Forces and Mechanics of Contact Sampling

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Overview

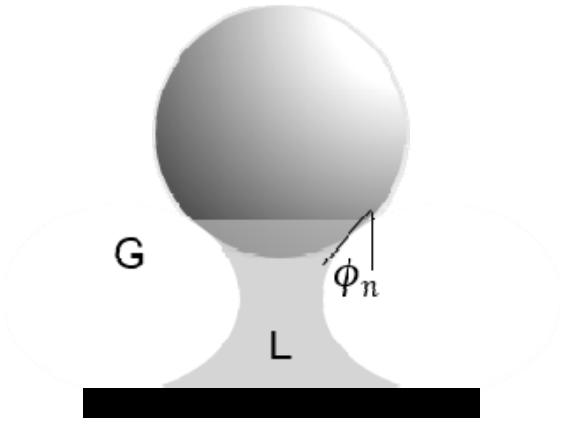
- Which forces matter in contact sampling?
  - Electrostatics
  - Capillary
  - van der Waals
- How do explosives contact a surface?
  - Point contact
  - Deformation leading to intimate contact
  - Solid-solid or solid-liquid-solid contact
- How do explosives come off surfaces during contact sampling?
  - Plastic deformation followed by internal failure
  - Adhesive failure
  - Cohesive failure
- And now for something completely different!!!

Electrostatic Forces

- Dry environments
  - Governed by Coulomb's law
  - As humidity ↑, adsorbed moisture drains surface charge and reduces ES effects
- Materials of our interest expected to have no net charge
  - Metals generally drain charge away – they are usually uncharged
  - Dielectrics and insulators are not manufactured to contain a fixed charge
  - Under certain conditions, charge and non-zero potential on surfaces may emerge
    - Materials may hold small surface charge if surface reactions have created oxides that can hydrolyze in humid environments
- Contact electrification may matter
  - Transfer of charge due to contact
    - For insulating materials, it is prudent to check charge build-up if materials are wiped or rubbed
      - Explosives crystals or powders may become charged due to rubbing
    - Compounded explosives likely will not accumulate charge
- <u>Experiments needed to investigate</u>

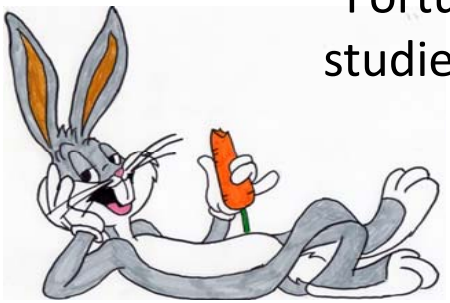
Capillary Forces

- Adhesion forces resulting from adsorbed water
  - Bulk water forms liquid bridges between surfaces
    - Kelvin equation classically used to describe the effect



$$R_s = \left(\frac{1}{R_1} + \frac{1}{R_2}\right)^{-1} = -\frac{V_{m,L}\gamma_{LG}}{RT\ln\left(\frac{p_G}{p^S}\right)} \qquad \Delta P \approx 2\gamma_{LG}\left(\frac{1}{R_1} + \frac{1}{R_2}\right)$$

    - R_s = Kelvin radius; R_1, R_2 = principle radii of curvature of liquid bridge; $V_{m,L}$ = molar volume of liquid; p_G/p^S = relative humidity; γ_{LG} = liquid-vapor surface tension; ΔP = Laplace pressure
  - Limits of the Kelvin equation
    - No dependence on surface energy of the solid surfaces between which the liquid bridge is suspended
    - It assumes that the surface tension of the liquid is constant, no matter how small the bridge
    - It assumes that the molar density of water is constant, no matter how little water there may be
    - It predicts that a liquid bridge will form at all humidity levels
    - Defies laws of physics

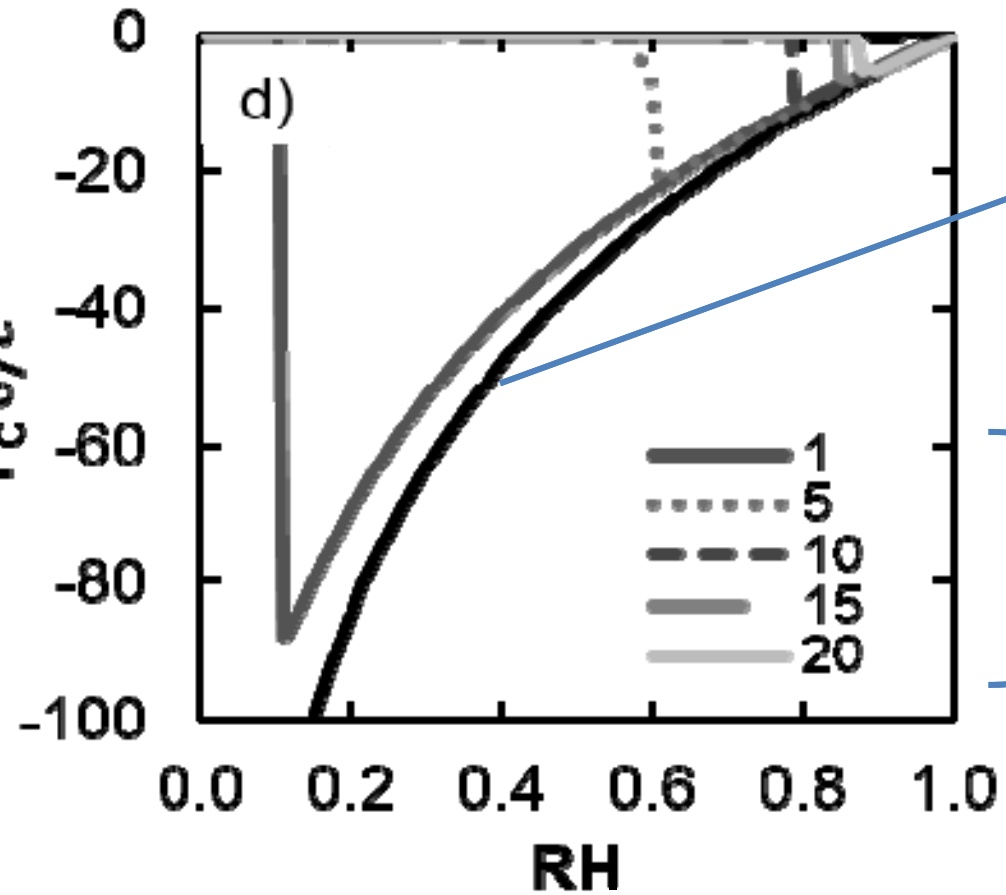


"Fortunately, I never studied law"

Kelvin Equation Limits

- Kelvin equation falls short at conditions most relevant to us
  - Low relative humidity
  - Close contact

Capillary force multiplied by ratio of water diameter to intermolecular attraction energy



Kelvin equation prediction

Intersurface separation distance divided by diameter of a water molecule

Capillary force as a function of humidity for superhydrophilic surfaces

Capillarity: What Does It All Mean

- There will be effects of adsorbed moisture at close separation distances
- Classic laws for prediction of such effects are overestimates at most humidities relevant to indoor environments
- Further study requiring detailed molecular simulation coupled with experimentation can elucidate these effects
- Must consider the following
  - Kinetics of bridge formation
  - How to quantify interfacial separation (our old friend, roughness)
  - How to model
    - Suggest applied model based on correction to Kelvin equation

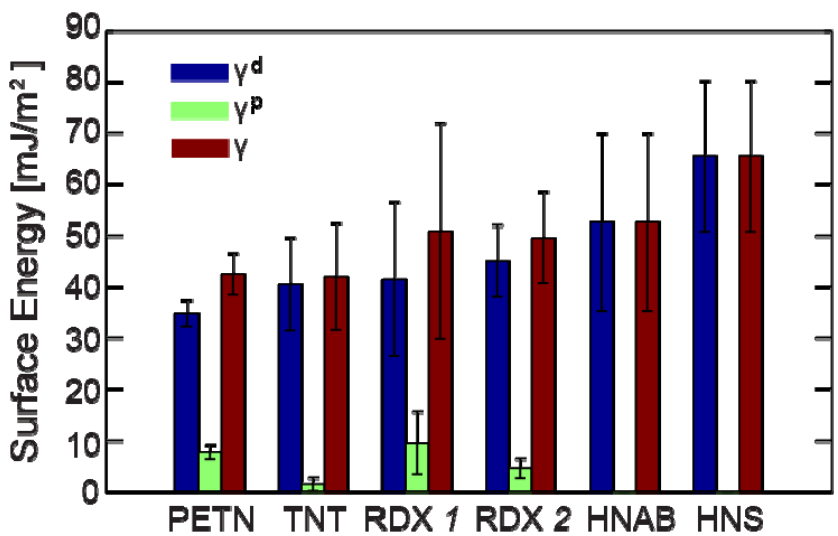
van der Waals Forces

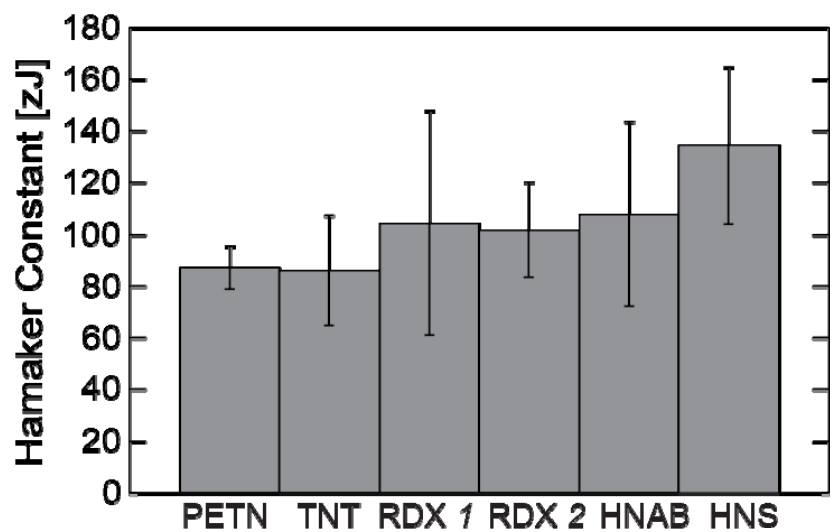
- Result from coupling of dipoles in adjacent surfaces
- Always present
- Generally strongest forces in adhesion when particles (residues) in contact with surfaces
- Substantially influenced by roughness of interacting surfaces
  - Alters the closeness of approach of the interacting surfaces
- Force proportional to
  - Composition-dependent constant (A_{132})
  - inversely proportional to separation distance squared (sphere-sphere, sphere-plate)
  - Inversely proportional to separation distance cubed (cylinder-plate)

van der Waals Forces

- Challenge: measure or calculate Hamaker constants
  - Range from 10^{-19} to 10^{-21} J for all materials (note: 1 zJ = 1×10^{-21} J)
  - Can be determined using atomic force microscopy, centrifuge, inverse gas chromatography (IGC), or surface energy measurements
    - IGC and surface energy both involve quite a bit of approximation

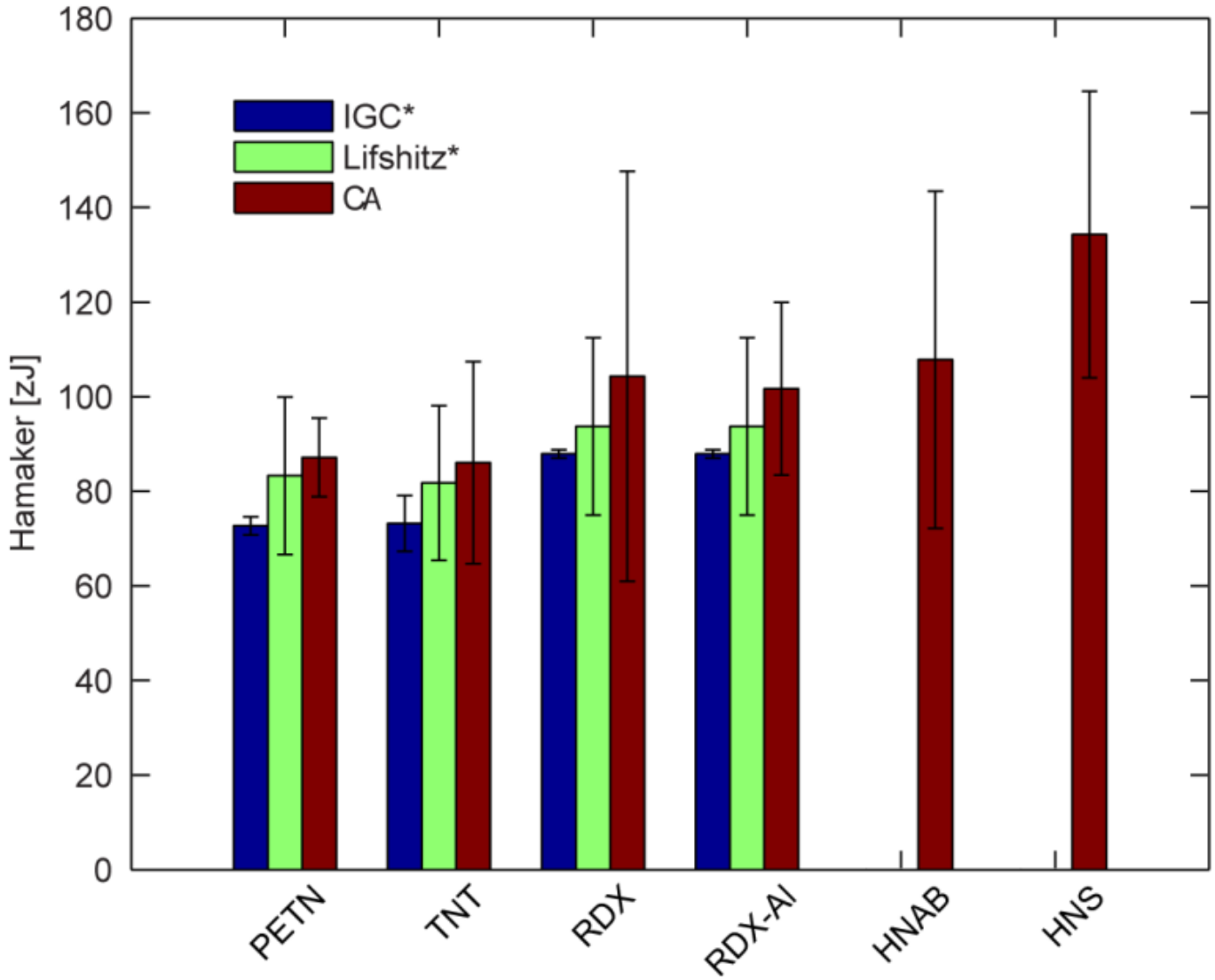
Recent Results of Surface Energy and Hamaker Constant Determination in Collaboration with Sandia National Labs





