Nanomechanical Probing With Scanning Force Microscopy

V. V. Tsukruk*, V. V. Gorbunov, Iowa State University
*vladimir@iastate.edu

Introduction

Highly localized probing of surface nanomechanical properties with a submicron resolution can be accomplished with scanning probe microscopy (SPM). The SPM ability to probe local surface topography in conjunction with mechanical, adhesive, friction, thermal, magnetic, and electric properties is unique.[1] However, the quantitative probing of the nanomechanical materials properties is still a challenge and only a few examples have been published to date.

In this note, we briefly review the latest developments in the nanomechanical probing of compliant materials (predominantly polymers). We solely focus our analysis of SPM-based approach in a so-called static force spectroscopy (SFS) mode. It is obvious that useful results can be obtained with classic nanoindentation technique and dynamic force spectroscopy (DFS). However, the first approach lacks the ability of micromapping surface mechanical properties with high spatial resolution (especially for the compliant materials considered here), and DFS still suffers from ambiguous interpretation. Finally, it is worth noting that this is not a comprehensive review with all developments meticulously listed but rather a brief sketch of recent findings from the authors' lab.

Basic Principles

SPM is a microcantilever-based experimental technique that uses a highly sensitive optical detection scheme to monitor a very minute (a small fraction of a nanometer) deflection of the microfabricated cantilever with a very sharp tip attached (Figure 1). Cantilever length is within 50 to 200 μm. The cantilever is usually tilted to assist optical detection. Typical tip radius is within 10 nm to 50 nm and its shape is, usually, close to paraboloid. For nanomechanical probing in the SFS mode, experimental data are collected in the form of so-called force-distance curve (FDC) that is, essentially, a cantilever deflection versus a piezoelement displacement during approach and withdrawal of the piezoelement.

A sketch of a typical FDC presented in Figure 2 displays four major regions for further analysis. Region I presents no tip-surface interaction and is assigned as a zero deflection range. Region II is related to non-contact interactions (measurements of weak surface forces, dominated by capillary forces in air, not of interest in this discussion) followed by a jump-in contact (important for the definition of contact point and initial indentation). Region III corresponds to the direct intimate contact of the SPM tip and the surface and is the base for the nanomechanical analysis. Region IV is the pull-off region during retracing of the cantilever and its returning to the zero deflection (measurements of adhesive forces, not discussed here).

The equation for the calculation of Young's modulus from the cantilever deflection data can be derived by using a two-spring linear model of the interacting cantilever and elastic surface (Equation 3).[2] Conditions for quasi-static equilibrium for this model are presented as the equality of cantilever spring forces exerted and elastic surface response:

$$k_n \bullet z_{defl} = P(h) \qquad (1)$$

where $P(h)$ is a surface response as a function of indentation depth, $h = z_{pos} - z_{defl}$, z_{defl} is a measured vertical deflection of the cantilever, z_{pos} is the vertical displacement of the piezoelement with attached cantilever chip (Figure 1), k_n is the normal spring constant of an AFM probe cantilever. By using the known relationship between $P(h)$ and materials parameters for the elastic contact, one can obtain analytical expressions for Young's modulus evaluation.[2-6]

A popular approximation frequently used for the analysis of the indentation data and calculation of Young's modulus from an overall FDC slope (Figure 2, region IV) is Sneddon's formula (Equation 2).[5] The Sneddon's model gives the relationship between dP/dh and Young's modulus, E, in the form:

$$dP/dh = (2\sqrt{A}/\sqrt{\pi}) \bullet E \qquad (2)$$

By estimating dP/dh and the contact area for the specific shape of the indentor (circular, pyramidal, and parabolic), one can evaluate the elastic modulus from Equation (2). For routine estimation of the elasticity modulus for small indentation depth, the Hertzian model of a sphere-plane contact is applied. For larger indentations, the Sneddon's model with parabolic tip and a plane surface contact (Figure 3) is used. The tip shape in the Sneddon model is described with equation $z = b \bullet x^2$, where b is a paraboloid focus. In the case of highly adhesive surfaces, the more complicated Johnson-Kendall-Roberts (JKR) model can be used.[6] For all models, Young's modulus is estimated from:

$$E = 3/4 \bullet (1-\nu^2)/(R^{1/2}) \bullet dP/d(h^{3/2}) \qquad (3)$$

where P is applied force for Hertzian and Sneddon's models. In the JKR model, the applied force is described with the additional tip-surface interaction due to adhesion in the contact zone.[2,6] The R in the equation (3) describes the tip radius in Hertzian and JKR models, or Sneddon's tip radius, $R = 1/(2 \bullet b)$, in Sneddon's model.

