Particle Characterization at the Nanoscale

Greg Meyers

Dow Chemical

Outline

- Experience with an Interlaboratory Study for Nanoparticle (NP) Sizing
- New NP Sizing Technology
- Mechanical Properties at the Nanoscale

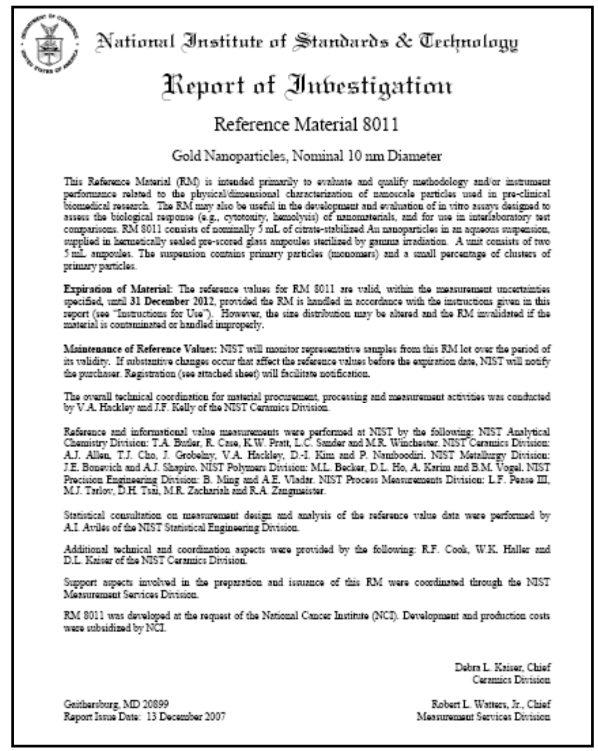
Interlaboratory Study

- ASTM Sponsored ILS#166 in 2008
  (basis for ASTM E 2490-09, published June 2009)

- Evaluation of Photon Correlation Spectroscopy (PCS)
  - with comparison by direct methods (AFM, TEM, SEM)
  - 26 participating laboratories

- NIST Au colloid reference materials

RM 8011 – nominal 10 nm
RM 8012 – nominal 30 nm
RM 8013 – nominal 60 nm



National Institute of Standards & Technology

Report of Investigation

Reference Material 8011

Gold Nanoparticles, Nominal 10 nm Diameter

This Reference Material (RM) is intended primarily to evaluate and qualify methodology and/or instrument performance related to the physical/dimensional characterization of nanoscale particles used in pre-clinical biomedical research. The RM may also be useful in the development and evaluation of in vitro assays designed to assess the biological response (e.g., cytotoxity, hemolysis) of nanomaterials, and for use in interlaboratory test comparisons. RM 8011 consists of nominally 5 mL of citrate-stabilized Au nanoparticles in an aqueous suspension, supplied in hermetically sealed pre-scored glass ampoules sterilized by gamma irradiation. A unit consists of two 5 mL ampoules. The suspension contains primary particles (monomers) and a small percentage of clusters of primary particles.

Expiration of Material: The reference values for RM 8011 are valid, within the measurement uncertainties specified, until **31 December 2012**, provided the RM is handled in accordance with the instructions given in this report (see "Instructions for Use"). However, the size distribution may be altered and the RM invalidated if the material is contaminated or handled improperly.

Maintenance of Reference Values: NIST will monitor representative samples from this RM lot over the period of its validity. If substantive changes occur that affect the reference values before the expiration date, NIST will notify the purchaser. Registration (see attached sheet) will facilitate notification.

The overall technical coordination for material procurement, processing and measurement activities was conducted by V.A. Hackley and J.F. Kelly of the NIST Ceramics Division.

Reference and informational value measurements were performed at NIST by the following: NIST Analytical Chemistry Division: T.A. Butler, R. Case, K.W. Pratt, L.C. Sander and M.R. Winchester. NIST Ceramics Division: A.J. Allen, T.J. Cho, J. Grobelny, V.A. Hackley, D.-I. Kim and P. Namboodiri. NIST Metallurgy Division: J.E. Bonevich and A.J. Shapiro. NIST Polymers Division: M.L. Becker, D.L. Ho, A. Karim and B.M. Vogel. NIST Precision Engineering Division: B. Ming and A.E. Vladar. NIST Process Measurements Division: L.F. Pease III, M.J. Tarlov, D.H. Tsai, M.R. Zachariah and R.A. Zangmeister.

Statistical consultation on measurement design and analysis of the reference value data were performed by A.I. Aviles of the NIST Statistical Engineering Division.

Additional technical and coordination aspects were provided by the following: R.F. Cook, W.K. Haller and D.L. Kaiser of the NIST Ceramics Division.

Support aspects involved in the preparation and issuance of this RM were coordinated through the NIST Measurement Services Division.

RM 8011 was developed at the request of the National Cancer Institute (NCI). Development and production costs were subsidized by NCI.

