Thermodiffusion of nanoparticles in water and the thermal boundary conditions of solid-liquid interfaces

David Cahill

Shawn Putnam, Zhenbin Ge,
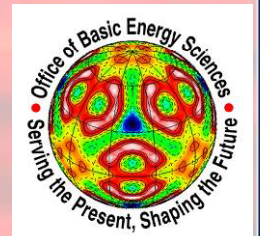
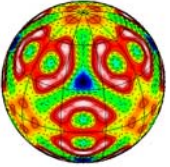Profs. Paul Braun, Gerard Wong

Center of Advanced Materials for the Purification of Water with Systems,

Frederick Seitz Materials Research Laboratory, Department of Materials Science, University of Illinois, Urbana, IL, USA
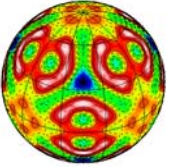
Outline

- Motivation
- Micron-scale beam deflection apparatus
  - short digression on thermal conductivity of particle suspensions
- Thermodiffusion of charged particles in water
  - thermoelectric fields in electrolytes
  - temperature dependence of the Soret coefficient
- Thermal conductance of solid-liquid interfaces
  - Transient adsorption and time-domain thermoreflectance
  - Hydrophilic and hydrophobic interfaces
- Summary and questions

An idea: Probe thermodynamics of aqueous interfaces through a transport measurement

Anderson, Ann. Rev. Fluid Mech. **21** 66-99 (1989), building on work by Derjaguin
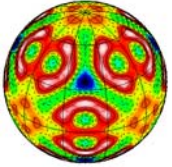
$$D_{\mathrm{T}} = -\frac{2}{\eta\, T}\left[\frac{2\Lambda_{\mathrm{l}}}{2\Lambda_{\mathrm{l}} + \Lambda_{\mathrm{p}}}\right]\int_0^\infty y\,\hat{h}(y)\,\mathrm{d}y$$

- In electrophoresis, we probe the charge distribution in the double-layer.
- In the Seebeck coefficient of a crystal, we probe the entropy of the charge carriers.

y = distance normal to the particle surface

$h(y)$ = the excess enthalpy per unit volume of the fluid created by the presence of the particle

Λ = thermal conductivity of liquid (l) and particle (p)

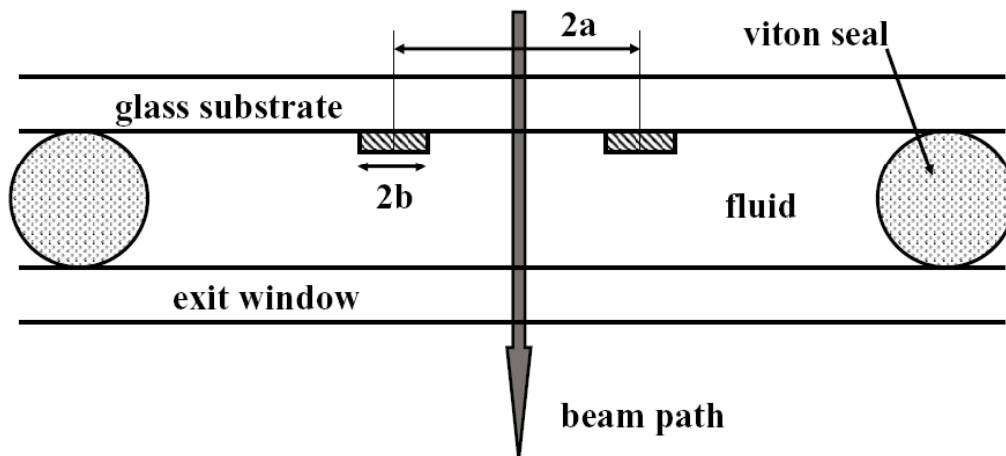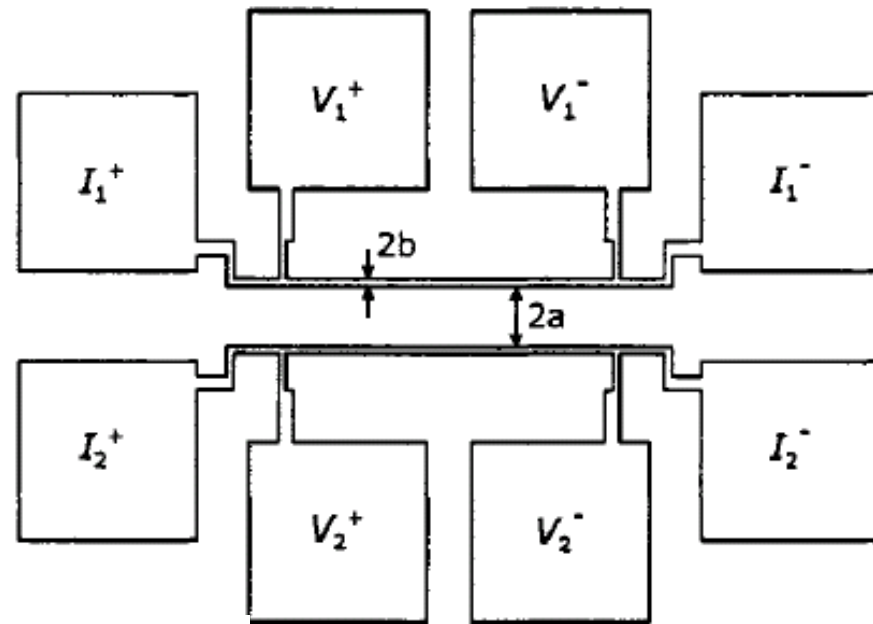# Build on our extensive experience with the "3ω method" for thermal conductivity
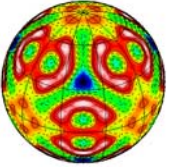
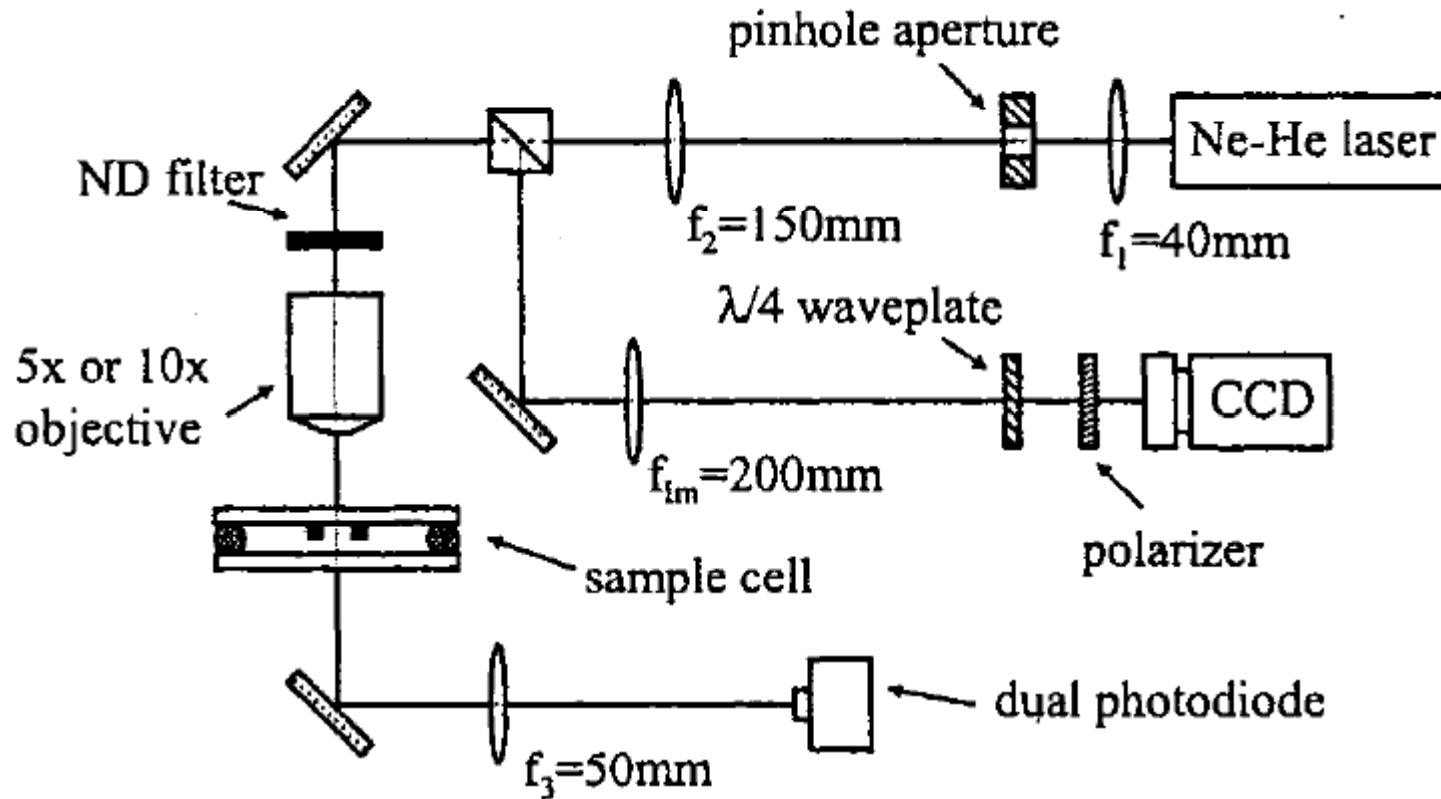Heater line separation:
$2a \approx 25\ \mu m$
Heater line width:
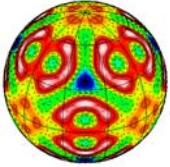$2b \approx 7\ \mu m$

Putnam and Cahill, RSI (2004)

Measurement of optical beam deflection

Small length scales increases frequency scales but may be introducing low-frequency noise due to $\sqrt{N}$ fluctuations in the number of particles in the probe volume.

