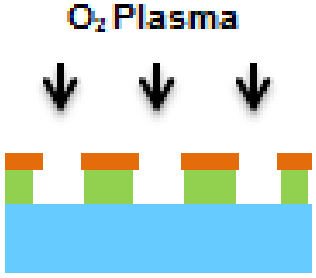
1) Spin-coating of resist and dispersion of spheres on top



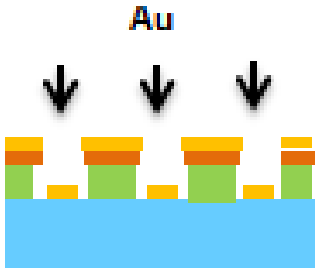
2) Evaporation of metal mask



3) Stripping off the spheres by sonication in IPA



4) Oxygen plasma etching



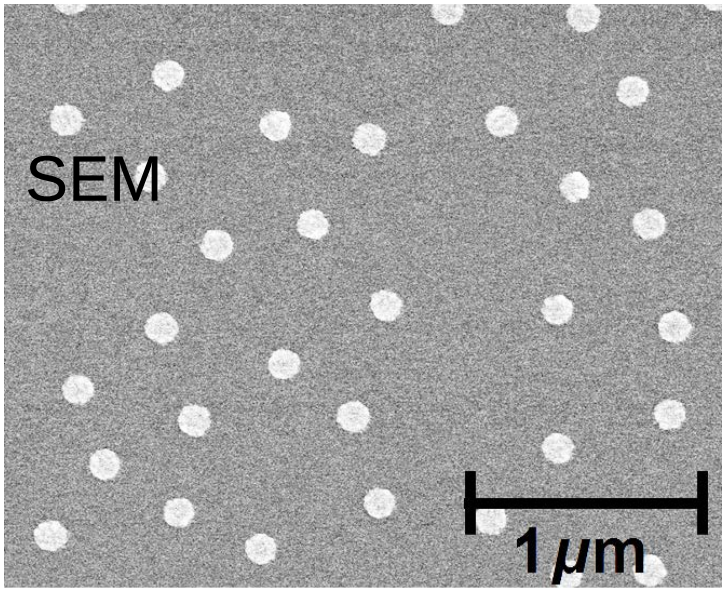
5) Au deposition

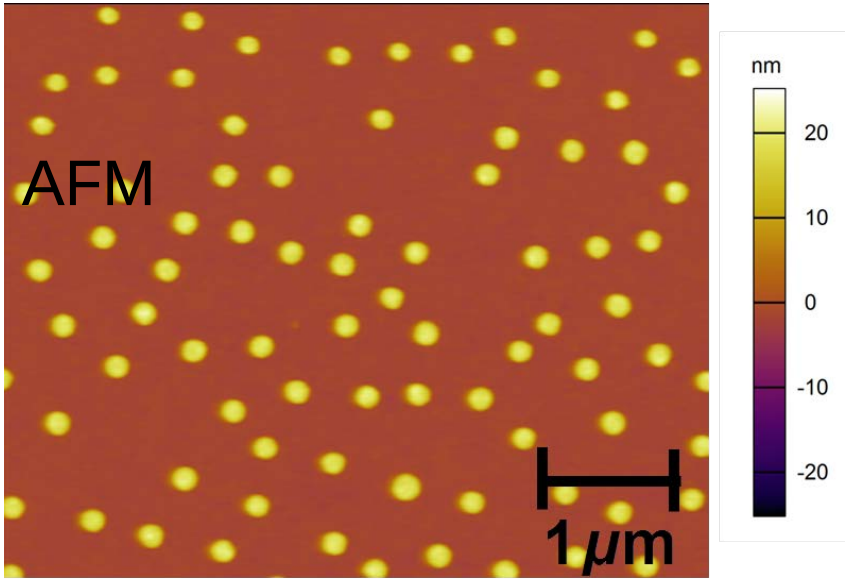
6) Lift-off

Nanodisk plasmonic sensors

- SEM gives the most accurate measurement of diameter
- AFM gives the most accurate measurement of height

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





Park and Cahill, J. Phys. Chem. C (2016)

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

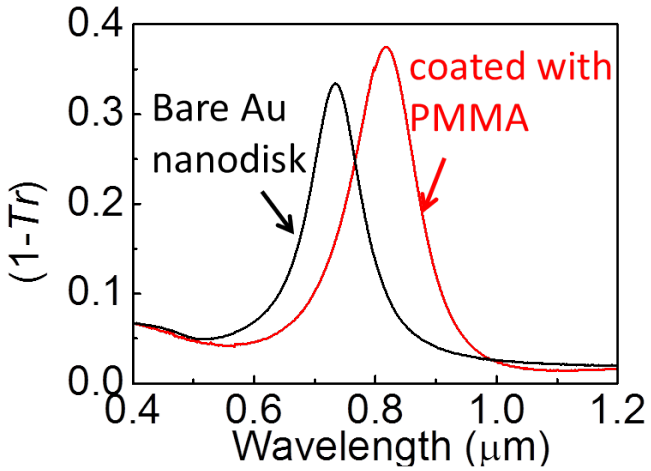
- Coat with PMMA and take difference spectra of the absorption.
- Noise floor of pump-probe measurements is

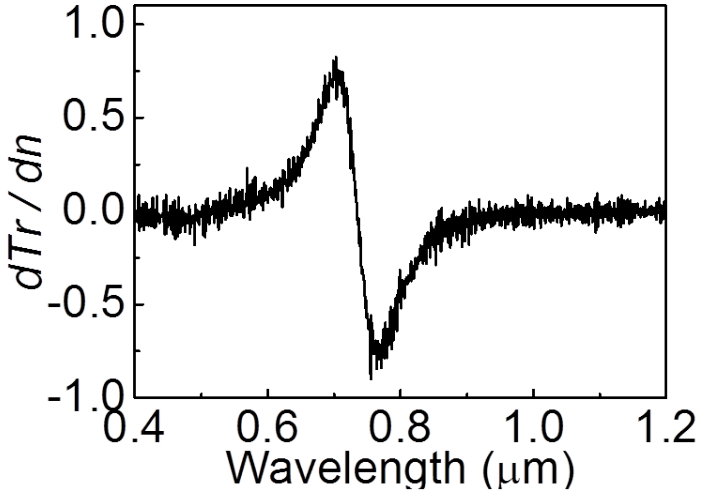
$$\Delta n \approx 0.3 \text{ ppm Hz}^{1/2}$$

