Phase imaging and stiffness in tapping-mode atomic force microscopy

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Abstract

The dependence of phase angles in tapping-mode atomic force microscopy on the magnitude of tip–sample repulsive interactions was investigated, and phase images of several hard and soft samples were recorded as a function of the free amplitude A_0 and the set-point tapping amplitude A_sp. The phase angle of probe oscillation increases with decreasing the set-point amplitude ratio A_sp/A_0. Phase imaging at moderate tapping (A_sp/A_0= ~0.5) allows one to distinguish different surface features of both multi-component materials and one-component systems with different density distributions. Phase images recorded at moderate tapping are related to surface stiffness variations associated with Young’s modulus change. © 1997 Elsevier Science B.V. All rights reserved.

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Use of oscillating probes and new imaging modes has led to significant progress in atomic force microscopy (AFM) in recent years. Tapping-mode AFM [1] was developed to avoid the surface damage accompanying contact-mode AFM imaging of soft samples and the inability of non-contact imaging to work reliably. In tapping mode, a fast oscillating probe is employed for surface imaging, and it minimizes inelastic surface deformation by reducing the duration of tip–sample contact. As a result, a broad range of soft materials are amenable for AFM studies. Nevertheless, the tapping mode does not completely remove tip–sample force interactions. In each cycle of oscillation, the tip apex spends some time close to and in contact with the sample surface. Consequently the tip experiences attractive and repulsive forces. Höper et al. [2] showed that the magnitude of tip–sample force interaction can be enhanced by increasing the amplitude A_0 of the driving oscillation and decreasing the set-point amplitude A_sp used for the feedback control. In understanding phase images of tapping-mode AFM, therefore, it is crucial to examine how phase angles of probe oscillation are related to tip–sample force interactions. In this letter we explore this problem in some detail.

Consider a freely oscillating cantilever characterized by the spring constant k, mass m, and quality factor Q [3]. Its resonance frequency ω_0 is related to k and m as ω_0 = \sqrt{k/m}. As a function of
the vibrational frequency \( \omega \), the phase angle \( \phi \) (in radians) of the free cantilever oscillation is expressed as:

\[
\phi = \tan^{-1}\left( \frac{m \omega \omega_0}{Q(k-m\omega^2)} \right).
\]  

(1)

As a function of \( \omega \), this angle varies sharply around \( \omega_0 \). \( \phi \) is \( \pi/2 \) at \( \omega = \omega_0 \), smaller than \( \pi/2 \) for \( \omega < \omega_0 \), and larger than \( \pi/2 \) for \( \omega > \omega_0 \). When an oscillating cantilever is brought close to a sample surface, its vibrational characteristics change due to tip–sample interactions. As a typical example, Figs. 1a–1d show a set of amplitude-versus-frequency (A-versus-\( \omega \)) and phase angle-versus-frequency (\( \phi \)-versus-\( \omega \)) curves recorded at different set-point amplitude ratio \( r_{sp} = A_{sp}/A_0 \). To obtain these data, the amplitude and phase angle of cantilever oscillation were recorded as the frequency is swept through the resonance frequency \( \omega_0 \) with the cantilever held at a constant height above the sample surface. The extent of tip–sample force interaction is increased by increasing the driving amplitude \( A_0 \) and by decreasing the set-point \( A_{sp} \). When the tip does not interact with a sample surface, the A-versus-\( \omega \) and \( \phi \)-versus-\( \omega \) curves are centered at \( \omega_0 \) (Fig. 1a), as expected for a freely oscillating cantilever [3]. Figs. 1b–1d show the changes in the A-versus-\( \omega \) and \( \phi \)-versus-\( \omega \) plots brought about by the tip–sample interaction on a polyethylene (PE) sample. When the frequency is swept at \( r_{sp} = 0.7 \) (Fig. 1b), the A-versus-\( \omega \) curve shows a cut-off at \( A_{sp} \), the amplitude peak is shifted to a lower frequency, and the phase angle at \( \omega_0 \) (hereafter denoted as \( \phi_0 \)) becomes larger than \( \pi/2 \). Increasing the tip–sample repulsive interaction, caused by lowering \( r_{sp} \), broadens the amplitude peak and shifts it toward a higher frequency (Figs. 1c and 1d). The phase angle curve follows this shift, so the \( \phi_0 \) value becomes smaller than \( \pi/2 \). Similar trends are found for a large number of different polymer samples.

