Confined Complex Fluids

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University of California – Davis

<u>Part 1: Confined Simple Fluid</u>

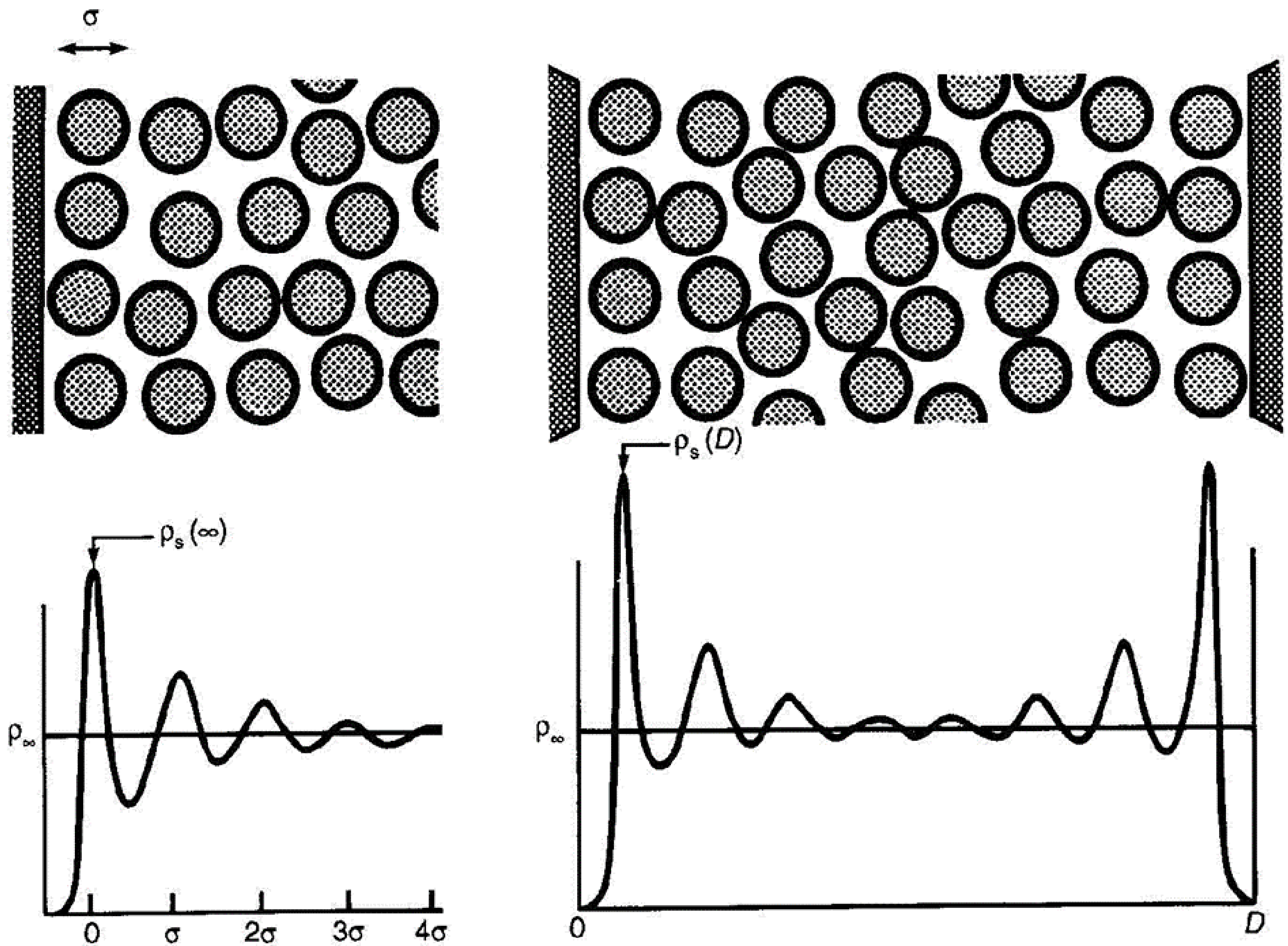
Daniel Kienle

<u>Part 2: Interpenetration of Confined Polymer Brushes</u>

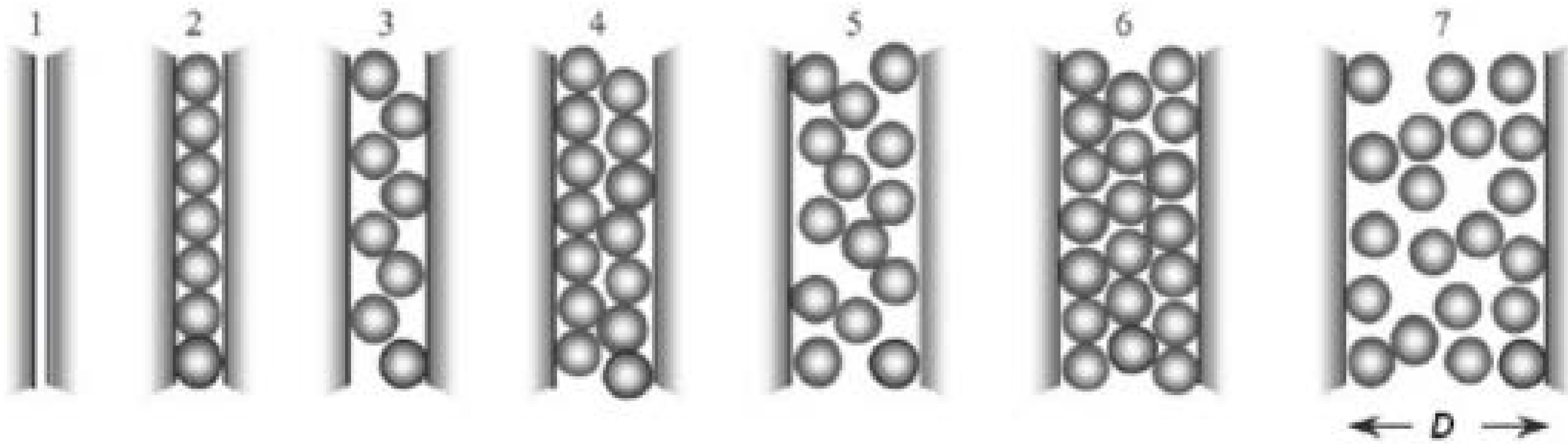
Dennis Mulder, **Wei-po Liao**, Suzanne Barber, Torsten Kreer, Carlos Marques, Greg Smith, Bill Hamilton, Jarek Majewski

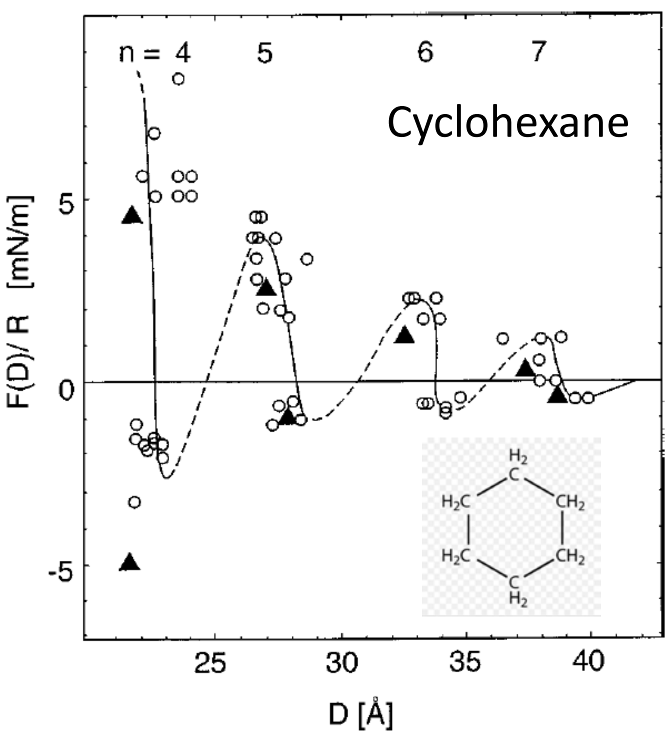
Support = ACS-PRF, UC LAB/ DOE, NSF

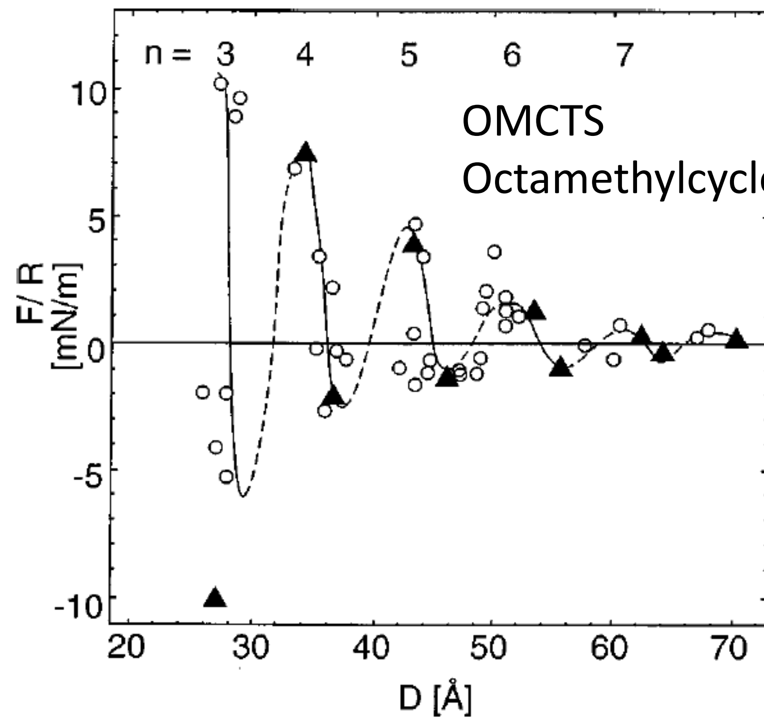
Confined Simple Fluids – Oscillatory Forces