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

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

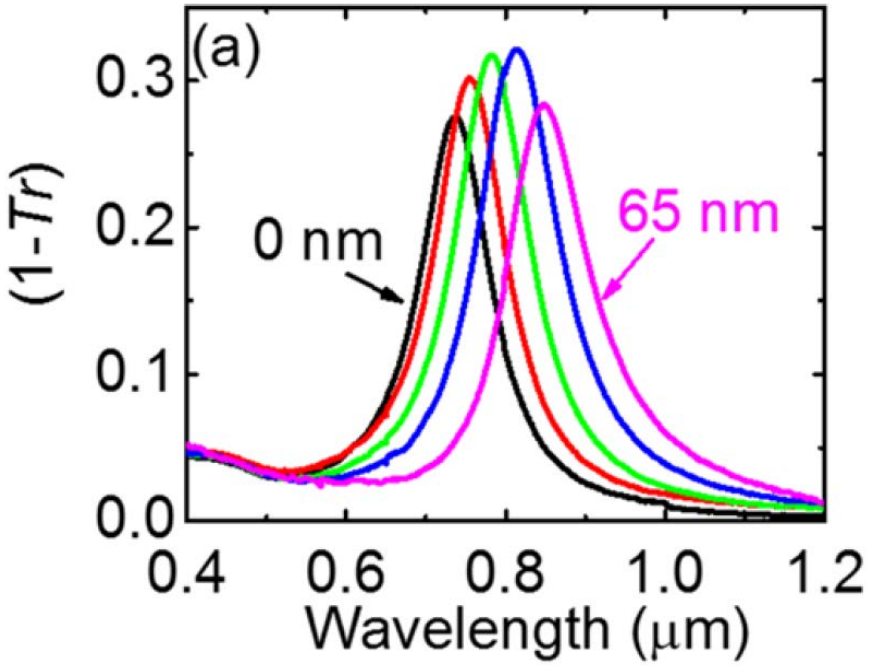
Tr = transmission

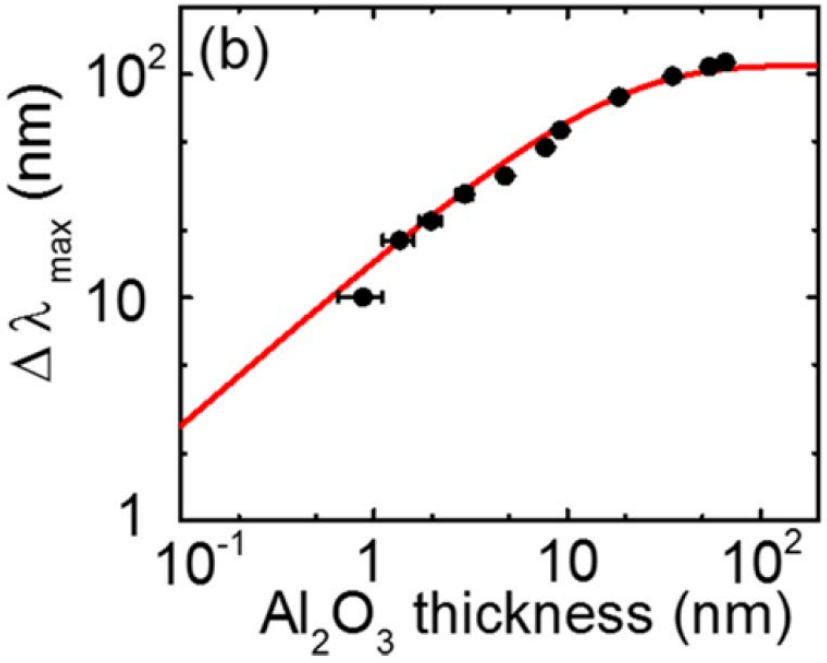




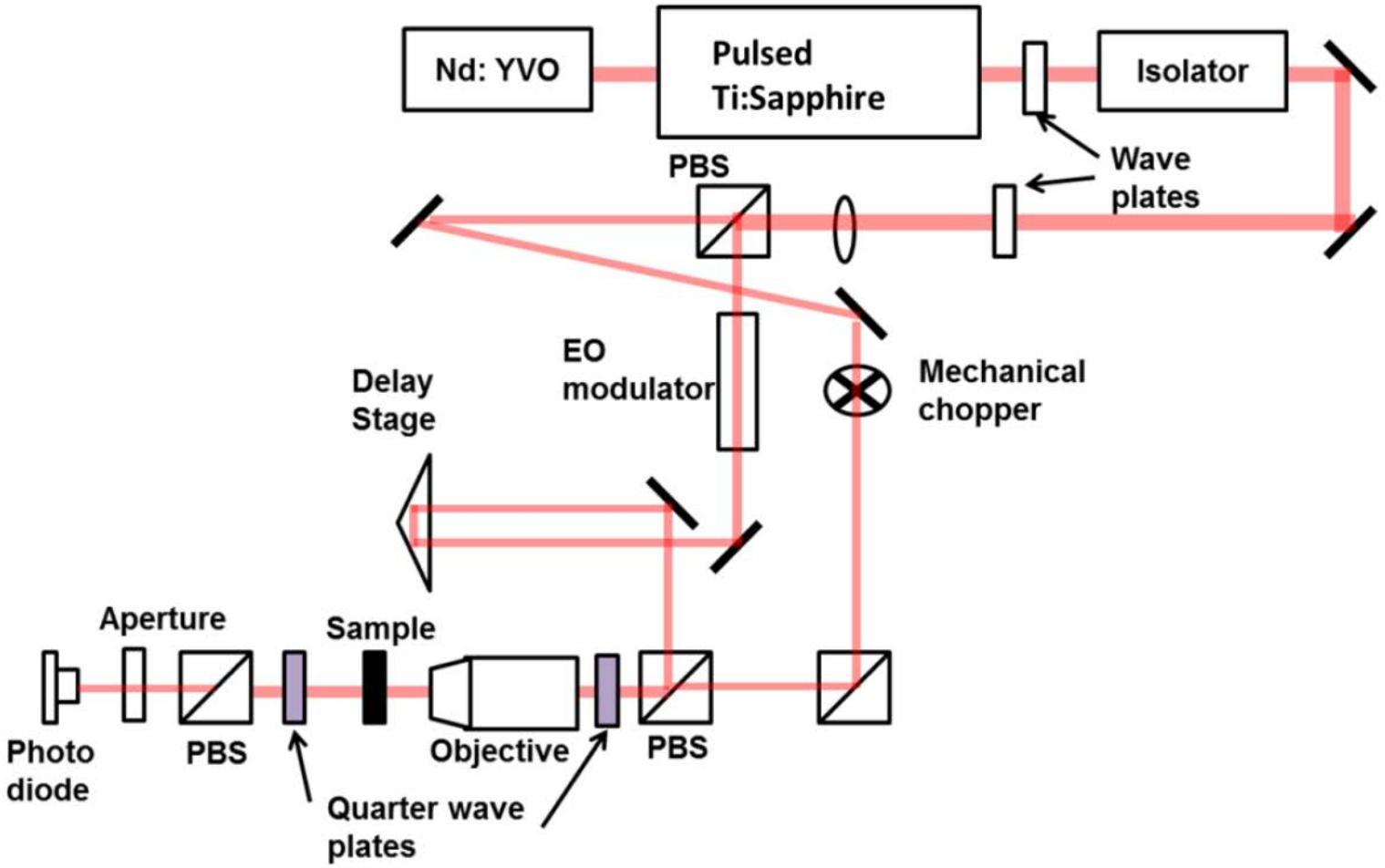
Sensitivity to *dn* is localized to within 13 nm of the Au surface

- Atomic-layer deposition of alumina
- Alumina thickness on planar Au surface measured by ellipsometry.





