In depth...

Comparative Atomic Force Microscopy Study of Soft Materials in the Hybrid and Amplitude Modulation Modes

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Hybrid Mode, which is based on the real-time detection and processing of temporal probe deflection signal reflecting tip-sample force interactions at non-resonant frequencies, is a valuable addition to the set of Atomic Force Microscopy (AFM) techniques. The essential elements of this mode and its implementation are presented. The value of Hybrid mode is verified through comparative studies of different materials with amplitude modulation mode - the resonant oscillatory mode that is most frequently applied in AFM analysis of soft materials. The synergistic benefits of both techniques for comprehensive analysis of surface structures and their properties are described. Quantitative nanomechanical studies associated with Hybrid mode are illustrated on multicomponent polymer materials.

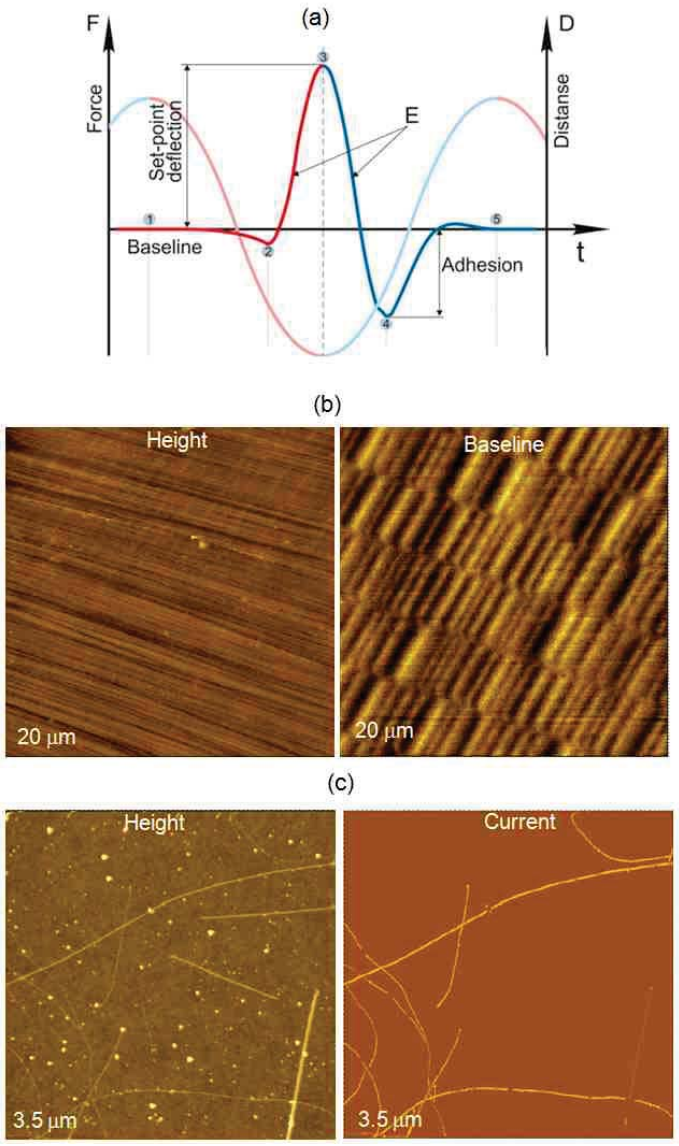
Introduction

Atomic force microscopy (AFM) [1] is broadly applied for high-resolution visualization of surfaces and studies of local materials properties. Initially, AFM was introduced with contact mode operation using the cantilever deflection for sensing the tip-sample forces. In this method the set-point deflection, which is proportional to the force experienced by the probe, was kept constant to retrieve the sample surface profile. In addition, the deflection-versus-distance traces recorded on soft materials were used for local nanomechanical studies [2]. The main drawback of contact mode is a strong shearing force during scanning that causes unwanted modifications of the probe and soft samples. Therefore, the development of oscillatory modes, in which the lateral force is minimized, has boosted many AFM applications. In oscillatory resonant modes the probe is driven at or near its resonant frequency and the tip-sample force interactions change its amplitude and frequency. The feedback that keeps these changes at the set-point values during scanning is employed for surface profiling, respectively, in amplitude modulation (AM) [3-4] and frequency modulation (FM) [5] modes. For many years AM mode has been the dominant choice for ambient studies, whereas FM is applied mostly in UHV [6] and much less in other environments [7]. The probe at its resonance is very sensitive to the tip-sample interactions but the conversion of the amplitude and frequency changes to the tip-force and sample deformation and, finally, to quantitative mechanical properties is quiet challenging and has not yet been accomplished. This situation leaves room for another oscillatory mode, in which the probe and the sample are brought into intermittent contact at frequencies below the resonances of the piezo-scanner and the probe. In this configuration the probe deflection is measured and applied for surface profiling and local studies of sample properties. The non-resonant operation has its own predecessors among which are the vibrating stylus profiler [8], the jumping mode [9] and others [10-12]. Practical realization of the non-resonant oscillatory mode largely relies on use of the real-time detection and processing of temporal probe deflection signal reflecting tip-sample force interactions. One of possible implementations is Hybrid (HD) mode [13-14], which embraces features of both contact and oscillatory modes. Here we describe this mode and compare it with AM to clarify the benefits of both techniques for comprehensive AFM analysis of surface structures and their properties.

