# Micro-rheometry for Polymer Melts and Concentrated Solutions


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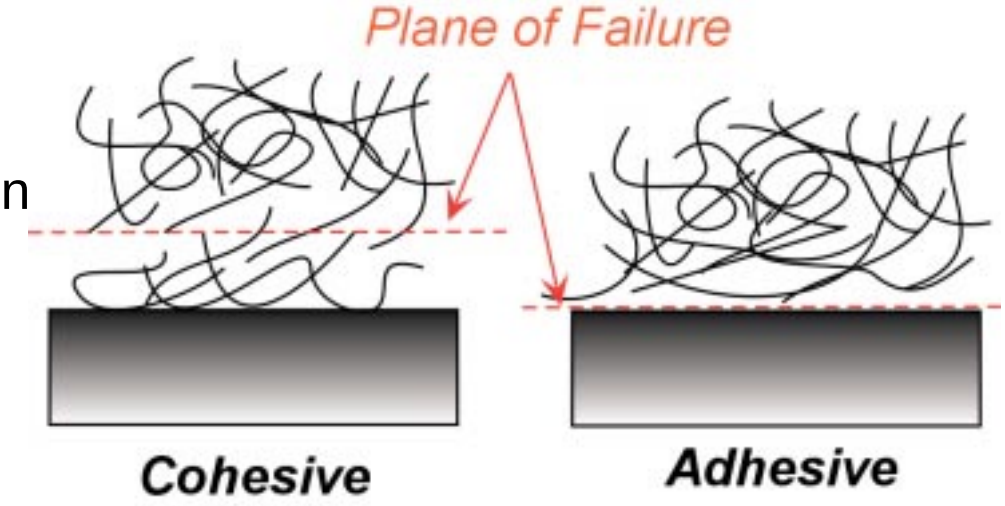
# Introduction 1

Concept: construct a rheometer capable of probing length scales similar to the size of industrially relevant macromolecules.

Aim: initially study effect of slip/no-slip on behaviour of high molecular weight material in narrow gap driven by desire to understand bulk instabilities.

Much recent work on elucidating the mechanism of instabilities in extrusion of polymer melts

Strong evidence of slip but not clear the mechanism or location (cohesive or adhesive failure).

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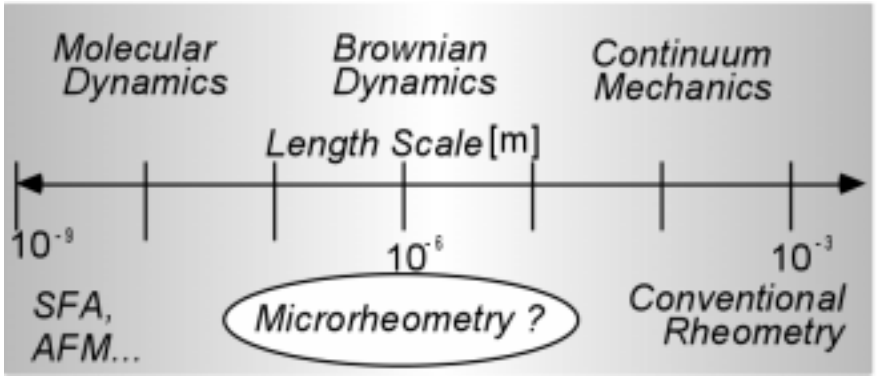
# Introduction 2

Clear that instrument capable of measuring molecular effects (at polymeric length scales) has other possible uses….

- » Expensive (low volume) samples
- » Samples used in small gap processes (e.g. inkjet ink?)
- » Awkward thin samples (e.g. Pressure Sensitive Adhesives films)
- » Aligning materials (e.g. Liquid Crystals)
- » Optically accessible materials (e.g. birefringence)

Fill experimental "gap" between "nanorheology" and bulk rheology hence "microrheometer"