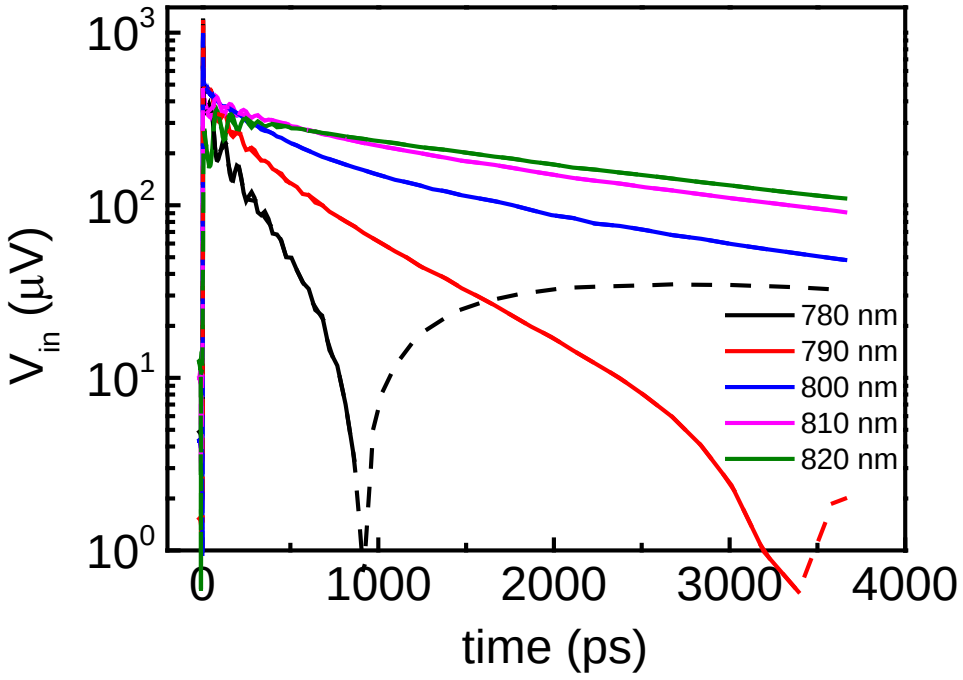
Transient absorption



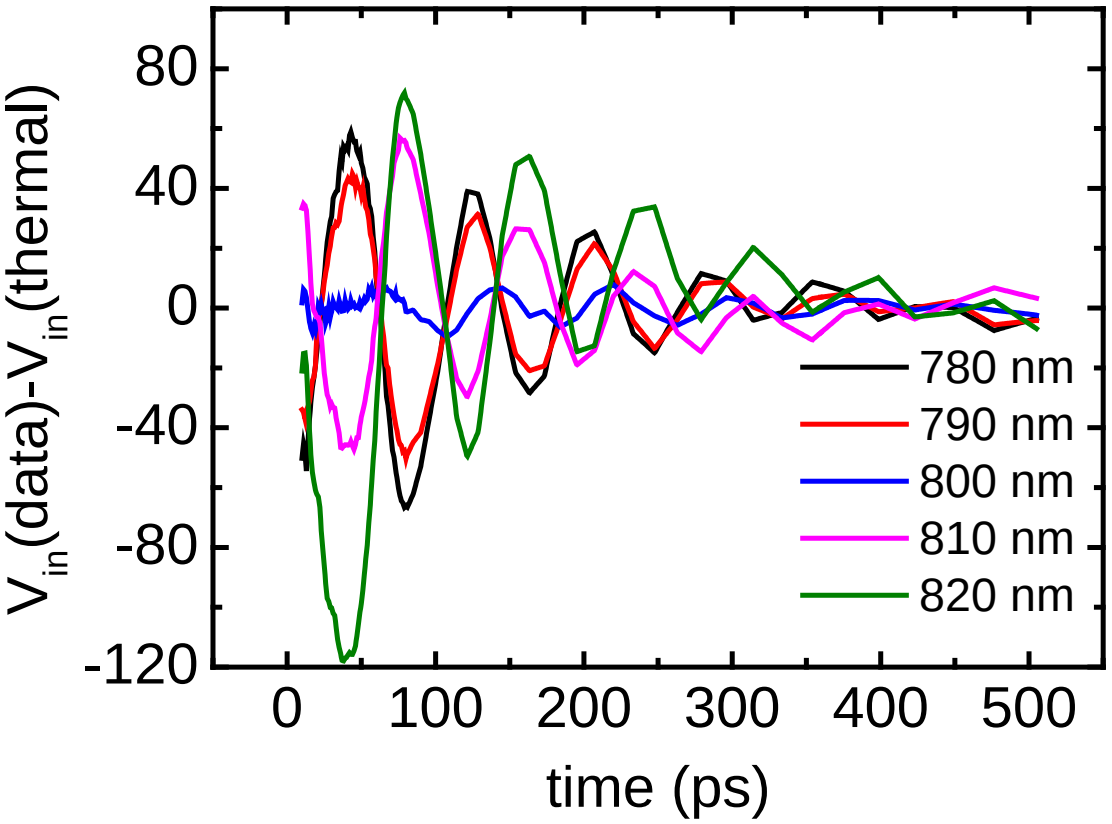
Signal is a combination of the temperature change of the Au and the temperature change of the surroundings

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

- Isolate the two terms using a linear combination of the response at two wavelengths.



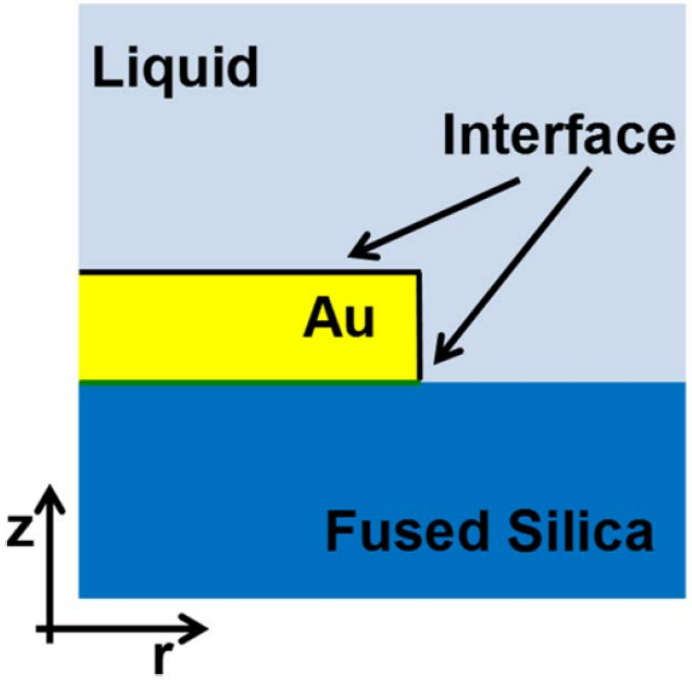
Signal from the lateral “breathing mode” acoustic oscillation is minimized at the same wavelength that minimizes the sensitivity to fluid temperature



Data after subtracting thermal response

Numerical modeling of the temperature field

- 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)*(n_{Al2O3}/n_{liquid}) of the Au nanodisk
- Au/silica interface conductance from an independent measurement.

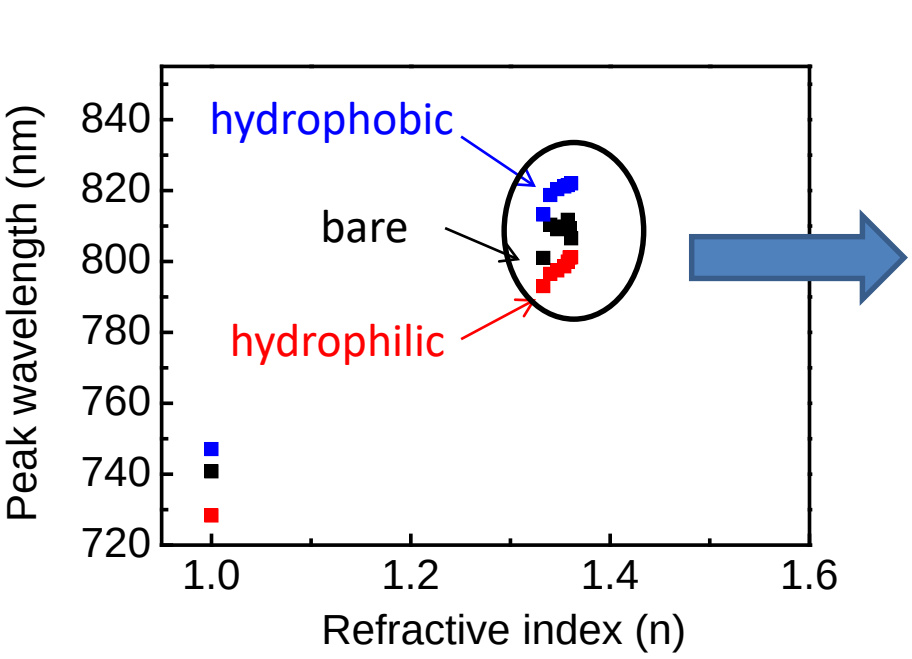


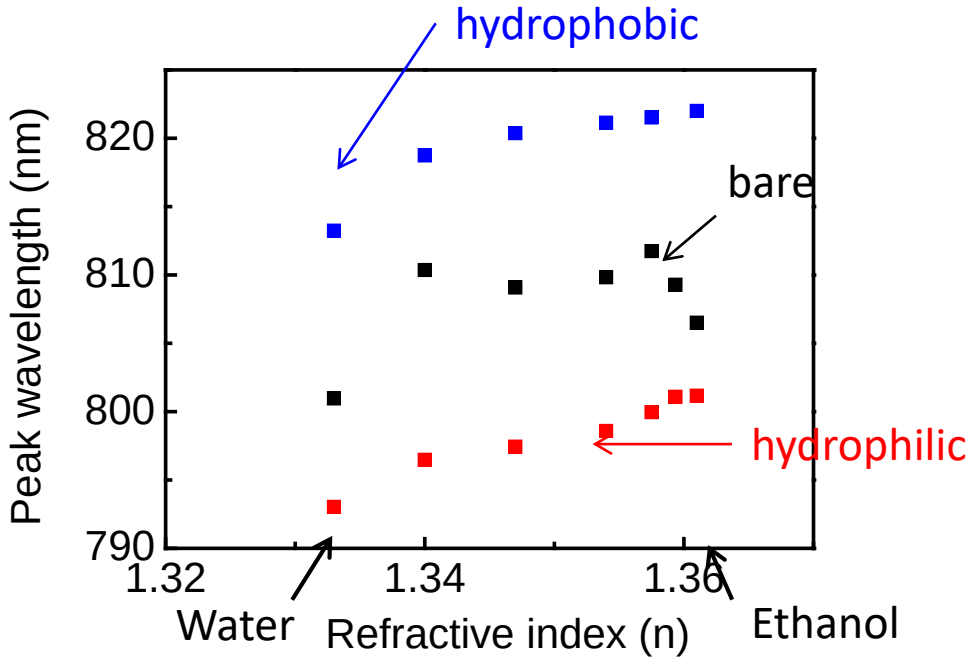
Park and Cahill, J. Phys. Chem. C (2016)

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.

