Explanation and correction of false step heights in amplitude modulation atomic force microscopy measurements on alkane films

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We use a prototypical alkane film (n-C32H66 or C32) adsorbed on a SiO2 surface to compare step heights measured by amplitude modulation atomic force microscopy (AM-AFM) with those measured in the contact mode. The C32 film exhibits layers in which the molecules are oriented with their long axis parallel to the SiO2 surface followed by partial layers of perpendicular molecules. We show that step heights measured in the AM and contact modes agree in all cases except where the step is between a surface formed by a layer of parallel molecules and one of perpendicular molecules. In this case, the AM mode gives a false step height that is as much as 20% lower than that measured in the contact mode and inferred from synchrotron X-ray specular reflectivity measurements. We propose that the weaker van der Waals forces between the AFM tip and a perpendicular layer compared to a parallel layer causes this discrepancy. We show how to correct the false step height by using the approximately linear relationship observed between phase angle (cantilever oscillation relative to the drive signal) and cantilever height measured in an approach curve.

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1. Introduction

Amplitude modulation atomic force microscopy (AM-AFM) has proved to be of great value in investigating the topography of soft films that would otherwise be damaged or deformed by measurements in the contact mode [12]. Due to its widespread use, it is important to have confidence that the height of topographic features can be measured quantitatively and reliably in the AM mode. Our purpose here is to compare step heights measured in the contact and AM modes for a prototypical alkane film adsorbed on a SiO2 surface, a system in which the dominant intermolecular and molecule–substrate interactions are of the van der Waals type. We find that the AM and contact-mode measurements of a step height agree in all cases except one where the step is between two surfaces for which the adhesion force acting on the AFM tip differs greatly.

Films of intermediate-length alkanes exhibit a rich structure and topography at room temperature when deposited from solution onto SiO2 surfaces. Ellipsometric [3], AFM [4], and synchrotron X-ray scattering measurements [5] on dotriacontane films [n–C32H66 or C32] support a model in which film growth begins with a two-dimensional (2D) phase consisting of one or two layers immediately adjacent to the SiO2 surface in which the C32 molecules are oriented with their long axis parallel to the surface. Above these parallel layers, partial layers of a second 2D phase can form in which the molecules are oriented perpendicular to the surface. Coexisting with these islands of perpendicular layers are three-dimensional (3D) mesa-shaped bulk particles. The 2D phase of perpendicular molecules is known to be crystalline and characterized by a rectangular unit cell [6] whereas the underlying phase of parallel molecules may be amorphous like the SiO2 substrate.

Fig. 1 contains a 3D AFM image from Ref. [4] illustrating these topographic features. We see that the substrate is covered by a nearly complete parallel layer (○) above which are regions that consist of either a single layer of perpendicular molecules (●) or smaller islands of double perpendicular layers (●). We note that the perpendicular layers are incomplete: in particular, an area depleted of perpendicular molecules (●) surrounds a larger mesa-shaped particle (○).

Although this film topography is complex, some of its features are known quantitatively. In particular, modeling of synchrotron X-ray specular reflectivity scans of solution-deposited C32 films gives the thickness of a perpendicular layer as 4.32 ± 0.01 nm [5] in reasonable agreement with the all-trans length of the C32 molecule. These X-ray scans are also consistent with the
molecules. These substrates were prepared specular reflectivity scans of similarly prepared samples [5] and a thickness in the range 1.2–2.5 nm as determined by modeling of identical structure. In addition, the presence of a perpendicular layer on top of a parallel layer affords the opportunity to measure the perpendicular layer thickness between surfaces of the same chemical composition but different molecular orientation for which one would expect different adhesive forces.

In this paper, we compare AFM topographic measurements on C32 films taken in both the contact and AM modes. We show that the AM mode yields a false step height for a perpendicular layer when residing on a surface formed by a layer of molecules that are oriented parallel to the SiO₂ surface. We explain this effect by the different strength of the van der Waals forces between the AFM tip and the film surface, depending on the orientation of the molecule in the underlying layer.

2. Experimental

The AFM measurements reported here were conducted on C32 films deposited from solution onto Si(10 0) substrates of area 12 × 12 mm² coated with their native oxide. The SiO₂ coating had a thickness in the range 1.2–2.5 nm as determined by modeling of specular reflectivity scans of similarly prepared samples [5] and was assumed to be amorphous. These substrates were prepared by an "acid cleaning" method in which the substrate was treated in a H₂O₂+sulfuric acid mixture to remove organic contamination [8]. The films were deposited by immersing a Si(10 0) wafer covered with its native oxide in a solution of C32 dissolved in heptane and then slowly withdrawing the vertical wafer (over a period of 5 min). Alkane purity was greater than 99.9%.

