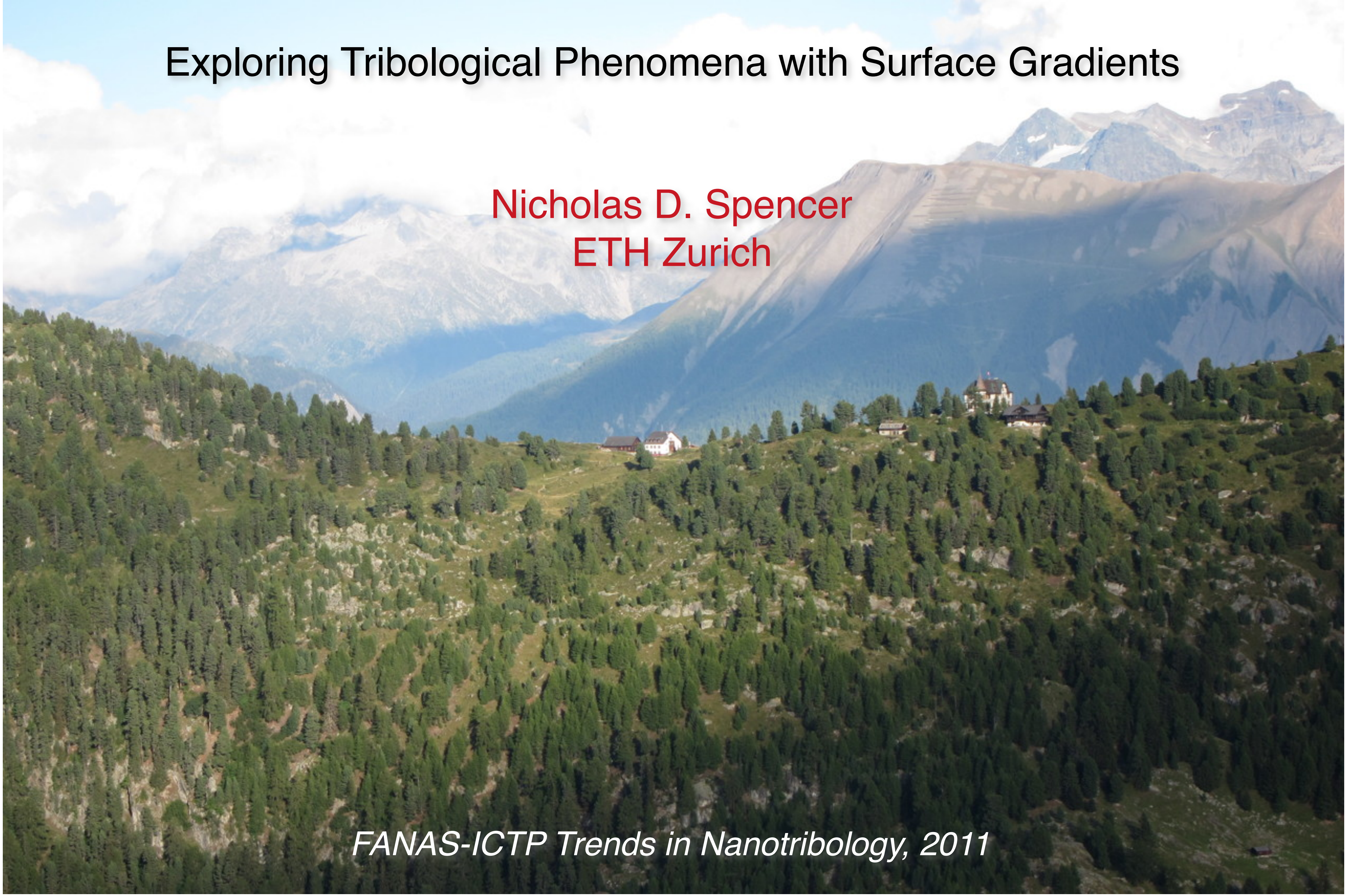

Exploring Tribological Phenomena with Surface Gradients

Nicholas D. Spencer
ETH Zurich

FANAS-ICTP Trends in Nanotribology, 2011

Outline

- Gradients
- Surface Chemical Gradients
- Example 1: Influence of polymer grafting density on friction
- Morphological Gradients
- Example 2: Influence of roughness on adhesion

Outline

- Gradients
- Surface Chemical Gradients
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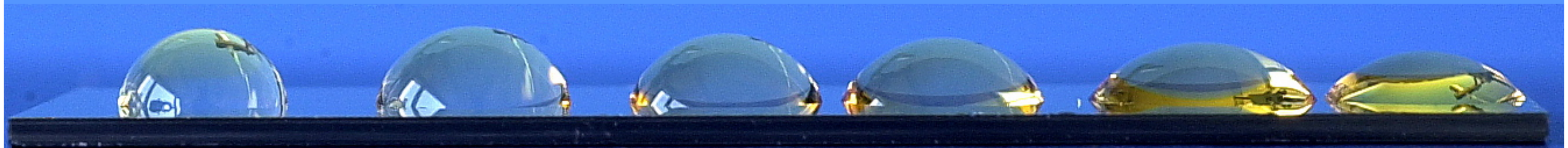
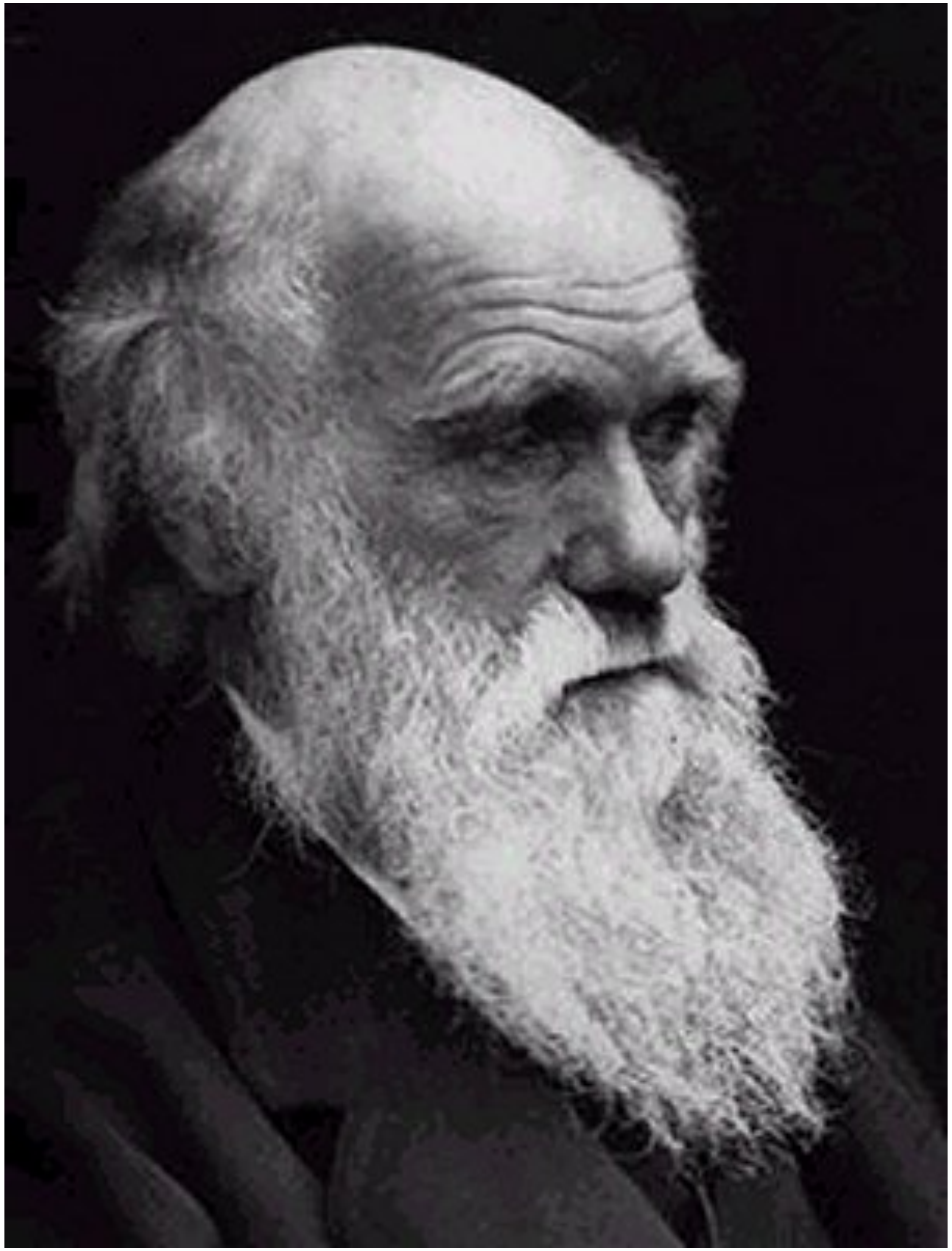
GRADIENTS





Charles Robert Darwin (1809 –1882)

Evolution and High-throughput Screening

•Nature designs systems by evolution

Random mutation and recombination, random genetic drift, natural selection, speciation, reproductive isolation....takes time

•Man can design systems by high-throughput screening (HTS)

Synthesis of a multitude of compounds followed by massively parallel testing

•HTS on surfaces involves spatial distribution

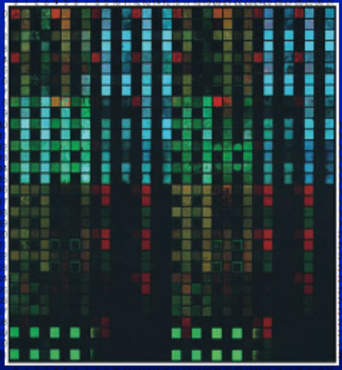
Early examples include arrays of phosphor compositions

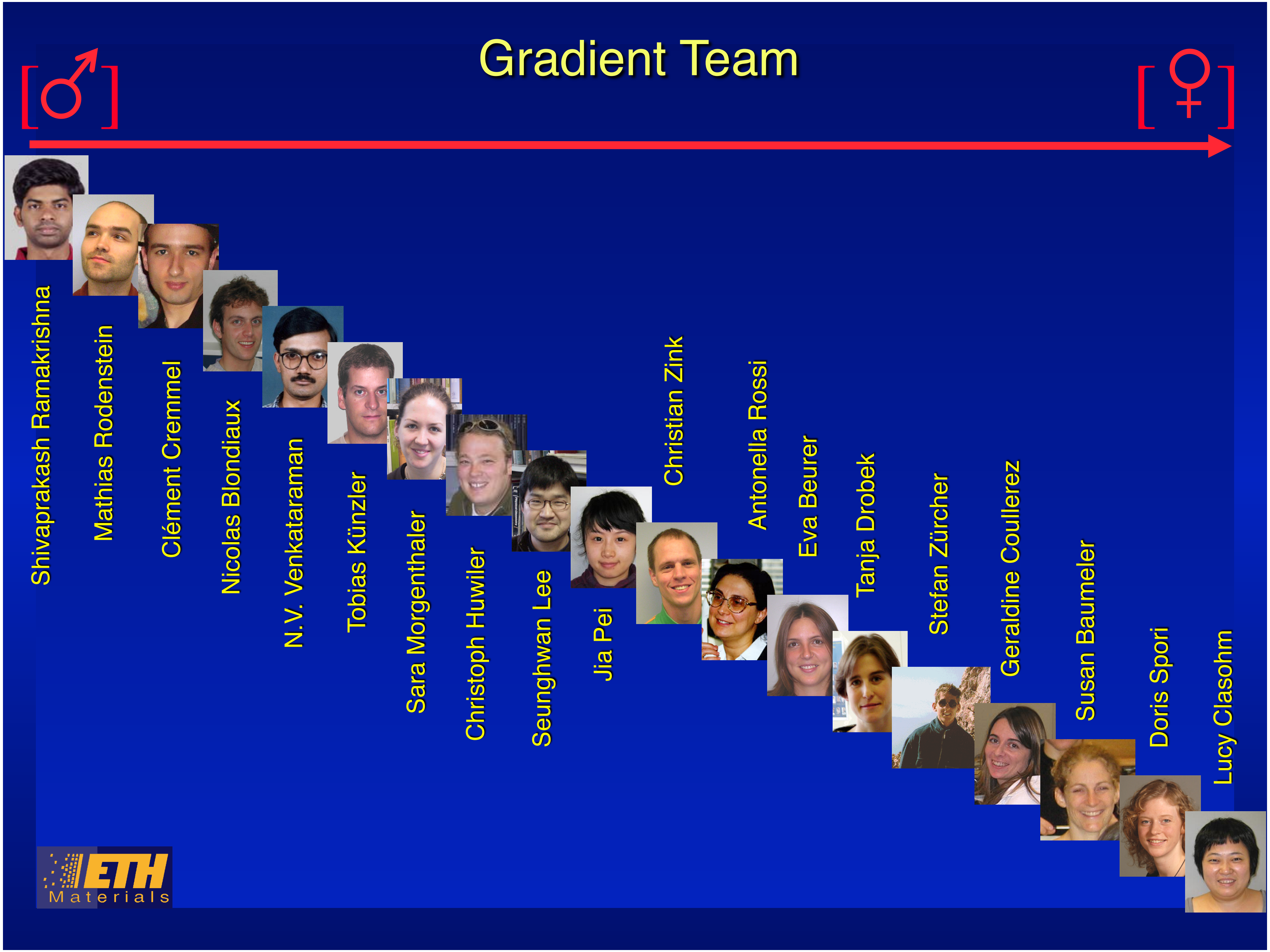
•Gradients provide the ultimate level of spatial discretization

Surface-chemical gradients and morphological gradients

•Gradients can help us understand parametric dependencies, i.e. how surface properties influence phenomena, such as adhesion and friction

Wang *et al*, *Science* **279** (1998) 1712




Gradient Team
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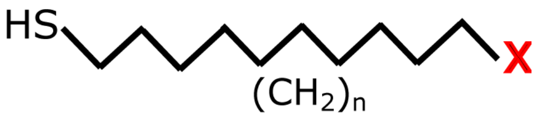
[♀]
Shivaprakash Ramakrishna
Mathias Rodenstein
Clément Cremmel
Nicolas Blondiaux
N.V. Venkataraman
Tobias Künzler
Sara Morgenthaler
Christoph Huwiler
Seunghwan Lee
Jia Pei
Christian Zink
Antonella Rossi
Eva Beurer
Tanja Drobek
Stefan Zürcher
Geraldine Coullerez
Susan Baumeler
Doris Spori
Lucy Clasohm
ETH
Materials

Outline

- Gradients
- Surface Chemical Gradients
- Example 1: Influence of polymer grafting density on friction
- Morphological Gradients
- Example 2: Influence of roughness on adhesion

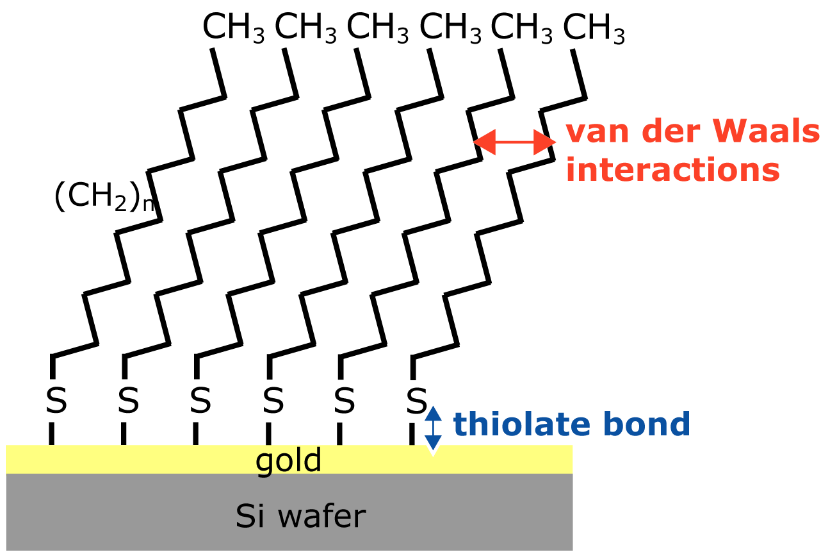
Surface-Chemical Gradients with Self-Assembled Monolayers

Alkanethiols:



X: $-CH_3$,
$-OH$,
$-COOH$,
etc.

spontaneous self-assembly

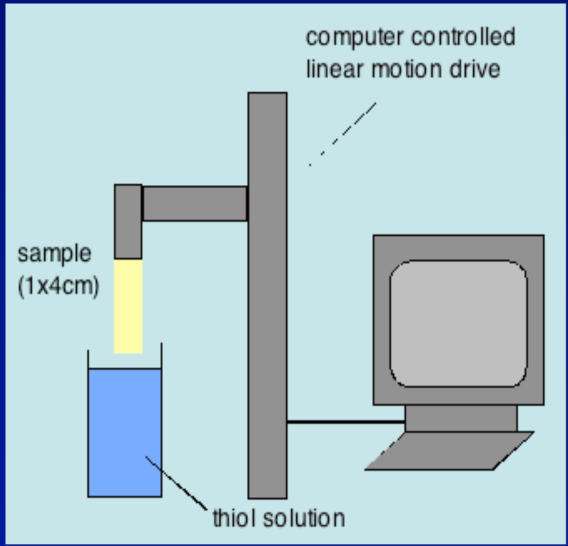


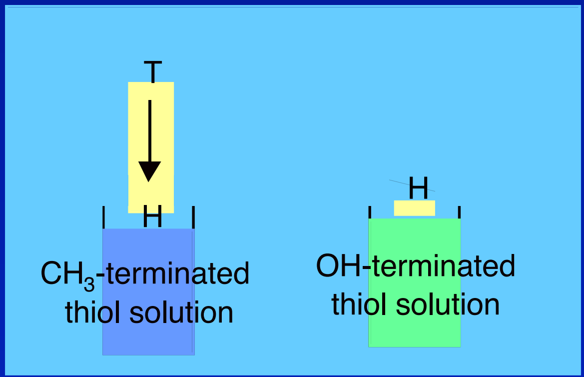
PLL-*g*-PEG :

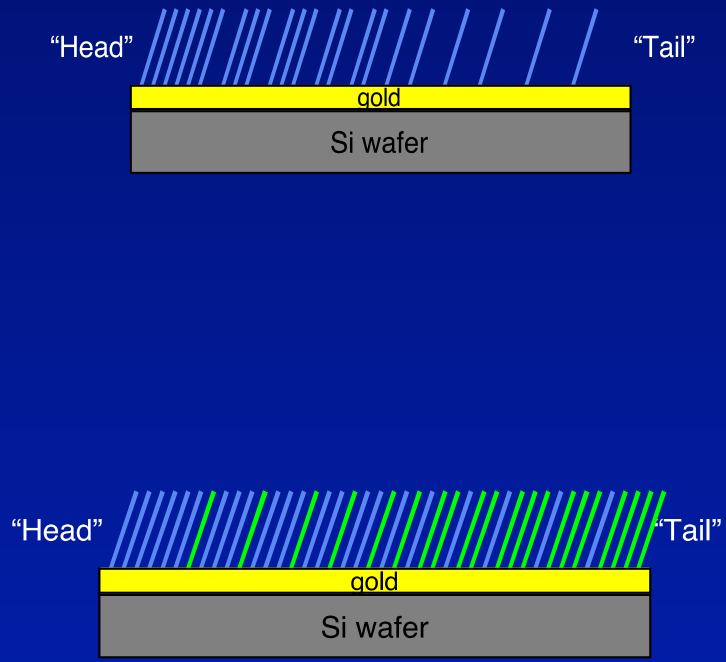
poly(ethylene glycol) side chain grafted onto a poly(L-lysine) backbone

X: –biotin,
–RGD,
–fluorine,
etc.

Chemical Gradients: Dipping Method



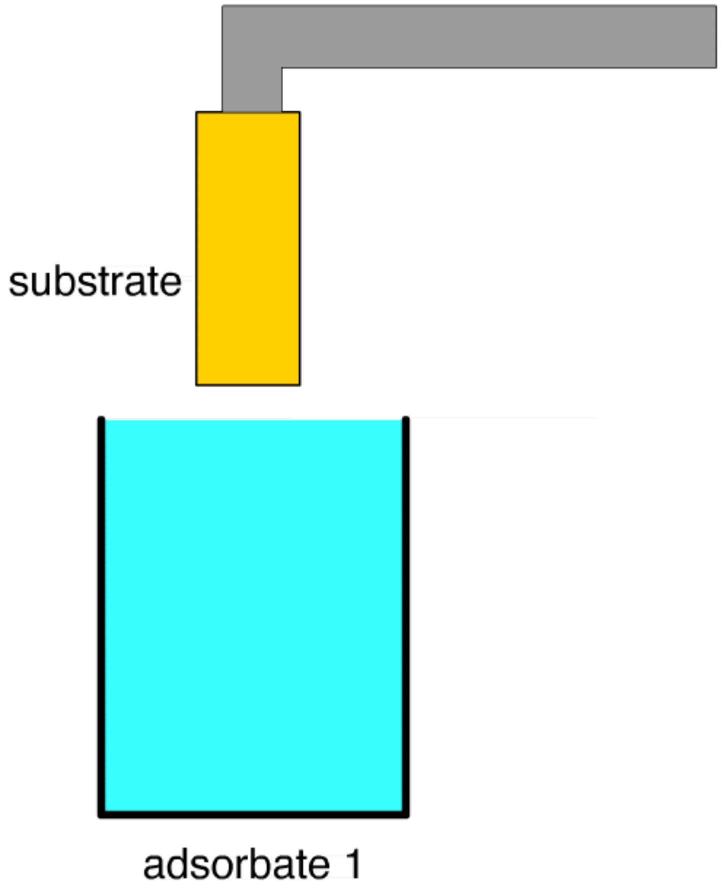




Applications in tribology, high-thoughput screening, cell/bacteria studies

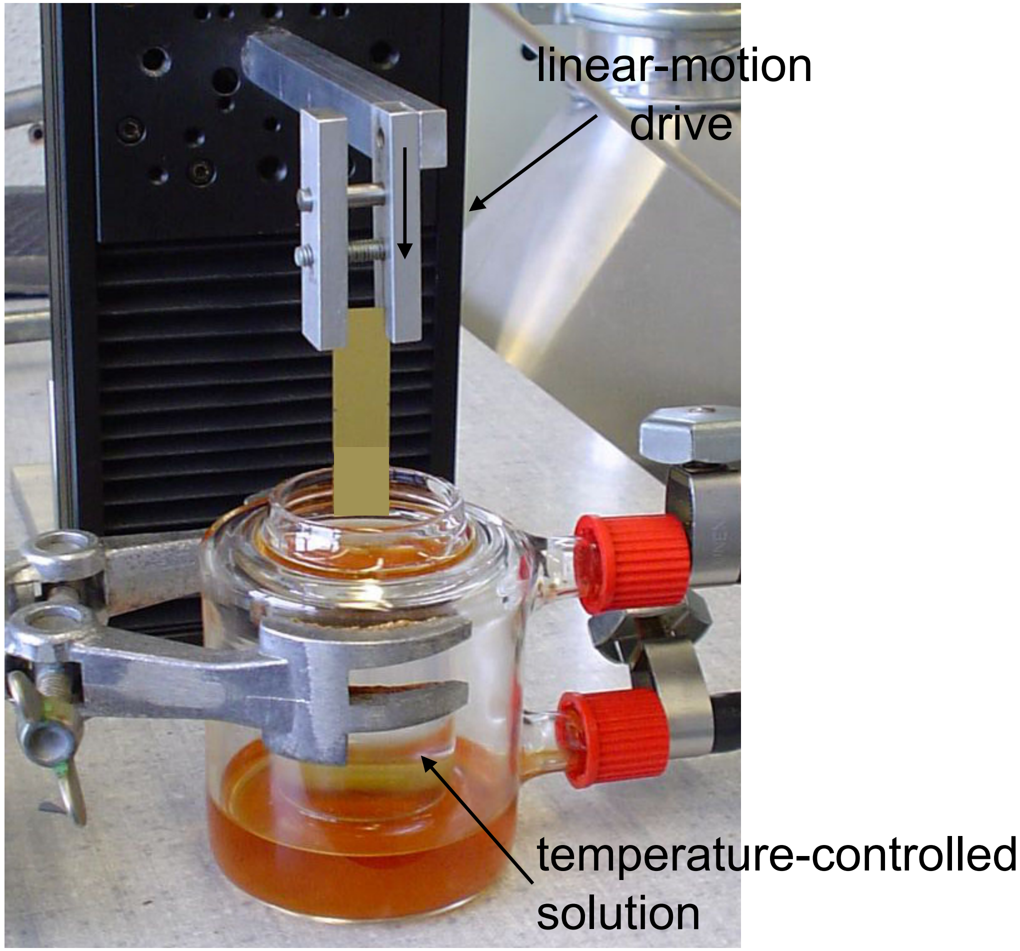
S. Morgenthaler, S. Lee, S. Zürcher, and N. D. Spencer
Langmuir; 2003; 19(25) pp 10459-10462

Gradient preparation



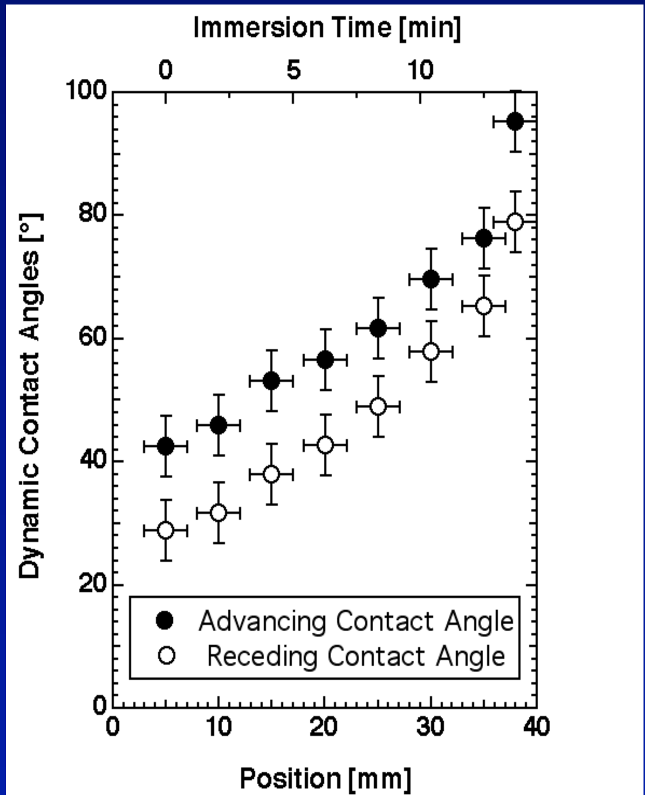
➡ generation of a gradient in coverage by controlling the adsorption kinetics through a gradual immersion

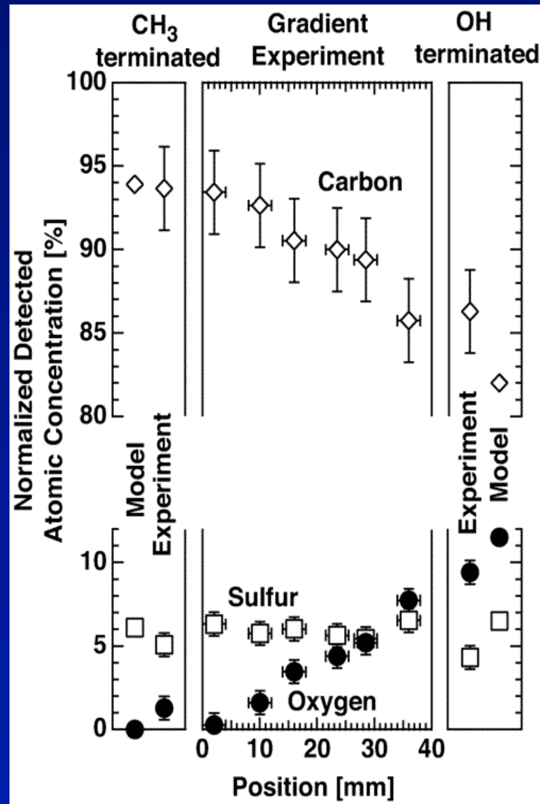
Gradient preparation - setup

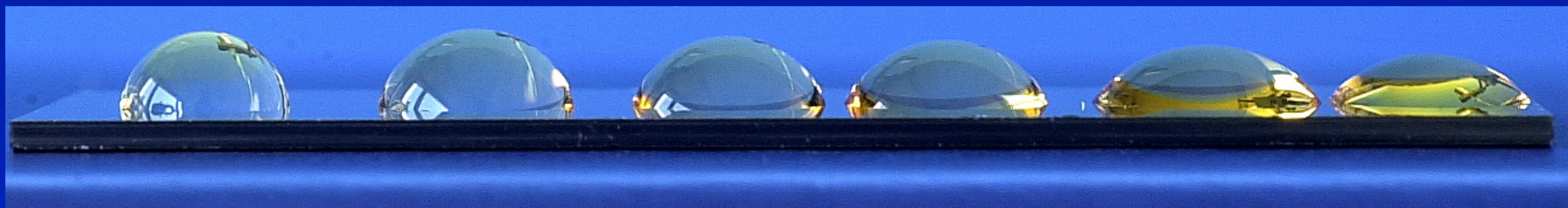


➡ generation of a gradient in coverage by controlling the adsorption kinetics through a gradual immersion