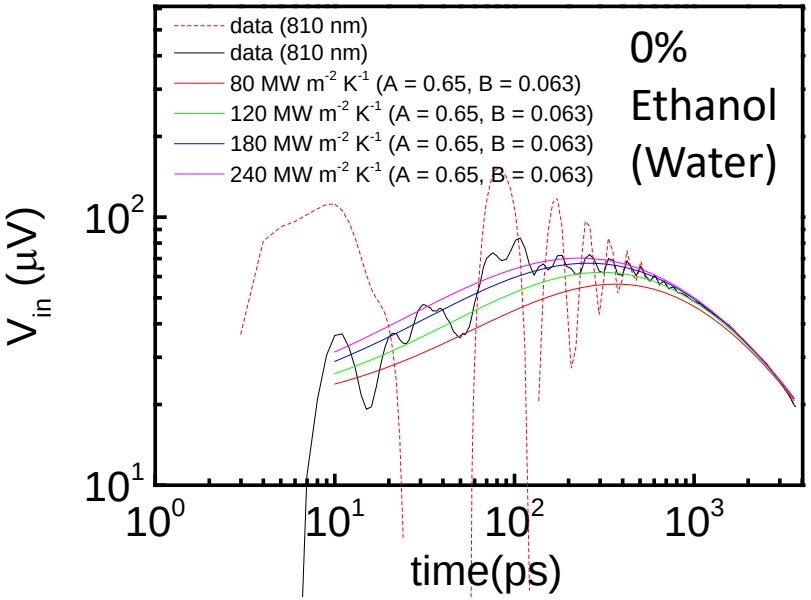
Hydrophilic $HS(CH_2)_3SO_3$ and hydrophobic $HS(CH_2)_9CH_3$

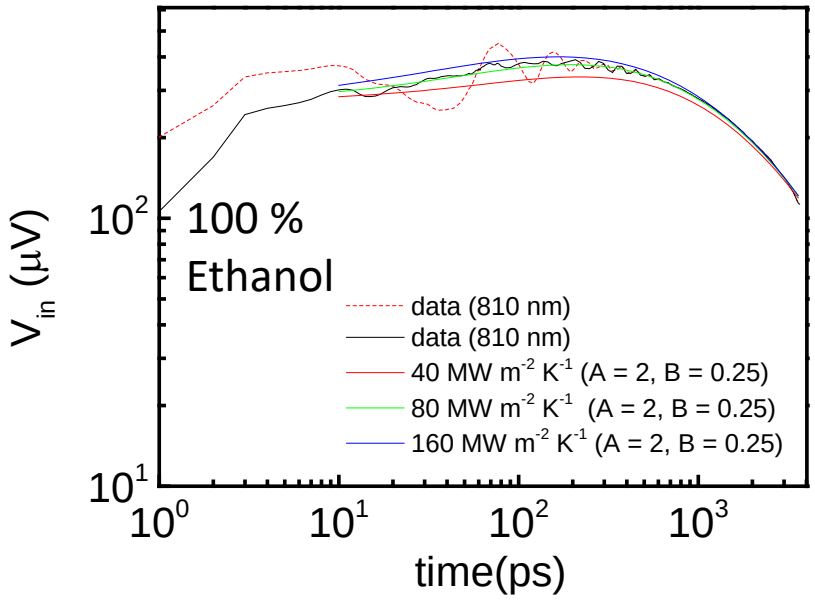




Data acquisition and analysis for interfaces with fluid mixtures

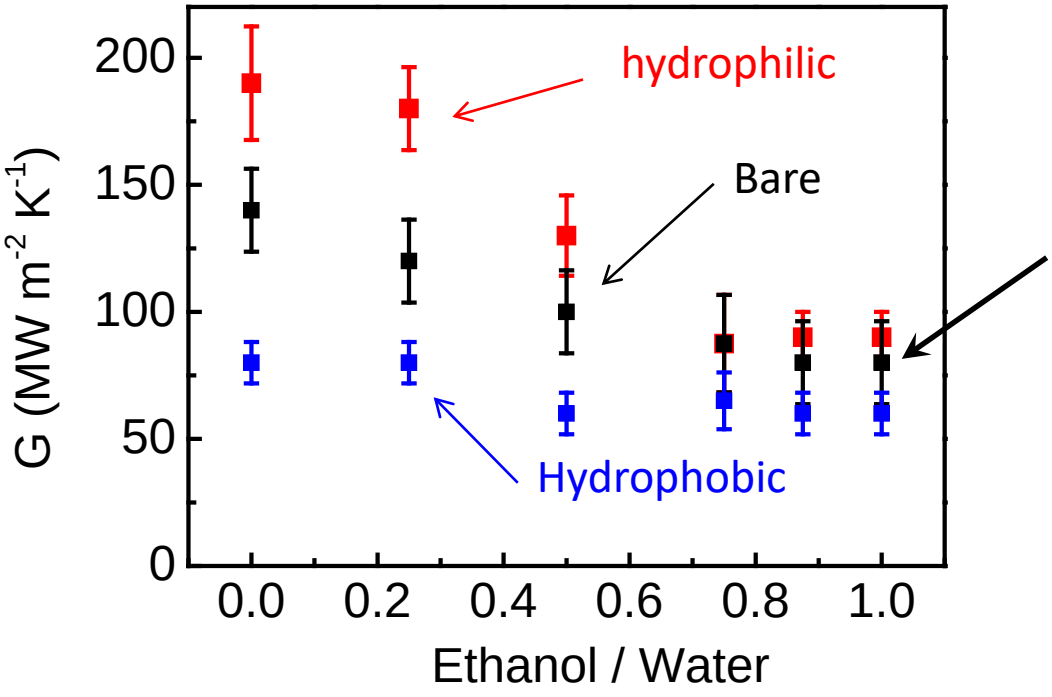
- Shift wavelength to optimize sensitivity to fluid temperature near the interface.
- Subtract breathing mode acoustic signal by fitting to a damped oscillator
- Compare to thermal model with interface conductance as a free parameter





Vary liquid composition between pure water and pure ethanol 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.



Kapitza length

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

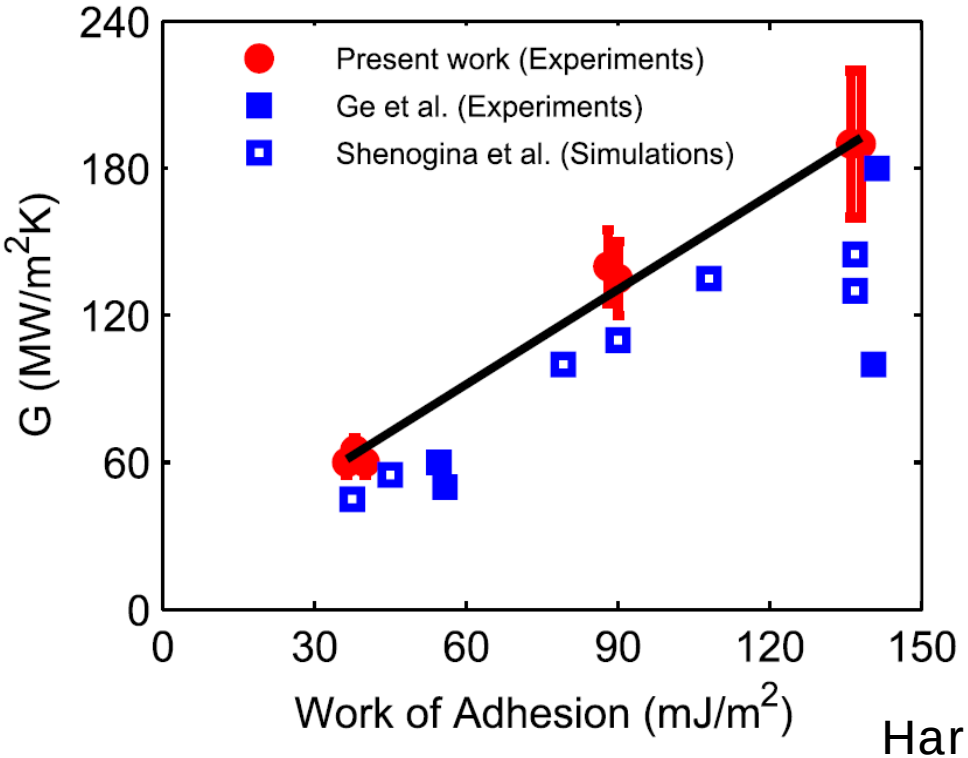
Convert the dependent variable from liquid composition to a thermodynamic parameter

