UNIVERSITÄT SIEGEN

Atomic Force Microscopy

Morphology and Surface Analysis Beyond Topography

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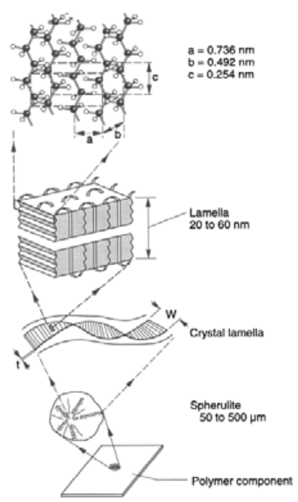
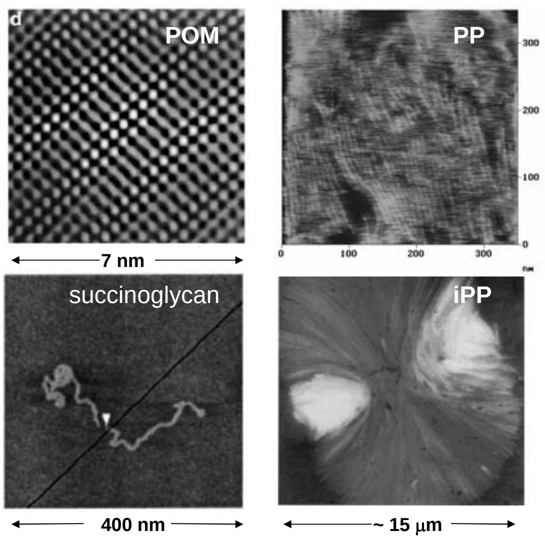
Polymer morphologies by AFM: structural hierarchy





Objectives

Introduction: Atomic force microscopy & polymers

- **– Polymer morphologies by AFM**
- **– AFM imaging principles and materials contrast**

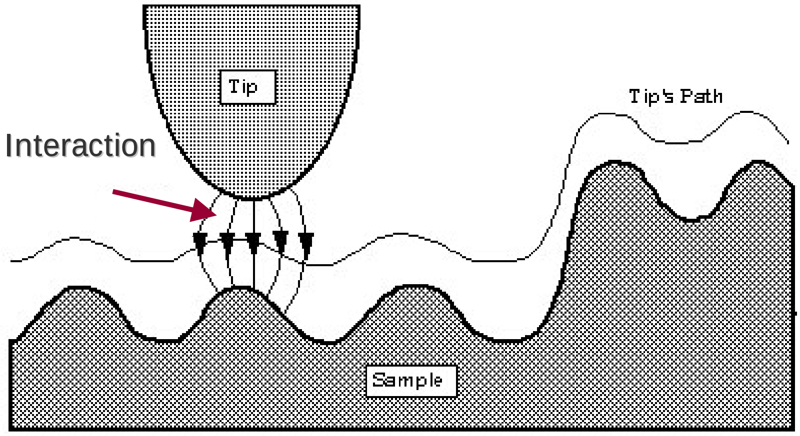
AFM beyond topography imaging

- **– Force – displacement curves: adhesion**
- **– Force – displacement curves: mechanical properties**

Outlook: new imaging modes

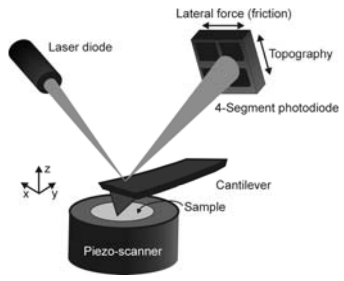
Scanning probe microscopy

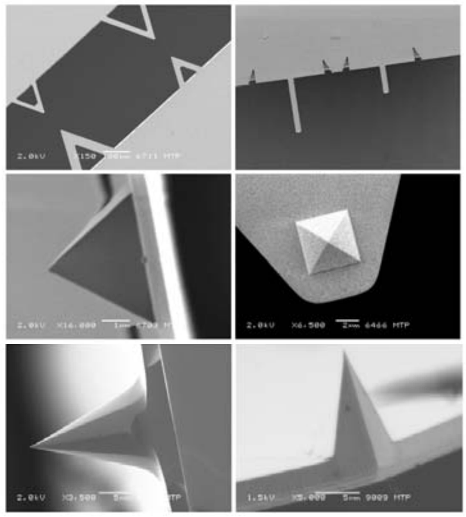
Surface profile by scanning the surface



Introduction: Atomic force microscopy in general

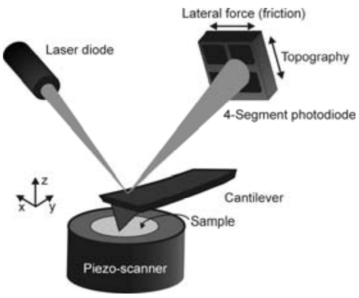
AFM

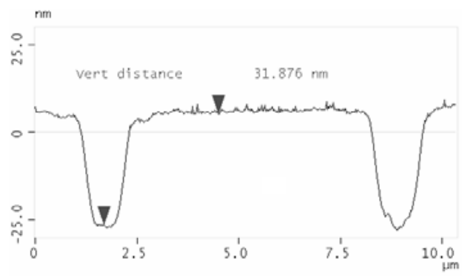


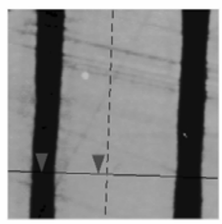


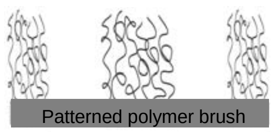
- Ultrasharp, ultrasensitive point probe
- Nanometer to 100 μm x,y displacement
- Various media and broad range of environmental conditions