Based on contact angles of a series of liquids on smooth thin films of explosive

Hamaker Constants Estimated by 3 Methods



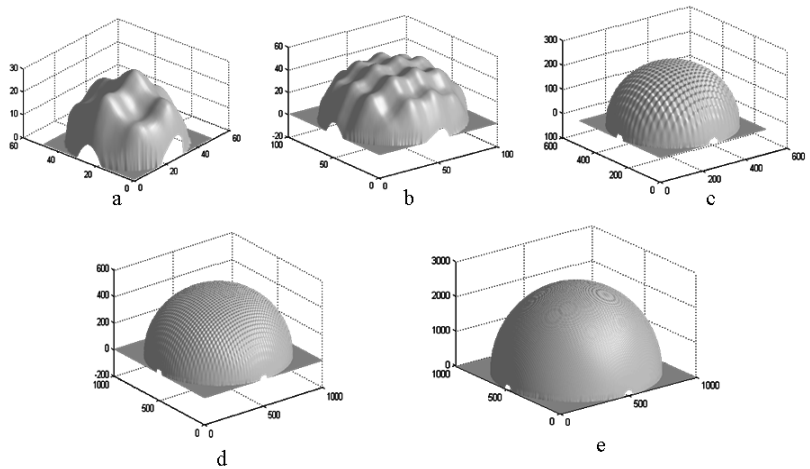
van der Waals Forces, cont'd

- Challenge: consider topographical effects of surfaces on vdW force
  - Total mass interacting within ~ 20-30 nm of point of contact drives vdW force prediction
  - We must accurately understand the roughness (soon) of the interacting surfaces, and we must have a way to model the effect of the roughness
- Modeling roughness effects on vdW forces
  - Simulator in existence
    - Inputs can be in form of topographical map, geometric form
    - Code discretizes the interacting surfaces and calculates vdW force based on separation distance of distinct nodes on each surface
- Modeling deformation effects on vdW forces
  - State of the art assumes equilibrium deformation
  - Does not consider kinetics of deformation in contact

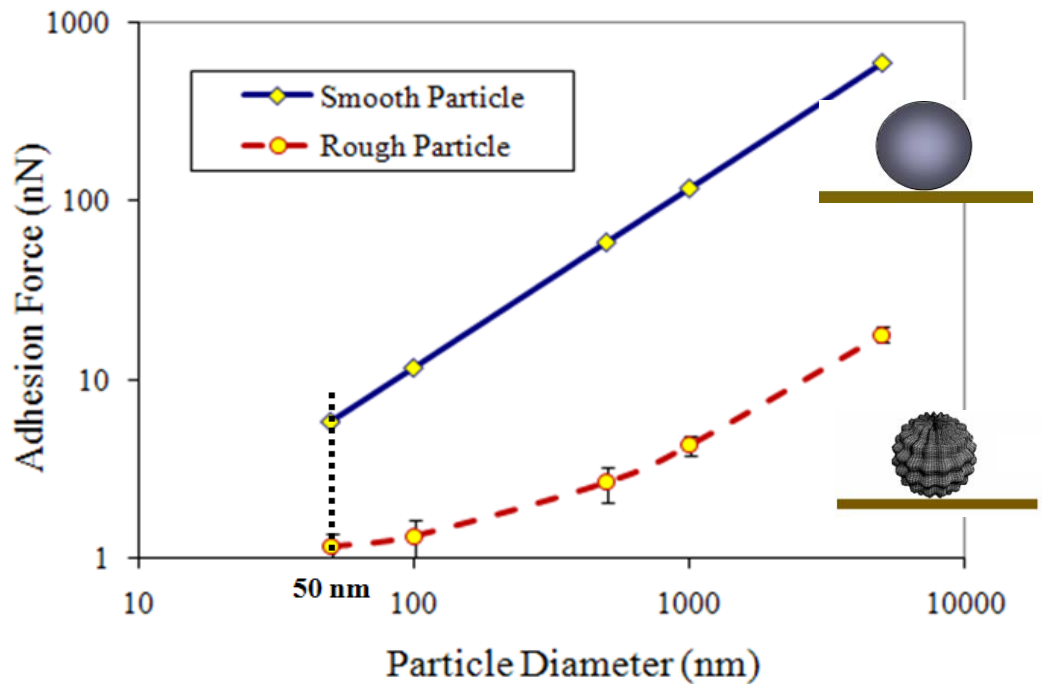
Roughness and van der Waals Forces

- Roughness simulated as 2d-sinusoids
  - Defined by amplitude and wavelengths

$$h(x,y) = 2a\left(\frac{Sin\left(\frac{2\pi x}{\lambda_x}+\varphi_x\right)+Sin\left(\frac{2\pi y}{\lambda_y}+\varphi_y\right)}{2}\right)$$



Identical roughness parameters
(max. height =5 nm; $\lambda_x = \lambda_y$ =20 nm)
(a) D = 50 nm (b) 100 nm (c) 500 nm (d) 1µm (e) 5 µm

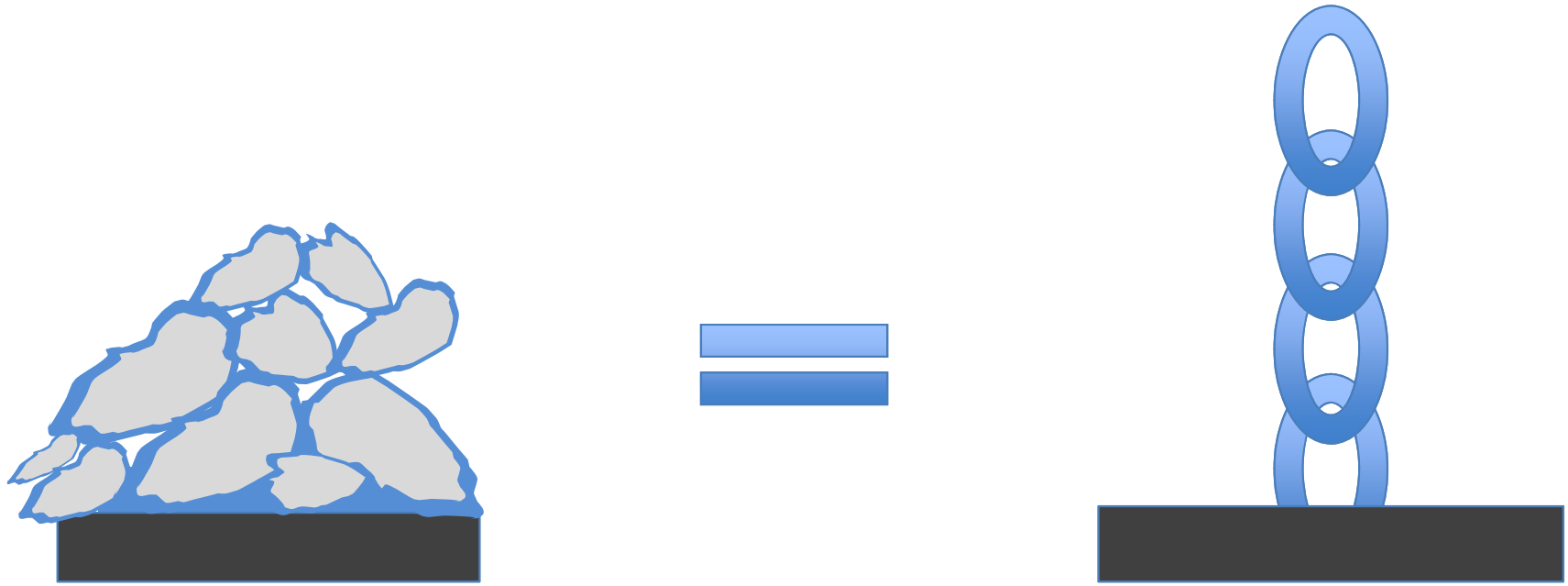


Deformation model still coming…

Explosives Contact with Surfaces

- Crystalline explosives will contact surfaces at distinct points
  - These materials are refractory and will not deform or will undergo only minimal deformation at points of contact
  - Possible to measure the mechanical properties of the crystals and describe the deformation that will occur due to the contact adhesion load
- Compounded explosives contact surfaces via solid-liquid-solid contact
  - Binders (liquids) in compounded explosives wet the crystalline explosives in the granules
  - These liquids flow in contact with surfaces
    - Create intimate contact between explosive and surface
    - An interconnected network of liquid binder completely surrounding all the solid explosives

How Are Residues Removed



Load applied on the residue (left) causes failure in the weak link in the chain (right)

Possible weak links

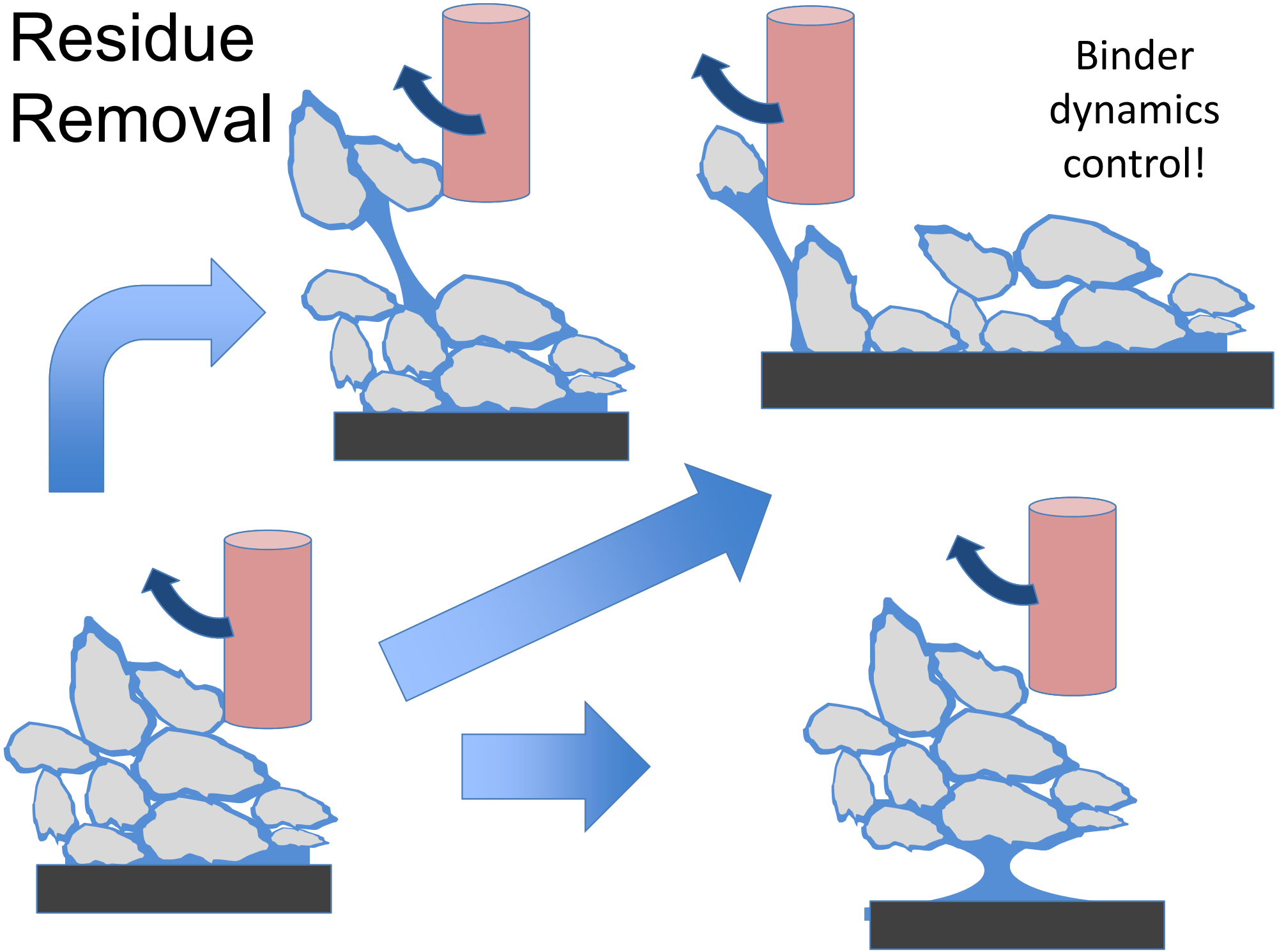
1) liquid binder – solid surface (adhesive failure);
2) liquid binder – liquid binder (cohesive failure);
3) liquid binder – explosive particle surface (adhesive failure);
4) within explosive particle (cohesive failure)