To a first approximation [4–7], the essential consequence of tip–sample force interactions is to change the force constant of the cantilever to a new effective value \( k_{eff} = k + \sigma \), where \( \sigma \) represents the sum of the force derivatives for all the forces \( F_i \) acting on the cantilever

\[
\sigma = \sum_i \frac{\partial F_i}{\partial z}.
\]  

(2)

Here \( z \) represents the relative displacement between the tip and sample. The phase angle \( \phi \) (in units of radians) of the interacting cantilever can be expressed as

\[
\phi = \tan^{-1}\left( \frac{m \omega \omega_0}{Q(k + \sigma - m\omega^2)} \right),
\]  

(3a)

provided that \( \sigma \) is very small in magnitude compared with \( k \). Then the phase angle \( \phi_0 \) (i.e. \( \phi \) at \( \omega_0 \)) is given by:

\[
\phi_0 = \tan^{-1}\left( \frac{k}{Q\sigma} \right).
\]  

(3b)

We define the phase angle shift, \( \Delta \phi_0 \), between the
free and interacting cantilevers as:
\[
\Delta \phi_0 = \frac{\pi}{2} - \tan^{-1} \left( \frac{k}{Q\sigma} \right) \approx \frac{Q\sigma}{k},
\]
(4)

where the approximate relationship holds when \( \sigma \) is very small in magnitude compared with \( k \). The sign of the phase angle shift \( \Delta \phi_0 \) (hereafter referred to as phase shift) coincides with that of the overall force derivative \( \sigma \). Thus the phase shift is positive when the overall force acting on the tip is repulsive, and negative when the over all force is attractive.

Recently, Sarid et al. [8] carried out numerical simulations of tapping-mode AFM using the attractive van der Waals and repulsive indentation forces acting between the tip and sample. Their work showed that the stiffness of the tip and sample is essential in determining the magnitude and duration of the tip–sample repulsive force and the magnitude of sample indentation. The elastic deformation associated with the tip–sample repulsive force can be estimated by the Hertz theory [9]. Provided that a spherical tip of radius \( R \) and a plane surface under force \( F \) leads to a circular contact area \( A \) of radius \( a \) and an indentation depth \( d \), the surface stiffness \( S \) is expressed as [5]:
\[
S = \frac{\partial F}{\partial d} = \epsilon a E^*,
\]
(5)

where \( \epsilon \) is a number between 1.9 and 2.4 [10], and \( E^* \) is the effective modulus,
\[
\frac{1}{E^*} = \frac{(1-v_1^2)}{E_1} + \frac{(1-v_2^2)}{E_2}.
\]
(6)

\( E_1 \) and \( E_2 \) are Young's moduli, and \( v_1 \) and \( v_2 \) are Poisson's ratios, of the tip and sample. \( S \) and \( a \) can be more accurately described in terms of a modified Hertz model given by Sneddon [11], but the Hertz model is more informative for our qualitative discussion.

When the tip and sample come into contact and their repulsive force indents the surface, it is reasonable to approximate the overall force derivative \( \sigma \) by the stiffness of the tip and sample [5,8]. The stiffness defined by Eq. (5) is valid when the tip is in permanent contact with a sample surface. In tapping mode, the tip makes only a momentary contact in each cycle of oscillation, and the tip–sample contact area varies with time through out the duration of each contact. For our qualitative discussion of phase angles, therefore, it is appropriate to use the time-averaged values of the contact area \( A \), contact radius \( a \) and stiffness \( S \) over one cycle of oscillation (i.e. \( \langle A \rangle \), \( \langle a \rangle \), and \( \langle S \rangle \), respectively). When the overall force derivative \( \sigma \) is dominated by the surface stiffness, \( \sigma \approx \langle S \rangle = \epsilon \langle a \rangle E^* \) so that Eq. (4) is rewritten as:
\[
\Delta \phi_0 \approx \langle S \rangle \frac{Q}{k} = \epsilon \langle a \rangle E^* \frac{Q}{k}.
\]
(7)

Eq. (7) shows that phase imaging provides a map of stiffness variation on the sample surface such that a stiffer region has a more positive phase shift and hence appears brighter in a phase image. The stiffness is proportional to \( E^* \), which is dominated by the modulus of the sample when the tip is much harder than the sample (e.g. \( E_1 \gg E_2 \)). Thus phase imaging provides a method of distinguishing surface features of different moduli.

