

Measuring phase shifts and energy dissipation with amplitude modulation atomic force microscopy

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Abstract

By recording the phase angle difference between the excitation force and the tip response in amplitude modulation AFM it is possible to image compositional variations in heterogeneous samples. In this contribution we address some of the experimental issues relevant to perform phase contrast imaging measurements. Specifically, we study the dependence of the phase shift on the tip–surface separation, interaction regime, cantilever parameters, free amplitude and tip–surface dissipative processes. We show that phase shift measurements can be converted into energy dissipation values. Energy dissipation curves show a maximum (~ 10 eV/cycle) with the amplitude ratio. Furthermore, energy dissipation maps provide a robust method to image material properties because they do not depend directly on the tip–surface interaction regime. Compositional contrast images are illustrated by imaging conjugated molecular islands deposited on silicon surfaces.

1. Introduction

Amplitude modulation atomic force microscopy (AM-AFM), also known as *tapping mode* AFM, is arguably the dominant technique for nanometre-scale characterization and/or manipulation of surfaces in air and liquids [1–8]. However, the ability to achieve quantitative chemical contrast by AM-AFM in particular, and AFM methods in general, is not as straightforward as topographic imaging.

In AM-AFM the cantilever–tip ensemble is excited at a fixed frequency, usually near or at the free resonance frequency, while the oscillation amplitude is used as a feedback parameter to control the operation of the microscope. Recording the phase shift between the excitation force and the tip response has been proposed and used to image compositional variations in heterogeneous samples [9–15]. In fact *phase imaging*, as it is known, has become a powerful method for mapping at high spatial resolution variations in composition, friction, viscoelasticity and adhesion of the sample surface with independence of the topographic features. However, compositional contrast has not yet been transformed into quantitative information about material properties. This is

probably due to the still emerging understanding of the various factors and interactions that affect and modify the phase shift during AM-AFM operation [1, 16–27]. Among those factors are the ratio between excitation and resonance frequencies, sample elastic and viscoelastic properties, the tip's radius, friction, lever tilt angle or crosstalk between morphological and compositional contributions. Nonetheless, numerical simulations as well as analytical expressions have clearly established that phase shift variations at a fixed feedback amplitude are directly linked to the energy dissipation process [27–31].

To develop *phase imaging* as a tool for quantitative analysis of material properties at the nanoscale requires, among other things, a precise theoretical and experimental understanding of the dependence of phase shifts on operational parameters such as the driving force and feedback amplitude and cantilever parameters as well as tip–surface energy dissipation processes.

In this contribution we address some of the experimental issues relevant to performing phase contrast imaging measurements. Specifically, we study the dependence of the phase shift on the tip–surface separation, interaction

regime, cantilever force constant and quality factor and free amplitude. Phase shift contrast images are illustrated by imaging conjugated molecular islands deposited on silicon surfaces.

Furthermore, energy dissipation studies by dynamic AFM methods are becoming an interesting subject on their own [31–36]. The direct link between phase imaging and energy dissipation measurements could also be applied to the emergence of the latest topic.

2. Experimental methods

Single-beam silicon cantilevers (Nanosensors, Germany) with spring constants in the $2\text{--}40\text{ N m}^{-1}$ range were used to perform the experiments. The cantilever was oscillated at its free resonance frequency ($50\text{--}350\text{ kHz}$ depending on the cantilever force constant) with a free amplitude A_0 in the $5\text{--}40\text{ nm}$ range. All the experiments were performed in air at room temperature and at a relative humidity of about 30%. The force constant was determined by characterizing the hydrodynamic response of the cantilever [37].

The amplitude and phase shift dependence on tip–sample separation, amplitude and phase shift curves respectively were obtained by approaching the tip towards the sample from a distance with negligible tip–sample interaction. Both the change of the oscillation amplitude and the phase shift were recorded as the tip–sample distance was modified. The curves were taken at 2 Hz .

To represent phase shifts, we have adopted the standard and physically sound convention that assigns a 90° phase shift lag between the excitation and the response when the free cantilever is excited at its fundamental resonance. Driving frequencies below the free resonance would produce phase shifts between 0° and 90° while excitation frequencies above resonance would produce phase shifts between 90° and 180° [16].