Our AFM measurements were performed with a Nanoscope IIIa (formerly Digital Instruments, Inc., now Veeco Instruments, Inc.) in air at room temperature. Cantilever tips for both the contact and AM modes were pyramidal in shape with a radius of curvature in the range of 10–40 nm. In the contact mode, we used cantilevers with small spring constants (0.01–0.03 N/m). We estimate that the normal force exerted by the cantilever on the sample in the contact mode is <5 nN.

In the AM mode (also known as Tapping Mode™), we used silicon cantilevers (MikroMasch CSC37) with spring constants and free resonance frequencies in the range 0.3–1.2 N/m and 25–55 kHz, respectively. We set the drive frequency less than 13% below the free resonance frequency of the cantilever and simultaneously recorded AFM images of topography and phase angle (cantilever oscillation relative to the drive signal). During the tuning operation that precedes recording of each phase image, the Nanoscope IIIa software sets the phase angle at the resonance frequency of the freely oscillating cantilever to zero so that the phase angle ranges from +90° to –90° on sweeping from low to high frequencies. The phase angle is recorded in “Bocek” degrees, which for small phase shifts are equal to true degrees.

3. Results

In Fig. 2, we show topographic AFM images of two similarly prepared low-coverage C32 films immediately after dip coating, one recorded in the contact mode (a) and the other in the AM mode (b). In contrast to higher coverage samples such as that shown in Fig. 1, our lower coverage films that are withdrawn slowly from solution have a tenuous, filamentary “seaweed-like” structure consisting of a partial layer of molecules oriented with their long axis perpendicular to the SiO₂ surface. This submonolayer structure of perpendicular molecules resembles the fractal-like islands previously observed by AFM at low coverages of C30 on SiO₂ [9]. It is also similar to the “dragonfly” structure shown in Fig. 1(a) of Ref. [5], which was obtained with a C32/C7 solution of slightly lower concentration. X-ray specular reflectivity [4,10] and previous AFM measurements in the contact mode [3] indicate that these perpendicular monolayer islands reside on one to two layers of C32 molecules oriented with their long axis parallel to the SiO₂ surface.

The histograms at the bottom of the AFM images in Fig. 2 show peaks separated by 4.58 and 3.76 nm measured in the contact and AM modes. These values correspond to a partial layer of molecules oriented perpendicular to the surface. At the bottom are height histograms showing a larger thickness of the submonolayer film measured in the contact mode (4.58 nm) compared to that in the AM mode (3.76 nm). AM mode measurement parameters are free amplitude A₀ = 30 nm; amplitude at set point A = 26 nm, cantilever resonant frequency = 46.02 kHz, and cantilever Q = 184.
AM modes, respectively. These results clearly indicate a smaller and false thickness of the perpendicular layer when measured in the AM mode. In a total of three films measured in the contact mode, we obtained step heights in the range 4.3–4.7 nm (average = 4.58 nm) whereas 14 films measured in the AM mode have perpendicular layer thicknesses in the range 3.7–4.17 nm (average = 3.95 nm), a decrease in the average thickness of ~14%. We also note that the average thickness of the perpendicular layer measured in the contact mode (4.58 nm) is in closer agreement with that inferred from synchrotron X-ray reflectivity measurements (4.32 nm) than with the average thickness measured in the AM mode (3.95 nm).

We also find that the step height of the first perpendicular layer is systematically less than that of the second perpendicular layer in the same sample when both are measured in the AM mode. In Fig. 3, we show an AFM image taken in the AM mode of a slightly higher coverage film than that in Fig. 2 so that there are now islands (colored light yellow) of a second perpendicular layer on top of the first. If we compare height histograms for the two rectangular regions of interest (the one in the lower left contains a bilayer island while the one in the upper right contains a monolayer island), we see a peak separation corresponding to a thickness of the second perpendicular layer of 4.63 compared to 3.86 nm for the first layer, a difference of 17%. A total of four samples measured in the AM mode gave step heights of the second perpendicular layer in the range 4.4–4.7 nm (average = 4.56 nm) whereas two samples measured in the contact mode gave second layer step heights of 4.5–4.7 nm (average = 4.61 nm). We conclude that the AM and contact modes give the same thickness of the second perpendicular layer to within the experimental uncertainty of ±0.1 nm.