Introduction: Atomic force microscopy in general







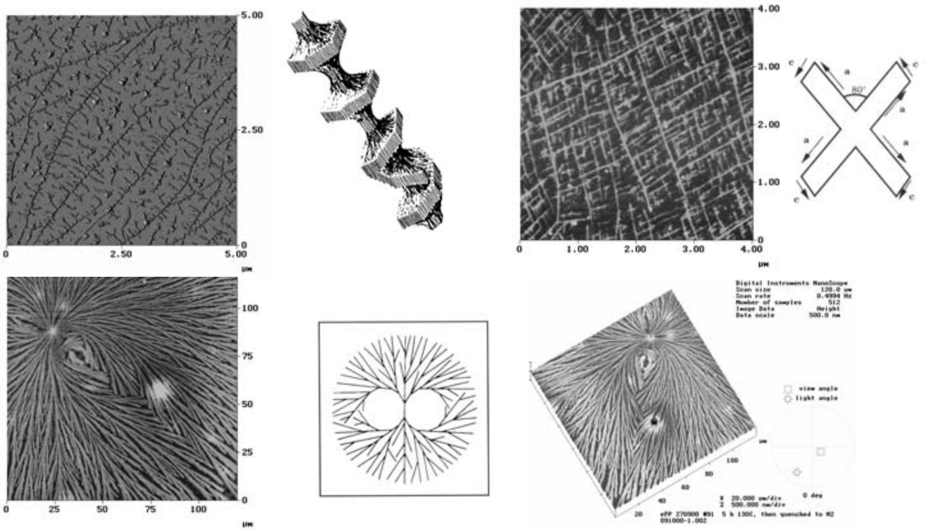


- constant force mode imaging:
  height information

Force-feedback

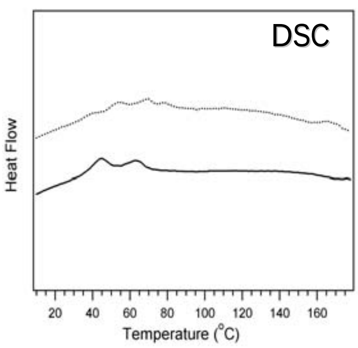
Introduction: Atomic force microscopy & polymers

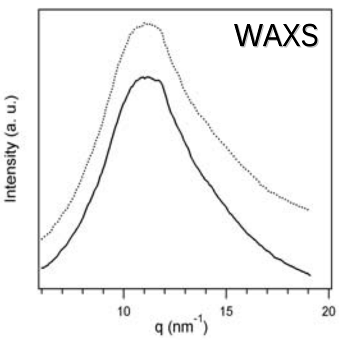
Polymer morphologies by AFM: isotactic polypropylene



Elastomeric Polypropylene

ether soluble fraction; < 1 - 2 % crystallinity





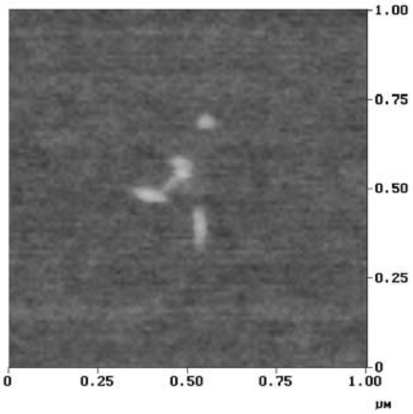
H. Schönherr, W. Wiyatno, J. Pople, C. W. Frank, G. G. Fuller, A. P. Gast, R. M. Waymouth Macromolecules 2002, 35, 2654-2666.

Elastomeric Polypropylene

ether soluble fraction

< 1 - 2 % crystallinity

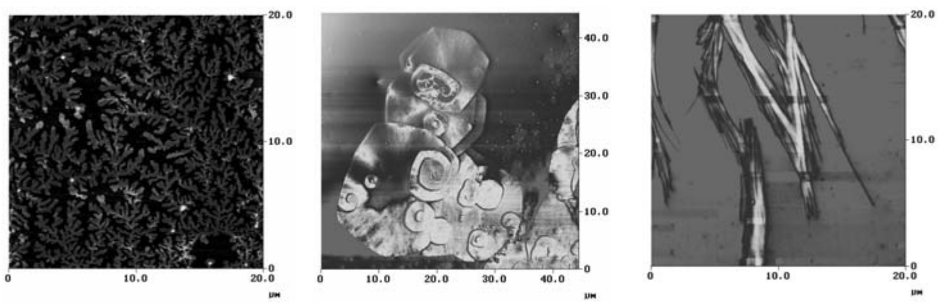
T = 40°C



H. Schönherr, R. M. Waymouth, C. W. Frank Macromolecules 2003, 36, 2412-2418

AFM imaging principles and materials contrast

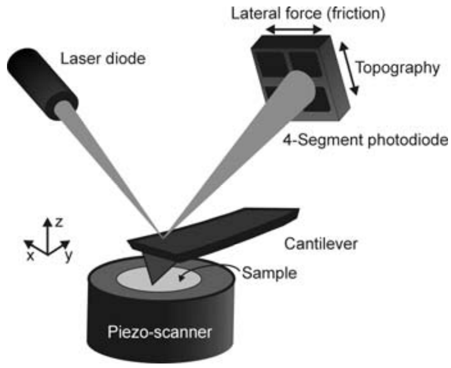
Polymer morphologies by AFM: poly(ethylene oxide)