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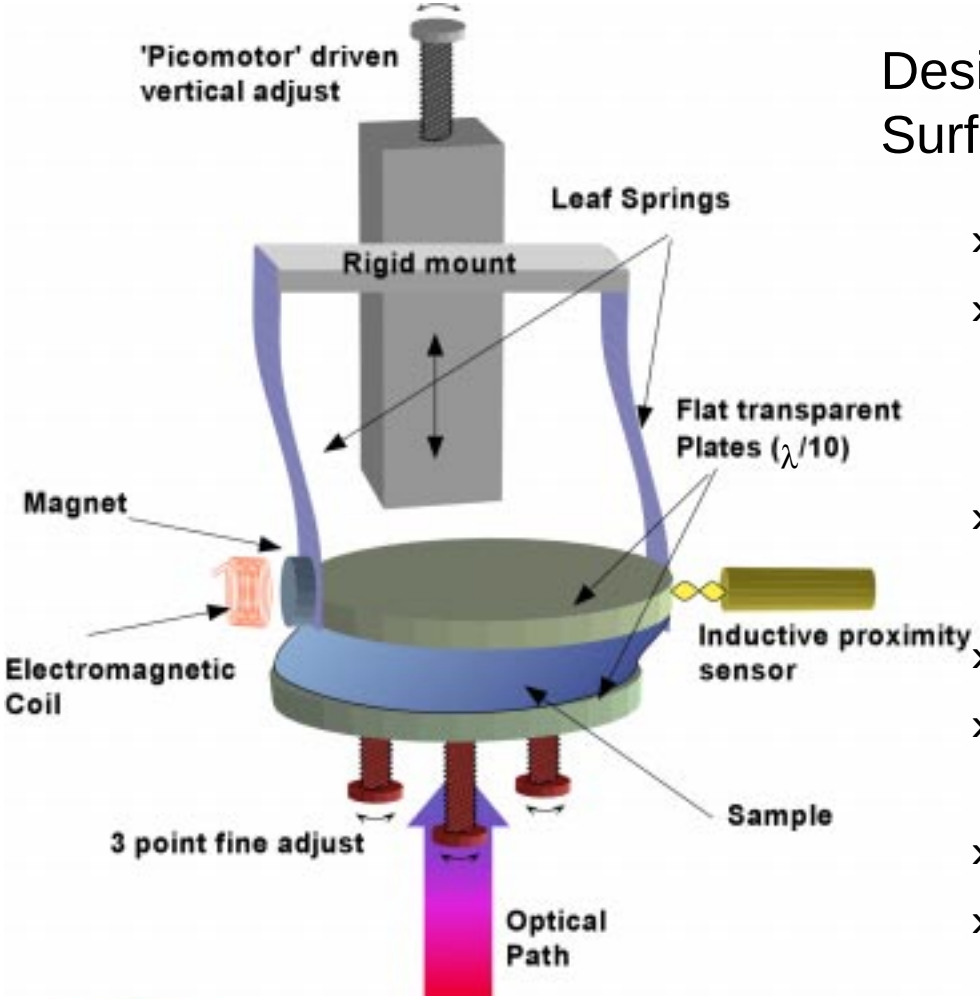
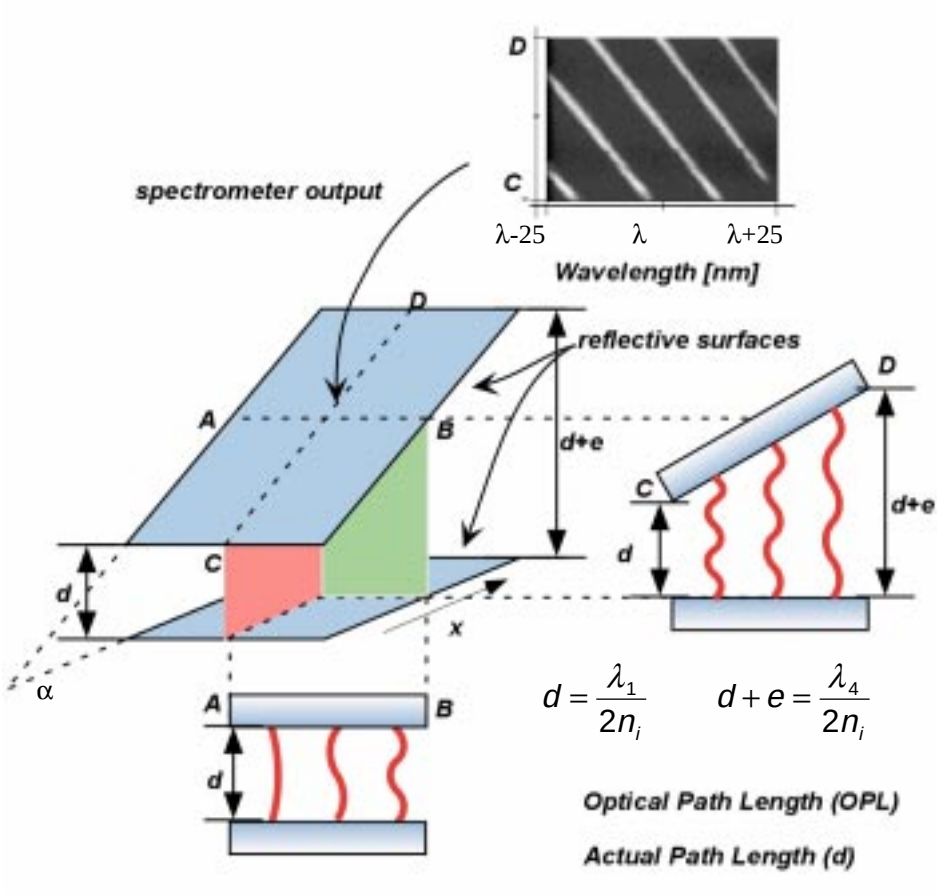
# Apparatus Description