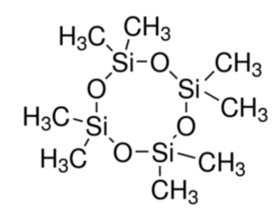


Confined Simple Fluids – Oscillatory Forces



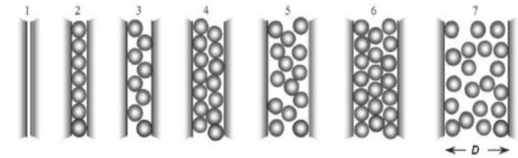


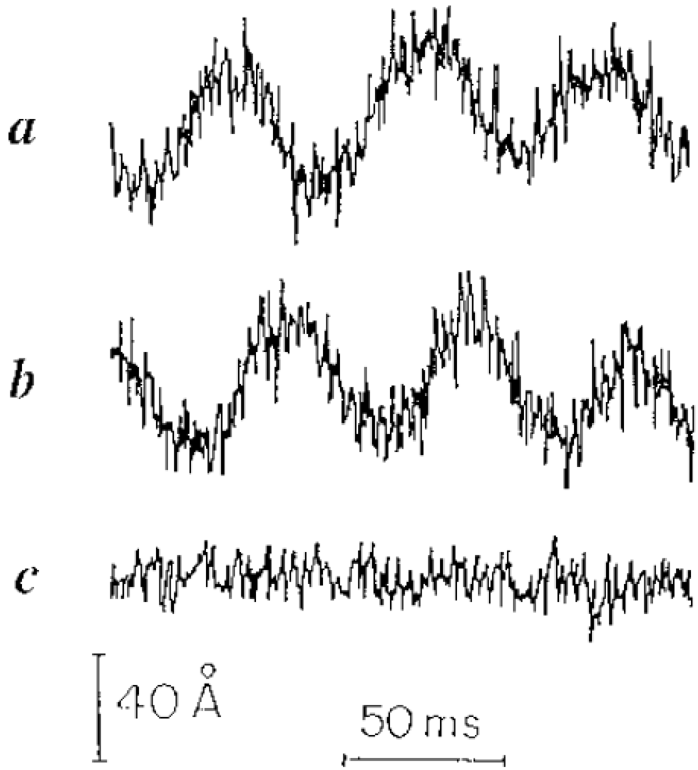


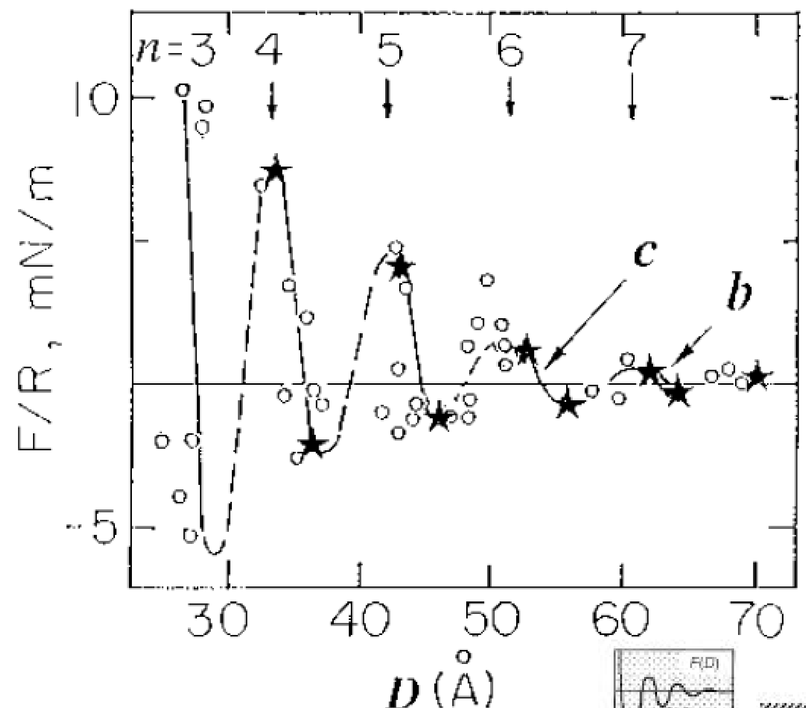


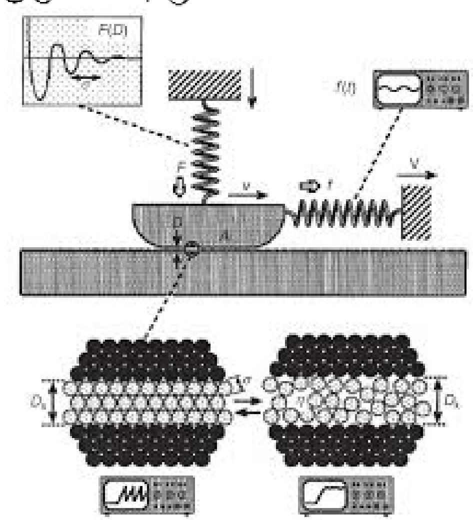
J Klein and E Kumacheva JChemPhys 1998

Confined Simple Fluids – Solidlike?







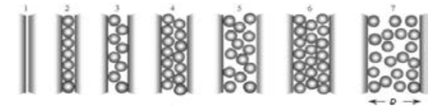


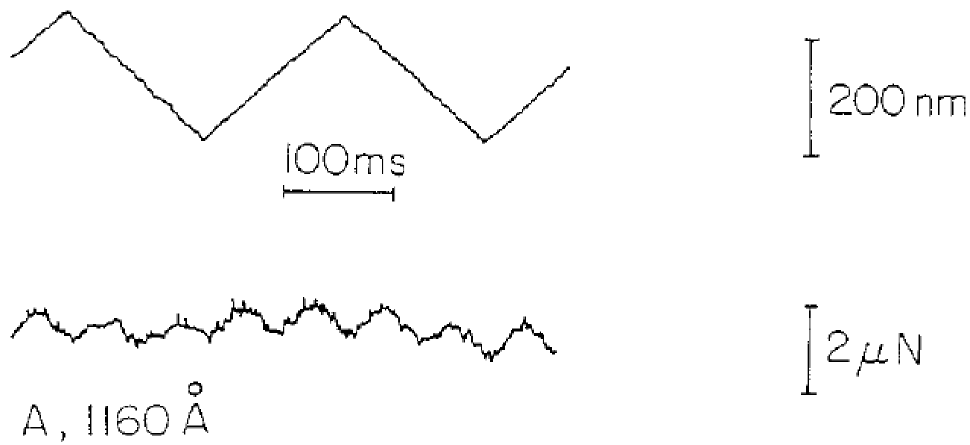
Almost no pressure applied!

Experimental temperature ONLY 8°C > T_{Melt}

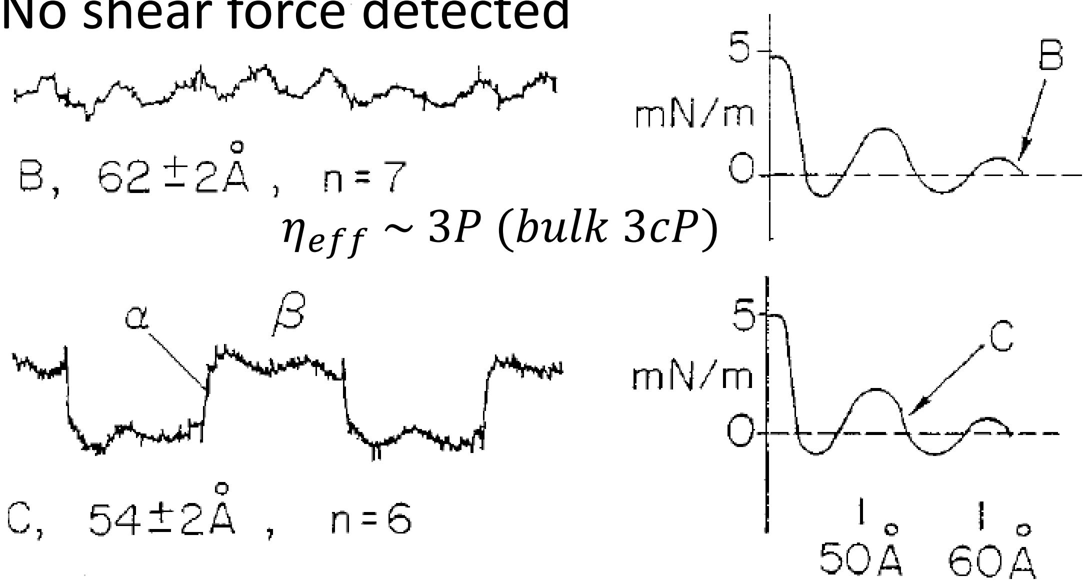
J Klein and E Kumacheva JChemPhys 1998

Confined Simple Fluids – Shear Forces

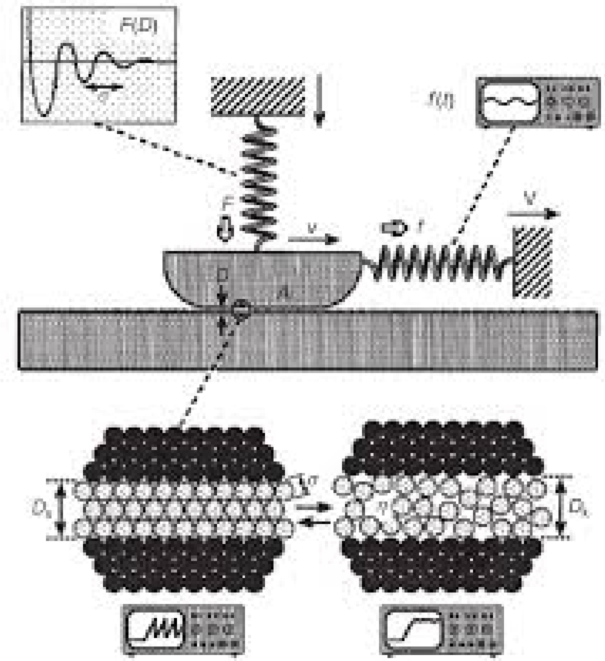


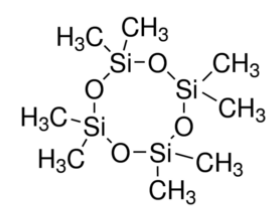


No shear force detected



$\eta_{eff} \sim 3P$ (bulk $3cP$)

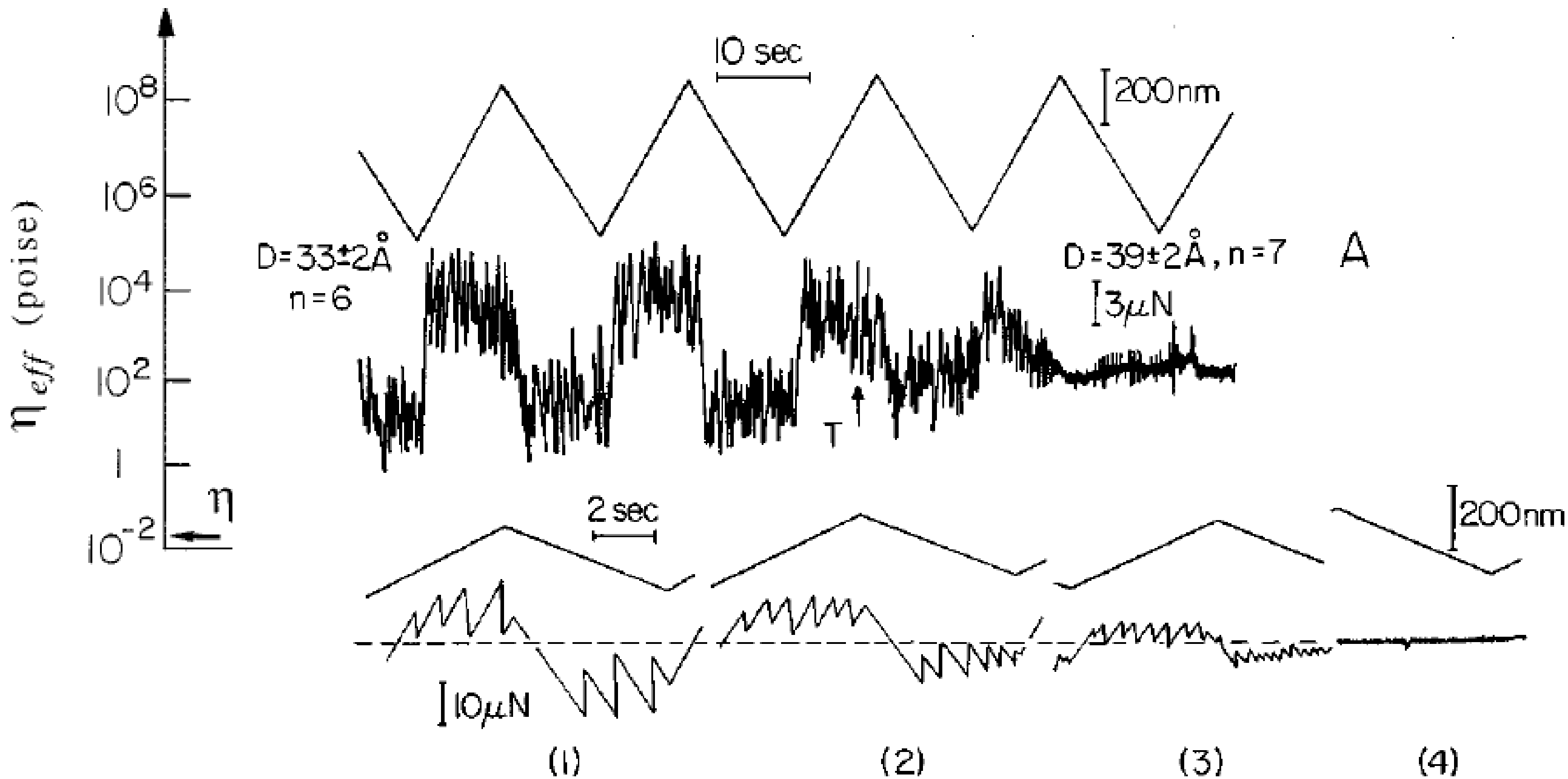




Shear force detected – yield point
transition from liquid to “solidlike” behavior

J Klein and E Kumacheva JChemPhys 1998

Confined Simple Fluids – Fluid/Glassy or Solid?