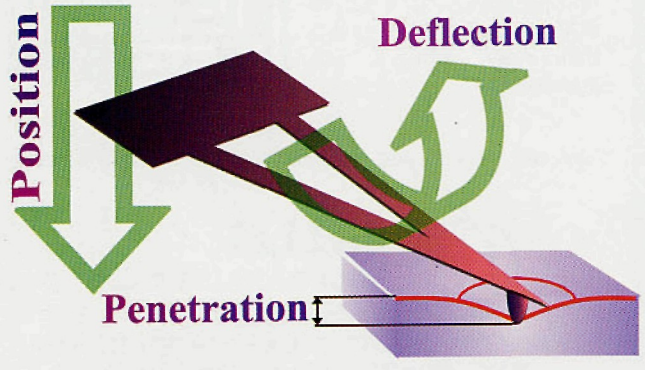


Figure 1. Scanning probe microscope cantilever in indentation mode.

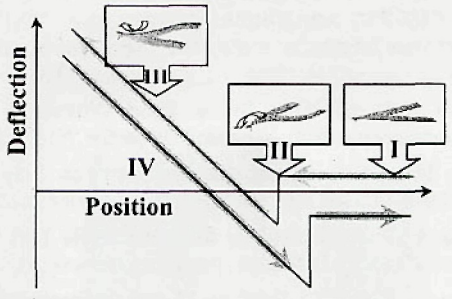
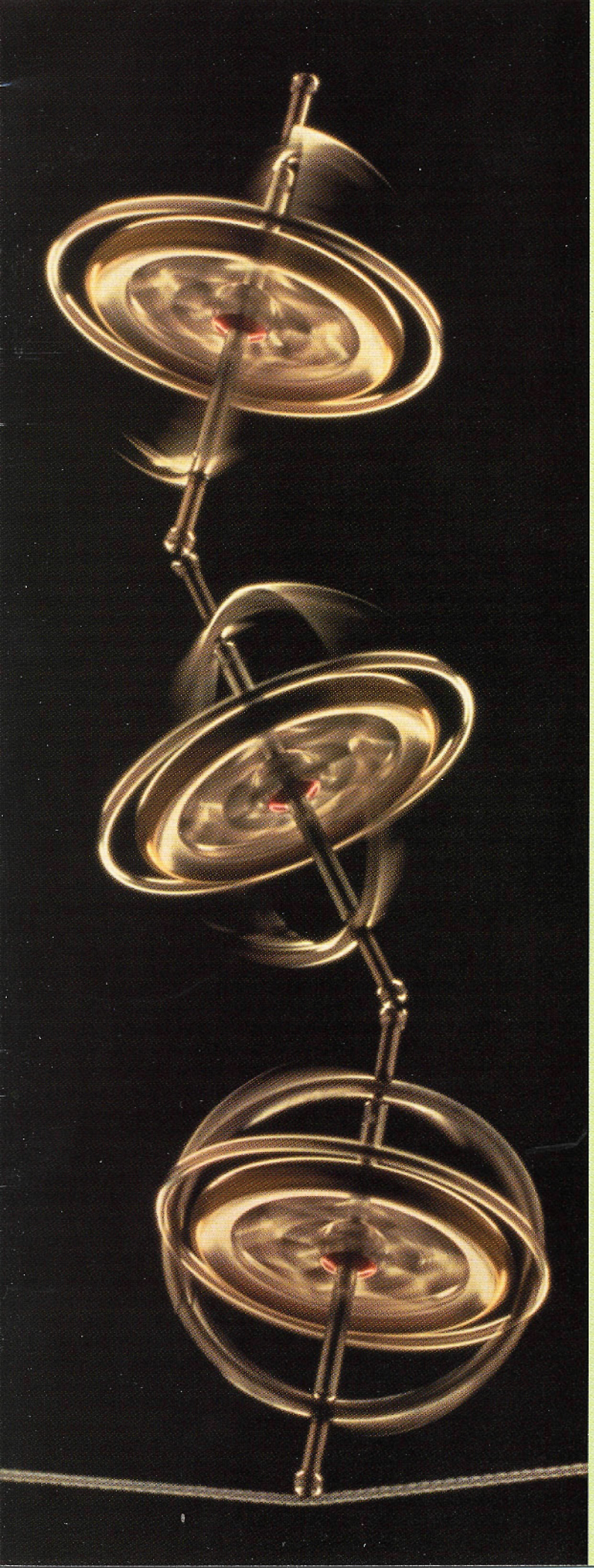


Figure 2. Force-distance curve (FDC) with major regions for nanomechanical analysis.

Continued on page 10



Getting All Your Detectors Working Together Can Be A Tough Balancing Act.

That's Where Emispec Comes In.

If balancing all components of your detectors has your head spinning, you should be talking to us.