Design based on ideas of Surface Forces Apparatus (SFA)

- Cantilever parallel motion
- Surfaces λ/10 optical flats
  - semi-silvered (~ 200 nm)
  - Other geometries possible
- Drive from electromagnetic coil
  - also piezos possible
- Inductive displacement sensor (~5 nm)
- Parallelism adjusted using 3-point micrometers
- Gap controlled micrometer
- Gap and parallelism determined using interferometery

# Gap Determination (absolute)




$$d = \frac{\lambda_1}{2n_i} \qquad d+e = \frac{\lambda_4}{2n_i}$$

$$OPL = \frac{\lambda_1}{2} \quad \frac{2\lambda_2}{2} \quad \frac{3\lambda_3}{2} \quad \ldots$$

$$d = \frac{\lambda_1}{2n_i} \quad \frac{2\lambda_2}{2n_i} \quad \frac{3\lambda_3}{2n_i} \quad \ldots$$

Two parallel mirrors act as Fabry-Perot interferometer

With polychromatic ("white") light, light passed at point is a combination of all possible integer wavelengths ($d \propto n.\lambda_n$, $(n-1).\lambda_{n-1}$….)

With gap varying a particular wavelength is only passed at specific gaps ($d \propto \lambda_1$ and $d$+e$\propto \lambda_2$)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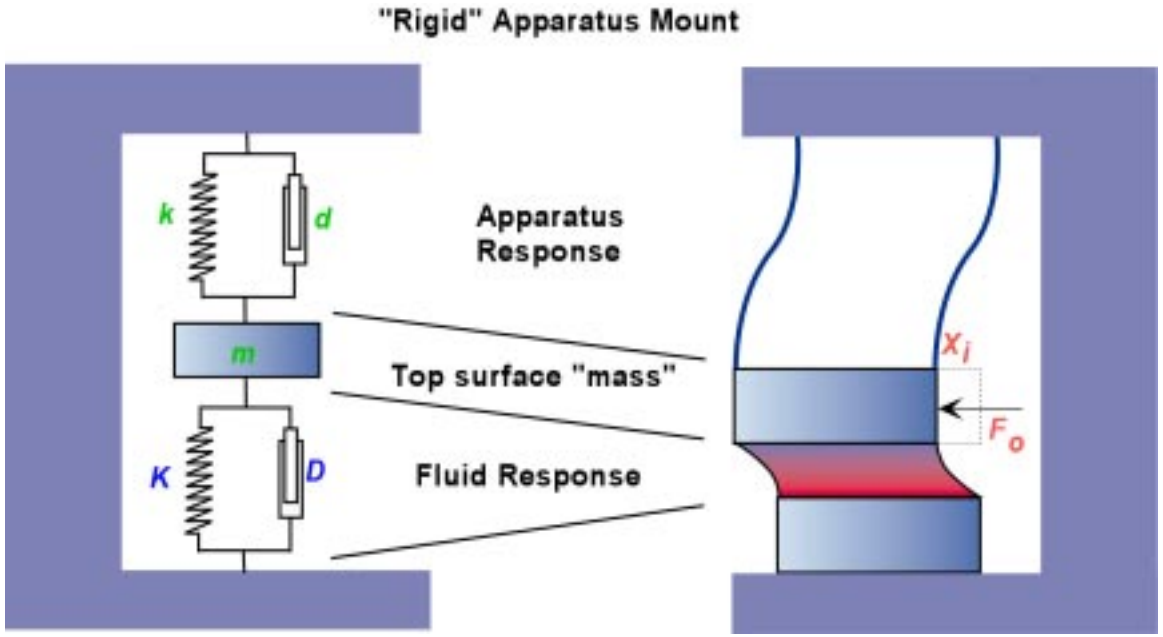
# Apparatus Model