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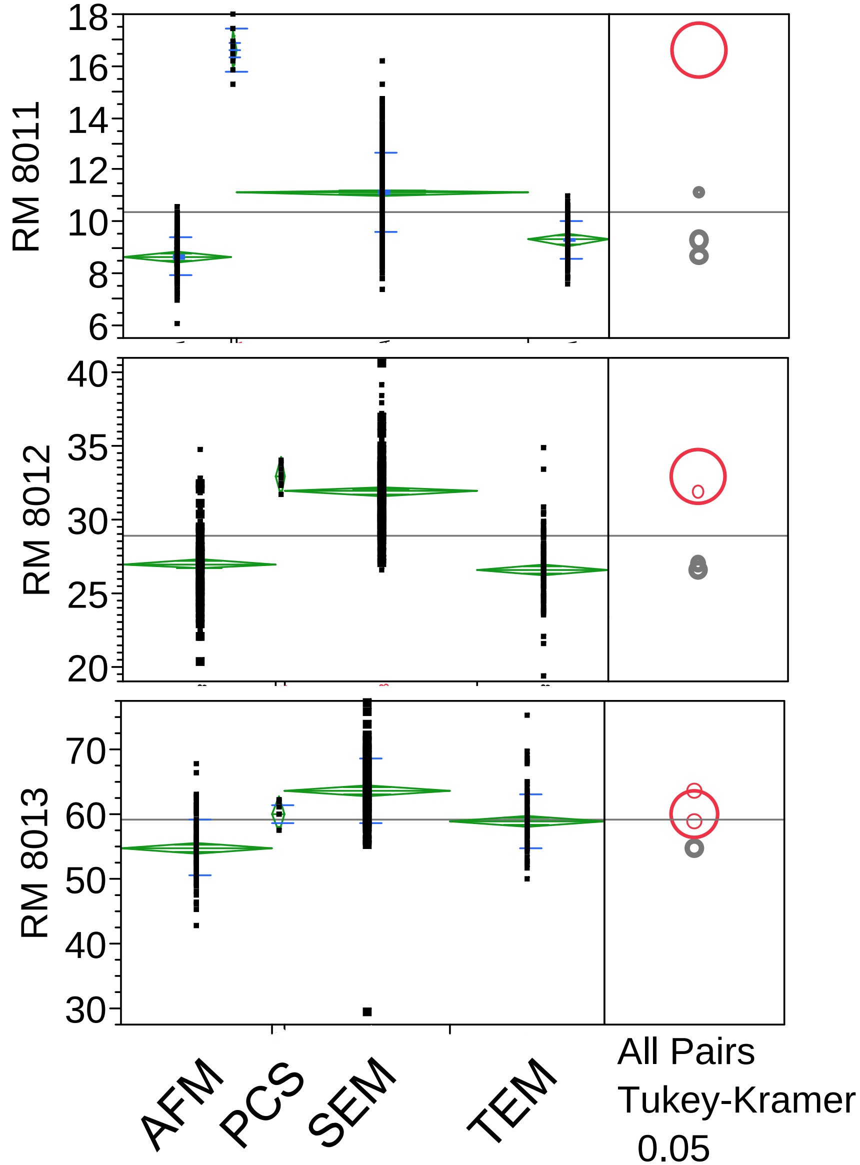
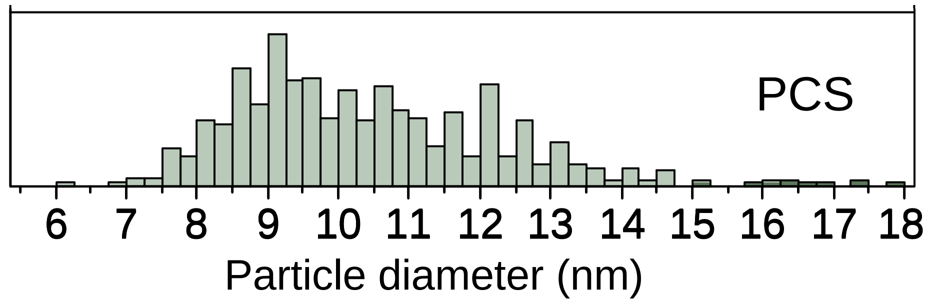
Ceramics Division

Gaithersburg, MD 20899
Report Issue Date: 13 December 2007

Robert L. Watters, Jr., Chief
Measurement Services Division

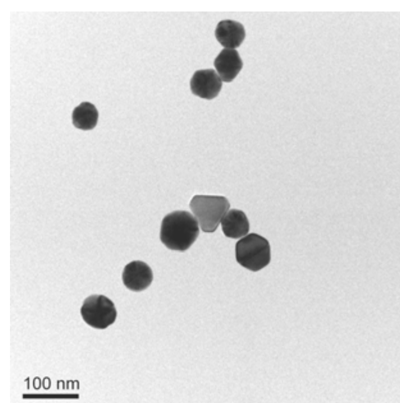
Our Results with Au NPs



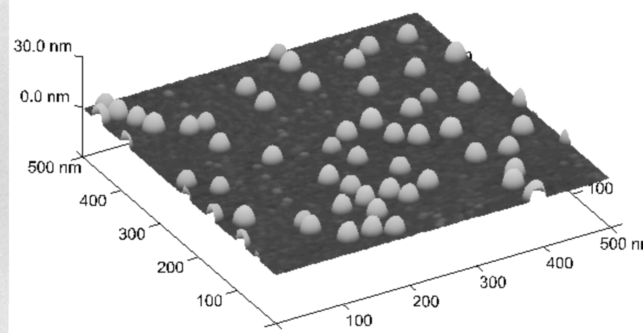


There are statistically significant differences between all techniques for the smallest particles