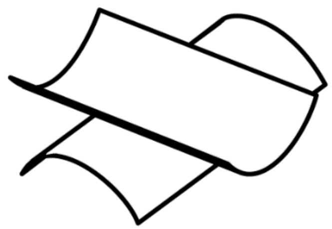
Reversible – glassy

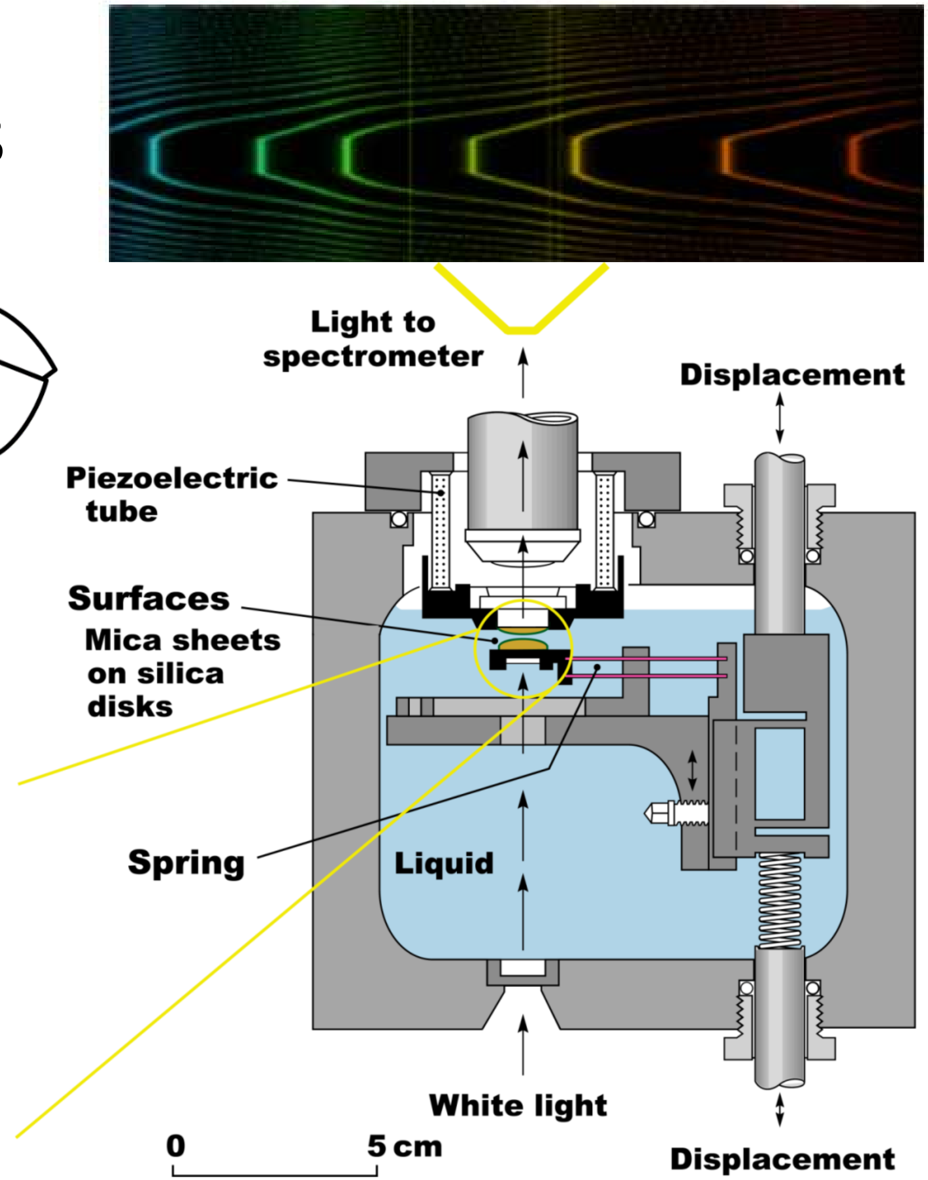
J Klein and E Kumacheva JChemPhys 1998

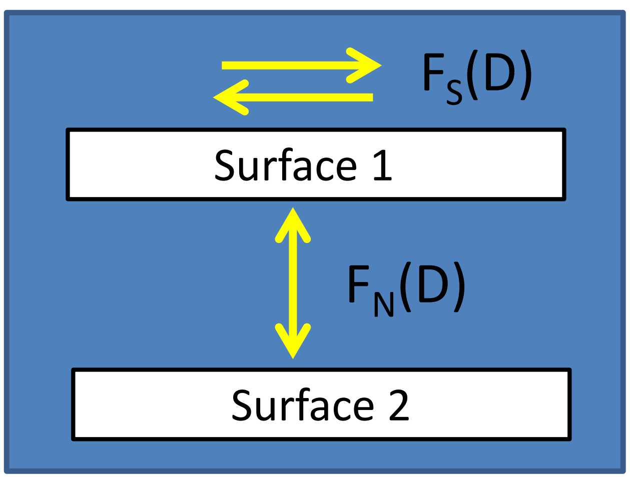
Measuring Colloidal Interactions at 0.1nm

Surface Force Apparatus

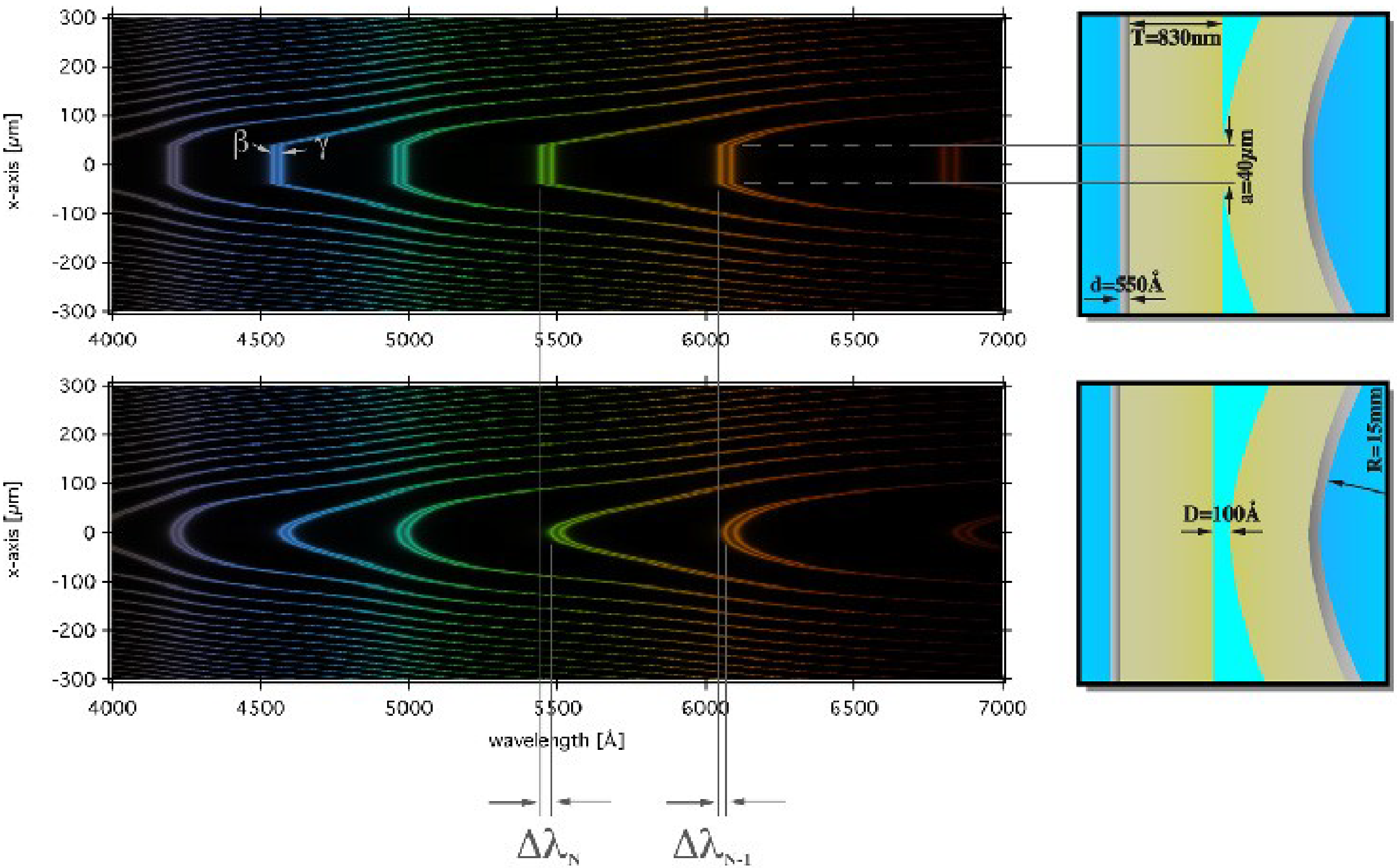
- Force Profile, $F_N(D)$
  - Force ~50nN
  - Distance ~ 1Å
- Friction, $F_S(D)$
- Thin Film Tribology/Rheology





