Project 1
Mechanical Characterization of Polymer Surfaces

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NIST National Institute of Standards and Technology

Outline

- Scratch and Mar Literature Update
  - Appearance and scratch / mar
  - Viscoelasticity and scratch / mar
- Surface Mechanical Property Measurements
  - Experimental method development
  - Tip shape determination methods
- Roughness literature study
- Updated Research Plan and Timeline
- Dissipative Particle Dynamics Model
- Light Scattering and Appearance Laboratory

Scratch and Mar Literature Update

Appearance and Scratch / Mar

- A recent paper was published (2001) on appearance aspects of surface scratches
  - Authors propose a new method for rendering “distributed visible defects” that are due to “nonvisible geometric variations”
    - » Link BRDFs with texture using a “theoretical scratch micro-geometry derived from physical measurements”
      - – Two peaks and a trough for scratch geometry plus a 2-D texture map to specify scratch locations
      - – Validated model with scratches on metallic surfaces
- Although limited and qualitative, previous studies of the links between appearance and scratch / mar have shown:
  - Differences in appearance for brittle vs. ductile scratch behavior
    - » Associated with topographic differences, stress whitening, etc.
  - Overall dimensions of scratches and material microstructure important
  - Color, orientation issues also important
  - Quantitative capabilities of instrumentation are limited

Our Approach

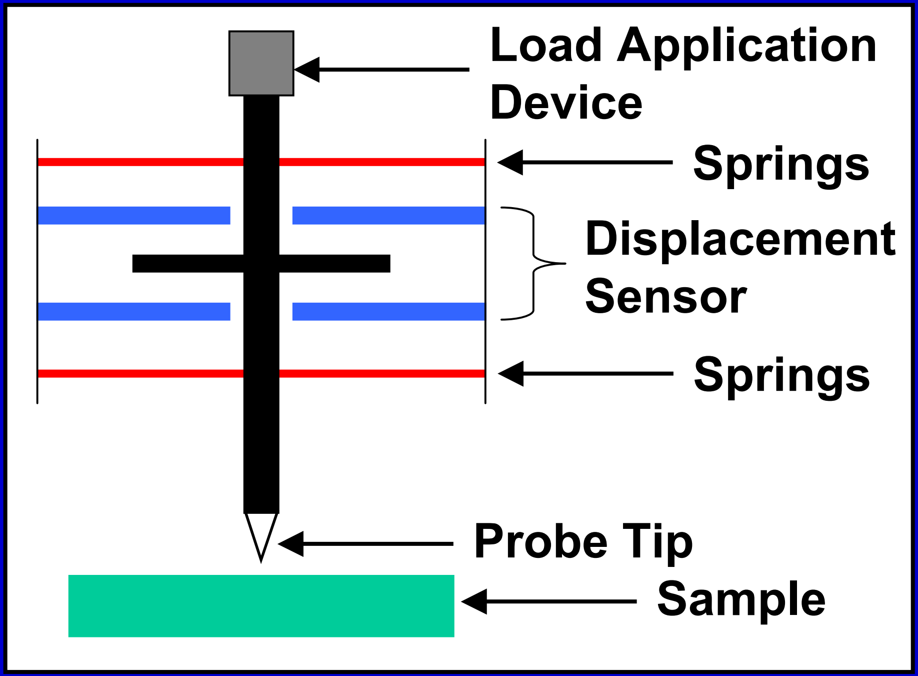
- In NIST Appearance project, BRDFs have been predicted for metallic flake coatings based on real microstructure maps measured using confocal microscopy.
  - Compared favorably to BRDF measurements
  - Rendered images showed realistic visual effects
- Our approach is thus to build on this success
  - Use techniques such as confocal microscopy and/or AFM to characterize surface topography, material microstructure, and scratch morphology
    - » Input into scattering models to predict BRDF
      - – Use scattering model to study relative importance of particular aspects of scratch morphology
  - Light scattering laboratory will be used for measurements of BRDF for the same samples
    - » Compare with model predictions and potentially use in rendering

Viscoelasticity and Scratch / Mar

- Scratch resistance is a function of the severity of contact conditions:
  - Elastic deformation $\Rightarrow$ smoothing of local asperities $\Rightarrow$ viscoelastic-plastic ploughing $\Rightarrow$ crack formation in or at the edges of the scratch groove $\Rightarrow$ more severe types of deformation
- Limited amount of experimentation or modeling that has included rate or temperature dependence related to scratch and mar.
  - Polymers exhibit a wide range of deformation modes, much wider than metals and ceramics, within a relatively narrow range of contact variables
  - Scratch rate has been found to be the most significant variable affecting the scratch behavior of polymers
    - » Also a function of contact geometry (strain) and penetration depth (strain density)
      - – Some inconsistencies regarding concepts of stress and strain
  - In a recently published study:
    - » For plastic type scratches, high minimum strain for plastic deformation related to high scratch resistance.
    - » For fracture type scratches, high E' related to high scratch resistance

Surface Mechanical Property Measurements

Depth-Sensing Indentation (DSI)



- Variations between different systems include:
  - How load is applied/measured
  - How displacement is applied/measured
  - Feedback control of system
  - Design for low load capabilities
- Commercial systems are available that either attach to or work with Scanning Probe Microscopes.