Key parameter: Capillary number (Ca)

$$Ca = \frac{viscous\ forces}{interfacial\ forces}$$

Ca for compounded explosives ~ 10^{-4} means viscous effects dominate

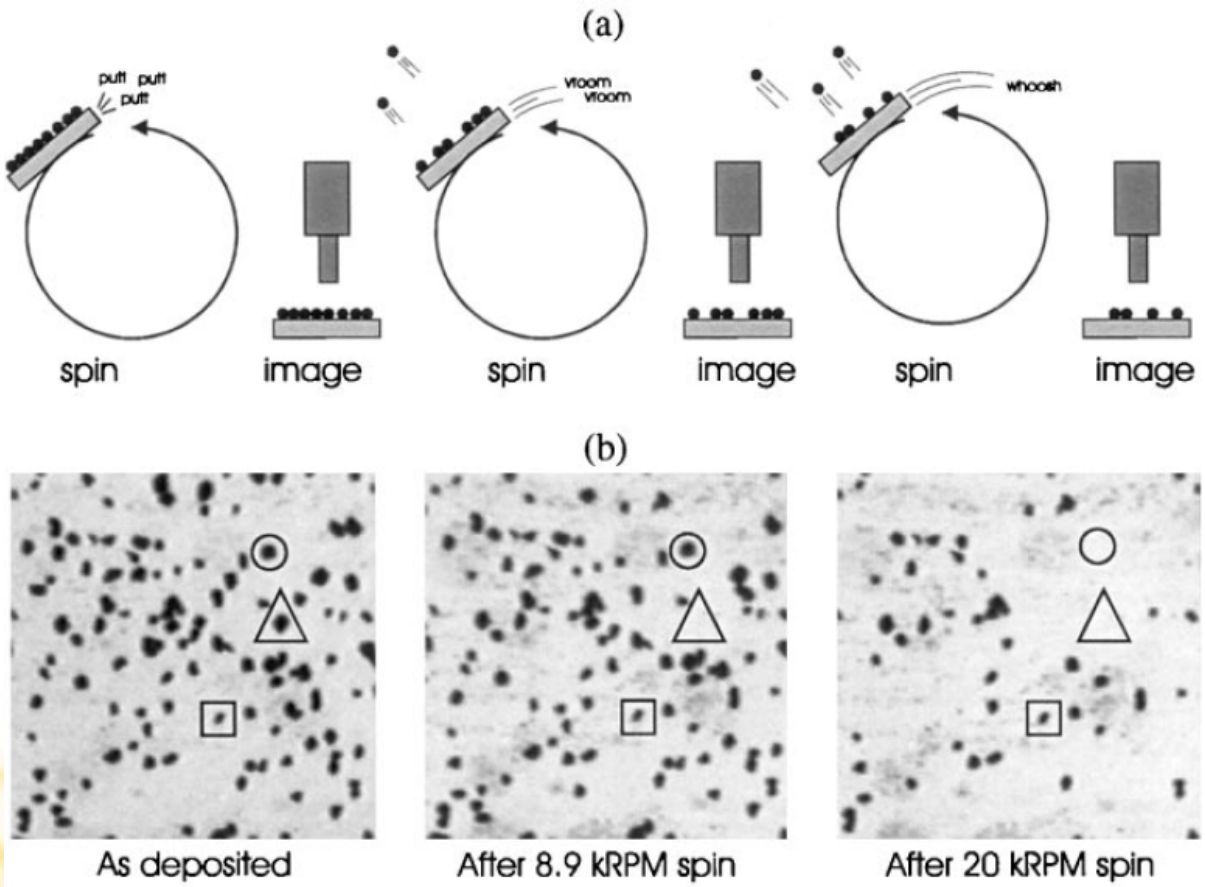
Residue Removal



A way to measure the adhesion of full residues to any surface!!!

Maybe…

Centrifuge Technique Description



$$F_{ad} = F_{cent} = m\omega^2 r$$

- Deposit particles and count the initial number of particles
- Run in centrifuge
- Capture an image of the surface to determine the number of remaining particles
- Repeat [1]

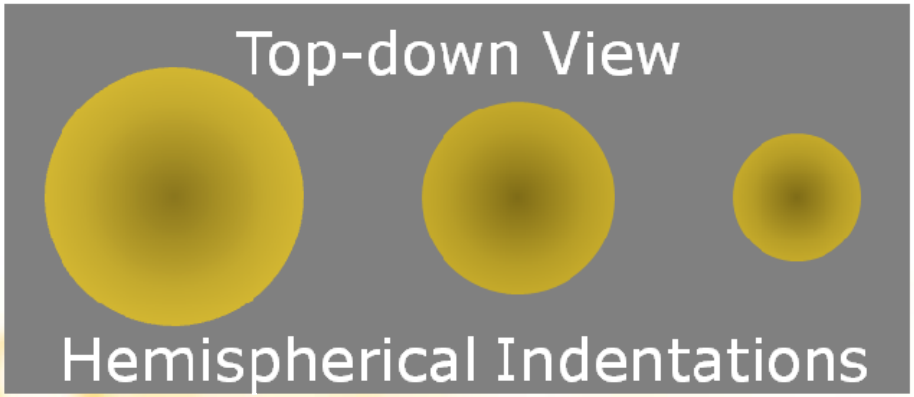
1. Mizes, "Small particle adhesion: measurement and control," *Colloid Surface A,* May 2000.

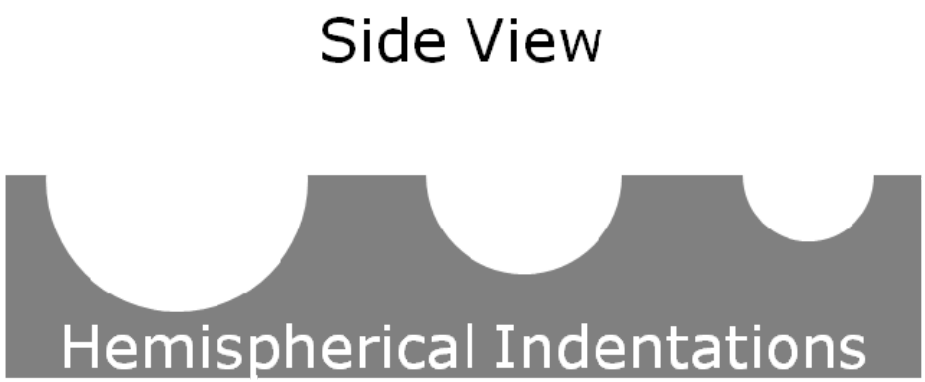
Enhanced Centrifuge Technique

Limitations of existing method:

- Only acquire geometric median adhesion force
- Doesn't provide insight on particle properties

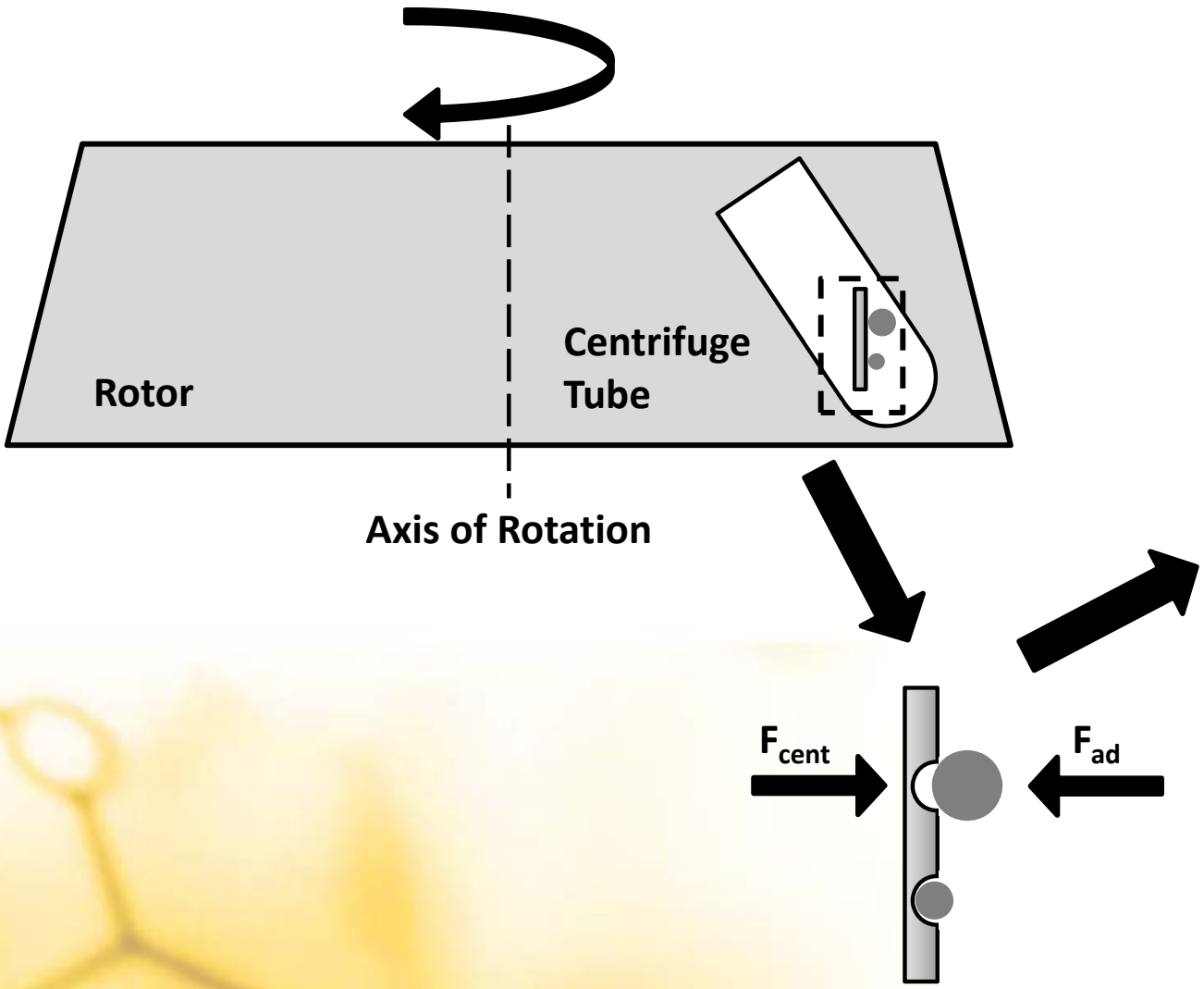
Enhancement:

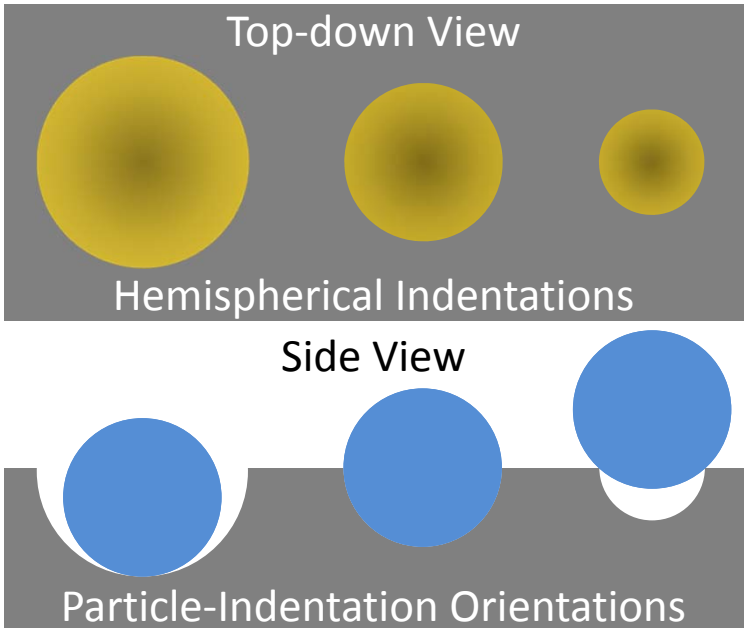




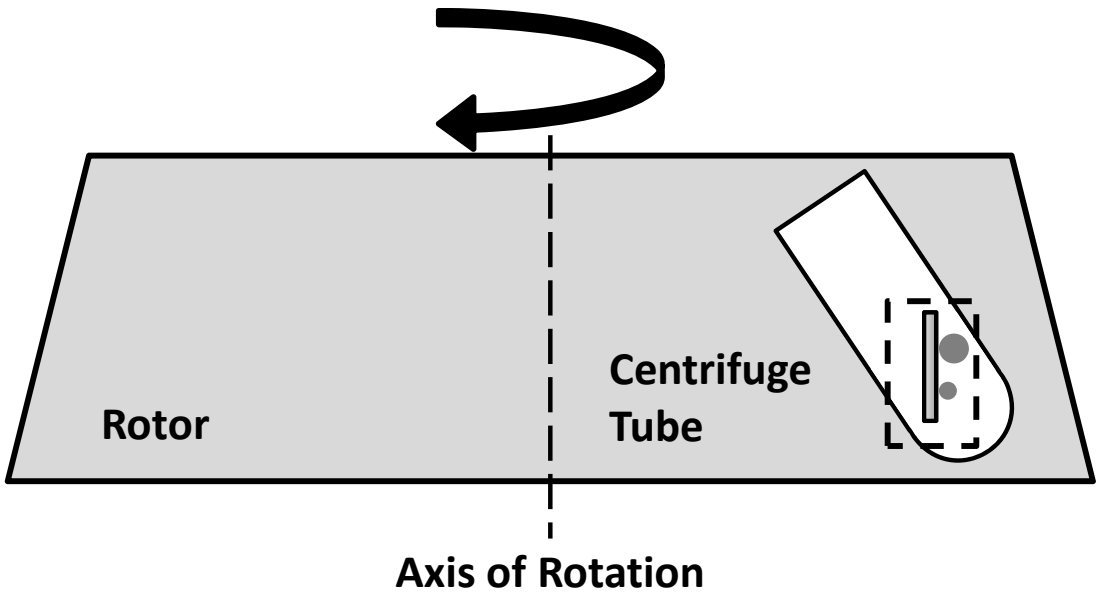
- Use specially designed substrates with hemispherical indentations to provide particle characterization