- Metrology: Quantitative profilometry !
- High resolution microscopy !
- Free sample surface, many media and environmental conditions
- ***Materials contrast – quantitative property determination*?**

AFM imaging principles and materials contrast

Contact mode AFM



• tip sample force measured via cantilever deflection

• constant force mode imaging: height information

AFM imaging principles and materials contrast

Contact Mode AFM

Feedback loop keeps a pre-set deflection of cantilever (force) constant by adjusting the piezo length in z direction:

Iso-force image = "height" (assume: same compliance)

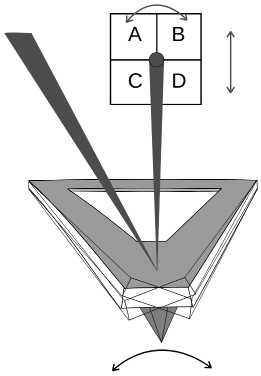
Deflection image (error signal) = outlines of features

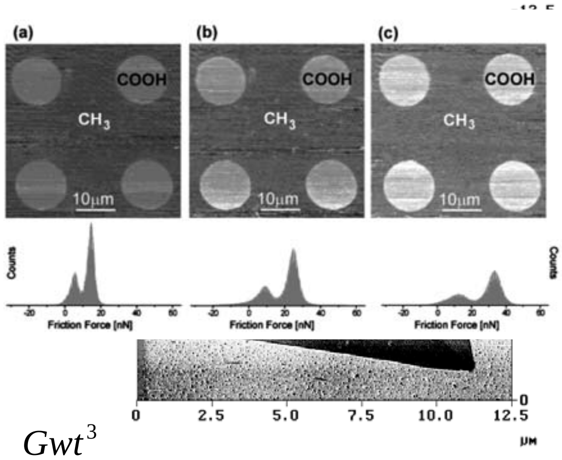
Friction image = materials contrast

Intermolecular Forces (force - distance curves)

AFM imaging principles and materials contrast: **friction**

AFM imaging principles and materials contrast



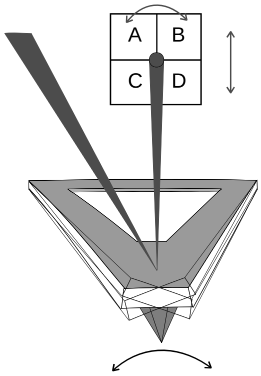


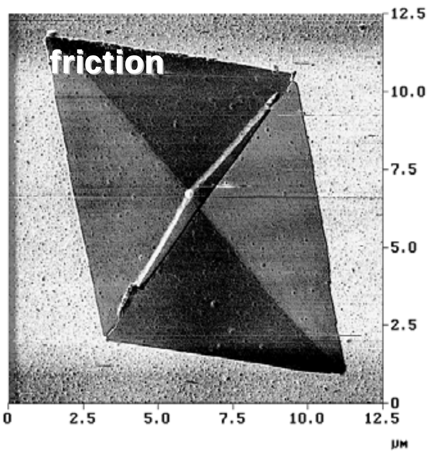
Single beam lever: $$k_L = \frac{k_\varphi}{h^2} = \frac{Gwt^3}{3lh^2}$$

with cantilever length *l*, cantilever thickness *t*, cantilever width *w*, tip height *h*, Young's modulus *E*, Poisson's ratio ν, and shear modulus $G = E / 2(1+\nu)$ Landau, L. D.; Lifshitz, E. M. *Theory of Elasticity*. Pergamon Press: Oxford, 1986; Vol. 7.

AFM imaging principles and materials contrast: **friction**

AFM imaging principles and materials contrast





Single beam lever: $$k_L = \frac{k_\varphi}{h^2} = \frac{Gwt^3}{3lh^2}$$

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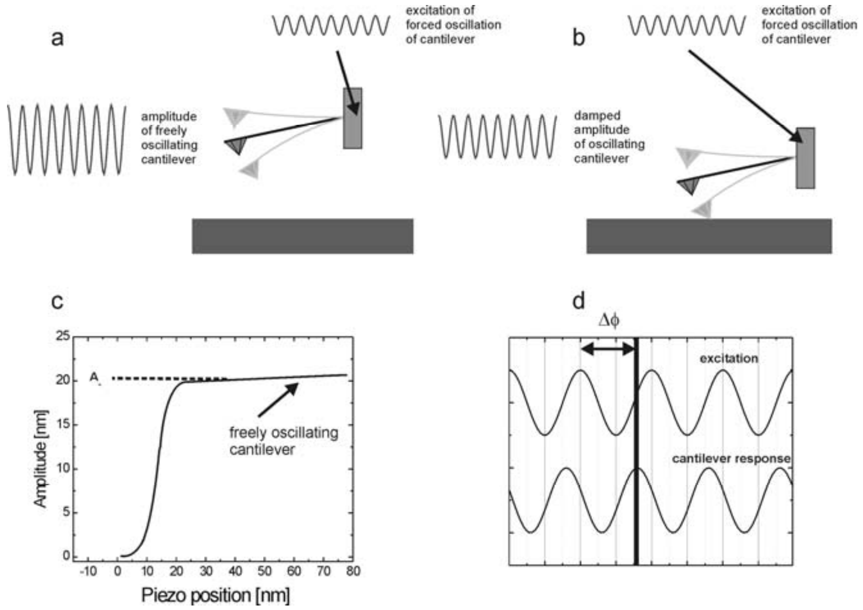
Tapping / Intermittent Contact Mode AFM