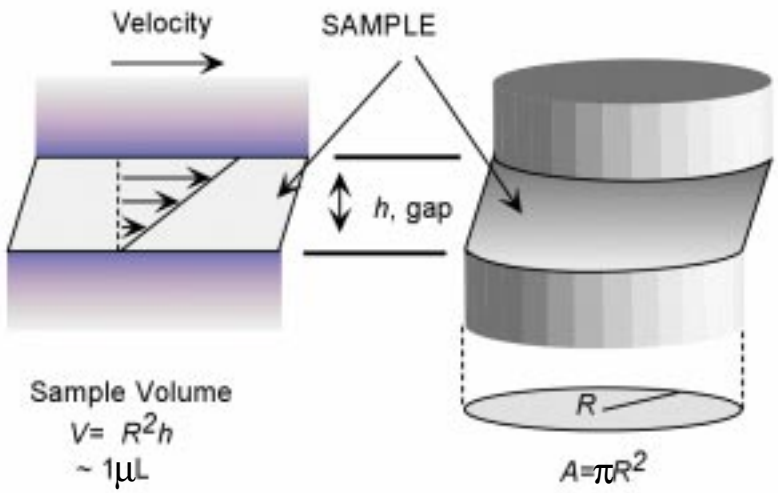

For all these models must remember that the apparatus itself is viscoelastic

$$K = \frac{F_0}{X_2}\cos\phi_2 - \frac{F_0}{X_1}\cos\phi_1; \qquad \omega D = \frac{F_0}{X_1}\sin\phi_1 - \frac{F_0}{X_2}\sin\phi_2$$

Apply a known Force ($F_o$) for a displacement ($X_i$)

$$K = \frac{F_0}{X_2}\cos\phi_2 - \frac{F_0}{X_1}\cos\phi_1 \qquad \omega D = \frac{F_0}{X_1}\sin\phi_1 - \frac{F_0}{X_2}\sin\phi_2$$

# Rheometer




SFA and hybrids allow mechanical study of fluids in small gaps (“nanorheology”).

Curved surfaces do not allow rheological parameters to be extracted easily.

Simple shear flow allows determination of rheological parameters (c.f. connection between torque and viscosity).

$$G^* = \frac{\sigma}{\gamma} = \frac{F^*}{A}\frac{h}{X^*} = p\frac{F^*}{X^*}; \qquad p = \frac{h}{A}$$

$$G^* = G' + jG'' = pK^* = p(K + j\omega D) \qquad j = \sqrt{-1}$$

# Instrument Parameter Space

| Parameter | Value | | Comment |
|---|---|---|---|
| Plate Size (diameter) | 13 mm | | Currently 5mm - 20mm possible |
| Gap Range | 500 nm — 500 μm | | Practical lower limit ~ 5 μm |
| Sample Size | 0.07 μL — 40 μL | | Governed by parameters above |
| Temperature Range | Ambient | | The design has been specifically considered with higher (~200 °C) temperatures in mind - since we measure the gap absolutely thermal expansion is not a problem |
| Stress Range | 8 mPa — 1 kPa | | This is drive current limited so different drive electronics would significantly increase the range |
| Dynamic Range (oscillatory) | <1 mHz — 500 Hz | | Governed by the stiffness of the springs and mass of surface. Note resonance currently at 50 Hz |
| Velocity Range (steady shear) | ~1 nm/s ? - 1 mm/s | | The lower limit at the moment is drift limited |
| | Gap = 1 μm | Gap = 500 μm | |
| Strain Range (gap dependent) | 0.5% — 5000% | 0.001% — 10% | |
| Strain Rate Range | $2\times10^{-6}$ $s^{-1}$ — 2 $s^{-1}$ | $1\times10^{-3}$ $s^{-1}$ — 1000 $s^{-1}$ | |
| Viscosity Range | 4 mPa.s — $500\times10^{6}$ Pa.s | $8\times10^{-6}$ Pa.s — $1\times10^{6}$ Pa.s | |