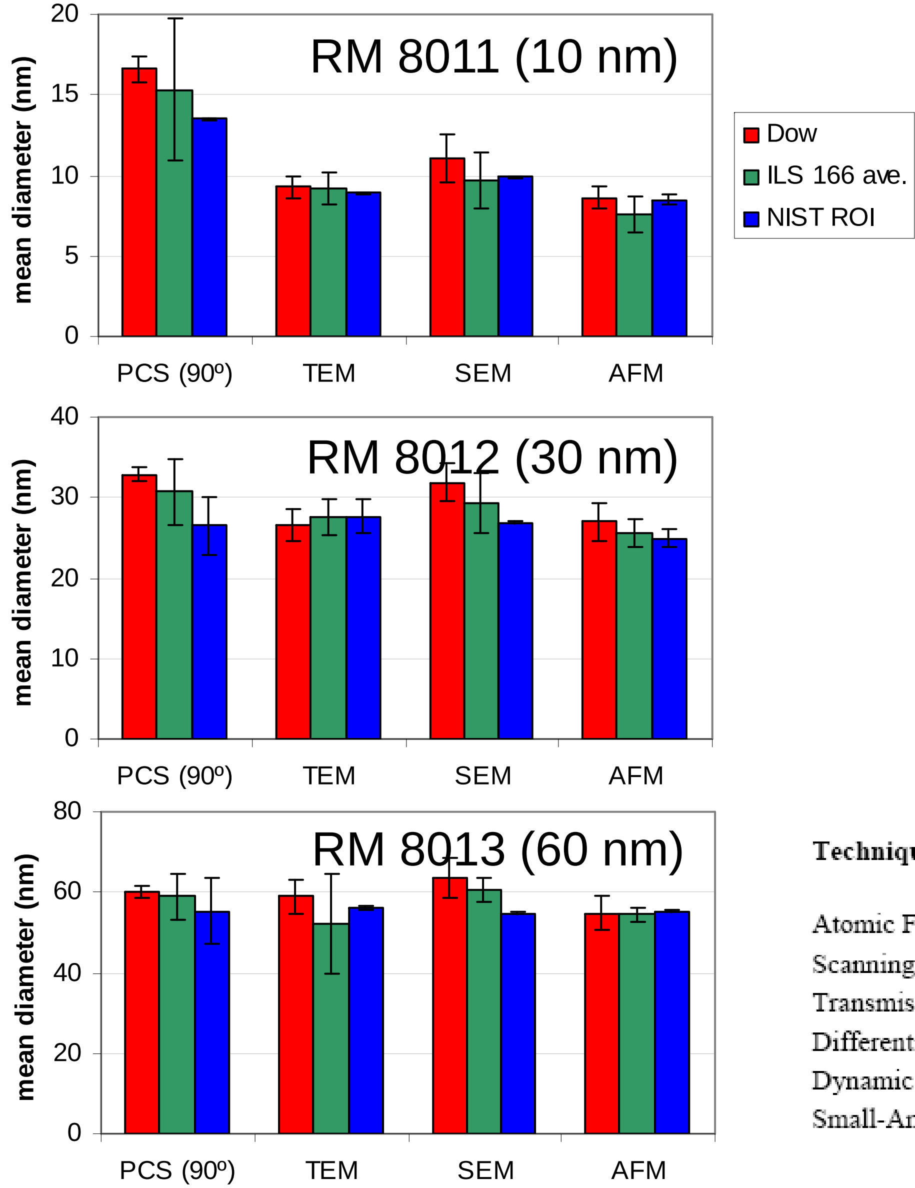
TEM of 8013



AFM of 8011



Interlaboratory Study



- ILS 166 average data is average of each laboratory's mean
- Quite good agreement across many labs, *primarily due to clear instructions for sample prep, data acquisition, and reporting*
- Recognition that different techniques can give statistically different values

From NIST RM8011 documentation...

Table 1. Reference Value Mean Size and Expanded Uncertainty [a]
Average Particle Size (Diameter), in nm

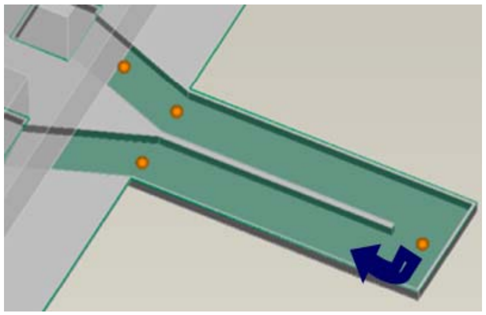
Technique	Analyte Form	Particle Size (nm)
Atomic Force Microscopy	dry, deposited on substrate	8.5 ± 0.3
Scanning Electron Microscopy	dry, deposited on substrate	9.9 ± 0.1
Transmission Electron Microscopy	dry, deposited on substrate	8.9 ± 0.1
Differential Mobility Analysis	dry, aerosol	11.3 ± 0.1
Dynamic Light Scattering	liquid suspension	13.5 ± 0.1
Small-Angle X-ray Scattering	liquid suspension	9.1 ± 1.8