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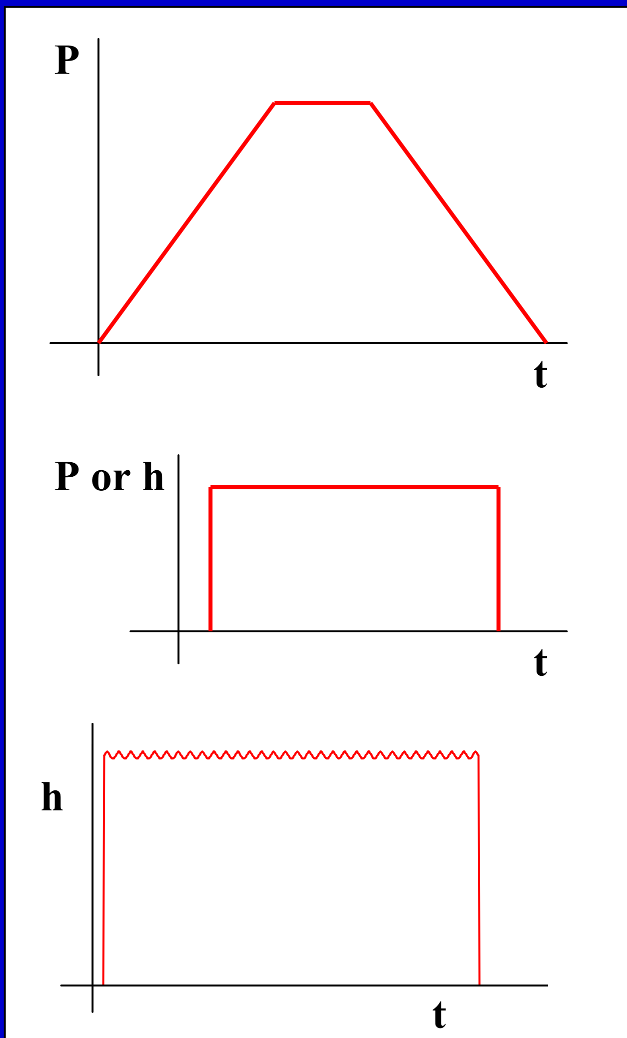
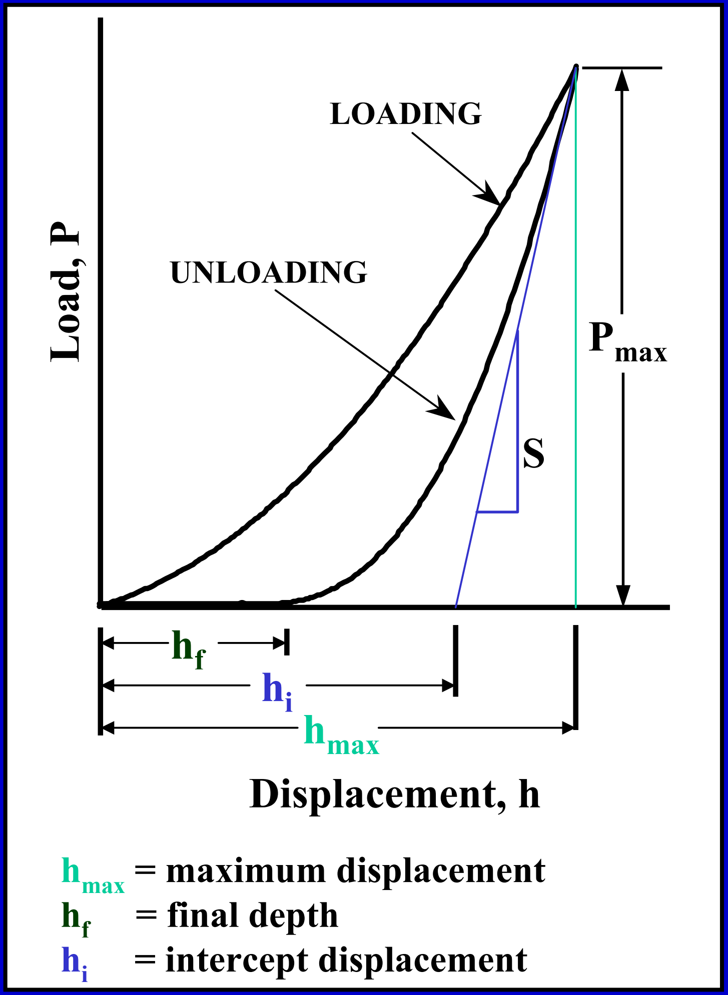
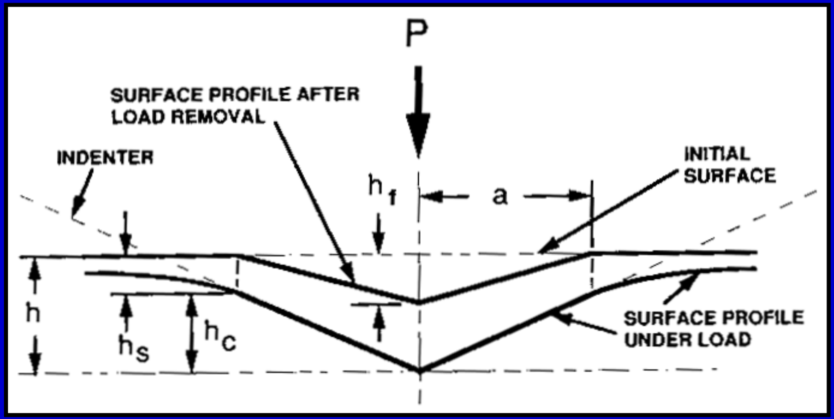
Experimental Method Development



- Typical quasi-static test:
  - Control loading/unloading rate, dP/dt
  - Hold period between loading and unloading
  - Can use small dynamic oscillation ($h_{dyn} \leq 1$ nm) during loading to estimate contact stiffness, S
- Other static and quasi-static tests:
  - Control strain rate
  - Step load or displacement
    - » Use appropriate feedback to maintain contant average stress or constant strain
- Dynamic tests:
  - Small dynamic oscillation over a constant load, displacement, stress, or strain
    - » Frequency range of 10-200 Hz