Solve heat diffusion equation and optical beam deflection in the frequency domain

$$q_j^2 = \frac{i\omega C_j}{\Lambda_j} \,, \qquad u_j = \left(k^2 + q_j^2\right)^{1/2} \,, \qquad \gamma_j = \Lambda_j u_j \qquad G_j(k) = \frac{k\sin(ka)}{u_j\left(\gamma_1 + \gamma_2\right)}$$
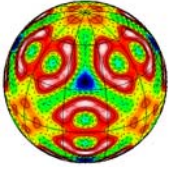
thermo-optic contribution from glass slide and liquid

$$n_j\theta_j = -\frac{2P}{\pi l}\frac{dn_j}{dT}\int_0^\infty \frac{\sin(kb)}{kb}G_j(k)dk$$

thermodiffusion

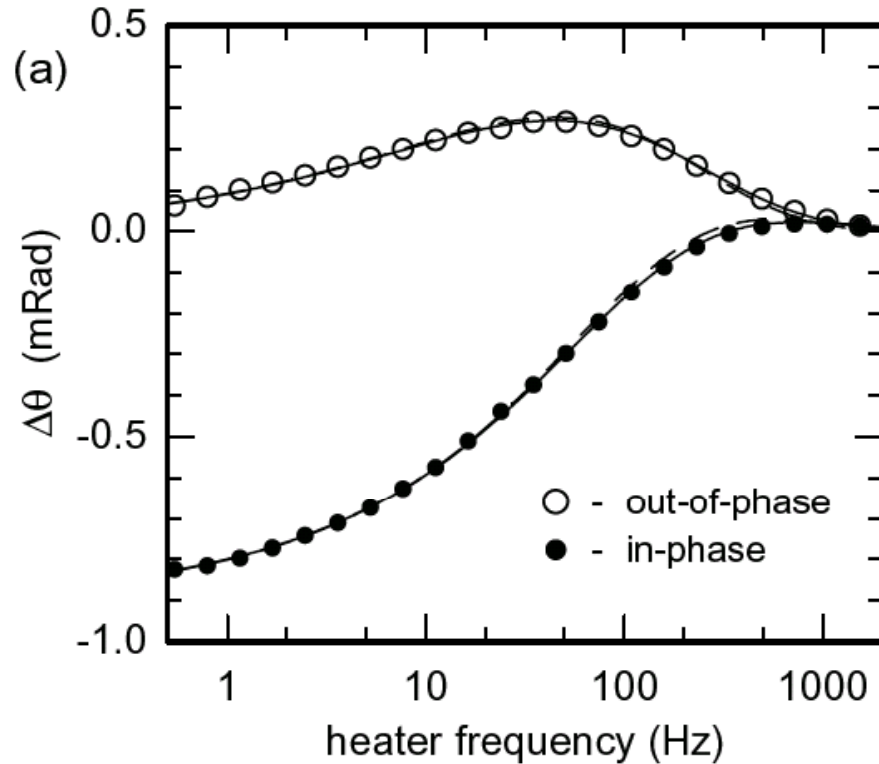$$n_2\theta_c = cS_T\frac{2P}{\pi l}\frac{dn_2}{dc}\int_0^\infty \frac{k^2\sin(kb)G_2(k)}{(kb)(k^2 + q_c^2)}\,dk$$

$$q_c^2 = \frac{i\omega}{D_c}$$
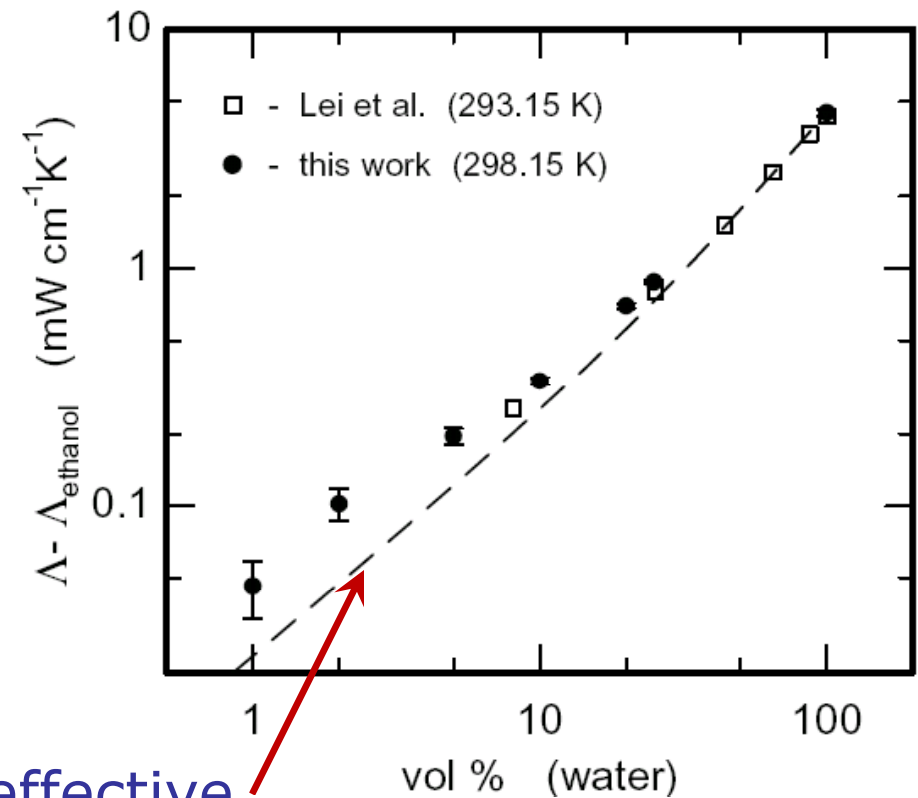
Putnam and Cahill, RSI (2004)

Also an excellent method for measuring heat diffusion in liquids
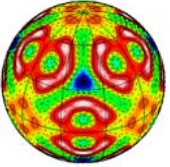
Raw data for ethanol

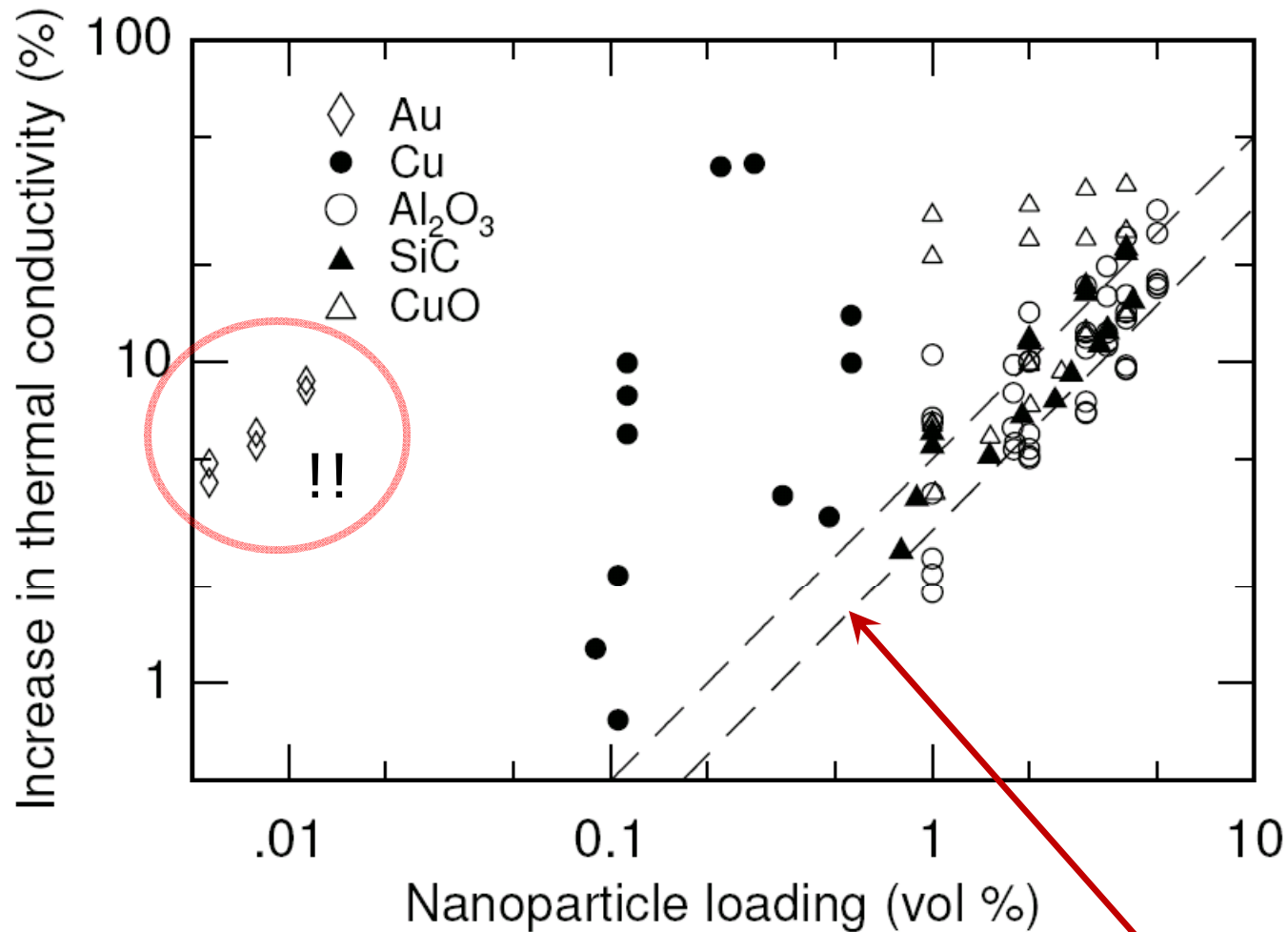Change in thermal conductivity upon adding water to ethanol
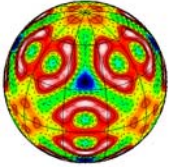

Symmetric effective medium theory

Putnam and Cahill, JAP (2006)

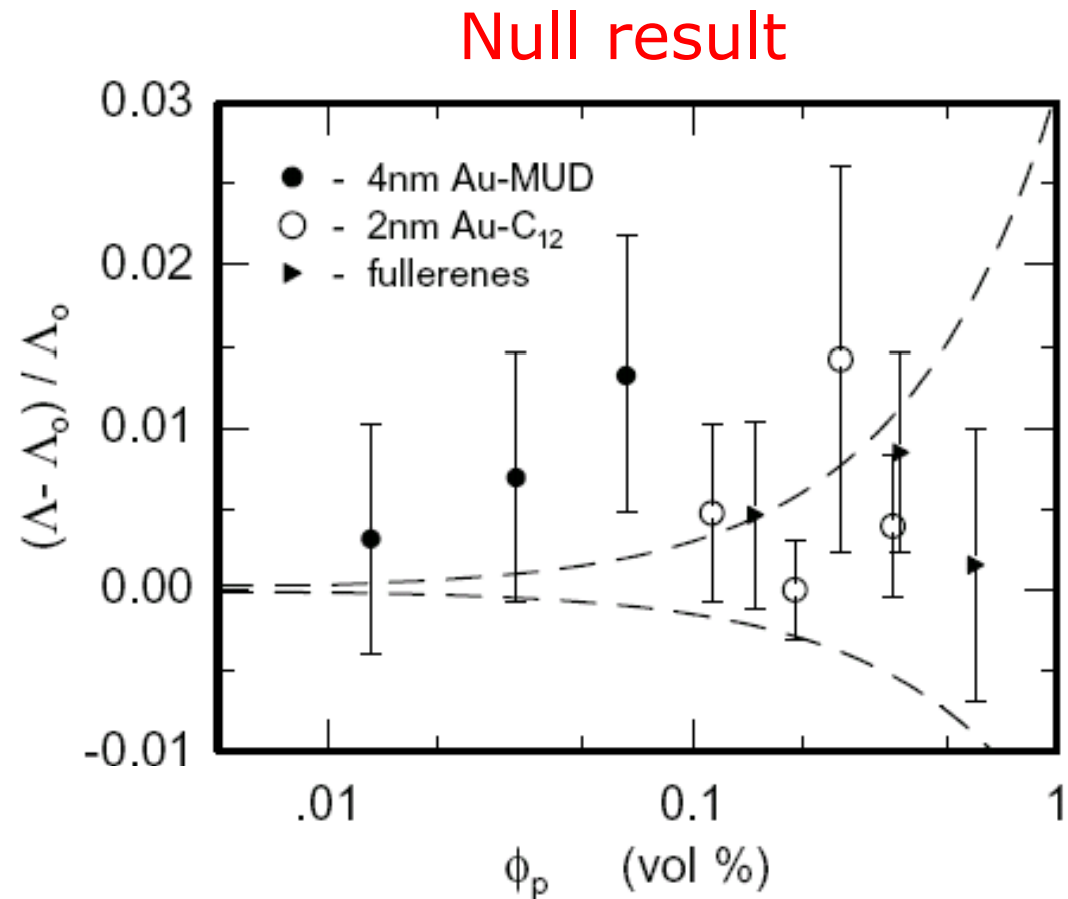# Reports of anomalous (wrong?) thermal conductivity of nanoparticle suspensions