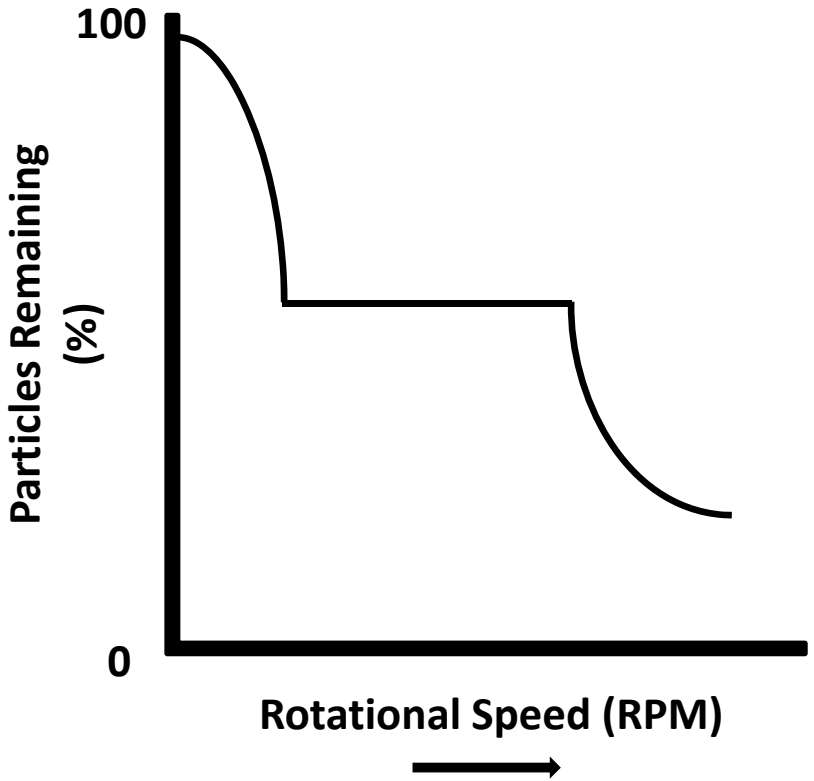
Enhanced Centrifuge Technique





Enhanced Centrifuge Technique





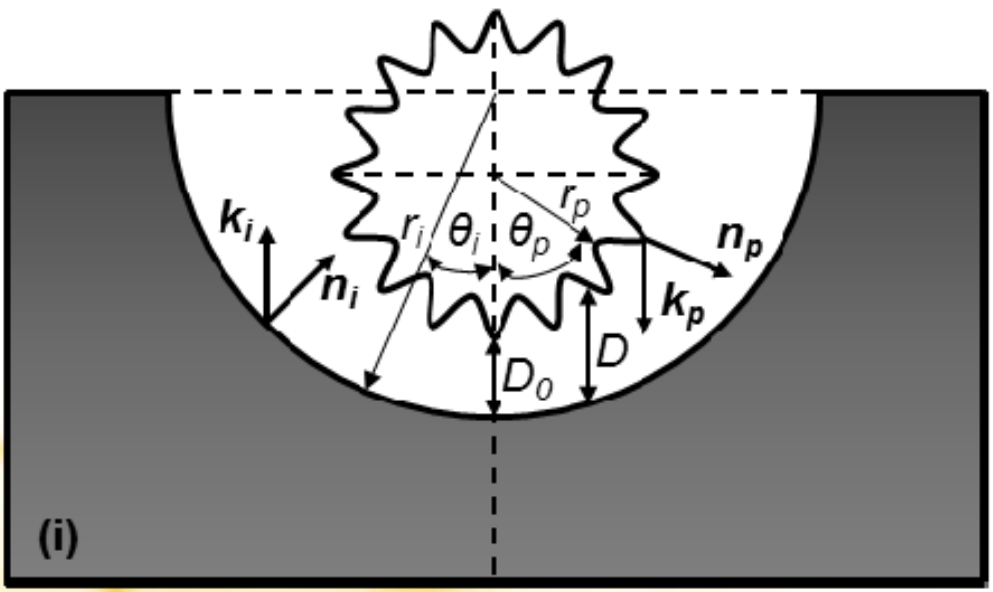
Surface Element Integration (SEI)

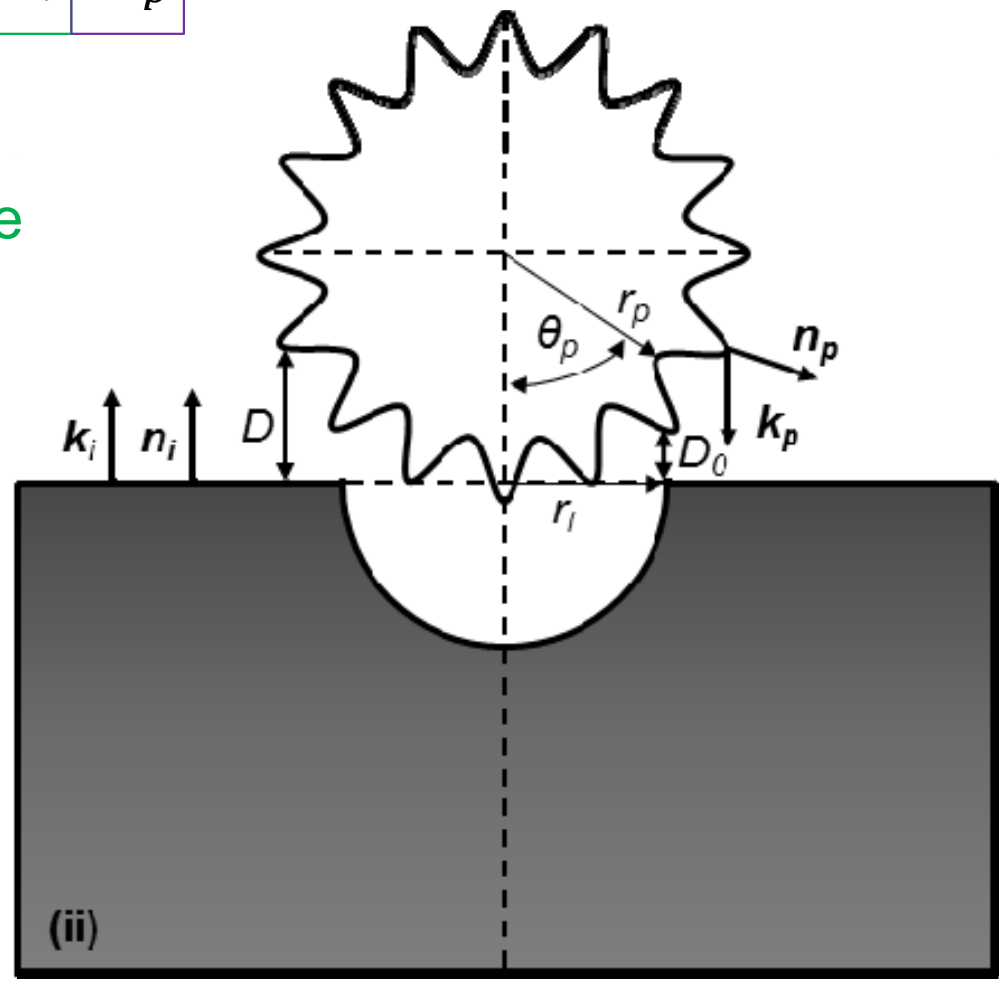
$$F_{ad} = \int_{S_p} dF_{ad} = \int_{S_p} (\boldsymbol{n_p} \cdot \boldsymbol{k_p})(\boldsymbol{n_i} \cdot \boldsymbol{k_i}) F_{vdW}(D)\, dS_p$$

Curvature

Flat plate – flat plate van der Waals force

Particle surface area





$$r_p = a\left[1 + \lambda_\theta \cos(n_\theta \theta_p) + \lambda_\phi \cos(n_\phi \phi_p)\right]$$

Roughness (Smooth = 0; Rough ≠ 0)

Asperity frequency

Particle Size Distributions

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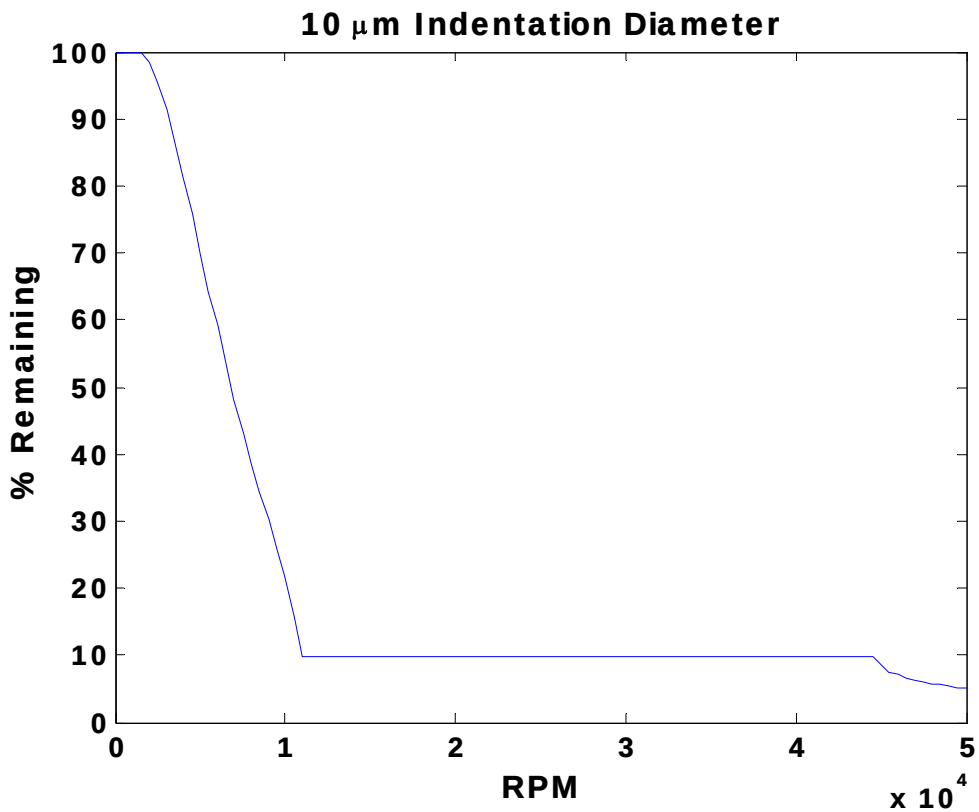
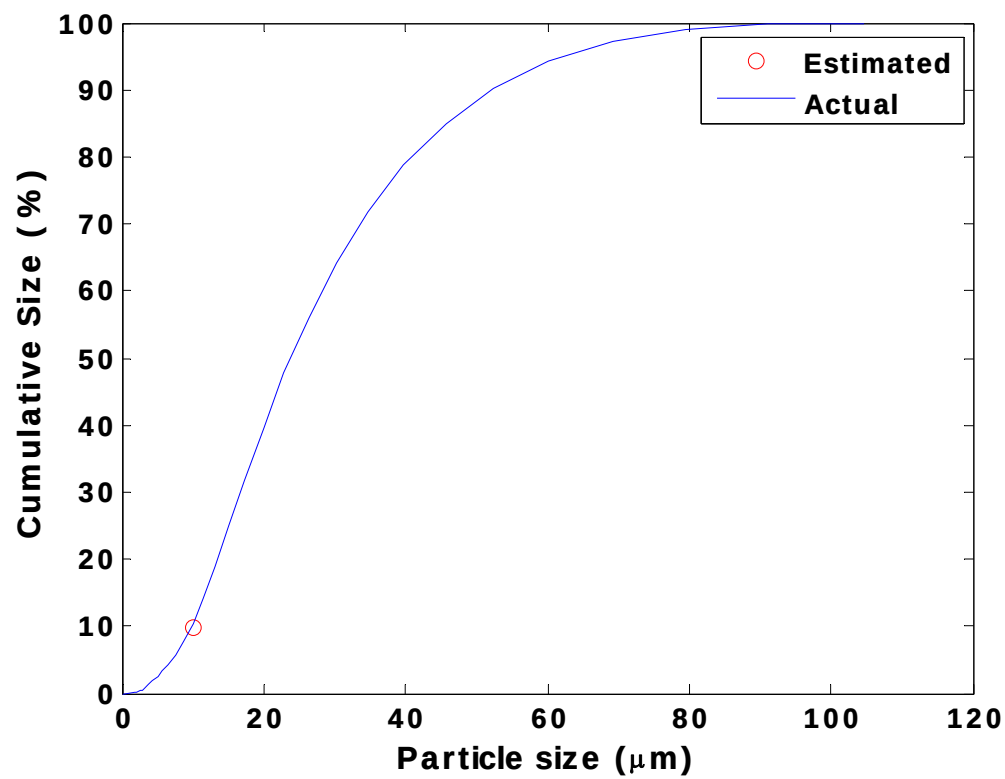
Simulated 10,000 particles of known size distribution adhering to plates with defined indentations

Cumulative size distribution built from Residual Adhering Particle (RAP) curves from each indentation size