Sexithienyl molecules (T6) were deposited onto silicon substrates by sublimation in ultra-high vacuum of the polycrystalline material from a Knudsen cell in an organic molecular beam deposition apparatus. In order to obtain the formation of two-dimensional ordered T6 layers, high substrate temperature during deposition, and low deposition rate and film thickness, were chosen on the basis of the T6 film ‘kinetic’ phase diagram [38]. Figure 1 shows a phase shift image of several T6 islands on a Si(100) surface. The cross-section (figure 1(b)) reveals a $\Delta\phi$ of 2.7° between Si and T6. The spikes at the island edges are due to topographic effects because of the finite feedback response time. Due to air exposure the silicon surface is covered by a native oxide about 1 nm in thickness.

3. Phase shift, dissipation and interaction regimes

The non-linear character of the interaction forces between tip and surface in AM-AFM gives rise to the coexistence of two oscillation states for the same external conditions [1]. This genuinely non-linear dynamic behaviour of the AFM is formally described in terms of the coexistence of two oscillation branches, low and high amplitude respectively. However, it is more common and intuitive to use a description

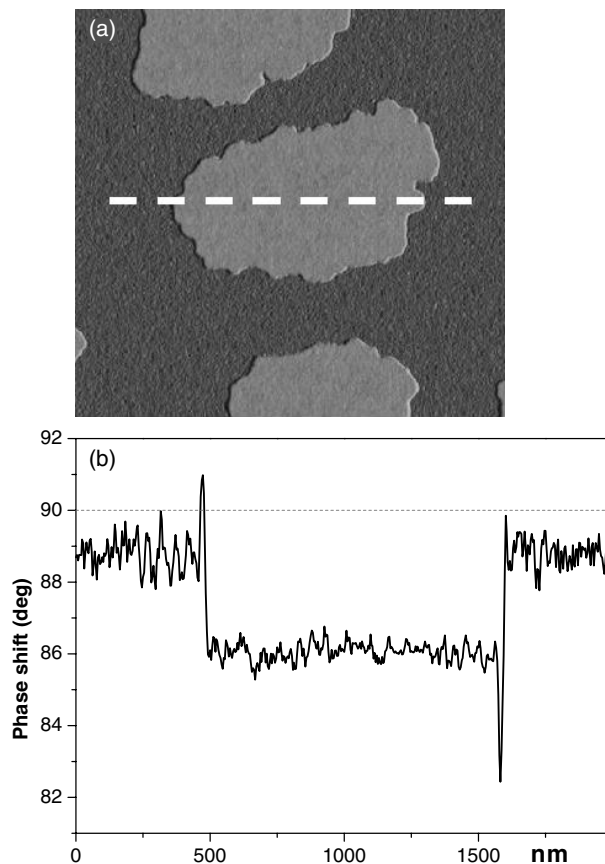


Figure 1. (a) Phase image of several monolayer islands (T6) on a silicon surface. The cross-section shows the phase angle difference between silicon and T6. (b) Cross-section along the dashed line of (a). The sharp peaks at the edge of the monolayer are due to topographic effects. In both regions the phase image is obtained in the repulsive regime (phase shift values below 90°).

based on terms of two dominant interaction regimes, *attractive* and *repulsive*. In the attractive interaction regime, a net attractive force dominates the amplitude reduction ($\langle F_{ts} \rangle \leq 0$) while in the repulsive regime the amplitude reduction is dominated by a net repulsive force ($\langle F_{ts} \rangle \geq 0$) [39]. Although the description of oscillation states in terms of attractive and repulsive regimes does not capture the whole complexity of AM-AFM operation [1, 40, 41] it can be applied to many experimental situations of interest, so the two descriptions will be used interchangeably here.

Phase-shift measurements have also been applied to determine the interaction regime [16, 39, 42]. This is justified by the equations deduced by applying the virial theorem to the average quantities of the tip motion at $\omega = \omega_0$ [40],

$$\cos \phi = \frac{2Q}{kAA_0} \left[\frac{\langle F_{ts} \rangle^2}{k} - \langle F_{ts} \cdot z \rangle \right]. \quad (1)$$