Oliver-Pharr Method

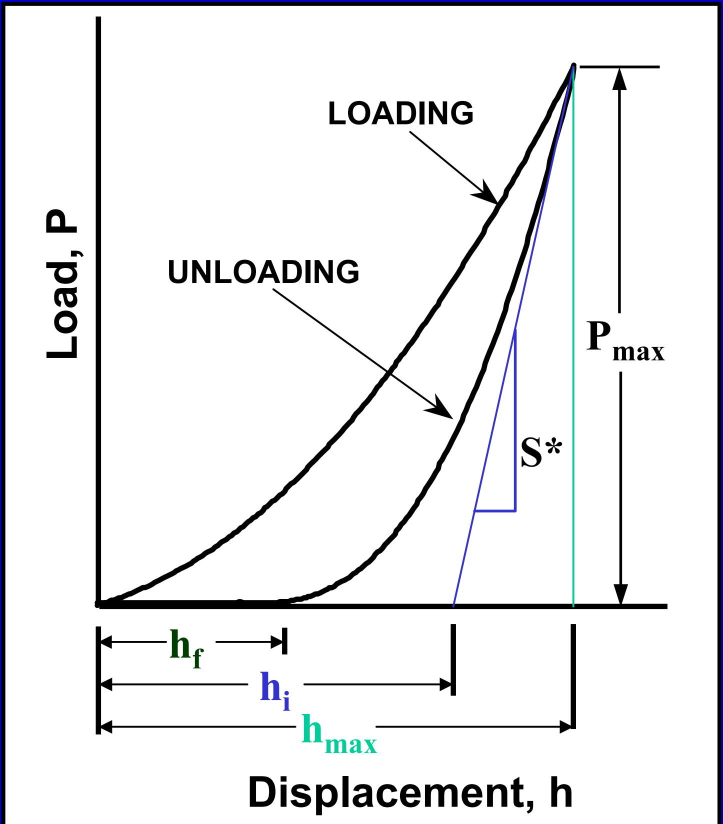


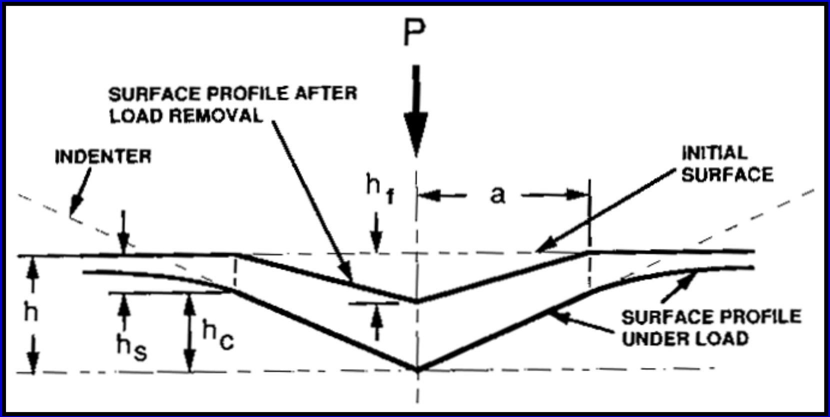


- Load-frame compliance and tip shape calibrations performed prior to indenting samples of interest.
  - Indentation of reference samples.
  - Several different procedures used.
- S is typically calculated from power law fits to the unloading curve.
  - Type of fit and amount of data used in fit varies.

Reference: W.C. Oliver and G.M. Pharr, *J. Mater. Res.*, 7(6), 1564-1583 (1992)

Calculating Elastic Modulus





- **Measurements on unknown samples:**
  - Indent sample using a range of maximum loads, fit unloading data with power law expression, and calculate S.
  - Determine contact depth, h_c and use with $A(h_c)$ to determine contact area, A.
  - Calculate modulus, E_r, from stiffness, S, and contact area A.

Reference: W.C. Oliver and G.M. Pharr, *J. Mater. Res.*, 7(6), 1564-1583 (1992)

$$E_r = \frac{\sqrt{\pi}}{2}\left(\frac{S}{\sqrt{A}}\right)$$

$$\frac{1}{E_r} = \frac{\left(1-\nu_s^2\right)}{E_s} + \frac{\left(1-\nu_i^2\right)}{E_i}$$

Dynamic Mechanical Analysis

- For linear viscoelastic behavior, application of a oscillatory stress results in an oscillatory strain that is out of phase with the stress and vice versa.

$$\varepsilon = \varepsilon_0 \sin \omega t$$

$$\sigma = \sigma_0 \sin(\omega t + \delta)$$

$$E' = (\sigma_0 / \varepsilon_0) \cos \delta$$

$$E'' = (\sigma_0 / \varepsilon_0) \sin \delta$$

- For dynamic indentation experiments:

$$E_r' = \left[\frac{P_0}{\Delta h_0} \cos \delta \right] \frac{\sqrt{\pi}}{2\sqrt{A}} = \frac{S\sqrt{\pi}}{2\sqrt{A}}$$

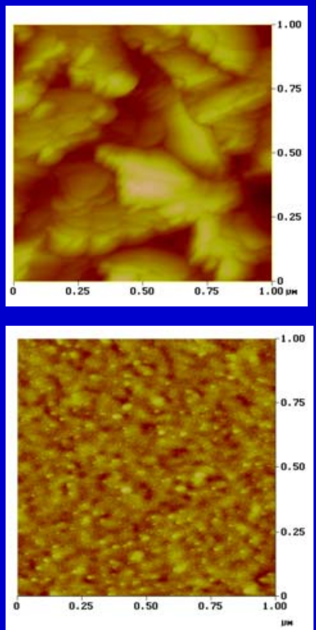
$$E_r'' = \left[\frac{P_0}{\Delta h_0} \sin \delta \right] \frac{\sqrt{\pi}}{2\sqrt{A}} = \frac{C\omega\sqrt{\pi}}{2\sqrt{A}}$$

- Linear viscoelasticity implies that the ratio of stress to strain is a function of time but not of stress magnitude.
  - Strains and strain rates are infinitesimal
    - » For nanoindentation and scratch experiments, it is likely that linear viscoelasticity is not obeyed.