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Particle Size Distributions

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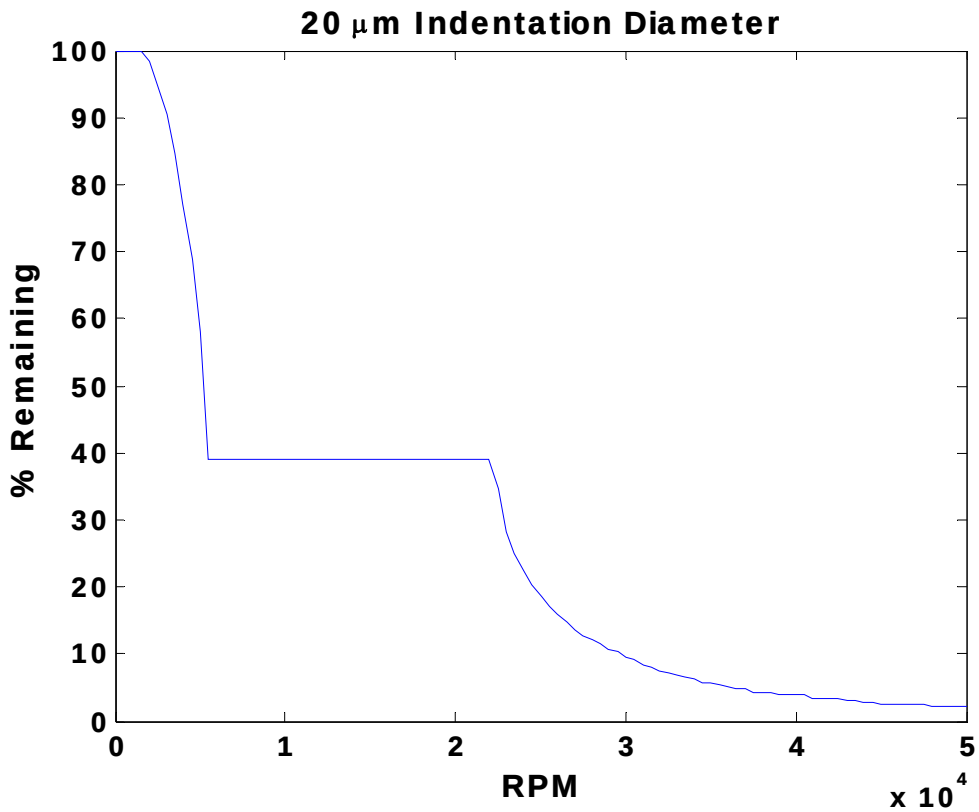
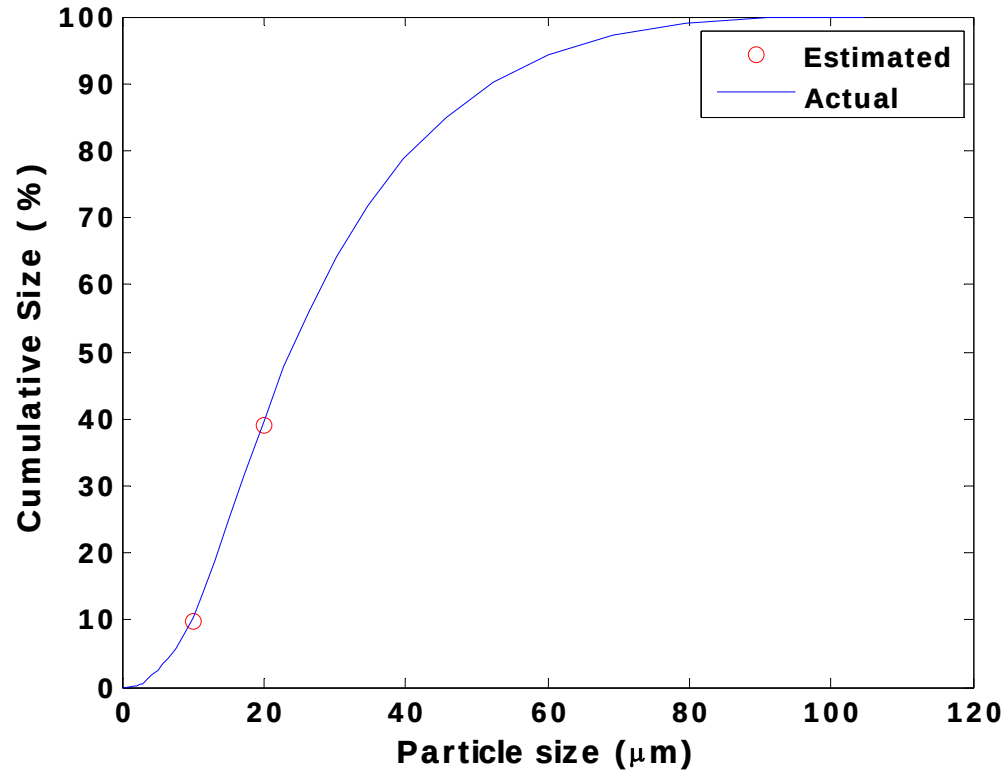
Cumulative size distribution built from RAP curves from each indentation size





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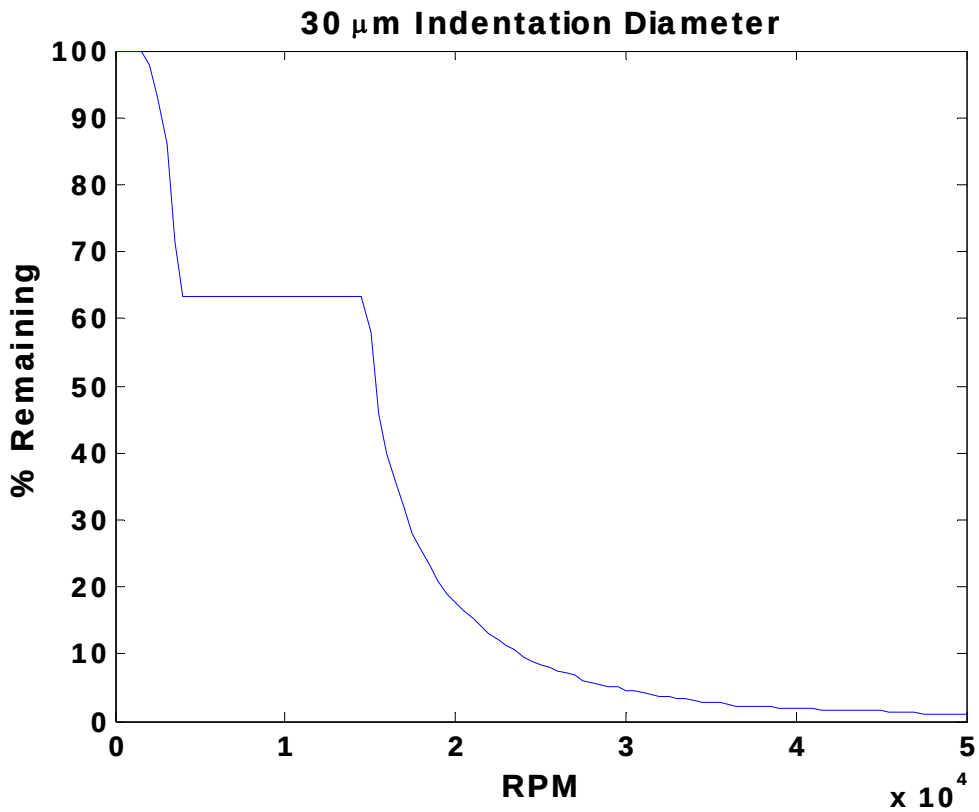

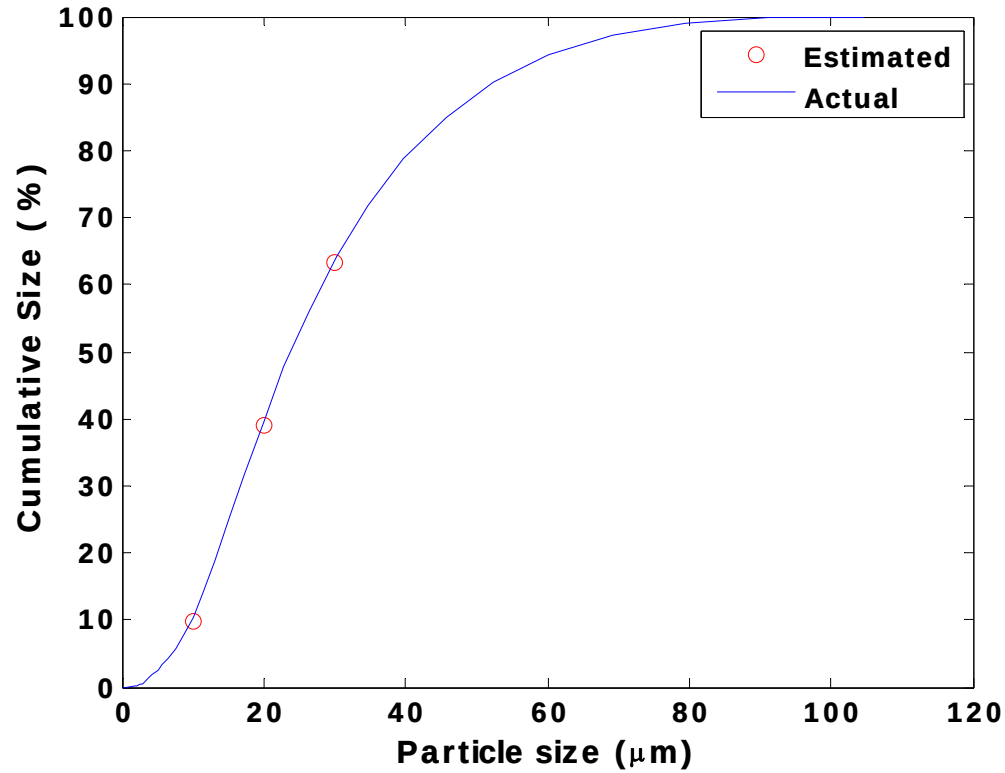

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Particle Size Distributions

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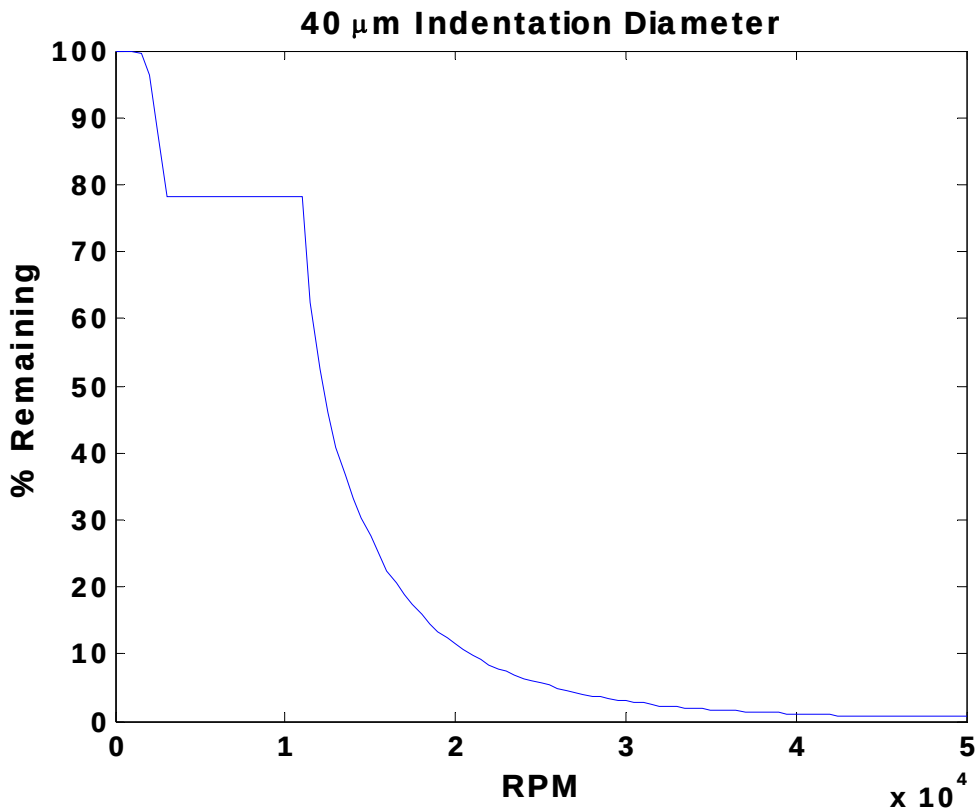
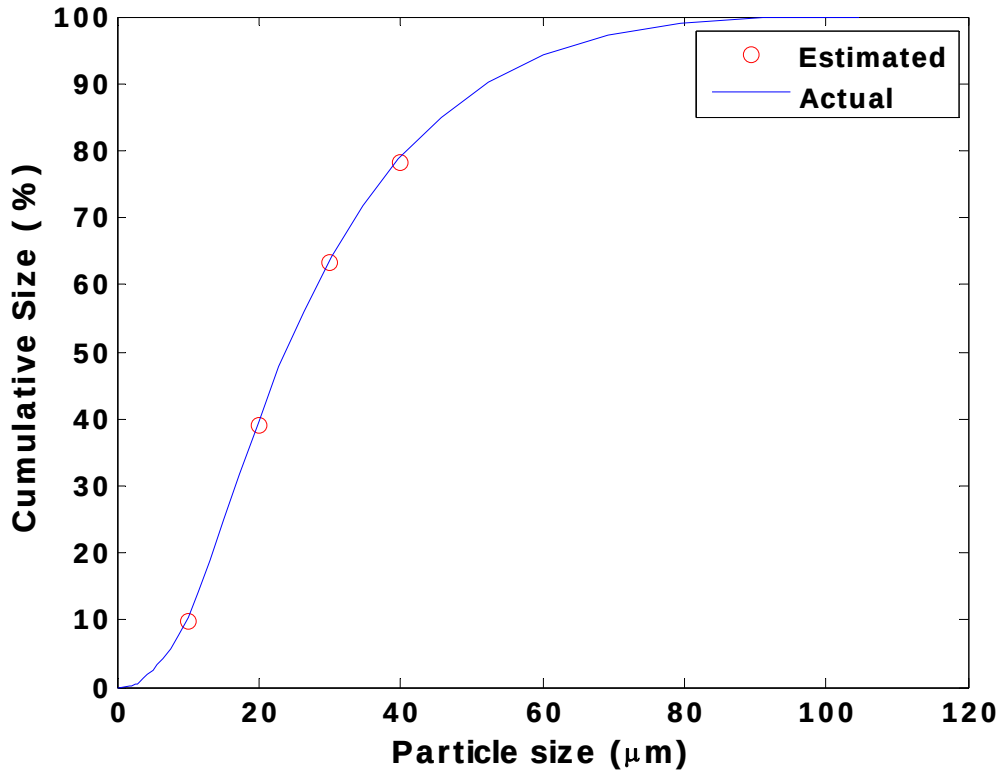
Cumulative size distribution built from RAP curves from each indentation size