The above equation can be further simplified whenever dissipation on the sample is smaller than hydrodynamic damping and when the interaction force only has significant values in the closest vicinity of the surface,

$$\cos \phi = 2 \frac{\langle F_{ts} \rangle}{F_0} \quad (2)$$

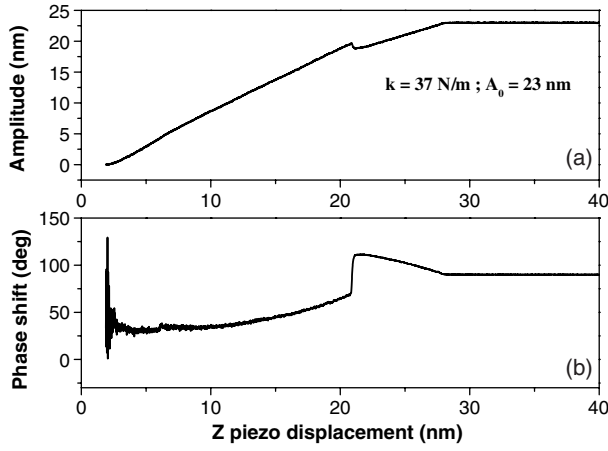


Figure 2. Amplitude and phase shift curves on a silicon surface. The steplike jump in both curves marks the transition between attractive and repulsive interaction regimes. Because of the direct dependence of the phase shift on the sign of the interaction force (equation (2)), the transition between regimes is better observed in phase shift curves (b) than in amplitude curves (a). The zero in the horizontal axis has been chosen arbitrarily, although it is close to the zero tip–surface distance.

where ϕ is the phase angle by which the driving force leads the displacement, $F_0 = kA_0/Q$ is the driving force and k and Q are the cantilever's force constant and quality factor respectively. Equation (2) indicates that the values of the phase shift depend on the sign of the average value of the tip–surface force.

Equations (1) and (2) have been deduced without any assumption regarding the dependence of the force on the distance or on the velocity. Note that the dependence of $\cos \phi$ on $\langle F_{ts} \rangle$ given by equation (2) is reminiscent of the relationship existing between frequency shifts and tip–surface forces for frequency modulation AFM [43].

Figure 2 shows amplitude and phase shift curves taken on T6. The sudden jump in the curves reveals a transition between the attractive (low amplitude) and repulsive regimes (high amplitude). At the transition point, the amplitude shows an increase of about 1 nm while the phase shift shows a remarkable reduction of 42° . The phase changes from values above 90° (attractive regime or low amplitude branch) to values below 90° (repulsive regime or high amplitude branch). This is exactly what is predicted by equation (2), where the cosine of the phase shift depends on the sign of the average value of the force (negative for attractive and positive for repulsive forces).

Another analytical relationship involving phase shifts and dissipation was proposed by Tamayo and Garcia and Cleveland *et al* [29, 30]. This expression links the phase shift with the energy dissipated in one cycle by the tip on the sample surface,

$$E_{\text{dis}} = E_{\text{exc}} - E_{\text{med}} = \frac{\pi k A A_0 \sin \phi}{Q} - \frac{\pi k A^2 \omega}{Q \omega_0}. \quad (3)$$

The above equation was deduced by considering that in the steady state (i) the energy per cycle supplied by the external force (E_{ext}) must be converted either into hydrodynamic damping in the medium (E_{med}) and energy dissipated in the sample (E_{dis}) and (ii) the tip motion is described by a sinusoidal function $z = z_0 + A \cos(\omega t - \phi)$. E_{med} is modelled by a linear

viscous damping law ($F_{\text{med}} = -b\dot{z}$); Q is the quality factor of the cantilever. The equation (3) allows us to turn the data of figure 2 into maps of energy (power) dissipation.

To separate the different contributions to the phase shift into elastic and inelastic components it is convenient to rewrite equation (3) as

$$\sin \phi = \frac{\omega A}{\omega_0 A_0} + \frac{Q E_{\text{dis}}}{\pi k A A_0} = \frac{\omega A}{\omega_0 A_0} \left(1 + \frac{E_{\text{dis}}}{E_{\text{med}}} \right). \quad (4)$$

In the right hand side, the first term represents the phase change associated with tip–sample elastic deformation while the second term includes both dissipation in the medium E_{med} and dissipation in the sample E_{dis} . The above equation contains a remarkable and counter-intuitive result. In amplitude modulation AFM operation ($A = cte$) phase shift changes are exclusively associated with tip–surface inelastic processes. In other words, a local change of an elastic property that is not coupled to an inelastic process would not imply any phase shift change.

Numerical simulations and experiments have confirmed the validity of the above equation when the source of dissipation is either viscoelasticity or surface energy hysteresis [29, 44, 45].