Both contact and AM mode measurements reveal that the 3D mesa-shaped particles (see Fig. 1) can have a terraced structure on their top. These terraces are clearly visible in the 3D topographic image in Fig. 4(a) taken from Ref. [3]. Measurements in both modes on these particles give the same step height from one terrace level to the next, which is about equal to the all-trans

![Fig. 3. A topographic image taken in the AM-AFM mode on a C32 film of slightly higher coverage than in Fig. 2. Islands (bright yellow) consisting of two perpendicular layers are now visible. Bottom: height histogram in red for the upper-right region of interest shows the thickness of the first perpendicular layer to be 3.86 nm; height histogram (black) for the lower-left region of interest (dotted rectangle) gives the thickness of the second perpendicular layer to be 4.63 nm. AM mode measurement parameters are free amplitude A₀ = 28 nm; set point amplitude A = 21 nm, cantilever resonant frequency f₀ = 43.39 kHz, and cantilever Q = 181.](image1)

![Fig. 4. (a) A 3D topographic AFM image taken in the contact mode of a typical mesa-shaped bulk particle showing the terraced structure on its top (from Ref. [3]). The total height of this particle ranges from 110 to 140 nm. The terrace depth is comparable to the all-trans length of the C32 molecule. Note that the particle sides represent a convolution of their true shape and that of the pyramidal cantilever tip. (b) A 2D topographic image taken in the AM-AFM mode of a mesa-shaped bulk particle. Bottom: height histogram from the region of interest showing two terrace steps of height 4.55 nm (lower) and 4.46 nm (upper), respectively. AM mode measurement parameters are free amplitude A₀ = 34 nm; set point amplitude A = 23 nm, and cantilever resonant frequency f₀ = 25.54 kHz. The cantilever Q is uncertain but believed to be in the range 100–230.](image2)
length of the C₃₂ molecule. In the contact-mode measurement in Fig. 4(a), the terrace step height is ~4.3 nm [3], while another particle gave a step height of ~4.4 nm (see Fig. 5 in Ref. [3]). Fig. 4(b) shows an AFM image of a mesa-shaped particle taken in the AM mode. A height histogram below the figure calculated for the indicated region of interest gives terrace step heights of 4.55 and 4.46 nm, respectively. Similar measurements on eight other samples gave terrace lengths in the range 4.2 to 4.7 nm. Therefore, within the measurement uncertainty, both the contact and the AM mode measurements give the same terrace height for C₃₂ particles. We note that this range of terrace step heights is in good agreement with what we have found above for the thickness of the second perpendicular layer (4.4–4.7 nm). It is also consistent with the c lattice constant of 4.25 nm determined for an orthorhombic phase in synchrotron X-ray scattering measurements on similarly prepared samples [4].

We have extended our AM mode measurements to nanoparticles of other intermediate-length alkanes supported on SiO₂-coated Si(10 0) substrates. The alkanes had a carbon number n in the range 24–36. The terrace step heights of these particles have a nearly linear dependence on n as shown in Fig. 5, and, in each case, the step height is close to the all-trans length of the alkane molecule. For comparison, we have also shown the perpendicular layer thickness (circles) for vapor-deposited alkane films (21 < n < 30) as determined from X-ray reflectivity measurements by Basu and Satija [10]. Their thicknesses are about 0.2 nm below our line for n = 27 and 30, and they did not find evidence of a second perpendicular layer. Also shown for comparison are measurements by Ocko et al. [11] (triangles) of the thickness of the surface frozen layer occurring at the bulk alkane liquid/air interface. Their values fall systematically below ours for n > 30, which can be explained by the tilting of the alkane molecules in the surface frozen layer for larger n [11].

4. Discussion and summary

To summarize, we find agreement between contact and AM mode measurements of the perpendicular layer thickness in all cases where the cantilever tip traverses a boundary between two surfaces of the same molecular orientation (long molecular axis perpendicular to the surface). This includes the step height measured from the top of the first to the top of the second perpendicular layer as well as the measurement of the terrace step height on top of the mesa-shaped bulk particles.