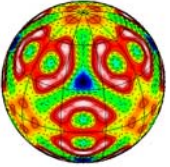Keblinski et al., Materials Today(2006)

Measure three types of nanoparticle suspensions

Null result

- 4 nm diameter Au in ethanol functionalized by 11-mercapto-1-undecanol (MUD)

- 2 nm diameter Au in toluene functionalized by dodecanethiol

- fullerene mixture of C_{60}-C_{70} in toluene

Plot: y-axis $(\Lambda - \Lambda_o) / \Lambda_o$ from -0.01 to 0.03; x-axis ϕ_p (vol %) from .01 to 1.
Legend:
● - 4nm Au-MUD
○ - 2nm Au-C_{12}
▶ - fullerenes

(No observable thermodiffusion in these samples)
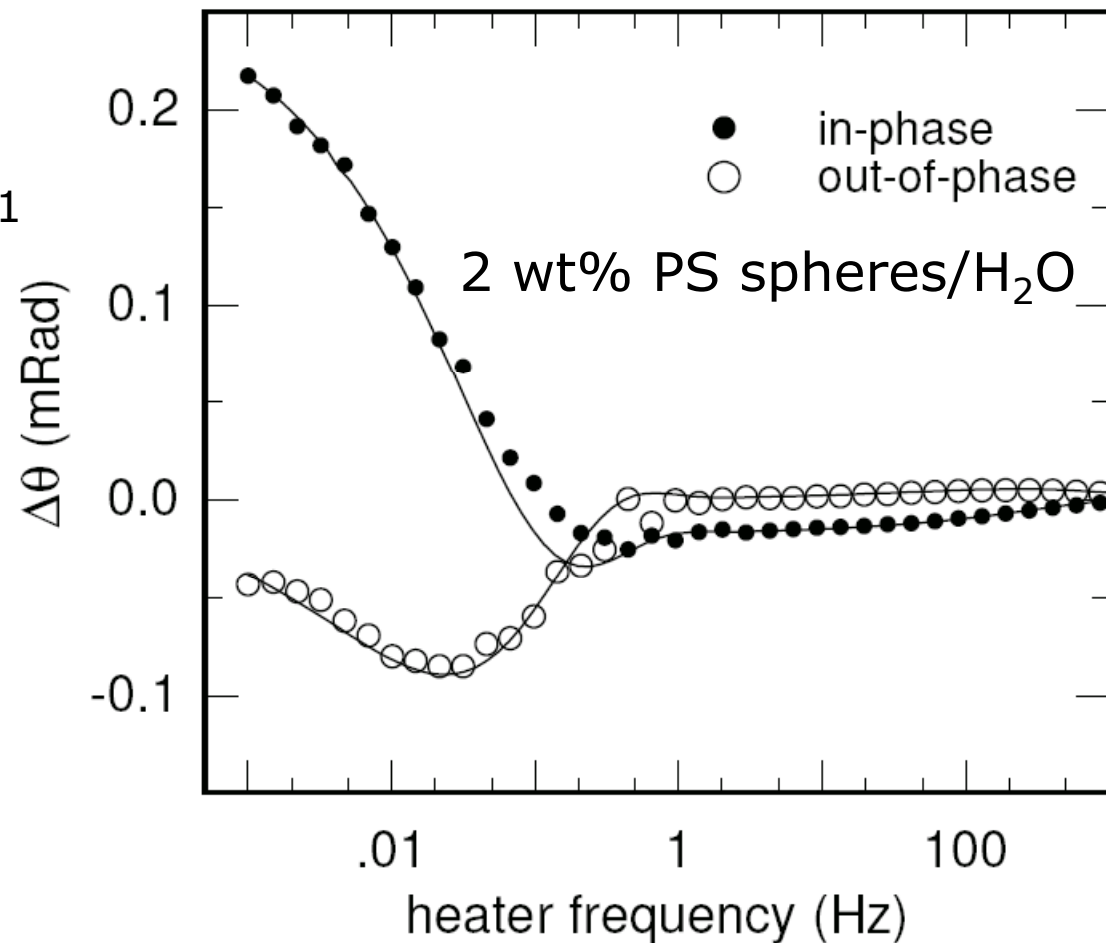
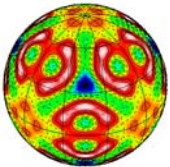Putnam and Cahill, JAP (2006)

Back to thermodiffusion

- Commercially supplied d=26 nm polystyrene latex spheres, COOH functionality

Fit <u>one</u> free parameter:

$$S_T = -0.30 \text{ K}^{-1}$$

Plot axes: $\Delta\theta$ (mRad) versus heater frequency (Hz); legend: in-phase (filled circles), out-of-phase (open circles); 2 wt% PS spheres/H_2O
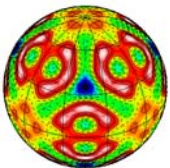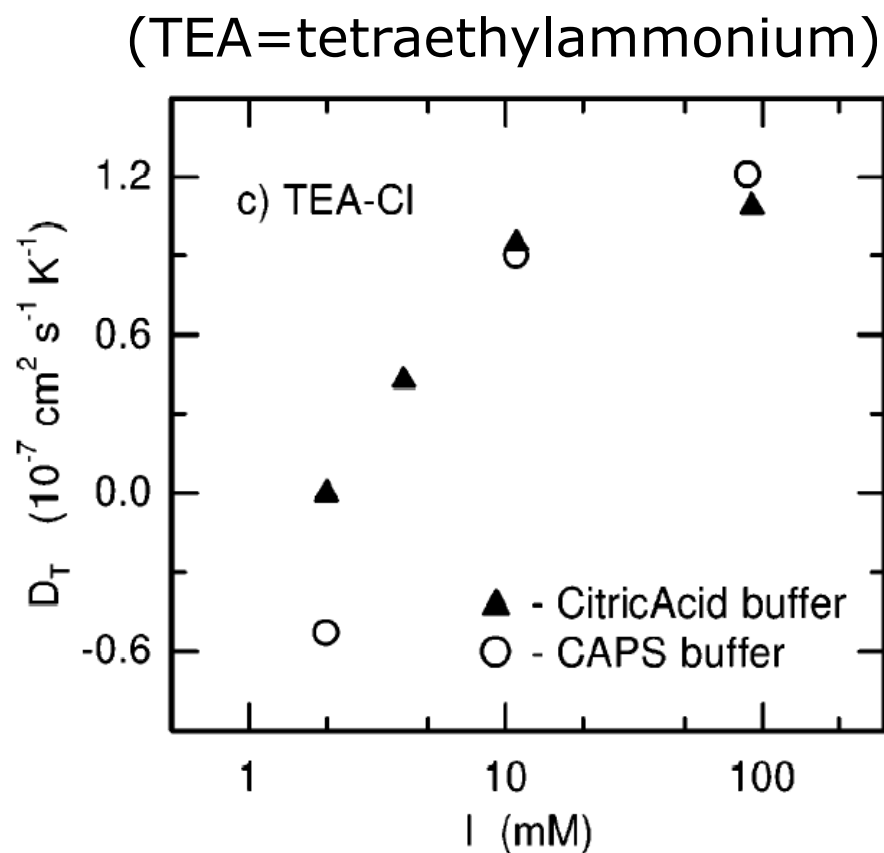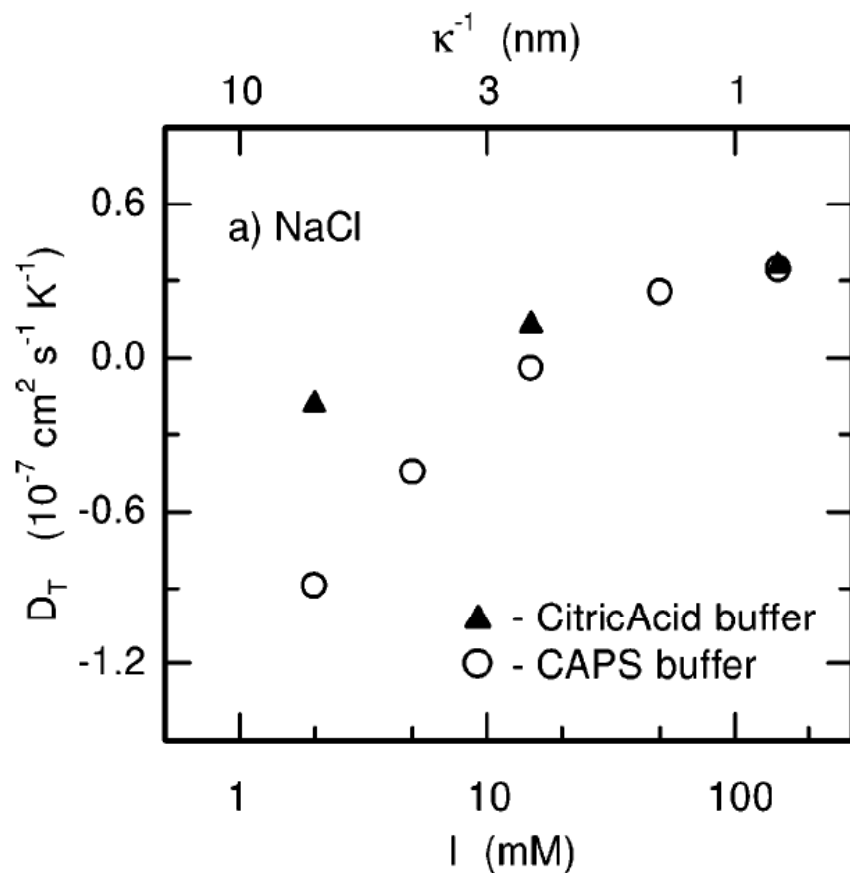
Survey of Interfacial Dynamics Corp. polystyrene latex suspensions (2%)
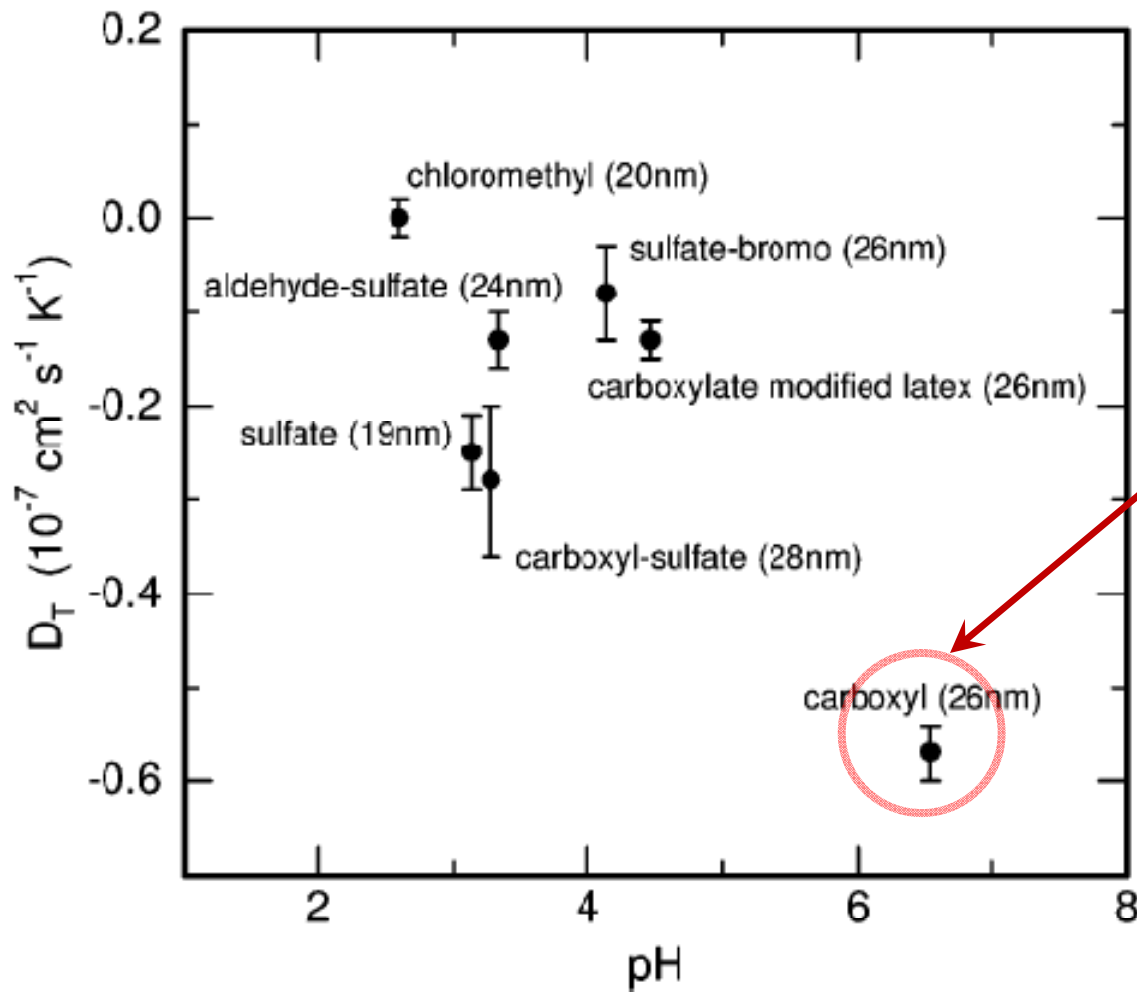
New experiment so pick the sample with the largest signal for further study (perhaps a poor choice in hindsight).
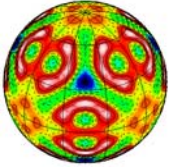
Putnam and Cahill, Langmuir (2005)