Chemical Gradients







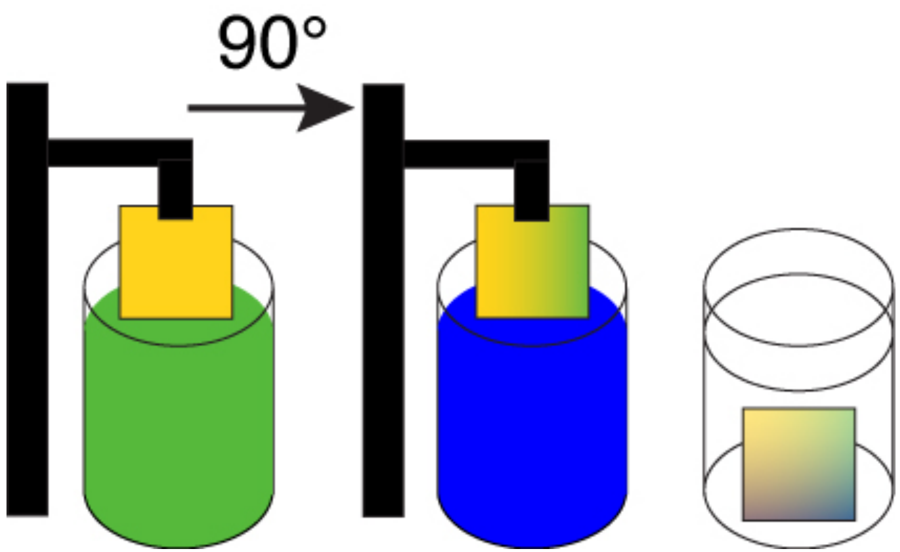
A Simple, Reproducible Approach to the Preparation of Surface-Chemical Gradients

Morgenthaler, S.; Lee, S.; Zurcher, S.; Spencer, N. D.; *Langmuir*; **2003**; 19(25); 10459-10462

Orthogonal Gradients

Orthogonal, Three-Component, Alkanethiol-based, Surface-Chemical Gradients on Gold
Eva Beurer, Nagaiyanallur V. Venkataraman, Antonella Rossi, Florian Bachmann, Roman Engeli, Nicholas D. Spencer
Langmuir; 2010 26(11) pp 8392-8399

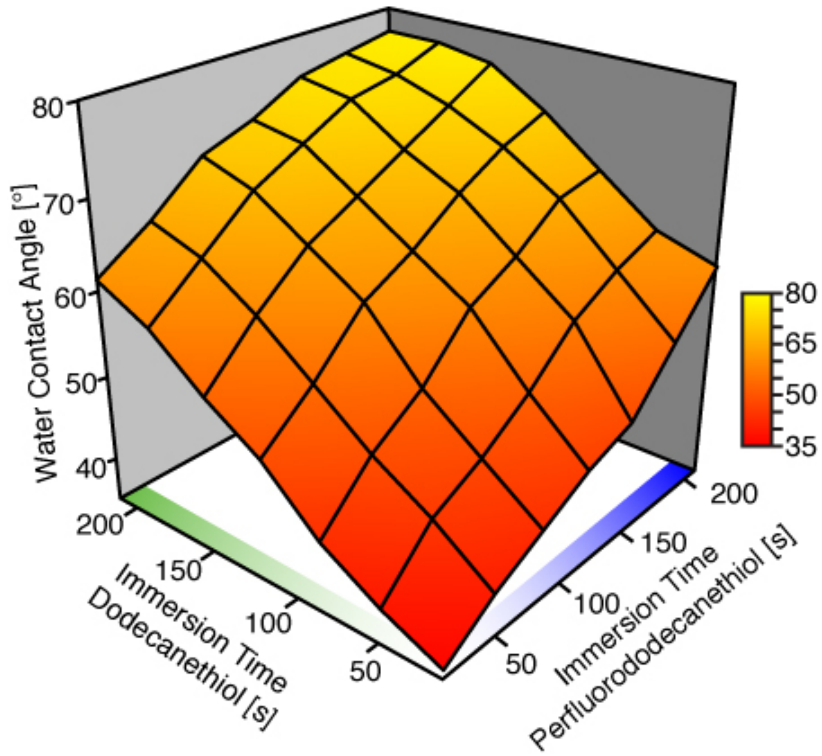
Preparation



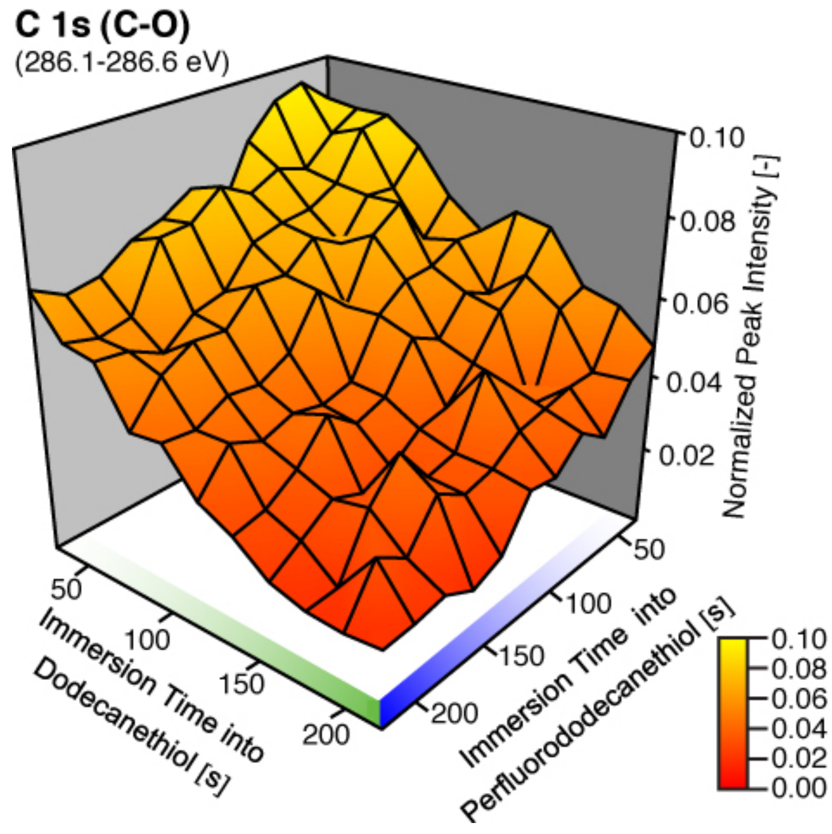
Thiol	Dodecanethiol	Perfluoro-dodecanethiol	Mercapto-undecanol
H_2O	hydrophobic	hydrophobic	hydrophilic
Hexadecane	oleophilic	oleophobic	oleophilic

Hydrophobicity

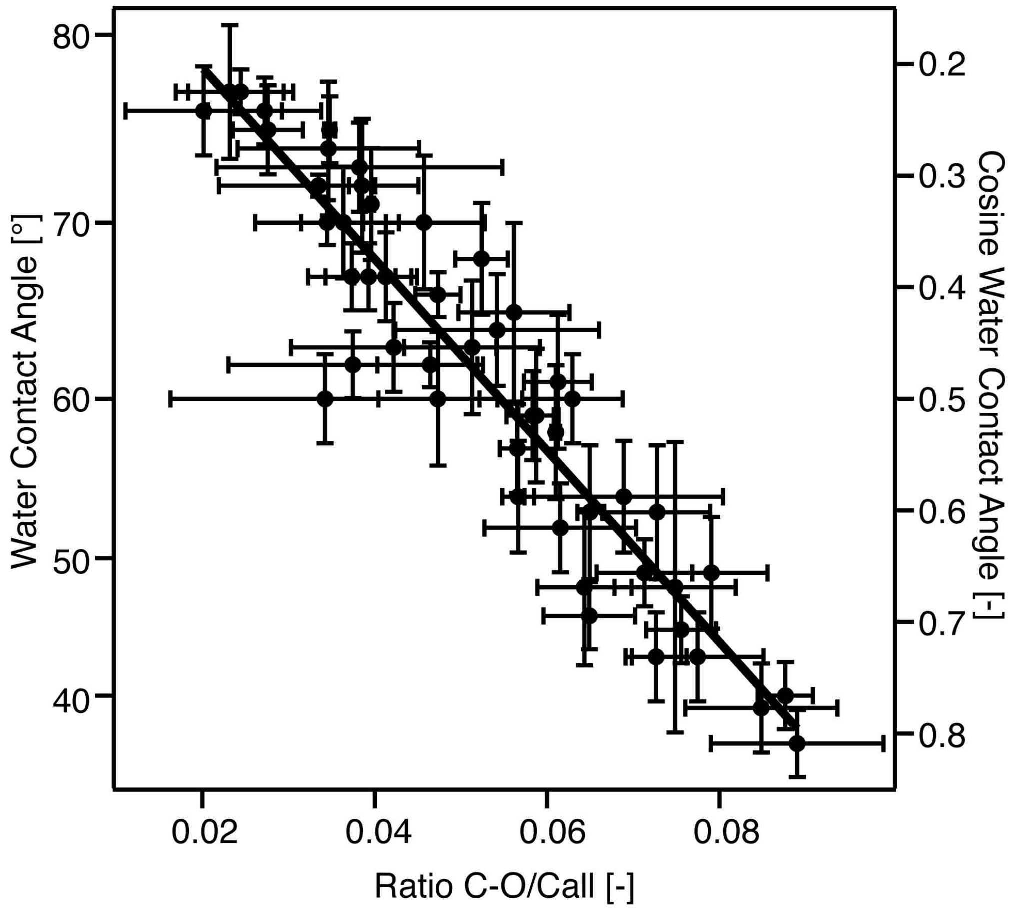
Water
Contact Angle

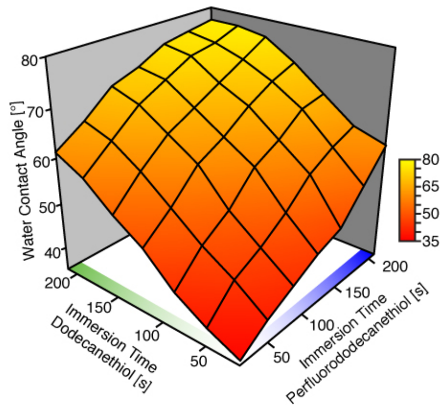


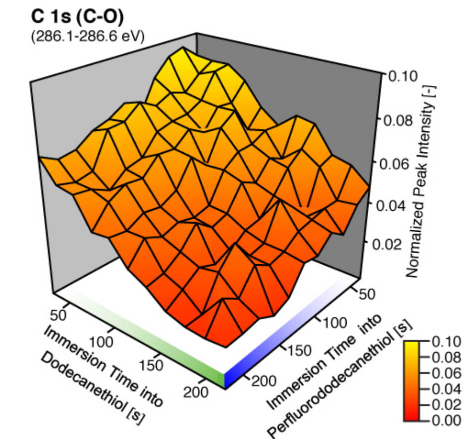
Mercaptoundecanol
Density



Correlation

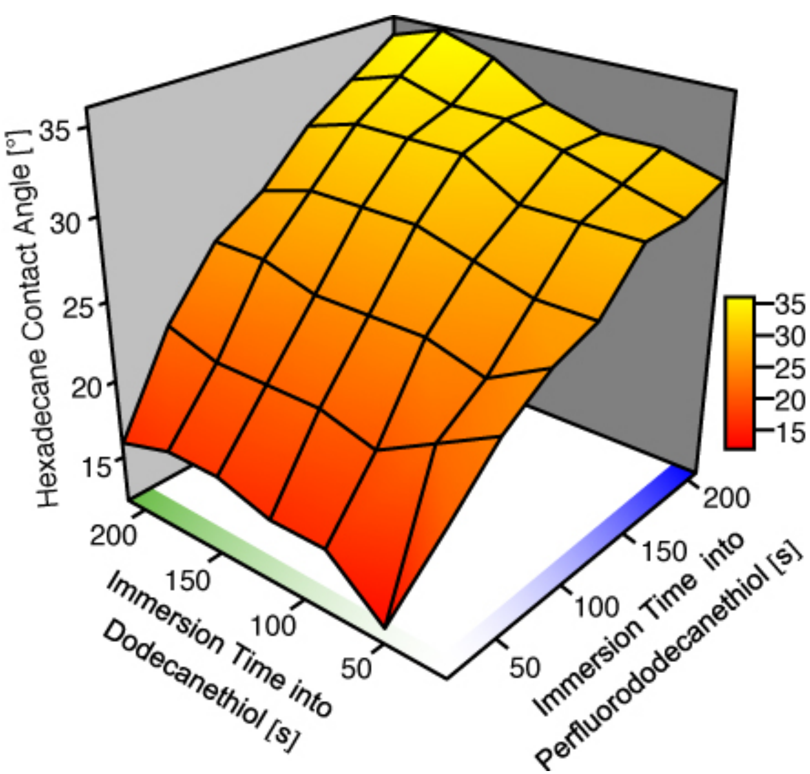




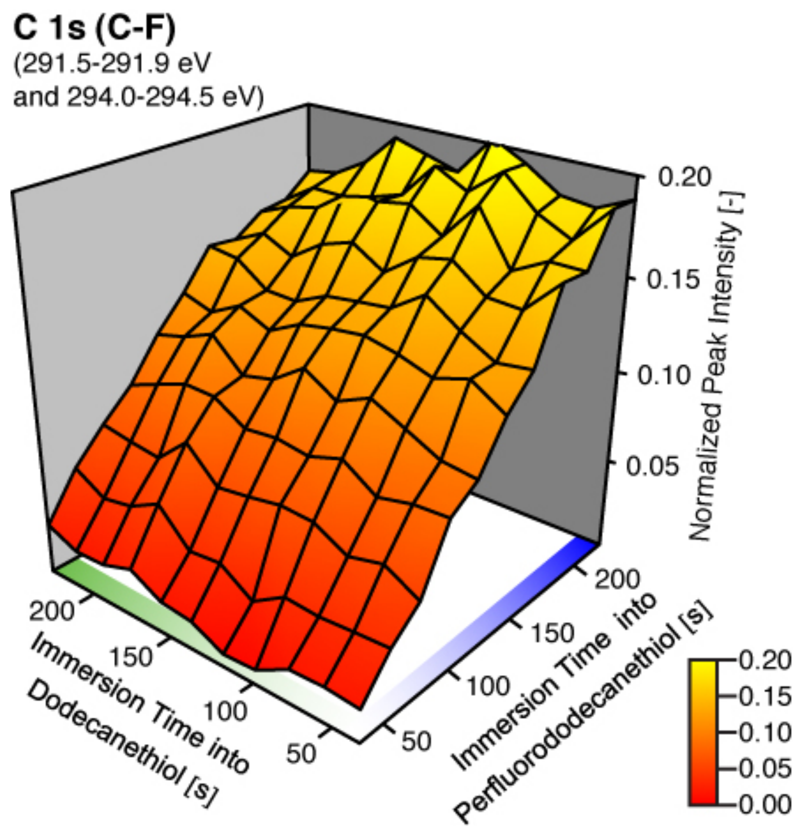


Oleophobicity

Hexadecane
Contact Angle



Perfluorododecanethiol
Density



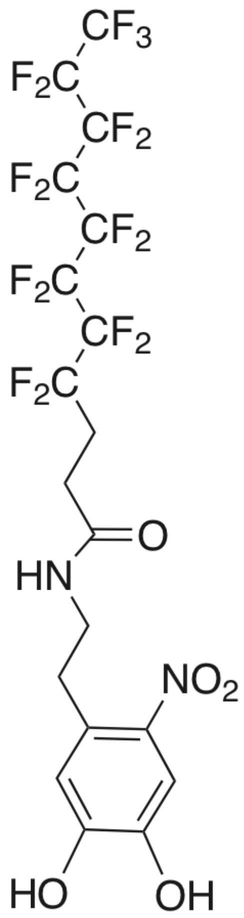
Beyond Thiols

Fabricating Chemical Gradients on Oxide Surfaces by Means of Fluorinated, Catechol-Based, Self-Assembled Monolayers

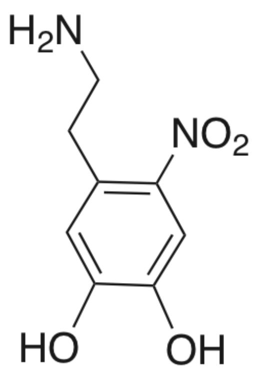
Mathias Rodenstein, Stefan Zürcher, Samuele G.P. Tosatti, Nicholas D. Spencer

Langmuir; ***2010*** 26(21) pp 16211–16220

Nitrodopamines!



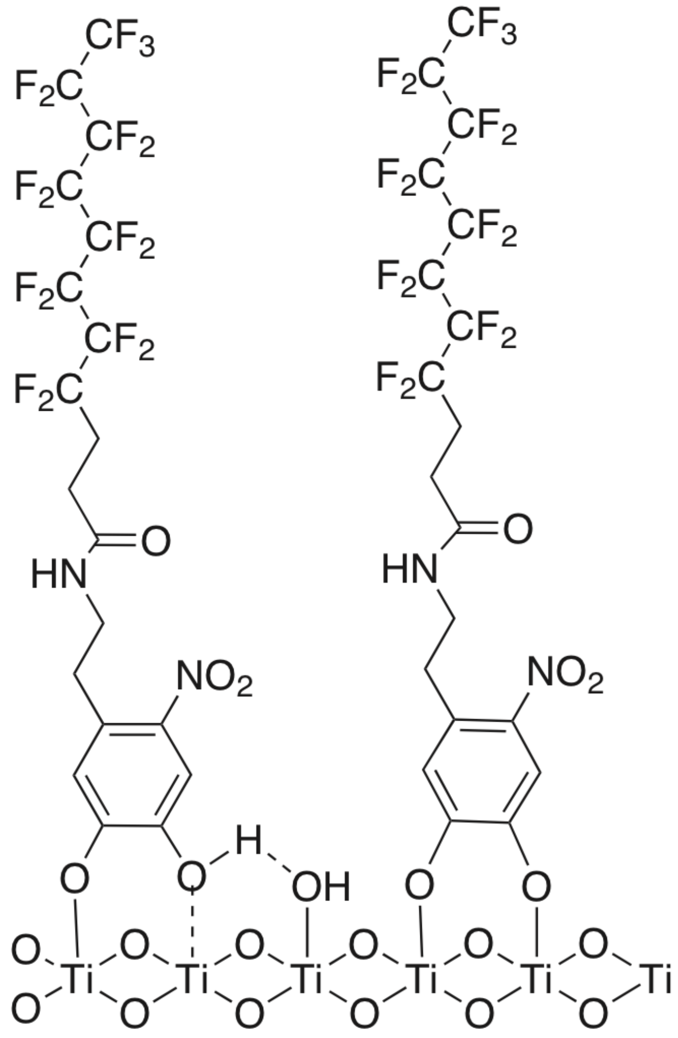
PFAND



ND

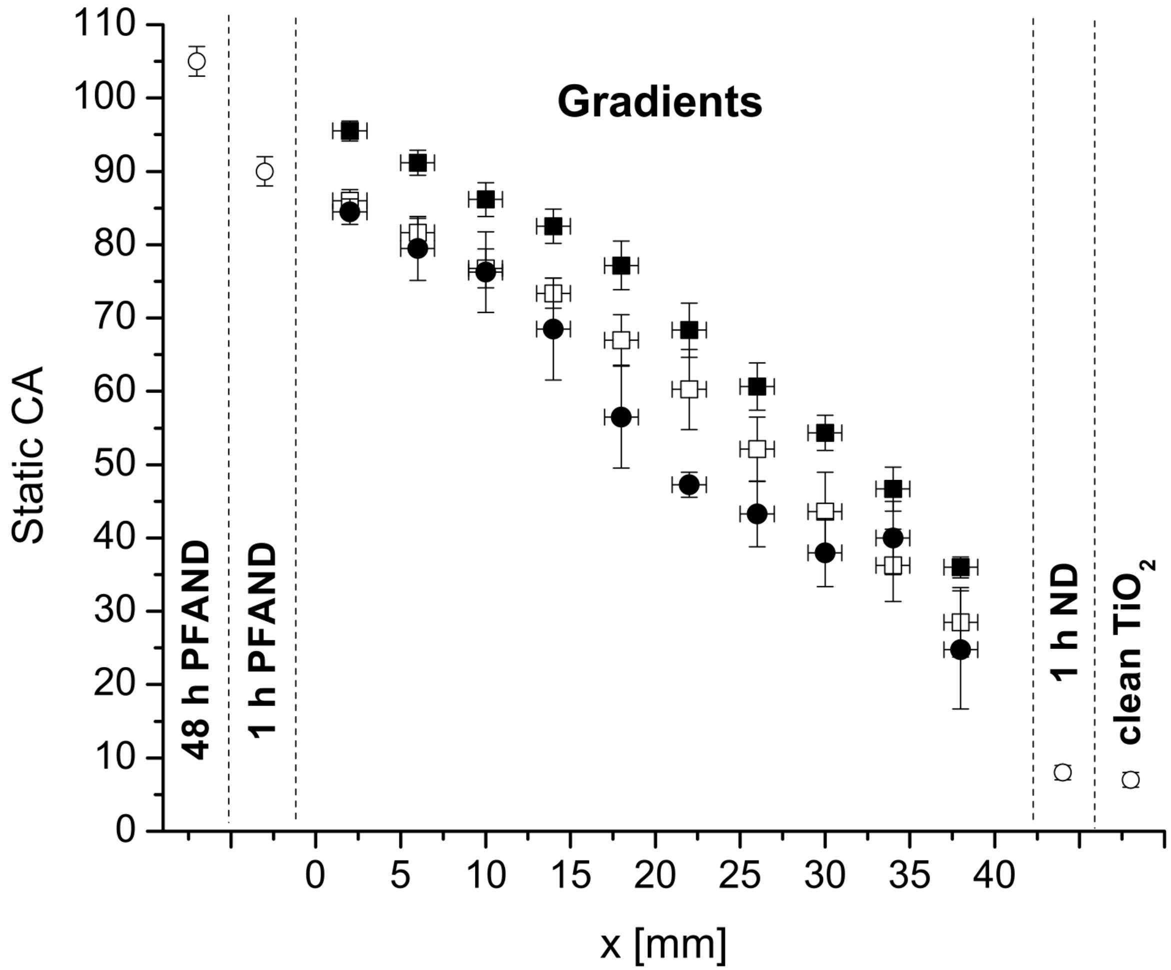
SuSoS

Nitrodopamines Adsorb Strongly on many Oxide Surfaces



I II

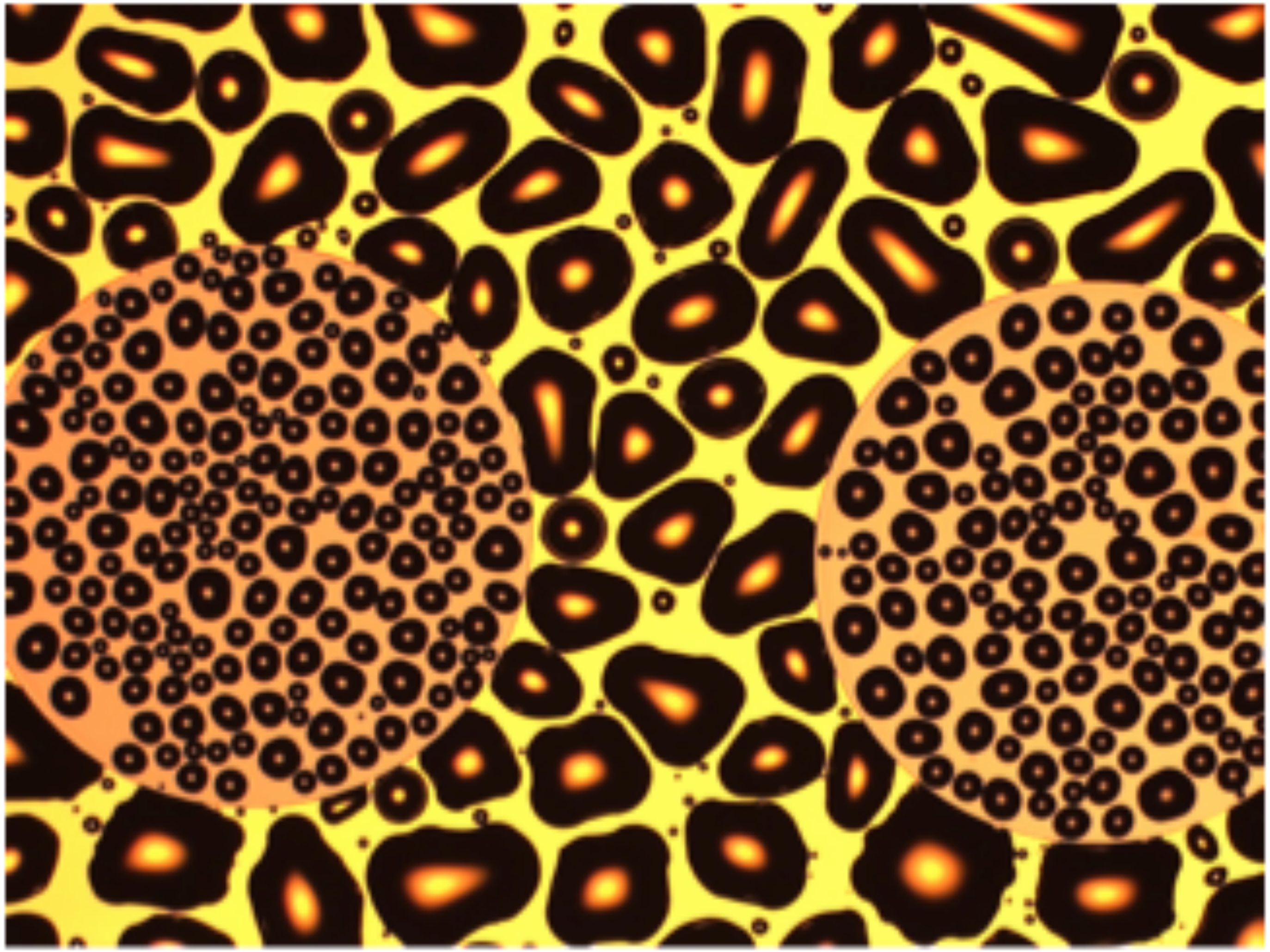
Nitrodopamines can be Used for Gradient Preparation on Oxides



PFAND one-component (■), ND backfilled gradients (□), after their additional immersion in H_2O for 14 h (●). Homogeneous samples (○).

