The effect of intrinsic instability of cantilever on static mode atomic force spectroscopy

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Abstract

We show that the static force spectroscopy curve taken in an atomic force microscope is significantly modified due to presence of intrinsic cantilever instability which occurs as a result of its movement in a nonlinear force field. This instability acts in tandem with such instabilities as water bridge or molecular bond rupture and makes the static force spectroscopy curve (including ‘jump-off-contact’) dependent on the step size of data collection. A theoretical model has been proposed to explain the data. We emphasize the necessity of taking care of this fundamental instability of the microcantilever in calculating the adhesive force and also in the interpretation of data taken using an atomic force microscope.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The atomic force microscope (AFM) is one of the most widely used tools in nanoscience and nanotechnology. Since its discovery, the AFM [1] has emerged as a very powerful tool in the characterization of various properties of materials at the nanometer scale. This is primarily because the AFM can not only image with atomic resolution but it can also measure interatomic forces which are of the order of piconewtons or even much less. These capabilities make the AFM a versatile enabling tool in nanotechnology. Since the time of its discovery by Binning [1], many attempts have been made to explain some of the non-intuitive features seen in these systems. For example, the force versus distance (f–h) curves [2, 3] depend on whether the cantilever is approaching the sample or retracting away from it (henceforth referred to as the ‘approach’ and ‘retract’, respectively), leading to a hysteresis like behavior. The hysteresis has traditionally been attributed to adhesion due to a layer of water existing on the surface [4, 5], or the rupture of molecular bonds [6, 7], and has indeed been used to measure the ‘snap-off’ force. There are several studies on measuring the ‘snap-off’ force using an AFM in different environmental conditions (in vacuum and also in ambient air or nitrogen atmosphere) [7] as well as on different kind of surfaces (hydrophilic and hydrophobic) [8] to quantify the meniscus effect in ‘snap-off’ force measurements. Weisenhorn et al [9] have studied the (f–h) curves using an insulating tip on an insulating sample and also a conducting tip on a conducting sample in different liquids to study the effect of different liquids on (f–h) curves. Stifter et al [10] have theoretically studied the distance dependence of the capillary force and van der Waals force in an AFM for different humidities, surface tension and tip geometries. Although there exist several studies on (f–h) curves using an AFM, none of these studies focuses on how the van der Waals force and the capillary force can be separated from the measured ‘snap-off’ force in a simple experiment. Understanding forces such as the van der Waals force, and the capillary force between surfaces is the key to understanding how best to operate an AFM.

In this paper we show that the widely used practice of determining the ‘snap-off’ force from the (f–h) curves can be erroneous because the intrinsic instability of the cantilevers can actually modify the (f–h) curves. We also show how one can properly interpret the (f–h) curves in the context of these
instabilities. In an actual experiment the quantity measured is the cantilever deflection ($d$) as a function of the distance between the sample and the cantilever tip when the tip is in the equilibrium position (in the absence of any external force) ($h$). The force $f = k_c d$, where $k_c$ is cantilever spring constant. It is important to note that although the steps in which the sample approaches or retracts from the cantilever (the $z$-controller resolution) is very small ($\approx 0.025$ Å), the cantilever deflection $d$ is only measured at discrete points in the whole path. In all our discussions below we will define ‘step size’ ($\delta h$) as the distance between two such neighboring points, and assume that the distance between these points is covered smoothly without any noticeable change to the deflection. This assumption will be discussed in more detail later in the paper.

The aim of this paper is to show that if one tries to estimate the ‘snap-off’ force by using any arbitrary discrete set of data points then there can be a problem because the point of ‘jump-off-contact’ (JOC) depends on ‘step size’ of data collection. In this paper we show (in case of the van der Waals force) that the ‘step size’ dependency is present in acquiring the ($f$–$h$) curves using an AFM and hence the estimate of the ‘snap-off’ force can be erroneous.