Add buffer, vary ionic strength

citric Acid pH ≈ 3.3; CAPS pH ≈ 10.5
26 nm polystyrene latex

(TEA=tetraethylammonium)

Putnam and Cahill, Langmuir (2005)

Temperature gradients separate cations and anions and produce an electric-field

$$\mathbf{J}_T^{Na} = -\frac{Q_a^* D^{Na}}{k_B T^2} c^{Na} \nabla T \qquad\qquad E = \frac{(Q_{Na}^* - Q_{Cl}^*)}{2eT} \nabla T$$

cation	Q_C^* (meV)	anion	Q_A^* (meV)
Li^+	0.4	F^-	34
Na^+	30	Cl^-	0
TEA^+	123	Br^-	0.9
H^+	133	OH^-	172

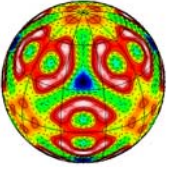Data from Snowden and Turner, *Trans. Farad. Soc.* (1960)

See also more thorough treatments:
Würger, PRL (2008)
Rasuli et al., PRL (2008)
Morthamus, et al., EPJ E (2008)
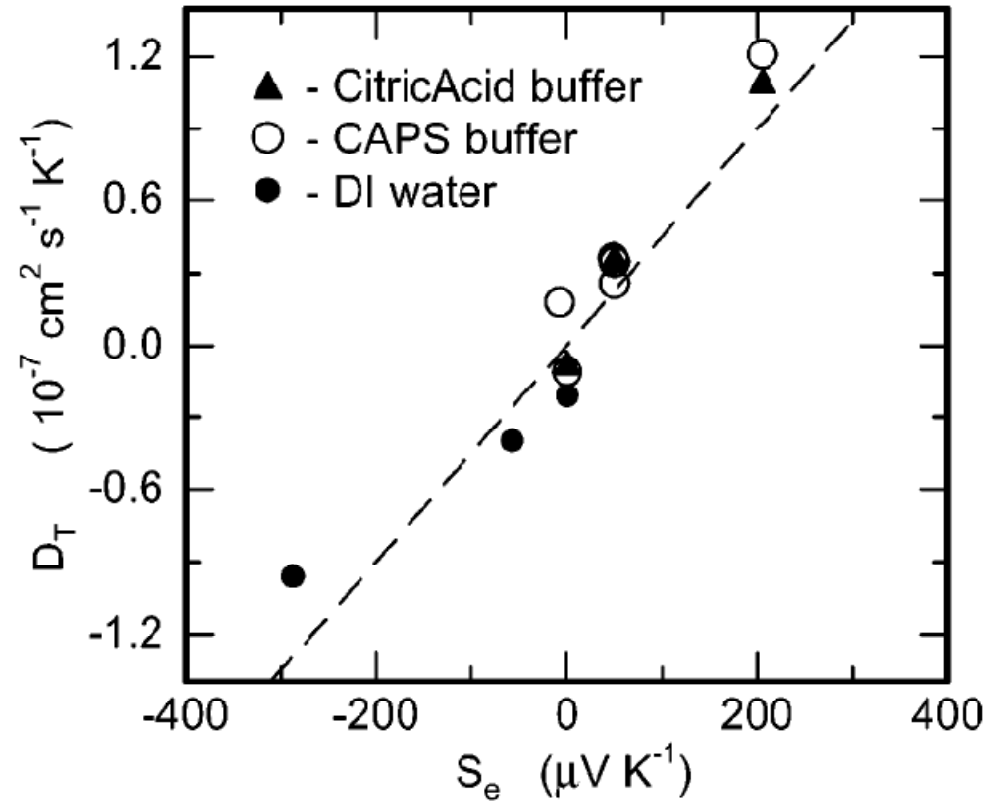Würger, *Langmuir* (2009)

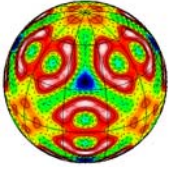# Electrophoresis driven by thermally generated fields might even be useful

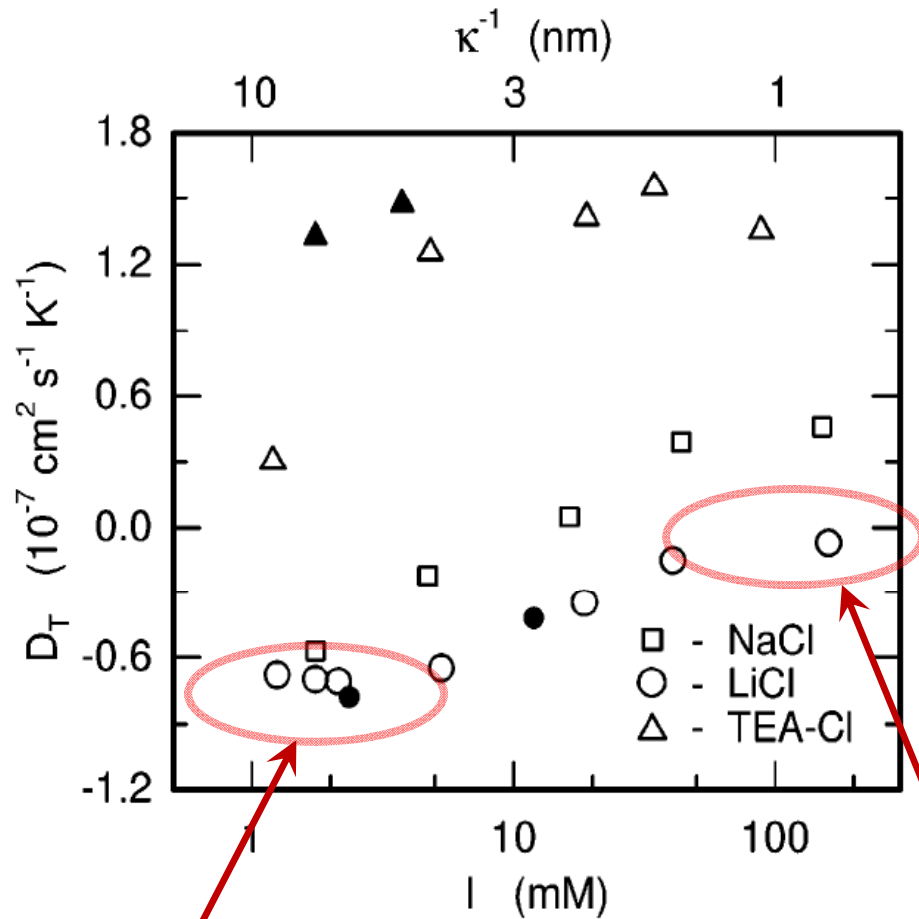Measured: $\mu_E = -4.5 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$

$$S_e = (Q_C^* - Q_A^*)/2eT, \qquad D_T = -S_e\,\mu_E$$

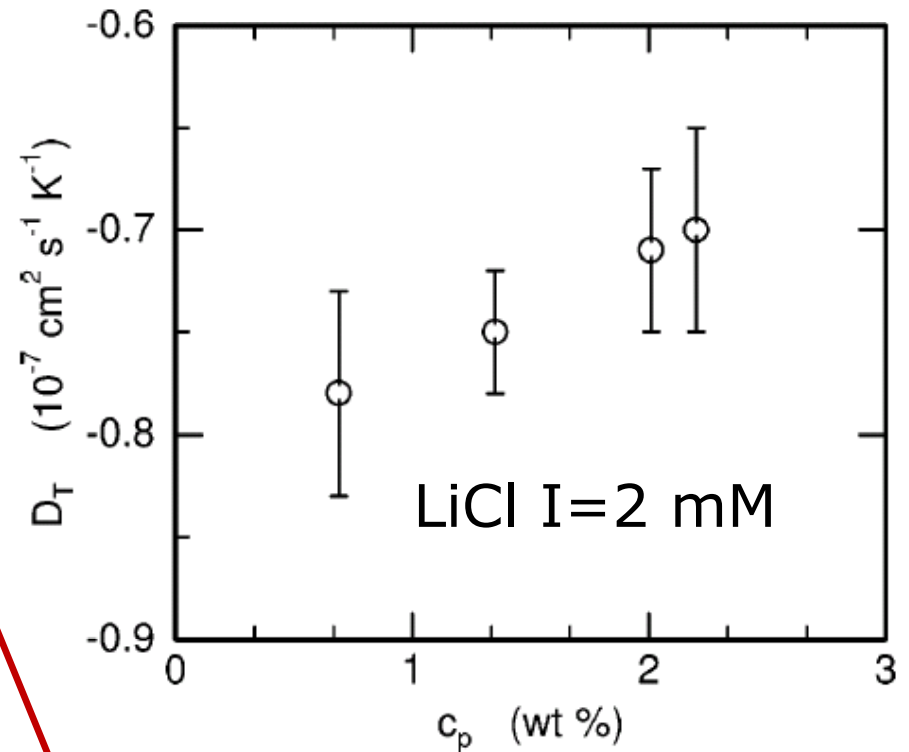Thermoelectric fields are on the order of k_B/e, as in semiconductors, $\sim 10^{-4}$ V/K