In general, a softer material leads to a larger contact area \( \langle A \rangle \), and the duration of tip–sample contact is longer on a soft than on a hard material. These effects are enhanced at large driving amplitude \( A_0 \) and small set-point amplitude ratio \( r_{sp} \). Consequently, a change in the stiffness \( \langle S \rangle \) can be dominated by a change in the contact area \( \langle A \rangle \) (i.e. \( \langle S \rangle \propto \langle a \rangle \propto \sqrt{\langle A \rangle} \)), which makes the phase shift greater on a softer than on a harder material. The contrast of a phase image recorded under this condition is reversed from that of the corresponding image recorded at small \( A_0 \) and large \( r_{sp} \). Therefore, it is important to examine how phase shifts depend on the parameters \( A_0 \) and \( r_{sp} \) and establish the regions of the parameters for which the surface stiffness is dominated by Young's modulus.

All our experiments were conducted with a commercial scanning probe microscope, a Nanoscope IIIa with MultiMode® head [1]. In tapping-mode operation in air, the amplitude \( A_0 \) of the driving oscillation needs to be chosen large enough to insure that the probe is not captured by the surface contamination layer. We used rectangular diving-board type Si probes.
(Nanoprobes®) with spring constant of ca 40 N/m and resonance frequencies in the 150–180 kHz range. During scanning with TappingMode®, the amplitude of the oscillating probe is maintained at a set-point value $A_{sp}$ by altering the vertical position of the sample, and the changes in the sample’s vertical position are presented as a height image. Changes in the phase angle of probe oscillation [as defined by Eq. (4)], which are simultaneously recorded, are presented as a phase image.

We used mica, Si and sapphire as representative samples of high Young’s modulus, and microlayered PE and polydiethylsiloxane (PDES) on a Si substrate as typical samples of low Young’s modulus. Microlayered PE samples consist of PE layers with low- and high-density, and their surfaces perpendicular to the layer plane, exposed by cutting with an ultramicrotome knife, were used for imaging. A layer of PDES on a Si substrate was prepared by rubbing a piece of this polymer on a Si wafer. The low- and high-density PE parts of a microlayered PE sample represent soft and hard regions of the surface. Likewise, the PDES and bare Si parts of a PDES/Si system constitute soft and hard regions of the surface.

To examine how phase shifts $\Delta \phi_0$ depend on measurement parameters $A_0$ and $r_{sp}$, we studied several different hard and soft compounds. Fig. 2a shows the dependence of $\Delta \phi_0$ on $r_{sp}$ recorded on mica at four different $A_0$ values. At $A_0 \geq 60$ nm, the $\Delta \phi_0$ versus $r_{sp}$ ($\Delta \phi_0$-vs-$r_{sp}$) plots are quite similar, and $\Delta \phi_0$ increases with decreasing $r_{sp}$ and gradually levels off at low $r_{sp}$ values. At $r_{sp}$ values >0.3, the $\Delta \phi_0$-vs-$r_{sp}$ plot for $A_0=20$ nm deviates considerably from those for $A_0 \geq 60$ nm. In addition, for small $A_0$ and large $r_{sp}$ values, the reproducibility of results is poor. This suggests that at small $A_0$ and large $r_{sp}$, the probe response is strongly influenced by the surface contamination layer. To reliably measure phase shifts induced by the tip–sample repulsive interaction, one needs to operate tapping-mode AFM at large $A_0$ and somewhat small $r_{sp}$.

The $\Delta \phi_0$-vs-$r_{sp}$ plots recorded on materials with different Young’s moduli reveal that the $\Delta \phi_0$-vs-$r_{sp}$ plots are very similar for materials of moduli larger than approximately 1 GPa (Fig. 2b). However, for materials with moduli of several GPa or smaller (i.e. a typical range for polymers), the plots show significant differences. For the low- and high-density parts of a microlayered PE sample (Fig. 2c) and for a PDES sample on Si (Fig. 2d), the phase shifts are substantially larger on the harder than on the softer part of the surface at moderate tapping ($r_{sp}=0.4–0.7$), the difference being about 20° in Fig. 2c and about 35° in Fig. 2d. At hard tapping ($r_{sp}<0.3$), however, the phase shift of the softer part becomes larger than that of the harder part. As already discussed, such a reversal indicates that at hard tapping, the stiffness is dominated by the tip–sample contact area, and the contact area becomes much larger on the softer part. At light tapping ($r_{sp}=0.8–0.9$) the hard and soft parts show similar phase shifts close to zero. At light tapping, the tip–sample contact is minimal so that the probe response is not dominated by the tip–sample repulsive force but is strongly influenced by surface forces such as capillary forces.