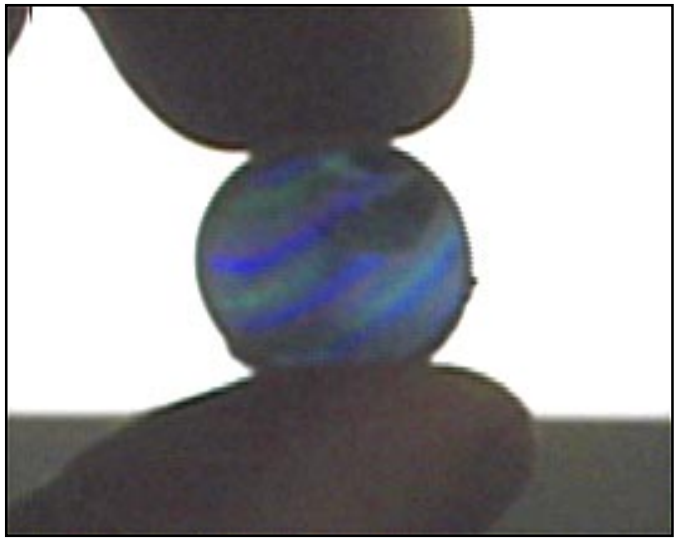
# Pressure Sensitive Adhesives

Example 1: a rubbery solid

3M Optically Clear Laminating Adhesive 8141

- ~25 μm acrylic adhesive on polyester release liners
- Isotropic, non-birefringent, 99+% transparent
- Shear modulus reported as $10^5$ Pa