- Prior theory, computation, and experiment has shown a linear relationship between *G* and work-of-adhesion *W*.

$$W = \gamma(1+\cos(\theta))$$

surface tension

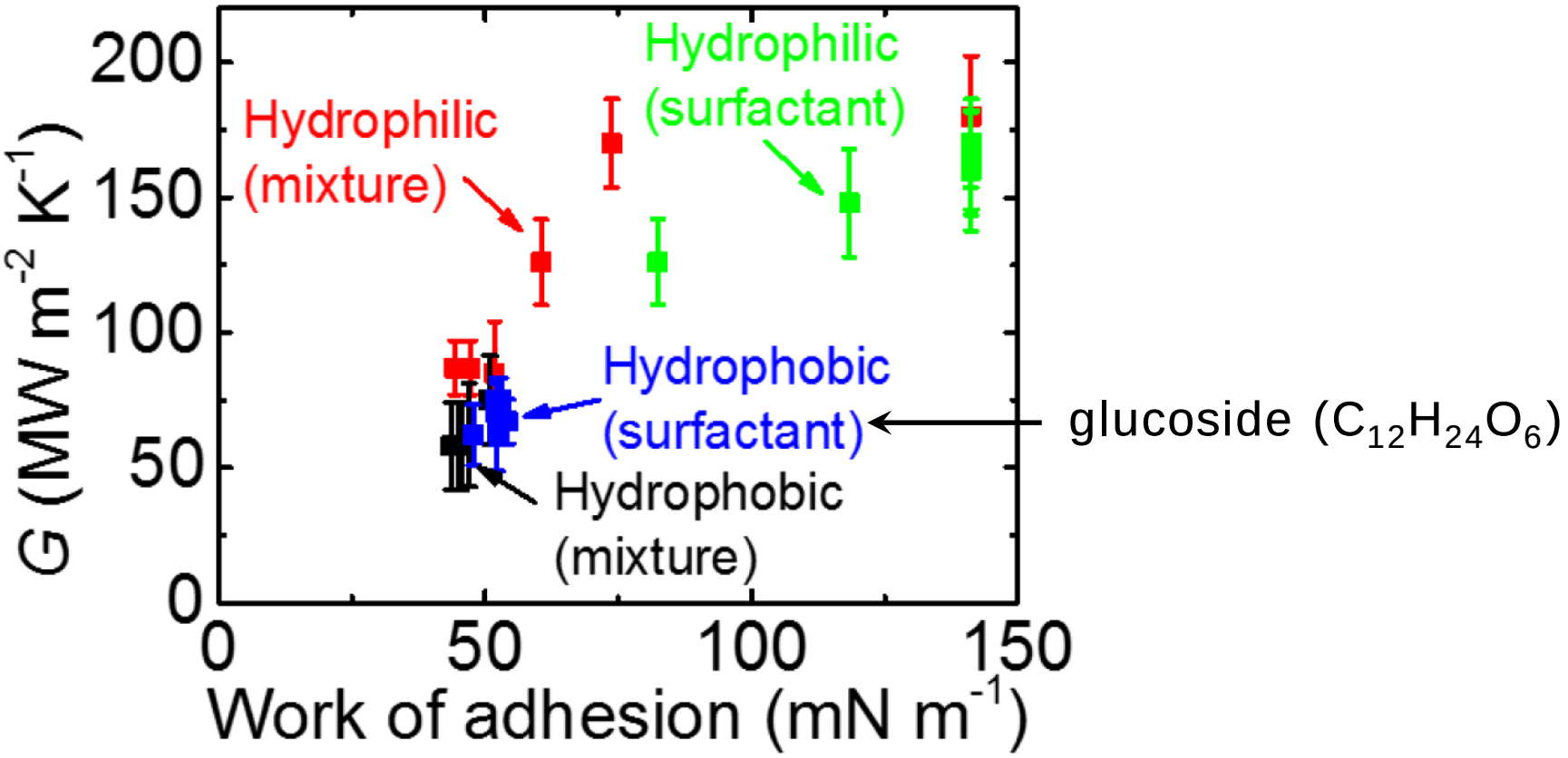
contact angle



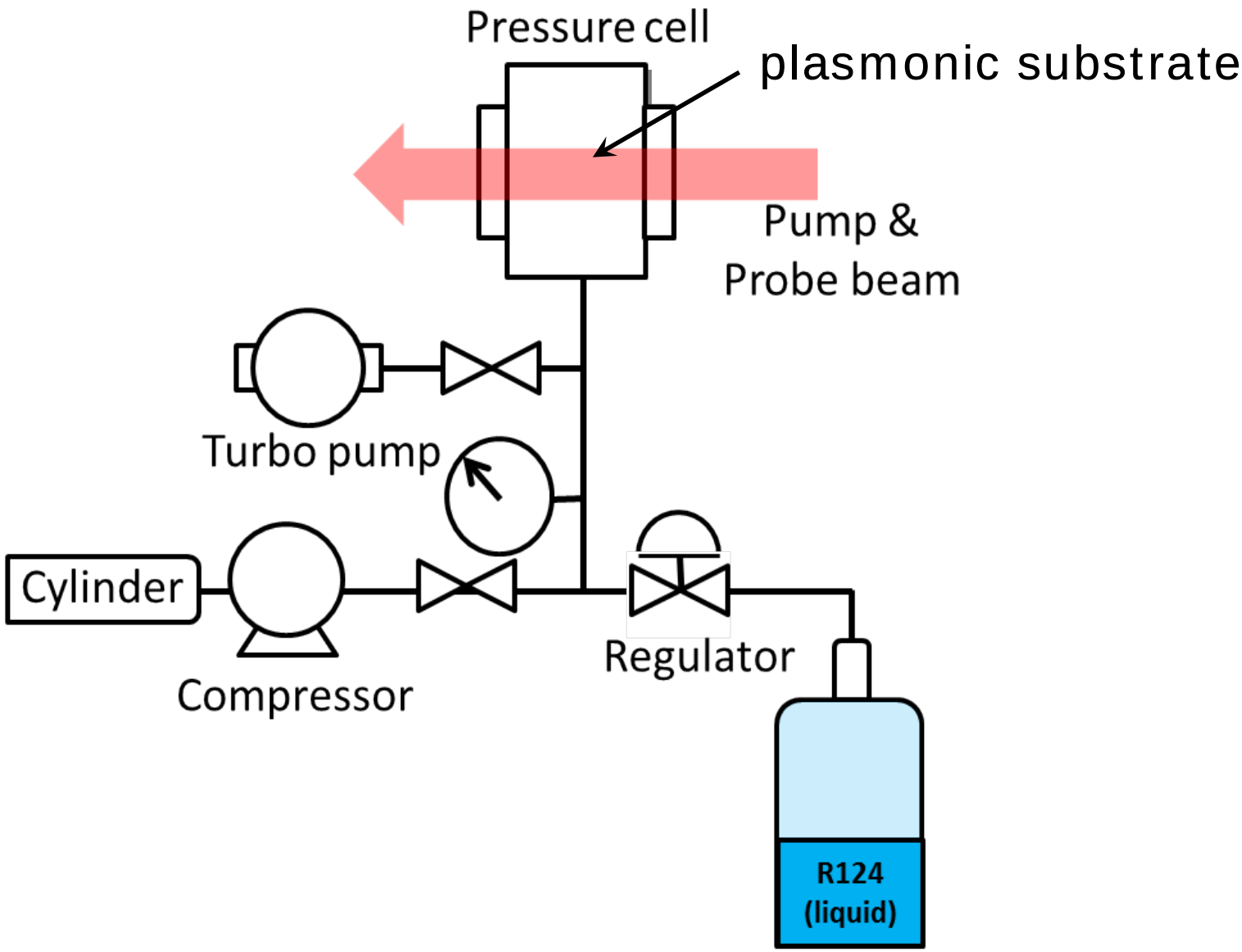
Harikrishna et al. (2013)

$G \propto W$ does not describe the interface thermal conductance of hydrophilic SAM for water/ethanol

- Water/ethanol mixture and water/surfactant,
- Work-of-adhesion to hydrophobic surfaces is essentially constant.