Legend:
▲ - CitricAcid buffer
○ - CAPS buffer
● - DI water

Y-axis: D_T (10^{-7} cm^2 s^{-1} K^{-1})
X-axis: S_e (μV K^{-1})

Cleaner experiment: dialyze, no buffers, focus on LiCl electrolytes

Weak dependence on particle concentration

Are thermoelectric fields unimportant here?

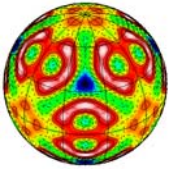High concentration LiCl electrolyte quenches thermodiffusion

Unfortunately, the 26 nm particles are somewhat anomalous

- Improved cell to control temperature and suppress convection.

- Temperature dependence of 26 nm polystyrene latexdiffers from the others samples.

I~1 mM

△ - 26 nm
▶ - 34 nm
□ - 67 nm
● - 90 nm
○ - 92 nm

S_T (K^{-1})

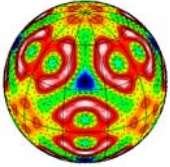Temperature (°C)
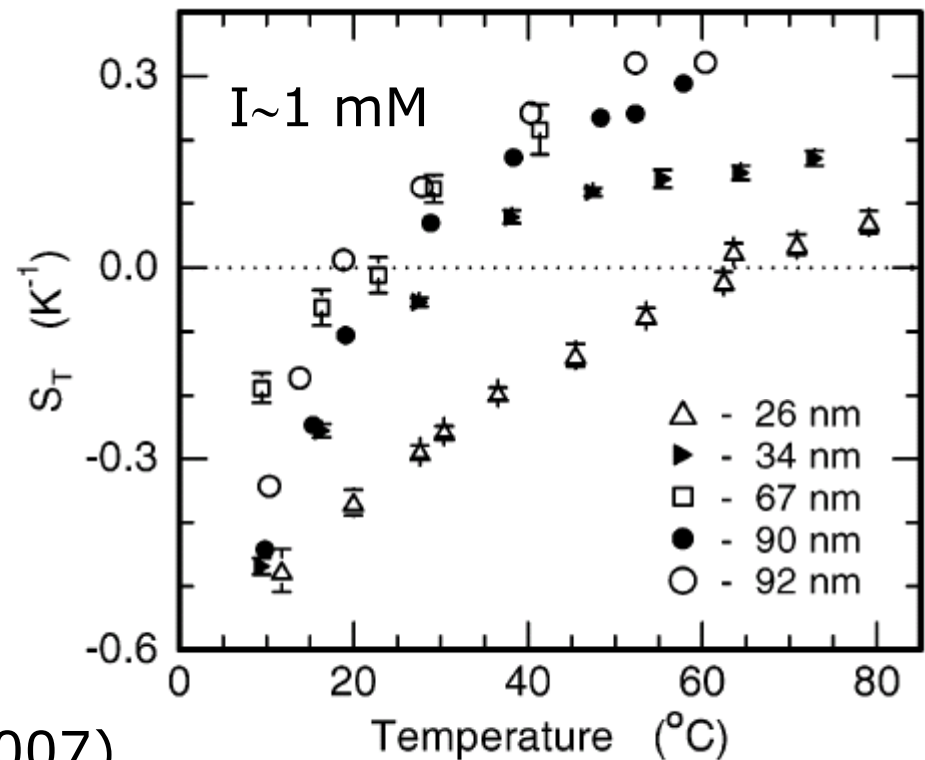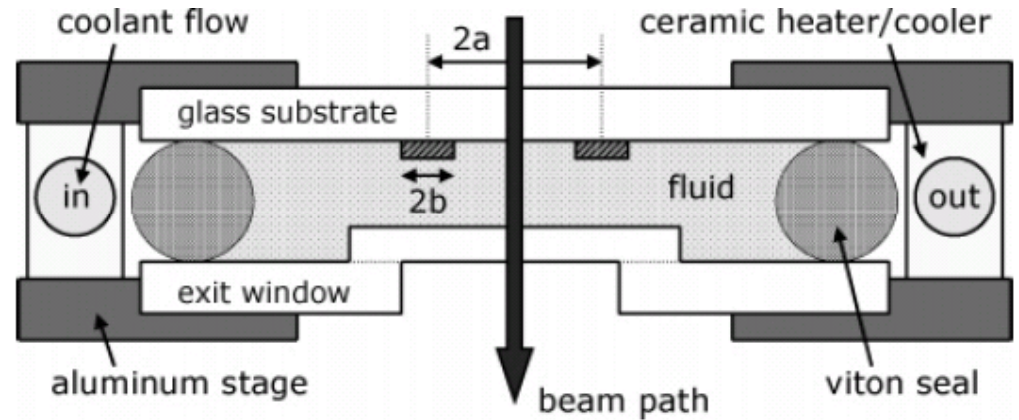
Putnam and Cahill, Langmuir (2007)

Mutant variants of lysozyme provide a unique way of controlling the charge of a "nanoparticle"

- T4 bacteriophage lysozyme kindly supplied by Dr. Lori Sanders and Prof. Gerard Wong.
- Hydrodynamic diameter is 3.6 nm, smaller compared to Debye lengths of 5-12 nm.

| protein suspension	formal charge	c_p (mg/mL)	g (μS/cm)	I (mM)	ζ](mV)
WT T4L	+9	22.0	510	4.0	67
single-mutant	+7	17.6	224	1.8	57
double-mutant	+5	10.5	119	1.0	43
triple-mutant	+3	16.8	100	0.8	26

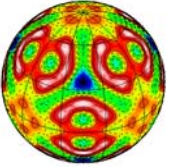Note we did not adjust ionic strength to a common value; perhaps a bad choice in hindsight

S_T does not seem to depend on charge

- Temperature dependence of S_T is approximately the same as for polystyrene latex.

- Thermoelectric fields so no seem to play an important role in this regime of low ionic strength : the particle charge is + for lysozyme and – for latex
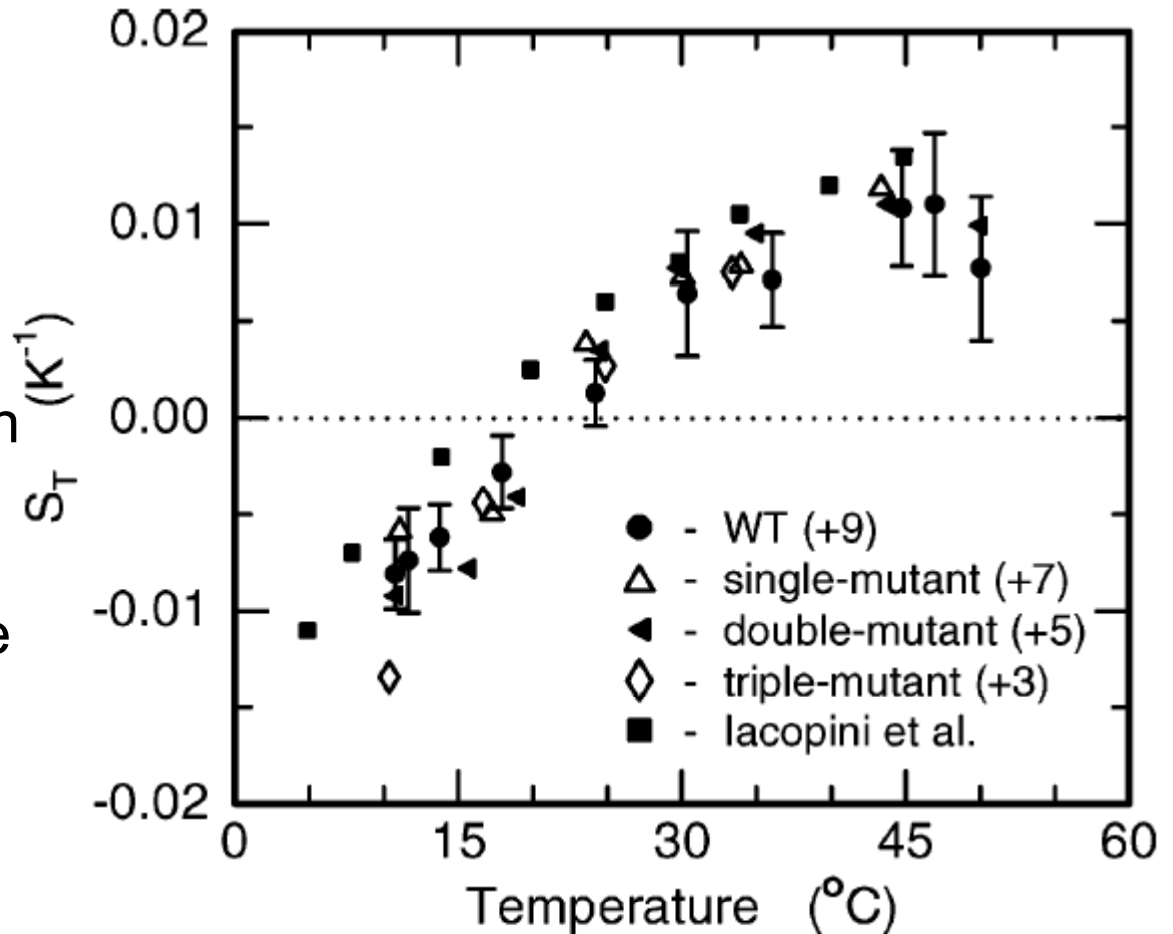
Putnam and Cahill, Langmuir (2007)

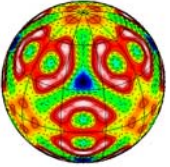# What mechanism creates the strong temperature dependence?