Sample Courtesy 3M



Standard approach 1 mm laminate

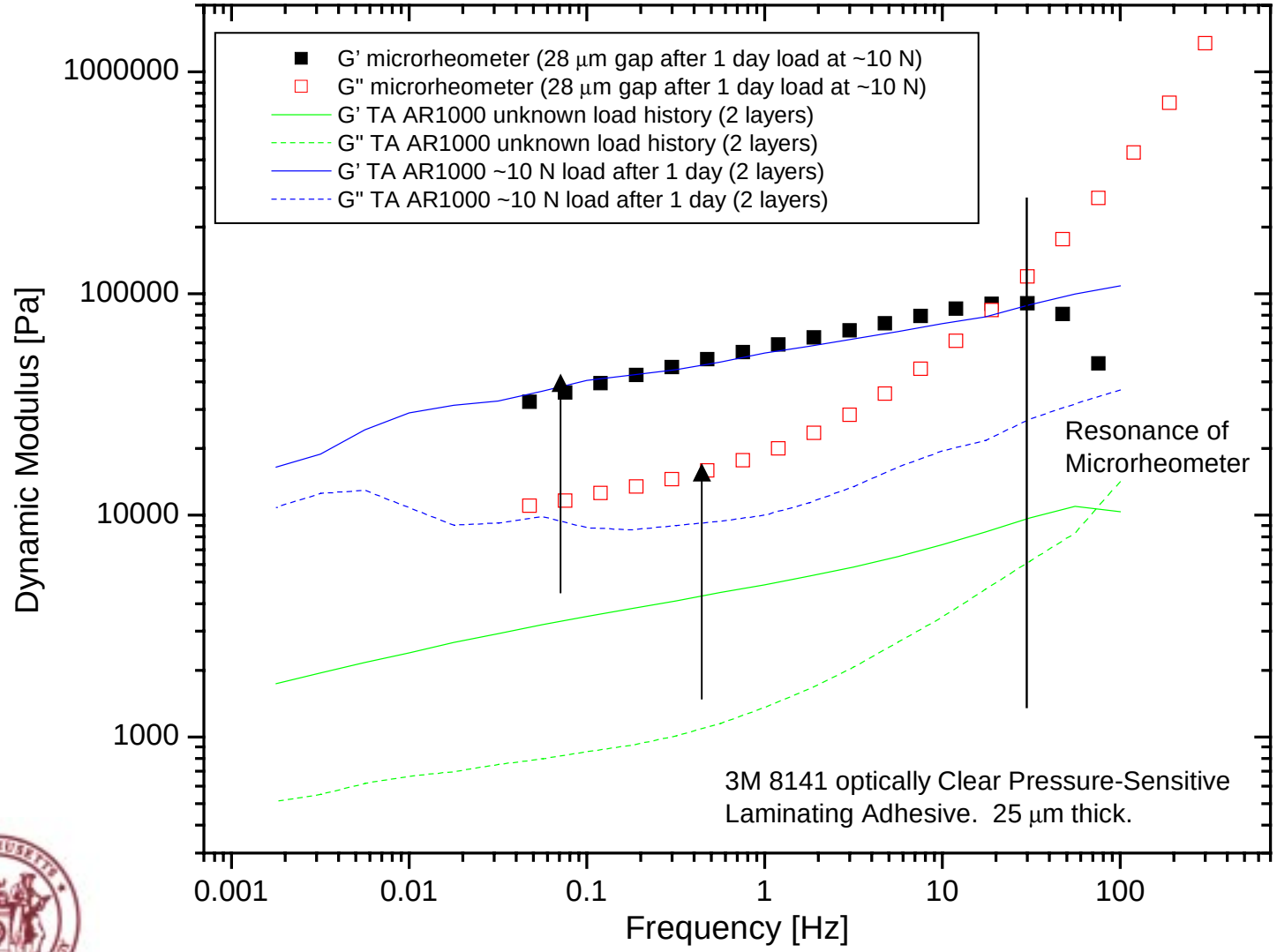
Plates parallel to resolution

Gap 28.32 μm ± 0.34 μm

Contact and loading history crucial

# Pressure Sensitive Adhesive

Note bulk data taken using two laminated layers (~ 100 μm) in parallel plate



# Polydimethylsiloxane (PDMS)

Example 2: Room Temperature Melt

Initially require a room temperature polymeric melt to test system.

