

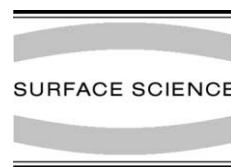


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Influence of volume and surface properties on phase contrast in tapping mode atomic force microscopy

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Abstract

Phase imaging angle of the cantilever oscillation in tapping mode scanning force microscopy can be related to the energy dissipated per oscillation. Nevertheless, in many cases, the physical properties (adhesion, viscosity...) of the sample that are sources of this energy dissipation are not clearly identified. We propose a simple method to distinguish the influence of surface and volume properties on phase imaging. This method is based on equalizing of surface properties by covering the sample surface with thin gold layers. As an example, in our specific working conditions (moderate tapping on glass–polyester composite), we show that volume properties have an important influence on the phase signal in comparison to surface properties.

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1. Introduction

Tapping mode [1] is the most commonly used AFM imaging mode. In this imaging mode, the cantilever is made to oscillate at a frequency close to its resonance frequency (typically ~50–300 kHz) with an amplitude of vibration maintained constant (a few tens of nanometers). The tip is brought in the vicinity of the sample surface so

that the tip/surface interaction causes a decrease of the vibration amplitude. Tapping mode is much less damaging for the surface than the contact mode, thanks to the reduction of the capillary force, friction and shear force and contact pressure, allowing observation of delicate material such as epitaxially deposited silicon, polymers [2–4] or biological samples [5–7].

The phase contrast is often associated with the tapping mode, the phase signal corresponds to the shift between the oscillations of the cantilever and the oscillations of the driver. It makes it possible to highlight changes of the sample properties. In the beginning, the tapping mode and the phase contrast data were difficult to interpret because of the

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strong non-linearity of attractive and repulsive forces that act on the tip when it oscillates to some nanometers of the surface. At present, phase imaging can be related to the energy dissipated per oscillation [8–10]. If the imaging parameters remain constant (frequency, vibration amplitude), the changes of the phase value can be directly related to changes of sample properties.

The behavior of the microlever can be studied under various conditions. When the tip does not interact with the sample, the system stiffness is the same as the microlever stiffness. On the other hand, when the tip vibrates in the field of attractive forces, the stiffness of the system is influenced by the gradient of attractive forces. If the oscillation of the microlever is sufficiently weak, the gradient of forces can be regarded as linear, and the stiffness of the system is the sum of the lever stiffness and the attractive gradient, thus the system stiffness remains linear. This is the case in non-contact mode [11].

If the vibration amplitude is more significant (tapping mode), the gradient of attractive and repulsive forces becomes strongly non-linear. It can hence exist, for the same operating conditions, an attractive and a repulsive regime [12–14]. We define the term soft tapping when the regime is attractive (the ratio set point (rsp) defined as the ratio as the oscillation amplitude A to the free amplitude A_0 , is then close to 1) and moderate tapping, when the regime is repulsive (rsp = 0.5–0.8). The transition between these two regimes induces a spectacular change of the phase value [12–14]. Even a very small change in the interacting forces can induce a spectacular change in oscillation amplitude and in phase value hence in image contrast. The $\Delta\varphi$ value is a possible way to determine the nature of the regime where the cantilever oscillates : for $\Delta\varphi > 90^\circ$, the regime is mainly attractive and for $\Delta\varphi < 90^\circ$, the regime is mainly repulsive [12–14].

Many numerical or analytical models were developed to understand [8,15–25] the behavior of the microlever when the tip interacts with the sample. These models solve the equation of the movement of the microlever when it interacts with highly non-linear gradient forces. In a complementary way, energy approaches show it is possi-

ble to connect the signal of phase to an energy dissipation [8–10].

$$\sin \varphi = -\frac{A}{A_0} \frac{\omega}{\omega_0} (1 + \eta) \quad (1)$$

where A is the working amplitude, A_0 the free amplitude, ω the working frequency, ω_0 the free resonance frequency and η the ratio between the additional oscillator damping coefficient due to the tip/sample interaction and the oscillator damping coefficient without any interaction. By deriving Eq. (1) we finally obtain:

$$d\varphi = \tan \varphi \left(\frac{dA}{A} + \frac{d\omega}{\omega} + \frac{d\eta}{1 + \eta} \right) \quad (2)$$