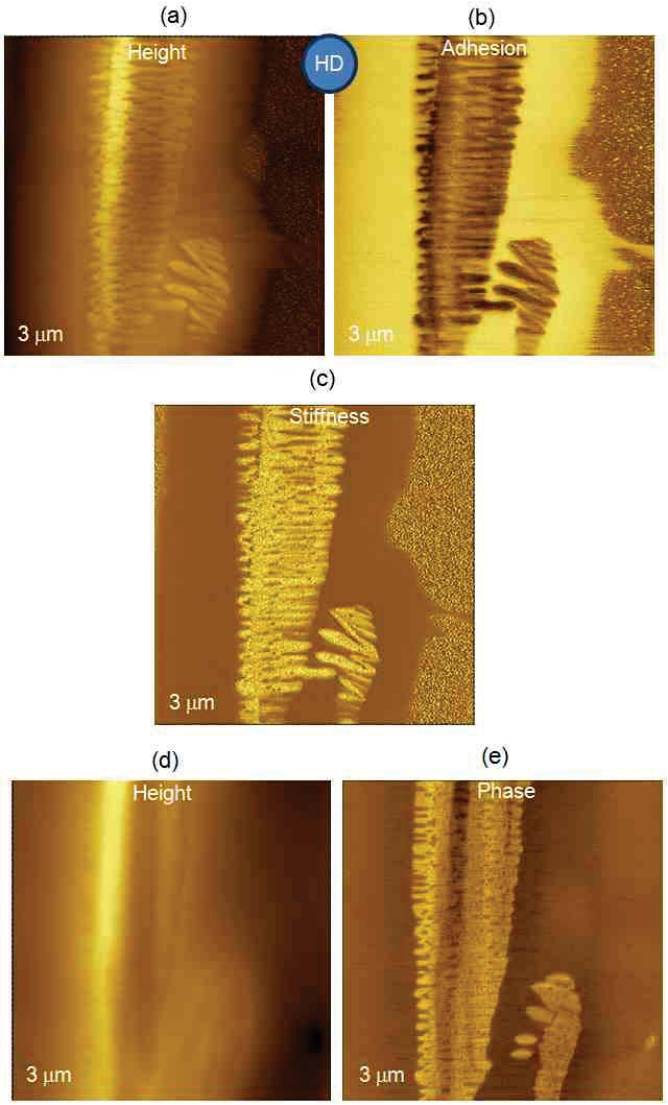
Non-resonant oscillatory Hybrid mode

In the NT-MDT microscopes HD mode is mainly realized by bringing the sample, which is placed on a vertically oscillating scanner, into periodic intermittent contact with the probe causing its deflection to the set-point level, Dsp. The scanner is oscillated at a frequency in the 0.5 - 6 kHz range, with amplitudes in the 5-500 nm range. In each oscillatory cycle, when the probe encounters the attractive and repulsive tip-sample forces, it bends from the baseline level, which is defined as the zero level, to Dsp and returns to the initial baseline position. Schematically, the temporal scanner motion and probe deflection are shown in Figure 1a. During lateral scanning the feedback loop, which controls the probe-sample separation, keeps the chosen Dsp constant. Depending on the quality of the deflection signal it is registered either at maximal rate of 20MHz or at smaller rates depending on a need of different averaging procedures. In practice, the temporal deflection trace can be complicated by cantilever ringing and waiving, which are caused, respectively, by the adhesive and viscous effects. The filtering of these wavy signals at frequencies near the probe resonance and at scanner oscillation helps in retrieving contamination-free deflection traces. In every oscillation cycle the probe experiences different force interactions reflecting various surface properties, and real-time acquisition and processing of the cantilever deflection facilitate their mapping, practically simultaneously with profiling