Mathias Rodenstein, Stefan Zürcher, Samuele G.P. Tosatti, Nicholas D. Spencer
*Langmuir; **2010*** 26(21) pp 16211–16220

Nitrodopamines on Oxides/Thiols on Gold



Simultaneous adsorption of OH-terminated thiol and PFAND
on an ultraflat Au and Ti surface (microdroplet density image)

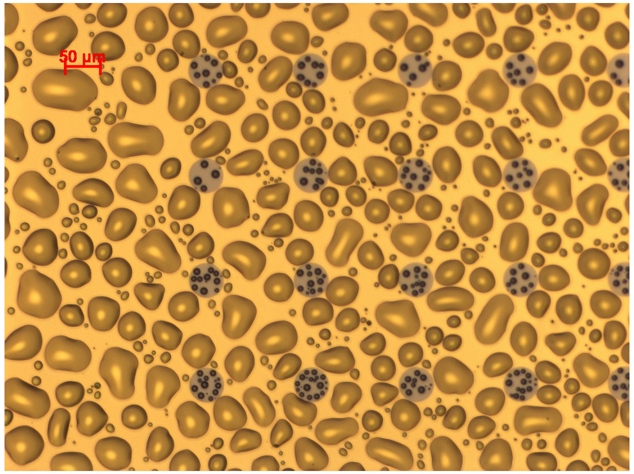
Bidirectional Gradient!
Nitrodopamines on Oxides/Thiols on Gold

Microdroplet density measurement of 1cm-long sample

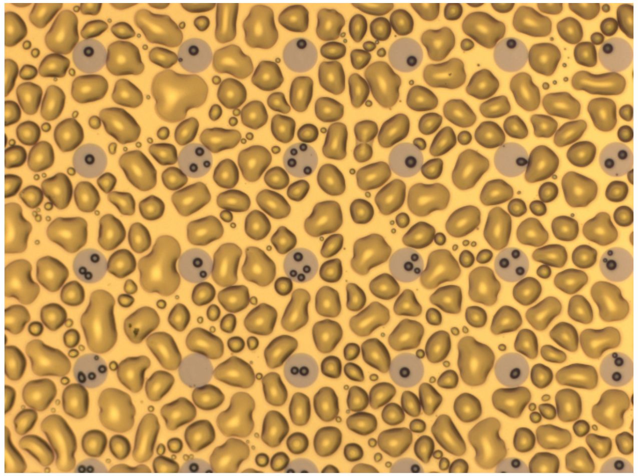
Ti/TiOx: Perfluoro-alkyl-nitrodopamine gradient

Au: 11-Mercapto-1-undecanol gradient

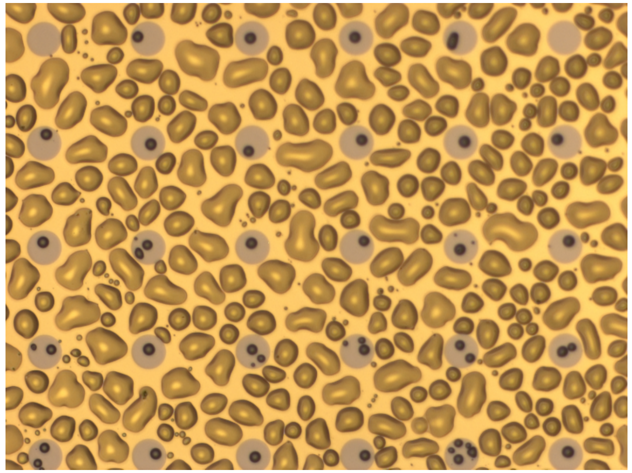
0mm



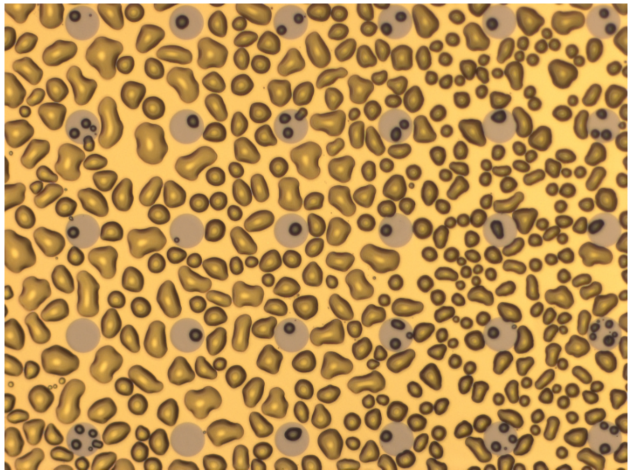
2mm



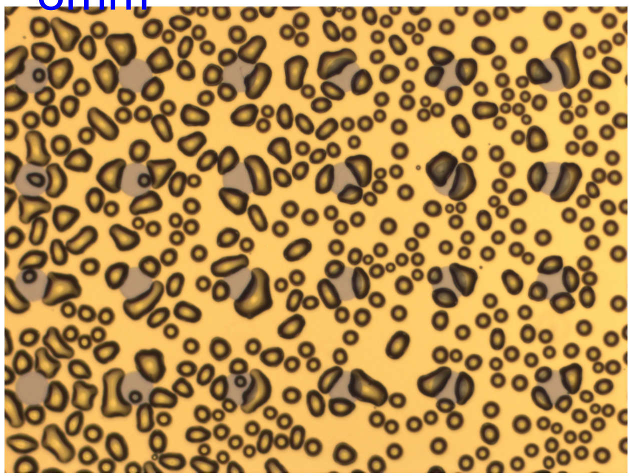
4mm



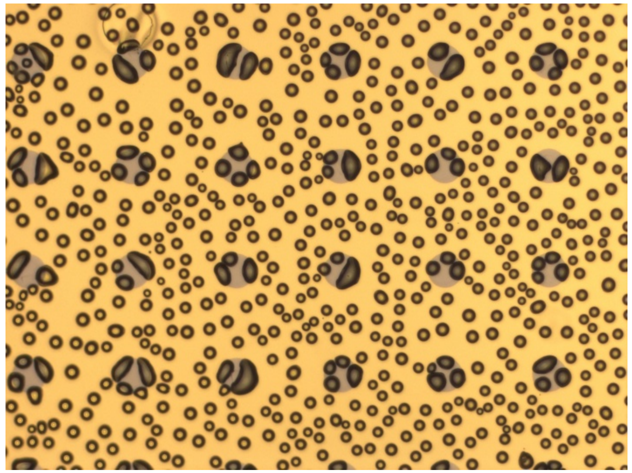
6mm



8mm



10mm



Outline

- Gradients
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- Example 1: Influence of polymer grafting density on friction
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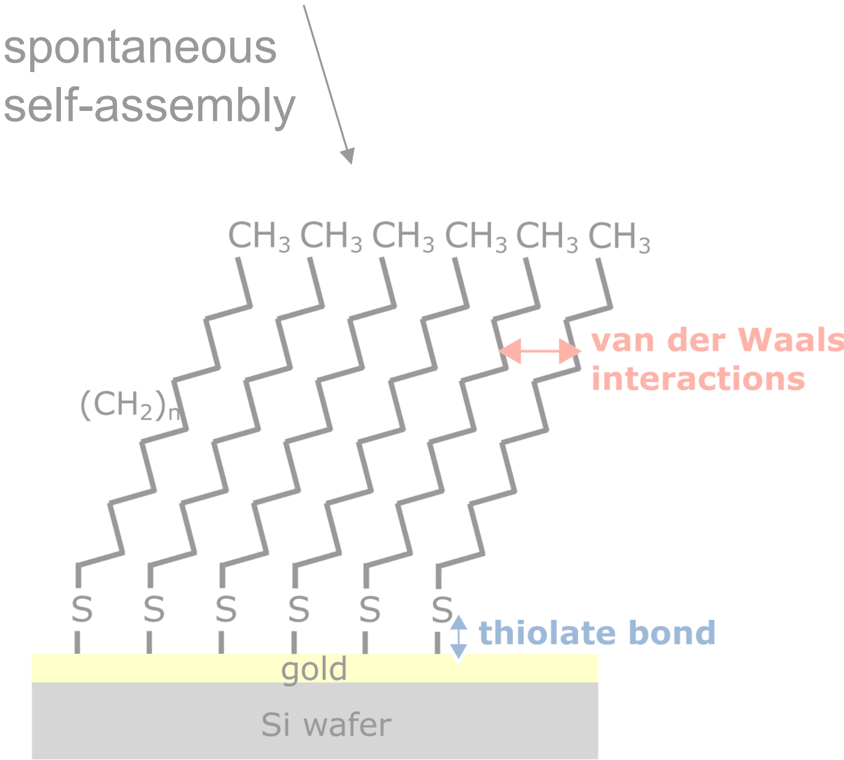
Surface-Chemical Gradients with Self-Assembled Monolayers

Alkanethiols:

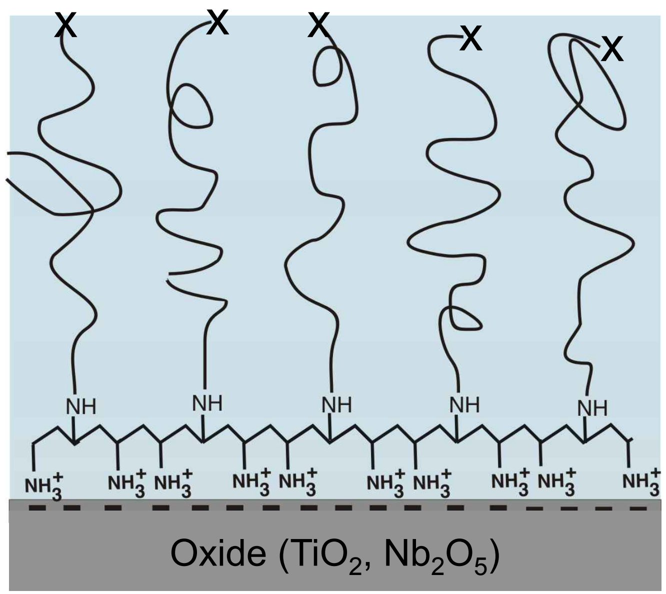
X: $-CH_3$,
$-OH$,
$-COOH$,
etc.



PLL-*g*-polymer:

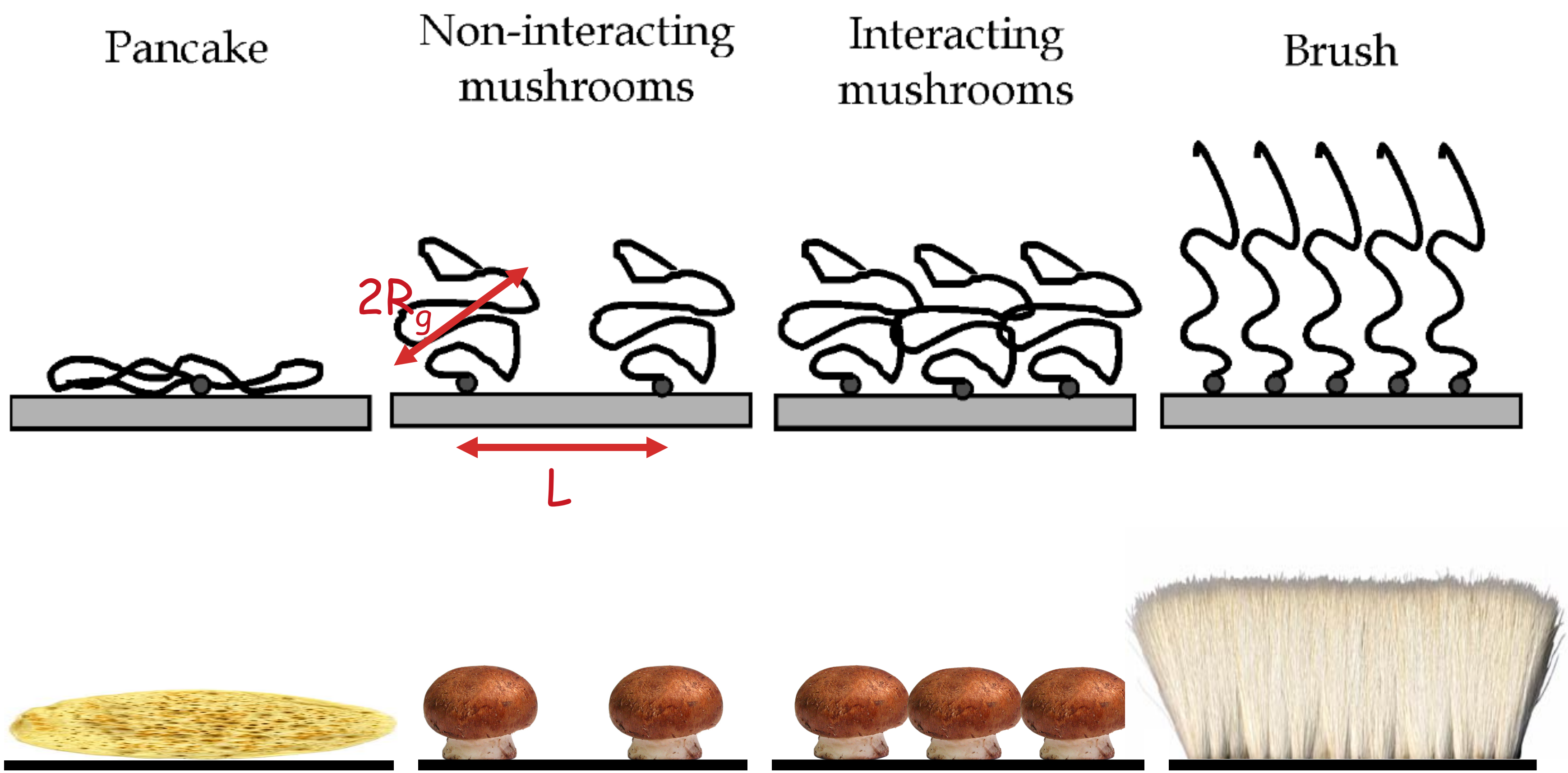
Polymer side chains grafted onto a poly(L-lysine) backbone

X: –biotin,
–RGD,
–fluorine,
etc.



Interlude: lubrication with polymer brushes

End-grafted polymers form brushes in a good solvent



The Brushettes:
World Premiere, Cargèse, 2010

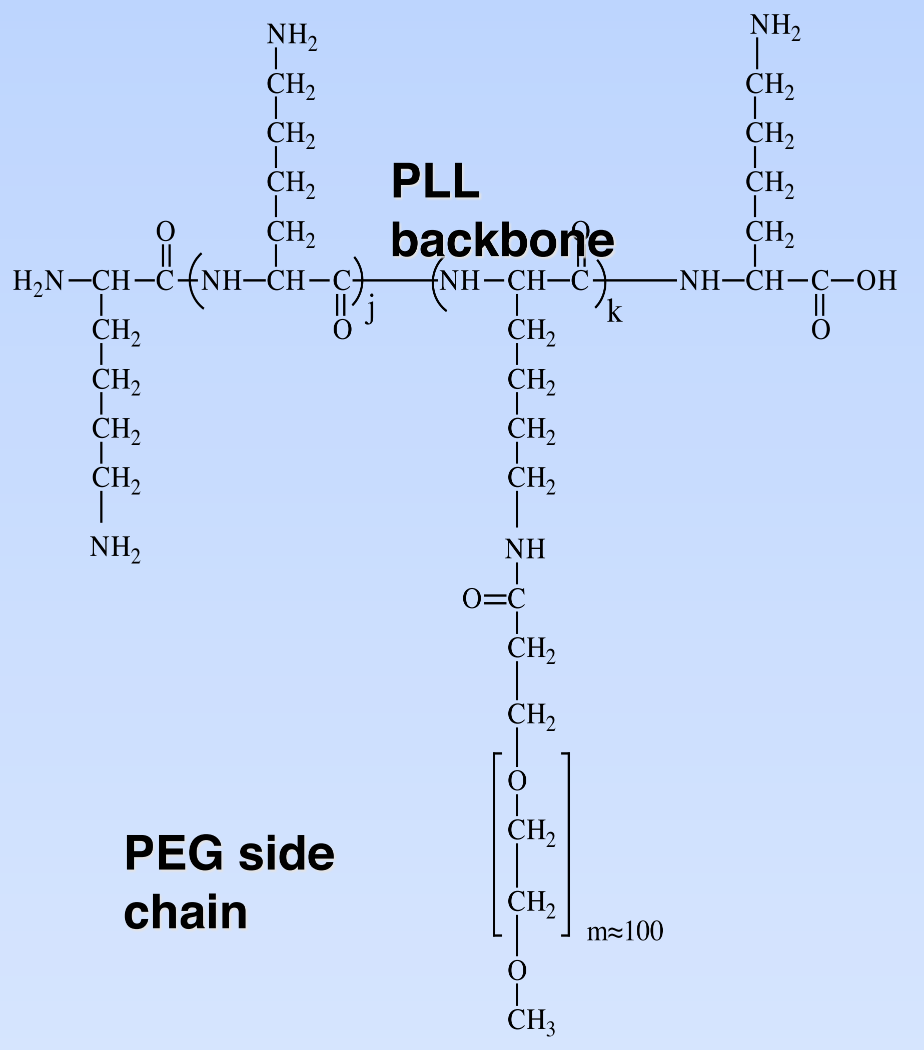
Poly-l-lysine (PLL)-*g*-polyethylene glycol (PEG)

PLL backbone

- MW: 20,000 to 350,000
- Positively charged at pH<10 (R= $–NH_3^+$)
- Approximate length of backbone: 90 to 1000 nm

PEG side chain

- MW: 2000 to 5000
- Adsorbs water and has properties similar to water
- Protein resistant
- Approximate length of side chain: 20 nm

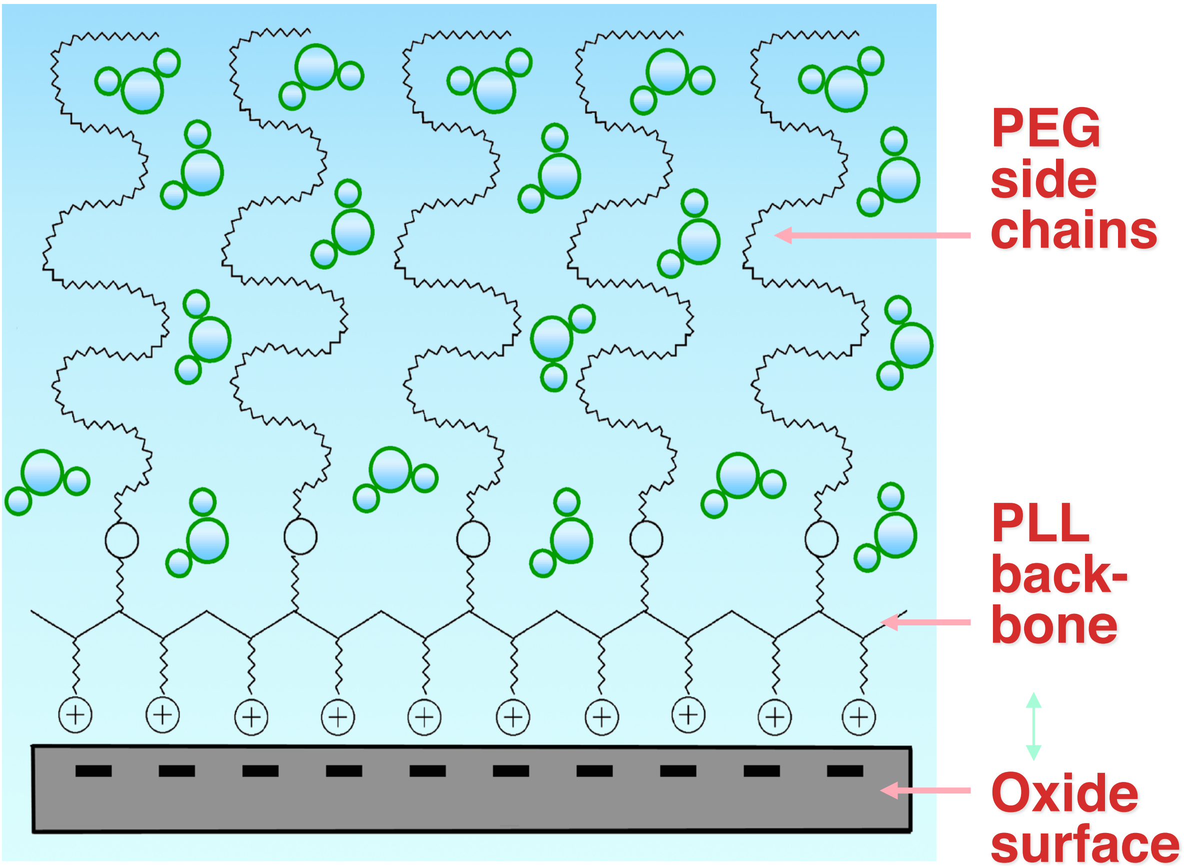


J. Hubbell, D. Elbert, Chem Biol 5: (3) 177-183 (1998)

Eidgenössische Technische Hochschule Zürich
Swiss Federal Institute of Technology Zurich

Laboratory for Surface Science and Technology

"Grafting to" of PEG, using a backbone



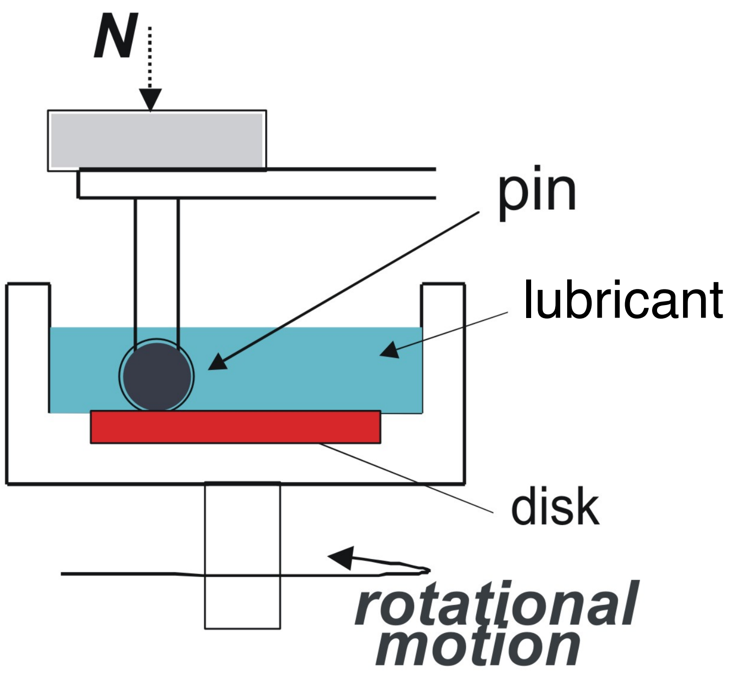
PEG side chains:

- Hydrophilic
- Uncharged
- Flexible chains
- High water content
- Steric repulsion
- Biocompatible

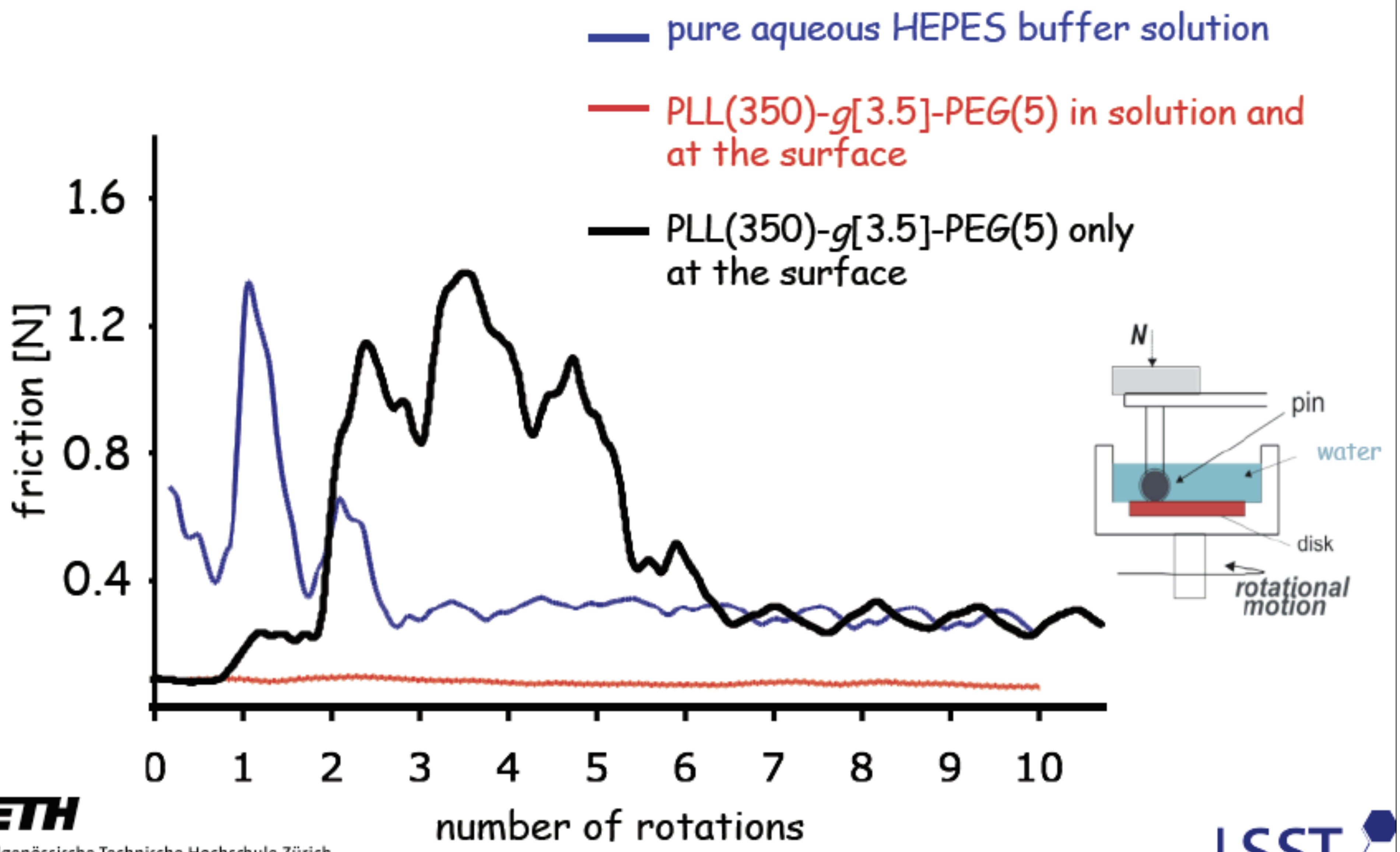
PLL backbone:

- Positive charge
- High coverage
- Kinetic inertness
- pH dependence

Pin-on-Disk Test
(sliding only)



Tribostress-Induced Polymer Desorption



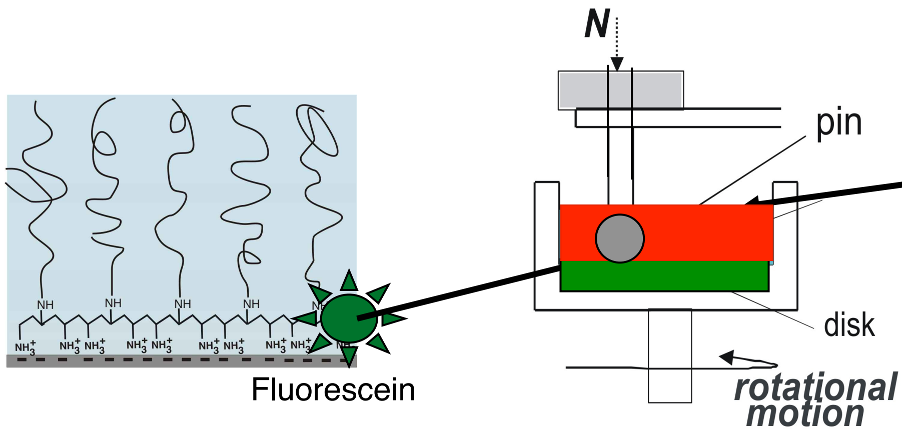
ETH

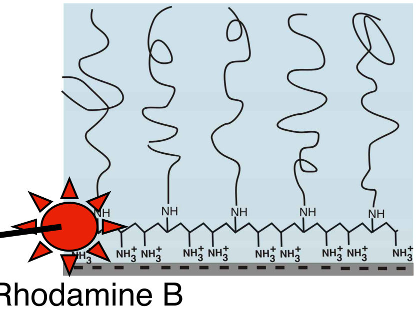
Eidgenössische Technische Hochschule Zürich
Swiss Federal Institute of Technology Zurich

LSST

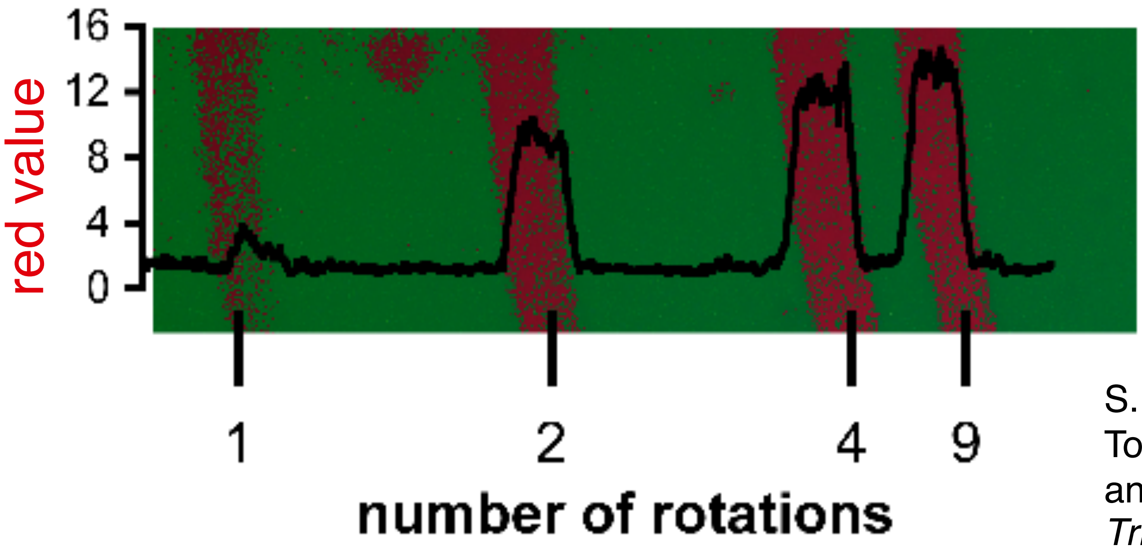
Tribostress-Induced Polymer Desorption

fluorescence microscopy



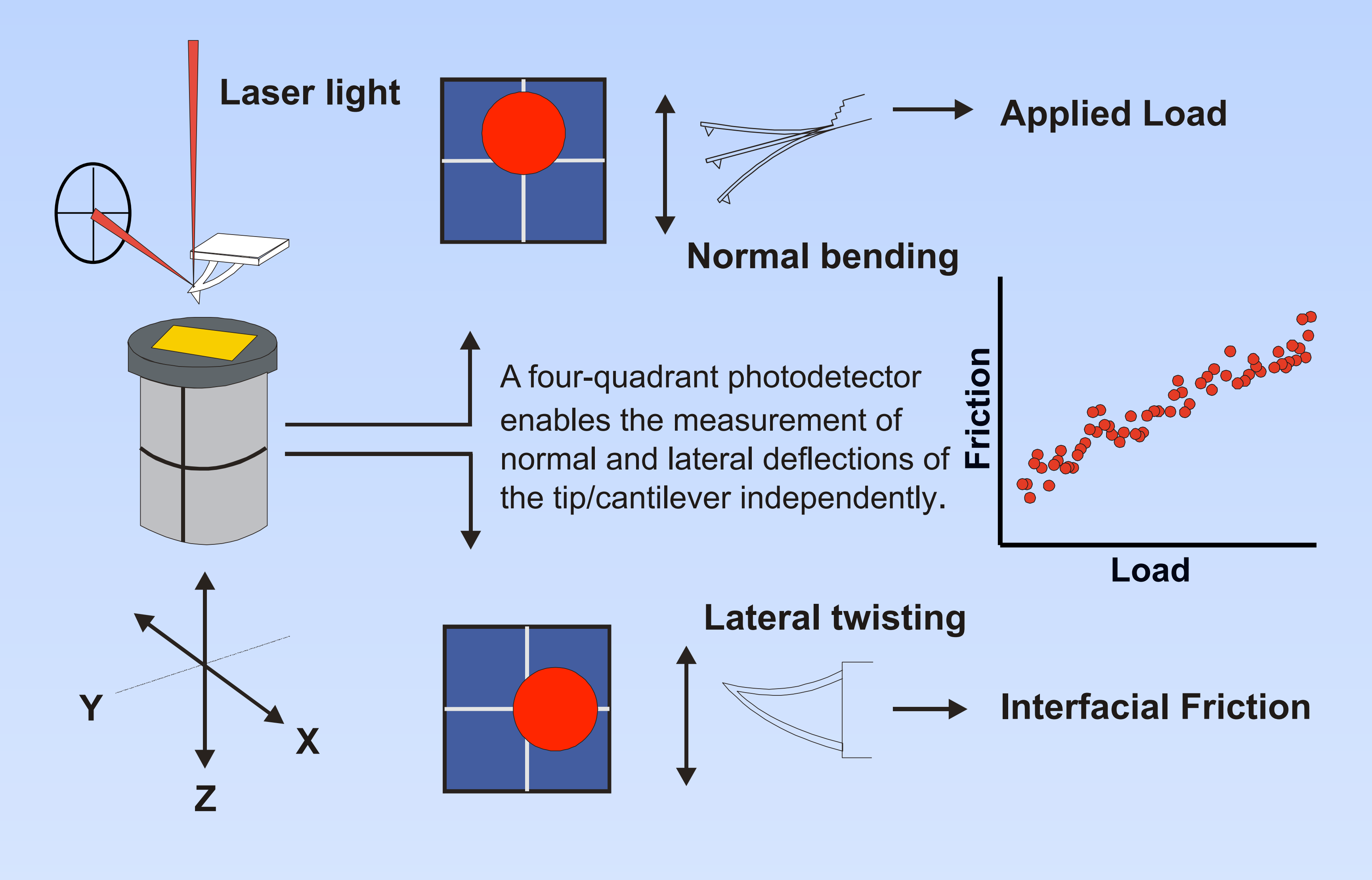


tribopair: steel/glass
load: 2N
pressure: 0.51 GPa
speed: 5 mm/s



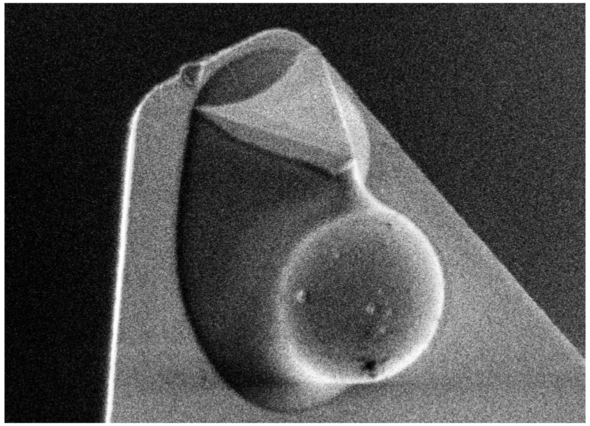
S. Lee, M. Müller, R. Heeb, S. Zürcher, S. Tosatti, M. Heinrich, F. Amstad, S. Pechmann, and N.D. Spencer
Tribology Letters; 2006 **24,** 217-223