~ no shear forces

- materials contrast in phase signal

AFM imaging principles and materials contrast

Tapping / Intermittent Contact Mode AFM

Feedback loop keeps a pre-set amplitude constant by adjusting the piezo length in z direction:

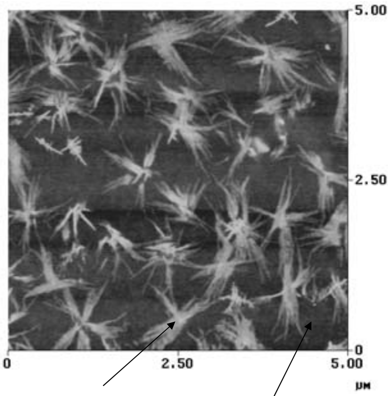
Iso-amplitude image = "height" (assume same damping characteristics)

Amplitude image = outlines of features

Phase image = materials contrast (energy dissipation)

AFM imaging principles and materials contrast: **phase**

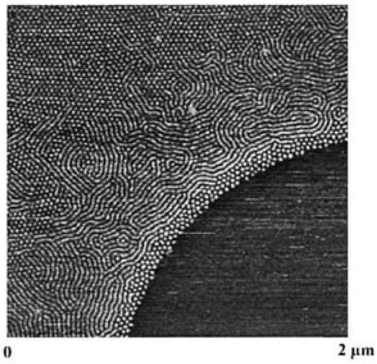
Elastomeric PP



crystalline phase

amorphous phase

Block copolymer



Materials properies ???

Polystyrene-b-polyisoprene-b-polystyrene

height phase height phase

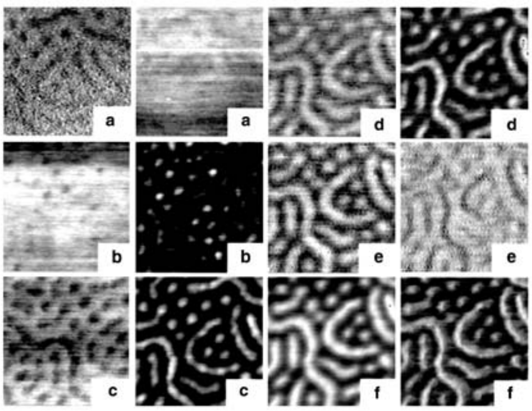
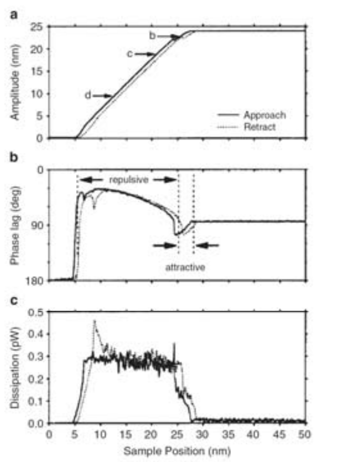


Fig. 3.57 Height (*left*, z-scale 8 nm) and phase (*right*) images (350 × 350 nm^2) of solution cast films of PS-b-PI-b-PS. The data were acquired using the following setpoint ratios A_r: (**a**) 0.99, (**b**) 0.95, (**c**) 0.70, (**d**) 0.50, (**e**) 0.40, (**f**) 0.20. With kind permission from Springer Science+Business Media from [130]. Copyright 1998. Springer

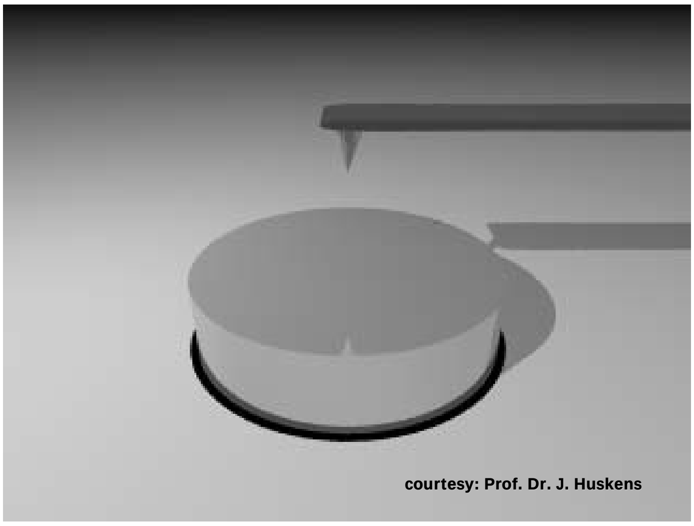
[130] Pickering JP, Vancso GJ (1998) Polym Bull 40:549–554