of the sample surface. The variations of the baseline level can be used for mapping the strength of long-distant electrostatic and magnetic interactions when probes with the appropriate coatings are applied. This capability is verified in a study of a hard drive surface, the height image shows its smooth topography whereas the baseline variations reflect the magnetic pattern, Figure 1b. With a conducting, biased, probe the tip-sample current can be measured at the maximal deflection for constructing conductivity maps as shown in the images of carbon nanotubes on Si substrate, Figure 1c.

The most commonly analyzed features of the deflection profiles are the "wells" and slopes observed on the advancing and receding parts of the deflection trace that can be used for mapping of sample adhesion and stiffness respectively. This HD capability is illustrated by the images of poly(diethyl siloxane) – PDES on Si substrate, Figures 2a-c. The same sample area has been examined with the same probe in AM mode, Figures 2d-e.

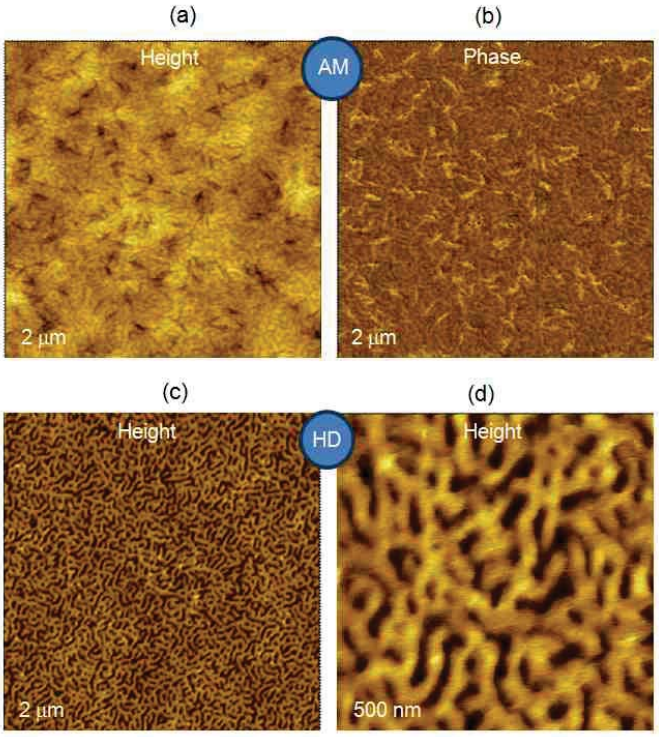


Figures 1a-c. (a) The idealized temporal deflection curve (dark red and blue) and sample displacement (light red and blue) during an oscillatory cycle. Baseline, attractive well on approach, set-point deflection, adhesive well on retract are pointed respectively with (1,5), (2), (3) and (4). (b) Images of hard drive obtained in the HD mode; (c) Images of carbon nanotubes on Si substrate obtained in the HD mode.



Figures 2a-e. AFM images of PDES layer on Si substrate obtained in the HD mode (a-c) and in the AM mode (d-e).