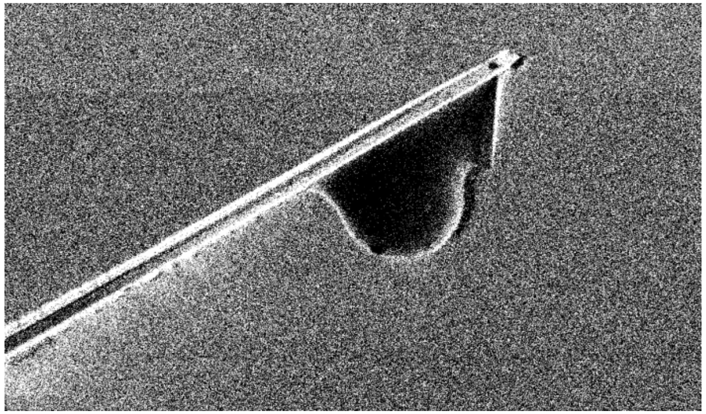
Friction Measurements with Beam Deflection AFM



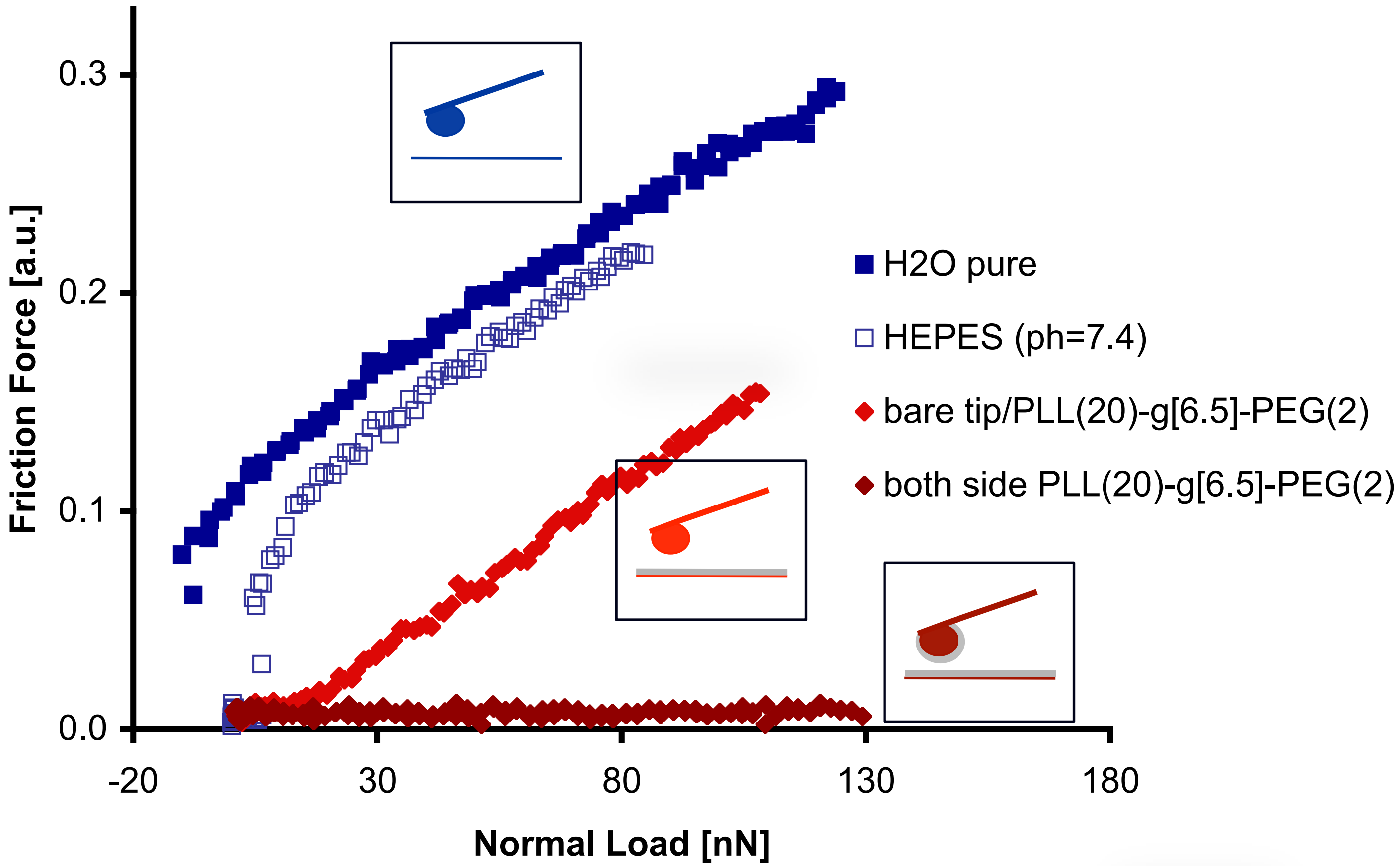
Sodium Borosilicate Microsphere

Cantilever:	Si_3N_4
Sphere radius:	2.5 μm
Image:	SEM
Beam energy:	1 kV



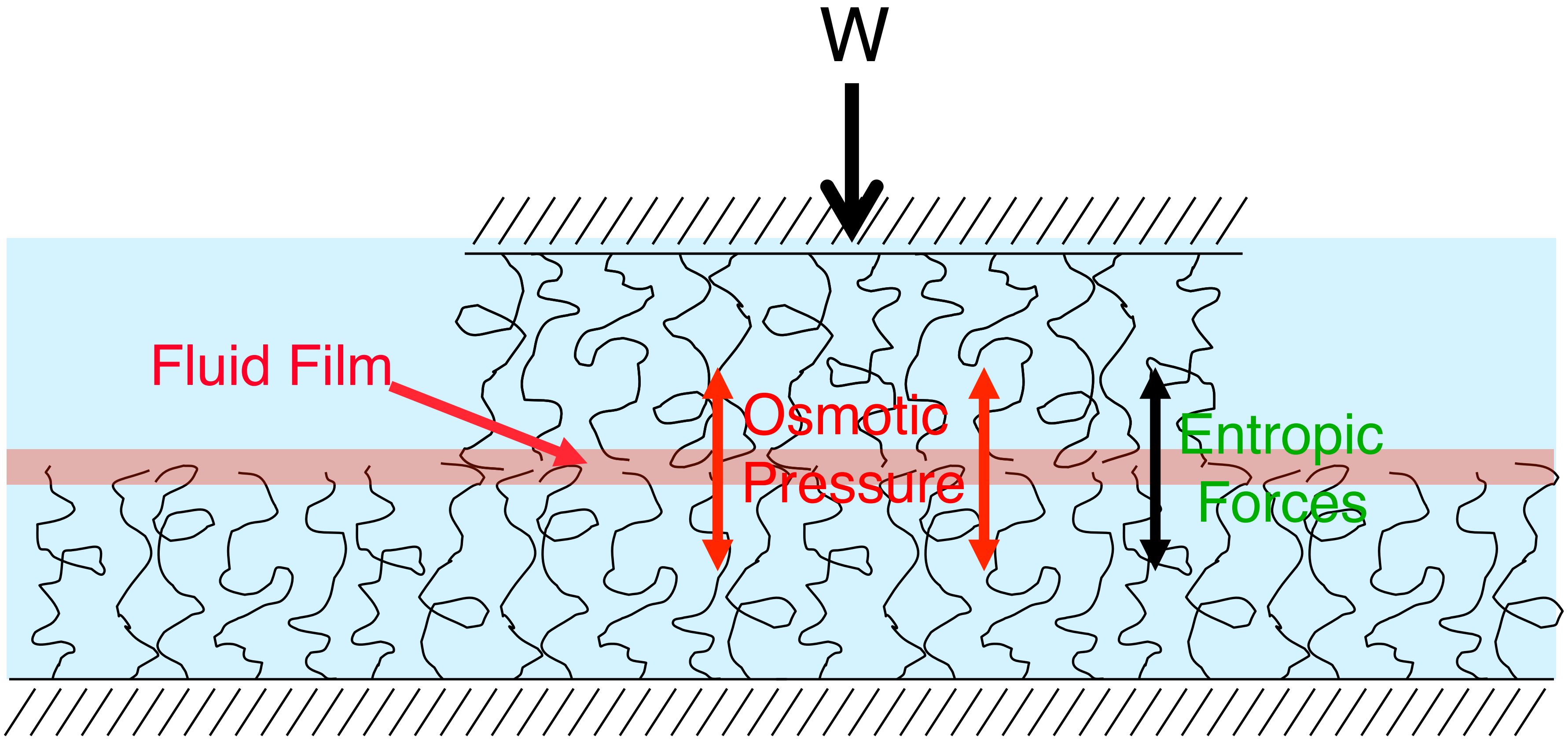


Polymer adsorption dramatically reduces nanofriction

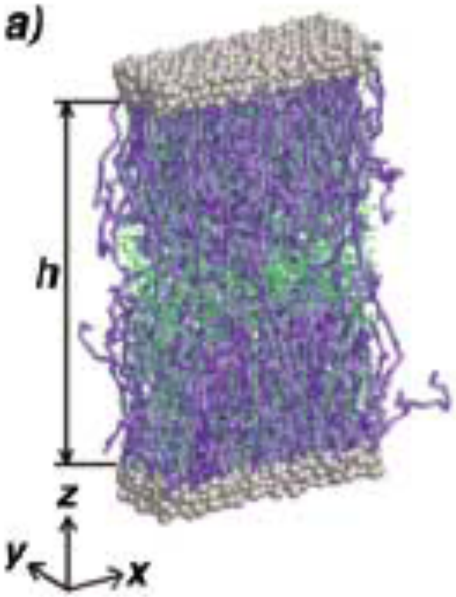


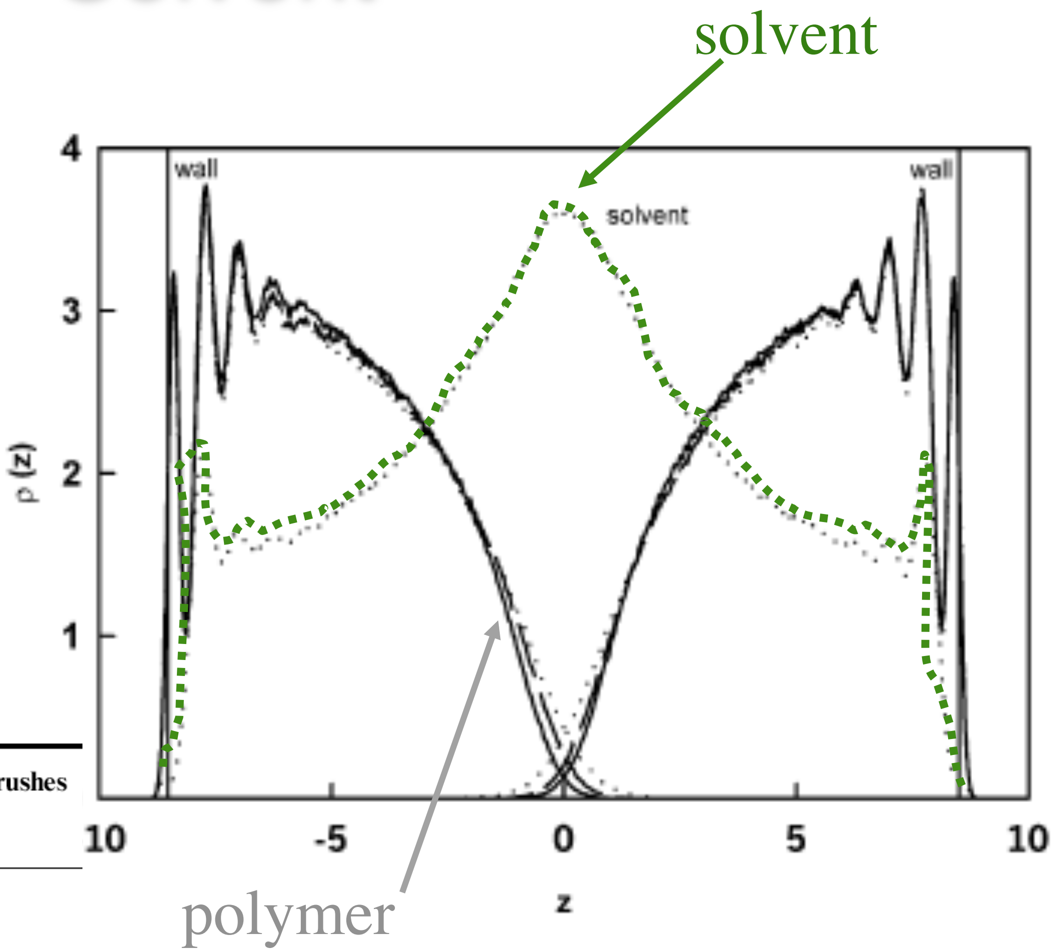
X. Yan, S.S. Perry, N.D. Spencer, S. Pasche, S.M. De Paul, M. Textor, M.S. Lim, *Langmuir* 2004, *20,* 423-428

“Enforced” Fluid-Film Lubrication by Polymer Brushes



Density Distribution of Polymer and Solvent





Dissipative particle dynamics simulation of grafted polymer brushes under shear

Danial Irfachsyad,[a] Dominic Tildesley[a] and Patrice Malfreyt[b]

[a] *Unilever Research Port Sunlight, Bebington, Wirral, UK CH63 3JW*
[b] *Laboratoire de Thermodynamique des Solutions et des Polymeres, UMR CNRS 6003, 24 avenue de Landais, Universite Blaise-Pascal, 63177, Aubiere Cedex, France*

Received 22nd November 2001, Accepted 22nd April 2002
First published as an Advance Article on the web 27th May 2002

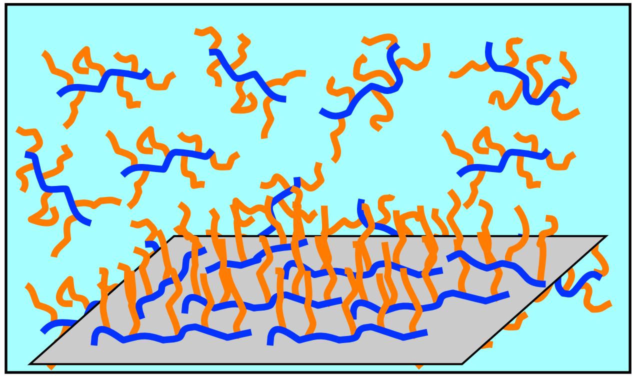
Problems with PEG

PEG is oxidationally unstable
PEG solubility decreases with temperature
PLL-g-PEG is expensive

Alternative: Sugar chains!

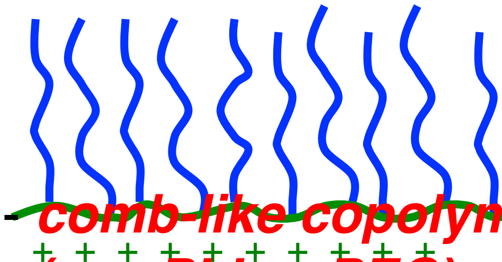
PEG immobilization to surfaces

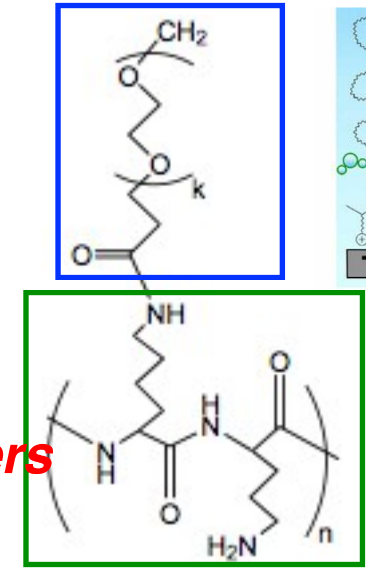
From PLL-g-PEG...

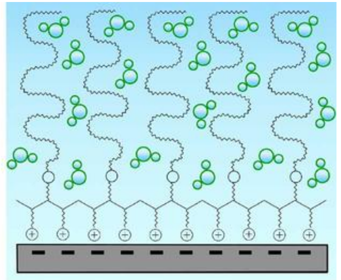


PEG side chains

- hydrophilic
- neutral
- flexible







- *comb-like copolymers (e.g. PLL-g-PEG)*

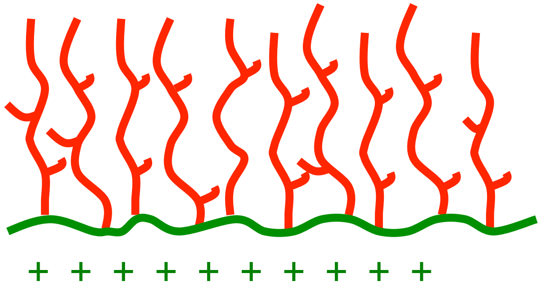
Backbone: PLL

- polycationic

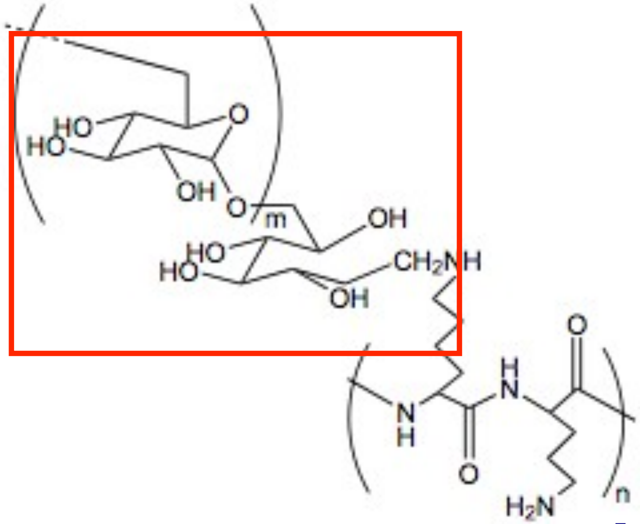
...to PLL-g-dex

Dextran side chains

- natural & neutral
- essentially linear
- water soluble
- biocompatible
- biodegradable
- branches: ~ 5% (1-2 glucose units long)



Backbone: PLL



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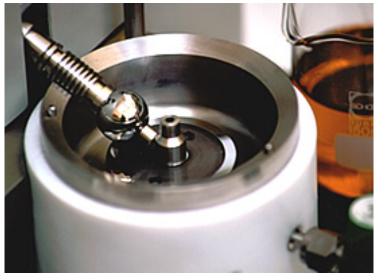
Swiss Federal Institute of Technology Zurich

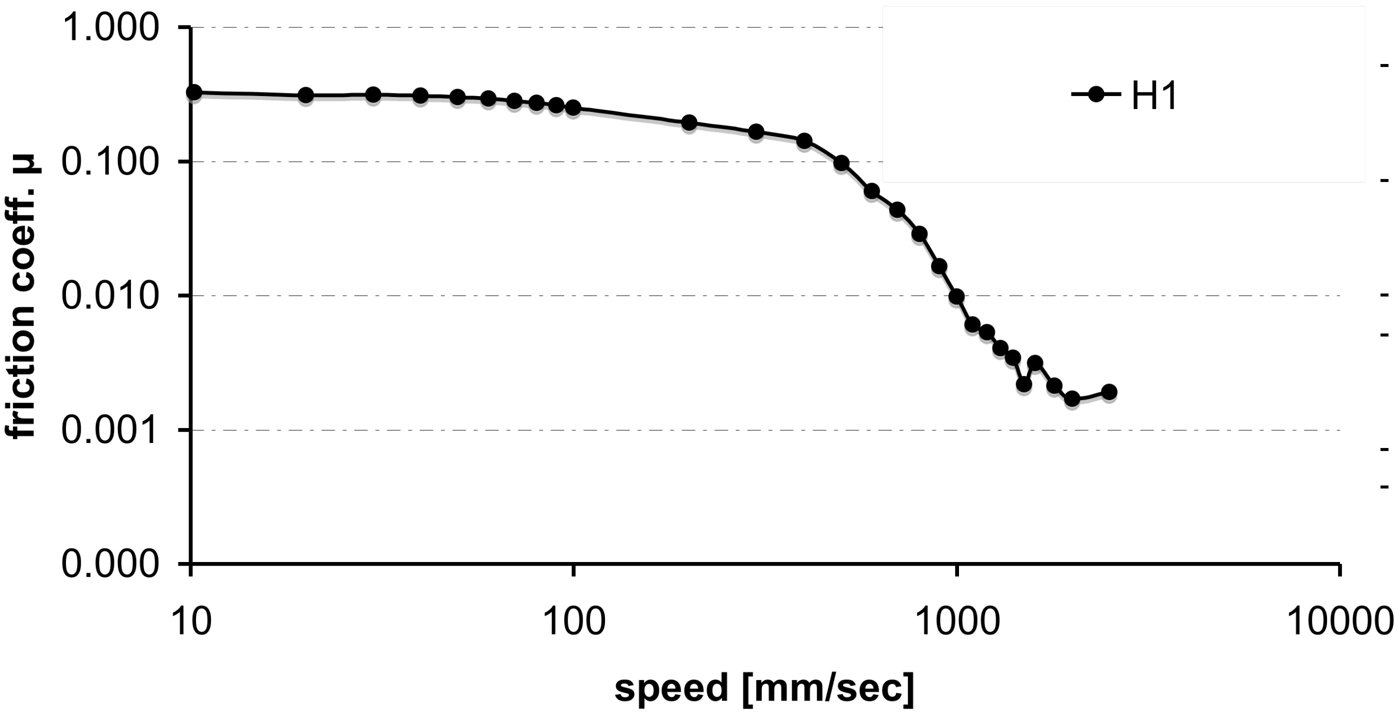
LSST Laboratory for Surface Science and Technology

PLL-*g*-dex lubrication

MTM Mini Traction Machine
Speed dependence



Mixed sliding/rolling regime

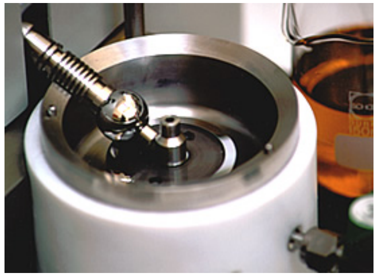


- tribopair: **steel ball** (r =9.5 mm, AISI 440) vs **glass disk**
- cleaning procedure: sonication in EtOH (10 min), O_2 plasma (1 min)
- SRR (slide/roll ratio) = 10 %
- samples incubated in the polymer solution (0.25 mg/ml) for 30 min
- load = **10 N**
- speed range = **2500-10 mm/sec**

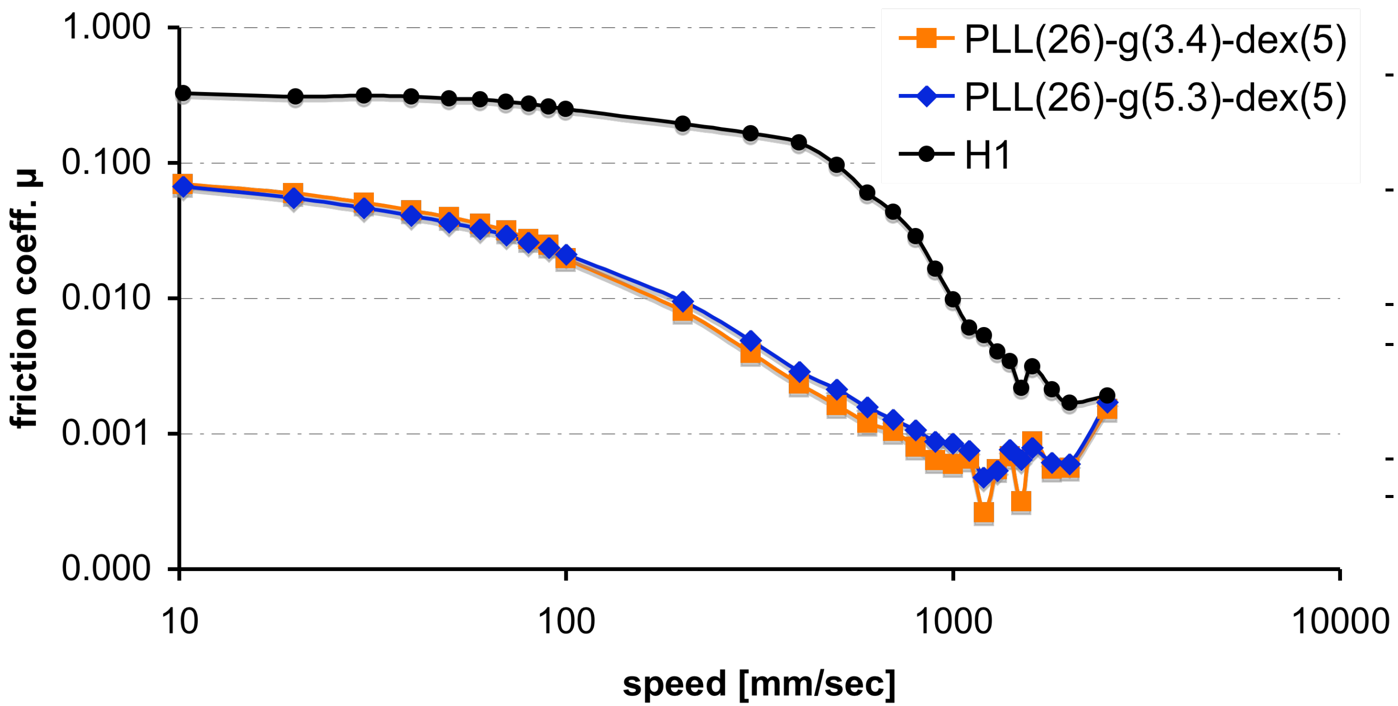
Eidgenössische Technische Hochschule Zürich
Swiss Federal Institute of Technology Zurich