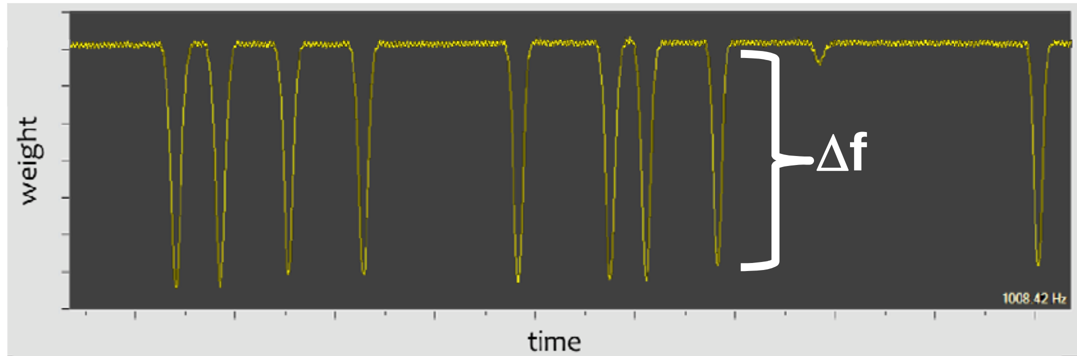
Current Challenges

- **Differences between techniques – *this is acceptable***
  - Different interactions are measured
  - Different assumptions are made
  - Different models may be applied
  - Sampling statistics variable
- **Real systems can be more complex**
  - May be multimodal, large dispersion
  - May have primary, aggregated, or agglomerated populations
  - May be heterogeneous in structure/composition
- **Quality of test methods used across laboratories are being addressed through interlaboratory studies**
- **Accurate sizing of particles that are non-spherical using indirect methods**
- **Relevant size, shape, surface area metrics for risk assessment**
- **Lack of standards for broader compositions, shapes, surface chemistries and physical properties**

Mass Selective Particle Sizing

<u>Suspended Microchannel Resonator</u> (commercialized as Archimedes*)



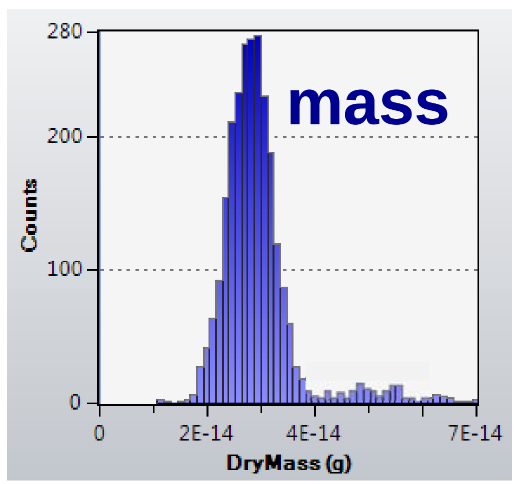


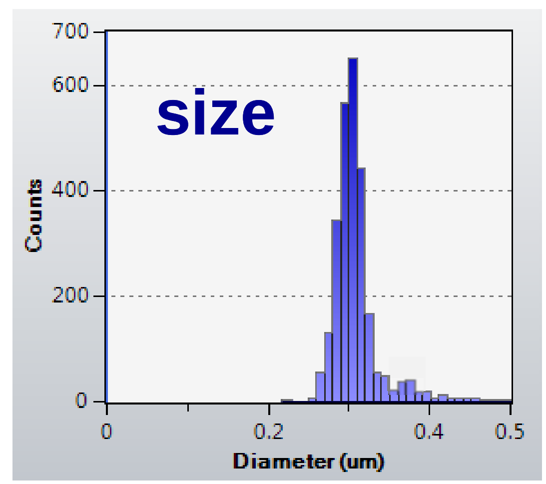
For each particle, relate buoyant mass to density, mass, and size via:

Buoyant mass

(density)

Spherical equivalent





NP Sizing Needs & Timing

- **Additional NIST particle standards mirroring manufactured NPs (1-3 years)**
  - SiO2 and CeO2 (slurry), TiO2 (cosmetic, paint), Ag (antimicrobial), CNT or graphene (fillers), dendrimer (drug delivery)

- **Techniques or algorithms to deal with non-spherical shapes (1-3 years)**
  - Fund research into new analysis methods
  - Improved throughput for direct imaging/analysis (microscopy)

- **More interlaboratory studies including *both* routine and developmental instrumentation for sizing, surface area (ongoing in standards bodies)**
  - Need to advertise participation opportunities more widely
  - *Surface area* techniques should be evaluated near term
  - Consider inversion algorithms for indirect methods as part of interlaboratory studies

NP Sizing Needs & Timing (con't)

- **Heterogeneous NP particle development (3-5 years)**
  - Physically heterostructured NPs
    - Porous (closed/open cell), core/shell
  - Chemically heterogeneous NPs
    - Hydrophobic/hydrophilic (surface functionalized particles)
    - Compositionally heterogeneous on the surface (Janus particles)