Indentation Creep and Stress Relaxation

- In published indentation creep studies:
  - A constant load is typically applied
  - Displacement changes are measured
  - Contact area changes are either ignored or assumed to be negligible
    - Thus, not really a creep test as both stress and strain change.
- Because most DSI systems are load control devices, stress relaxation experiments are not often possible.
  - Only one published account using the IFM.
- Improved control capabilities allow:
  - Creep tests in which a mean stress, P_0/A_0, can be held constant
  - Controlled constant displacement for stress relaxation tests
- Linear viscoelasticity will be checked using:
  - Homogeneity tests (constant strain rate tests)
  - Additivity tests (creep / stress relaxation tests)
  - Dynamic tests

Blind Reconstruction of AFM Tips

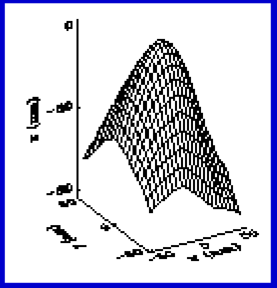


AFM images of "tip characterizer" surfaces

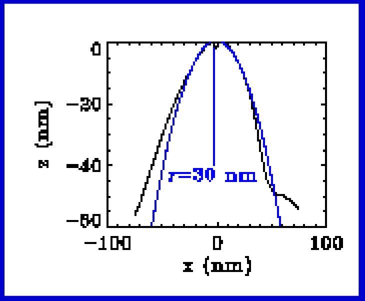
$$I = S \oplus P$$

Tip Reconstruction
Solve: $(I \ominus P) \oplus P = I$
Result: $P_R = f(I, S, \ldots)$

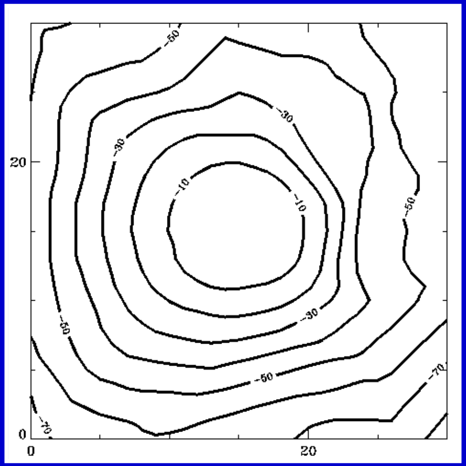
Where:
- I represents the image
- S represents the sample
- P represents the AFM probe tip



3-D tip geometry



tip cross section

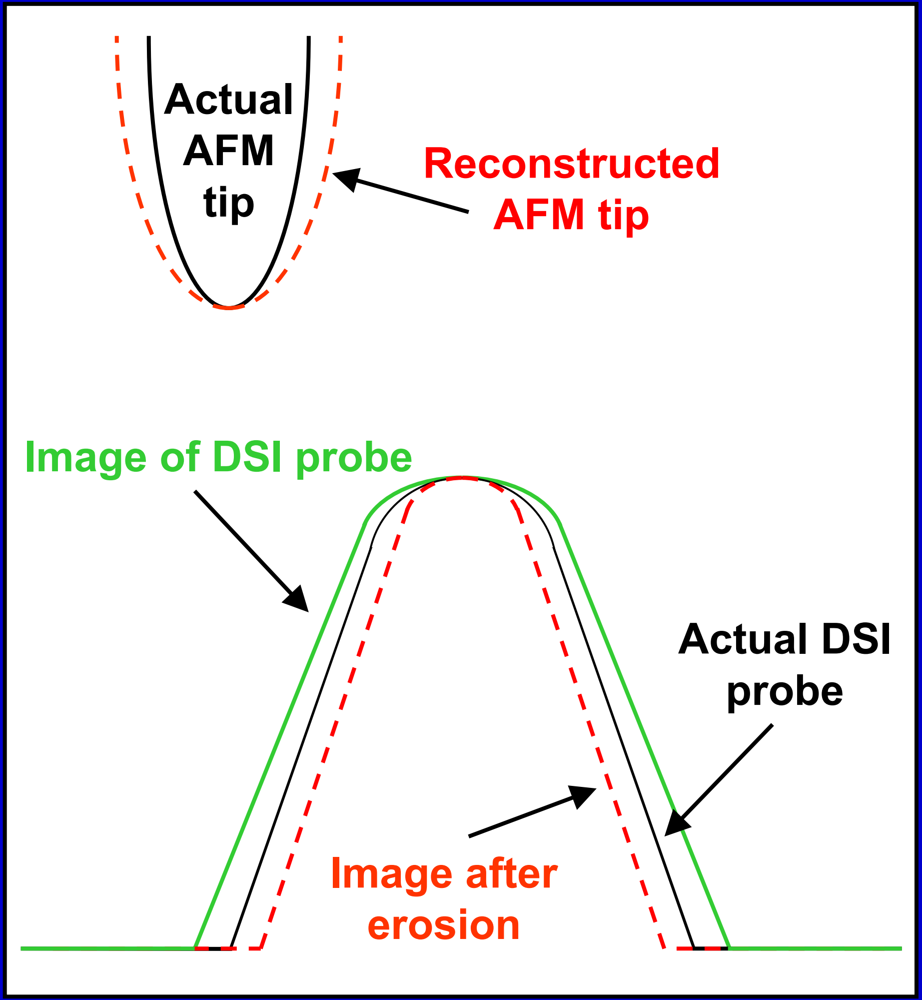


contour plot of tip

Calculated tip shape will be an outer bound

Only the region of the AFM tip near the apex will contact the indentation tip and thus needs to be estimated.

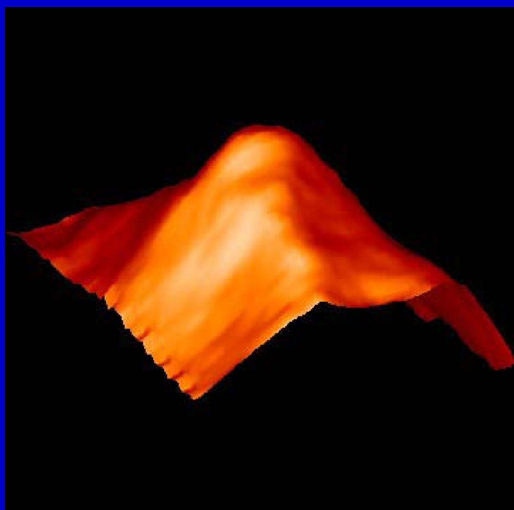
Estimation of DSI Probe Tip Geometry



- AFM image of a DSI probe tip will be a combination of the two tip geometries:
  - Constitutes an outer bound on the true DSI probe geometry.
- Using mathematical morphology:
  - Determine an outer bound on the AFM tip shape using blind reconstruction.
  - Use erosion to produce a lower bound on the true DSI probe geometry.