![Fig. 2. Plots of phase angle shift (in degrees) versus set-point amplitude ratio recorded on different surfaces. (a) On mica with $A_0=20, 60, 100$ and 140 nm. (b) On mica, Si and sapphire with $A_0=140$ nm. (c) On low- and high-density polyethylene with $A_0=100$ nm. (d) On amorphous PDES layer and Si substrate with $A_0=140$ nm.](image_url)
and adhesion. In order to relate contrast changes in phase images to local stiffness variations on sample surfaces, phase imaging should be performed at moderate tapping around $r_{sp}=0.5$. This aspect is illustrated in the next section.

The $\Delta \phi_0$-versus-$r_{sp}$ plot for the PDES/Si system (Fig. 2d) shows a negative phase shift for the PDES part at moderate tapping, which indicates that the attractive force causing tip's adhesion to PDES is larger in magnitude than the repulsive force resulting from the surface indentation. As shown in the next section, the phase images of PDES parts recorded at moderate tapping exhibit fine details of surface features. Although the overall force is attractive, it is most likely that the fine image features are still determined by variations in the repulsive force, as discussed elsewhere [12].

The height and phase images recorded for a microlayered PE sample at different $r_{sp}$ are given in Figs. 3a and 3b. The height image (Fig. 3a) does not reveal the microlayer pattern. The corresponding phase image exhibits a superior contrast of nanoscale features. This is also found for many different samples. On going from light to moderate to hard tapping, the height images do not show much difference but the phase images do. Strong contrast variations revealing the microlayer pattern are found in the phase image at moderate tapping (Fig. 3b), where the bright and dark stripes of 0.5–1.0 $\mu$m in width are related to the high- and low-density PEs, respectively. The contrast of the phase image is reversed at hard tapping (Fig. 3c). (Similar results were obtained from the phase imaging of another microlayered PE sample in which high- and low-density layers possess different widths, so that the assignment of hard and soft regions is unambiguous [13].) This example shows that phase imaging can be very powerful for studying multi-component surfaces of block copolymers, polymer blends and composite materials.

For semicrystalline and mesomorphic polymers, structures with different density are common. A recent AFM study of thermotropic phase transitions in PDES demonstrated how phase images allow the visualization of mesomorphic structures embedded in amorphous polymer and the monitoring of structural transitions on cooling [14].

Several images of PDES on Si substrate are presented in Figs. 4a–4c. In the surface area where these images were taken, the polymer coverage is low so that 200–300 nm high islands of PDES and
bare Si can be seen. At light tapping the tracking of surface topography is not perfect, and the phase image is made up of negative $\Delta \phi_0$ values with no resolved structures (Fig. 4a). At moderate and high tapping conditions, there is no evident change in the height images recorded, but more structural features are resolved in the phase images (Figs. 4b and 4c). The phase image at moderate tapping exhibits a bright contrast on bare Si and a dark contrast on PDES islands (Fig. 4b). The PDES islands show aggregates of elongated lamellar structures, which are the main structural elements of PDES in mesomeric state. Since the lamellar structures are partially ordered and are thus harder than the amorphous PDES, the contrast of the aggregates is closer to that of bare Si. At hard tapping (Fig. 4c), the contrast of bare Si and partially ordered PDES become darker while that of amorphous PDES becomes brighter. This reflects that the effect of the tip-sample contact area and contact time on the stiffness increases as the set-point amplitude ratio is lowered.

In tapping-mode AFM, the phase angle of probe oscillation is sensitive to the stiffness of the sample surface, and increases with increasing the surface stiffness. When Si probes of $k \approx 40$ N/m and $\omega_0 \approx 150-180$ kHz are used, phase imaging at moderate tapping ($A_{sp}/A_0=0.4-0.7$) and $A_0 \geq 60$ nm provides information about surface stiffness variations related to changes in Young’s modulus. Phase imaging at moderate tapping is a powerful technique for distinguishing different surface features of both multi-component compounds and one-component systems with different density distributions. Surface stiffness cannot be detected unless the tip makes contact with surface. Thus stiffness-related images cannot be recorded with non-contact imaging, and are difficult to obtain with light-tapping AFM because the tip-sample repulsive force is minimal.

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