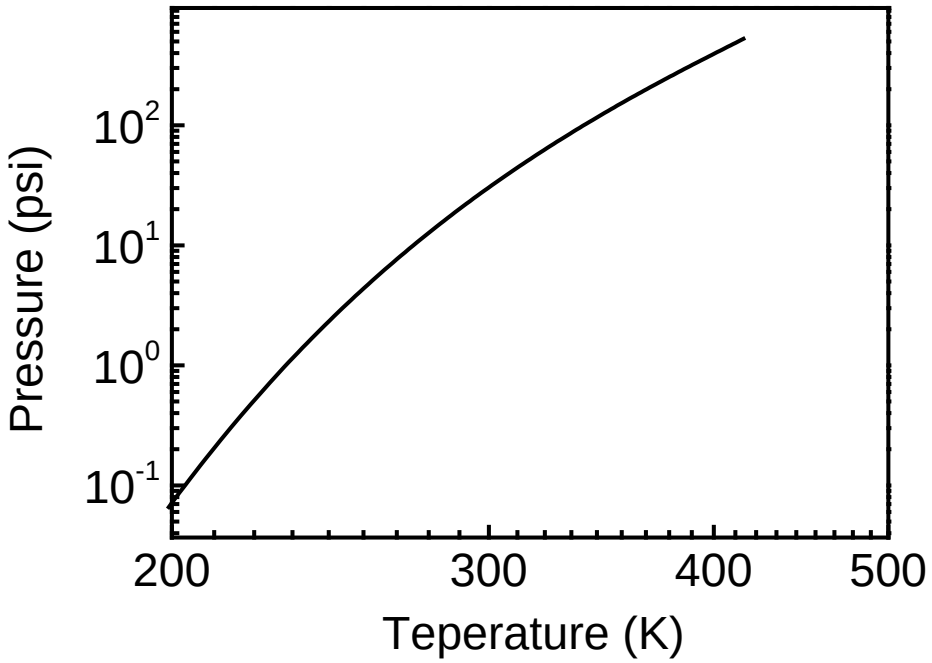


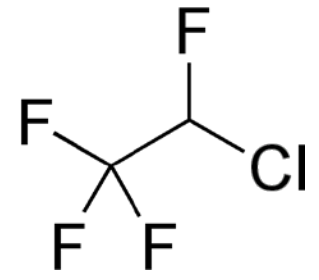
Replace bulk liquid with an adsorbed refrigerant layer as a function of pressure

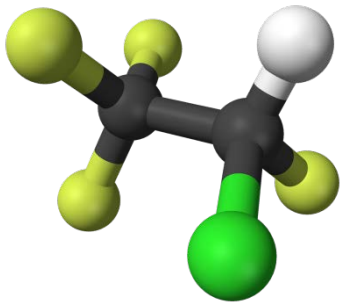


R124 gas chromatograph analysis
1-chloro-1,2,2,2-tetrafluoroethane (99.79%)
1,1,1,2,2 – pentafluoropropane (0.21 %)

- Vapor pressure is ≈40 psi at lab temperature





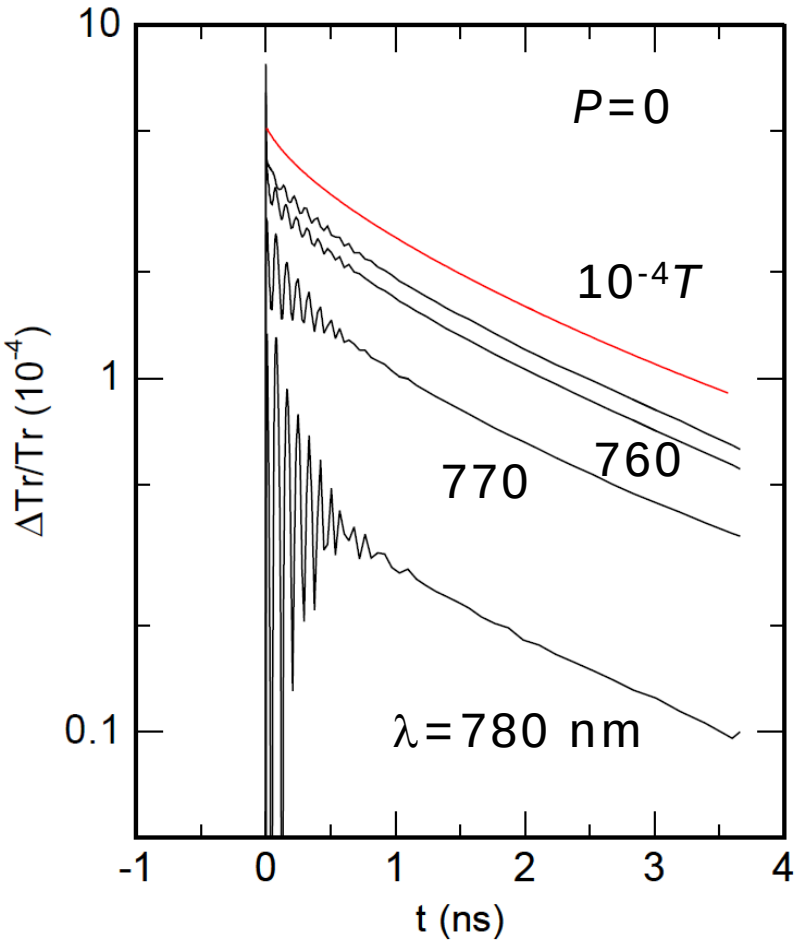


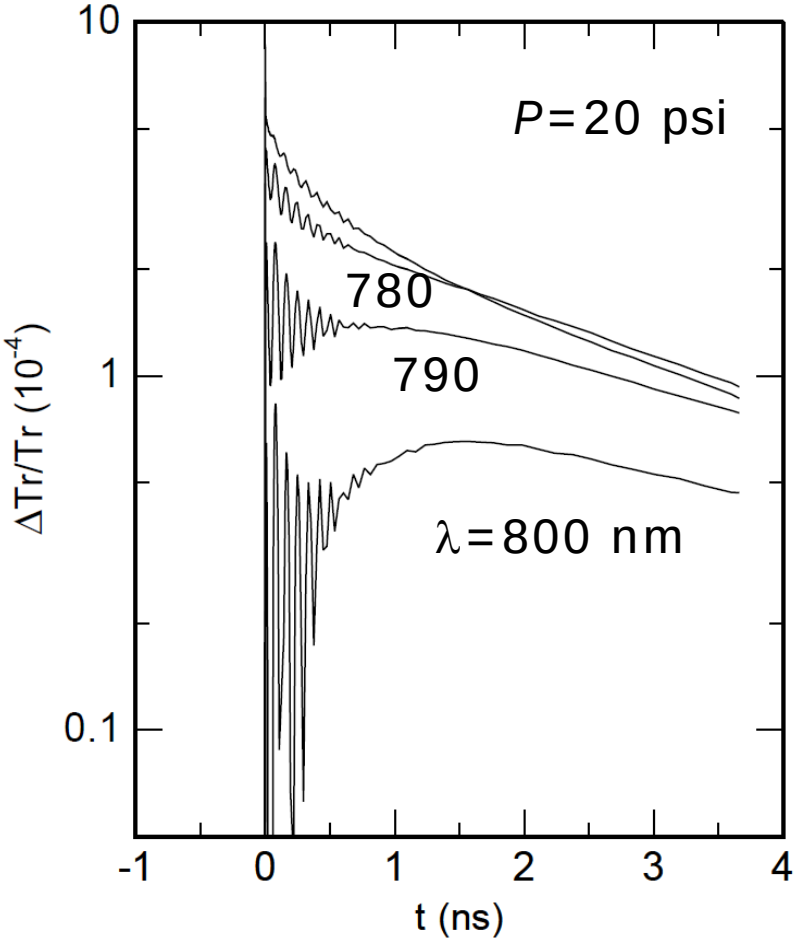
wikipedia.org

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

Same approach: measure response at peak absorption (Au temperature) and red-shifted (changes in thickness of adsorbed layer)