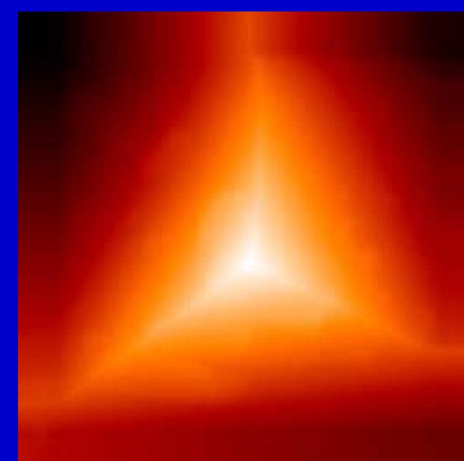
$$S = I \ominus P$$

Example of Tip Shape Estimation



Reconstructed AFM Tip

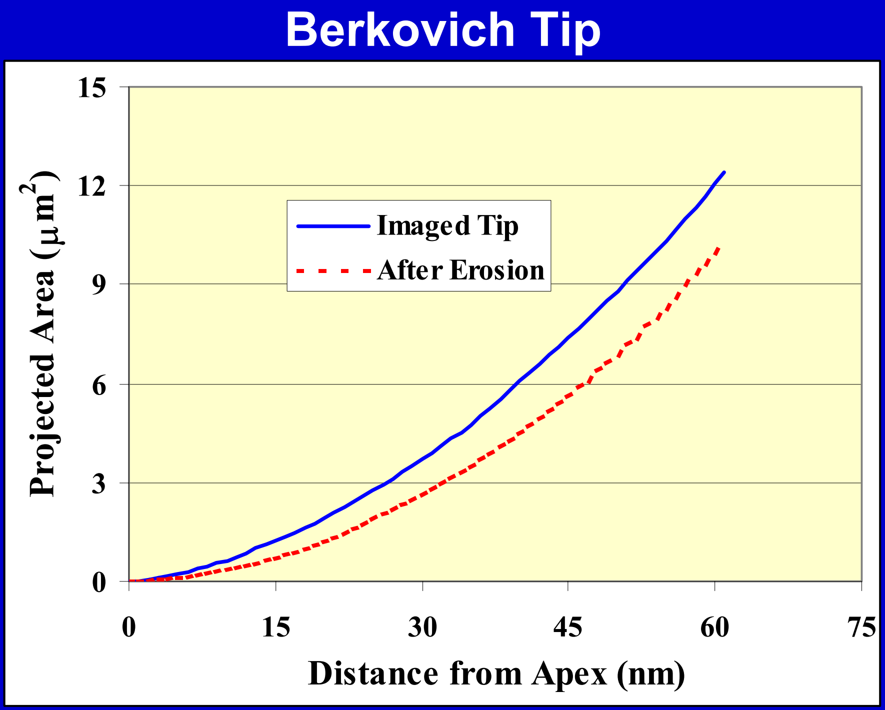
AFM Image

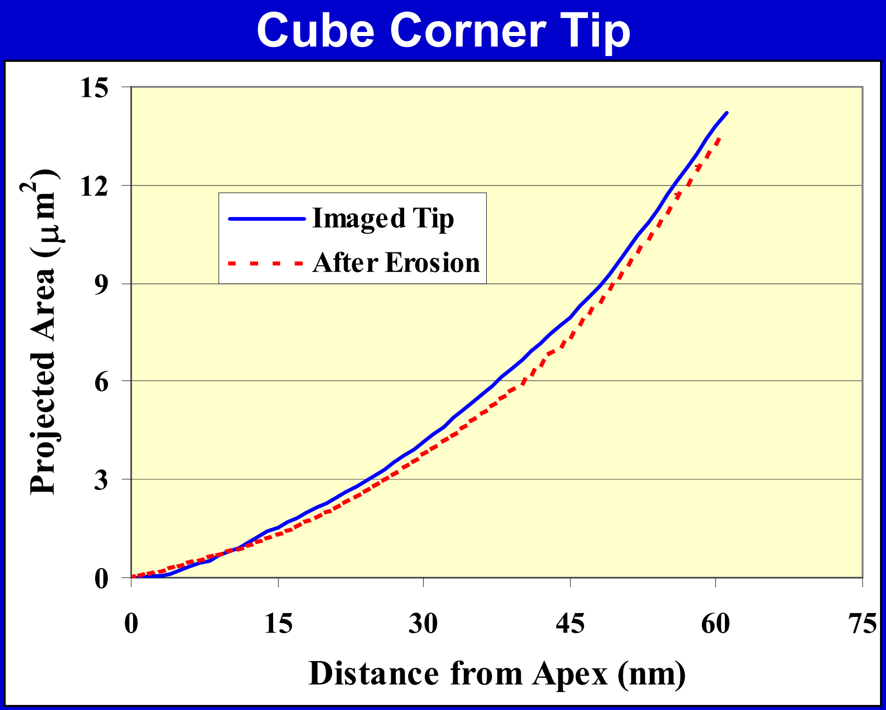


After Erosion

AFM tip shape eroded from AFM image of indenter tip, which is an upper bound on the indenter geometry, yielding a lower bound on the indenter geometry.

Examples of Tip Area Data





- Actual tip area has upper and lower bounds, the difference between which is a function of the geometries of the AFM tip and the indenter tip.