The one discrepancy between measurements in the contact and AM modes is the smaller thickness of a perpendicular layer when measured from the top of a parallel layer to the top of a perpendicular layer. A similar error in step height may also have been observed for C₃₀ films deposited on a SiO₂ surface [9]. AM-AFM measurements on domains believed to consist of perpendicularly oriented molecules gave a thickness of ~30 Å compared to a value of 40 Å inferred from X-ray reflectivity scans.

The fact that contact and AM modes agree on the perpendicular layer thickness in all other cases suggests that this discrepancy is not related to compression of the perpendicular layer by the tip as found in some soft materials [12]. In particular, we note that the AM mode gives a lower step height for the first perpendicular layer than for the second perpendicular layer (see Fig. 3). Because we believe these layers are identical, it is difficult to explain how there could be a compressive effect for the first layer but not the second. Instead, we propose that the false-step-height measurement in the constant-amplitude AM mode is caused by the weaker adhesion force of the cantilever tip to a perpendicular layer compared to a parallel layer.

To estimate this difference in adhesion forces, we assume that the SiO₂-coated tip and the alkane film interact by van der Waals forces alone and first consider the tip interaction with the top surface of a perpendicular layer. Due to the short range of the van der Waals force, we further assume that the tip interacts principally with the top layer of exposed terminal methyl (CH₃) groups of the alkane molecules, whereas, on approaching a parallel layer, the tip interacts with methylene (CH₂) groups along the whole length of the molecule. From the known structure of a perpendicular layer [5] and reasonable assumptions about the density of a parallel layer [6,13], we estimate a ~2.8 times higher areal density of methylene groups in a parallel layer than methyl groups at the surface of a perpendicular layer [14]. Finally, assuming the same strength of interaction of a clean SiO₂-coated tip with a CH₃ group as with a CH₂ group [15], we estimate that the tip is roughly 2 to 3 times more strongly attracted to a parallel than a perpendicular layer.

To characterize the relative force of adhesion between the tip and the C₃₂ film, we compared the force curves on a parallel and perpendicular layer as measured by the cantilever deflection in the contact mode on approaching and then retracting from the film. The spring constant of the tip was 0.03 N/m. In Fig. 6, we see that the displacement required to detach the tip from a parallel layer is greater than for a perpendicular layer, indicating that the attractive forces on the tip are 1.22 times larger on the parallel layer. Three other measurements gave ratios of the parallel-to-perpendicular “snap-out” force of 1.21, 1.22, and 1.96, respectively. All of these values are smaller than our crude estimate above from the relative density of the CH₃ and CH₂ groups. However, in addition to the assumptions that went into our estimate, there may be other factors that affect the snap-out force such as contamination of the tip by C₃₂ molecules, the tip-sample contact area, the presence of water molecules, and nonlinearity of the piezoelectric scanner. These other factors may also explain the slight deviation from linearity in the dependence of cantilever deflection on piezo displacement z in Fig. 6.

Now, let us consider operation of the AFM in the constant-amplitude mode with the cantilever driven just below its free resonance frequency. The microscope is scanning over a parallel layer with the tip in the net attractive regime so that the cantilever resonance frequency is shifted downward from its free
value to below its driving frequency. If the AFM tip were to cross the boundary to the more weakly attractive perpendicular layer and maintain the same mean tip-to-sample distance, then the amplitude of the tip's oscillation would increase due to the decrease in the adhesion force (more precisely, the decrease in the sum of the force gradients of all attractive and repulsive forces acting on the cantilever [16]). Therefore, with the microscope operating in the constant-amplitude mode, the cantilever body will be driven toward the sample to maintain the constant tip amplitude. The control software interprets the feedback signal required to make this correction as a decrease in the step height, yielding a false step height that is less than the true value.

This explanation of a false step height in the AM-AFM mode based on the change in the attractive van der Waals force between tip and surface is essentially the same as that proposed for the height variations observed for nanoparticles residing on substrates having different attractive capillary forces [16]. However, these capillary forces appear to be substantially greater in magnitude than the attractive van der Waals forces to the parallel and perpendicular alkane layers that we have investigated. They also result in a much larger error in the measured step heights than we observe. We do not believe these larger capillary forces are present in our samples. The nearly complete layers of parallel alkane molecules adjacent to the SiO$_2$ substrate provide a hydrophobic surface that inhibits formation of a uniform water layer. It may be possible to perform our measurements in a fluid medium in order to eliminate capillary effects entirely (see Fig. 12(a) in Ref. [21]); however, we have not pursued this possibility and are uncertain as to which liquid would be optimal. We also note that there are applications, such as the studies of the structure and phase transitions of alkane films above room temperature [5] that would preclude the use of a liquid medium.