In an AFM experiment, the frequency is maintained constant, the signal of phase is thus only sensitive to the changes of the cantilever amplitude and the changes of the energy dissipation. Working with high rsp $A/A_0 \approx 0.9$ –1, it can be noted that the phase signal can be directly connected to the amplitude signal. This drawback can be eliminated by using the original set-up of Anczykowski et al. [10], in which case, the energy dissipation can be directly measured. In the other hand, when the rsp is low, the phase signal becomes very sensitive to the change of energy dissipation. This variation of energy dissipation can be due to various sources such as adhesion, friction, viscosity, plasticity, and/or indirectly by properties such as elasticity or surface curvature which modify the contact area and thus indirectly the dissipated energy.

Experimental results have shown the relationship between the curvature of the sample and the phase contrast [26,27]. The sample curvature can thus be regarded as an indirect source of the phase contrast insofar as the modification of sample curvature modifies the reduced curvature radius. Consequently, the radii of contact as well as attractive and adhesive forces change and thus induce a change in energy dissipation. In the same way, a modification of the elastic properties modifies the contact radii and the indentation depth [28,29] and can be indirectly responsible for a change in the energy dissipation. It has often been reported that the phase contrast is generally brighter on the most compliant surfaces [30–32].

Experimentally, the influence of sample properties like viscoelasticity or adhesion forces on phase contrast are difficult to investigate due to the fact that it is difficult, if not impossible to modify one of the properties of the sample without changing the others. Nevertheless, Dubourg et al. have shown that the variation of the phase signal during an approach curve can be correlated to a model that takes into account a viscous force proportional to the indentation depth [28,29]. Furthermore, Tamayo and Garcia have shown convincing results which show that the adhesion energy hysteresis is a source of phase contrast [33]. Likewise, experimental results have shown that the capillary forces and thus the hydrophobic/hydrophilic properties [18] or Coulomb force [34] can have a minor influence on the phase contrast. Furthermore, according to the microlever used (stiffness, resonance frequency, quality factor and tip radius) or to the applied conditions (working frequency, free amplitude, and *rsp*), the phase contrast can be very affected and an inversion of contrast can be observed [30–32,35]. In this paper, we propose a method that allows us to distinguish the influence of volume properties. The main idea is to equalize the surface properties by covering the sample surface with a thin gold layer.

2. Experimental results and discussion

All measures were done with a Dimension 3100 Nanoscope IIIA AFM, from Digital Instruments. We used classical tapping cantilevers Olympus OTESPA, from Digital Instruments, having a resonance frequency near 280 kHz, and a quality factor close to 400. The free amplitude was about 40–50 nm and the *rsp* value was equal to 0.5. We choose a low *rsp* value in order to create experimental conditions where the phase is sensitive to sample properties and where the phase contrast is important. For higher *rsp* (0.9–1), the phase can be directly related to amplitude vibration changes by comparing the phase signal to the amplitude signal. Concerning the imaging conditions, when examining the frequency response of the cantilever for a downward and an upward sweep, a hysteresis loop can be noted on each side of the free reso-

nance frequency corresponding to transition from the attractive to the repulsive regime [13,25]. The peak offset was thus set on the low frequency side of the resonance peak, at a median frequency between the borders of these two hysteresis as to avoid instability between the attractive and the repulsive regime. The gains were fixed as low as possible.

Our goal is to determine if phase signal is more sensitive to surface or to volume properties. When the tip interacts with the sample, the surface area of a few nanometers in radius and the half sphere volume of a few nanometers in radius dissipate energy. To be able to distinguish the influence of both contributions, we propose to equalize the surface properties without modifying the volume properties. In order to do that, we coat the sample surface with a thin gold layer. Gold is a non-oxidizable metal that is easy to deposit by an evaporation process.