The comparison of the images shows that the lamellar aggregates, which are covered by an amorphous polymer, are barely seen in the AM height image but are pronounced in all others. This suggests that imaging in HD mode was performed at sufficient force that the probe depressed the soft material making the lamellae visible in the height image in Figure 2a. AFM has been proven as a valuable technique for the elucidation of the micro-phase morphology of different block copolymers. The contrast differentiating the individual nanoscale blocks of polymers in glassy and rubbery states is pronounced in the AM phase images, particularly, at elevated tip-force interactions [15]. Specific features of these materials, such as enrichment of top surface layer(s) in low energy component(s) can be also detected in variable-force imaging. The sub-surface morphology can be visualized by lowering the ratio of the set-point and free amplitudes that caused a tip-induced depression of top surface as it was shown for a number of block copolymers including the triblock copolymer poly(styrene)-b-poly(butadiene)-b-poly(styrene), SBS [15]. In AM and HD mode studies of SBS films, we expanded such observations to the visualization of nano-crystals of antioxidant, which are used in the preparation of this material, Figures 3.



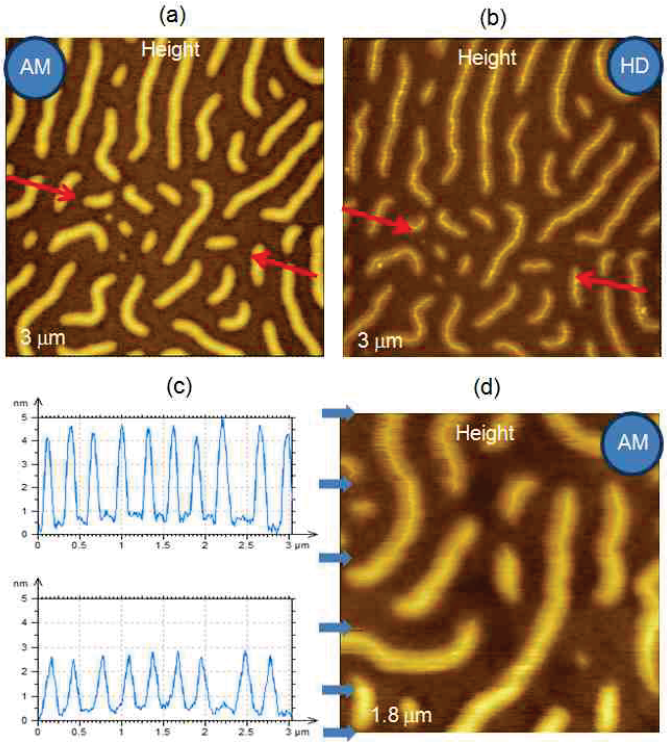
Figures 3a-d. AFM images of triblock copolymer SBS layer on Si substrate obtained in the AM mode (a-b) and in the HD mode (c-d).

In the AM experiments with the probe having stiffness below 0.1 N/m the stable imaging of this film, which is countered by tip-surface stickiness, was possible only at amplitudes above 200 nm. At such conditions, numerous extended platelets of antioxidant were observed with pronounced bright contrast in the phase images. In the height images these objects are vaguely distinguished as darker patches with the crystal-like edges. Such appearance of top nano-crystals is not surprising for AM height

images of heterogeneous surfaces with structures of nanometer-scale height [16]. The AM imaging of the same sample with a much stiffer probe with spring constant of 40 N/m and amplitudes in the 8-25 nm range showed traces of the antioxidant crystals only in studies at the lowest amplitudes. At higher amplitudes, as well as in the images obtained in the HD mode with soft and stiff probes, we observed the microphase separation common to the sub-surface morphology with the alternation of soft rubber blocks with rigid plastic ones.

Starting with visualization of DNA molecules on mica, AFM examination of single macromolecules of biological and synthetic origin provides unique data about molecular dimensions, conformation, branching and other structural features of these objects. In this respect, the use of HD mode is quite valuable as seen from visualization of brush-like poly (n-vinyl acrylate) macromolecules with side chains. In AM mode the macromolecules with side chains of 80 polymer units, which were spread on mica substrate, are seen as the extended stripes of different length (60 - 1000 nm), Figure 4a. The width of the objects is around 30 nm in width and their height is slightly below 4 nm as seen from the related cross-section taken along the direction marked by the arrows, Figure 4c. The same surface area, which was examined with HD mode, shows different shape of the macromolecules with elevated core and depressed entities of side groups, Figure 4b. This change is caused by the tip-depression of the side chains. The cross-section shows the effective height of the macromolecules' cores of 2.5 nm, and the height of side chains regions smaller than 2 nm. Important observations were made when a stiff probe of 150 N/m was applied in AM studies of these macromolecules. When imaging has proceeded in the up scan direction, the ratio of set-point amplitude to free amplitude was reduced in steps, with the regions of different ratios marked by the arrows on left side of the height image, Figure 4d.