The larger capillary forces present in the nanoparticle systems [16] also cause a larger downward shift in the resonant frequency during imaging as confirmed by the use of different cantilever drive frequencies [16]. In the case of the weaker van der Waals attractive forces, we have been unable to observe a dependence of the false step height on drive frequency.

In order to correct the false-step-height measurement, we need a determination of the difference in the mean tip-to-sample distance on the parallel and perpendicular molecule surfaces when scanning in the net attractive regime. In principle, any microscope parameter that is a function of this distance could be used. While this clearly eliminates use of the tip amplitude in the constant-amplitude AM mode, we can use the phase angle between excitation signal and cantilever deflection for this purpose. In Fig. 7, we compare (a) the amplitude and (b) the phase approach curves on a parallel layer with those on a perpendicular layer and on a bare SiO$_2$ surface. In order to reduce scatter, each curve represents an average over four to six measurements. As noted in the captions to Figs. 2–4, all AM-mode images were taken at a set point $A/A_o > 68\%$ where $A$ and $A_o$ are the amplitude at the set point and of the freely vibrating cantilever, respectively. In Fig. 7, we see that set points in the range $A/A_o > 68\%$ (indicated by the horizontal double arrow) correspond to a phase shift greater than $-48^\circ$, which we interpret as being in the net attractive or “light tapping” regime as will be discussed in more detail below.

The fixed amplitude or set point used to record the AM-mode images in Fig. 8 corresponds to a particular height $z_{sp}$ above the surface indicated by the vertical dotted line in Fig. 7. For all three surfaces, we see that the phase angle measured on approach has a nearly linear dependence on $z$ near the set point. The inset shows that at each $z$ the phase angle on approaching the perpendicular layer is a few degrees more positive than for the parallel layer, although the slopes of the two curves are experimentally indistinguishable. We attribute the slightly lower value of the phase on the parallel layer in the neighborhood of the set point to the stronger binding of the tip to the parallel surface and hence a greater energy dissipation than for the perpendicular surface. We note, though, that the slope of this linear region can be affected by tip damage and by C$_{32}$ molecules adhering to the tip. Such cases can usually be identified by a large snap-out distance.

![Fig. 6. Force curves as measured by the cantilever deflection in the contact mode as the tip approaches and then retracts from the film. The larger $z$ displacement required to detach the tip from a parallel layer indicates a larger force of attraction on this surface compared to that of a perpendicular layer.](image)

![Fig. 7. The amplitude (a) and phase (b) of the cantilever as a function of its height $z$ on approaching a parallel layer of molecules (black line), a perpendicular layer (red line), and the bare SiO$_2$ surface (green line). The curves for both the amplitude and the phase represent an average over six measurements (only four measurements for the perpendicular layer). The horizontal double arrows indicate the range of set points $A/A_o > 68\%$ used to record the images in Figs. 2–4. The dotted vertical line indicates the height $z$ at the set-point ($A/A_o = 68\%$) used to record the topographic and phase images in Fig. 8. In (b) the zero of phase and sign convention are discussed in the text. Measurement parameters are free amplitude $A_o = 12\,\text{nm}$, cantilever resonant frequency $= 50.0\,\text{kHz}$, and cantilever $Q = 200$.](image)
For clarity, we have omitted from Fig. 7 the amplitude and phase curves recorded on retracting from the respective surfaces. The ratio of the snap-out distance from the parallel layer to that from the perpendicular layer, averaged over four measurements, is 1.19, in good agreement with three of the values obtained in the contact mode from the deflection vs. $z$ curves.

In Fig. 8, we show AFM topography and phase images recorded from the sample same whose amplitude and phase approach curves are in Fig. 7. From the height histogram calculated for the rectangular region sample in Fig. 8(a), we infer a false step height of 3.85 nm between the surfaces of adjacent parallel and perpendicular layers. Similarly, the phase histogram at the bottom of Fig. 8(b) indicates the phase on the perpendicular layer is 3.52° lower than that on the parallel layer. Using the common slope of 8.35 deg/nm of the phase vs. $z$ curve for the parallel and perpendicular layers at the set point [see inset in Fig. 7(b)] and the phase shift of 3.52° between parallel and perpendicular surfaces, we obtain a correction to the step height of ~0.42 nm. This yields a thickness of the perpendicular monolayer of 4.27 nm within the range measured in the contact mode and in reasonable agreement with the all-trans length of the C32 molecule.