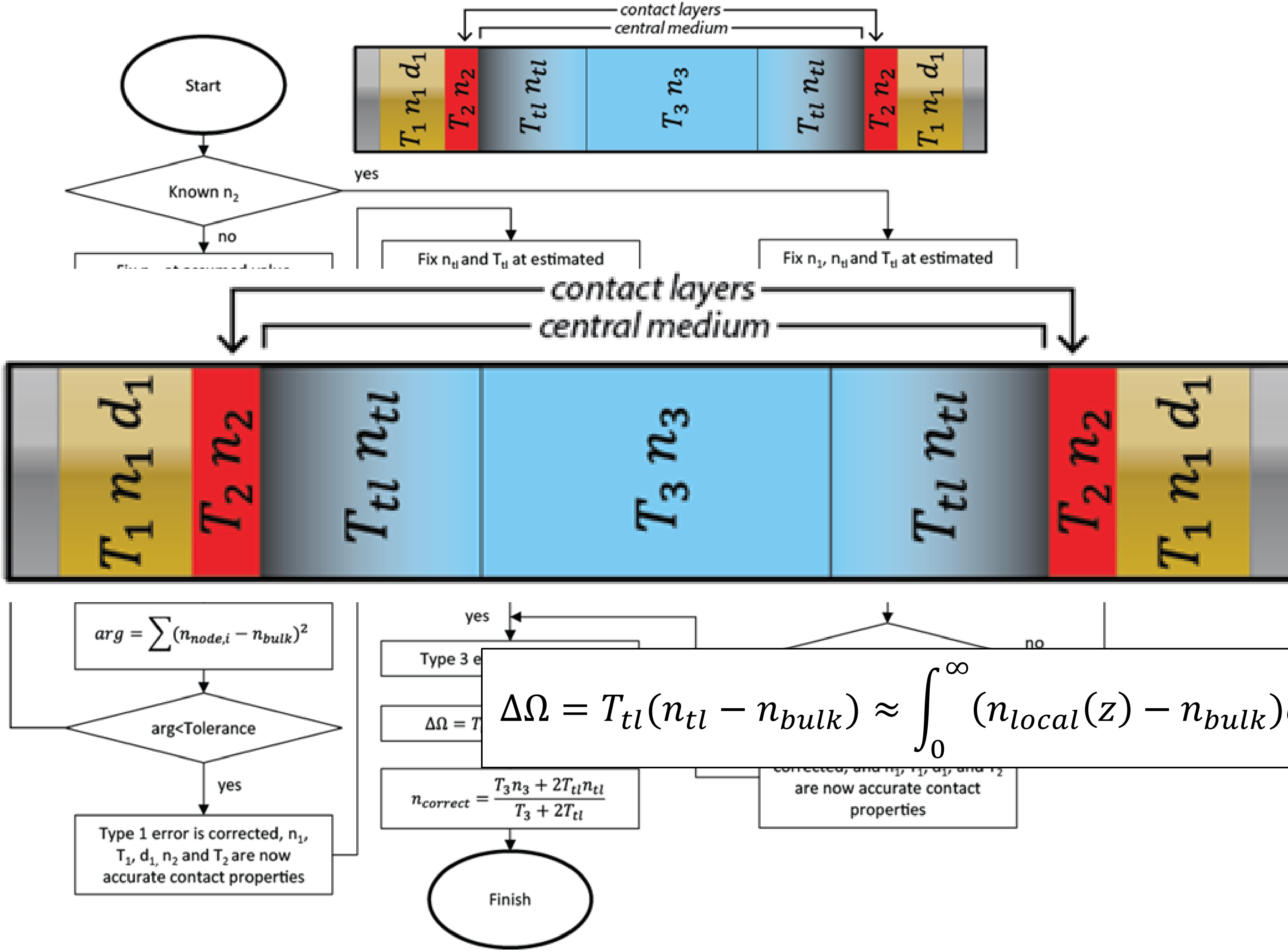


Multiple Beam Interferometry



Heuberger et al Langmuir 1997

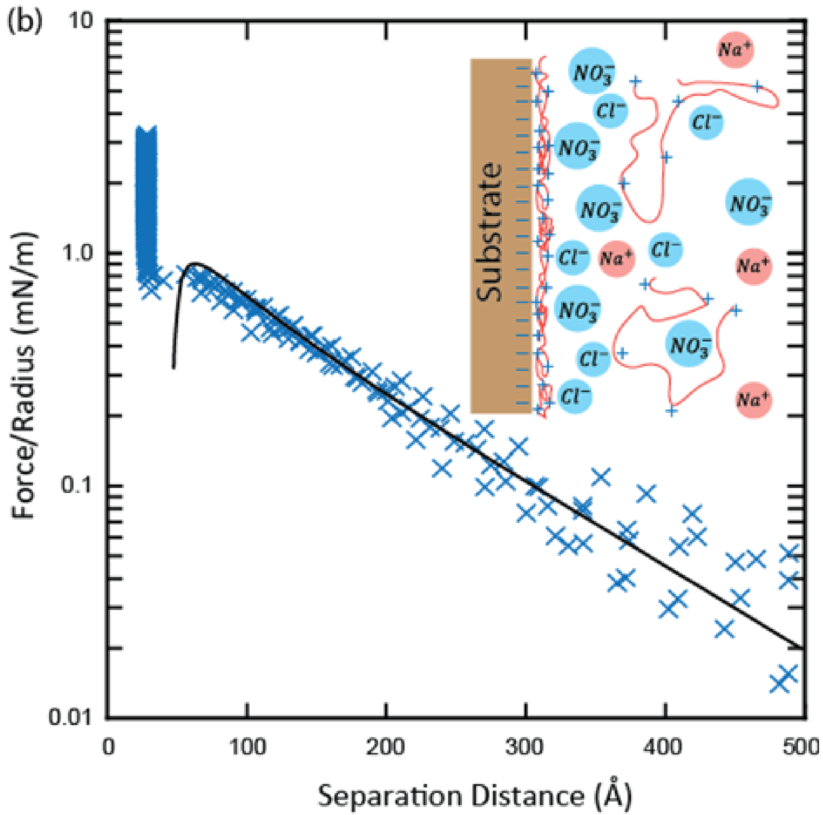
Modeling Multiple Beam Interferometry



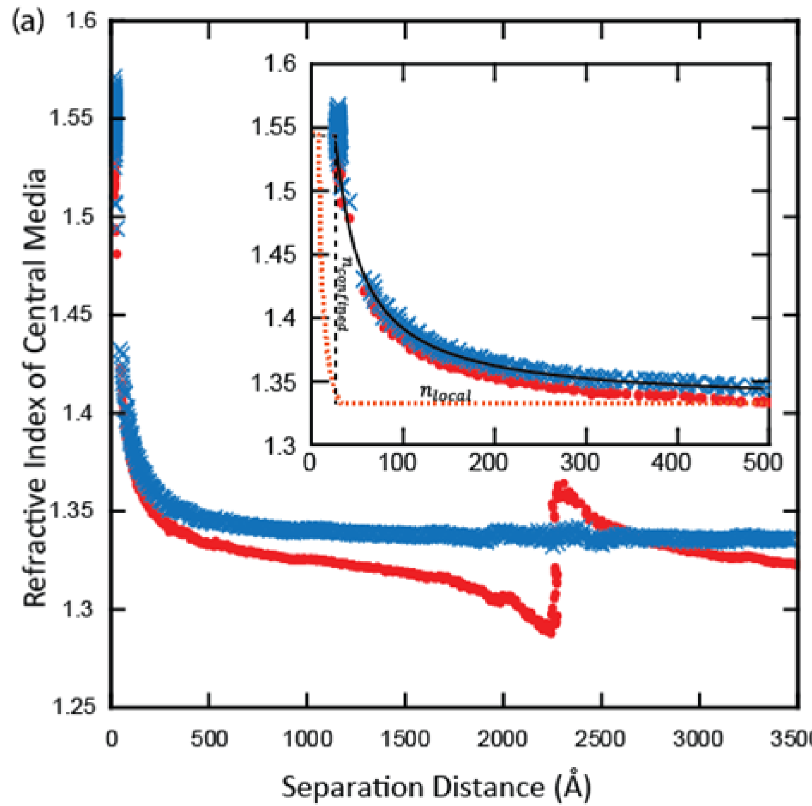
$$\Delta\Omega = T_{tl}(n_{tl} - n_{bulk}) \approx \int_0^\infty (n_{local}(z) - n_{bulk})dz$$

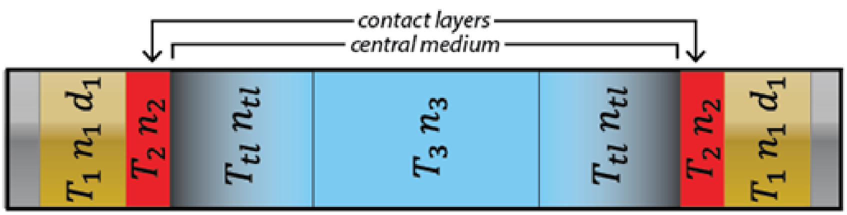
Confined Complex Fluids – Adsorbed polymer layer

linear polyethyleneimine (PEI)
in 0.5 mM NaNO3



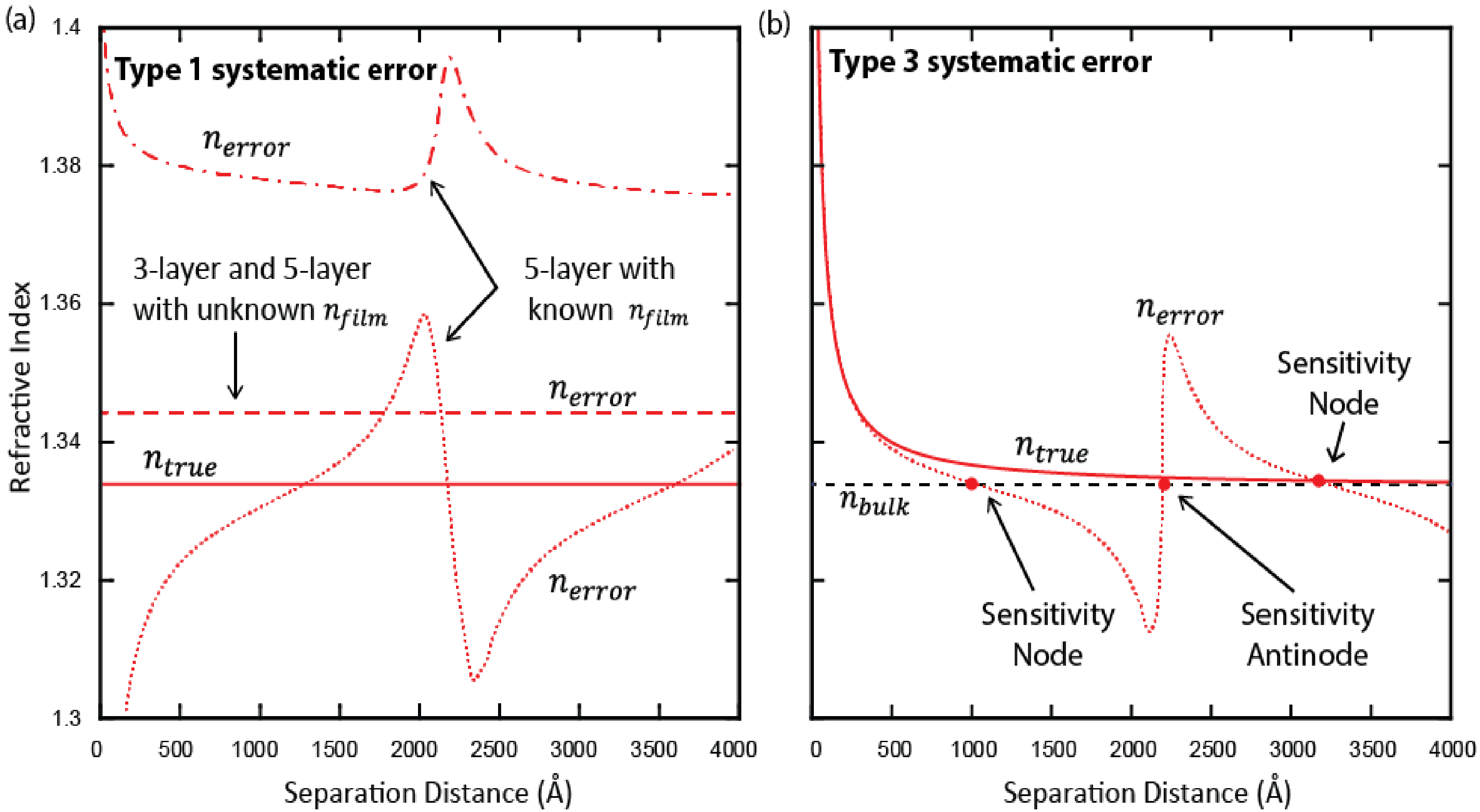
Refractive Index Modeling





Kienle et al Analytical Chemistry 2014
Kienle et al Analytica Chimica Acta 2016

Modeling Multiple Beam Interferometry

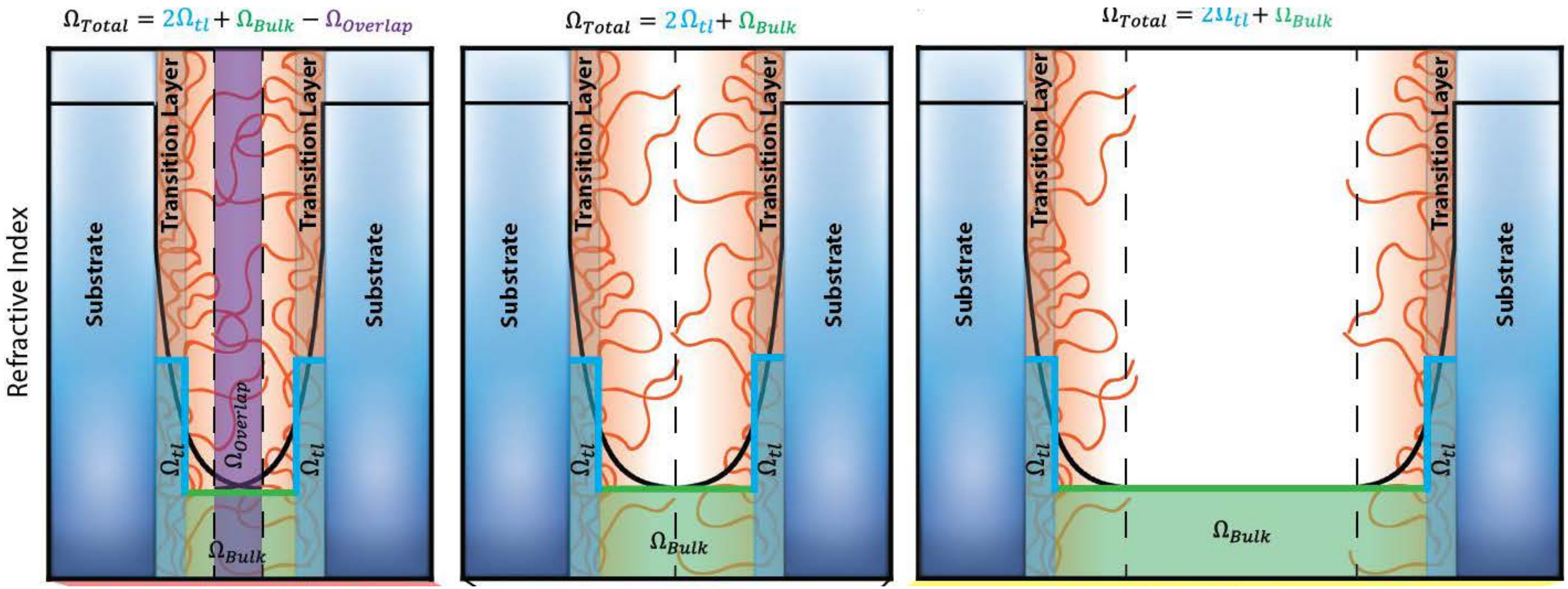


Type 1 error = systematic error in substrate T and η

Type 2 error = systematic error in FECO λ, optical noise, different orientation, contamination