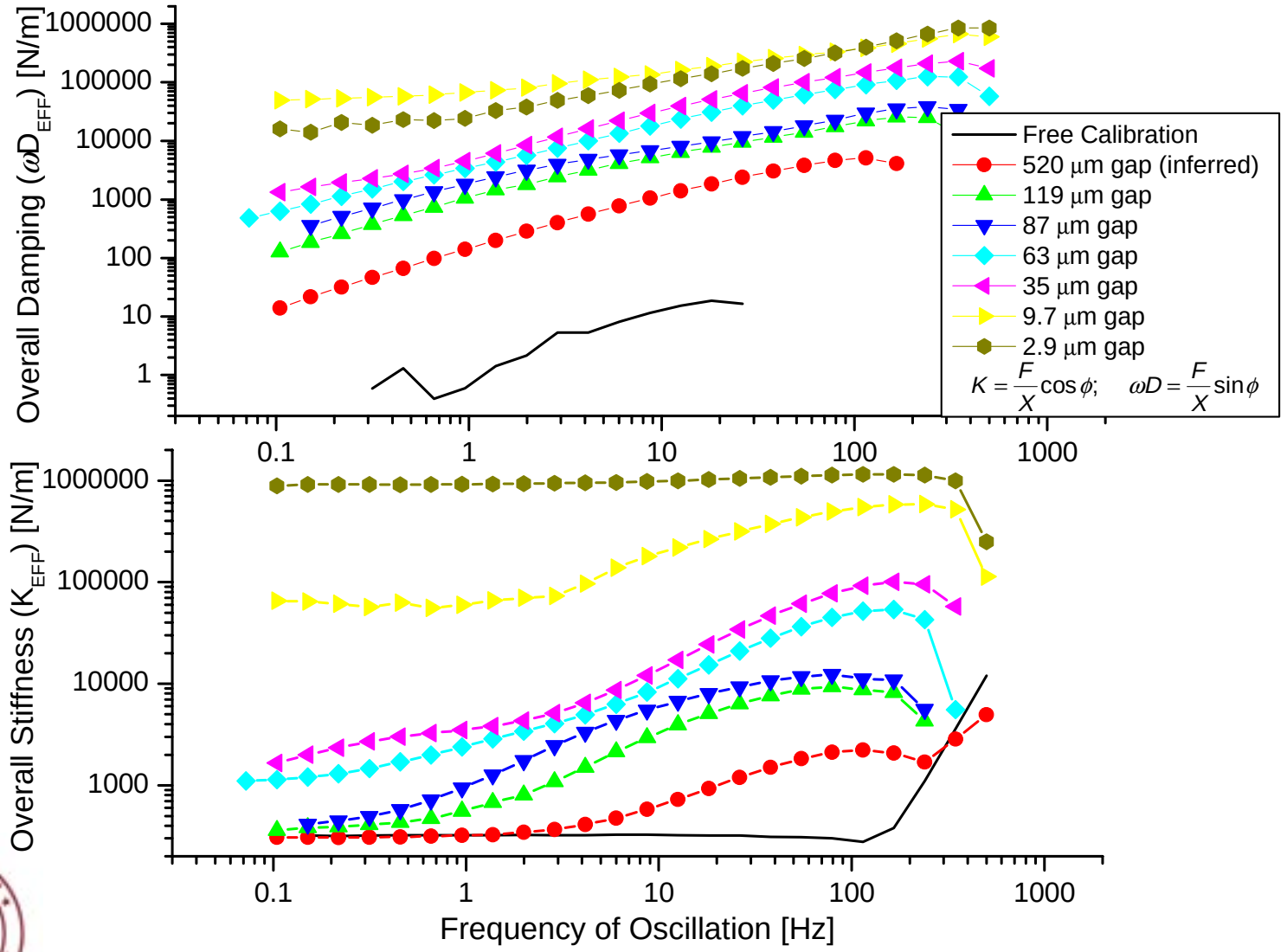
PDMS a good candidate:

- Strongly adsorbing to glass
- High molecular weight (139,000) polydisperse (Gelest Inc)
- High viscosity (Shear viscosity ~100 Pa.s)
- Inert
- Transparent

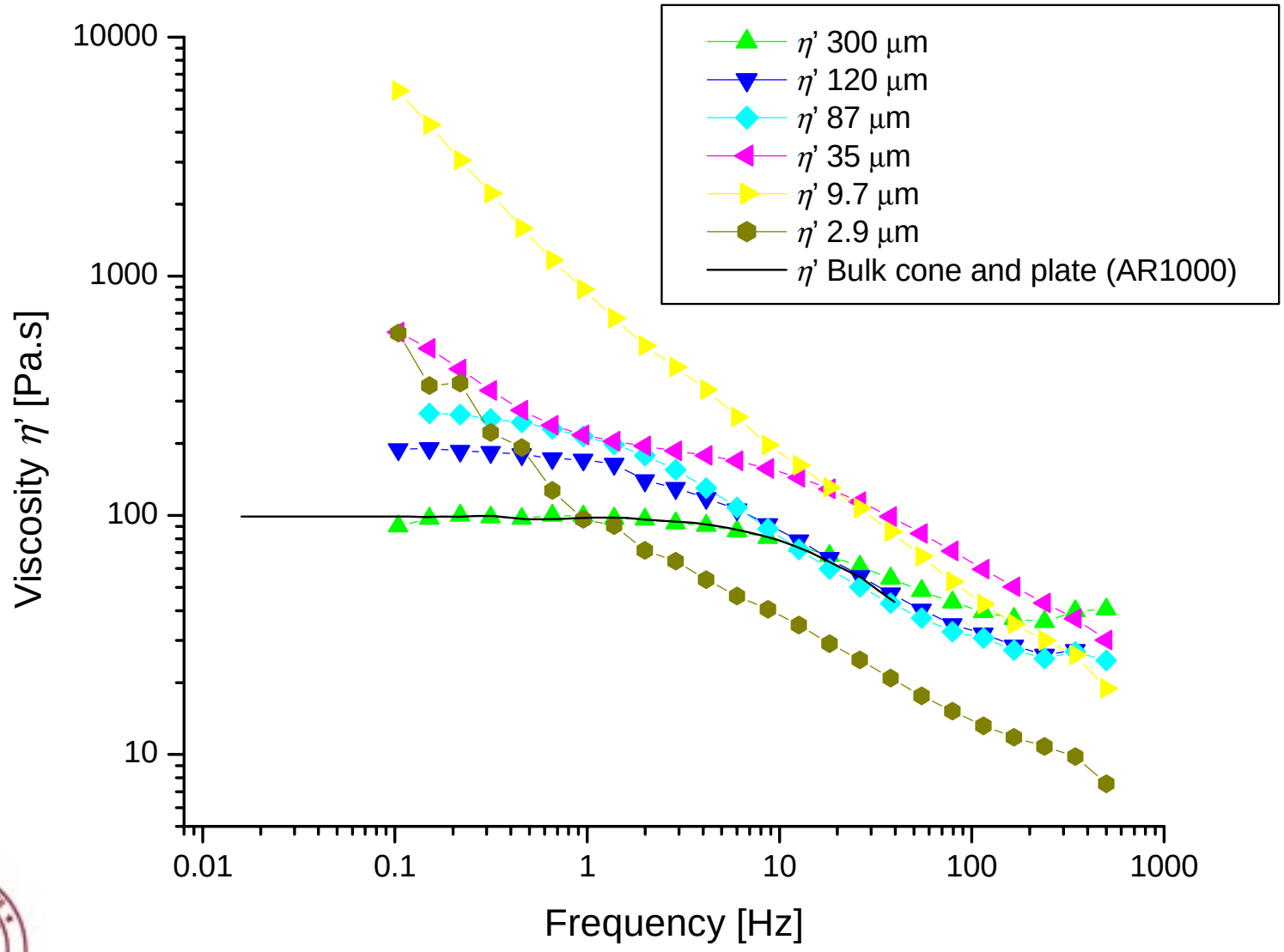
Entanglement weight ~30,000 (weakly entangled)