Roughness Literature Study

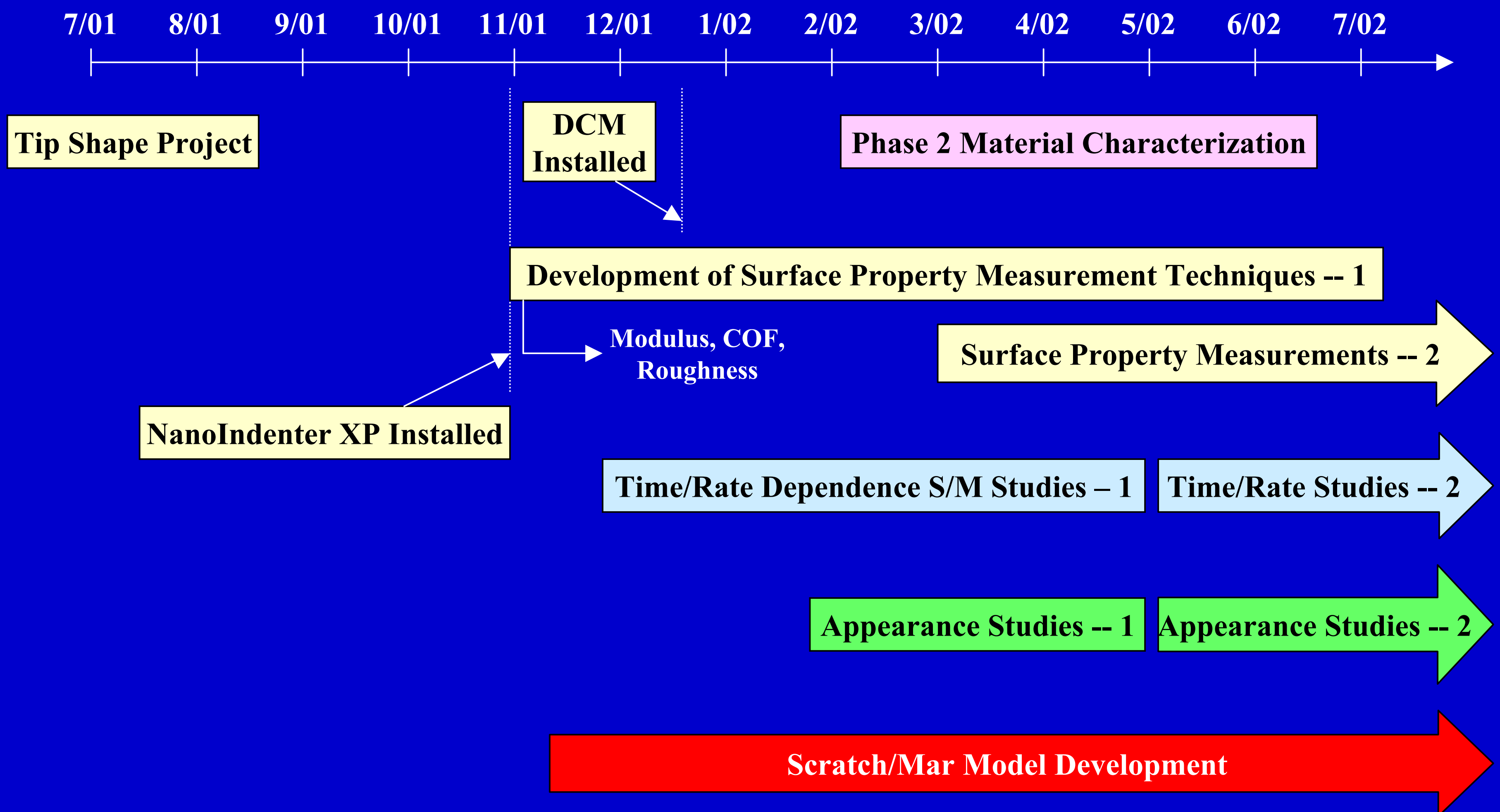
Roughness Characterization

- Concept of roughness depends on sample interval / size and scale of analysis.
  - Sectional vs. areal measurements
- Two principal planes of roughness
  - At right angle to surface – height
    - » Single value parameters
      - Extreme value parameters
      - Average parameters
    - » Statistical distributions
      - Height distribution
      - Bearing area
  - In the plane of the surface – texture
    - » Random-process functions
      - Autocovariance function (ACVF) and power spectral density function (PDSF)
      - Autocorrelation function (ACF) is normalized version of ACVF
      - Structure function is related to the ACF but is stable, easy to compute, does not require prior high-pass filtering, and related to fractal roughness
      - Correlation length is a single value based on the ACF
    - » Fractal Roughness
      - Fractal constants are intrinsic properties of the surface
      - Difficult to characterize anisotropy

Next Steps

- With NanoIndenter:
  - Characterize time-dependent and dynamic mechanical response of surfaces for Phase 1 and Phase 2 materials
    - » Link to time/rate-dependent response to scratch/mar
  - Explore the usefulness of friction coefficient measurements in single-probe scratch/mar testing.
    - » Effects of probe geometry
- Begin appearance studies
  - Determine best methods for characterizing surface roughness as related to scratch/mar.
- Continue model development
  - Link measured material response to model parameters
  - Explore whether non-linear viscoelasticity is necessary

Updated Research Plan and Timeline



Dissipative Particle Dynamics
+
Spring Network

- Looks like Molecular Dynamics but at coarser scale.
- Viscosity: velocity dependent dissipation
- Spring network: $F_{ij} = -k_{ij} (x_i - x_j + xeq_{ij})$.
- To account for plastic deformation allow k_{ij} and xeq_{ij} to be function of time, temperature and history.

Model Details

- Start with square lattice.
- Nearest and next nearest interactions.
- Construct model of probe (sphere, pyramid…)
- Supply loading history.

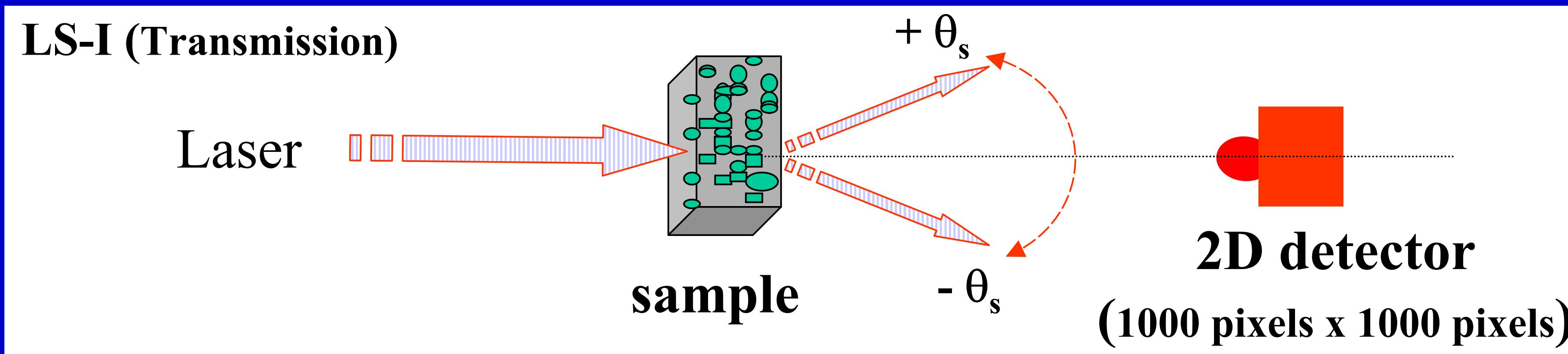
Future Research

- Validation of model.
- Compare to experiment.
- Link model parameters to material behavior.
- Include scratching of surface.