If the phase lag is mostly due to surface properties, thin gold layers are able to annihilate the phase lag. Nevertheless, if the thickness is too thin, there is a risk that the surface properties are not perfectly uniform. The thickness of the gold layer required as to enable the surface properties to remain uniform is difficult to estimate even if the range of interaction forces is generally of a few atomic distance [36]. On the other hand, if the phase lag is due to volume properties, the phase lag should disappear as a function of the gold layer thickness, and should be zero when the volume which interacts with the tip corresponds entirely to the gold layer. According to the elastic theories [37], this volume can be estimated to 10 times the contact radius and thus to a few tens of nanometer. Due to the fact that the thickness of the gold layer required as to enable the surface properties to remain uniform or to mask the active volume is unknown, it is thus necessary to plot the phase lag as a function of the gold layer thickness. Obviously, this method could be extended to thin films of different nature using other deposit methods. Nevertheless, the material used for the thin films should be of a low source energy dissipation compared to the sample material and should be of constant thickness, therefore, organic or polymer films should be avoided.

We use a composite material constituted of two elements with very different Young's moduli: 70 GPa for glass (fibers randomly oriented) and 3 GPa for polyester (polymeric matrix). Odoni and Loubet have shown that the surface curvature can be a contrast source [26,27]. A very meticulous polishing procedure permits us to obtain a flat surface, where the ratio of the curvature radii for the two materials are close to 1.5 and are much higher than the tip radius. Under these conditions, the curvature has no influence on the phase signal (Appendix A). Thin gold layers were deposited using an evaporation system (Edwards Coating System E306A) and all the thicknesses were controlled by a crystal monitor (Edwards). After deposition, the sample was kept in a vacuum chamber to limit surface contaminations.

Fig. 1 shows a phase image achieved at the interface of the two elements, with a phase contrast of about 33° between glass and polyester. As previously reported in similar working conditions, the more compliant region (polymer) looks brighter than the stiffer one (glass) [30–32,35]. This high phase contrast is probably the sum of several contributions, so to specify the origin of the con-

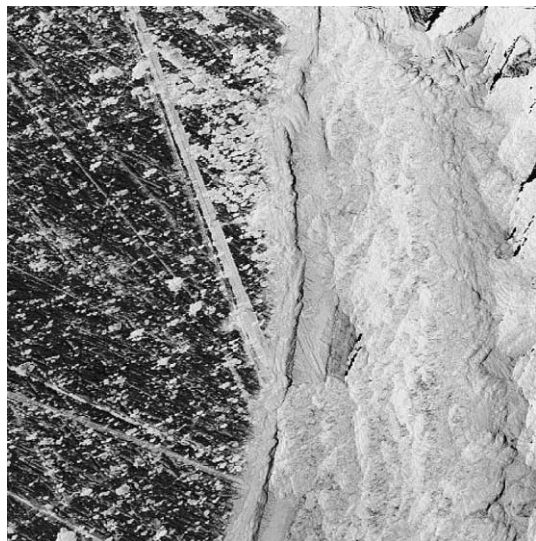


Fig. 1. $20 \times 20 \mu\text{m}$ phase image ($z\text{-scale} = 50^\circ$) of the composite material showing the high contrast between glass (dark phase) and polyester (bright phase) after polishing and before gold coating.

trast, we cover the composite sample with thin gold thin of increasing thickness. After the coating, the surface properties between glass and polyester must be similar, whatever the thickness, whereas volume properties are modulated as a function of the gold thickness. So if phase contrast suddenly decreases to zero when the thickness is increased, phase signal will be mostly related to surface properties such as adhesion forces. If the decrease is progressive though, the phase signal will be more related to volume properties such as viscosity, than to surface properties. In Fig. 2 are plotted the values of the phase contrast as a function of gold thicknesses going from 0 to 30 nm. The gradual decrease is in agreement with a model sensitive to volume properties. The relationship between the logarithm of the phase contrast and the gold layer thickness seems to be linear for a thickness between 0 and 20 nm. Beyond this value, the phase contrast is not relevant. This enables us to estimate the half sphere that dissipates energy to about 20 nm. There is no abrupt change at the beginning of the curve. We interpret this by the fact that the surface properties played a minor role in the phase contrast. In our specific conditions, using this sample, we can conclude that the phase lag is mostly due to a change in volume properties. Obviously, for other operating conditions, using other materials, the