PLL-*g*-dex lubrication

MTM Mini Traction Machine
Speed dependence



Mixed sliding/rolling regime



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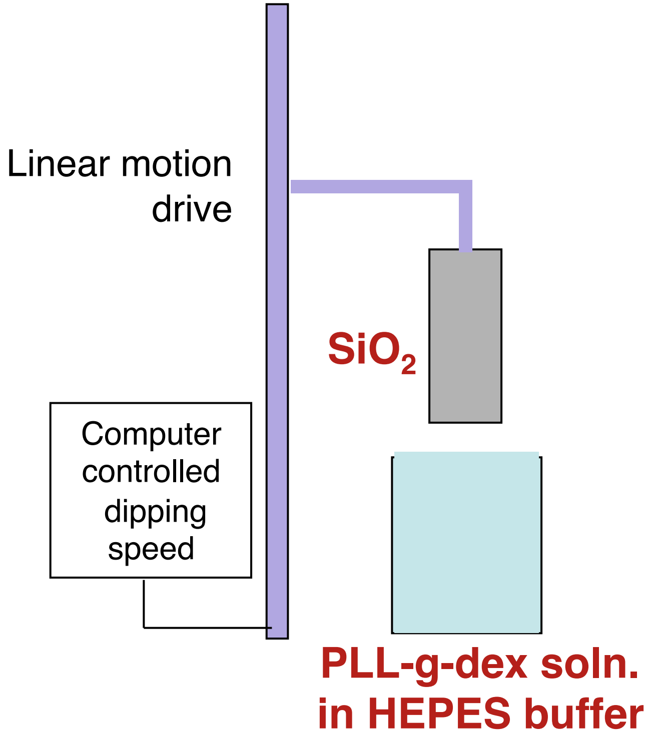
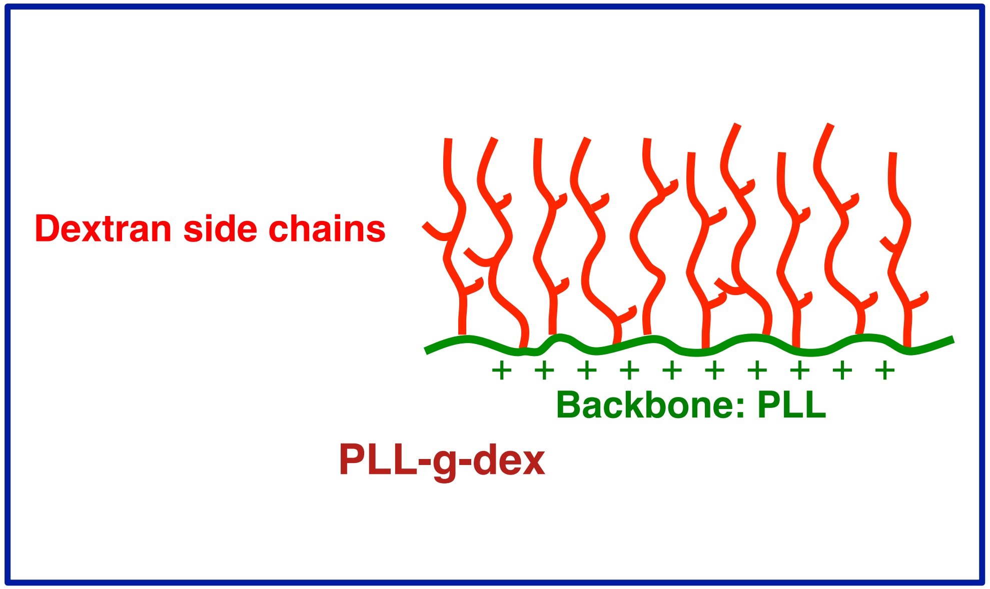
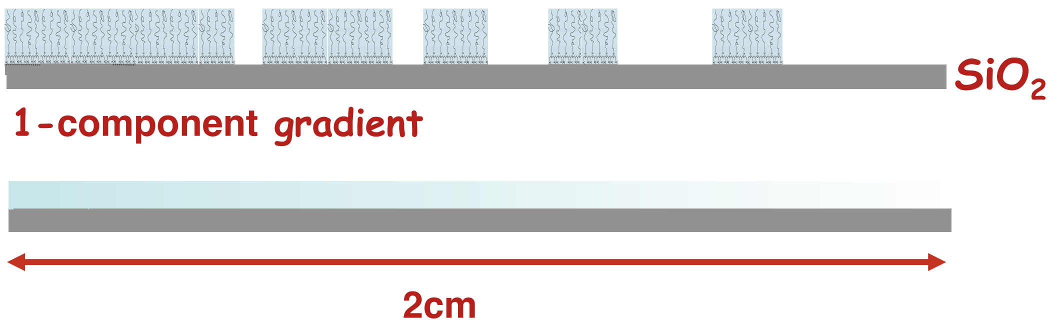
Chiara Perrino, Seunghwan Lee and Nicholas D. Spencer
Tribology Letters; 2009 **33(2)** pp83-96

Dextran gradients on Silicon Wafers







ETH
Eidgenössische Technische Hochschule Zürich
Swiss Federal Institute of Technology Zurich

Morgenthaler, S. et al *Biointerphases* **1** (2006) 156-165

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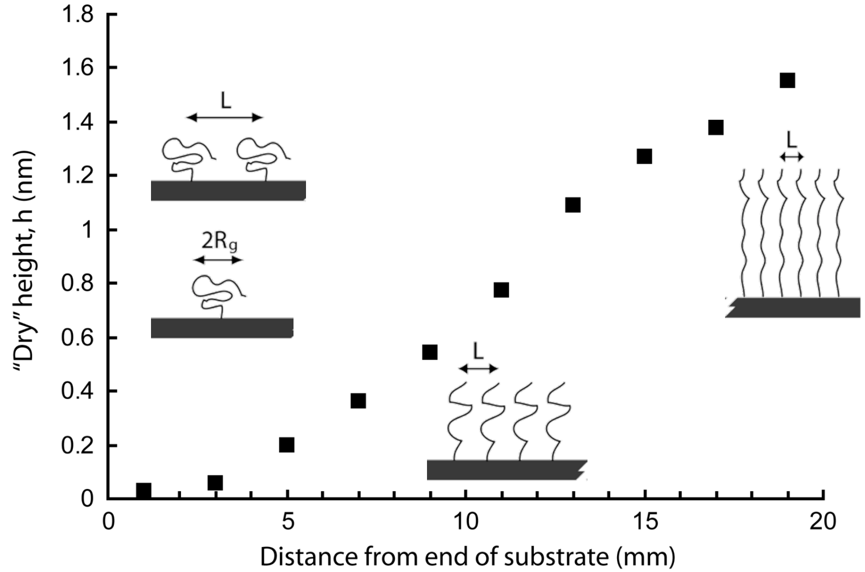
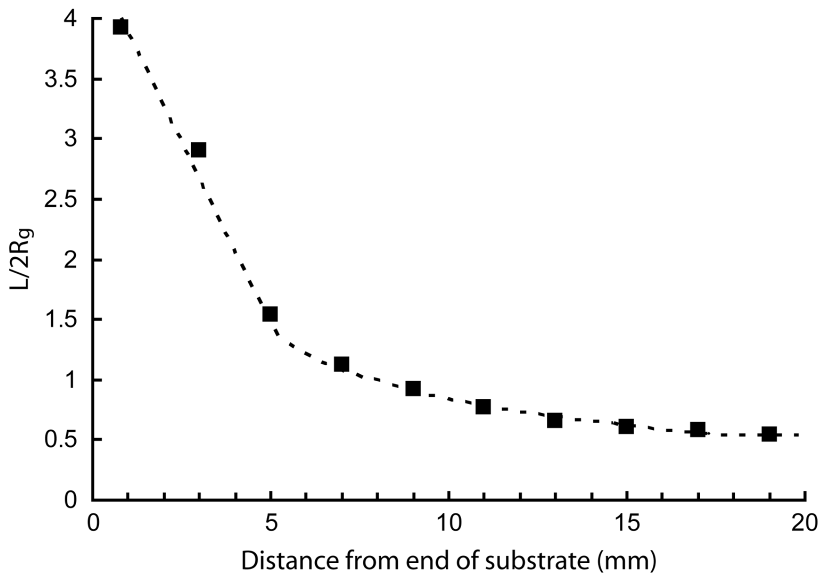
Laboratory for Surface Science and Technology

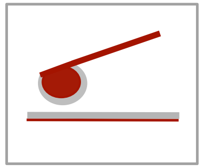
Dextran gradients on Silicon Wafers

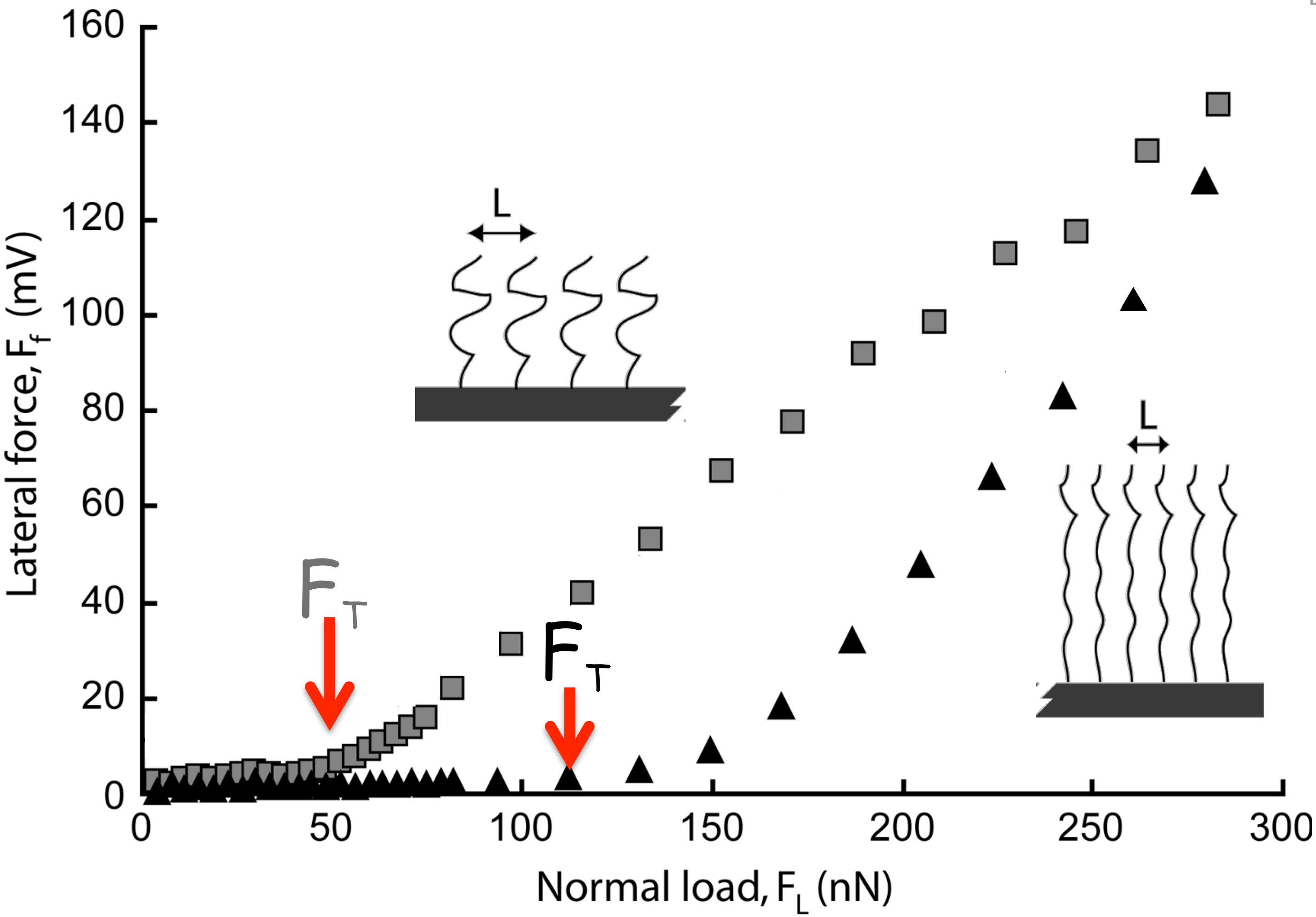




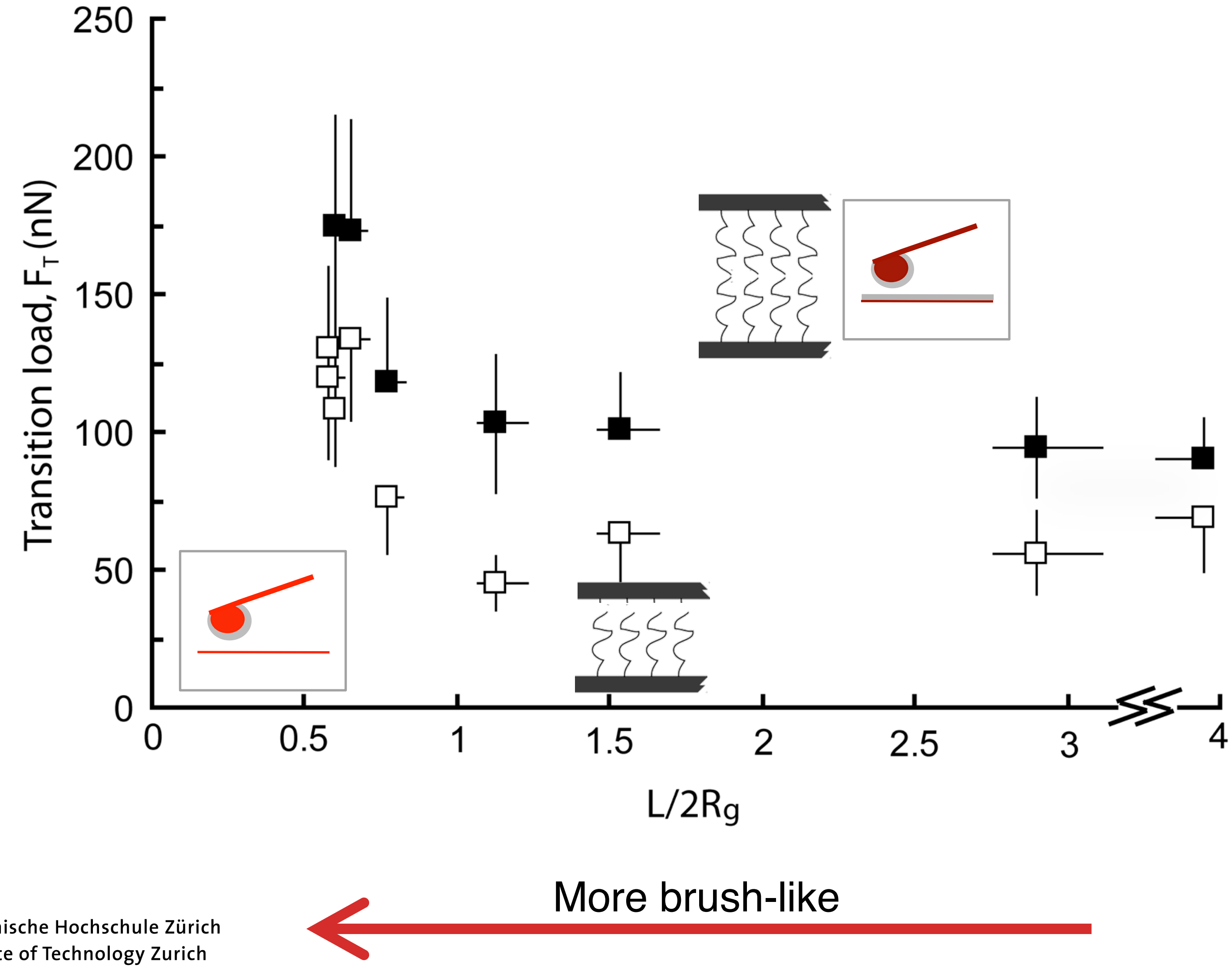
Dextran gradients on Silicon Wafers

Friction in low-load and high-load regimes by colloidal-probe AFM

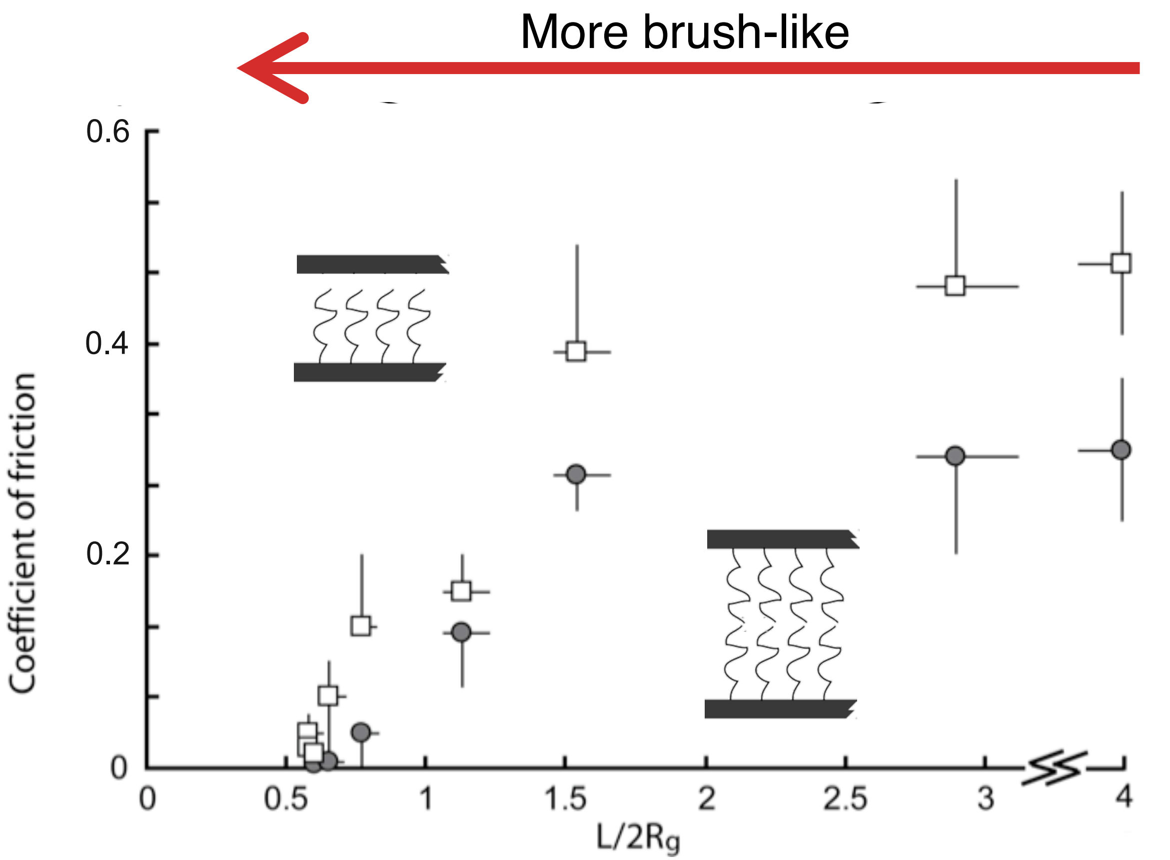




Dextran gradients on Silicon Wafers



Dextran gradients on Silicon Wafers



Possible interpretation: at low loads, stiff brushes help separate sliding surfaces and lead to low-friction sliding across solvent-rich interface.

Low-load regime

At high loads, when interpenetration occurs, the stiffer the brush, the greater the resistance.

Eidgenössische Technische Hochschule Zürich
Swiss Federal Institute of Technology Zurich

Kenneth J. Rosenberg, Tolga Goren, Rowena Crockett, Nicholas D. Spencer
ACS Applied Materials and Interfaces; ***2011 3 (8), pp 3020-3025***

Laboratory for Surface Science and Technology

Outline

- Gradients
- Surface Chemical Gradients
- Example 1: Influence of polymer grafting density on friction
- Morphological Gradients
- Example 2: Influence of roughness on adhesion

Morphological Gradient Preparation

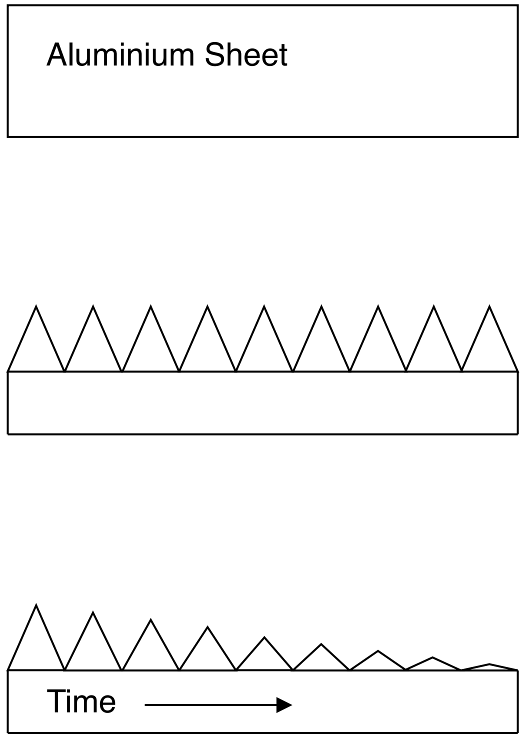
Surface

↓

Bead Blasting

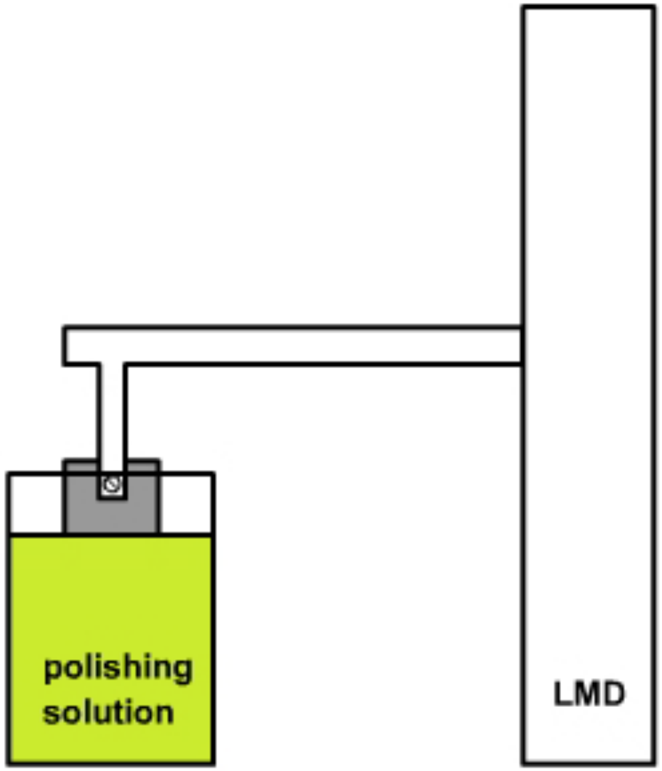
↓

Chemical Polishing



Tobias P. Künzler, Tanja Drobek, Christoph M. Sprecher, Martin Schuler, Nicholas D. Spencer
Applied Surface Science; 2006 253, pp2148-2153

Procedure: Chem. Polishing



Polishing Solution

Phosphoric Acid

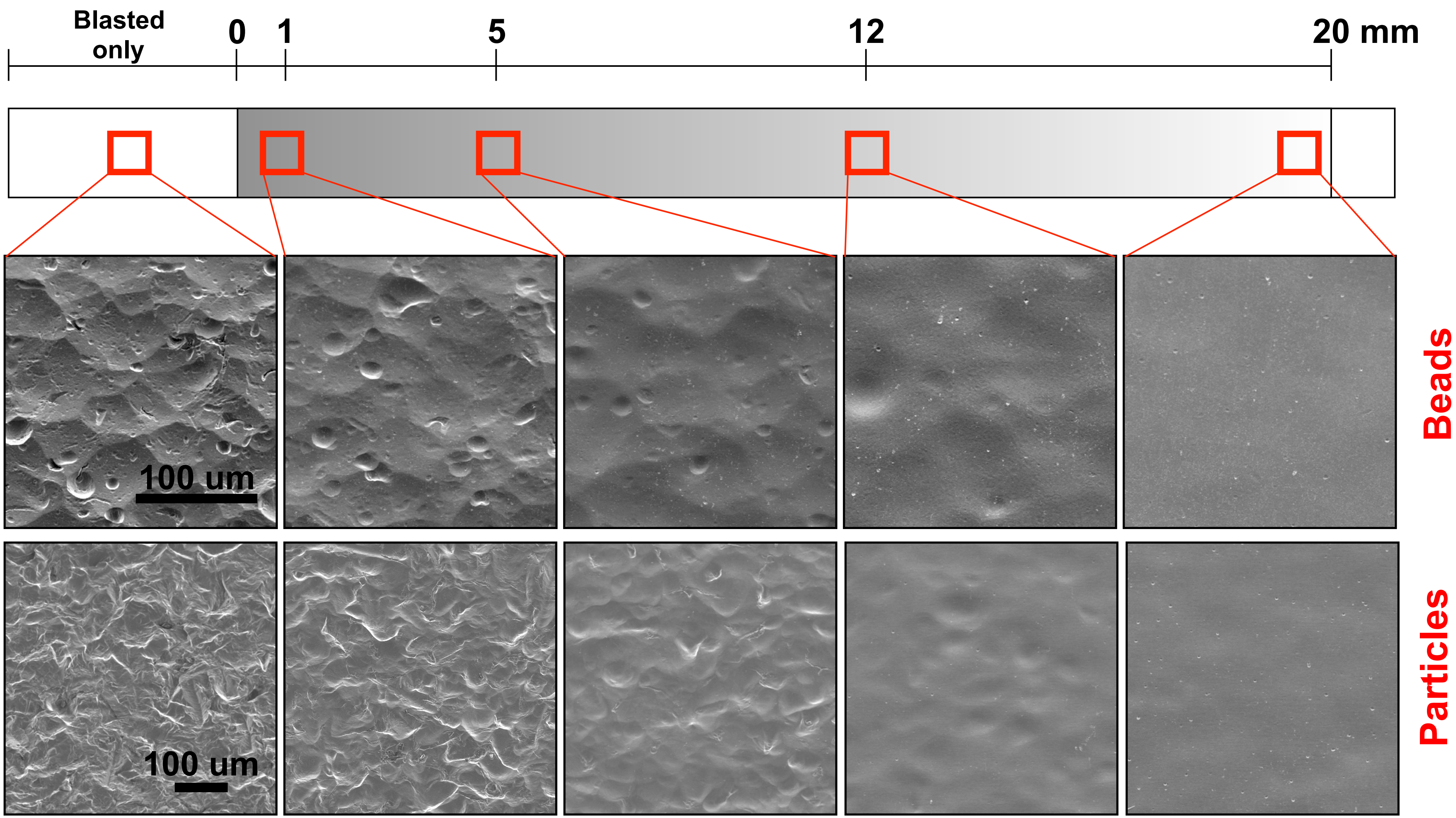
Sulphuric Acid

Nitric Acid

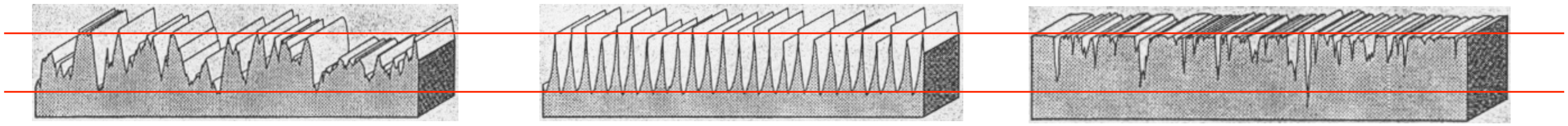
Copper Nitrate

@ 80°C for 0 to 40 minutes

Characterization (SEM)

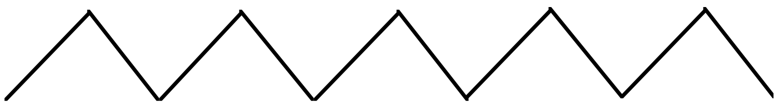


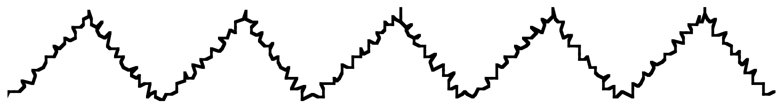
Roughness Parameters



Amplitude Parameters (e.g. Ra) are identical, Spacing and Statistical Parameter are different