Variations in the slope of the phase vs. $z$ curve in the neighborhood of the set point contribute uncertainty to the correction in the false step height. For example, in Fig. 7(b), the slope of the parallel and perpendicular layers varies from 7.3 deg/nm at $z = 5.8$ nm to 9.0 deg/nm at $z = 6.7$ nm. From the width of the peaks in the height histograms at the bottom of Fig. 8, we estimate an uncertainty in $z_{so}$ of about ±0.7 nm from which we infer an error in the correction to the step height of about ±0.05 nm. For another sample, we measured the step height of the first perpendicular layer for a range of set points lying within the linear region of the phase approach curve ($A/A_o$, in the range 23–63% where the amplitude of the freely oscillating cantilever is the linear region of the phase approach curve) for a range of set points lying within the linear region of the phase approach curve. For a range of set points, our analysis, we found the same false step height, within the measurement uncertainty, for this range of set points. Our analysis is also supported by measurements on top of the mesa-shaped particles as in Fig. 4(b) that gave the same terrace step height in both the AM and contact modes. These measurements showed a negligible phase shift between terrace surfaces in the AM mode. Similarly, there is negligible phase contrast between the monolayer and bilayer islands of perpendicular molecules in the dotted rectangle at the bottom of the topographic image in Fig. 3.

The lower value of the phase angle on the perpendicular layer in Fig. 8(b) is consistent with the results in the inset to Fig. 7(b), which show near the set point that the phase curve for the parallel layer lies about 3° below that for the perpendicular layer. The phase images in Fig. 8(b) are taken at constant amplitude, not at constant tip–sample separation. At the set point [dotted horizontal line in the inset to Fig. 7(b)], we see that the height $z$ of the tip above the more weakly binding perpendicular surface is ~0.4 nm lower than above the parallel surface in reasonable agreement with the step height correction of 0.42 nm that we have calculated from the slope of the phase vs. $z$ approach curve near the set point.

To avoid the need to correct for the false step height effect in the AM mode, one might consider operating the microscope in the net repulsive mode by reducing the mean tip–sample distance (lower set point). In this case, we would expect the false step height effect to decrease; i.e., there should be closer agreement with the perpendicular layer step height measured in the contact mode. The reason for this is that if, on average, the tip feels a repulsive force on both the parallel and perpendicular layers (even if they are of different magnitude), the amplitude of the tip’s oscillation will not increase on crossing the boundary from the parallel to the perpendicular layer at constant tip–sample distance.

To address this issue, we measured the step height and phase shift of a perpendicular layer residing on parallel layer as a function of set point down to $A/A_o = 10\%$ as shown in Fig. 9. By phase shift, we mean the difference between the phase angle measured on a surface of parallel molecules minus the value on a perpendicular surface. For $A/A_o > 40\%$, we see that the phase shift approaches a constant value of 2.6°, in reasonable agreement with the phase contrast shown in Fig. 8(b). This range of constant phase shift provides a more precise identification of the net attractive regime. The step height of 3.76 nm at $A/A_o = 40\%$ is in good agreement with the values given in Figs. 2(a) and 8(a) and is consistent with our false step-height interpretation.

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**Fig. 8.** AM-AFM topology (a) and phase (b) images recorded from the monolayer C32 film whose amplitude and phase approach curves are shown in Fig. 7. Bottom left: histogram showing a false step height for the perpendicular monolayer of 3.85 nm. Bottom right: histogram showing a phase angle that is 3.52° lower on the top of perpendicular layer than on the parallel layer. AM mode measurement parameters are free amplitude $A_o = 12$ nm; set point amplitude $A = 8$ nm, cantilever resonant frequency $f = 50.0$ kHz, and cantilever $Q = 200$. (a) and (b) images recorded from the monolayer C32 film whose amplitude and phase approach curves are shown in Fig. 7. Bottom left: histogram showing a false step height for the perpendicular monolayer of 3.85 nm. Bottom right: histogram showing a phase angle that is 3.52° lower on the top of perpendicular layer than on the parallel layer. AM mode measurement parameters are free amplitude $A_o = 12$ nm; set point amplitude $A = 8$ nm, cantilever resonant frequency $f = 50.0$ kHz, and cantilever $Q = 200$. (c) and (d) images recorded from the monolayer C32 film whose amplitude and phase approach curves are shown in Fig. 7. Bottom left: histogram showing a false step height for the perpendicular monolayer of 3.85 nm. Bottom right: histogram showing a phase angle that is 3.52° lower on the top of perpendicular layer than on the parallel layer. AM mode measurement parameters are free amplitude $A_o = 12$ nm; set point amplitude $A = 8$ nm, cantilever resonant frequency $f = 50.0$ kHz, and cantilever $Q = 200$.