- Thermodiffusion is probably driven by a combination of mechanism.
- Importance of the thermal expansion of solvent has been discussed, see, e.g., Iacopini *et al.*, EPJ E (2006), Brenner, PRE (2006)

$$S_T \approx \frac{D_s}{D_c} \beta$$

D_s = solvent self diffusivity
D_c = particle concentration diffusion
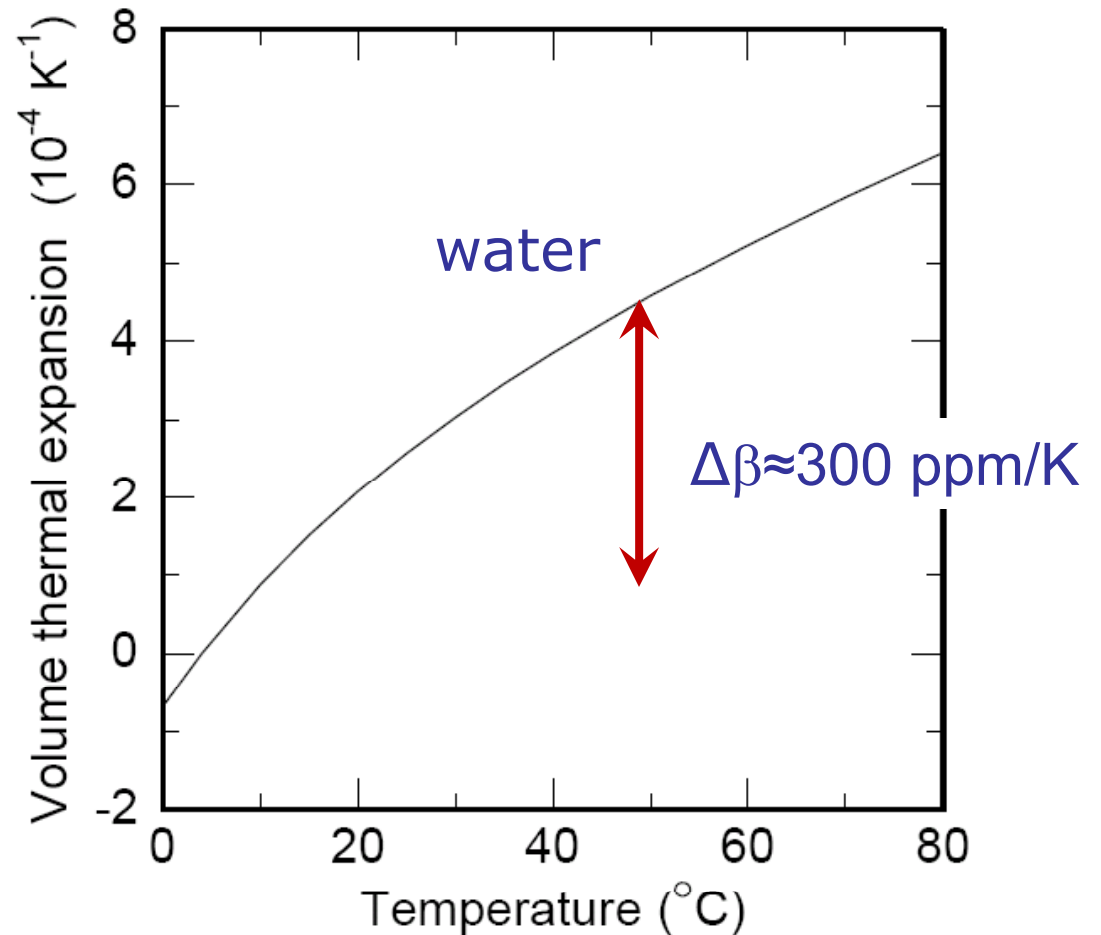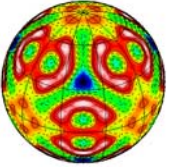β = thermal expansion coefficient of the solvent

What mechanism creates the strong temperature dependence?

$$S_T \approx \frac{D_s}{D_c} \beta$$

- D_s/D_c ~20 for lysozyme; ~400 for largest latex particles.
- In both cases, this mechanism is a factor of 3-to-4 too small to explain the data.
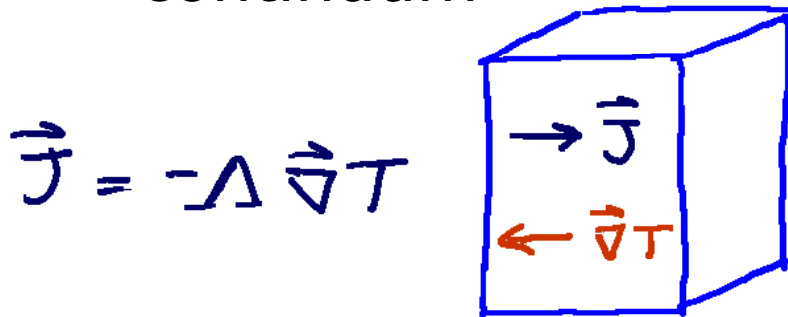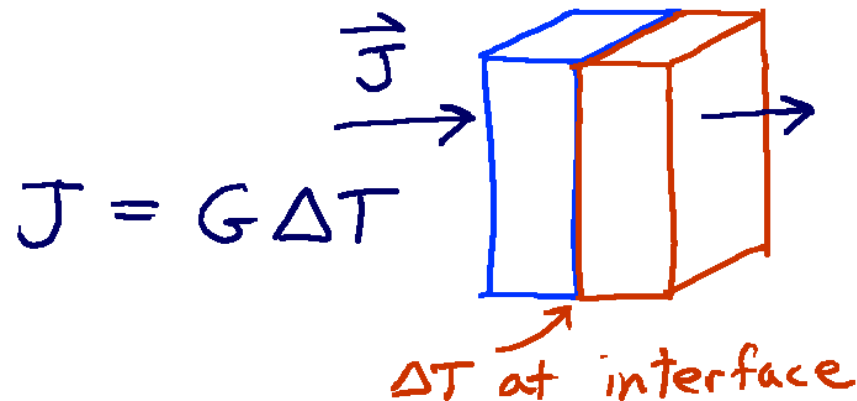- Is that close enough?

water

Δβ≈300 ppm/K

Interface thermal conductance

- Thermal conductivity Λ is a property of the continuum
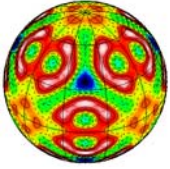
$$\vec{J} = -\Lambda \vec{\nabla} T$$

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

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

$$J = G \Delta T$$

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

ΔT at interface

Factor of 60 range at room temperature
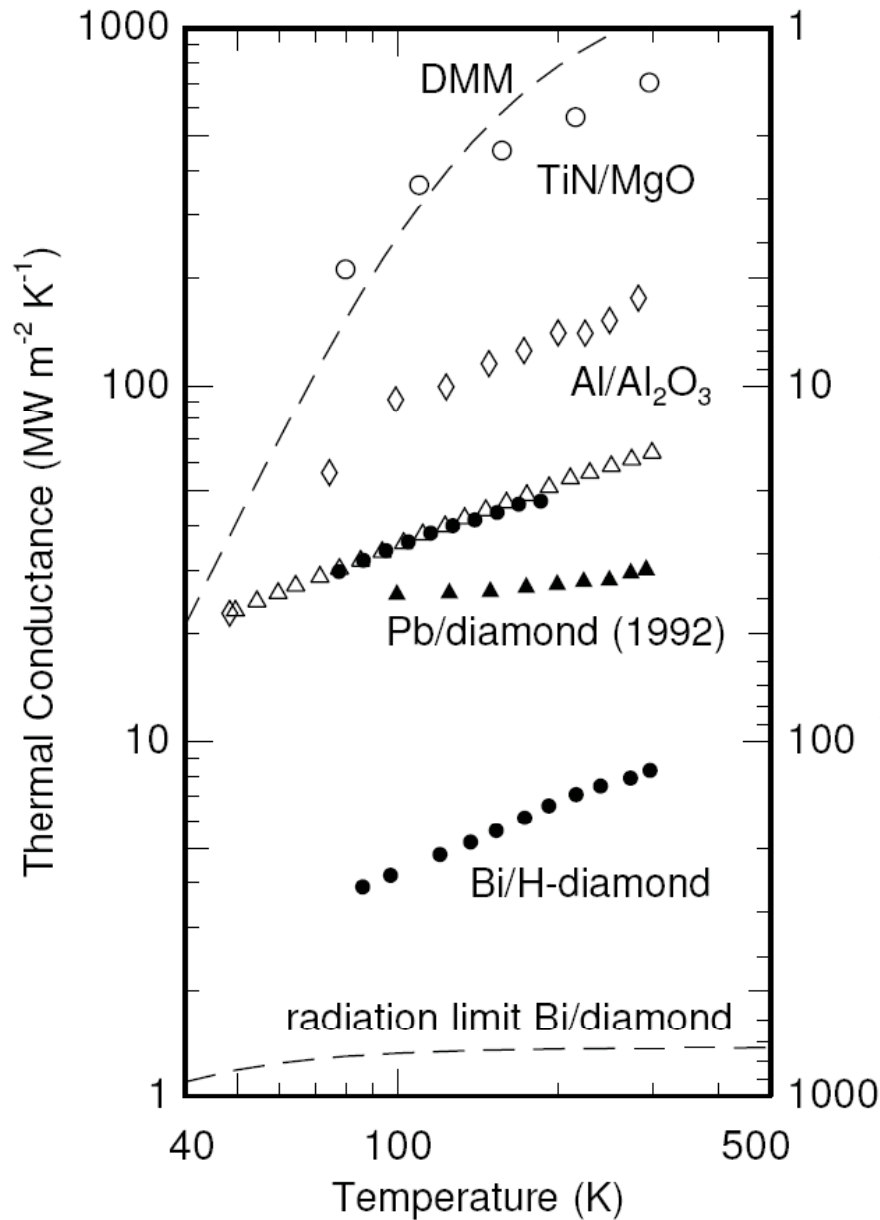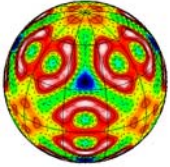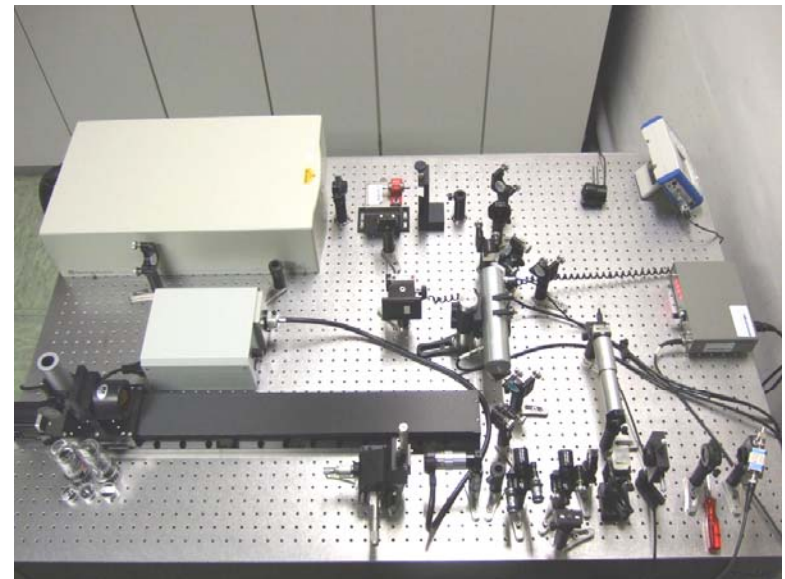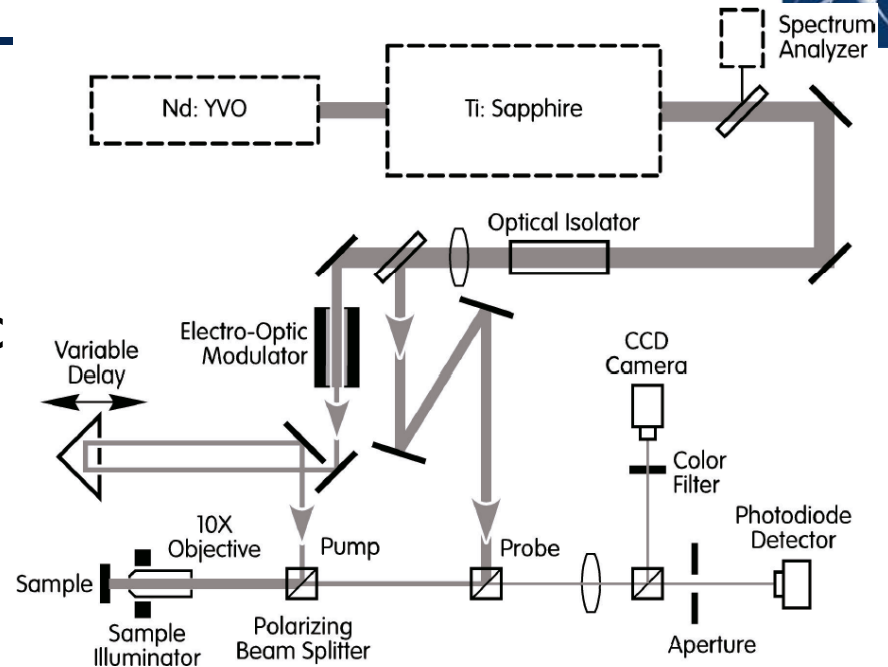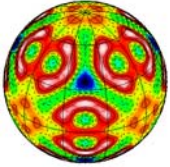
Time domain thermoreflectance since 2003