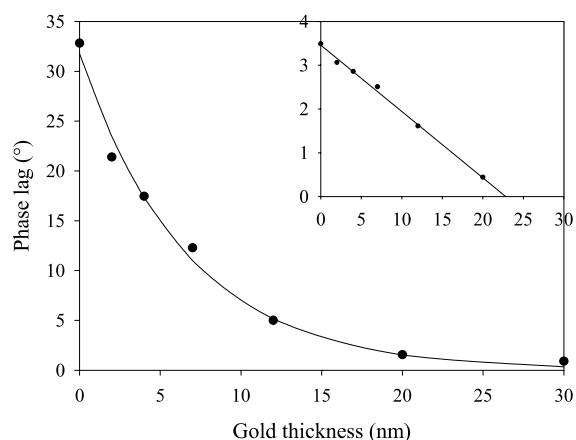


Fig. 2. Effect of gold thickness on the phase contrast between glass and polyester. Inset: logarithm of the phase contrast as a function of the gold thickness.

phase contrast can be related to surface properties [18,33,34].

3. Conclusion

We present a method which enables us to distinguish the influence of surface and volume properties on phase contrast in tapping mode experiments by modifying the surface properties. The surface properties are equalized by covering the surface sample with thin gold layers. As an example, this method applied on a glass/polyester composite shows that the phase contrast is mainly due to volume properties. On other materials, and different experimental conditions, this method can enable to distinguish volume properties such as viscosity and plasticity and surface properties such as attractive or adhesive forces.

Appendix A

A curved surface can be described by two radius of curvature R_1 and R_2 that are the maximum and the minimum curvature radii, respectively. The Gaussian curvature K (total curvature) is calculated by:

$$K = \frac{1}{R_1 R_2} \quad (3)$$

If the surface is described by the equation $z = f(x, y)$, R_1 and R_2 are the solutions of the following equation:

$$K = \frac{rt - s^2}{(1 + p^2 + q^2)^2} \quad (4)$$

with

$$p = \frac{dz}{dx}, \quad q = \frac{dz}{dy}, \quad r = \frac{d^2z}{dx^2}, \quad s = \frac{d^2z}{dx dy} \quad \text{and} \\ t = \frac{d^2z}{dy^2}$$

According to Hertz [26], if $R_x \approx R_y$, the surface can be approximately represented by a sphere having a radius R such as $R = (R_x R_y)^{1/2}$. Then the equivalent radius R^* can be found as follow:

$$\frac{1}{R^*} = \frac{1}{R_{\text{sample}}} + \frac{1}{R_{\text{tip}}} \\ = \frac{1}{\sqrt{R_{1\text{sample}} R_{2\text{sample}}}} + \frac{1}{\sqrt{R_{1\text{tip}} R_{2\text{tip}}}} \quad (5)$$

$$\frac{1}{R^*} = \frac{\frac{1}{\sqrt{K_{\text{sample}}}} + \frac{1}{\sqrt{K_{\text{tip}}}}}{\frac{1}{\sqrt{K_{\text{sample}} K_{\text{tip}}}}} \quad (6)$$

giving

$$R^* = \frac{\frac{1}{\sqrt{K_{\text{sample}} K_{\text{tip}}}}}{\frac{1}{\sqrt{K_{\text{sample}}}} + \frac{1}{\sqrt{K_{\text{tip}}}}} \quad (7)$$

In our experiment, the sample curvature radii are very inferior to the tip curvature, the equivalent radius is thus equal to the reciprocal of the square root of the tip curvature and thus constant.

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