You see, at Emispec Systems, Inc., we approach data acquisition differently. Instead of creating systems targeting one detector, we focus on integration. This concept can be applied equally to new and existing electron microscope installations. Core acquisition capabilities of our products include:

- **Digital scanning** for **STEM**.
- **Digital EDX** acquisition and analysis.
- **EELS** acquisition and analysis.
- **CCD** and **TV** imaging.

Integrated microscope control, imaging and spectroscopy allows automation of demanding experiments, such as **spectrum imaging**. Emispec enhances these capabilities with extensive on-line and off-line processing.

To find out how Emispec can help your lab keep in balance, visit our Web site today at **www.emispec.com.** See why we are fast becoming the leader in microscope detector technology solutions.

Emispec

Emispec Systems, Inc
2409 South Rural Road, Suite D
Tempe, Arizona 85282 USA
Phone: 480.894.6443 ▪ Fax: 480.894.6458
Web: www.emispec.com

thinking beyond the box™

Nanomechanical Probing With Scanning Force Microscopy

Continued from page 8

For the polymer systems considered here, we assume: $E_{tip} >> E_{polymer}$ (the elastic modulus of a silicon tip is 160 GPa versus 0.01 to 5 GPa for polymers).

These approaches were tested for a number of compliant materials and showed reasonable results for polymers ranging from very compliant rubbers with E = 2 MPa to hard glassy polymers with E = 5 GPa.[2,3] Below, we present some of these findings and summarize major technical steps to be taken to get practical and reliable results. Major issues in the SFS probing will be briefly discussed as well.

Selected results and practical advice

Young's modulus for amorphous elastomeric materials is virtually constant at indentation depths larger than 30 nm.[3] At small indentation depths (below 30 nm), unstable results are caused by the initial tip jump-in phenomenon. The approaches mentioned above give convergent results and close absolute values of Young's modulus as demonstrated for a wide range of polymeric materials. That is, the absolute value for polyisoprene rubber is determined to be within 2 to 3 MPa, that is close to its measured bulk modulus of 2 MPa. The Hertzian model systematically overestimates the absolute value of Young's modulus by 20 to 30% due to underestimation of the initial contact area (zero adhesive force assumption).[3] However, for routine calculations we usually select the Hertzian model, which is relatively simple, gives reliable results, and does not require additional measurements of surface energy. The Hertzian approximation works quite well for hard materials far from the glass transition temperature, as can be seen from Figure 4, where a Hertzian approximation is applied to stiff, epoxy-based composites. However, for compliant materials in a viscoelastic state, significant deviations from the Hertzian behavior are observed at higher normal loads as demonstrated for Kraton resins in Figure 4.

Micromapping of surface mechanical properties can be achieved by repeating FDC pixel-by-pixel within a selected surface area.[7] Reasonably stable sets of data can be collected for surface areas from a few micrometers to a few tens of a micrometer across with 32 x 32 or 128 x 128 pixels and a lateral increment better than 100 nm. Ultimate lateral resolution (level of localization of nanomechanical probing) can be as low as 2 to 5 nm for ultrasharp tips and modest indentation depths. Keeping a constant Z-range and a threshold level for cantilever deflection are critical for quality data collection. From collected data, histograms of the surface distribution of elastic modulus can be calculated as demonstrated in Figure 5 for composite rubber-plastic films. Separate elastic modulus values for rubber (dispersed) and glassy (matrix) phases can be resolved by this micromapping technique.

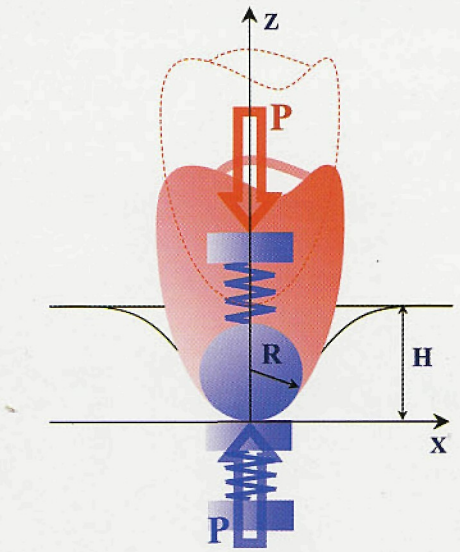


Figure 3. Tip indentation experiment with two-spring model and sphere-plane and parabola-plane approximations.