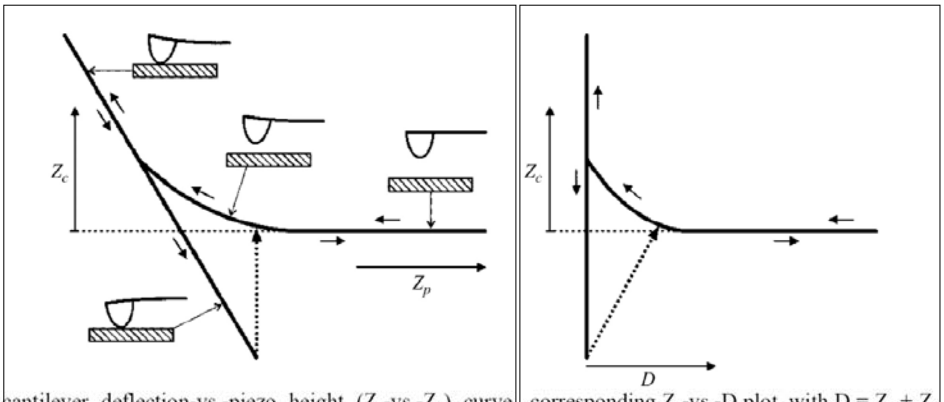
Cleveland JP, Anczykowski B, Schmid AE, Elings VB (1998) Energy dissipation in tapping-mode atomic force microscopy. Appl Phys Lett 72 (20):2613–2615

Phase contrast may depend on setpoint ratio, contrast inversion may occur.

AFM Force - Displacement Measurements



AFM Force - Displacement Measurements

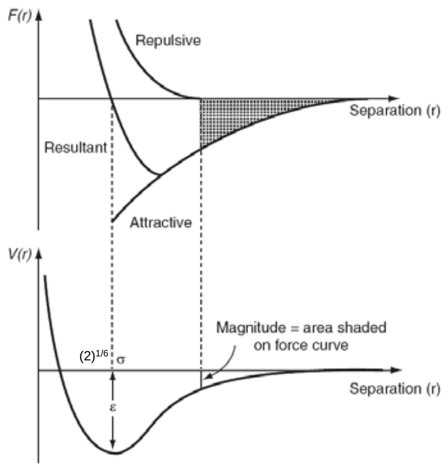


cantilever deflection-vs.-piezo height (Z_c-vs.-Z_p) curve | corresponding Z_c-vs.-D plot, with $D = Z_c + Z_p$

$$F = k_s \, \Delta Z_C$$

Butt HJ, Cappella B, Kappl M (2005) Surf Sci Rep 59:151–152

Forces between atoms



$$V(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

Lennard – Jones 6-12 potential

Forces between bodies

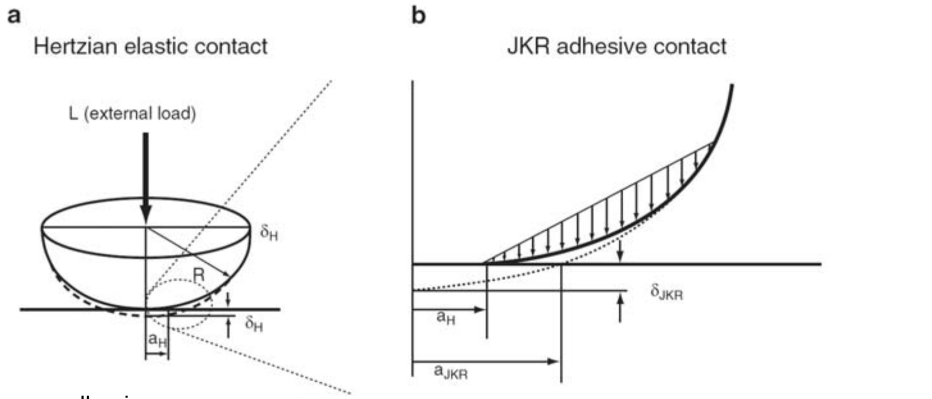
van der Waals interaction energies between macroscopic bodies

	Molecule	Sphere	Surface	Cylinder (↑)
Molecule	$-\frac{C}{D^6}$		$-\frac{\pi C\rho}{6D^3}$	
Sphere		$-\frac{AR'}{6D}$	$-\frac{AR}{6D}$	
Surface			$-\frac{A\ell^2}{12\pi D^2}$	
Cylinder (↑)				$-\frac{A\ell R'^{1/2}}{12\sqrt{2}D^{3/2}}$
Cylinder (→)				$-\frac{A(R_1R_2)^{1/2}}{6D}$

$R' = R_1R_2(R_1 + R_2)$
$A = \pi^2 C\rho_1\rho_2 \simeq 10^{-19}$ J = Hamaker constant
ℓ = length

J. Israelachvili: Intermolecular and Surface Forces, Acad. Press, London, 1992.

Continuum contact mechanics



no adhesion

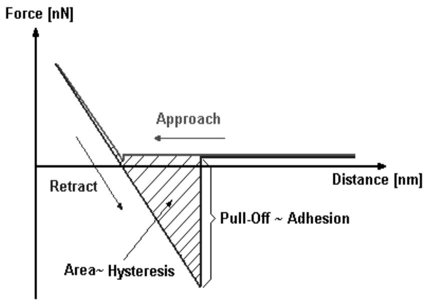
$$a^3{}_{\mathrm{JKR}} = \frac{R}{K}\left[L + 3\pi W_{132}R + \left(6\pi W_{132}RL + (3W_{132}\pi R)^2\right)^{1/2}\right]$$