- **Particles for physical property testing (5-10 years)**
  - Sized NP series for mechanical, thermal, optical, magnetic properties

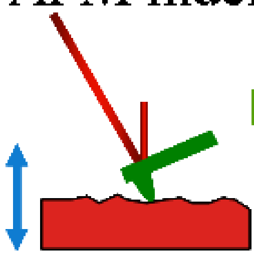
Nanoscale Mechanical Properties

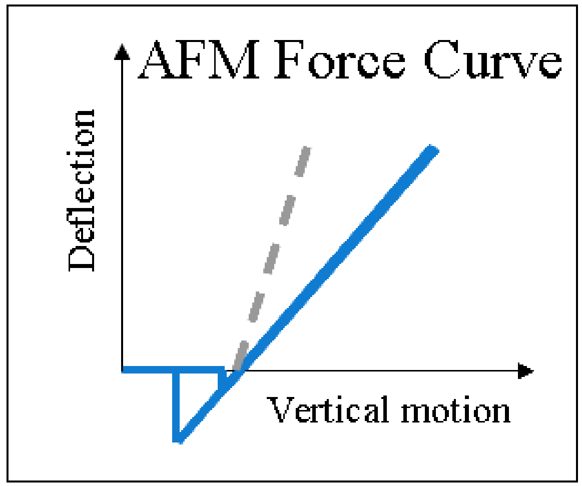
Dow – Veeco NIST ATP Program 2004-2007

Quantitative Nanoindentation in the AFM