**Fig. 9.** Measurement of the thickness of a perpendicular layer residing on a parallel layer as a function of the set point $A/A_o$ as discussed in the text. The phase shift is the phase angle measured on top of the perpendicular layer minus the angle on a parallel layer. Both height and phase are modal values determined from a histogram computed over a square scan area of side 5 µm. AM mode measurement parameters are free amplitude $A_o = 15$ nm; cantilever resonant frequency $f = 45.2$ kHz, and cantilever $Q = 141$.
At set points below 40%, the phase shift plotted in Fig. 9 begins to drop off rapidly to zero. This means the phase angles on the perpendicular and on the parallel surfaces approach each other as one enters the net repulsive regime so that the correction term vanishes and there is no false step-height effect as anticipated above.

However, as the phase shift approaches zero at the lowest set points, we see the step height of the perpendicular layer actually decreases more rapidly rather than increase to its true value. We suggest that this increase in the false step-height effect results from penetration of the perpendicular layer by the vibrating tip. We believe this penetration does not occur in the contact mode (the observed step height is in agreement with our X-ray measurement) due to the much softer cantilevers used (see Section 2) and our operation in the attractive regime. Thus, for the very soft materials that we are investigating, imaging in the net repulsive regime does not appear to be an option. We emphasize that there is no compressive effect when operating in the AM mode in the net attractive regime. As shown in Fig. 7(a), the amplitude on approaching both the perpendicular and parallel layers tracks that for a bare SiO$_2$ surface. The approach curves onto the C$_{32}$ layers do not show the delay in damping characteristic of tip penetration into the film (see, e.g., Fig. 14(c) in Ref. [2]).

In Fig. 9, we are uncertain as to the origin of the slight decrease in the perpendicular step height as the set point $A/A_c$ decreases from 80% down to 40%. This slight slope in the step height was not reproducible and occurs in a region where the phase shift is constant.

Theoretical understanding of the phase shift measured in the constant-amplitude AM mode is still incomplete. Both numerical simulations and analytical results show that phase shift variations can be caused by energy dissipation associated with the tip-sample interaction [17–20]. One of the sources of this energy dissipation identified by scanning in the attractive regime is hysteresis in the loading and unloading force [18,19]. We suggest that the alkane films considered here may be favorable systems to investigate the microscopic origin of inelastic tip–sample interactions in combination with molecular dynamics simulations [15]. The structure of the perpendicular layer is known and the adhesion forces to the adjacent parallel and perpendicular layers differ despite their identical chemical composition. Such studies will require improved control over tip wear and cleanliness than achieved in the measurements reported here.

5. Conclusion

We have shown that AFM measurements in the AM mode on films of C$_{32}$, a prototypical alkane molecule of intermediate length, yield false step heights between two surfaces that exert significantly different van der Waals forces on the cantilever tip. Such a step occurs in C$_{32}$ films between the top of a layer of molecules oriented with their long axis perpendicular to the surface residing on a layer of parallel molecules. In this case, the AM mode gives a false step height that is as much as 20% lower than that measured in the contact mode and by X-ray specular reflectivity measurements. However, when the perpendicular layer resides on another perpendicular layer, the AM and contact-mode measurements are both in reasonable agreement with the perpendicular layer thickness inferred from X-ray reflectivity measurements. Finally, we have shown how to correct the false step height by using the approximately linear relationship observed between phase angle and cantilever height measured in an approach curve.

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References

[14] This conclusion assumes the same interaction strength between the AFM tip and a methyl or methylene group in the film for the same separation distance. The estimate of the methyl group density is based on an area per molecule of 18.8 Å$^2$ for a C$_{32}$ perpendicular layer on SiO$_2$ (Ref. [4]). The methylene group density is based on an area per molecule of 209 and 196 Å$^2$ found for parallel C$_{32}$ layers on a Ag(111) (Ref. [6]) and a graphite (0 0 0 1) (Ref. [13]) surface, respectively.