When the set-point amplitude was chosen close to the free oscillation amplitude, the macromolecules' shape was similar to that seen in the AM images with



Figures 4a-d. AFM images of brush macromolecules on mica in the AM mode (a, d) and in HD mode (b). (c) The cross-sectional height profiles taken in the images in (a) and (b) along the direction marked with the arrows. The arrows at the left side of the image in (d) indicate the regions where the set-point amplitude was kept the same: the largest at the bottom region and gradually smaller in the top regions.

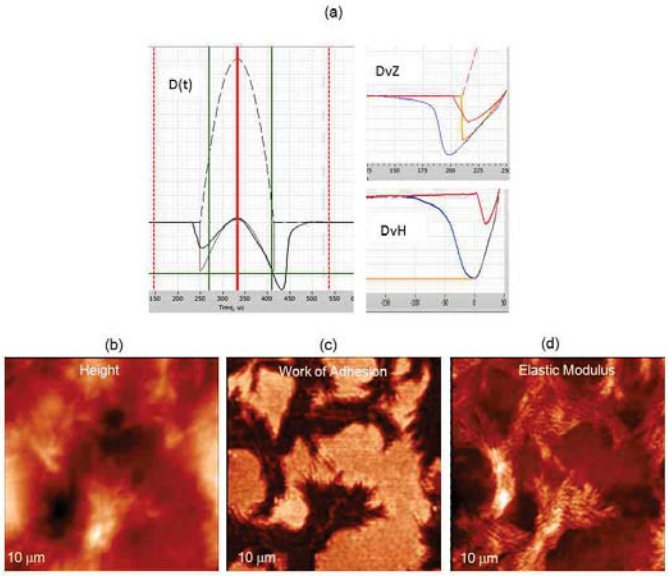
softer probes. As the set-point was lowered, the depressions of the side chains become more substantial compared to the macromolecule's core, similar to the observation in the HD mode with softer probes. The reversible changes might be explained by a stronger elastic deformation of side chains compared to the main chain. This example demonstrates how elevated force imaging in HD mode helps visualize the structure of the brush macromolecules.

So far, we have compared the AFM data obtained on the same samples in two modes and found out that the results complement each other. Now we consider the unique HD application related to the on-line mapping of sample elastic modulus and work of adhesion. The example is taken from studies of biocompatible coating formed by a film of block-copolymer of poly(ethylene glycol) and a peptide, which are connected via urethane bonds. Self-assembly of peptide blocks lead to the micron-scale

sheaf-like structures embedded in an amorphous matrix. In HD mode, the temporal deflection and sample motion traces can be converted to deflection-versus-distance (DvZ) curves or to deflection-versus-penetration curves (DvH), which are used in quantitative nanomechanical analysis. Typical temporal deflection trace, DvZ and DvH curves, which were obtained on this film, are shown in Figure 5a. These curves can be treated on-line and also can be saved as arrays (up to 1024x1024 curves) for detailed off-line analysis. In the temporal deflection graph the tall dotted profile represents the response on a hard material, whereas the deflection profile measured on the block copolymer film is in black. The height difference of these profiles corresponds to the tip depression of the soft coating. The gray trace, which closely mimics the black profile, is the result of the best mathematical fit of the deflection curves using the DMT model with a particular elastic modulus and work of adhesion. This fit is shown as the yellow trace in the corresponding DvZ graph. The red and blue curves present the loading and retracting parts of the force curve. The fit is actually the average of the loading and retracting profiles and their attractive wells. Our software also provides another approach to the quantitative analysis of the DvH curves. Instead of finding the best fit curve, the on-line DMT calculations of the elastic modulus and work of adhesion can be performed for loading and retracting parts of the DvH curve. The yellow traces in the middle and bottom DvH curves (left part of Figure 5a) illustrate these calculation results. Finally, we present the height image and elastic modulus and work of adhesion maps (Figures 5b-c) where the contrast covers the modulus variations in the 50-110 MPa range and work of adhesion changes in the 300-500 mN/m range.