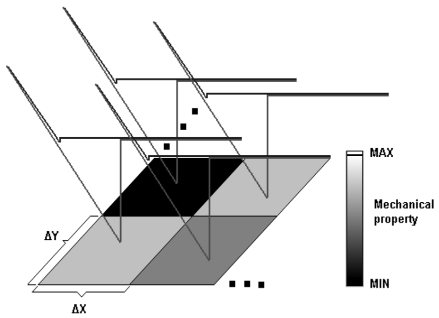
pull-off force $L_{\mathrm{pf}} = -\frac{3}{2}(W_{132}\pi R)$

AFM Force - Displacement Measurements

- **Attractive and repulsive intermolecular forces**
- **Adhesion**
- **Elastic properties**
- **Plastic behavior** **etc.**

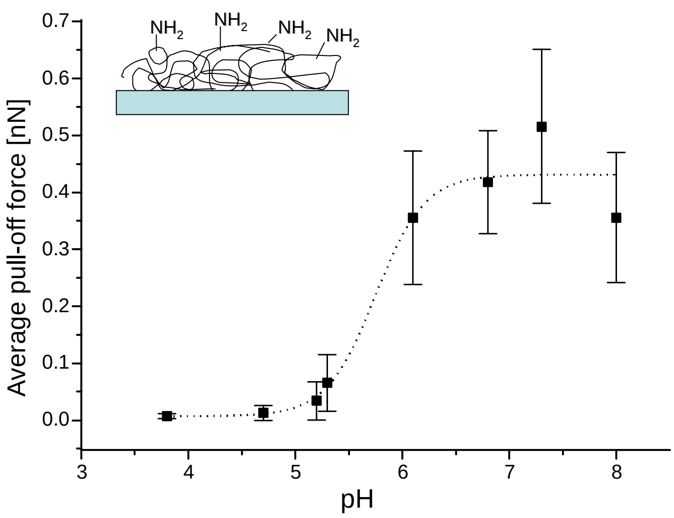
Force data acquisition

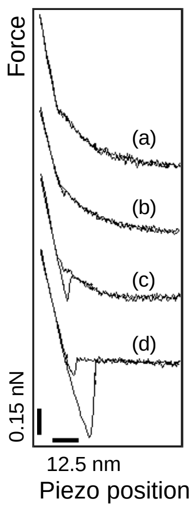




One f-d curve per pixel: “Force volume (FV) imaging”

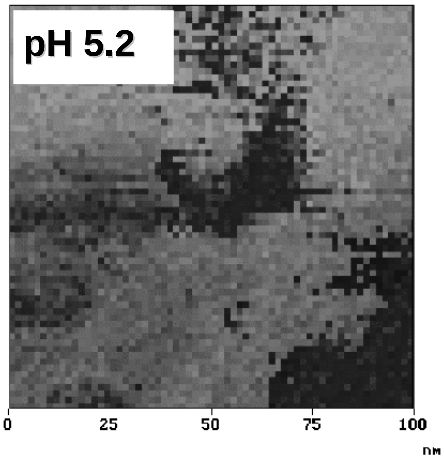
Plasma polymerized allylamine films:
Pull-off forces with OH tips at different pH

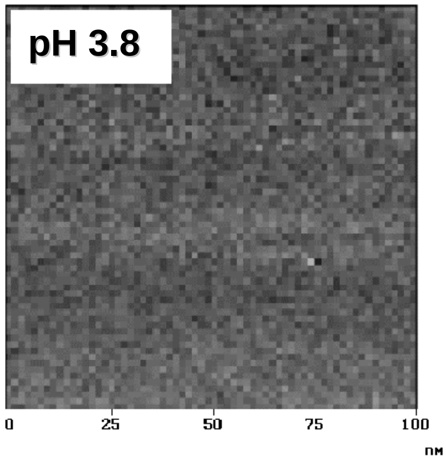




H. Schönherr, M. T. van Os, R. Förch, R. B. Timmons, W. Knoll, G. J. Vancso Chem. Mater. 2000, 12, 3689-3694

Adhesion images of plasma polymerized allylamine film (OH tip)





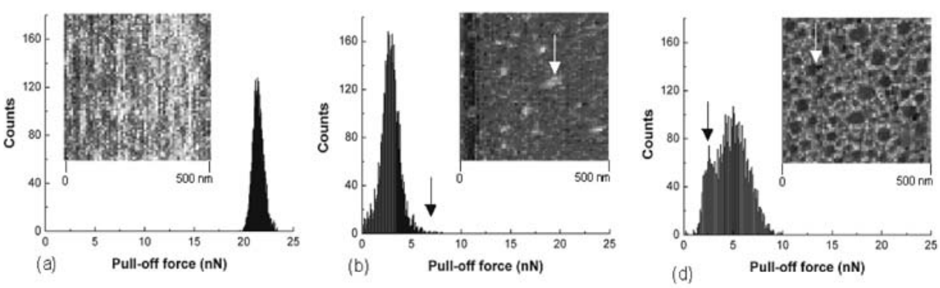
bright 0.0 nN, dark - 2.0 nN **bright 0.0 nN, dark - 0.1 nN**

H. Schönherr, M. T. van Os, R. Förch, R. B. Timmons, W. Knoll, G. J. Vancso Chem. Mater. 2000, 12, 3689-3694

Hydrophobic recovery of partially oxidized poly(dimethyl siloxane) PDMS

(60 minutes exposure) : Adhesion

unexposed PDMS **0.1 days recovery** **40 days recovery**



Histograms of pull-off forces and corresponding adhesion images acquired with OH-terminated tip in water. The color scales are scaled from dark (low pull-off force) to bright (high pull-off force).