- Instead of measuring $\Delta n(15\ nm)$; measure $(n-1)\Delta h$



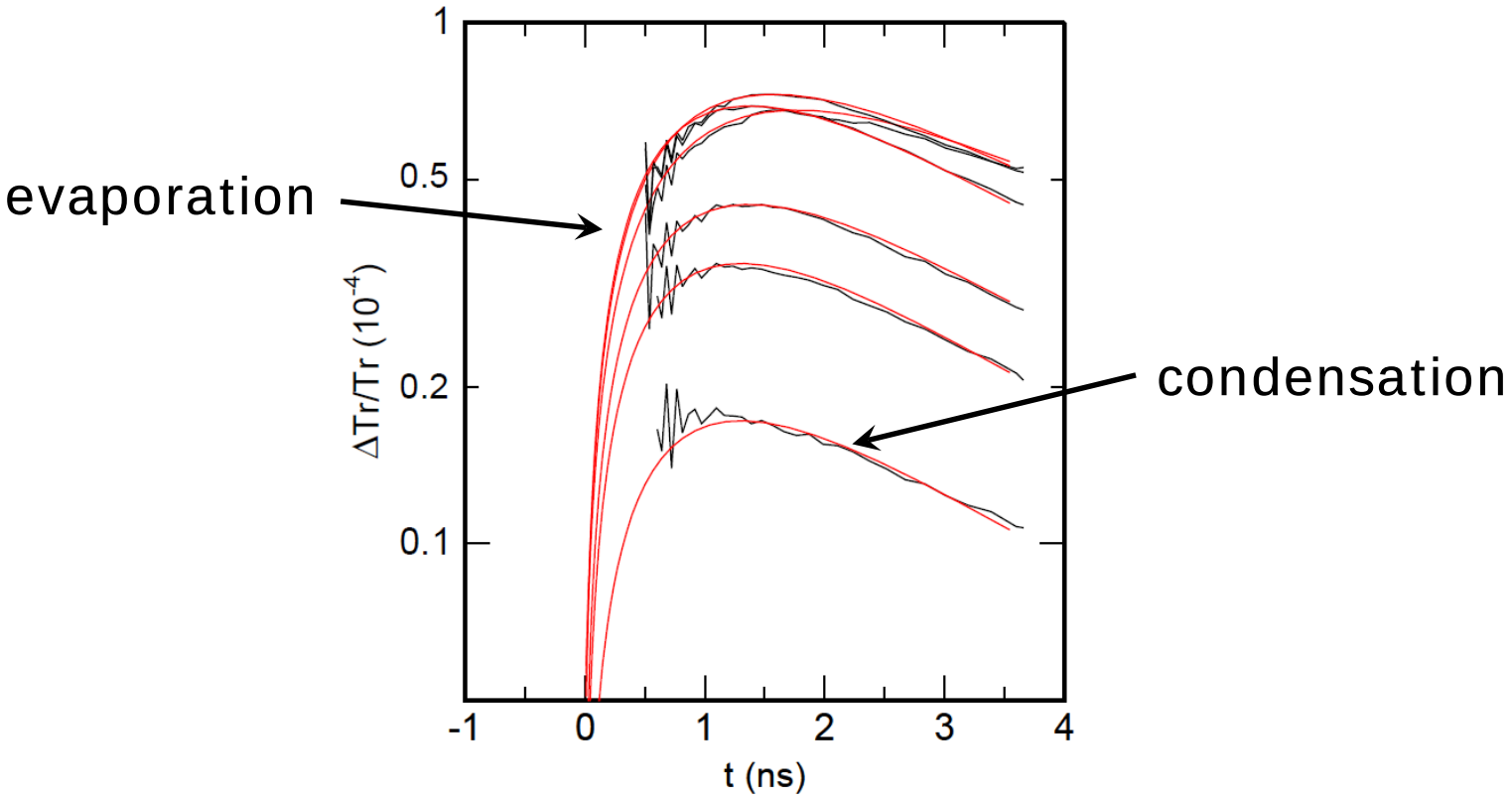


Isolate contribution from Δh and compare to model

- Model assuming linear response
- In the frequency domain, thickness response is simply a low-pass filter applied to the temperature response

$$\Delta h = g(t) * T(t)$$

$$g(t) = \frac{A}{\tau} \exp\left(-\frac{t}{\tau}\right)$$



Relate the interface velocity $v(t)$ to kinetic and thermodynamic factors

volume per molecule

vapor pressure at T(t)

equilibrium vapor pressure at T_0

$$v(t) = \eta\Omega \frac{P(t) - P_{eq}}{\sqrt{2\pi M k_B T}}$$

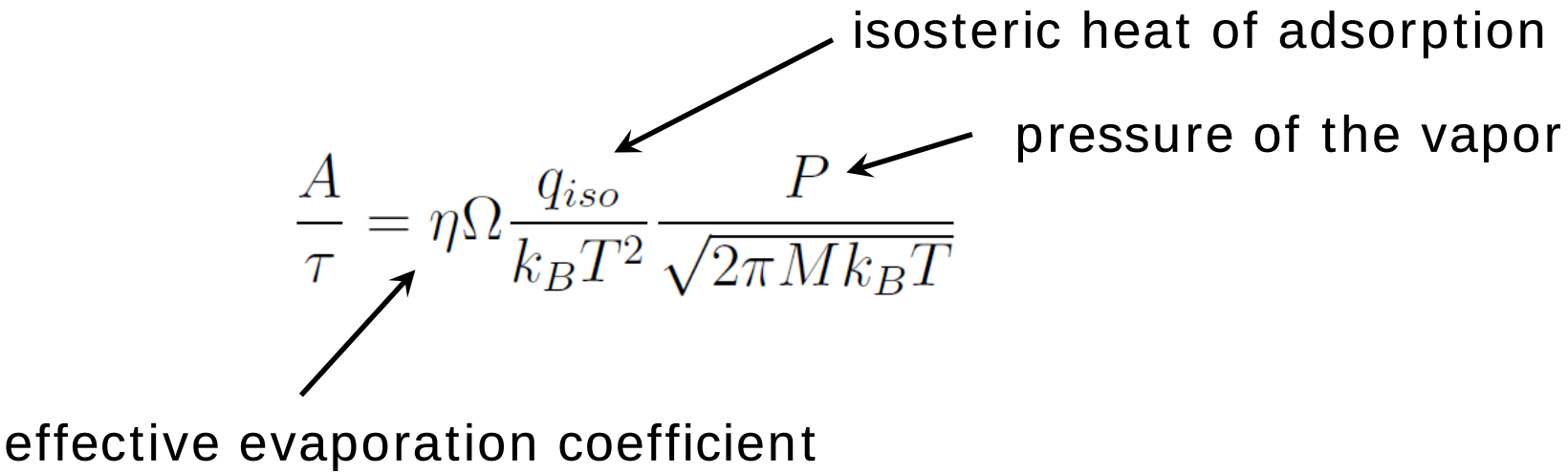
effective evaporation coefficient

- Isosteric heat of adsorption q_{iso} relates changes in P to changes in T at constant coverage

$$\Delta P = P \frac{q_{iso}}{k_B T} \frac{\Delta T}{T}$$

Consider a linear model where changes in *P*,*T* of the vapor are small compared to changes in vapor pressure of the adsorbed layer

- Essentially hiding all the complicated (and interesting) kinetics in the “effective evaporation coefficient”