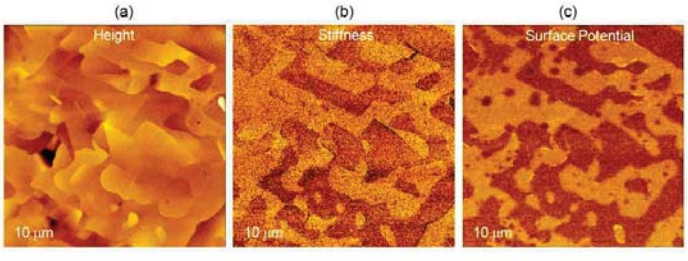
The final example of HD applications is related to mapping of mechanical properties of a hard material such as an incomplete alloy of Bi and Sn whose surface topography is shown by height image in Figure 6a.

By performing an HD study of such sample using a very stiff probe (spring constant ~ 300 N/m) one



Figures 5a-d. Temporal deflection plots, DvZ, DvH plots and AFM images, which were obtained on a biocompatible coating of block copolymer of poly(ethylene glycol) and peptide. (a) Left - Temporal deflection plots on a sample – black line, theoretical fit with DMT model – gray line and plot of a reference Si substrate – dashed line. Right – DvZ and DvH plots with traces in red and blue corresponding to tip approach and retract. Yellow curve shows the DMT fit with average adhesion (top) and with DMT analysis of the retract curve. (b-d) AFM

can get the stiffness map (Figure 6b), in which individual crystalline domains can be identified due to differences of the components' elastic modulus (32 GPa – Bi, 50 GPa – Sn). Such compositional imaging based on variations of local mechanical properties of metals is practically impossible with AM mode. Yet the difference of the work function of these metals can readily be detected in Kelvin Force Microscopy – an offspring of AM mode, Figure 6c.



Figures 6a-c. AFM images of incomplete alloy of Bi and Sn obtained in the HD mode (a-b) and KFM mode (c).

Conclusions

The value of the Hybrid mode, in which the probe deflection is applied for measurements of sample

topography and on-line mapping of sample properties including elastic modulus and work of adhesion, is verified by several examples. The comparison of this mode with commonly used amplitude modulation mode shows that the modes complement each other in the comprehensive nanoscale analysis of materials. By applying stiff probes one can extend the Hybrid mode to mapping mechanical properties of materials with high elastic modulus.

Experimental Part

Materials The polymers: polystyrene (PS), polybutadiene (PBD) and triblock copolymer polystyrene-b-polybutadiene – b – polystyrene (SBS) were purchased from Polymer Source Inc. The samples of polymer brush macromolecules and film of poly(ethylene glycol) and peptide blockcopolymer are courtesy of Prof. S. Sheiko (UNC, Chapel Hill, NC), and Prof. D. Sarkar and Dr. G. R. Krishnan (SUNY, Buffalo). The polymer samples for AFM studies were prepared by spin cast of polymers in toluene on mica and Si substrates. The sample of carbon nanotubes is courtesy of Prof. I. Kuljanishvili (SLU, Saint Louis, MO).

Measurements AFM studies were performed with the scanning probe microscopes NTEGRA Prima and Titanium (NT-MDT, Zelenograd, Russia), which are equipped with a controller that integrates 5 lock-in amplifiers enabling multi-frequency mechanical and electric modes. The microscopes are characterized by a small optical deflection noise below 25fm/√Hz as measured with 95μm long probe with a source power of 2 mW. Low noise high voltage electronics (<1mV over the 600V range) facilitates the high-resolution imaging. Additional capabilities are enabled by Hybrid Mode module providing fast (20 MHz) data acquisition and processing at the rates up to 120 MHz. The latter is essential for real-time filtering, calculations and presentation of the results.

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