- Improved optical design
- Normalization by out-of-phase signal eliminates artifacts, increases dynamic range and improves sensitivity
- Exact analytical model for Gaussian beams and arbitrary layered geometries
- One-laser/two-color approach tolerates diffuse scattering

Clone built at Fraunhofer Institute for Physical Measurement, Jan. 7-8 2008

Solid-liquid interfaces: Two approaches

- Transient optical absorption of nanoparticles and nanotubes in liquid suspensions.
  - Measure the thermal relaxation time of a suddenly heat particle. Interface sensitive if the particle is small enough.
  - limited to interfaces that give good stability of the suspension, e.g., hydrophilic particles in H_2O
- Time-domain thermoreflectance of thin planar Al and Au films.
  - heat flows both directions: into the fluid and into the solid substrate.
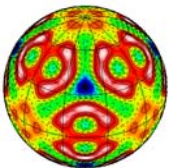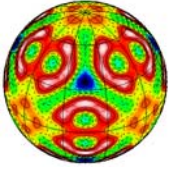
Hydrophilic metal nanoparticles:
4 nm diameter Au:Pd nanoparticles in water

transient absorption data
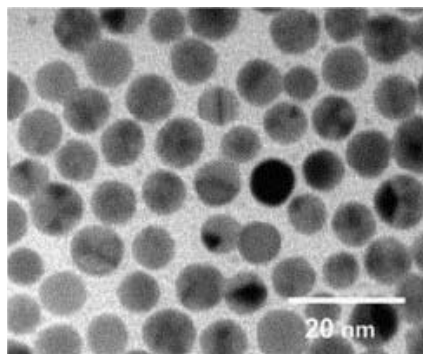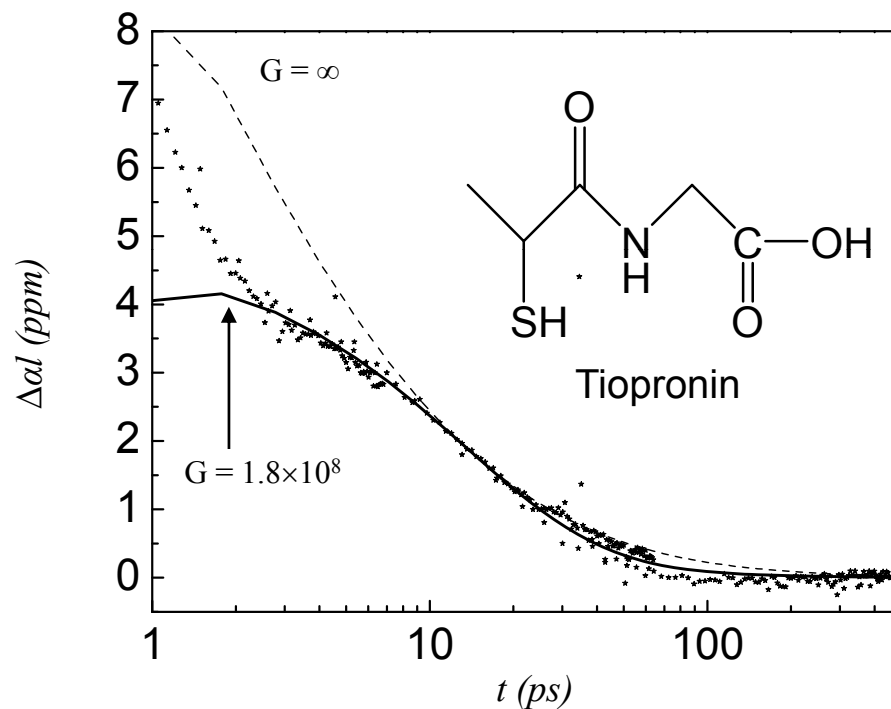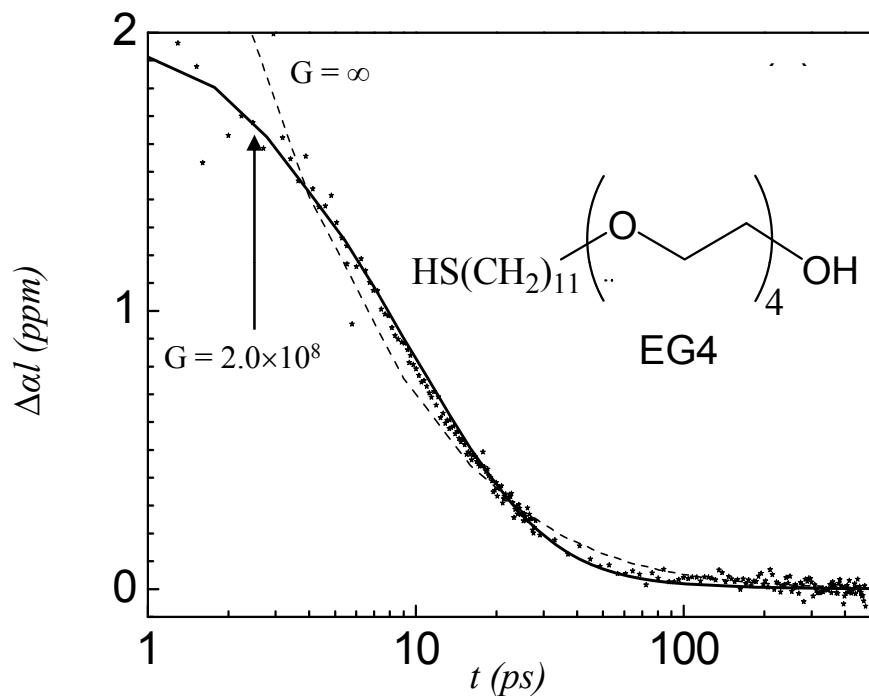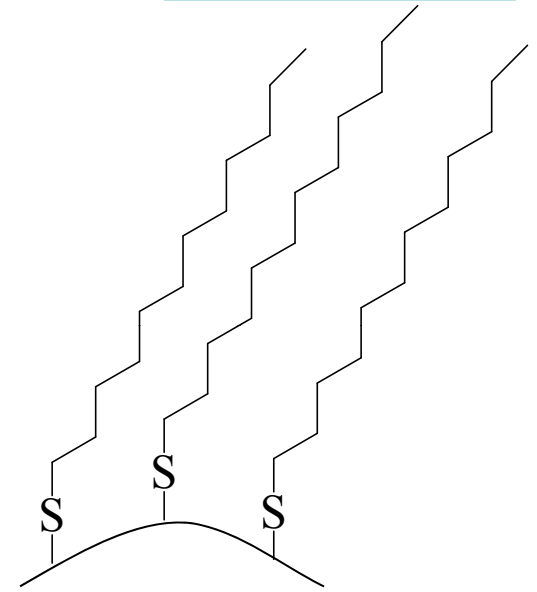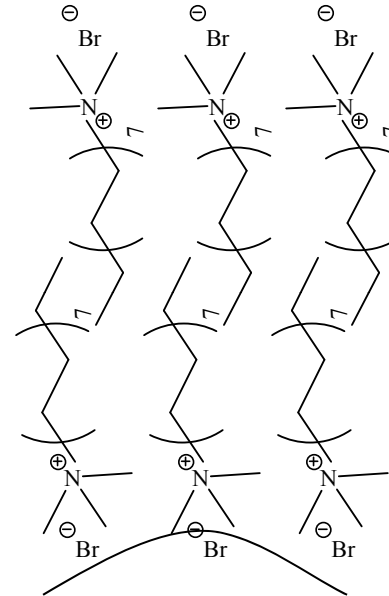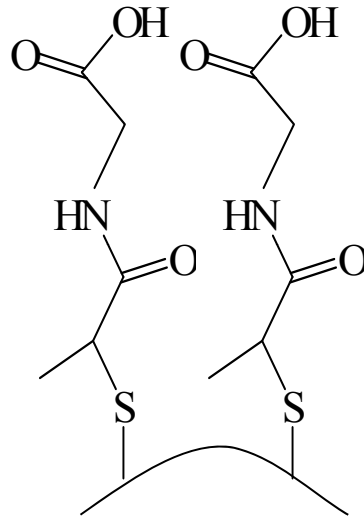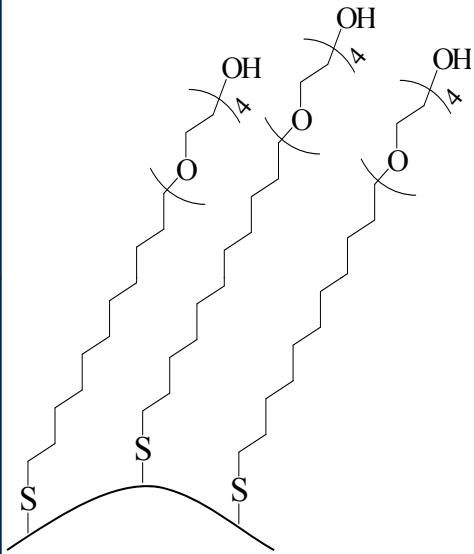