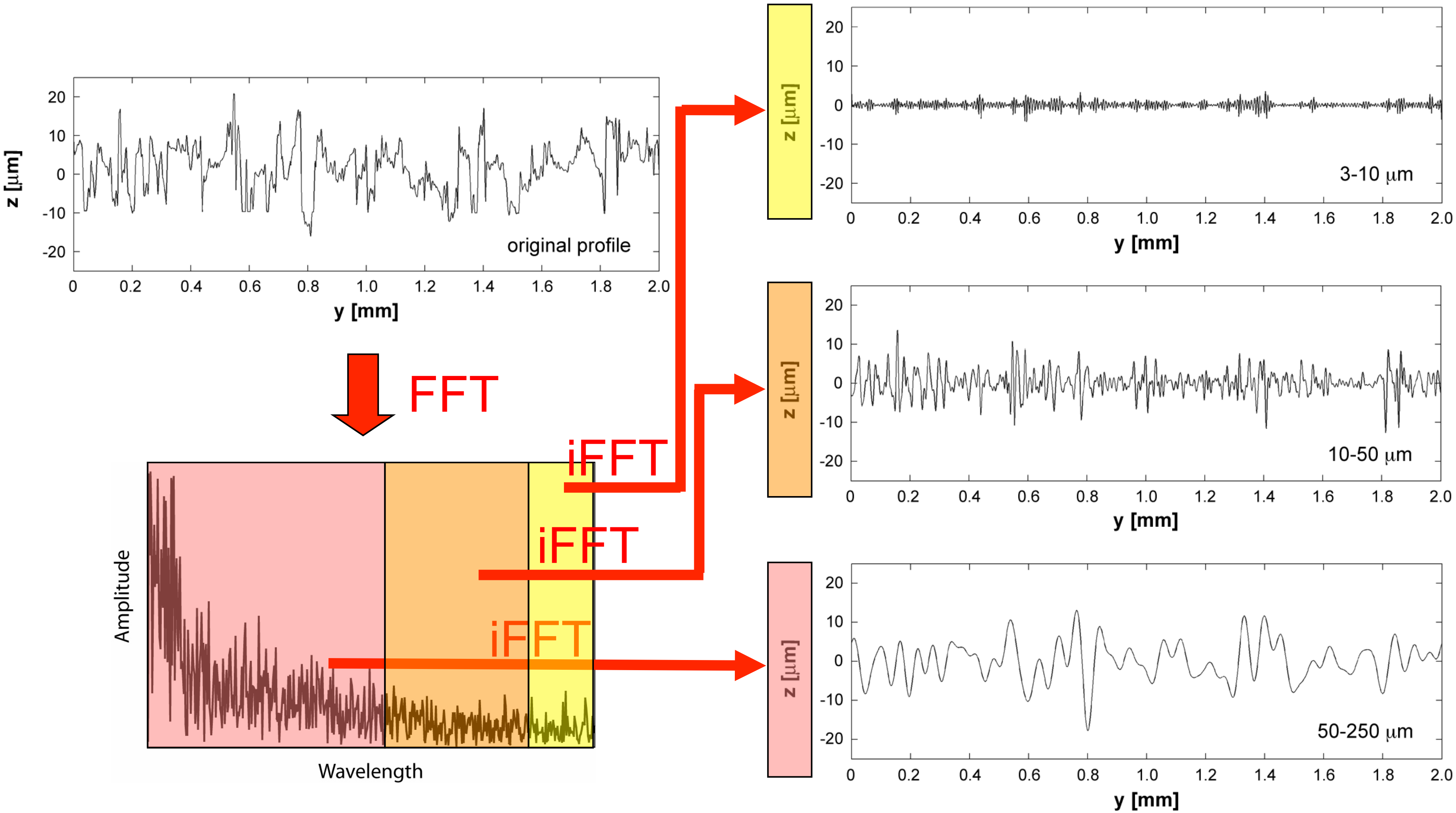
→ Some Roughness Parameters are identical





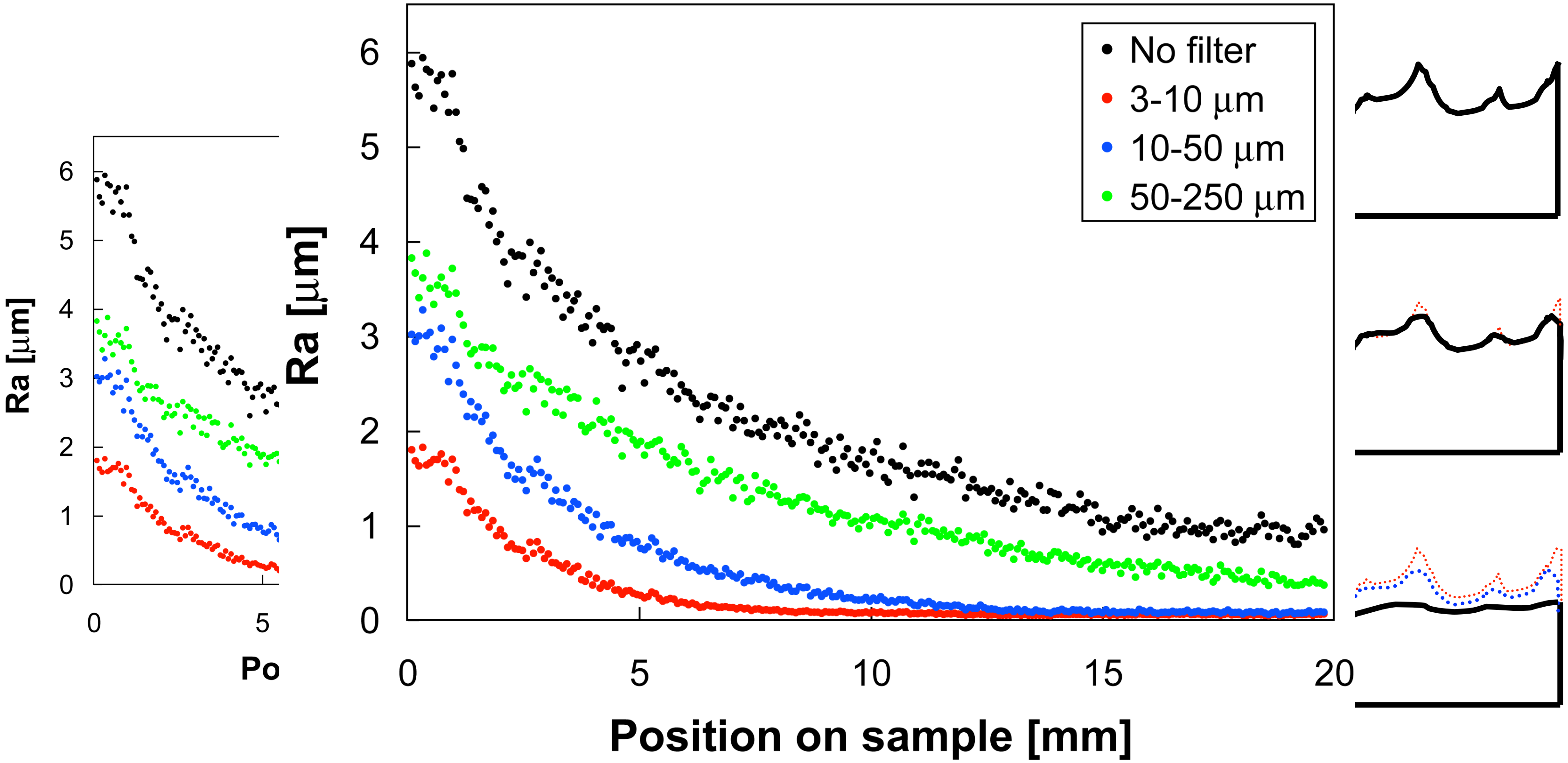
→ Roughness Parameters are identical

FFT (Wavelength dependent)



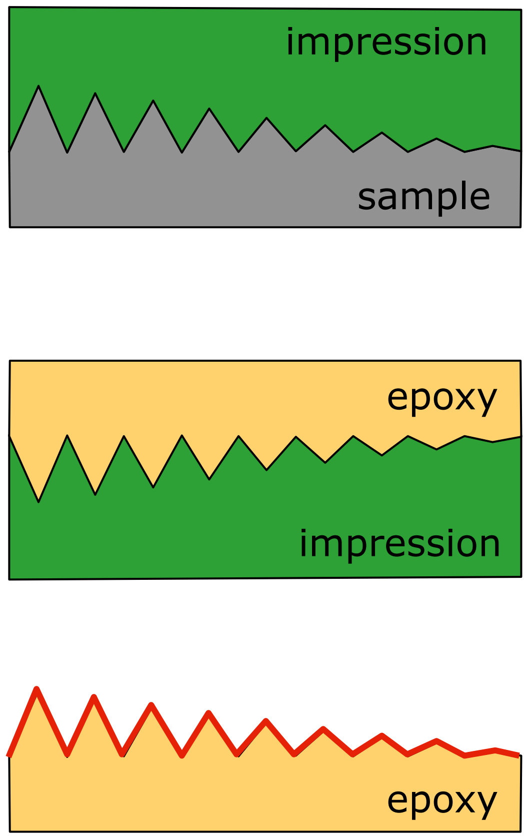
Characterization (LP)

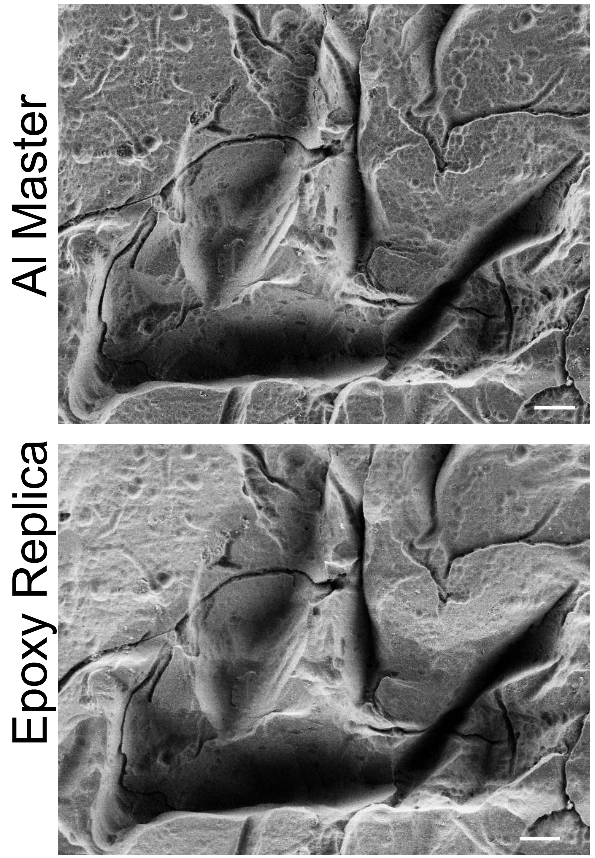
Wavelength dependent analysis[1)] with FFT (Fast Fourier Transformation)



1) M.Wieland et al, Wear 237, 2000, p. 231-252

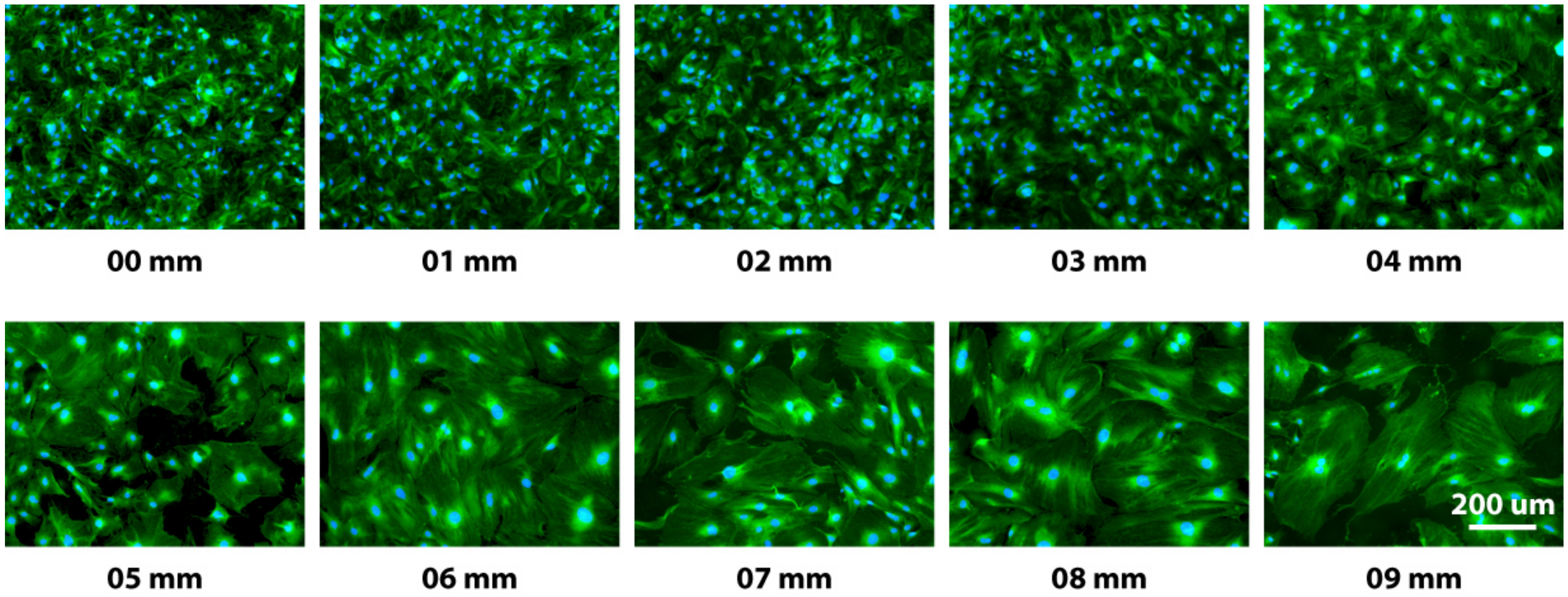
Epoxy-replica fabrication technique





M.Schuler, T.P.Künzler et al., J Biomed Mater Res, 2006, *submitted*

Osteoblast morphology along roughness gradient



RCO (rat calvaria osteoblasts)
7 days after seeding
Seeding density: 4500 cells/cm2
Staining: nucleus=DAPI (blue), cell membrane=FITC (green)

Systematic Study of Osteoblast and Fibroblast Response to Roughness by means of Surface- Morphology Gradients
Tobias P. Kunzler, Tanja Drobek, Martin Schuler, and Nicholas D. Spencer *Biomaterials*; 2007 **28**, pp2175-2182

Outline

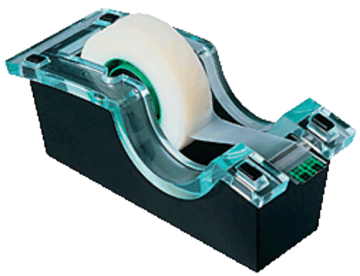
- Gradients
- Surface Chemical Gradients
- Example 1: Influence of polymer grafting density on friction
- Morphological Gradients
- Example 2: Influence of roughness on adhesion

Tape Adhesion on Roughness Gradients

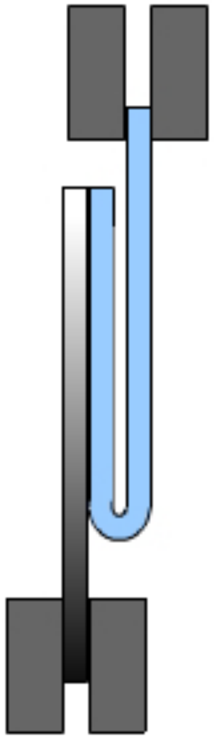
Tape Adhesion Measurement

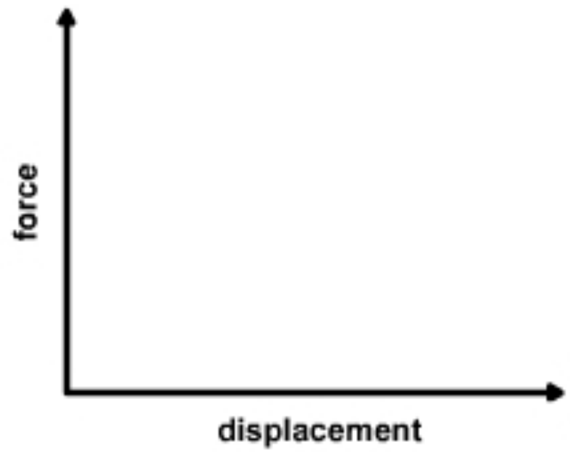
Peel Tests

1. Clean sample
2. Press tape onto sample with a defined pressure



3. Peel off tape with constant speed



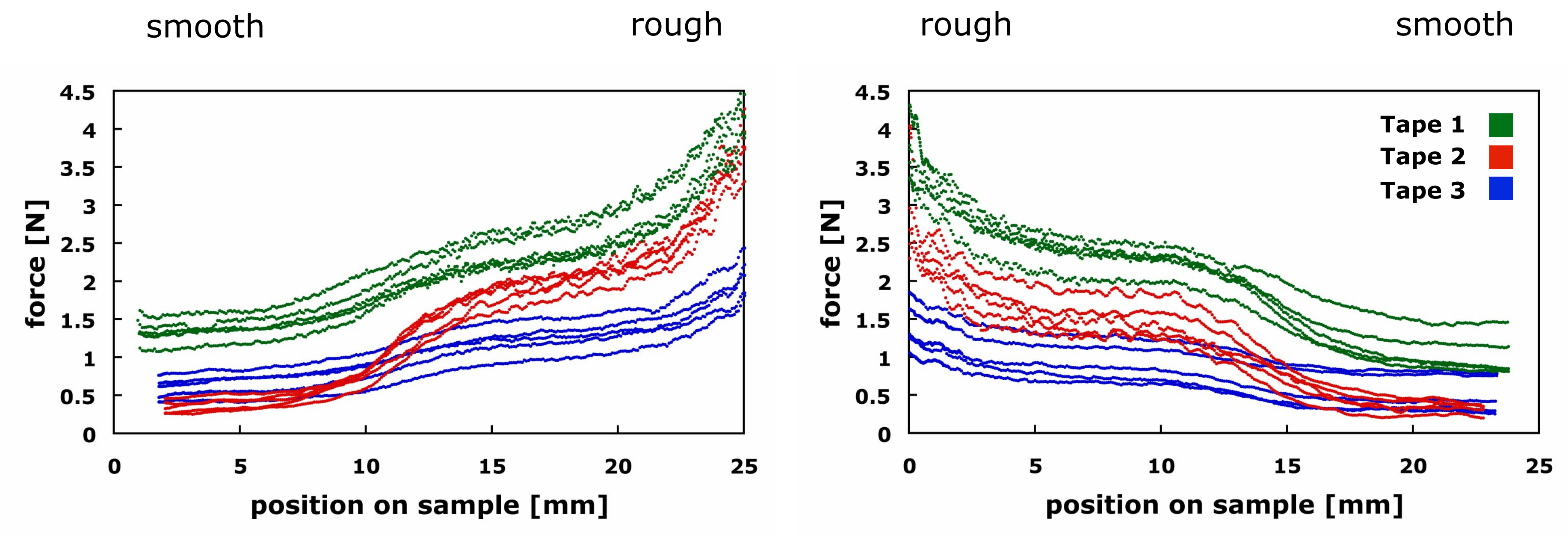


International Standard ISO 8510-2: 1990

Tape Adhesion Results

Peel Tests

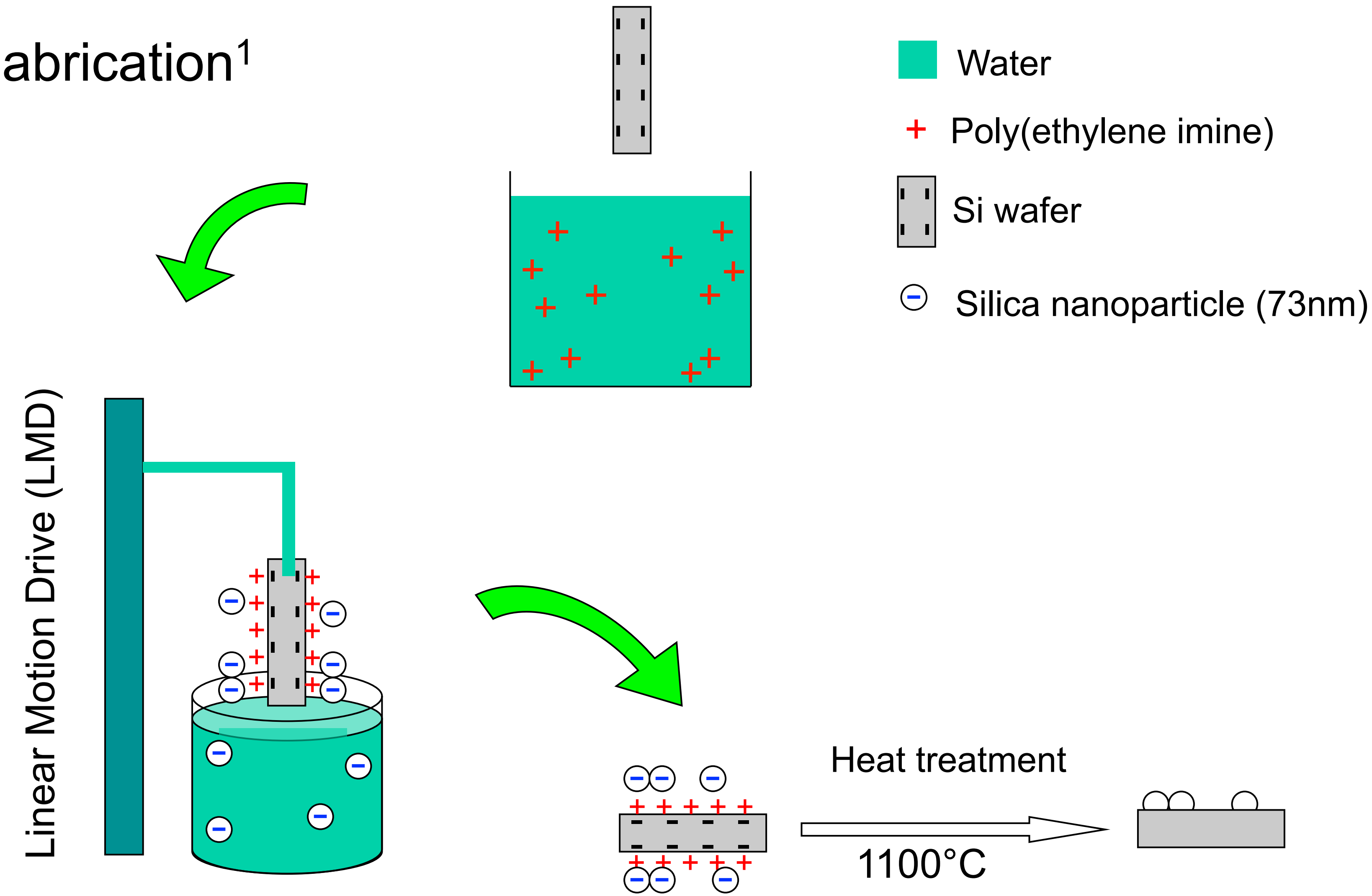
N/tape:	5
Pressure:	0.5t
Speed:	10 mm/min
Load cell:	0-10 N
Peel-Angle:	180°



Nanoparticle Gradients

Nano-featured Gradients

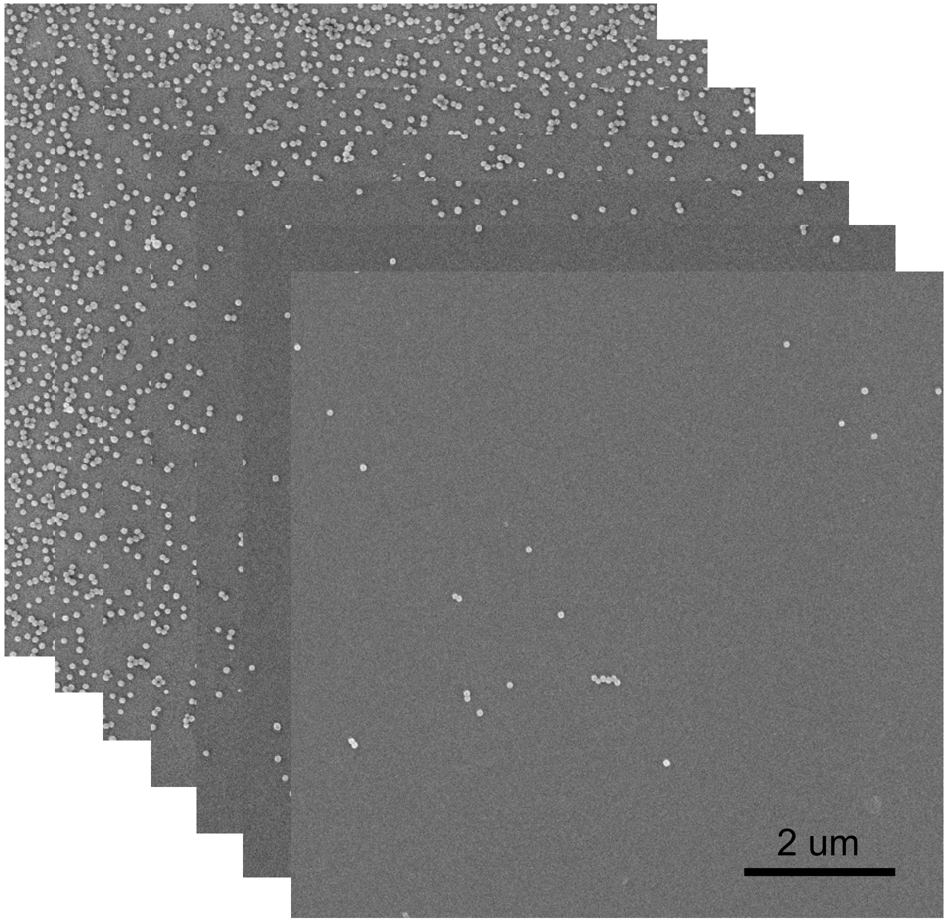
Fabrication[1]

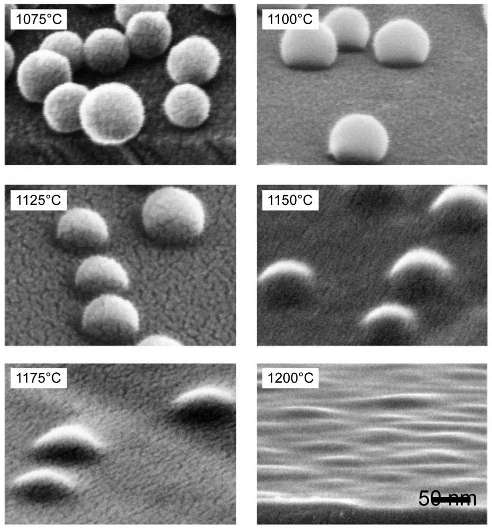


1) C. Huwiler et al., *Langmuir*, 2007, 23, 5929 - 5935

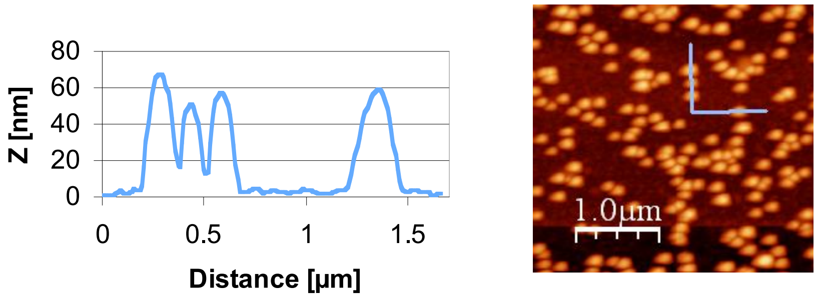
Nano-Featured Gradients

Scanning electron microscopy (SEM) images





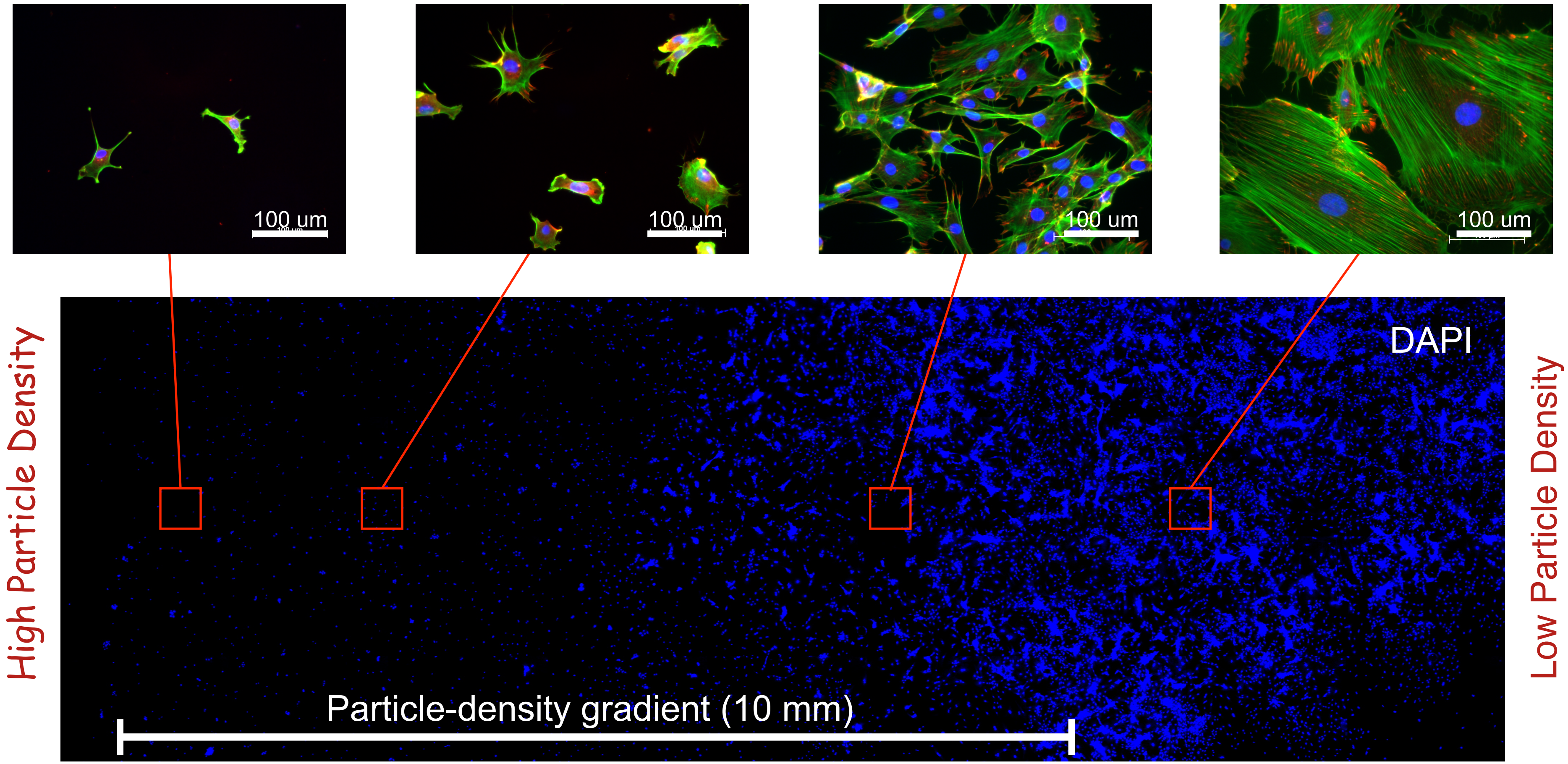
Sintering of particles at different heat-treatment temperatures