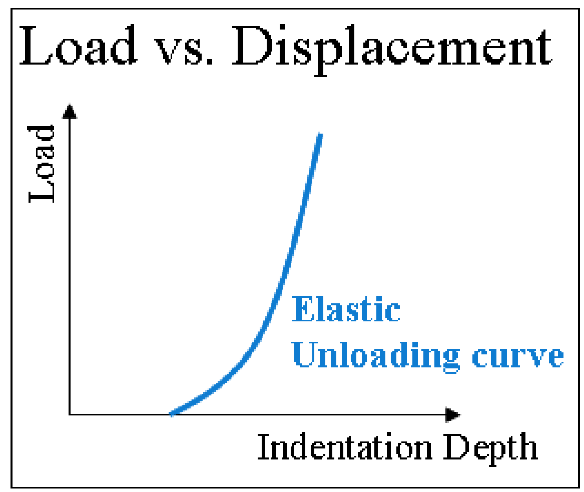
Vertical

AFM indentation

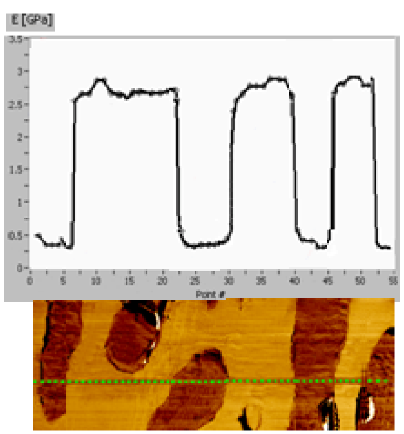




Spring constant, optical sensitivity

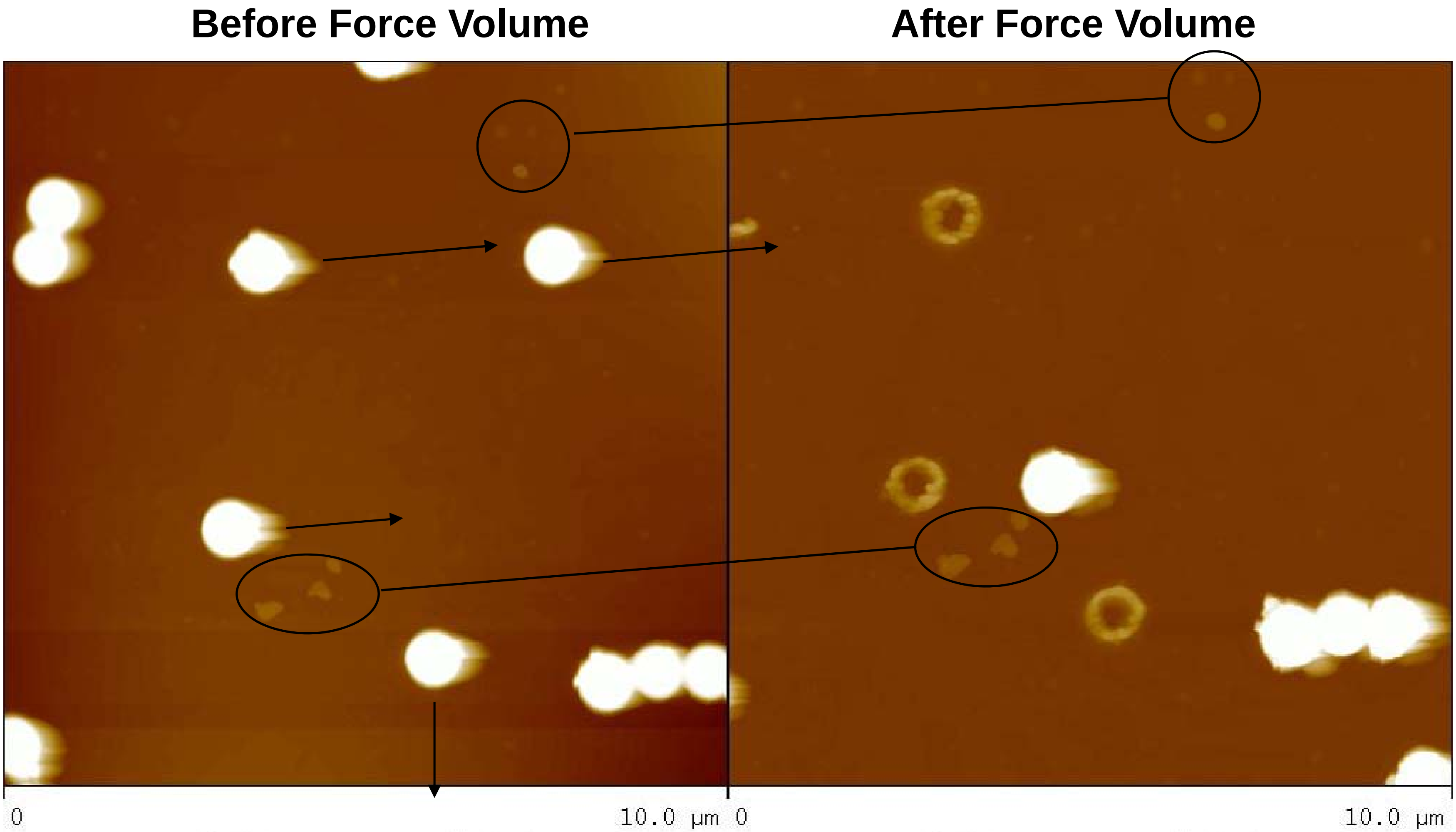


Tip shape, Nanomechanical models



Elasticity Profile

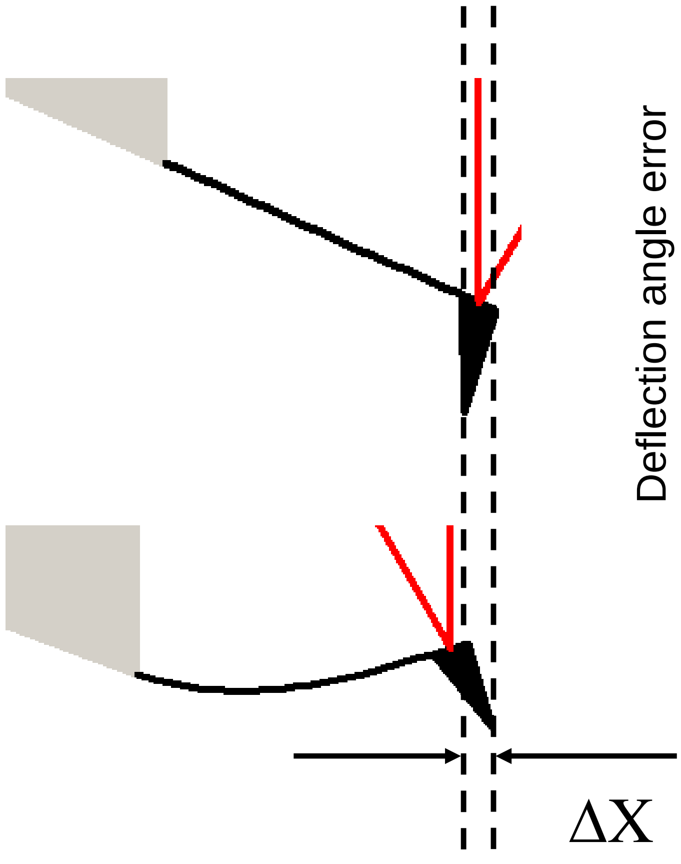
Lateral Forces