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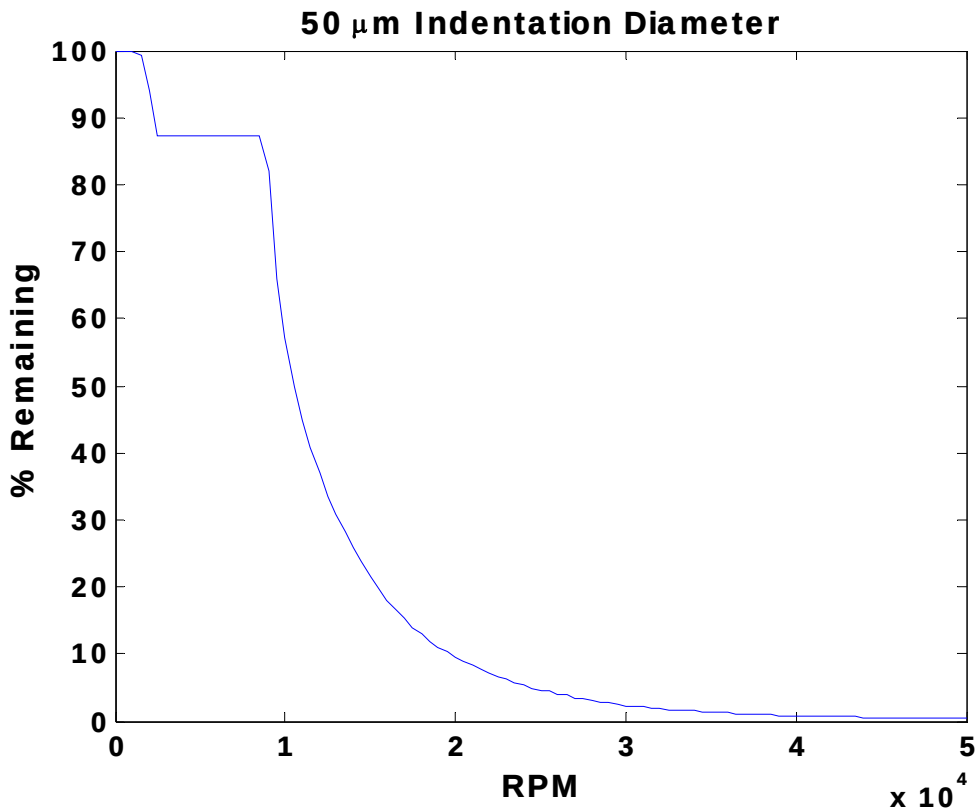

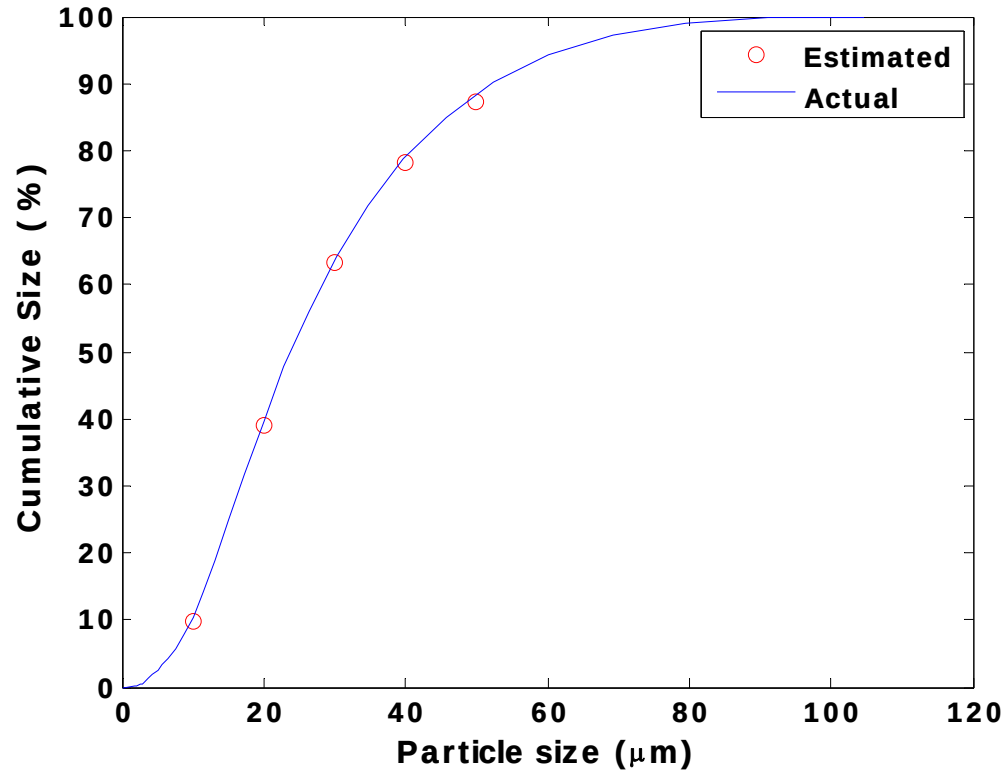

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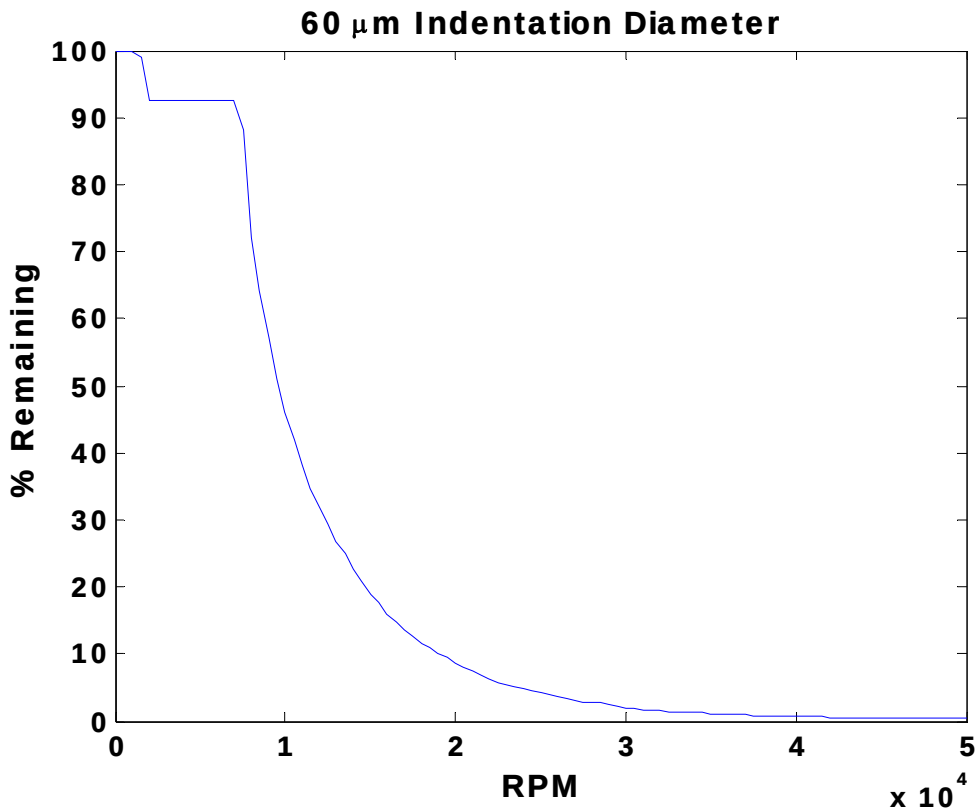

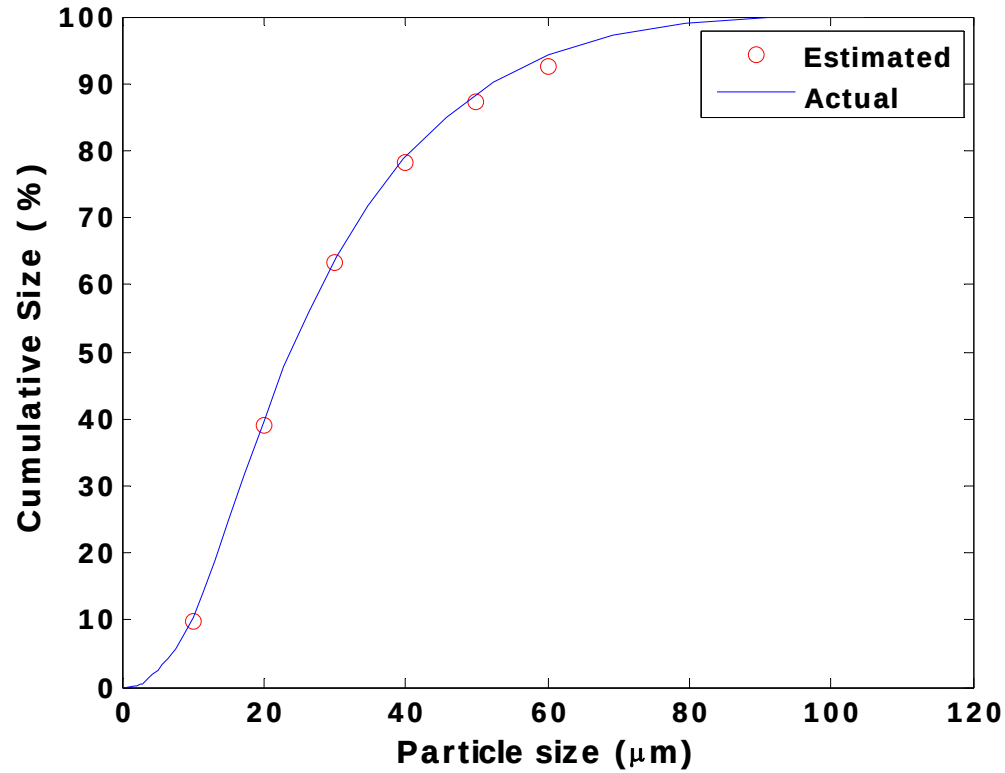

Enhanced centrifuge technique developed to discriminate particle size

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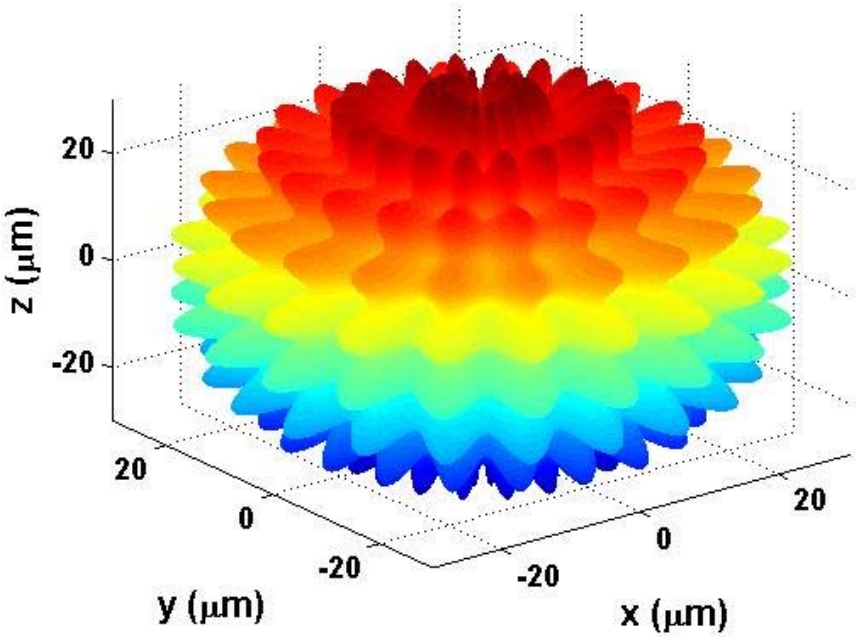
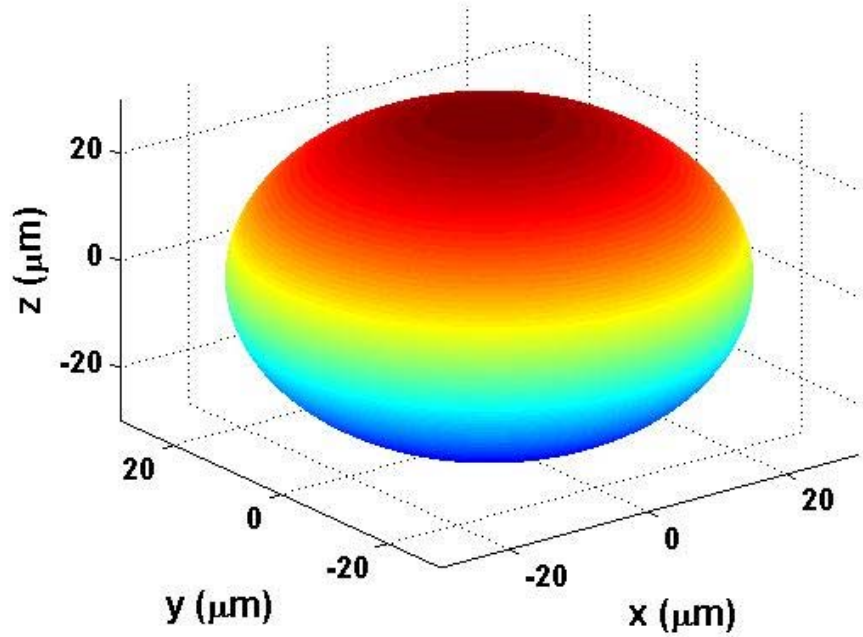
Simplify Powder Characterization