Cantilever choice. SPM probing routine controls only a piezoelement displacement but not a cantilever deflection. Actual indentation depth can be calculated from a cantilever deflection data. To get the "right" indentation depth, the appropriate stiffness of the microcantilever should be selected. Typical indentation depths for elastic compliant materials are within 50 to 400 nm, but should be limited to 10 to 30 nm for glassy polymers to avoid plastic defor-

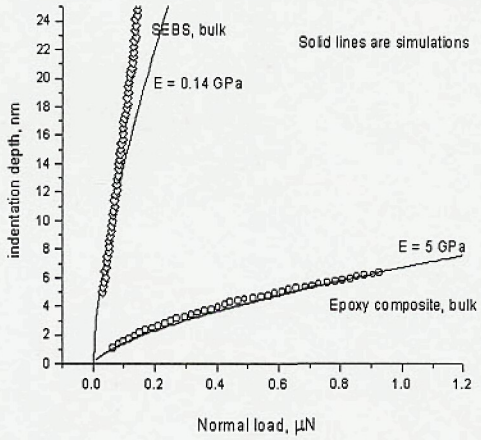


Figure 4. Experimental loading parts of FDC data for stiff (epoxy composite) and compliant (Kraton elastomeric resin = SEBS) surfaces along with their Hertzian approximations and corresponding elastic moduli.

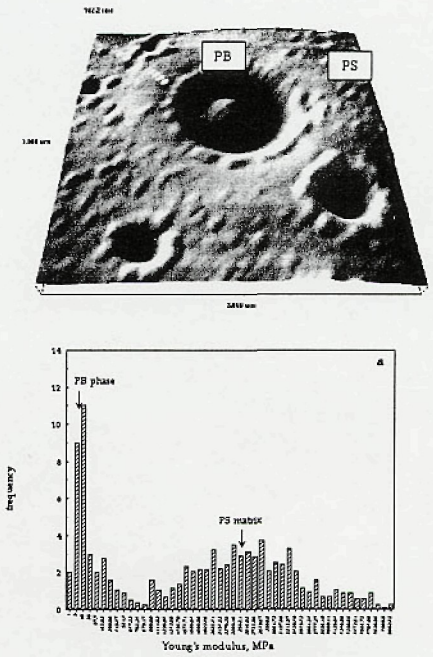
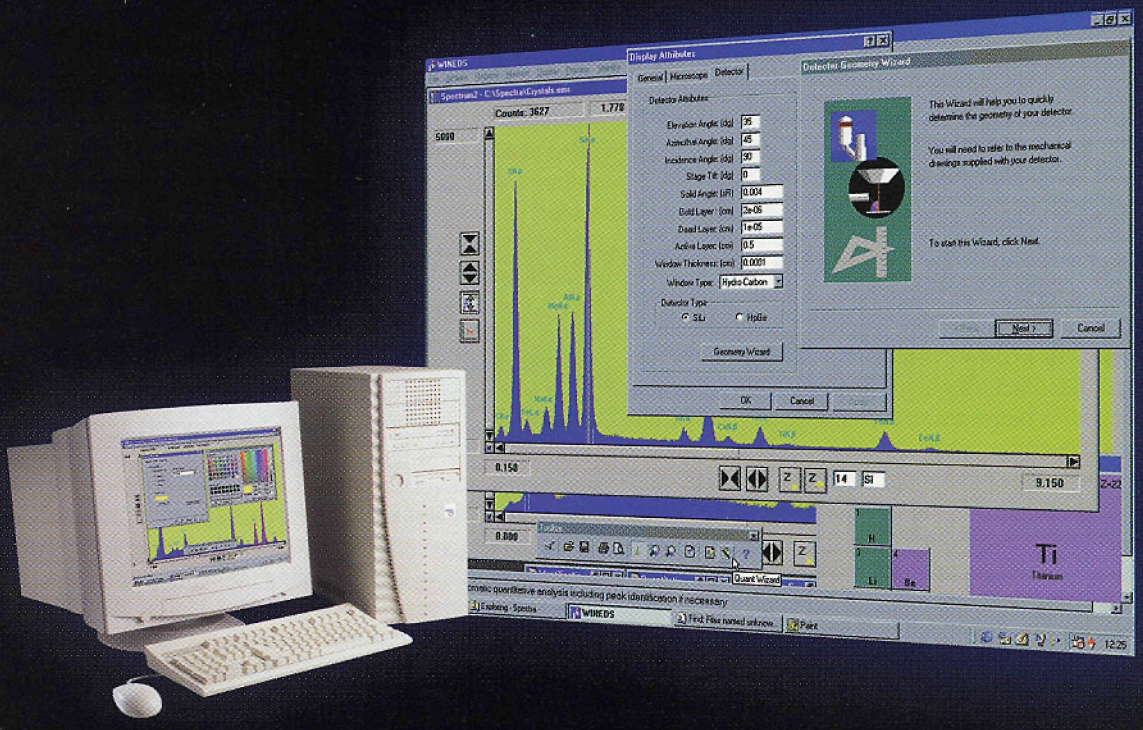


Figure 5. Surface topography of rubber-glass (polybutadiene (PB)-polystyrene(PS)) polymer composite film and corresponding histogram of surface distribution of elastic moduli with two peaks for rubber and glassy phases.