Type 3 error = incorrectly using a continuously varying, mean refractive index

Refractive Index of Confined Adsorbed Polymer



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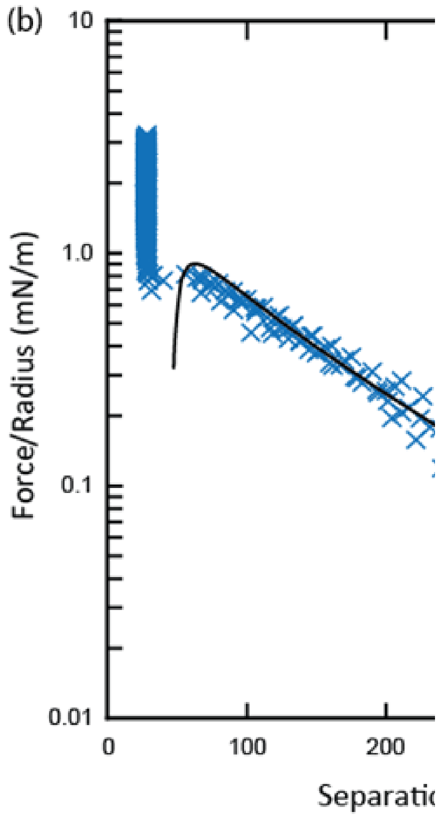
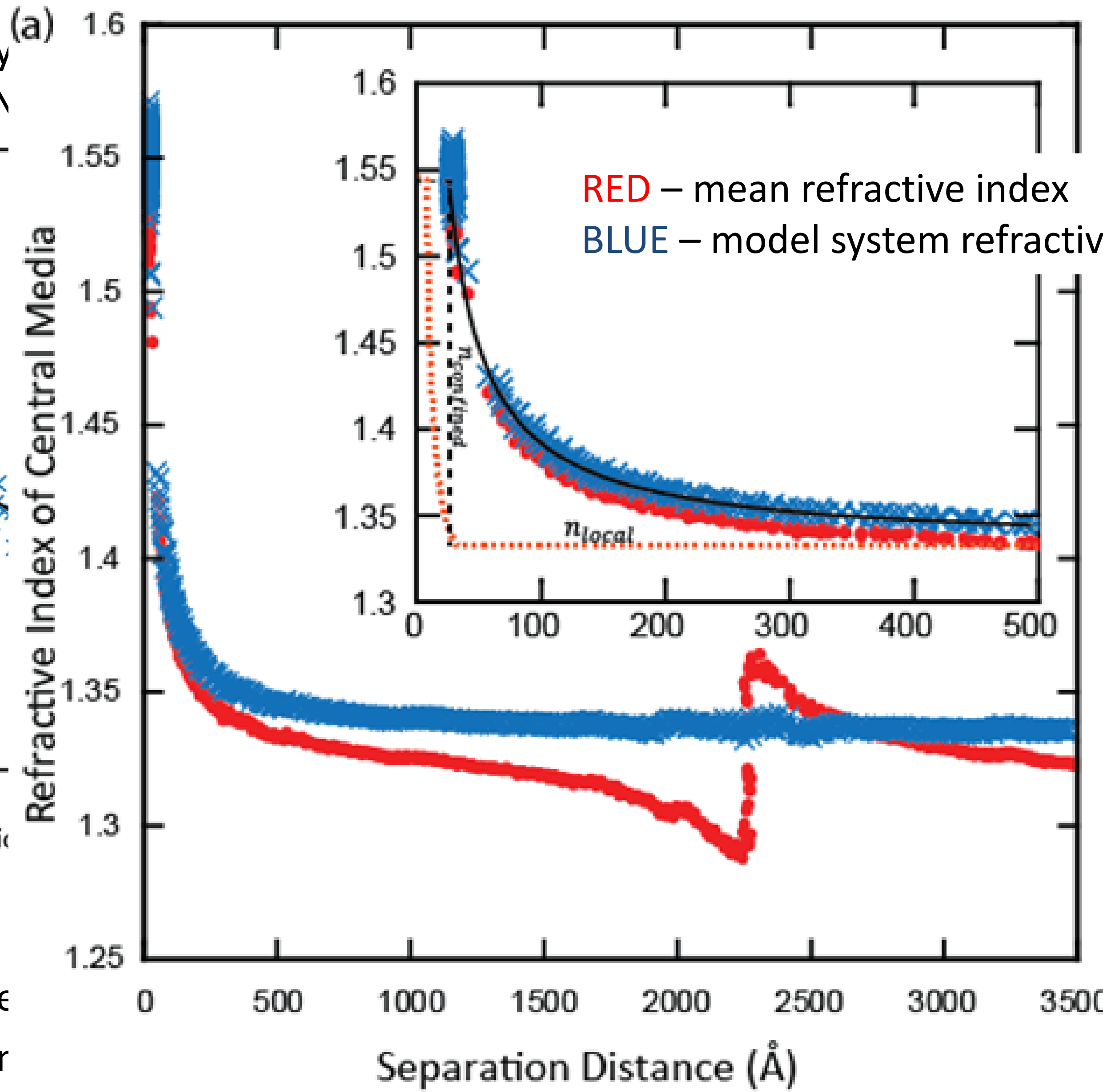
Kienle et al Analytical Chemistry 2014

Kienle et al Analytica Chimica Acta 2016

Confined Complex Fluids – Adsorbed polymer layer

linear polyethy
in 0.5 mM NaN





Kienle et al Analytical Che
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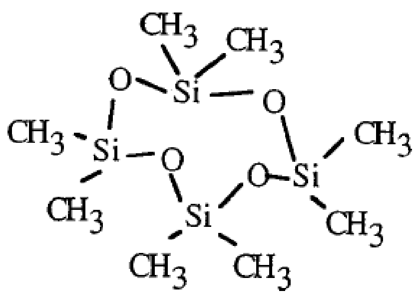
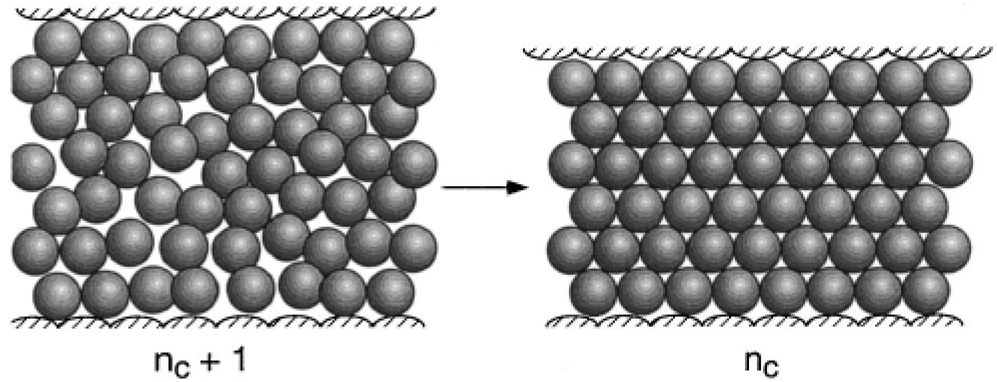
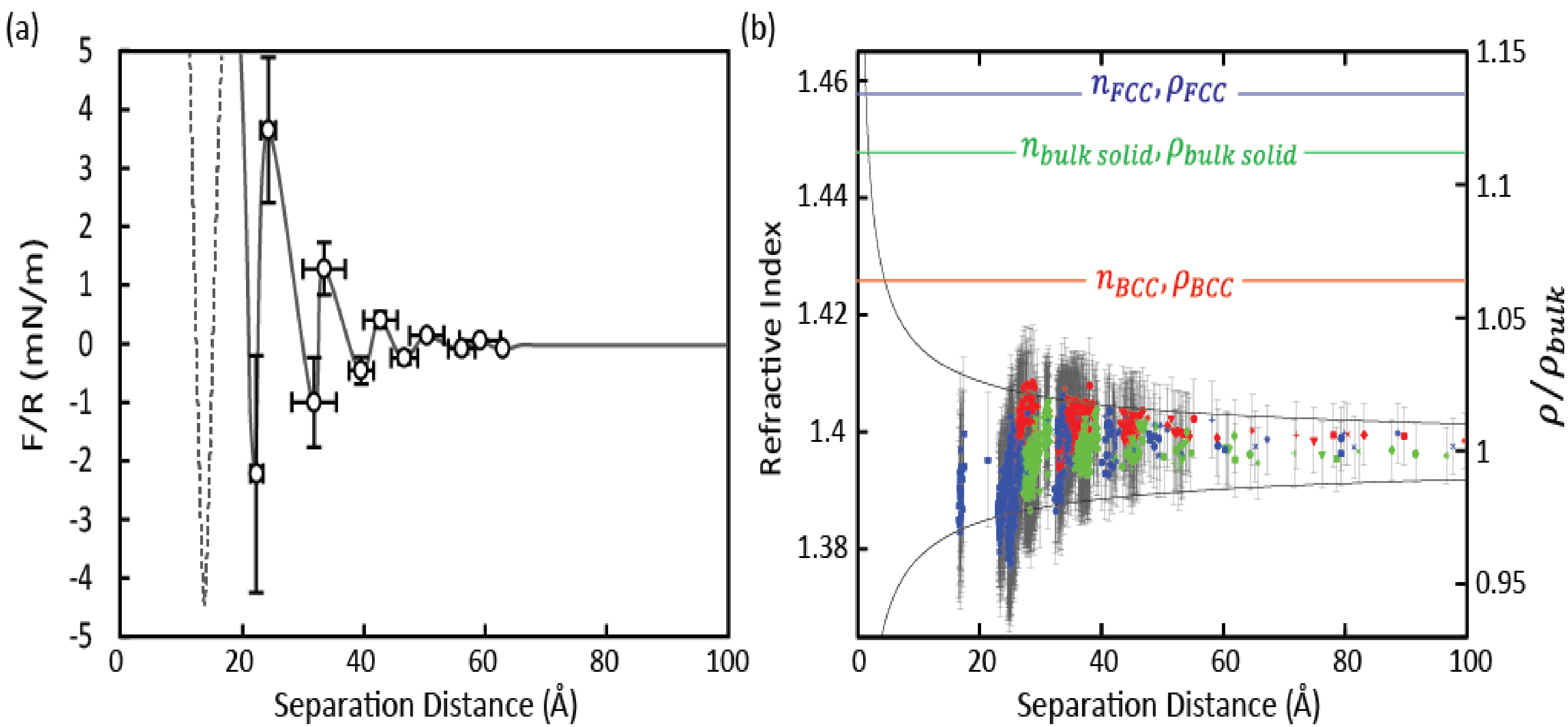
Confined Fluids - OMCTS

Octamethylcyclo-
tetrasiloxane
(OMCTS)