Blend of poly(methyl methacrylate) and polybutadien

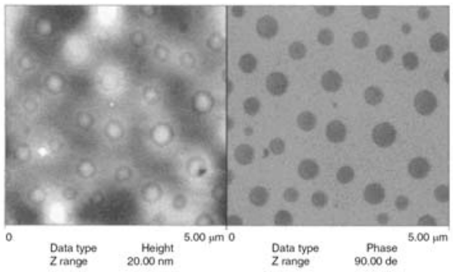
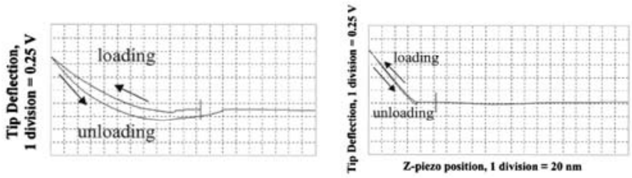
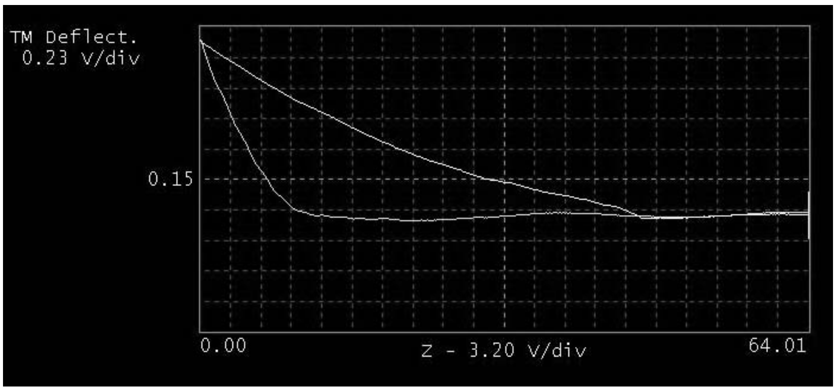


Fig. 3.60 **(a)** Tapping mode AFM height image (*left*) and phase image (*right*) for PMMA – PB 80 – 20 blend after 24 h of ambient conditioning [134]. Contrast variations are 20 nm from *white to black* for the height images and 90° from *white to black* for the phase image. Reprinted with permission from [134]. Copyright 2000. American Chemical Society

Raghavan D, VanLandingham M, Gu X, Nguyen T (2000) Langmuir 16:9448–9459



AFM Nanoindentation



Deflection: V to nm to µN

Deflection sensitivity

Cantilever elastic constant

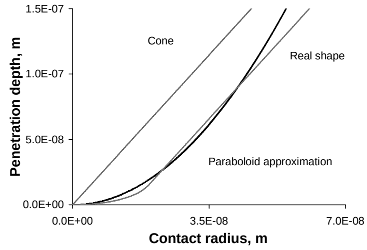
Piezo displacement: V to nm

Piezo sensitivity

Courtesy: Dr. Davide Tranchida

Contact mechanics models, e.g. Sneddon's model

Relationship between applied load and penetration depth in the case of:

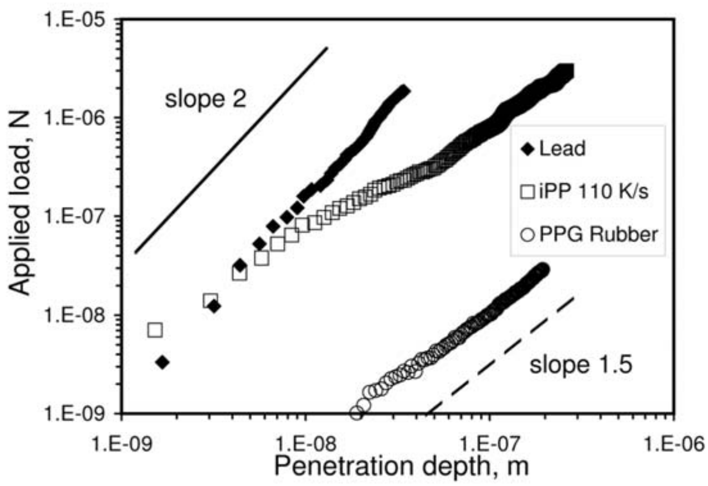


- Flat punch $F \propto p$
- Cone $F \propto p^2$
- Paraboloid $F \propto p^{1.5}$ $\quad F = \dfrac{4E}{3(1-\nu^2)}\left(2qp^3\right)^{1/2}$
- Sphere $p = \dfrac{1}{2} a \log \dfrac{R+a}{R-a}$ $\quad F = \dfrac{\mu}{1-\nu}\left\{\left(a^2 + R^2\right)\log \dfrac{R+a}{R-a} - aR\right\}$