Continued on page 12



When looking at things closely, *WINEDS*® is easier to use and better value than any other Microanalysis system.

THE SOFTWARE

The clever thing about WINEDS® is it behaves just like all your other Windows™ applications. In fact you probably already know how to use it because it is fully compliant with Windows™ 95/98/2000 and NT 4.0 interfaces. It features:

- New Quant Wizard one step analysis
- New Geometry Wizard interactively determines detector geometry
- Smart validation of analysis parameters
- New "Tool Tips" and "Hint Text" captions
- Multiple fully re-sizeable Spectrum Windows
- Easy report generation
- Windows™ 2000 ready / Y2K compliant

THE COMPLETE SYSTEM

We offer a complete range of high performance micro-analysis systems including: PC, detector electronics, detector and digital imaging.

Our products are also available as an ideal **upgrade** package for older microanalysis systems.

THE VERDICT

WINEDS®—the world's most user friendly microanalysis system that **will** fit your budget.

WINEDS®

HIGH PERFORMANCE XRAY MICROANALYSIS

Thomson Scientific Instruments Pty Ltd
ABN 37 005 720 945
216 DRUMMOND ST, CARLTON 3053, VICTORIA AUSTRALIA
TELEPHONE (03) 9663 2738 (03) 9663 2742 FAX (03) 9663 3680
INTERNATIONAL FAX 61 3 9663 3680
E-MAIL: tsi@mira.net
WEB PAGE: www.tsi.com.au

American Agent
TN Analyzer Service, Inc.
7897 Highway 19
Dane WI 53529
USA Telephone 608 798 2005
Fax 608 798 1675
Email doug_tnas@classic.msn.com

3011/G 28872e

Nanomechanical Probing With Scanning Force Microscopy

Continued from page 10

mation. Typically, a set of silicon and silicon nitride cantilevers with spring constants from 0.1 N/m for very compliant surfaces (E ~ 1 MPa) to 50 to 70 N/m for hard materials (E ~ 1 to 10 GPa) can be used. Harder materials will require a diamond tip with spring constants higher than 100 N/m. The plot for the microcantilever selection is presented in reference 8.

Vertical spring constants. To obtain a quantitative value of elastic modulus, accurate values for vertical spring constant and tip radius must be known. Vertical spring constants are very uncertain and manufacturers usually provide a very crude estimation (±100%). If a better accuracy is desired, one of the handy but labor-consuming methods can be used. Added mass technique, spring-against-spring, damping in fluids, and modeling resonant response are the most popular approaches that give precision within ±20% (for a brief review see reference 9). Commercially calibrated tips are available.

Tip radius. To estimate tip radius, one can use a specially prepared reference sample introduced by Butt. This is a mix of gold nanoparticles (diameters of 5 to 100 nm) tethered to a smooth surface (Figure 6). From nanoparticle cross-sections, the tip radius can be calculated by using a simple spherical model, or tip shape can be restored by mathematical morphology. Tip radii for commercial tips vary in the range from 10 nm for silicon ultrasharp tips to 20 to 60 nm for silicon nitride pyramidal tips. Ultrasharp tips provide much higher resolution (contact area for modest loads (nN) is close to 1 nm) but usually are much less stable and prone to brittle fracture.

As is clear from preceding the discussion, comprehensive analyses of nanomechanical properties requires extensive data processing and analysis. The authors are developing a software package, *MMA (MicroMechanical Analysis)*, that allows processing of a single FDC and its arrays for surface histogram evaluation. The detailed description of the calculation routines applied will be published elsewhere[10] and the initial version of this package will be available soon with a request to the authors for testing and evaluation.

Issues

Several important "issues" that complicate nanomechanical probing are briefly discussed in this section.

Probing procedure. The jump-in contact is usually caused by strong capillary forces. This results in initial uncontrolled surface deformation and instabilities in tip deflection measurements for small indentation depths. Usually this range is limited to several nanometers, but for very compliant materials, it can reach 30 to 50 nm. This contribution can be reduced by using low initial forces (low set point voltage), softer cantilevers, larger tip radii, and probing in fluid or in dry gas.

Piezoelement nonlinearities. Non-linearity of the SPM piezoelement is usually not an issue for compliant and low adhesive materials like polymers. However, for harder surfaces with E > 5 GPa, these phenomena require special attention. Linear behavior within 1% is observed when "infinite" stiff surface (*e.g.*, a silicon wafer) is used for a sensitivity calibration under modest (10^0 to 10^2 nN) loads.