$(SiO)_4(CH_3)_8$







Kienle et al PRL 2016

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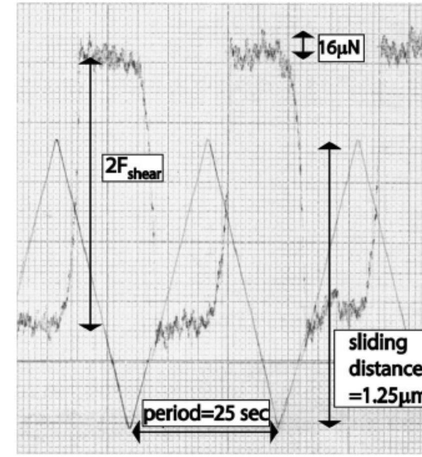
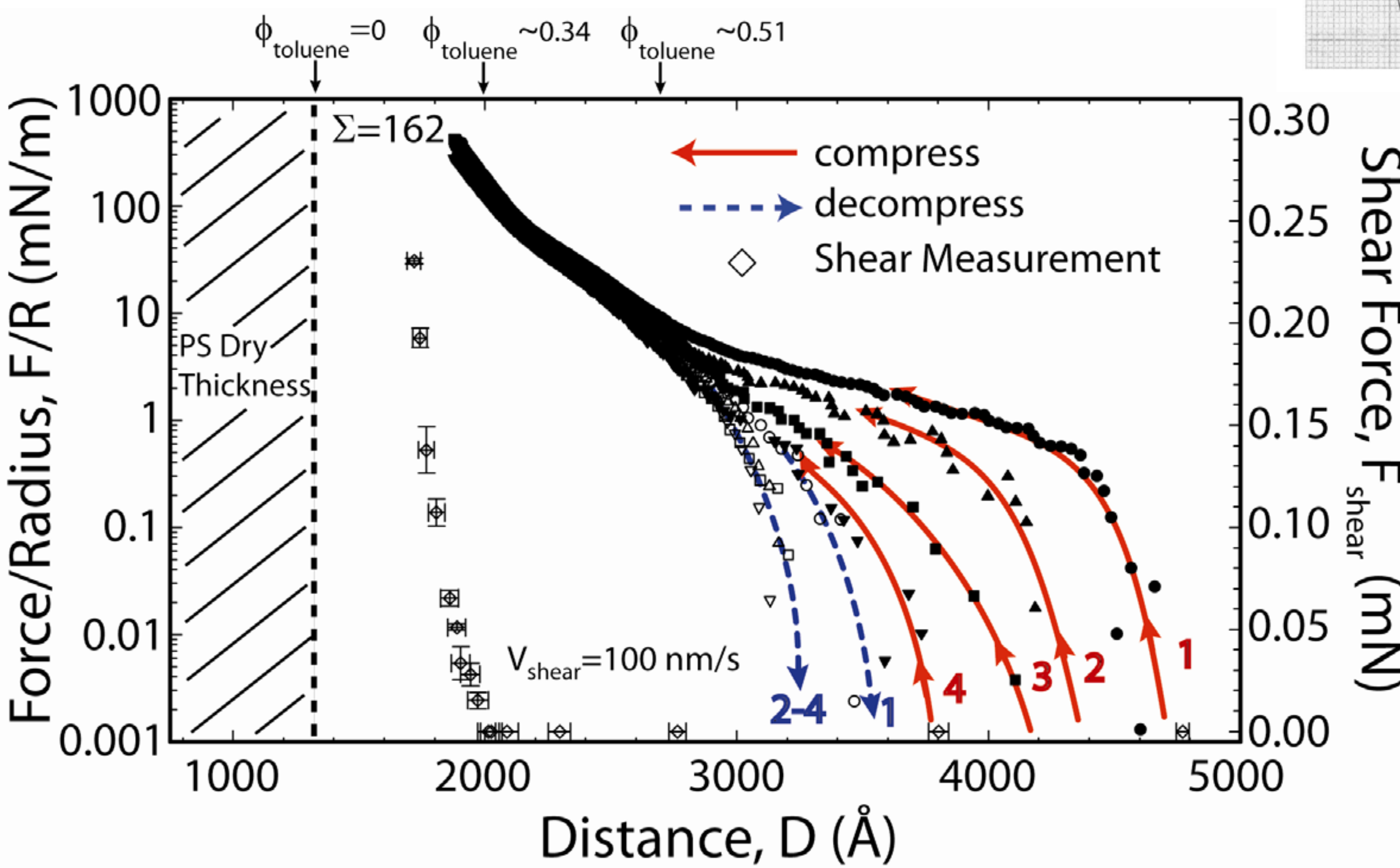
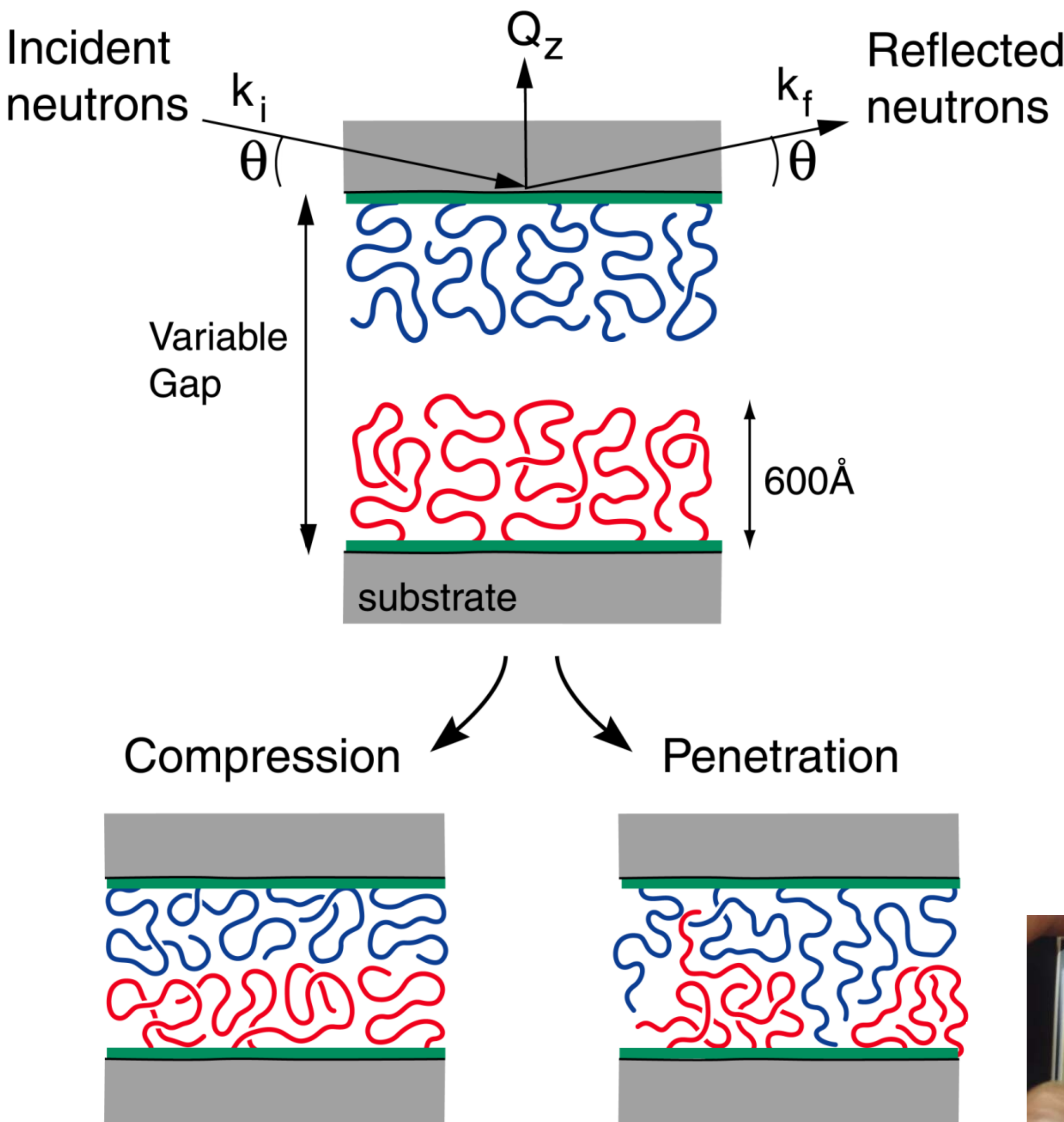
Dynamics of Polymer Brushes



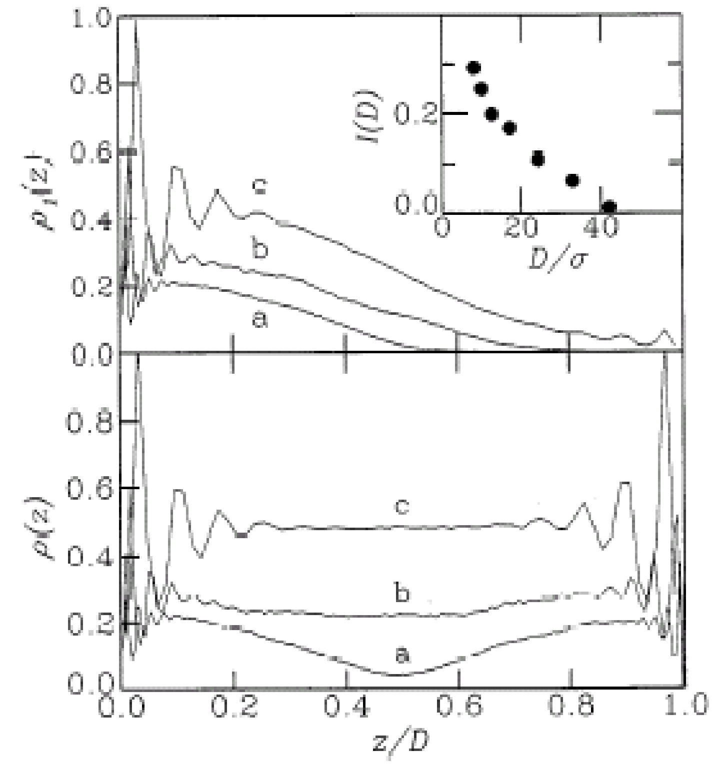


Liao et al Soft Matter 2013

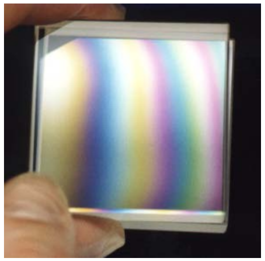
Neutron Scattering – Compression vs. Interpenetration