Ge *et al.*, JPC B (2004)

Nanoparticle summary

In water

In Toluene

$$G \sim 200 \text{ MW m}^{-2} \text{ K}^{-1}$$

$$G \sim 15 \text{ MW m}^{-2} \text{ K}^{-1}$$
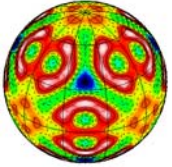
Ge *et al.*, JPC B (2004)
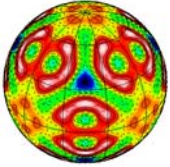
- Interface conductance and thermal conductivity of the fluid determine a critical particle radius
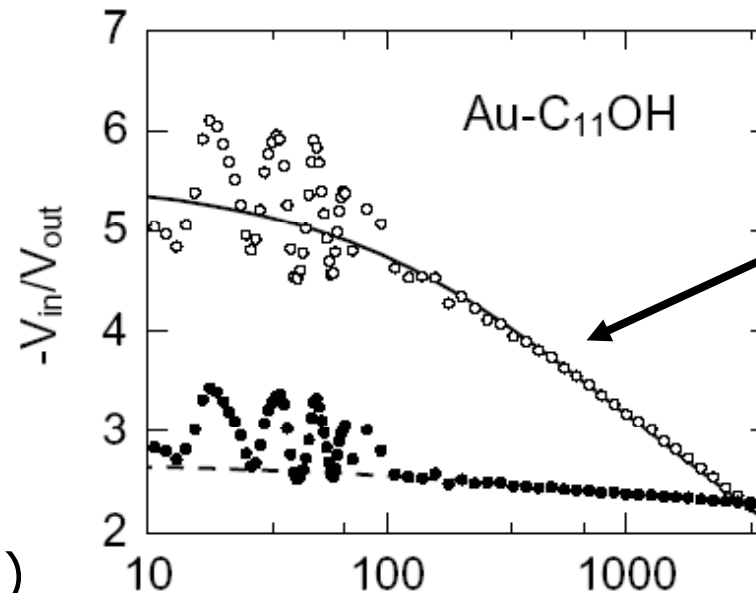
$$r_c = \Lambda/G$$

- For particles in water, $r_c = 3$ nm.

- For high thermal conductivity particles, dilute limit of effective medium theory

$$r >> r_c \qquad \Delta\Lambda = (1+3\phi)\Lambda$$
$$r << r_c \qquad \Delta\Lambda = (1-1.5\phi)\Lambda$$

Thermoreflectance of solid/H₂O interfaces

Layer stack (top to bottom): Water / SAM / Au 10nm / Ti 2nm / Al 20nm / Ti 5nm / polyimide~30nm / sapphire substrate 1mm / SiO₂ 130nm

Au-SC$_{18}$ plot — hydrophobic 50 MW/m²-K; no water

Au-C$_{11}$OH plot — hydrophilic 100 MW/m²-K
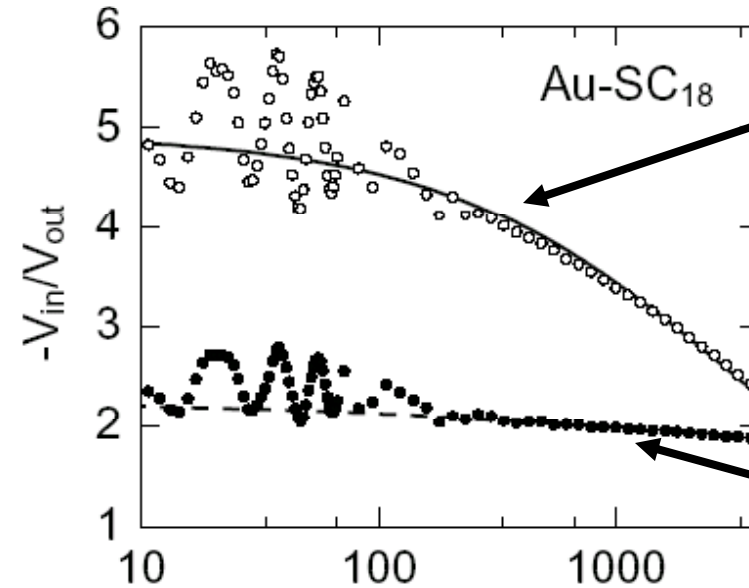
Ge *et al.*, PRL (2006)

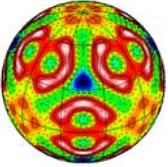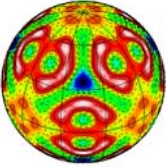# Thermoreflectance of solid/H$_2$O interfaces

- Experiments contain many interfaces and layers so look at the difference in the conductance created by changing from hydrophobic to hydrophilic.

- Define Kapitza length, equivalent thickness of water: $h = \Lambda / G$
  - Au/hydrophobic h = 12 nm
  - Au/hydrophilic h = 6 nm

- Difference $\Delta h = 6$ nm

Summary

- At high ionic strength, thermodiffusion of charged particles in water is driven by thermoelectric fields.
  - This might be useful for generating small electric fields.
- Mechanisms driving thermodiffusion at low ionic strength are still unclear (at least to me).
  - Rule out thermoelectric fields at low ionic strength (?).
  - At high temperatures, enthalpy of dielectric in an electric field gives the right magnitude but lysozyme does not show the expected dependence on zeta-potential. (Theory is incomplete? Experiments are incorrect?)
  - Temperature dependence of thermodiffusion is stronger than predicted by the thermal expansion of water.
- Kapitza lengths for hydrophilic interfaces are on the order of a few nm. For sufficiently small nanoparticles, even high thermal conductivity particles behave as thermal insulators.
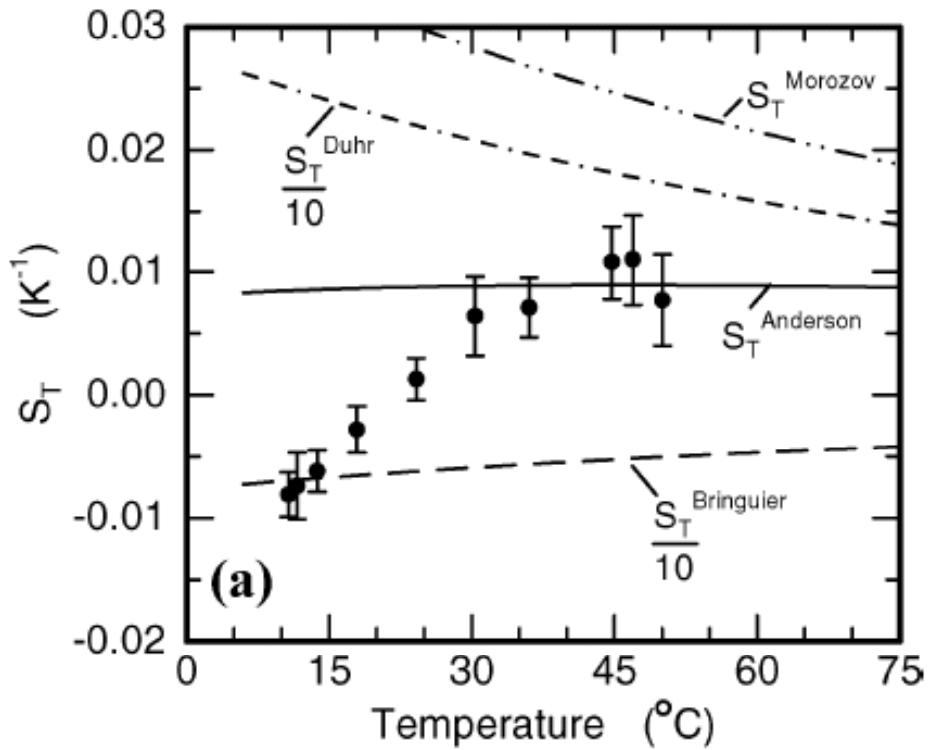
- What is the temperature dependence of the thermoelectric voltage?

  - Is there a convenient way to measure these small fields directly?

- Could we advance the subject using "pressure-tuning" of thermodiffusion, i.e., hydrostatic pressure up to ~1 GPa?

- How can we experimentally explore the role of particle thermal conductivity and interface thermal conductance on the thermodiffusion of nanoparticles?
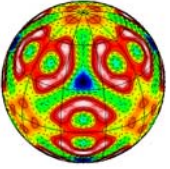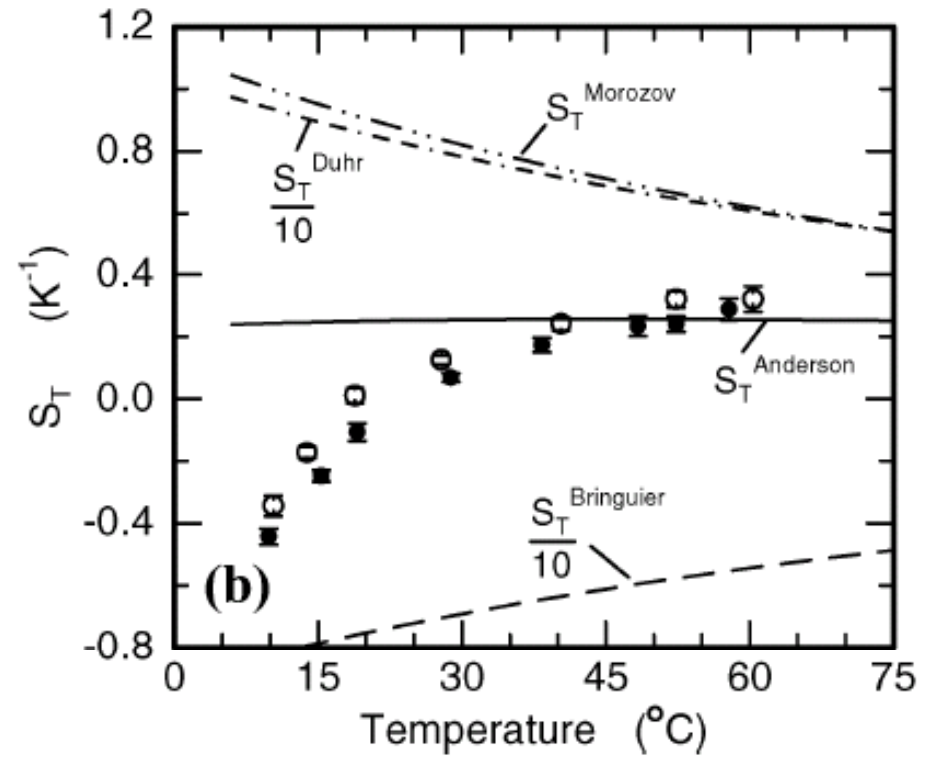
Backup slide—comparisons to theories

lysozyme

90 nm latex

Putnam and Cahill, Langmuir (2007)