Tilted cantilever. Small tilting of the SPM cantilevers (usually <10°) results in non-axial normal load, lateral movement that can be as large as 5% of vertical motion, and buckling of the SPM tip. Complicated vertical-lateral motion of the piezoelement can be used to compensate for this problem. However, for the vast majority of polymers and under elastic deformation conditions, the stiffness of the SPM tip in the buckling mode is much higher than the vertical cantilever deflection, and a non-axial contribution does not significantly affect the data measured.

Topographical contribution. The topographical contribution is a serious issue for the nanomechanical probing. Having local groves and ridges with tilting angles higher than 20 to 30° and elevations and depressions on a sub-micrometer scale can completely change conditions for the local mechanical contact. Actual contact behavior can be very different from the sphere-plane model used for data processing. As a result, significant overestimation/underestimation of elastic modulus (100% to probably not more than 200%) can be observed for concave/convex surface areas. There are no simple ways to remove this contribution and analytical models do not exist for the general case. On the other hand, numerical solution of the contact problem is too cumbersome and prone to instabilities to be practical. Working with smooth, strictly horizontal surfaces, blunter tips, and selecting local areas with modest fluctuations of elevations is helpful. Reasonable results can usually be obtained for surfaces with microroughness of less than 1 μm within a 100 x 100 μm area.

Thickness dependence and gradient properties. The nanomechanical probing of thin films on solid substrates is limited due to the influence of a stiff substrate on the elastic response. Depending upon the ratio between elastic moduli, reliable results can be obtained for and indentation depth less than 20 to 40% of the whole film thickness. The variable mechanical properties in the direction normal to the surface cause deviations from the Hertzian behavior and can be treated with more complicated contact mechanics models.

Rate dependence. The viscoelastic nature of polymeric sur-

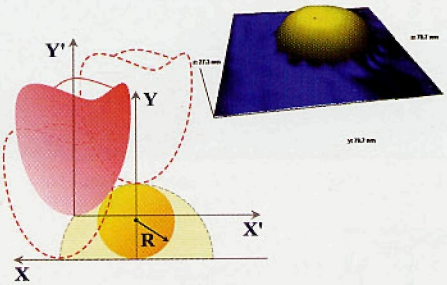


Figure 6. Tip radius evaluation from imaging of gold nanoparticles (3D image, top) for parabolic and spherical approximations.

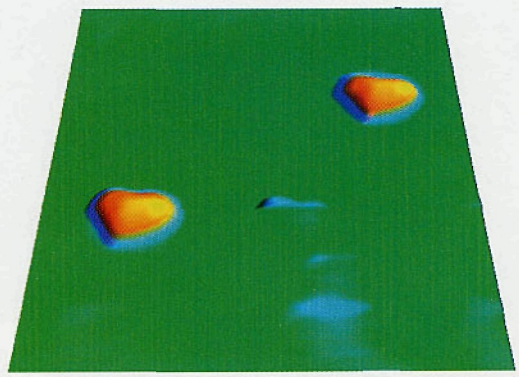
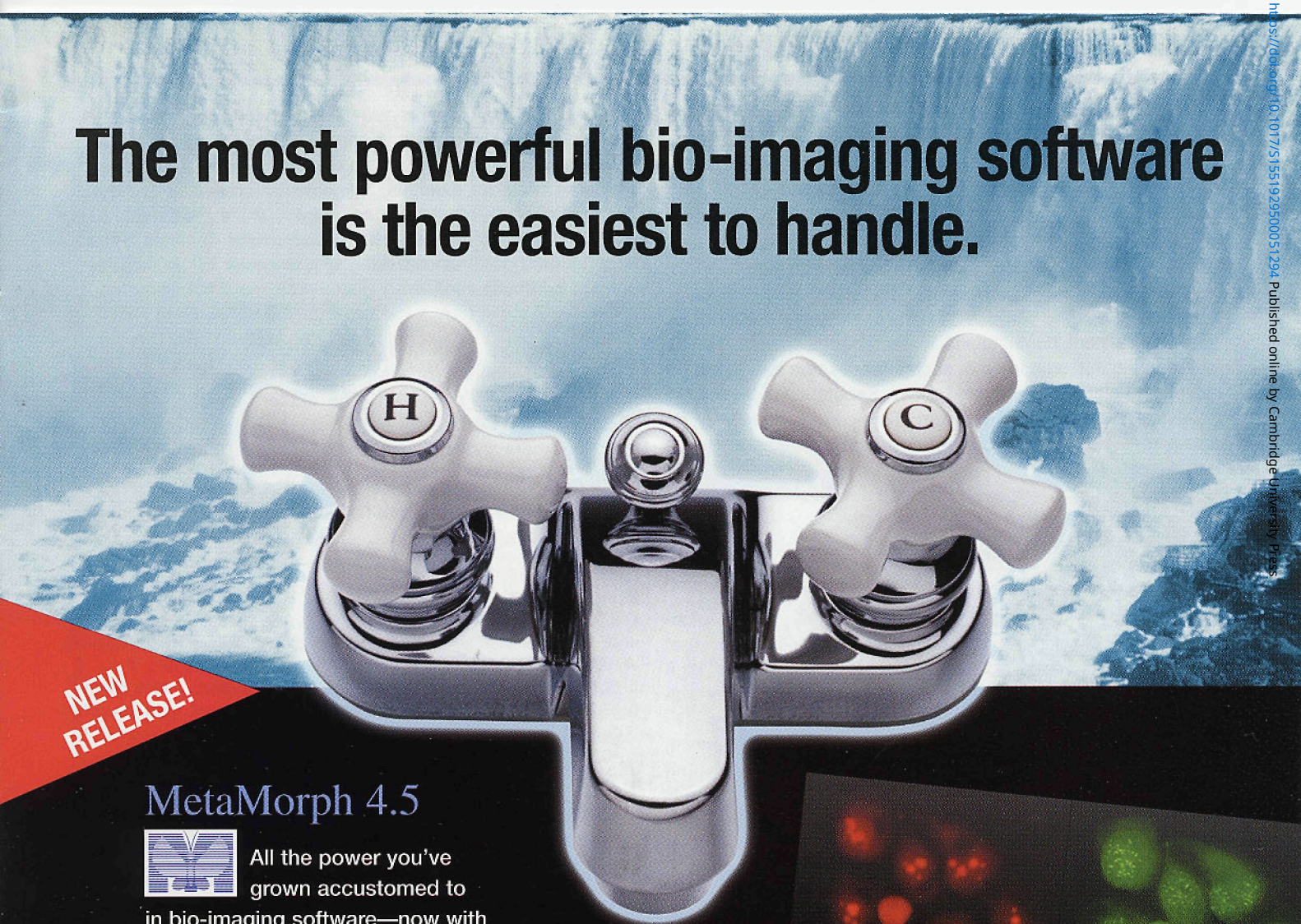