Radius of gyration approximately 20 nm

# PDMS - gap dependence



# PDMS - viscosity



# Possible Explanations


- Drive Mechanism?
  - » Changed to piezo drive
- Compliance in Instrument?
  - » See previous experiment

- Surface Tension?
  - » Immersed plates
  - » Different Geometries
- Flow edge effects?
  - » ?

# Conclusions

Demonstrated viable design for a microrheometer

Good dynamic range, Small sample size (~1 μl)

Adjustable surface chemistries and geometries

Optically accessible

PSA results very promising.

Difficult experiment relatively easy.

Excellent agreement

PDMS correct order of magnitude. Gap dependence as yet unexplained.

Potential systems for study:

- Liquid Crystals (e.g. birefringence, coarsening)
- colloids/suspensions
- soft solids (e.g. PSA, tire elastomers, food stuffs)
- biofluids (e.g. blood, synovial fluid)

# Multiple Beam Interferometry (extra information)

At a particular point on the surfaces (or on line A-B):

$$d = \frac{\lambda_1}{2n_i} = \frac{2\lambda_2}{2n_i} = \frac{3\lambda_3}{2n_i} = \cdots$$

$$\Rightarrow d = \frac{n\lambda_{(n)}}{2n_i} = \frac{(n+1)\lambda_{(n+1)}}{2n_i}$$

$$\text{hence } d = \frac{1}{2n_i}\frac{\lambda_{(n)}\lambda_{(n+1)}}{\lambda_{(n)} - \lambda_{(n+1)}}$$

Also along plane of tilt of surface (*i.e.* line C-D):

$$d = \frac{n\lambda_{(n)}\Big|_{x=d}}{2n_i}; \quad d+e = \frac{n\lambda_{(n)}\Big|_{x=d+e}}{2n_i}; \quad n \text{ is constant but } \lambda_{(n)} \text{ depends on } x$$

$$\text{hence tilt} = \frac{e}{x} = \frac{\lambda_{(n)}\Big|_{x=d+e} - \lambda_{(n)}\Big|_{x=d}}{2n_i}$$

Error in wavelength determination is 1 nm. Therefore at 600 nm 0.2%.

Error in gap is $\sim 5\%$, error in tilt $\sim 1$ nm / mm