Equation (3) can be re-written in a more compact form as ($\omega = \omega_0$)

$$E_{\text{dis}} = \left(\sin \phi - \frac{A}{A_0} \right) \frac{A}{A_0} F_E \quad (5)$$

with

$$F_E = \frac{\pi k A_0^2}{Q}. \quad (6)$$

4. Phase shift and energy dissipation measurements

4.1. Energy dissipation measurements deduced from phase shift curves

Figure 3 shows several phase shift curves obtained with a cantilever of $k = 2 \text{ N m}^{-1}$ and $Q = 150$ on a silicon region. Each curve has been obtained with a different free amplitude. For relatively small A_0 values (6–23 nm) phase shifts are above 90° , which implies that the amplitude reduction is dominated by attractive forces. Approaching the tip towards the sample implies increasing the strength of the attractive force; consequently and according to equation (2), the phase shift increases. For larger A_0 values, the phase curves show low amplitude (attractive) and high amplitude (repulsive) sections and a transition between them. In the repulsive regime, the net force is negative, and according to equation (2) the phase shift should decrease by increasing the force, i.e., by approaching the tip towards the sample. This behaviour is clearly reproduced by the experimental curves taken at $A_0 = 26.6$ and 32.5 nm.

The sine function has a maximum at 90° ; consequently, a change of the interaction regime could introduce substantial changes in the phase shift without involving substantial changes in the sample's properties ($\sin(90^\circ - \Delta\phi) = \sin(90^\circ + \Delta\phi)$). For this reason, it is more convenient to transform phase shift measurements into energy dissipation values by means of (5). Then these measurements could be used to map variations in material properties.

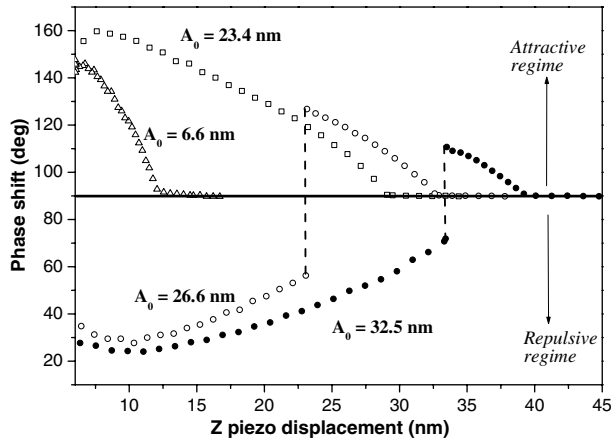


Figure 3. Phase shift curves as a function of the free oscillation amplitude. For smaller free amplitudes the operation regime is dominated by attractive forces while for larger amplitudes attractive and repulsive regimes coexist. The attractive regime is characterized by phase shifts above 90° while the repulsive regime implies phase shifts below 90° . Far from the sample (negligible interaction) the phase shift is 90° ($\omega = \omega_0$) because the cantilever is excited at its first resonance. Data obtained on a silicon region.

Figure 4 shows the dependence of the dissipated energy as a function of the amplitude ratio (A/A_0) for several A_0 . The curves obtained in the attractive regime ($A_0 = 6.6, 23.4$ nm) show a maximum with respect to the amplitude ratio. The maximum increases with A_0 and its position is slightly shifted to higher A/A_0 ratios when A_0 increases. For $A_0 = 26.5$ and 32.5 nm the curves show sections dominated by attractive and repulsive regimes. The transition between interaction regimes is accompanied by a 10–15% increase in the dissipated energy. The data also become noisier in the repulsive regime section (see error bars). The current experimental results for the repulsive regime section do not show a clear tendency with the amplitude ratio. In this experiment, the maximum of the dissipated energy is 10 eV.

Figure 4(b) shows a comparison between an energy dissipation curve obtained in the attractive regime and a curve obtained under the same experimental parameters and cantilever–tip ensemble, that shows both attractive and repulsive sections. The comparison illustrates the increase in E_{dis} associated with the repulsive regime. Notice that for large amplitude ratios, here from 0.6 to 1, it was not possible to place the tip in the repulsive regime (high oscillation state). Although the repulsive regime also exists for these amplitude ratios ($A_0 = 23.4$ nm), the basin of attraction of the repulsive state is very small; consequently, it can be very hard to observe the repulsive regime [1, 16].