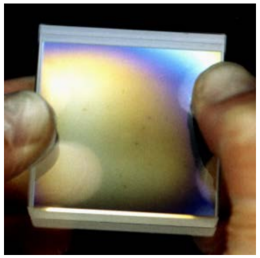


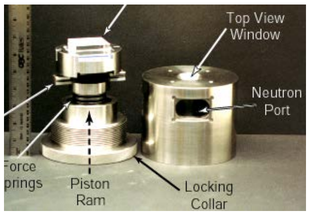
Mulder et al Soft Matter 2010



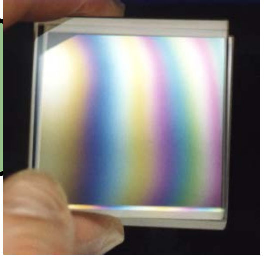
Grest, Adv Poly Sci, 1998

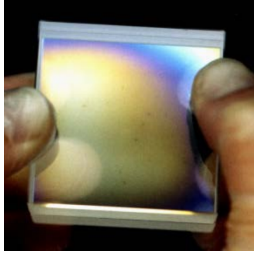


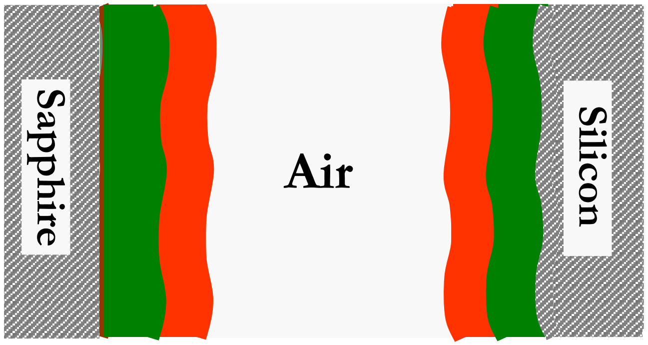


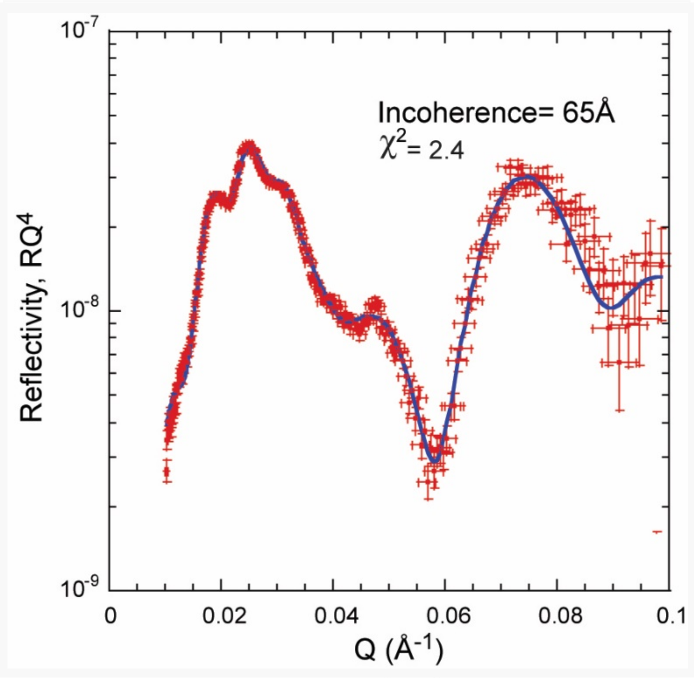


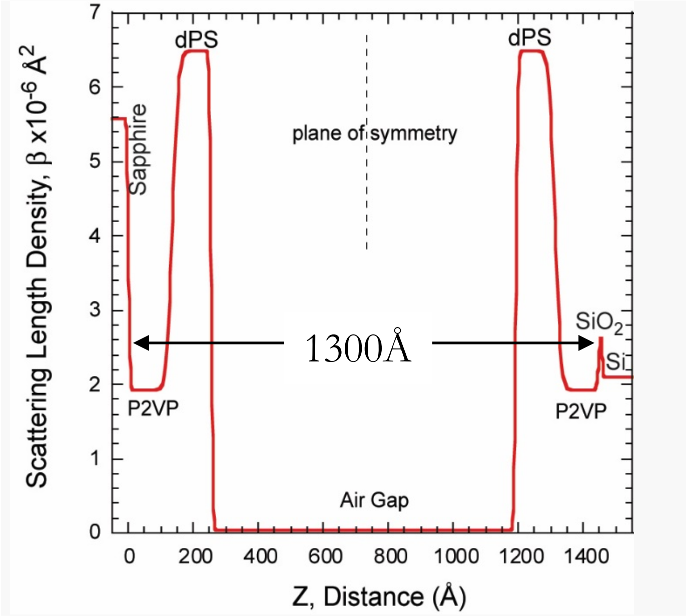
Neutron Reflectivity Measurements

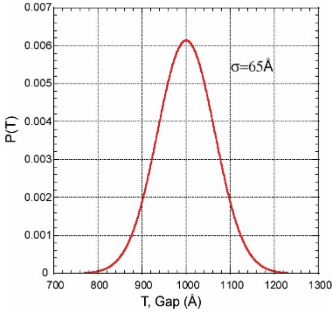












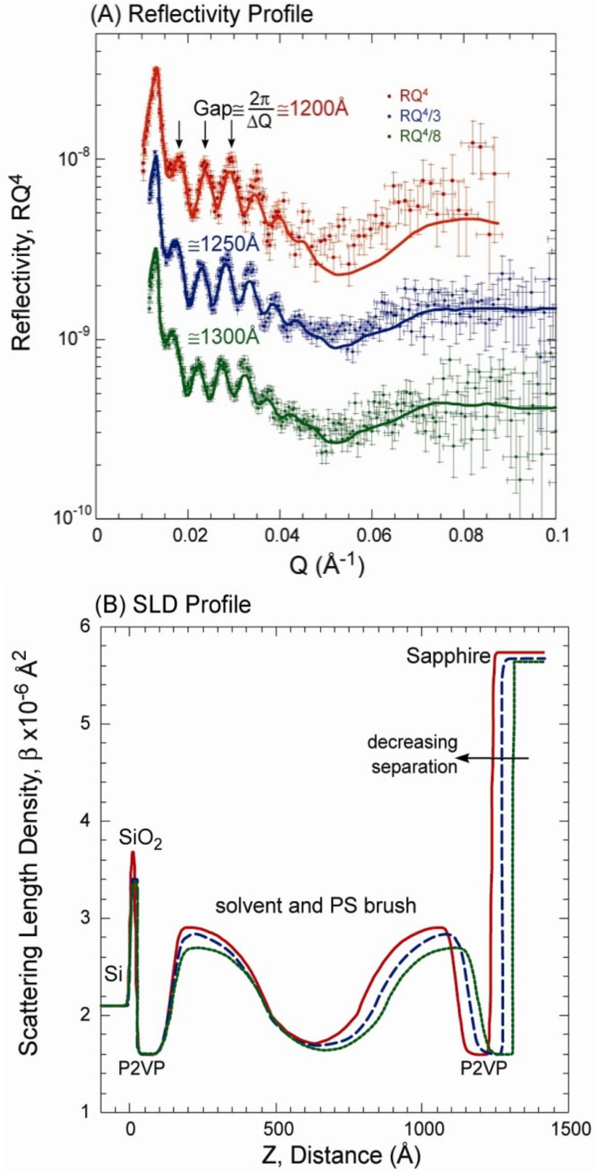
High frequency fringes blurred by averaging over the gap spacing

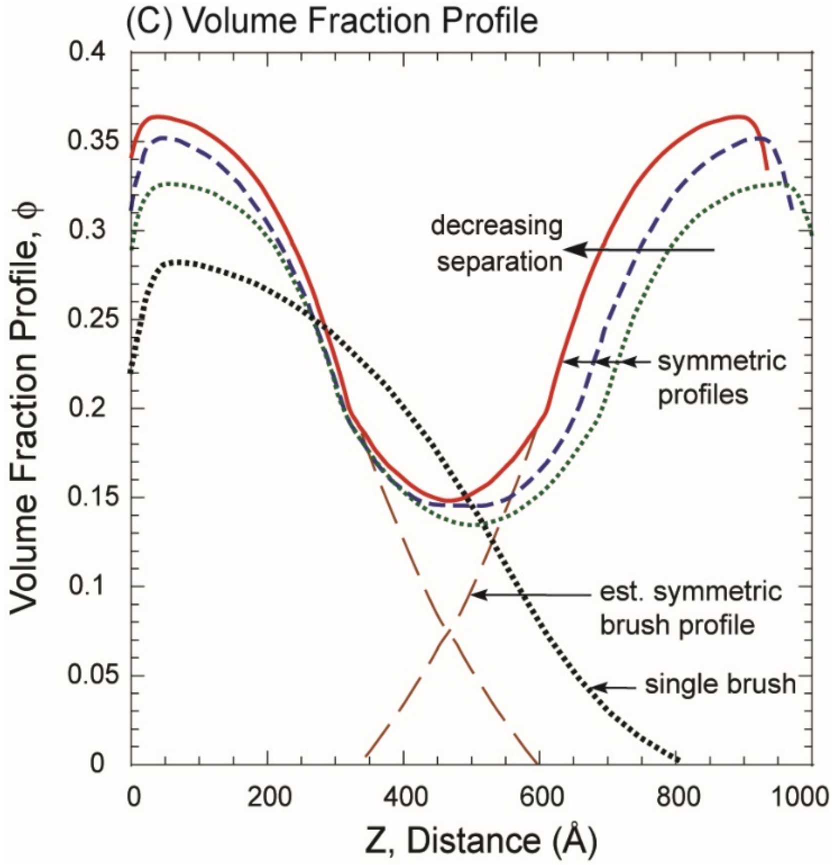
Variation in substrate spacing T from T_{avg}
Reflectivity calculated by incoherently averaging

$$R(q_z, T_{avg}) = \frac{1}{\sigma\sqrt{2\pi}} \int R(q_z, T)\; e^{-\frac{(T-T_{avg})^2}{2\sigma^2}}\, dT$$

Mulder et al Soft Matter 2010

Structure of Confined Polymer Brushes



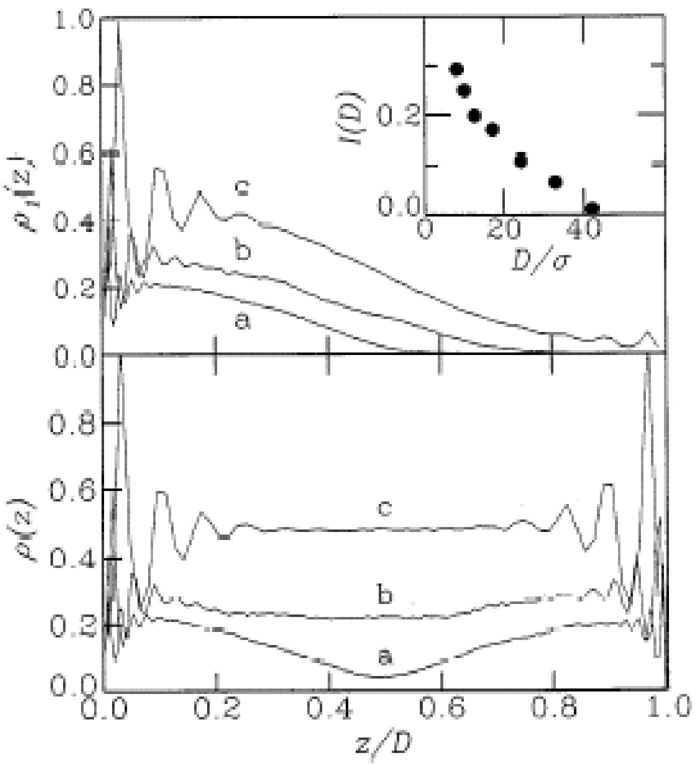


Polymer compresses and mostly collapses at the surfaces

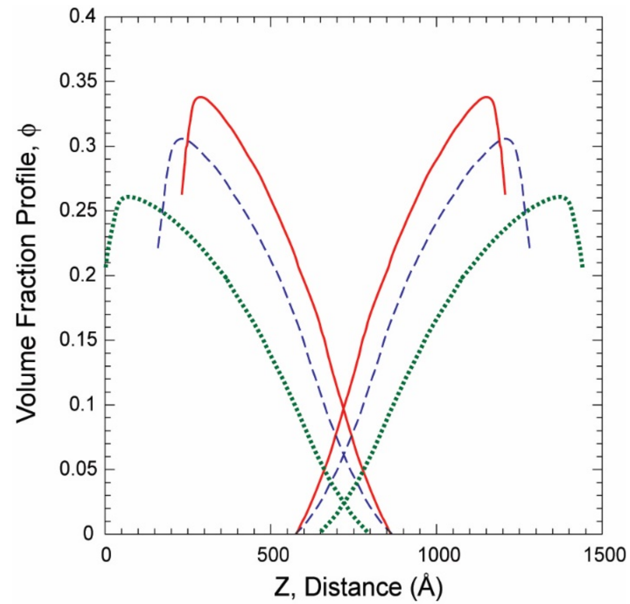
Conservation of mass

Mulder et. al Soft Matter 2010

Neutron Scattering – Compression vs. Interpenetration



Grest, Adv Poly Sci, 1998



$$I(D) = \int_{D/2}^{D} \phi_1(x)\,dx \Big/ \int_{0}^{D} \phi_1(x)\,dx$$

Gap	D (Å)	$I(D)$	$I(D)_{complete}$
Large	1440	0.006	0.010
Medium	1125	0.029	0.089
Small	980	0.048	0.162

Mulder et al Soft Matter 2010

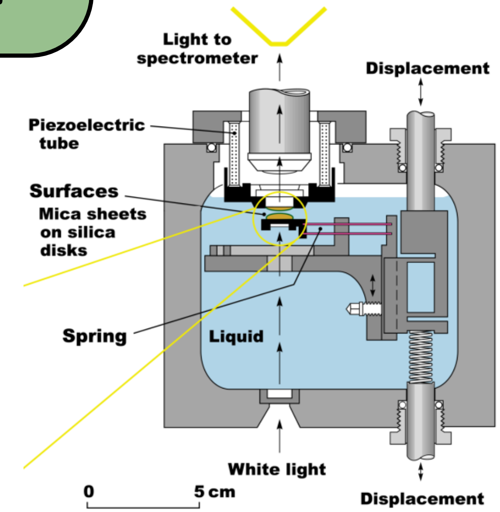
Possibilities…

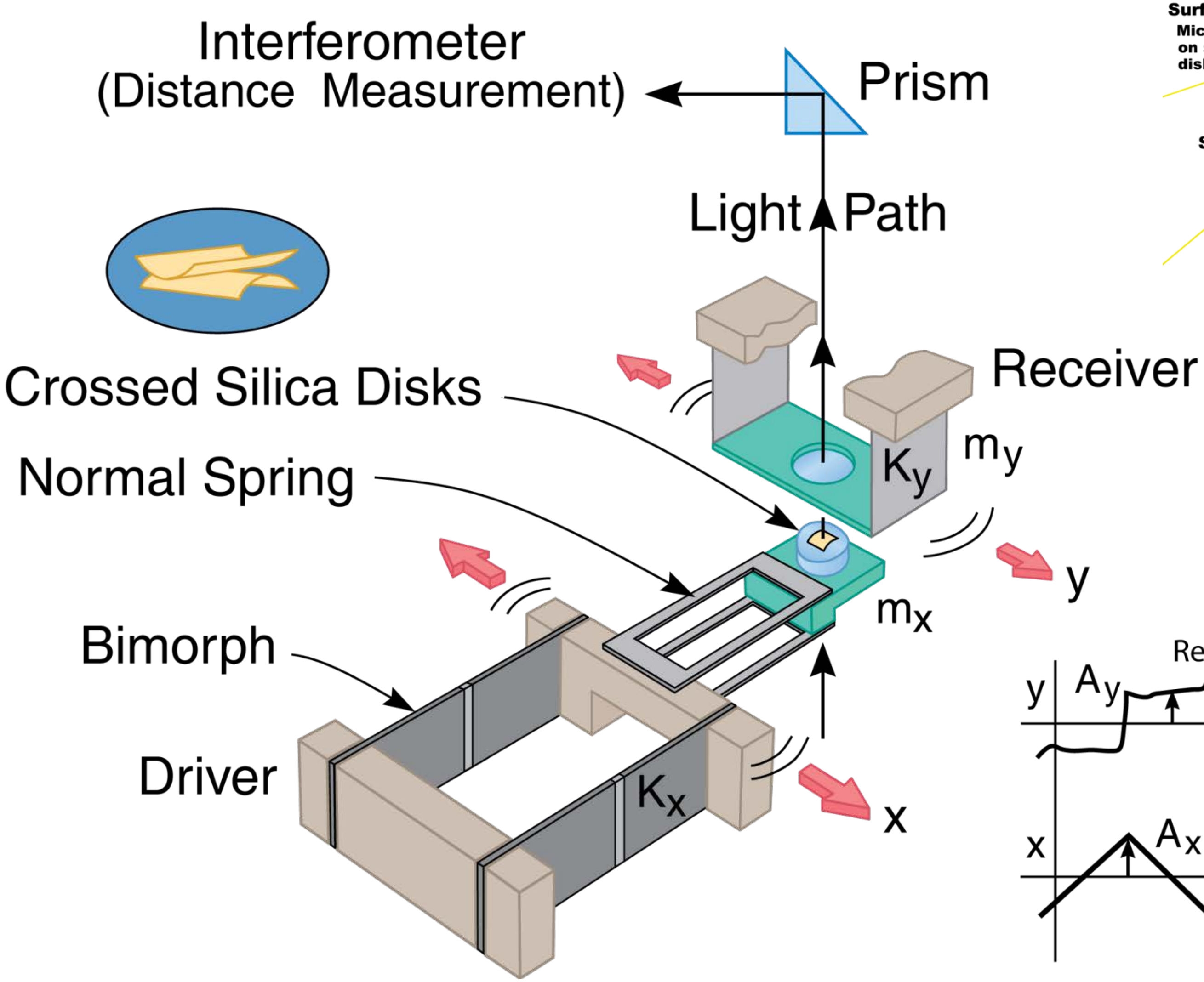
SFA can measure interactions and friction/shear force at with molecular

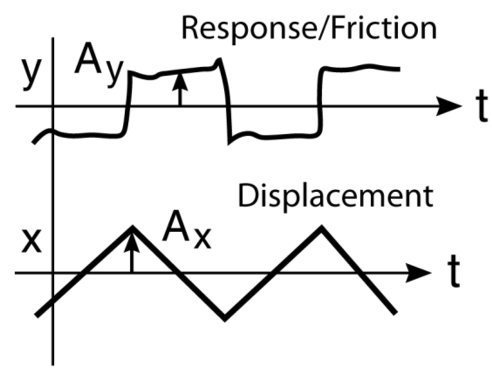
What's going on in the gap?