Relate the amplitude of the response to parameters that describe thickness *h* versus *T* at constant P

$$h = BT^n \exp(\epsilon / k_B T)$$

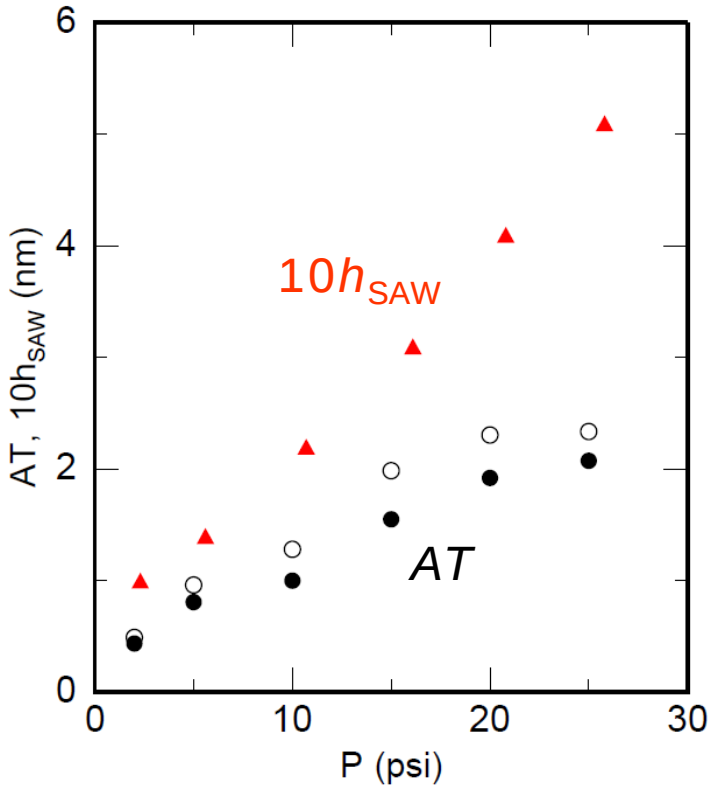
$$A = \left(\frac{\epsilon}{k_B T} + n \right) \frac{h}{T}$$

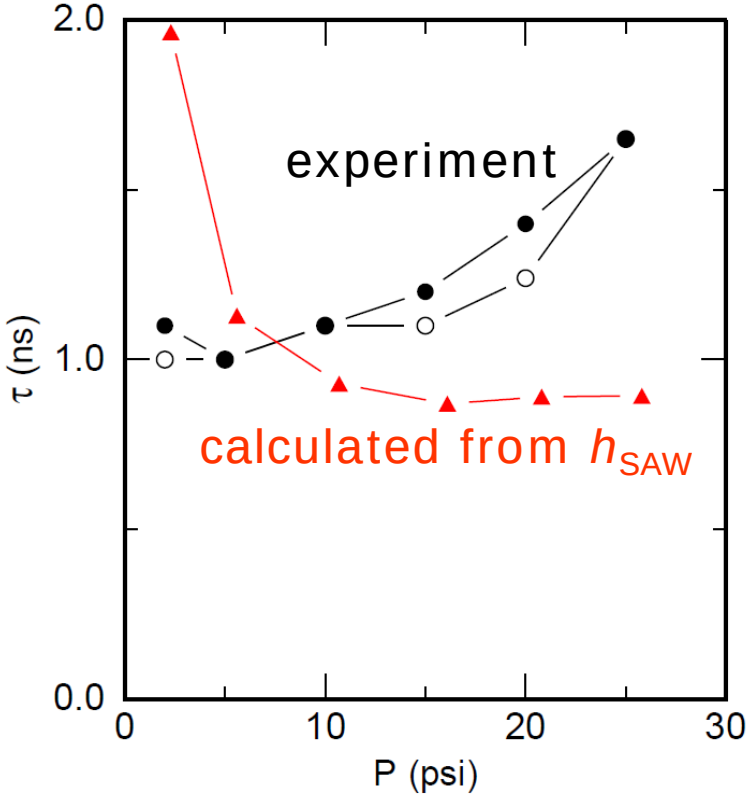
- Combine with previous definitions to yield an expression for time-scale on which thickness relaxes to a new equilibrium

$$\tau = \frac{h}{\eta \Omega} \frac{\sqrt{2\pi M k_B T}}{P} \left(\frac{\epsilon + n k_B T}{q_{iso}} \right)$$

Look at response amplitude *A* and relaxation time τ independently and then as the ratio *A*/τ

- *AT* should be on the order of 10 times thickness *h*
- τ is a more robust measurement and should scale with *h*/*P*
- open circles for hydrophilic SAM, solid circles for hydrophobic SAM

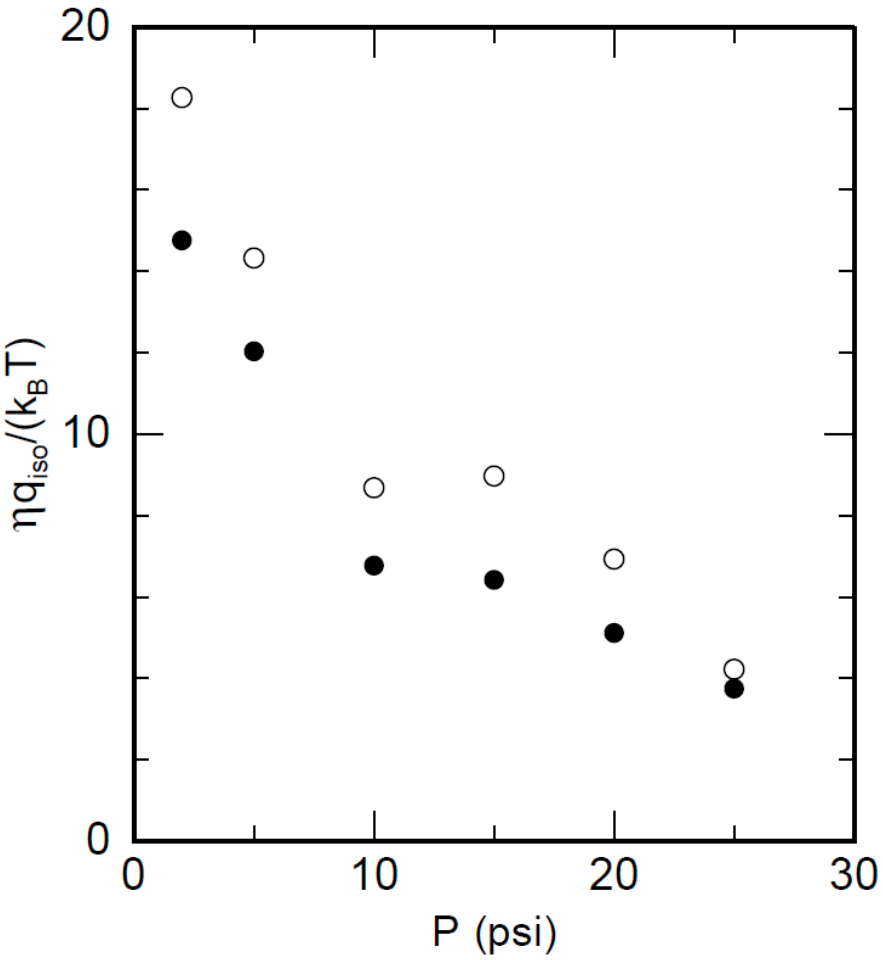




...then the ratio A/τ

- For bulk liquid R124 at saturation pressure and room temperature $\frac{q_{iso}}{k_B T} \approx 8$

$$\eta \frac{q_{iso}}{k_B T} = \frac{AT}{\tau} \frac{\sqrt{2\pi M k_B T}}{P\Omega}$$



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 adsorbed layers.
- Conductance and work-of-adhesion at hydrophobic interfaces are insensitive to the liquid composition.
- At hydrophilic interfaces, conductance is not a linear function of work-of-adhesion.
- Noise floor of 10^{-13} m $Hz^{-1/2}$ for measurements of phase change from liquid to vapor.
- Adsorbed layers of R124 on the order 1 nm thickness have a time-constant on the order of 1 ns.
- Potential for studies of accommodation coefficients and vapor velocity distribution near an interface during evaporation/condensation.