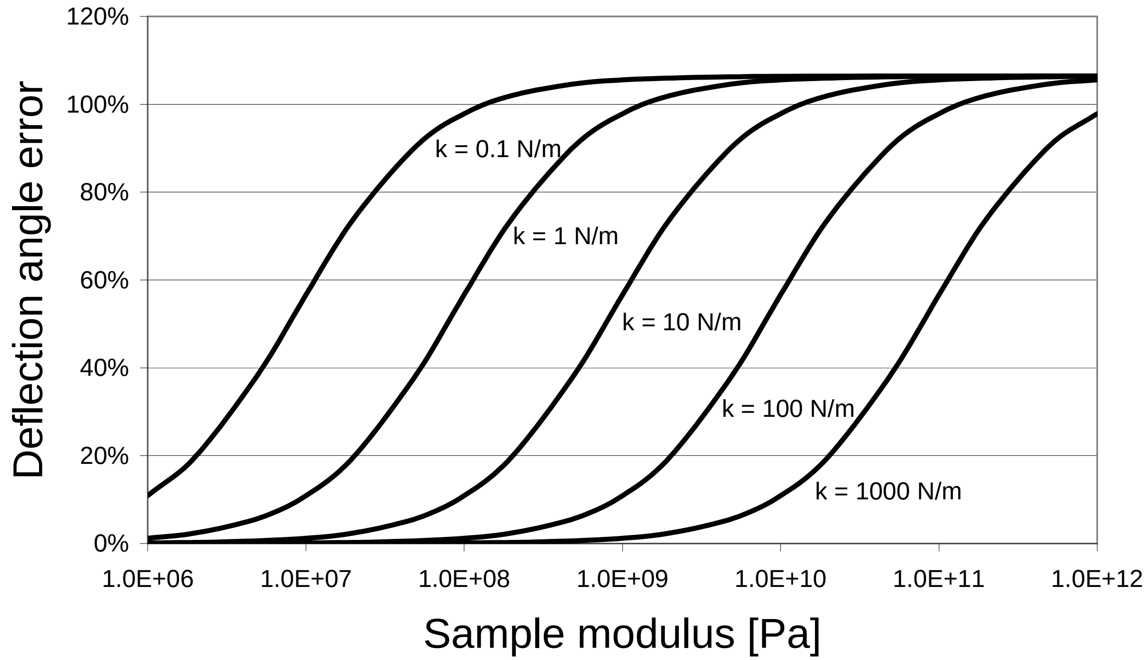
- solid 700nm PS latex particles dislodged from surfactant rings

Lateral Forces

The problem



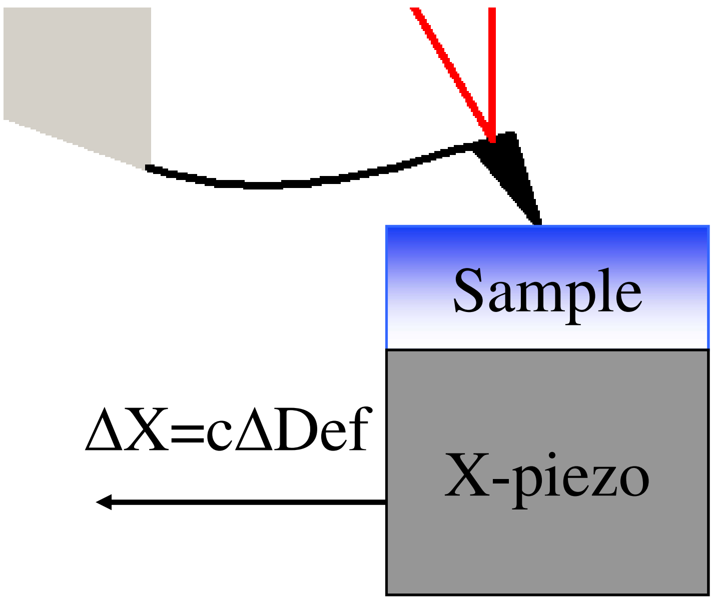
Deflection Error vs. Sample Modulus



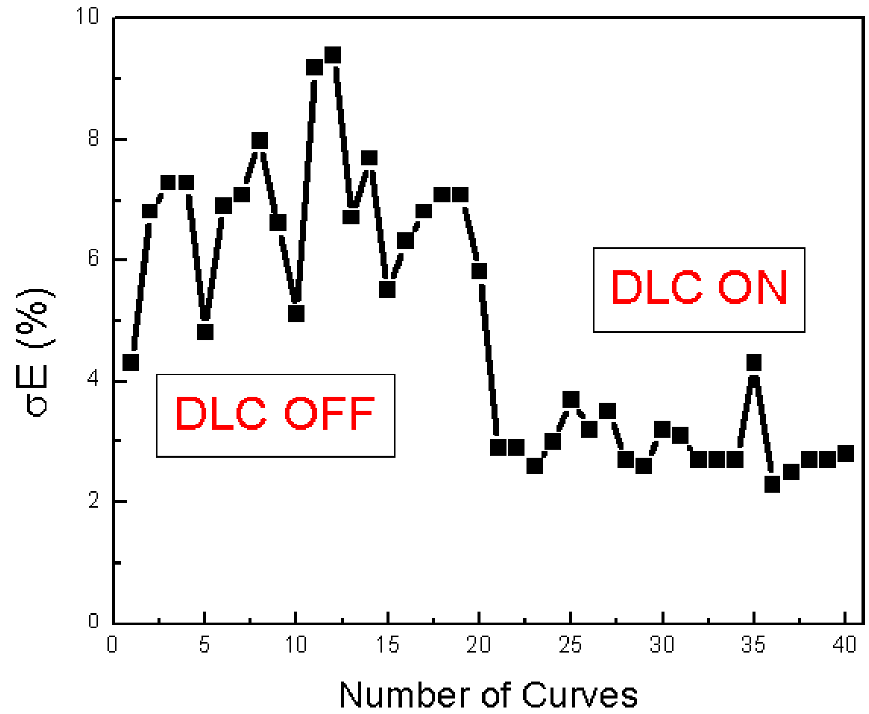
Errors can be reduced using
- passive levers with stiffer springs
- active levers