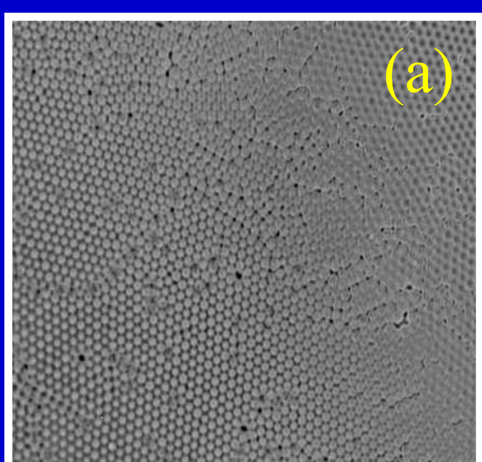
Light Scattering Laboratory

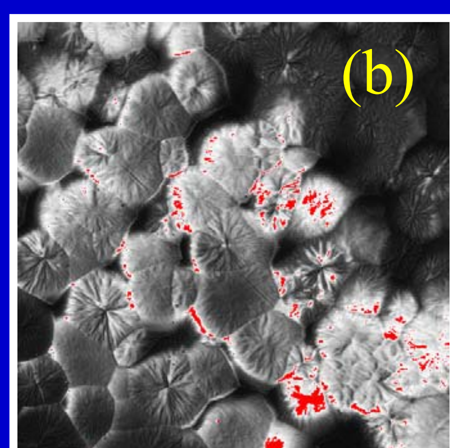
Forward Scattering Configuration

film samples (no substrate), plastic sample, epoxy in liquid cell

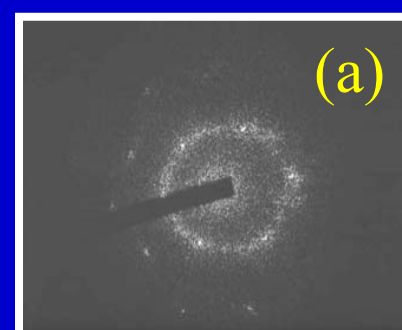


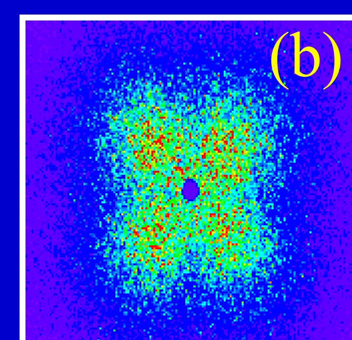
Microstructure/Morphology





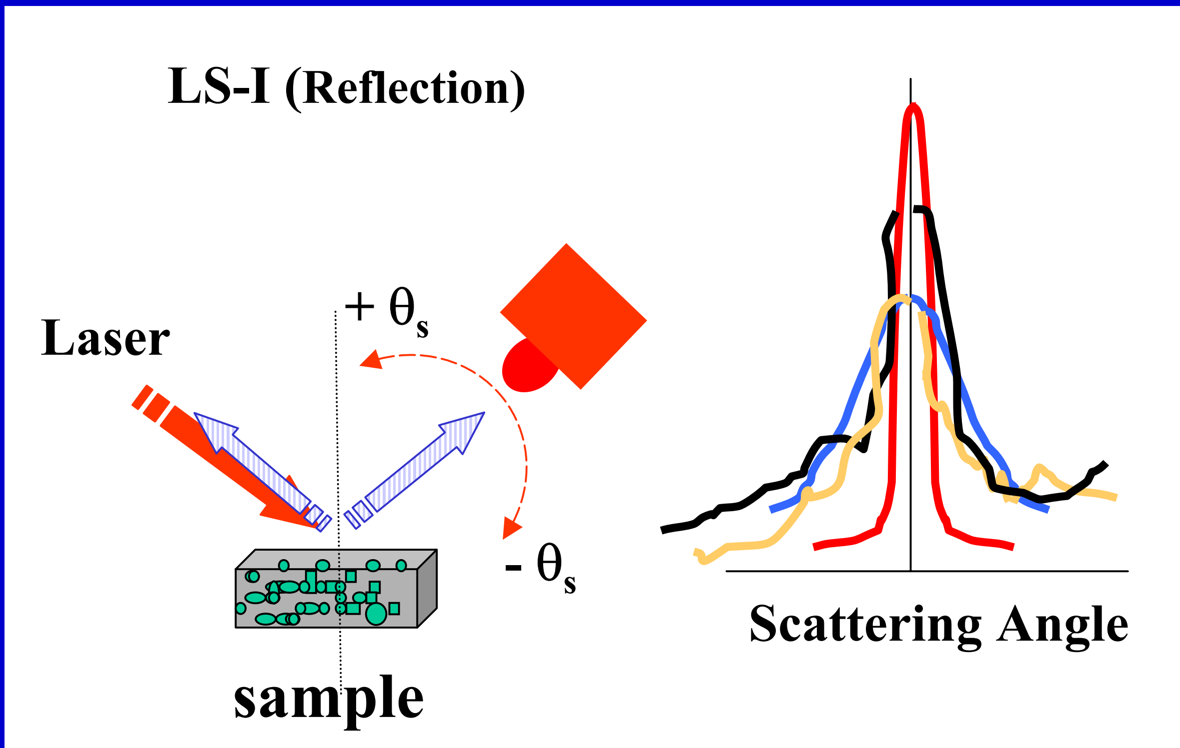
Output Scattering Patterns (In Fourier Space)