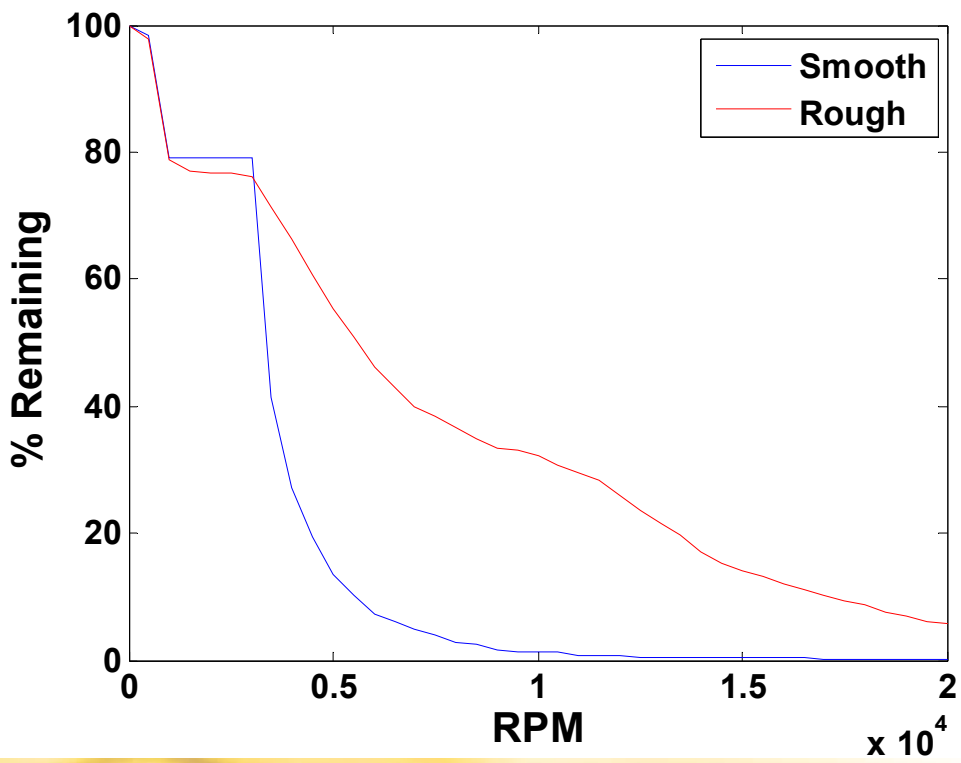
- Size: Known
- A_{132}: Known
- Roughness: ?

- Size: Known
- $A_{132,eff}$: Determine

Effective Hamaker Constants

Consider the behavior of particles with same size distribution as before but arbitrary nanoscale roughness…

40 µm Diameter Indentation



Effective Hamaker Constants

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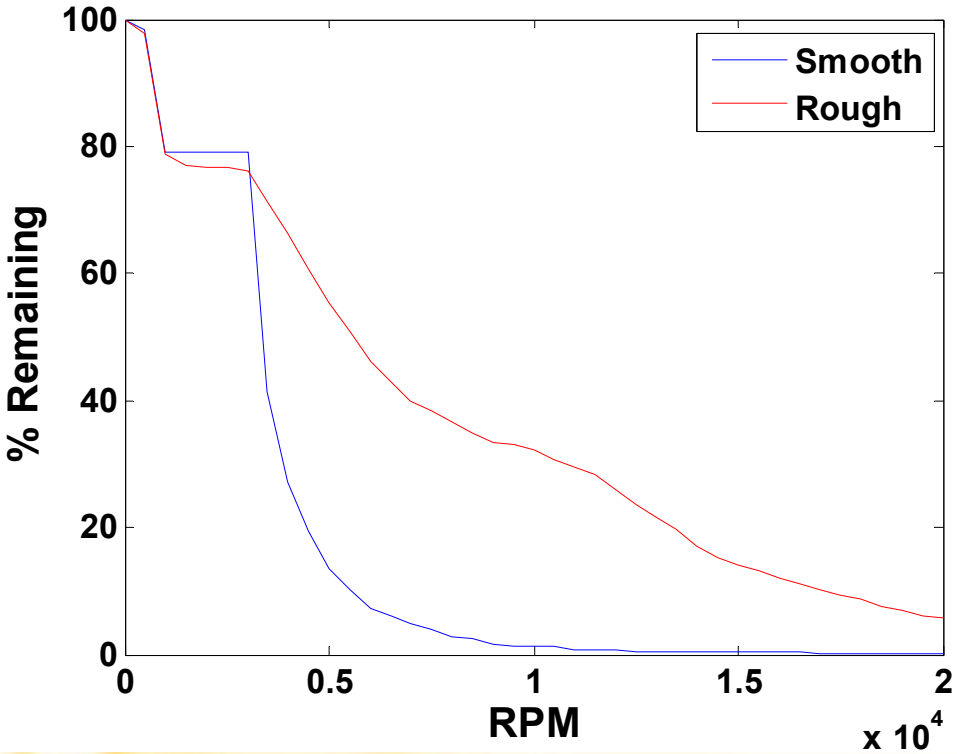

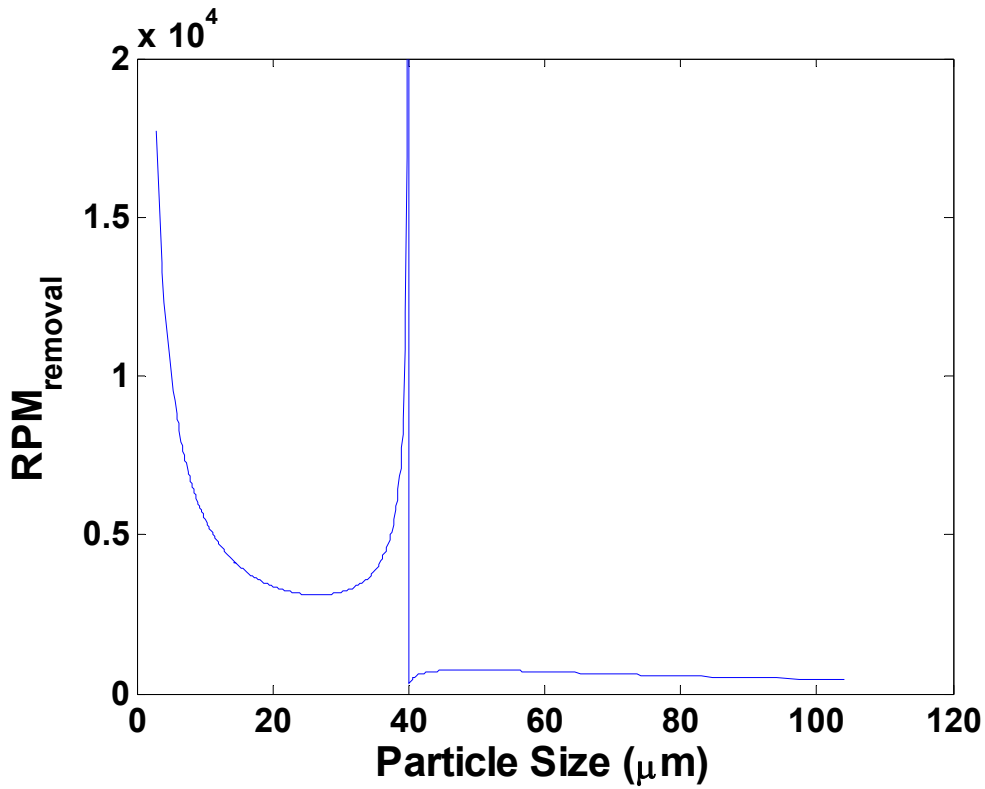

Replot the ideal RAP curve in a new way

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Effective Hamaker Constants

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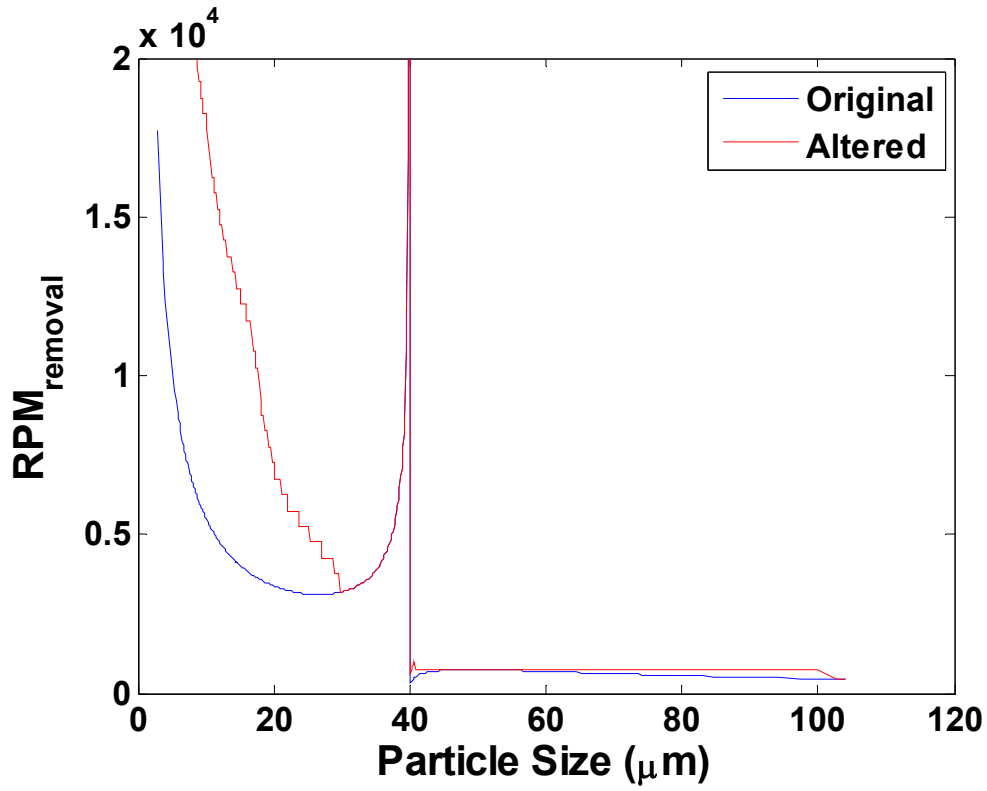
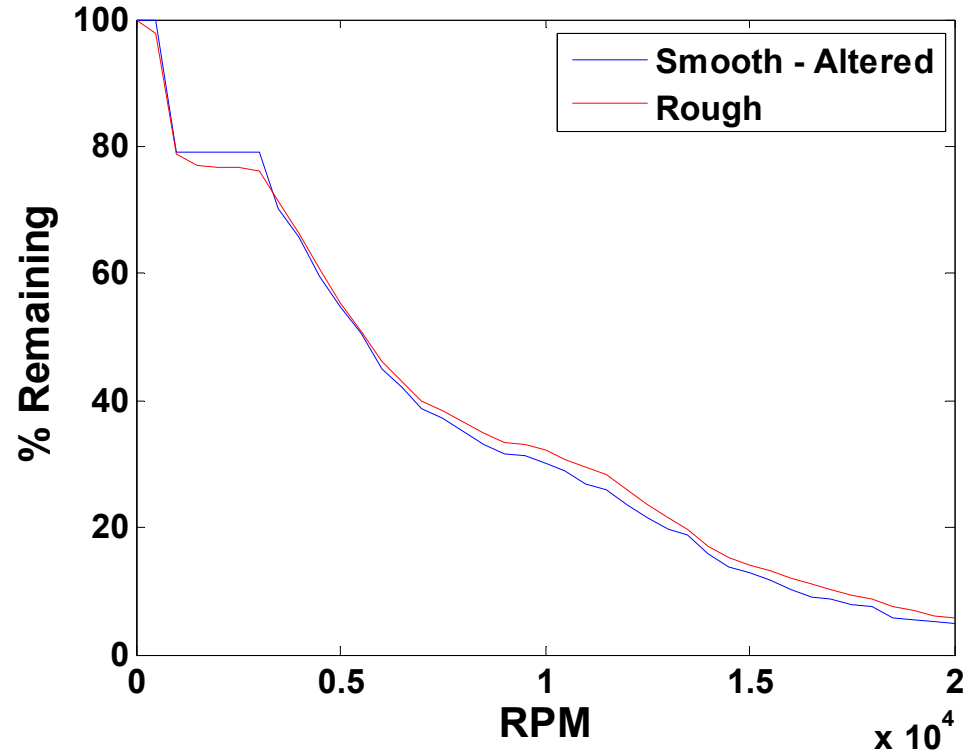
40 µm Diameter Indentation





Fit roughness PRE with A_{132_eff}

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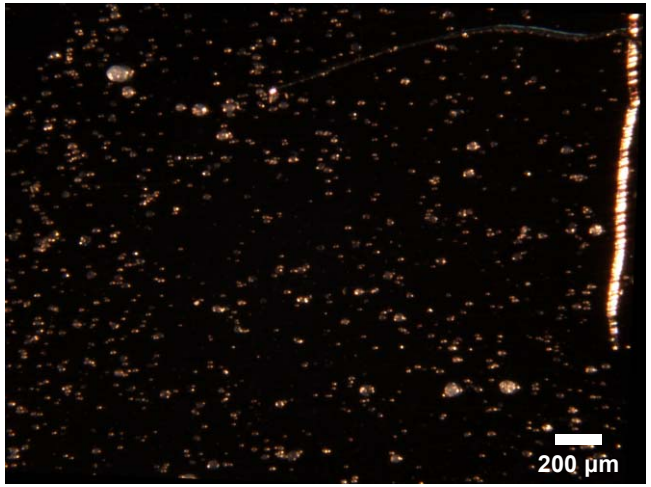
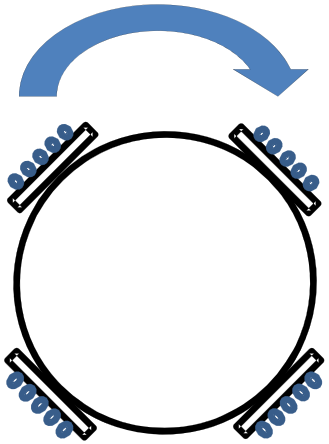
Centrifuge Technique – Silica on Steel