Christoph Huwiler, Tobias Künzler, Marcus Textor, Janos Vörös, Nicholas D. Spencer
Langmuir; ***2007*** 23(11) pp5929-5935

Nano-Featured Gradients

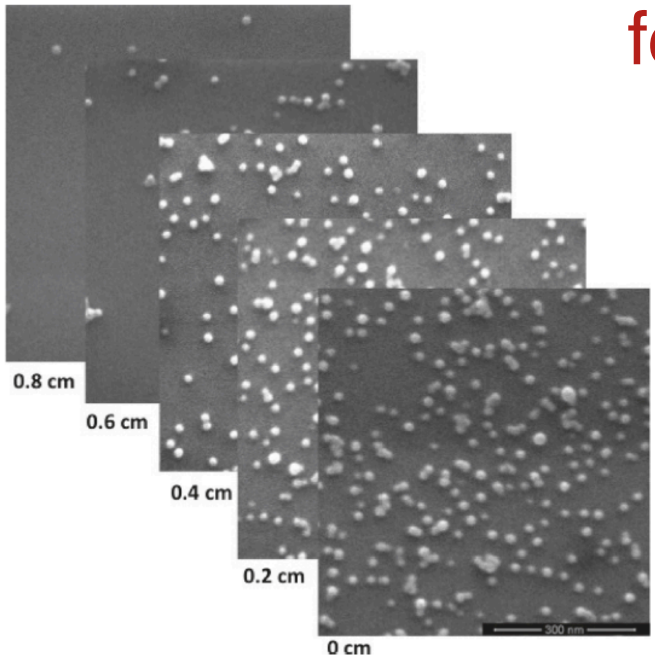
Morphology of Rat Calvarial Osteoblasts (RCO), 7 days post seeding



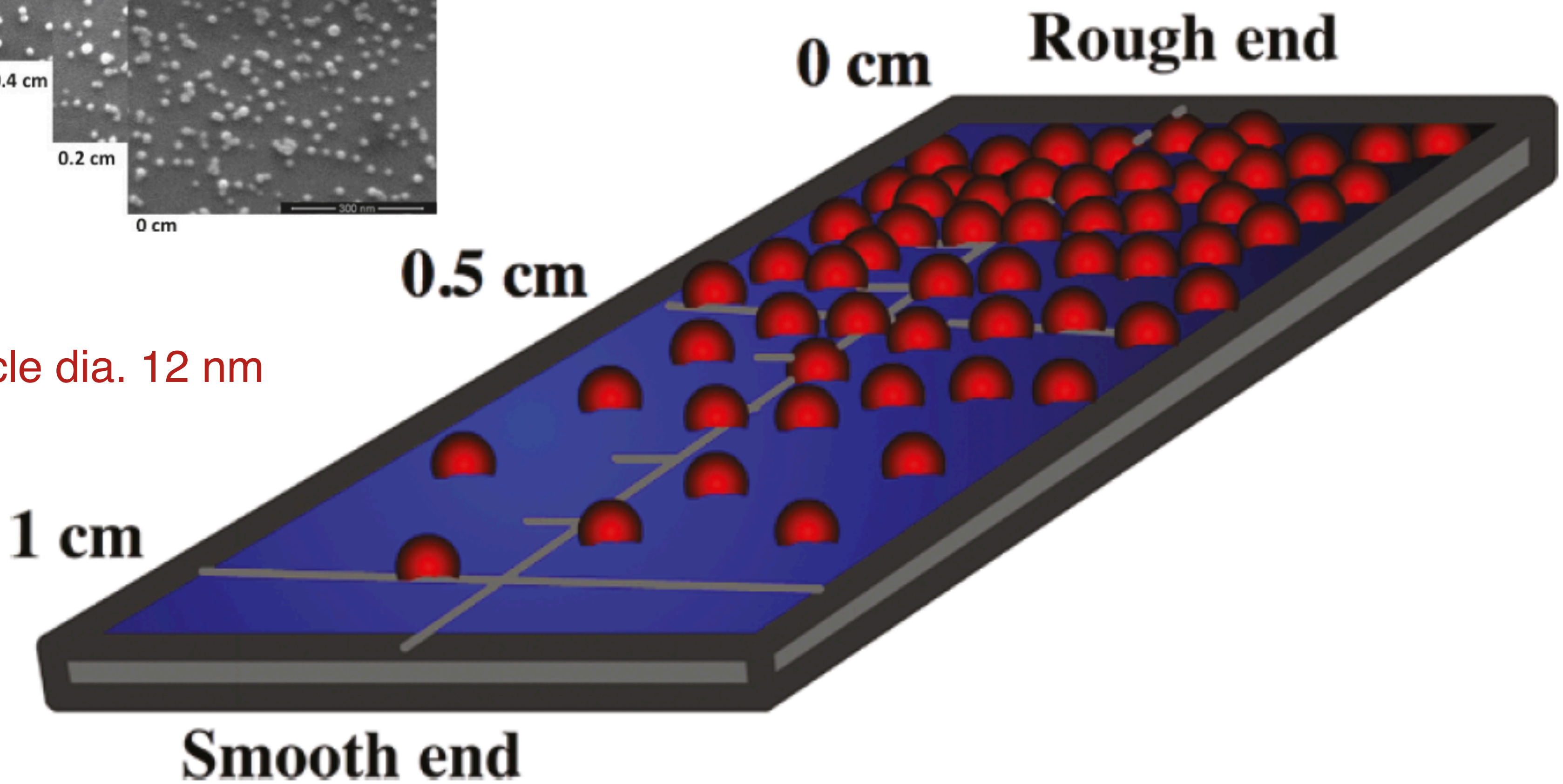
Tobias P. Kunzler, Christoph Huwiler, Tanja Drobek, Janos Vörös, Nicholas D. Spencer
Biomaterials; ***2007*** 28 pp5000-5006

Adhesion Studies on Nanoparticle Gradients

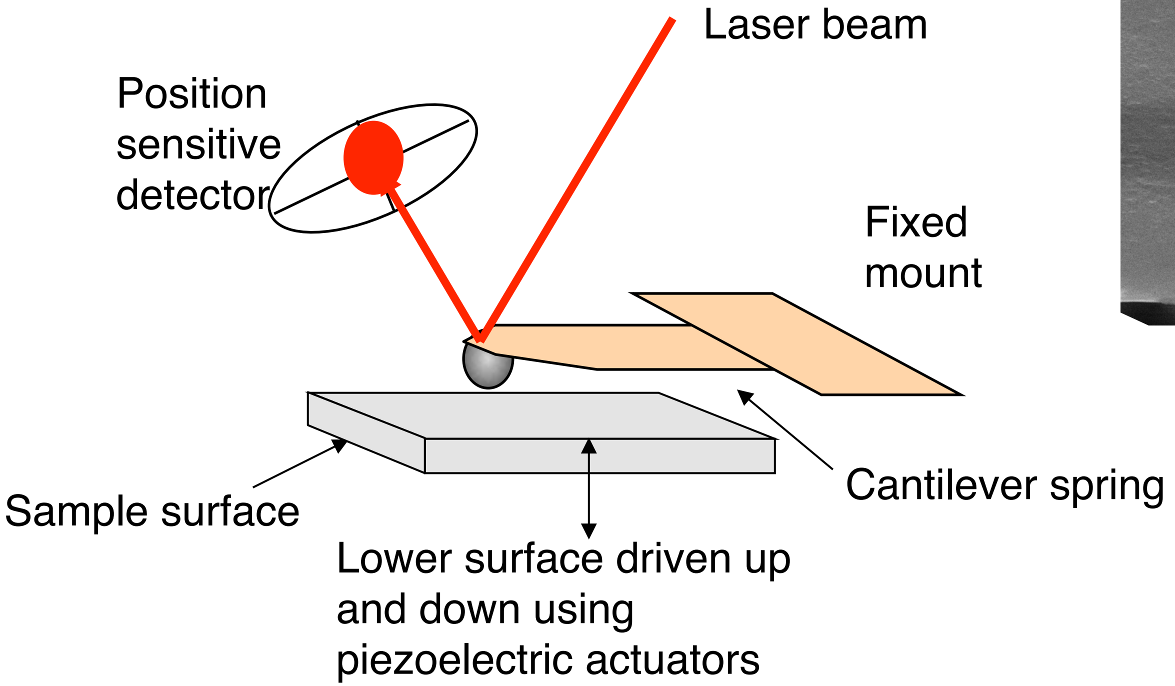
Cartoon (not to scale)
and SEM of Nanoparticle gradient
for adhesion studies

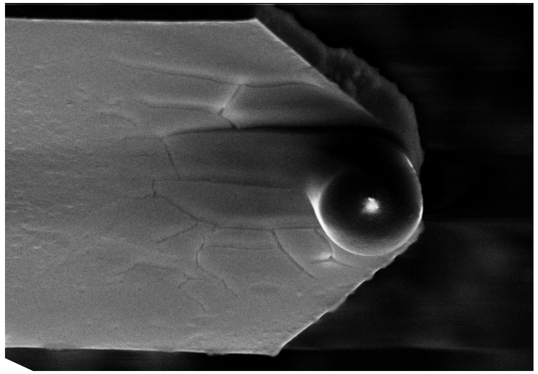


Particle dia. 12 nm



<u>Adhesion</u> measurements between a **PE** colloid-probe AFM and a gradient surface

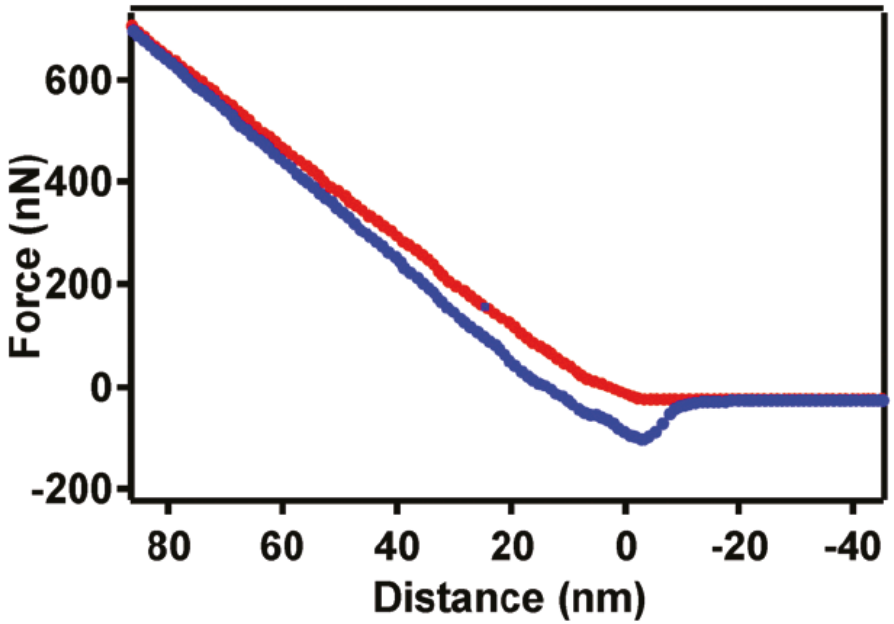




All measurements with **polyethylene** colloidal probe, carried out under **perfluorodecalin** (n= 1.313, ε = 1.8) to exclude water and enhance Hamaker constant

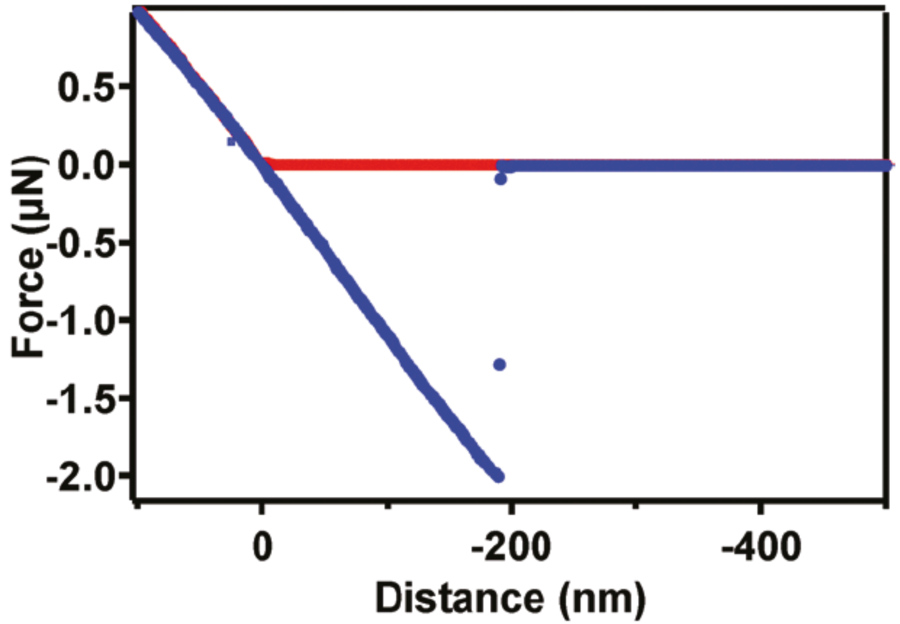
Pull-off behavior contrasted at each end of the nanoparticle gradient

Multiple detachments with hysteresis

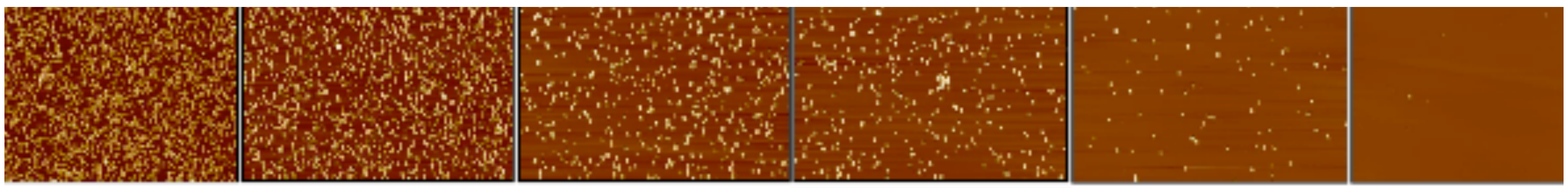


Rough end

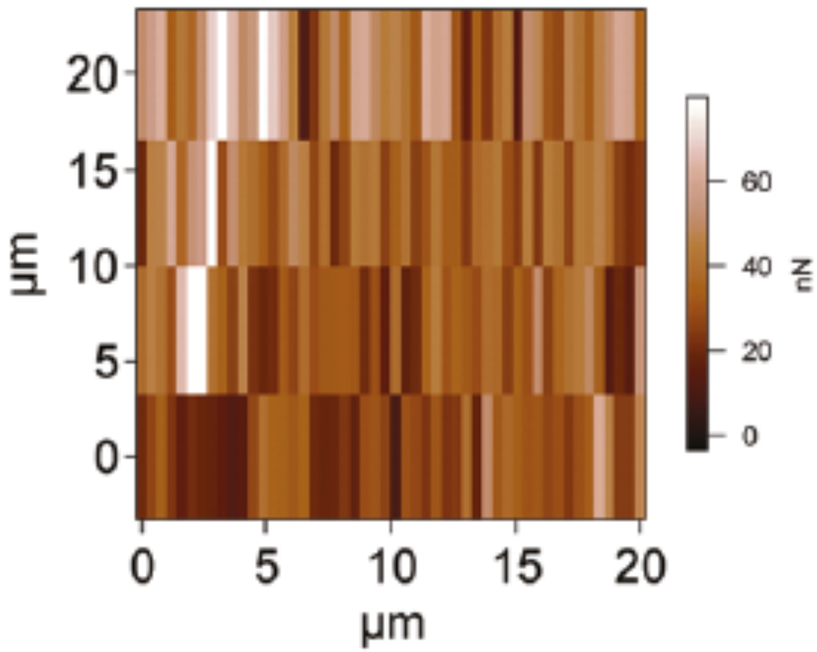
“snapping off”

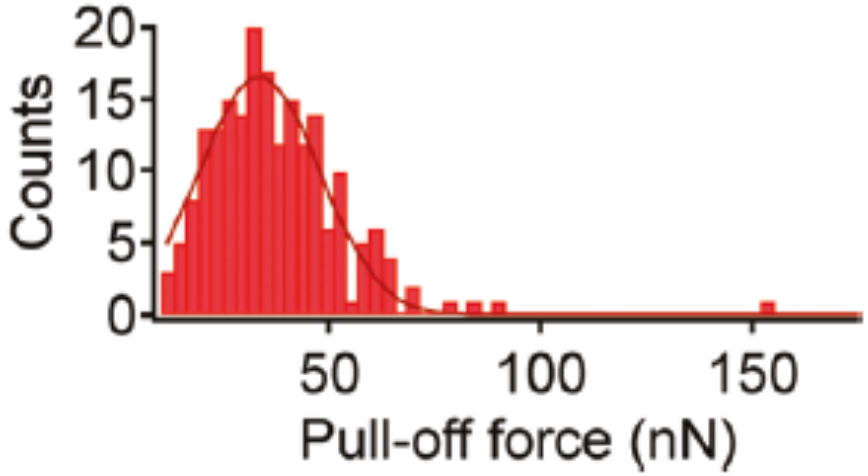


Smooth end

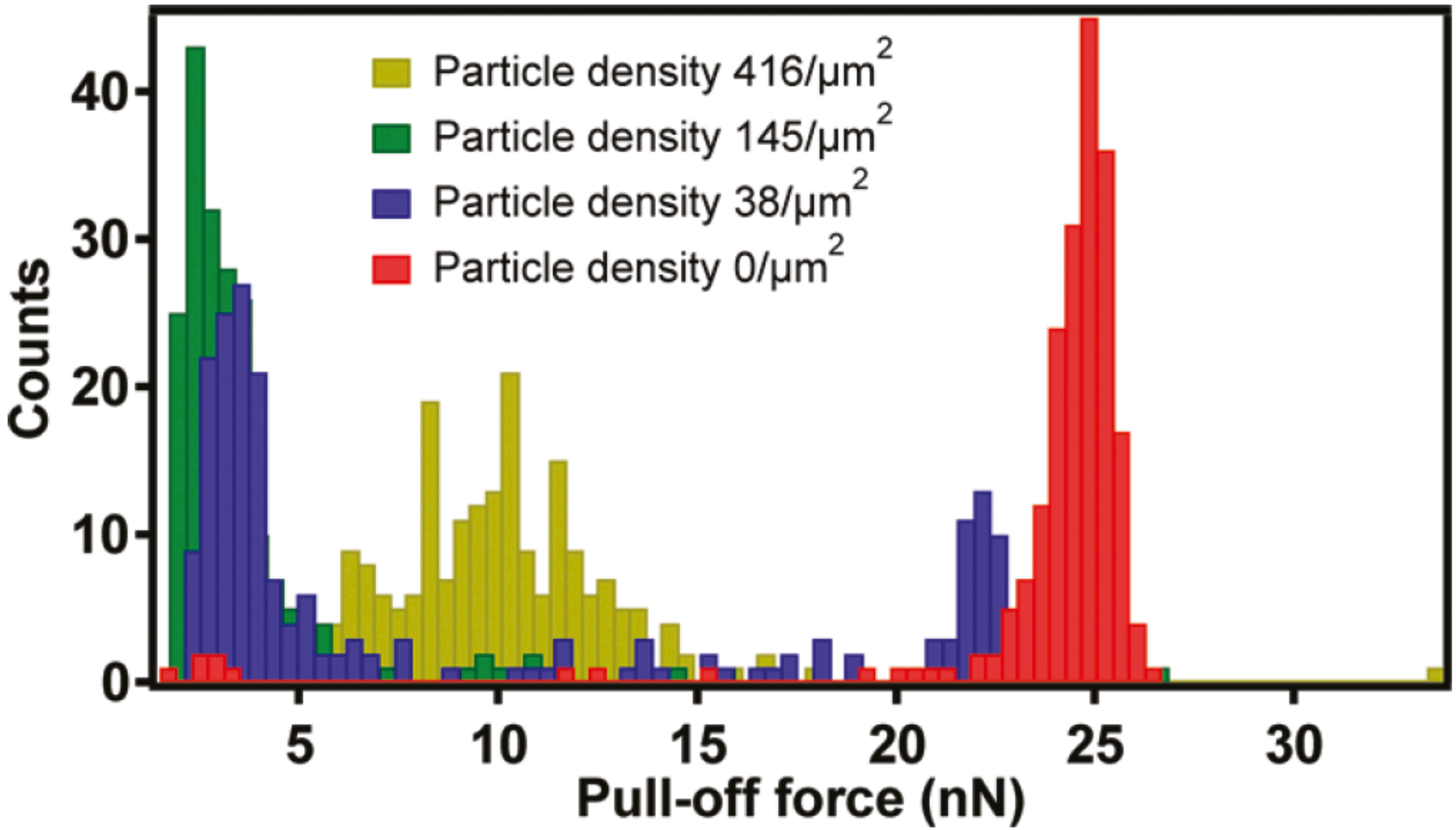


Adhesion mapping procedure: 200 pull-off measurements over a 20 μm x 20 μm area

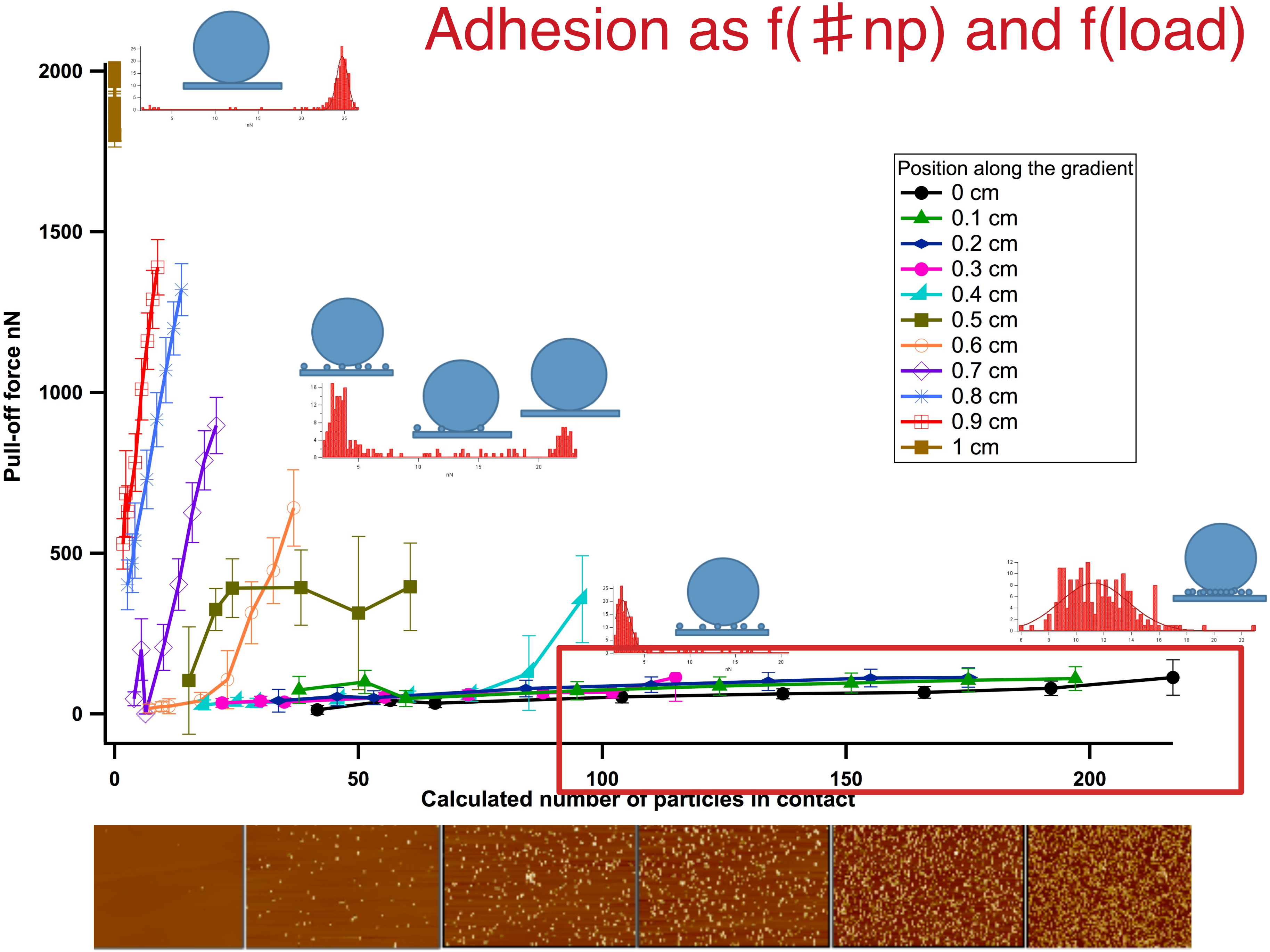




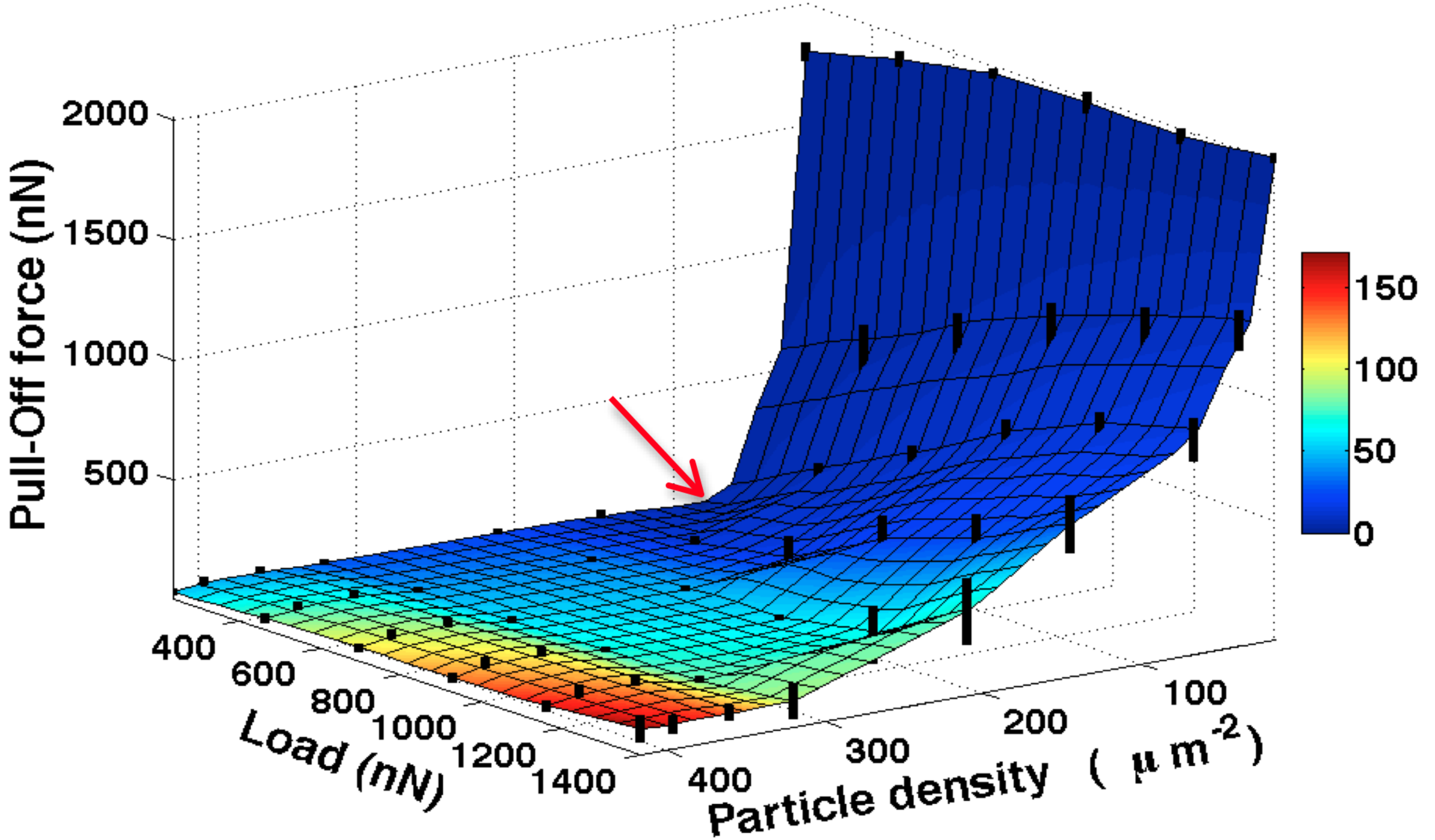
Pull-off force distributions at various particle densities



Adhesion as f(#np) and f(load)



Effect of load and particle density on the pull-off force:
A minimum is reached at a combination of particle density and load that lead to a minimum number of particles under the sphere that still prevent contact with the silicon substrate.