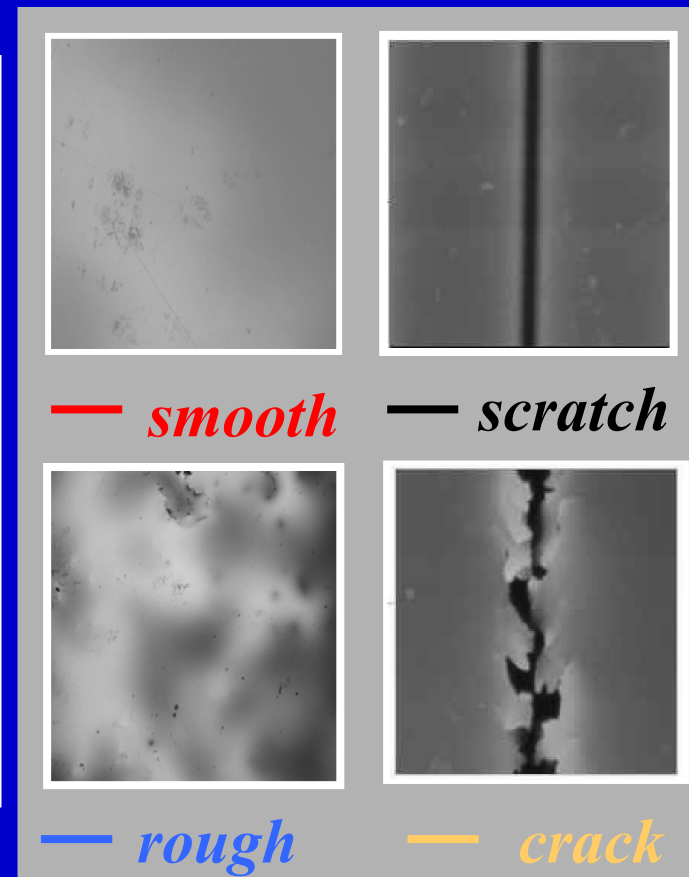




Back Scattering Configuration

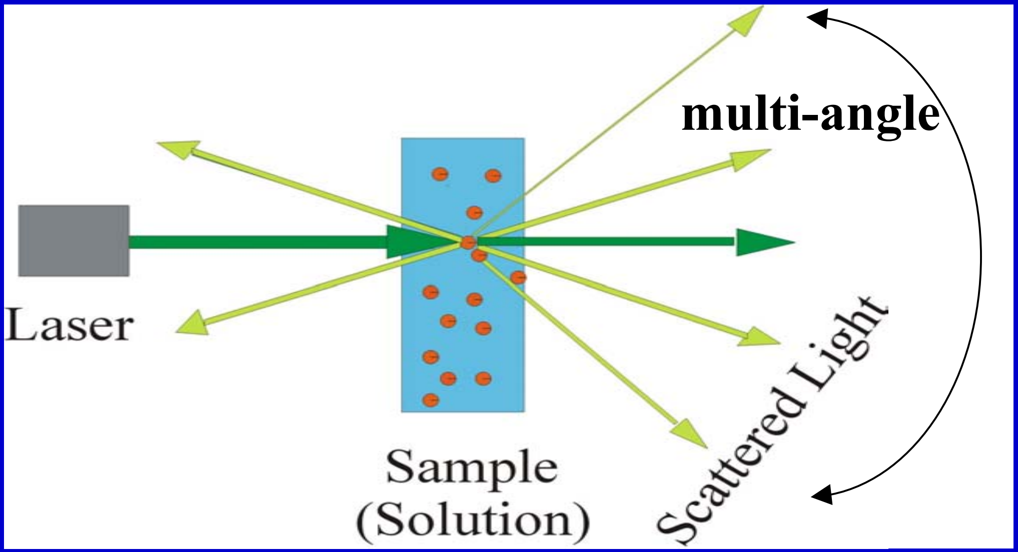
samples on substrate, plastic coatings



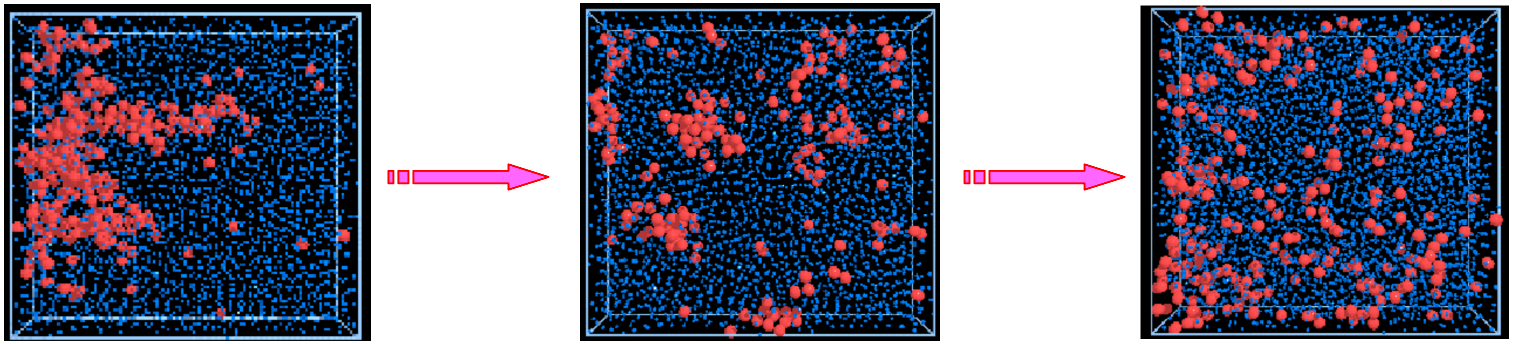


Surface Morphology and Scattering Profiles

LS - II (Static & Dynamic)



- Static (5 nm – 10 μm)
  - Time-averaged
  - Particle size
  - Network structure
- Dynamic (1 nm – 5 μm)
  - Time-dependent
  - Cluster size
  - Curing process
  - Diffusive motion
  - Includes multiple scattering



Particle Dispersion in Solutions