Figure 7. Visualization of the crashed tip end shape in the form of "nanohearts" of about 100 nm across by scanning tethered gold nanoparticles. Image size is 715 x 715 nm, Z scale is 19 nm.

Continued on page 14

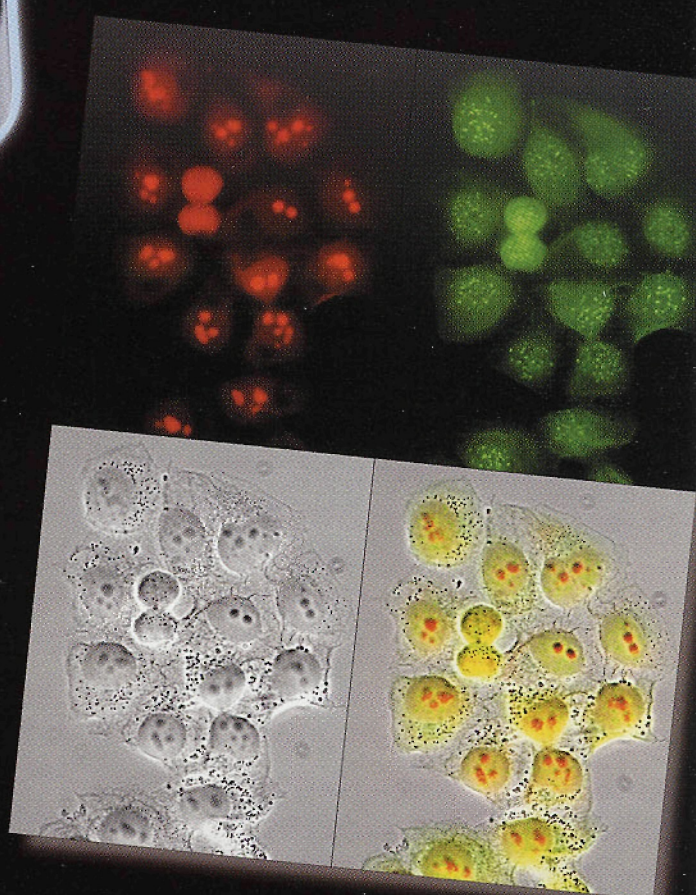
The most powerful bio-imaging software is the easiest to handle.



NEW RELEASE!

MetaMorph 4.5

All the power you've grown accustomed to in bio-imaging software—now with a more Intuitive User Interface. And, with the introduction of our interactive training CD, you won't waste a drop of your time getting acclimated.