The maximum observed in the curves obtained in the attractive regime is consistent with a dissipation process dominated by hysteresis in the adhesion energy. This means that attractive forces in the approaching half cycle are slightly different from the attractive forces in the retracting half cycle. The area enclosed by the loop represents the dissipation. The energy dissipated in the sample should increase when the amplitude ratio decreases from unity to smaller values because the interaction is increased (from negligible to an observable interaction). On the other hand, at a certain tip–surface distance a reduction in the tip–surface separation will

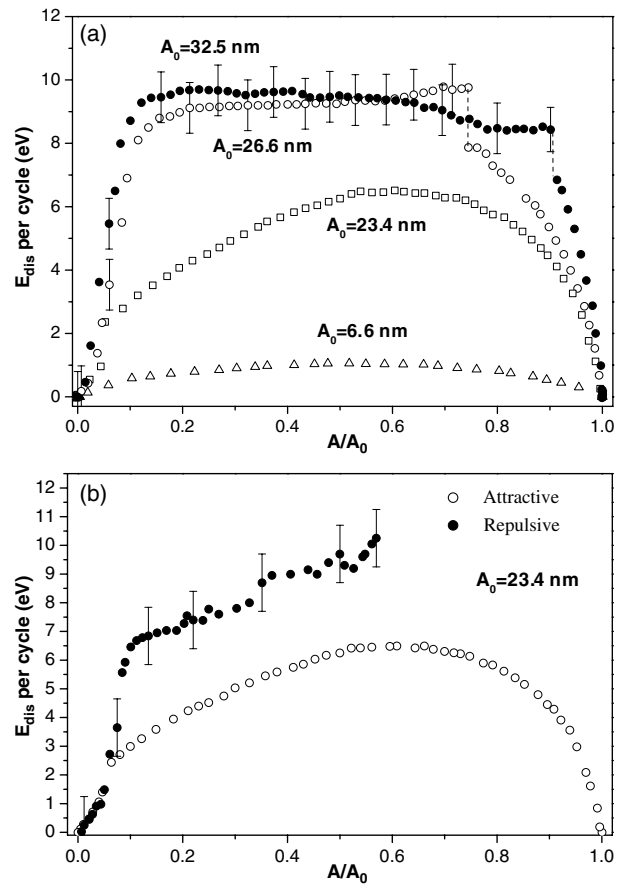


Figure 4. (a) Energy dissipation curves deduced by applying equation (5) to the data presented in figure 3. The curves show a maximum with the amplitude ratio. The transition between attractive and repulsive regimes is usually marked by a small jump in the dissipated energy. (b) Comparison between dissipation in the attractive (low branch) and repulsive (high branch) regions for the same cantilever and operating conditions. Data obtained on a silicon region.

imply a reduction of the force–distance area enclosed by approaching and retraction curves, consequently a reduction of the dissipated energy. These competing effects give rise to the observed maximum.

Dissipation in the sample should not be associated with sample irreversible deformation. Notice that for contact radii of 1 and 2 nm, a total dissipation of 10 eV implies that the energy dissipated per atom is roughly 0.15 and 0.04 eV respectively. Furthermore, the maximum E_{dis} in figure 4 represents a small amount of the hydrodynamic damping with the medium (~ 100 eV) in the same experiment.

4.2. Dissipation dependence on cantilever properties and tip geometry

To test the dependence of energy dissipation measurements with the operating conditions and cantilever properties, we have performed E_{dis} versus amplitude ratio curves for different microcantilevers. The energy factors of the used cantilevers (see equation (5)) range from 31.5 to 55.6 eV ($F_E = \pi k A_0^2 / Q$). Figure 5 shows that the overall dependence of dissipation on the amplitude ratio is quite similar; however, at first sight there

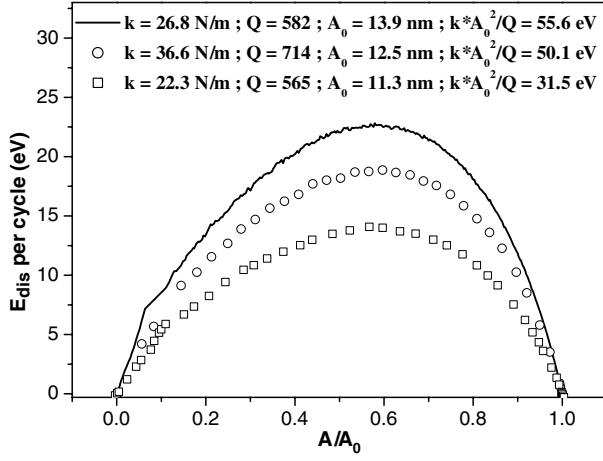


Figure 5. Energy dissipation curves for different cantilevers. The curves were obtained in the attractive regime. The dissipated energy per cycle increases with kA_0^2/Q and the amplitude ratio. Data obtained on a silicon region.