Sneddon IN Int. J. Eng. Sci. 1965, 3, 47

Courtesy: Dr. Davide Tranchida

Elastic contact



Plastic

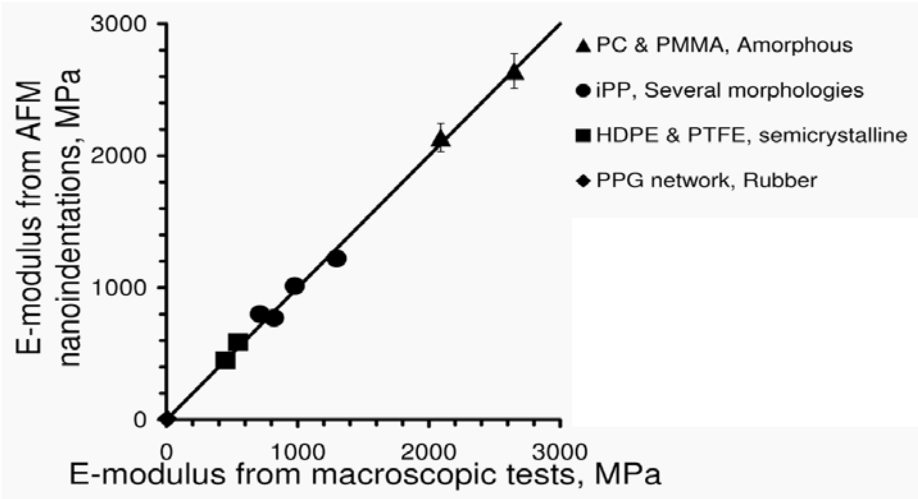
$$F = \frac{Eh^2}{\left[\frac{1}{\sqrt{\pi}\tan\gamma}\sqrt{\frac{E}{H}} + \frac{\varepsilon}{\beta}\sqrt{\frac{\pi}{4}}\sqrt{\frac{H}{E}}\right]^2} f(n)^2$$

elastic

$$F = \frac{4}{3\left(1-\nu^2\right)} E\sqrt{R}\, h^{3/2}$$

Courtesy: Dr. Davide Tranchida

Accuracy of the technique



Tranchida D., Piccarolo S., Soliman M. Macromolecules 2006, 39, 4547

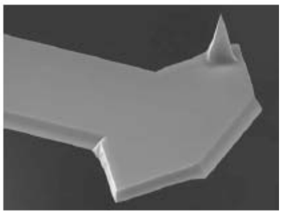
Problem with adhesion and indentation mapping:

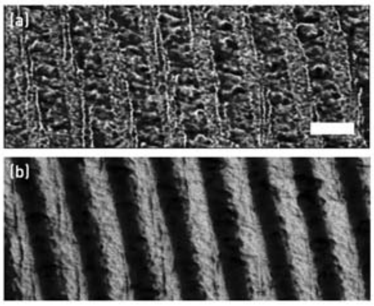
Slow data acquisition rates.

Outlook

Rapid measurements of adhesion force data and mechanical properties:

HarmoniX™ Nanoscale
Material Property Mapping





Simultaneously collected Adhesion (a) and Stiffness (b) maps of PET multilayer. Length of scale bar is 200 nm.

Torsion during tapping mode: torsional and flexural motion are decoupled and adhesion and stiffness data are extracted; oscillations vary between 2 to 10 nm amplitudes.

Each cantilever must be calibrated with a reference sample, does not work in liquid.

O. Sahin, C. Su, S. Magonov, C. F. Quate, and O. Solgaard, “An atomic force microscope tip designed to measure time-varying nanomechanical forces” Nature Nanotechnology, 2, 507 (2007)

Outlook

Rapid measurements of adhesion force data and mechanical properties:

During intermittent contact mode imaging, the cantilever deflection is determined, the **peak force** is measured.

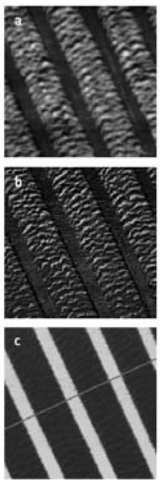
~ FV imaging at 2 kHz

z-travel distance can be adjusted to up to 150 nm

Height

Adhesion

Modulus

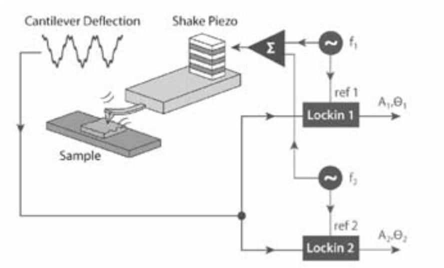


Outlook

Rapid measurements of adhesion force data and mechanical properties:

Dual AC mode

Overtones are also excited and amplitudes may contain additional information.



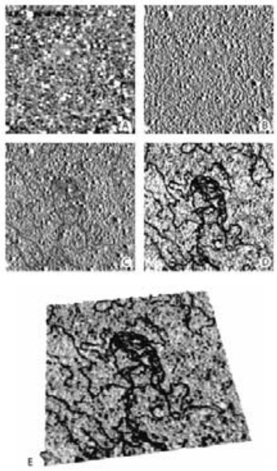
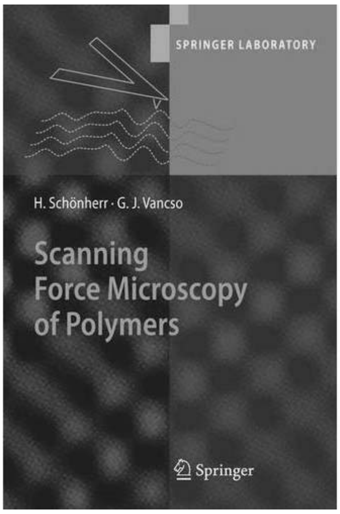


Figure 5: (A) topography, (B) fundamental amplitude, (C) fundamental phase, (D) bimodal Dual AC second mode amplitude of DNA, 750nm scan. (E) Second mode amplitude data overlaid on rendered AFM topography.

Acknowledgement: Dr. Davide Tranchida



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