Confinement
Boundary layers
Fluid to glass transition
Measure interactions
Effect of surface roughness
Friction and Shear

Friction or Shear Force Measurement

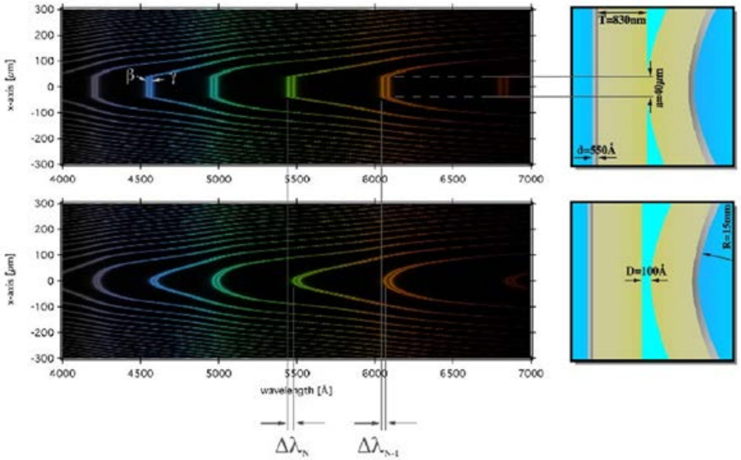


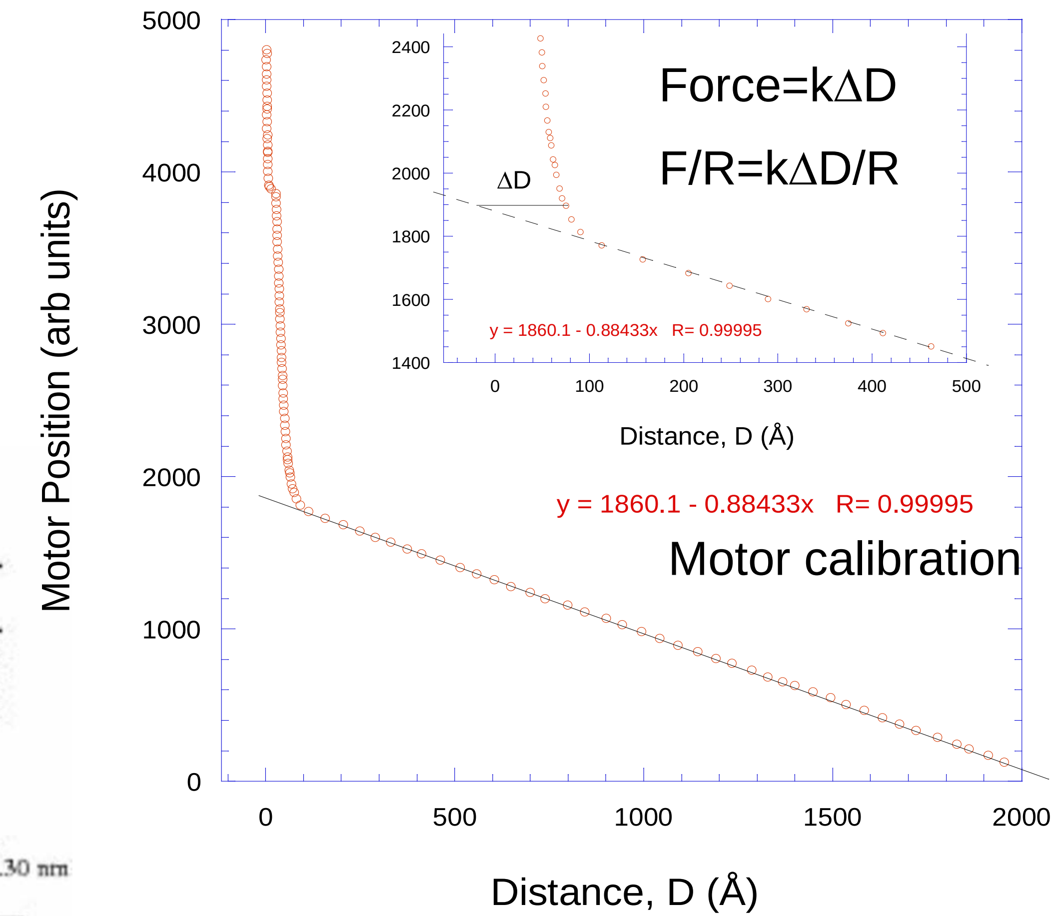


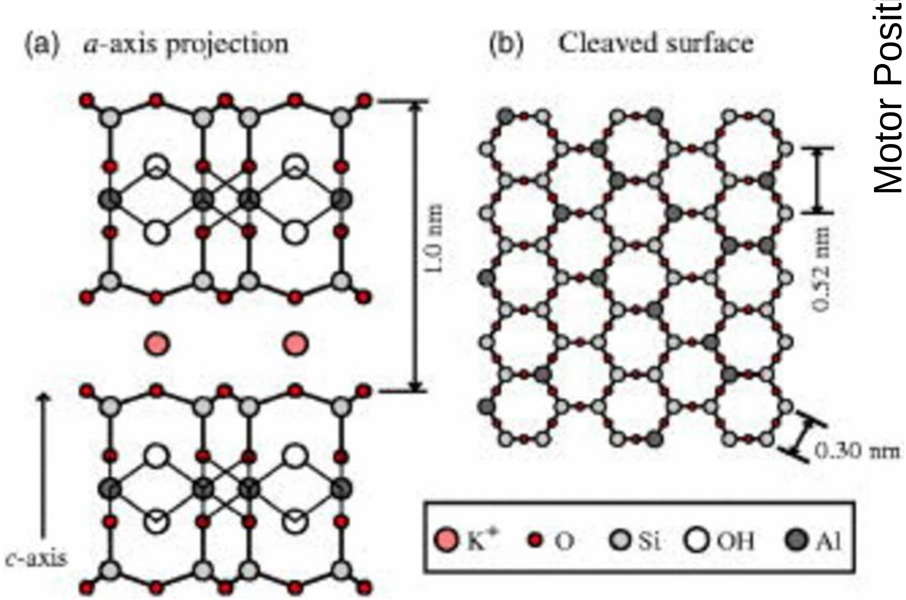


Interaction Force Profile

SFA: 0.1 nm in distance
Radius and image of the contact
Force to 50nN

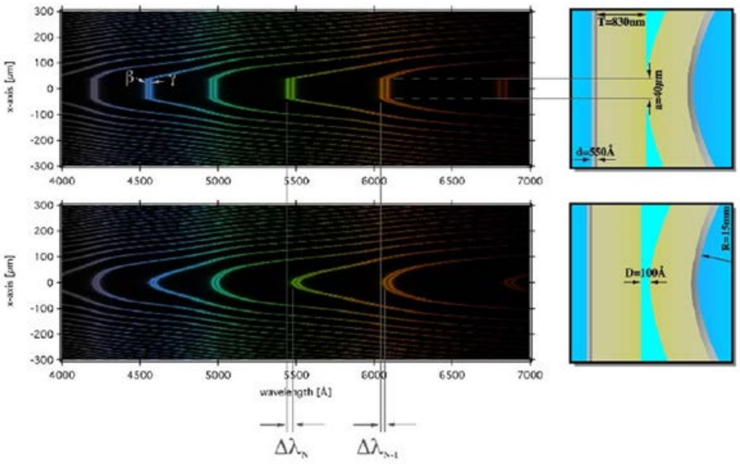




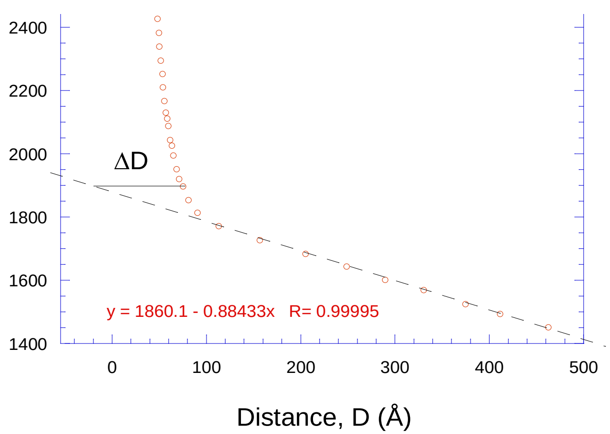


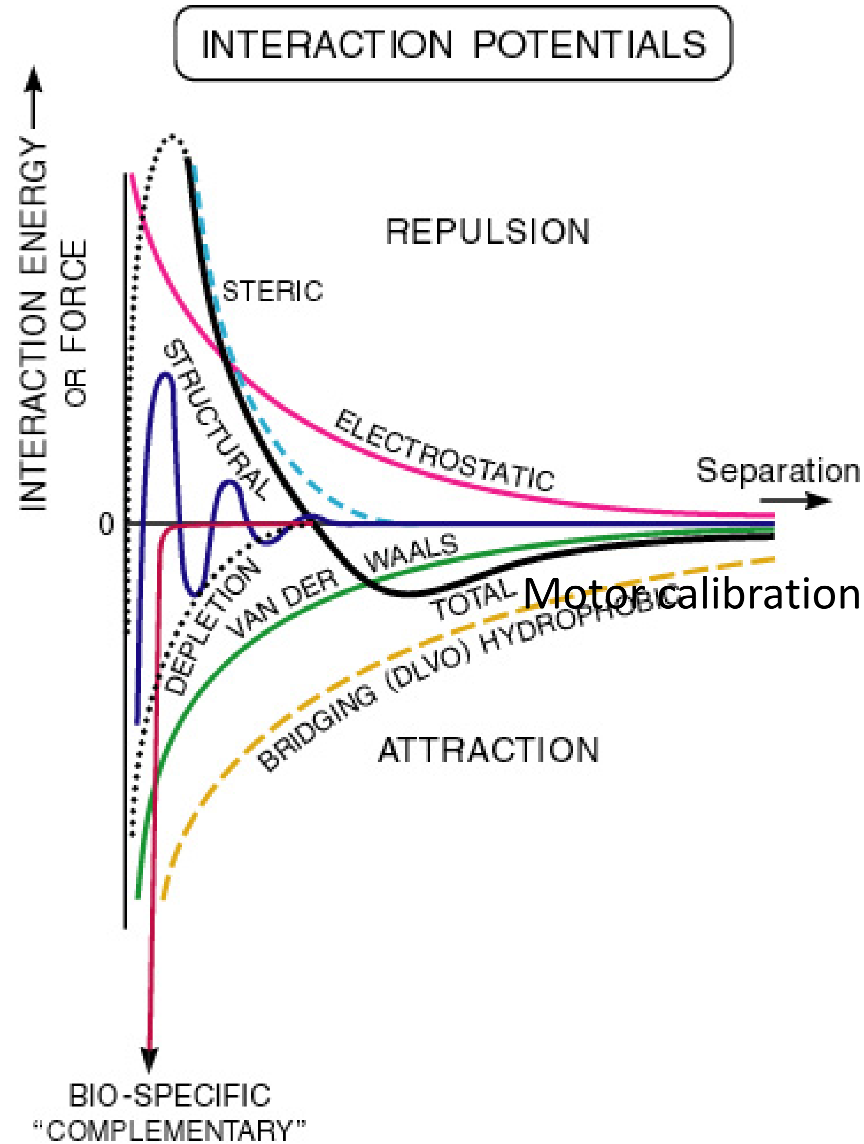
Surface – molecularly smooth mica

Interaction Force Profile



0.1 nm in distance
Radius of the contact





Motor calibration