Lateral Forces

Deflection Lateral Compensation (DLC)*
– works with any cantilever



Use the cantilever deflection signal to control the AFM's X-piezo and compensate for the lateral motion



Improved accuracy on homogeneous material standards

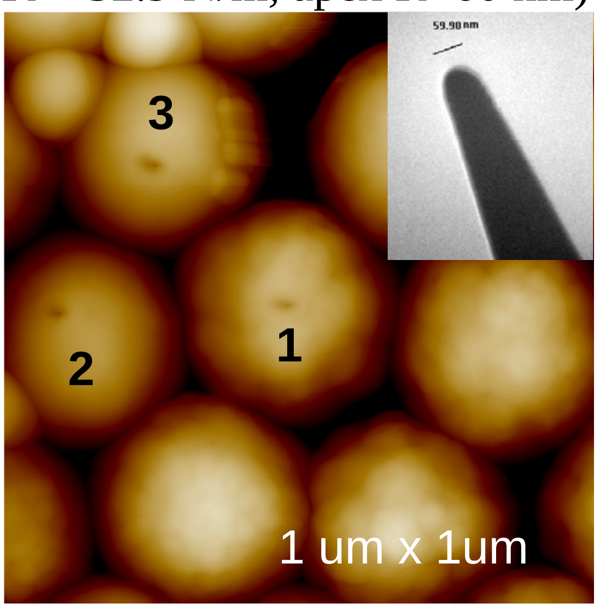
*L Huang, C Meyer and C Prater, Journal of Physics: Conference Series **61,** 805–809 (2007)

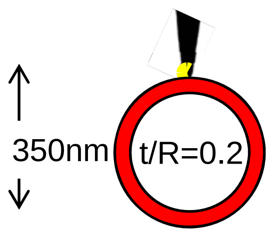
Regimes of Deformation

- Hollow Latex Used in Coatings
- Understanding deformation of nanostructured particles *at the particle level*
- Requires very stable AFM platform

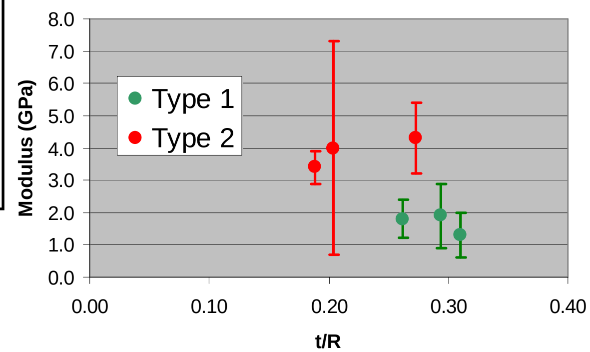
Spherical tip

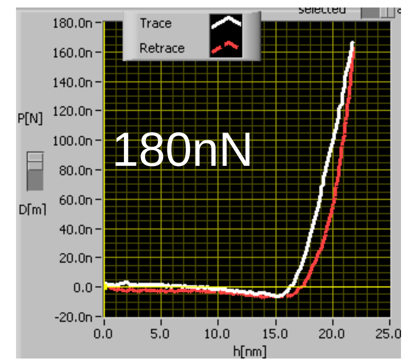
(K = 32.9 N/m, apex R~60 nm)



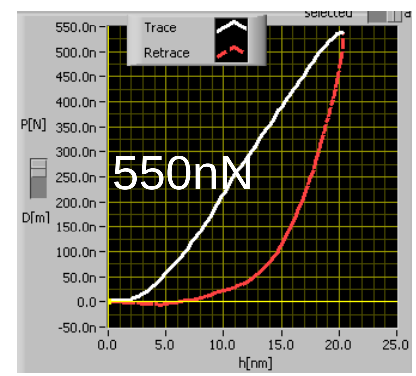


Elastic Response of shell

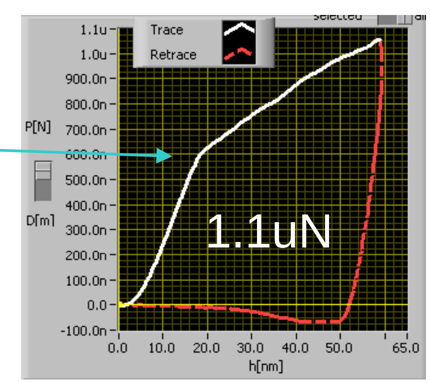




Elastic-Plastic Response of shell



'Kink' at point where shell buckles



In-situ TEM Deformation of CdS NP

YouTube video

Needs for NP Mechanics & Timing

- Accessible methods for calibrating spring constant of high stiffness probes (40-1000N/m) of arbitrary cross-section for AFM indentation into materials with E>10 GPa (1-3 years)
- Alternative tip geometries including flat punch for AFM indentation (1-3 years)
- Libraries of NPs of various sizes on rigid substrates (3-5 years)
  - Metal cluster deposition; centrifugal force deposition/separation by spin coating
- Develop nanoscale test for NP adhesion in biological, ceramic, or polymeric material matrix (3-5 years)
- Models and simulation to support experimental deformation and fracture regimes for NPs (ongoing)
- Interlaboratory studies on AFM based indentation of NPs are needed (ongoing)

Acknowledgements

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