Controlling adhesion force by means of nanoscale surface roughness
Shivaprakash N Ramakrishna, Lucy Y. Clasohm, Akshata Rao, Nicholas D. Spencer, *Langmuir; 2011; 27 p 9972-9978*

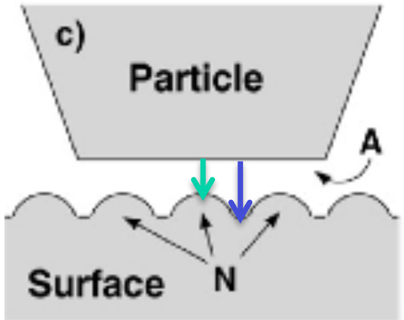
Calculated Van der Waals Force

For smooth end of the gradient

Sphere vs the flat surface, $F_{adh} = A_H R / 6H_0^2$

(Calculation yields 1420 nN, experimental = 1800 nN)

For rough side of the gradient



$$F_{adh} = \frac{A_H A}{6H_0^2}\left[\rho r + \frac{1}{\pi H_0 (1 + y_{max}/H_0)^3}\right].$$

Contact part

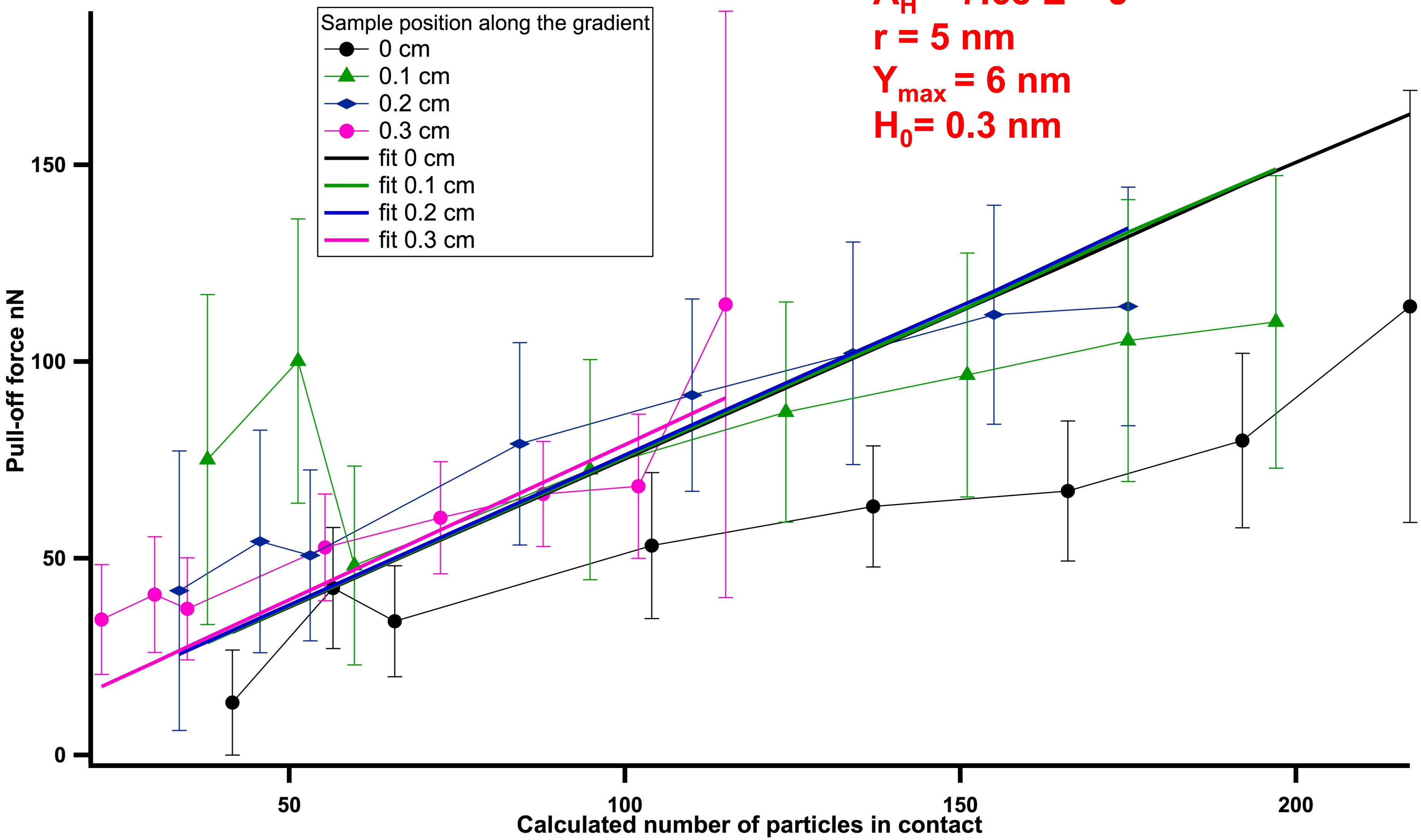
Non contact part

where A_H is the Hamaker constant, R is the radius of the adhering particle, H_0 is the equilibrium distance, r is the radius of the asperity on the surface, and y_{max} is the height of the asperity.

A is flattened part of colloid probe (from Hertz Eq.)
A_H = 7.68 E^{-20} J (from Lifshitz Eq.)
r = 5 nm (asperity radius)
Y_{max} = 6 nm (max asperity height)
H_0=0.2 - 0.3 nm

J. Katainen, M. Paajanen, E. Ahtola , V. Pore , J. Lahtinen
Journal of Colloid and Interface Science 304 (2006) 524–5

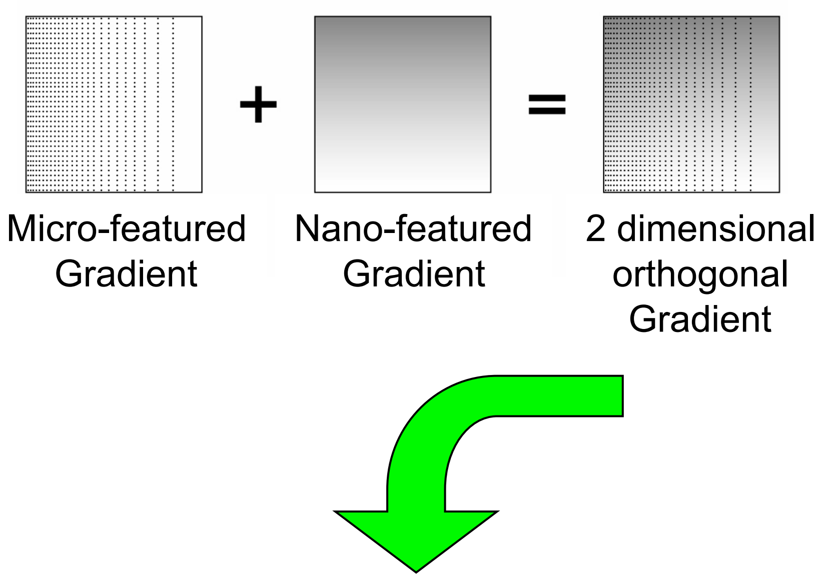
Calculation and Exptl. data



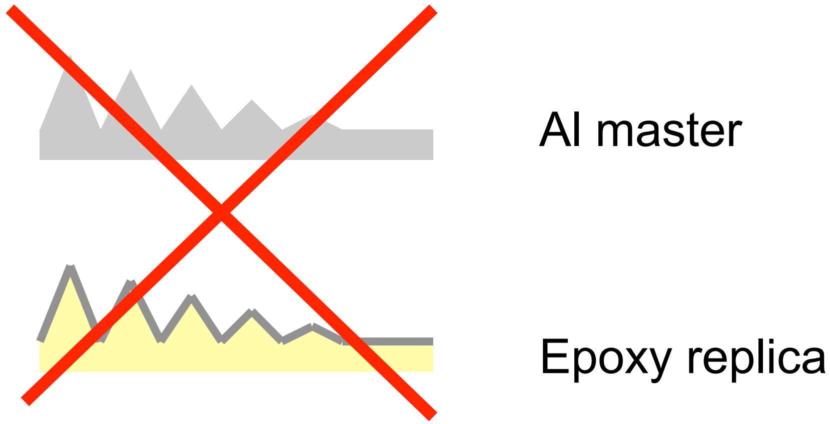
A_H = 7.68 E^{-20} J
r = 5 nm
Y_{max} = 6 nm
H_0= 0.3 nm

Combining Microscopic and Nanoparticle Gradients

Combined Micro-, Nano-Morphology Gradients



Sinter temperature too high for:



A. Substrate material replaced by temperature resistant material

B. Different nanoparticles that can be attached at lower temperatures

Combined Gradients

A

Epoxy can be replaced by temperature resistant material

→ Ceramic materials are suited most

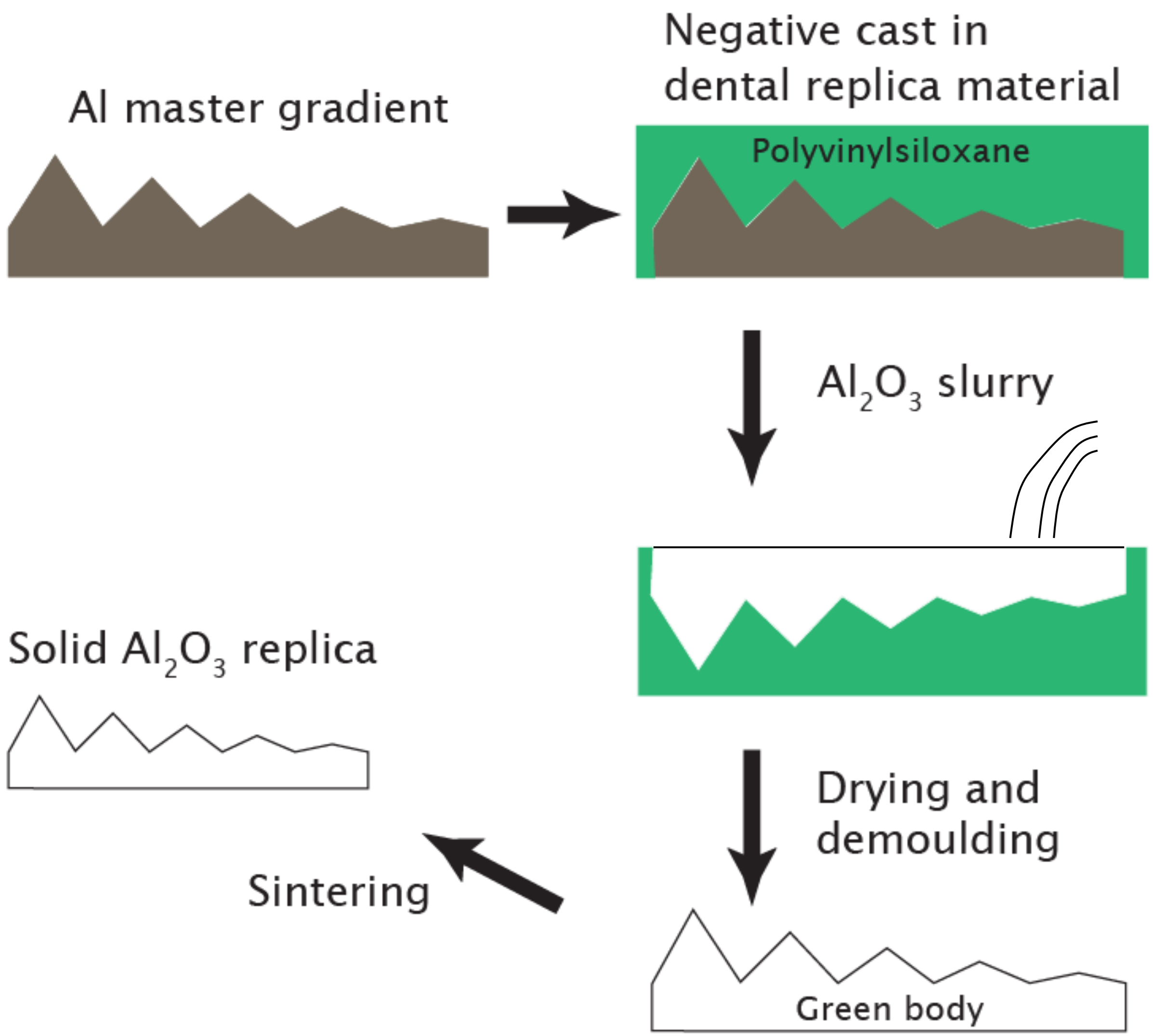
Pros	Cons
👍 well established shaping processes	👎 many parameters to test (material, powder grain size, shaping technique, T_{SINTER} etc.)
👍 easy and fast applicable	👎 grains add additional roughness
👍 interesting for other high T experiments	
👍 chemical inert oxide surface	

Alumina: high availability, well established microfabrication techniques

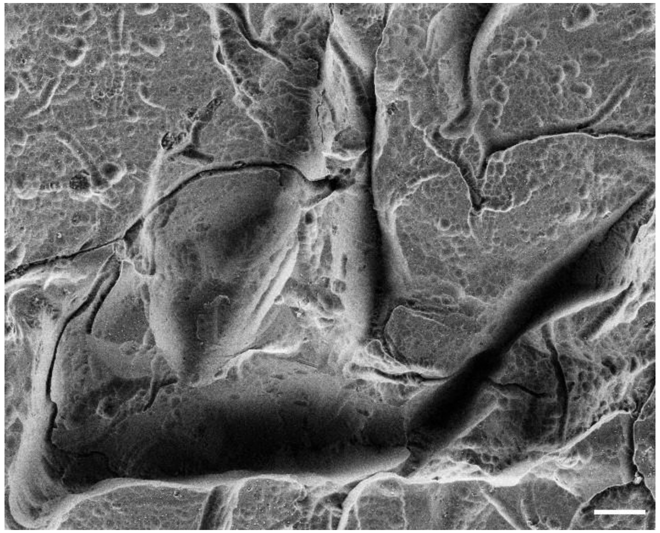
→ Slurry casting[1]: simple process, shrinkage while drying, cracks possible

1) Schönholzer U.P., Microfabrication of Ceramics (2000), PhD Thesis, 13473, ETH Zurich

Alumina Replica Technique

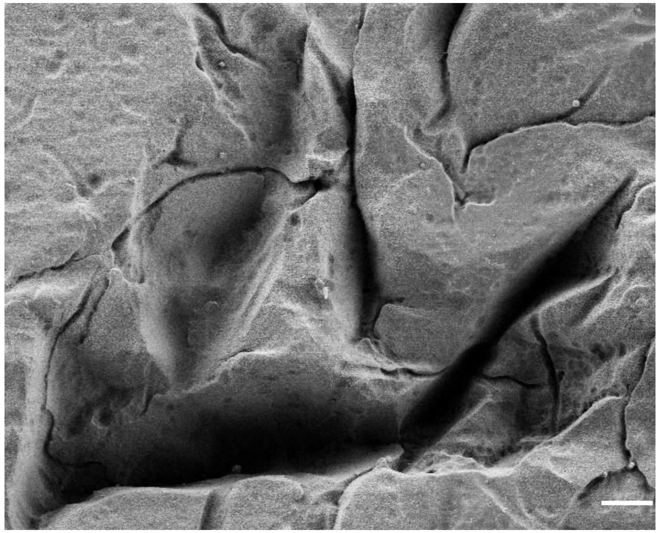


Alumina Replica Technique



Al Master

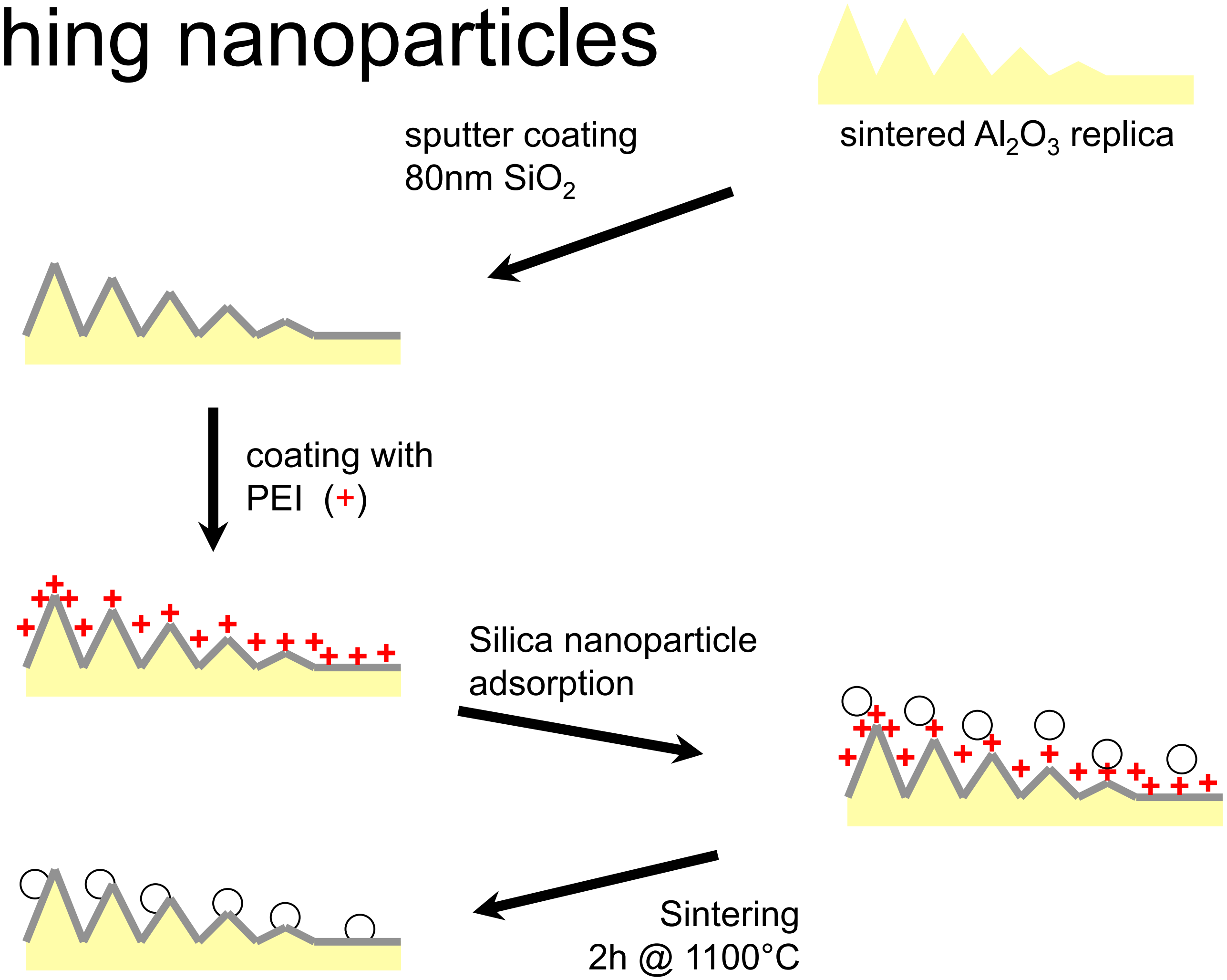
Alumina Replica



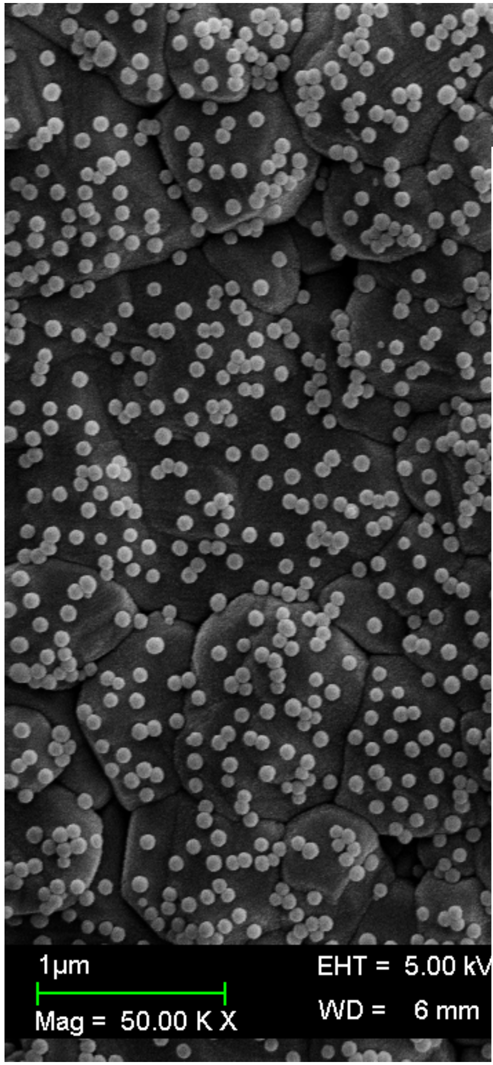
Epoxy Replica

Alumina Replica Technique

Attaching nanoparticles

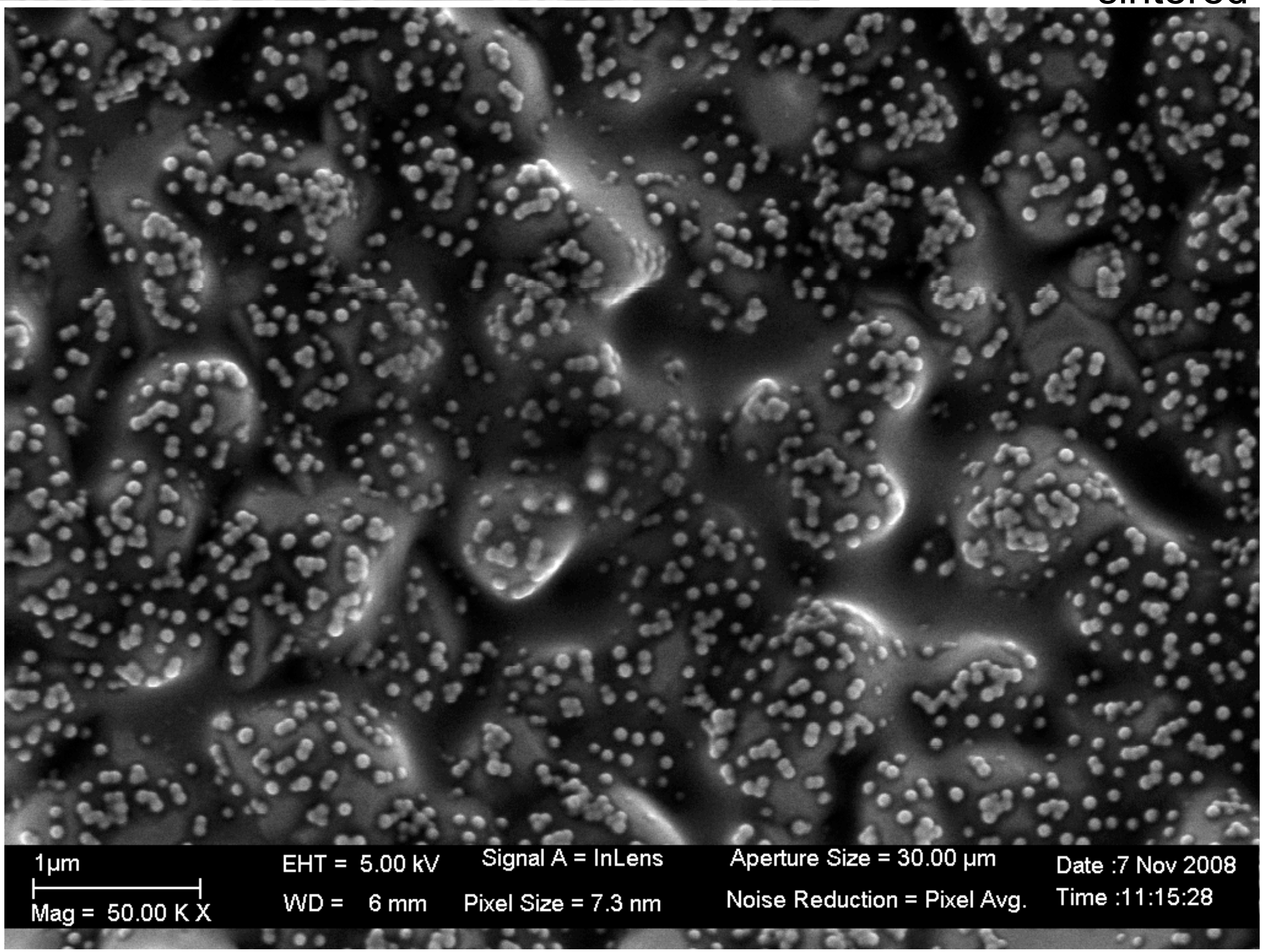


Alumina Replica Technique



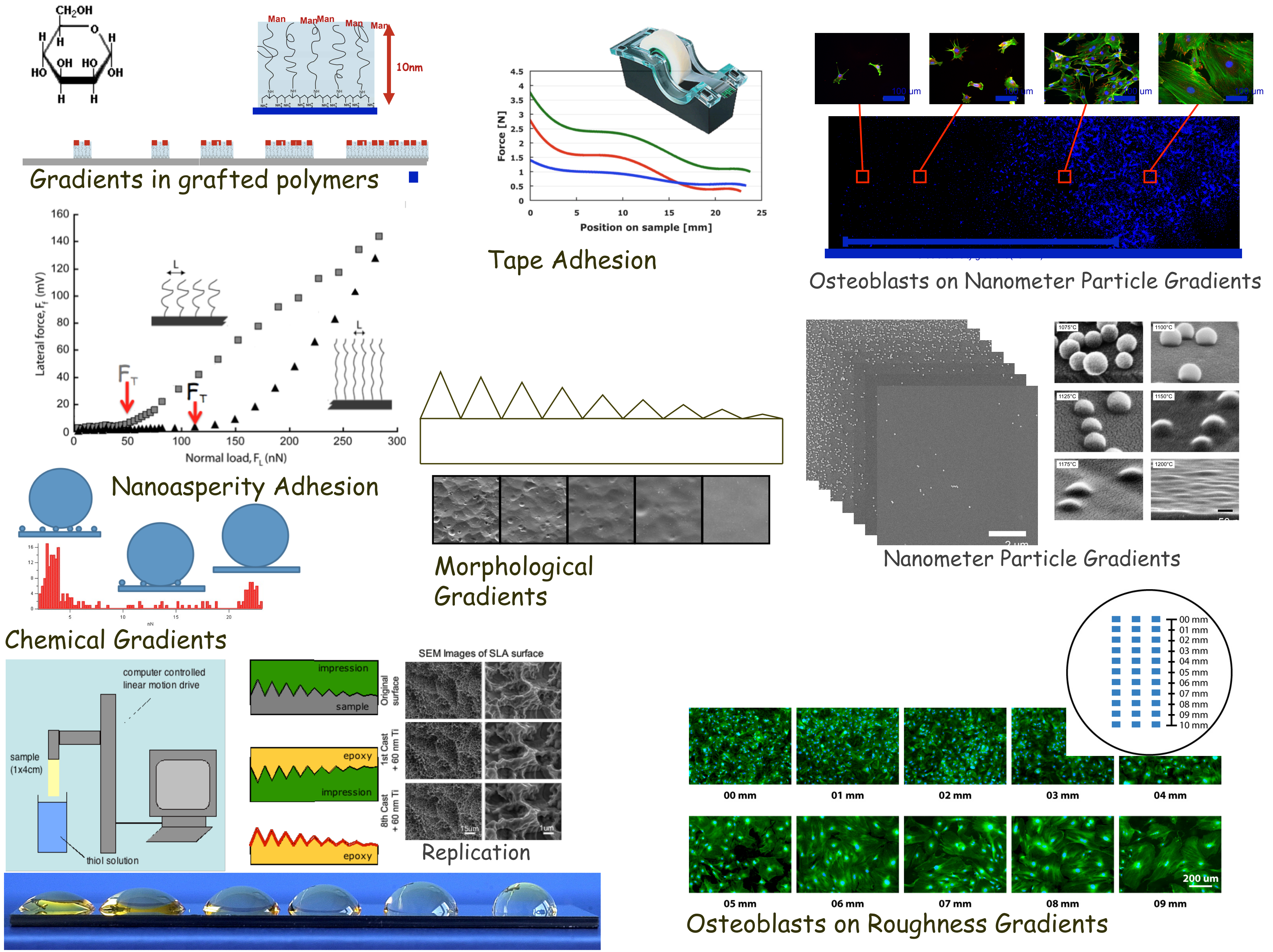
unsintered

sintered



Chemical Gradients: The Movie

Sara Morgenthaler
Manfred Heuberger


Gradients in grafted polymers
CH_2OH
Man
10nm
Nanoasperity Adhesion
Lateral force, F_f (mV)
Normal load, F_L (nN)
F_T
Tape Adhesion
Force [N]
Position on sample [mm]
Osteoblasts on Nanometer Particle Gradients
Morphological Gradients
Nanometer Particle Gradients
1075°C
1100°C
1125°C
1150°C
1175°C
1200°C
Chemical Gradients
computer controlled linear motion drive
sample (1x4cm)
thiol solution
impression
sample
epoxy
SEM Images of SLA surface
Original surface
1st Cast + 60 nm Ti
8th Cast + 60 nm Ti
Replication
00 mm
01 mm
02 mm
03 mm
04 mm
05 mm
06 mm
07 mm
08 mm
09 mm
10 mm
200 um
Osteoblasts on Roughness Gradients

Laboratory for Surface Science and Technology

Aletsch Glacier, August, 2011