Join us at
the Society for Neuroscience
30th Annual Meeting
Nov. 4–9, New Orleans
Booth 1718

For more information contact:

www.universal-imaging.com
Universal Imaging Corporation
West Chester, PA USA
610-344-9410

Nanomechanical Probing With Scanning Force Microscopy

Continued from page 12

faces contributes to their mechanical response, especially in the vicinity of the glass transition temperature where dramatic variations of both storage and loss moduli are observed. As a result, significant deviations from the Hertzian behavior are observed (*e.g.*, see Figure 4) and "apparent" elastic modulus varies with probing frequency, vertical range and forces applied. Significant contributions in recorded response can be seen during micromapping of such surfaces due to a lag in recovery of neighboring indented areas. Separation of these contributions is a non-trivial problem. This can be done only for relatively simple cases by using one of the viscoelastic models like the Maxwell or Voight models. Keeping, if possible, identical probing conditions for different surfaces helps to create comparable measurements. Thermal drift can be also an issue if the thermomechanical properties are probed at elevated temperature and high-resolution (time-consuming) micromapping is exploited (with pixels 64 x 64 and higher).

Tip crashes and contaminations. This is a common problem for nanomechanical probing of compliant materials that can prevent any meaningful data processing. Hunting for high resolution requires ultrasharp silicon tips, which are very unstable against multiple probing and calibration on a stiff (*e.g.*, silicon) surface. Usually tips with R < 10 nm cannot pass this test. Stable results can be obtained with silicon nitride or silicon nitride coated tips with R > 20 nm. Contamination of SPM tips is always an issue and periodic cleaning with solvent or under UV-light is needed. Checking of the tip shape before and after a series of measurements with, for example, gold nanoparticles imaging is required to have a correct "current" value of tip radius. As a result of tip crashes, the tip end can assume a very frivolous shape such as, for example, "nanohearts" presented in Figure 7. Two "nanoheart" images with apparent lateral sizes about 100 nm and one "broken" nanoheart in-between were obtained by scanning tethered gold nanoparticles with diameter of 10 nm with the damaged SPM tip.

Acknowledgments

This authors' work in this field is continuously supported by The Solid Mechanics and Materials Engineering Program, The National Science Foundation. The authors thank S. Chizhik, N. Myshkin, and I. Luzinov for collaboration on nanomechanical testing of polymers and N. Fuchigami for providing image presented in Figure 7. ■

1. D. Sarid, *Scanning Force Microscopy*, Oxford University Press, New York, 1991.
2. S. A. Chizhik, Z. Huang, V. V. Gorbunov, N. K. Myshkin, V. V. Tsukruk, *Langmuir, 14,* 2606, 1998.
3. V. V. Tsukruk, Z. Huang, S. A. Chizhik, V. V. Gorbunov, *J. Mater. Sci. Lett., 33,* 4905, 1998.
4. M. R. Vanlandingham, S. H. McKnight, G. R. Palmese, R. F. Eduljee, J. W. Gillespie, R. J. McCulough, *J. Mat. Sci. Lett., 16*, 117, 1997.
5. G. M. Phart, W. C. Oliver, F. B. Brotzen, *J. Mater. Res., 7,* 613, 1992.
6. K. L. Johnson, K. Kendall, A. D. Roberts, *Proc. R. Soc., London, A324,* 301, 1971.
7. V. V. Tsukruk, Z. Huang, *Polymer, 41*, 5541, 2000.
8. V. V. Tsukruk, V. V. Gorbunov, Z. Huang, S. A. Chizhik, *Polymer Intern. 49,* 441, 2000.
9. J. L. Hazel, V. V. Tsukruk, *Thin Solid Films, 339,* 249, 1999.
10. V. V. Gorbunov, V. V. Tsukruk, *Probe Microscopy,* in preparation

INCACrystal offers EBSD with all the productivity benefits of the INCA platform:

- New, high sensitivity camera for fast Crystal Orientation Mapping at low current
- INCA Navigator makes complex operations easy to follow
- Integrated processing generates meaningful results
- Customized reports in seconds

Fast, simple and powerful, in fact EBSD Crystal Clear.

INCA *INCA-power and productivity in EBSD*

For more information on INCA visit our website today at
www.oxford-instruments.com
Or call us on:

USA 1 (978) 369 9933,
UK +44 (0) 1494 442255,
France (33)-01-69 85 25 21,
Germany (49) 06122 937-176,
Austria (43) 1 710 6198,
INCA is a trademark of Oxford Instruments

Scandinavia (46) 8 590 725 50,
Australia (61) 29484 6108,
Japan (81) 3-5245-3591,
Singapore (65) 337-6848,
China (86) 10 6833 0336.

OXFORD INSTRUMENTS