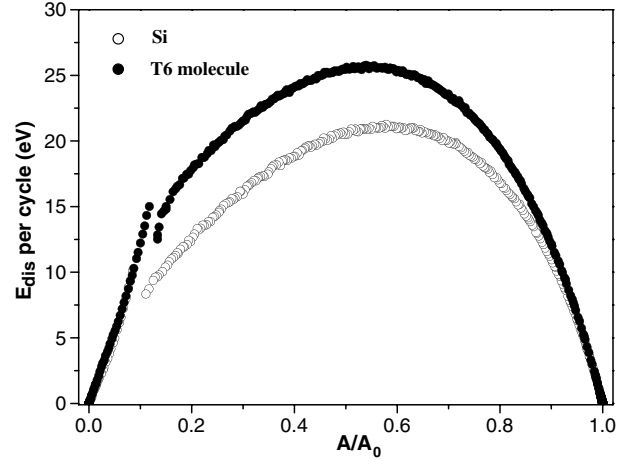


Figure 6. Compositional contrast between T6 and silicon as a function of the amplitude ratio. The curves show that the compositional contrast between Si and T6 is not inverted by changing the A/A_0 ratio, i.e., E_{dis} is always larger in T6 than in Si.

are some quantitative differences. These differences could be explained in part by the differences in the energy factors; for example, the dissipated energy difference $\Delta E_{dis}/E_{dis} \sim 56\%$ obtained between top and bottom curves (at the peak's maximum) is fully matched by the difference between energy factors $\Delta F_E/F_E \sim 56\%$. For top and middle curves we obtain a $\Delta E_{dis}/E_{dis} \sim 19\%$ while the difference of energy factors is $\Delta F_E/F_E \sim 10\%$. For middle and bottom curves we obtain a $\Delta E_{dis}/E_{dis} \sim 33\%$ while the difference of energy factors is $\Delta F_E/F_E \sim 49\%$. We attribute the remaining differences (9% and 16% respectively) to two factors. On one hand, for the same amplitude ratio, the cantilever with the larger A_0 dissipates more energy on the sample (see figures 4(a) and 5). On the other hand, there is the influence of the tip's radius. Although there is not an explicit dependence of the tip's radius in equation (5), energy dissipation should depend on the tip's radius (R) because the strength of interaction forces scales with it (van der Waals forces $\sim HR/6d^2$). Consequently, any hysteresis in the interaction forces should scale with the radius [16]. We find it very encouraging that the quantitative differences could be accounted by small changes in the geometry of the tip because we did not select the cantilever–tip ensembles to provide the same tip radius.

4.3. Compositional contrast in heterogeneous samples

The curves presented in figure 5 show a smooth behaviour for all relevant A/A_0 ratios. In this range, there were no multiple crossings among the curves. This is important for using energy dissipation measurements to map reliably compositional variations. To see this directly we have taken dissipation curves with the same cantilever–tip ensemble ($k = 31 \text{ N m}^{-1}$, $Q = 570$) and operating conditions ($A_0 = 14.2 \text{ nm}$ and $\omega = \omega_0$) on a T6 region and on a bare silicon region of the sample shown in figure 1 (figure 6). The curves show that the compositional contrast between Si and T6 is not inverted by changing the A/A_0 ratio. They also indicate that dissipation is always larger on T6 than on Si. The precise physical origin of this effect is currently under study.

5. Summary

Phase imaging is a powerful and versatile tool to characterize compositional contrast variations at the nanoscale. However, the still emerging understanding of the various factors and interactions that affect and modify the phase shift during tapping mode AFM operation does not allow us to transform phase shift maps into material property maps. In this contribution we have studied the dependence of the phase shift on the tip–surface separation, interaction regime, cantilever properties and excitation force. Phase shift data depend on the sign of the average value of the interaction force; consequently, they can be used to characterize the interaction regime controlling the tip motion. But it is the very dependence on the interaction regime that renders direct phase shift measurements less useful to map quantitatively material properties. We propose and demonstrate that by converting phase shifts into energy dissipation data the characterization of material properties is less sensitive to the interaction regime and more to the tip–surface interactions. We also show that energy dissipation curves obtained in the attractive regime have a maximum with respect to the amplitude ratio. This maximum has its origin in the existence of hysteresis in the long range interaction forces. The amplitude ratio that gives rise the maximum is the optimum point to maximize compositional contrast.

Compositional contrast images are illustrated by imaging conjugated molecular islands deposited on silicon surfaces. Because the maximum in the energy dissipation curves is about 25 eV, material contrast may be achieved without introducing irreversible tip–surface modifications.

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