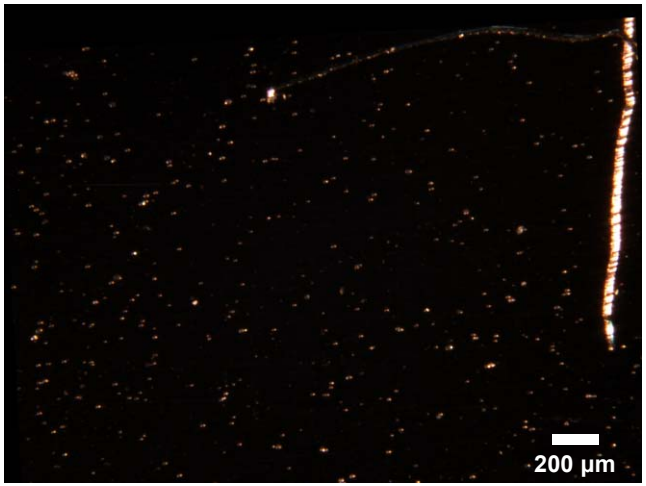
Initial Image



Centrifugal Rotation

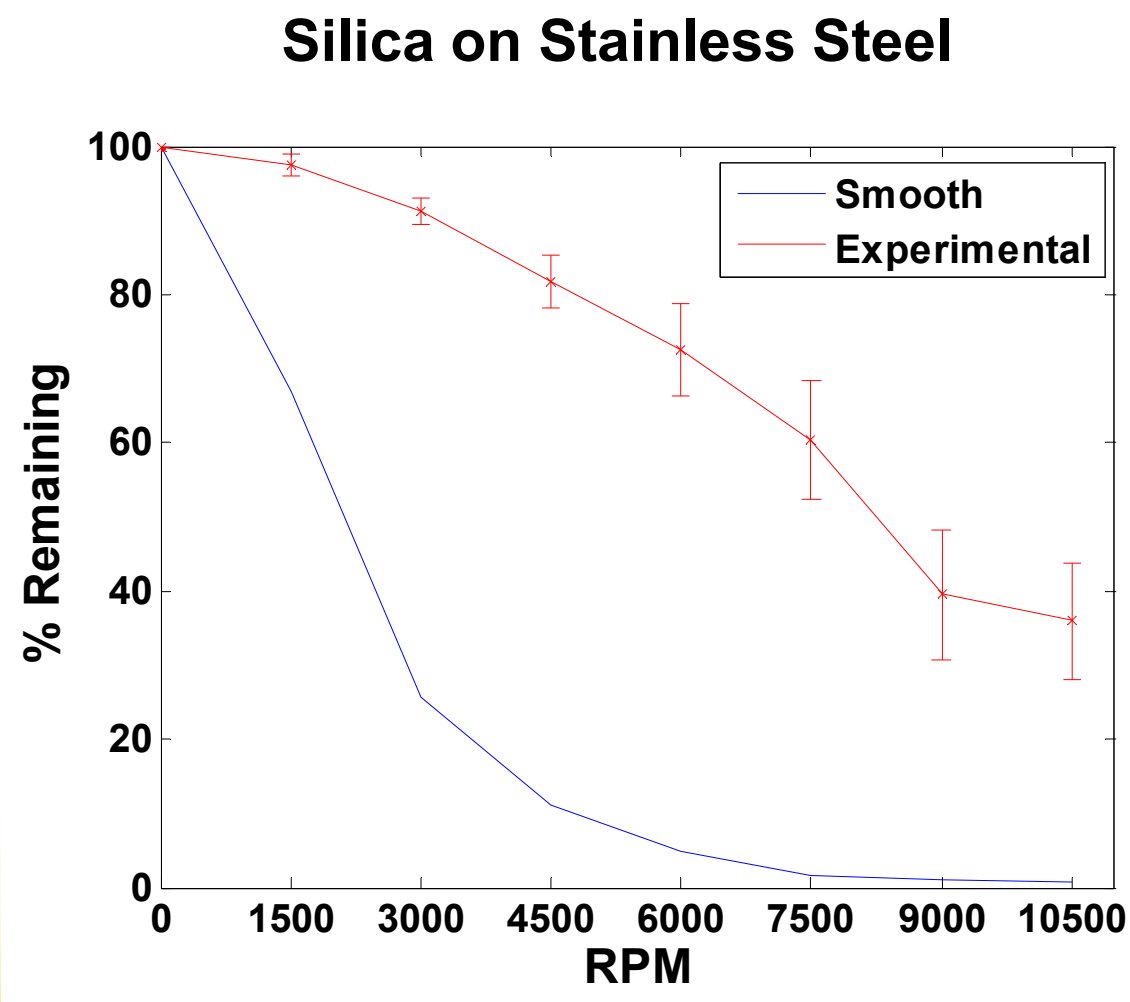


After 10500 rpm

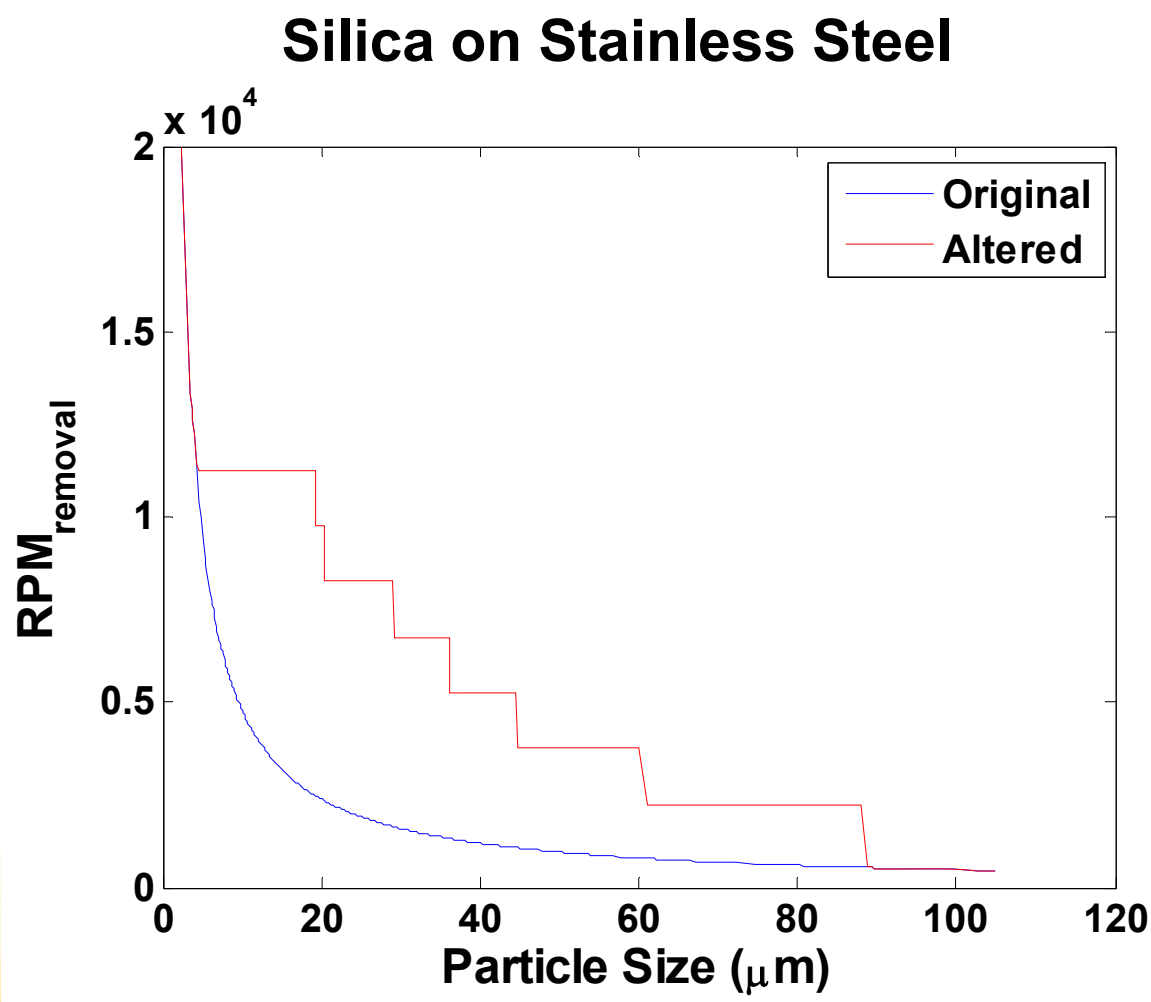


- Silica particles dispersed on stainless steel plates
- Rotate plates in centrifuge
  - 1500 to 10500 rpm
  - One minute run time

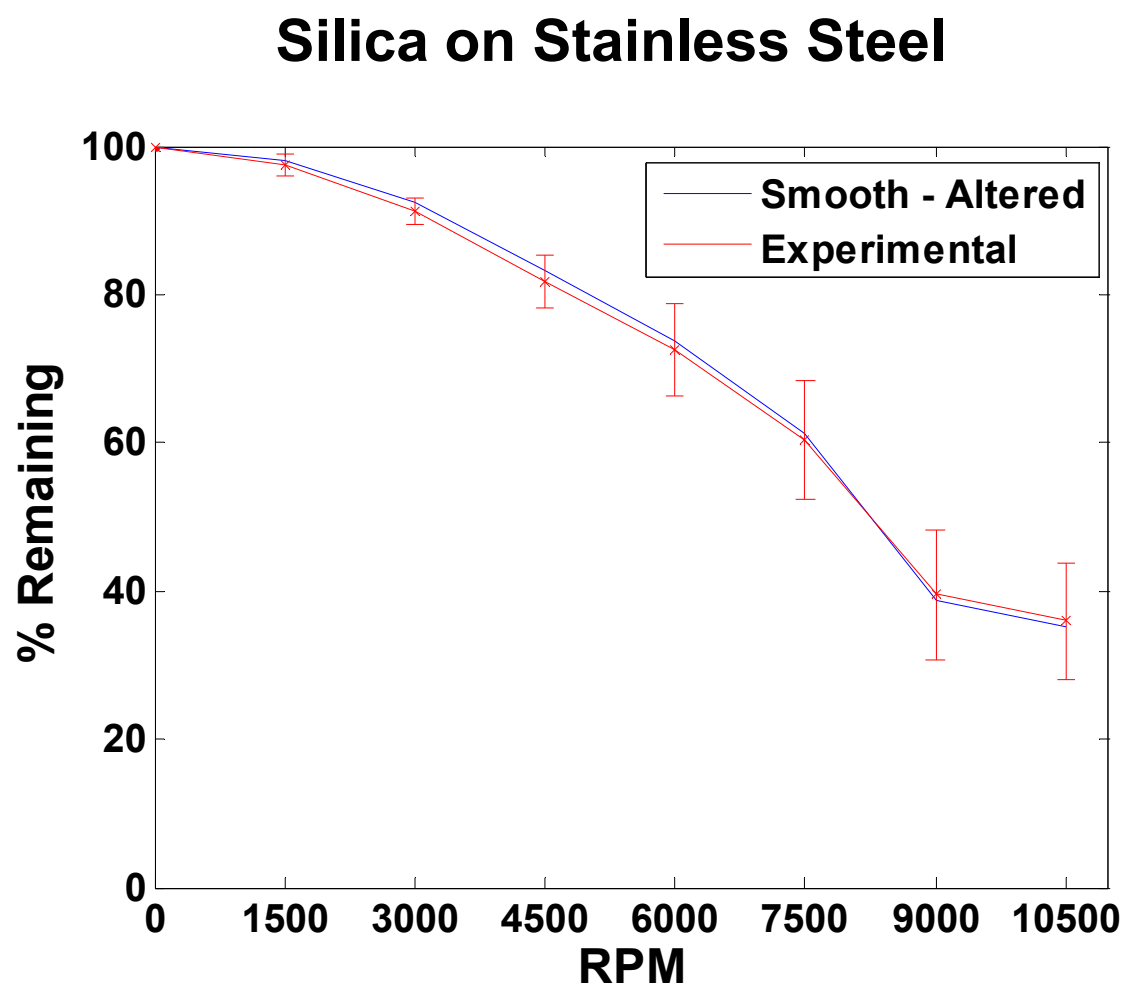
Experimental and Smooth RAP



Effective Hamaker Constants



Effective Hamaker Constants



New Challenge

- Modify the enhanced centrifuge technique to work with compounded residues
  - Proof of concept
  - Quantitative demonstration (including models)
- Deliver effective Hamaker constants to DHS and community
  - Capable of predicting residue adhesion to all substrates of interest using validated constants
  - Models residues as smooth spheres – simple
    - ‘Magic’ is in the fitted constants

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Centennial Celebration
A Century of People and Progress
1911-2011

Circled:

- Melissa Sweat
  - Dec. 2015
- Leonid Miroshnik
  - 2018/2019

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- Johanna Smith
  - Grad. May 2014
  - Employed at General Mills
- Chris Browne
  - Grad. May 2017
- Alyssa Bass
  - Grad. May 2017
- Hannah Burnau
  - Grad. H.S. May 2017

Top: Leonid Miroshnik, Sean Fronczak, Jenny Laster, Darby Hoss, Andrew Parker
Bottom: Aaron Harrison, Caitlin Schram, Myles Thomas, Melissa Sweat, Jordan Thorpe

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