If the maximum distance between the cantilever and the surface is $h_{\text{max}}$, and the number of data points acquired is $N$, then $h_{\text{max}} = Nh$. In the case of experiments done in ambient conditions, $N$ has been kept fixed at 500 (in one direction) and hence $\delta h$ can be varied by varying $h$, but for the experiments done in UHV, $h$ has been kept fixed while $N$ has been varied to vary the ‘step size’. The two important parameters that one obtains from the experimental $f$–$h$ curves are the ‘jump-into-contact’ (JIC) distance obtained from the approach part and the ‘jump-off-contact’ (JOC) from the retract part, as shown in figure 1(b). The force, defined by $f^* = k_c d^*$, where $d^*$ is the cantilever deflection at JOC, has traditionally been attributed to adhesion or molecular bond rupture. However, we observe experimentally that $d^*$ and $h^*$ (the tip–sample separation at JOC) depend on the ‘step size’ ($\delta h$). In this paper we show both experimentally, and through theoretical analysis, that these observed dependencies of $d^*$ and $h^*$ on $\delta h$ arise due to an intrinsic instability in the cantilever dynamics, which manifests itself mainly due to the procedure of data acquisition in most AFM. We show, in particular, that both the instabilities (the intrinsic instability and the ‘snap-off’ instability) occur in tandem. We also find that in an UHV-AFM where the ‘snap-off’ instability is absent, one observes the JIC and JOC arising solely from the intrinsic instability. The intrinsic instability arises mainly due to the motion of the cantilever in a nonlinear force field, and the two instabilities can be separated in a real AFM experiment by acquiring data as a function of $\delta h$. We find that the shift of the observed $d^*$ and $h^*$ on $\delta h$ can be clearly explained by our model. In this regard, we want to mention here that the inherent instability of the cantilever has been addressed previously in the context of amplitude modulation (AM) AFM [11, 12]. The paper is organized as follows. In section 2, we have provided the experimental details. In section 3, we introduce our simple spring–ball model for the motion of the cantilever. We solve the static force equation analytically to locate the instability that causes the JIC and JOC. Section 4 shows the simulated results to understand our experimental observations. We discuss the results in section 5. Finally in section 6, we present our conclusions.

2. Experimental results

2.1. Experiments done in ambient condition

The experiments were carried out using a commercial AFM (Model CP II, Veeco) [13] using cantilevers ($k_c = 0.1$ N m$^{-1}$) with a Si$_3$N$_4$ tip. The samples were clean Si wafers with a natural oxide layer unless otherwise stated. The cantilever tip had a radius of curvature, $R_t \approx 30$ nm, as determined by direct imaging with a scanning electron microscope (SEM). Experiments were carried out in a glove box with controlled RH using a flow of Ar gas at a temperature controlled environment at $28 \pm 2$°C. We have done the experiments at two different RH values—30% and 55%. We have also taken data on a hydrophobic Si surface created by etching the oxide layer using a 50:1 (v/v) HF:H$_2$O solution for 30 s. The rate of data collection was 0.1 Hz for all the experiments presented here.

Figure 2 shows a set of $d^*$ and $h^*$ plotted as a function of $\delta h$. The data have been obtained from the typical ($d$–$h$) curves. The data are taken with two representative humidities (RH = 30% and 55%) on a Si surface with an oxide layer (hydrophilic), as mentioned earlier. The formation of the water bridge depends on the hydrophilic nature of the surface. To investigate what happens in the absence of the water bridge, another set of data (figure 3) were taken on a hydrophobic surface. All the data show a definite trend. There are three regions in the data (barring the data taken on the hydrophobic surface). In region A, occurring at highest ‘step size’, we find that for $\delta h \geq \delta h_{c1}$, $d^*$ and $h^*$ reach a limiting value which is independent of $\delta h$. We call these limiting values $d^*_{\text{min}}$ and $h^*_{\text{min}}$, and they are almost independent of the RH values. In region C, occurring for smaller $\delta h$, the $d^*$ and $h^*$ again reach a limiting value $d^*_{\text{max}}$ and $h^*_{\text{max}}$ for $\delta h \leq \delta h_{c2}$ for a hydrophilic surface. However, in contrast to the region B, $\delta h \geq \delta h_{c1}$, $d^*_{\text{max}}$ and $h^*_{\text{max}}$ are not independent of the RH values. In particular $\delta h_{c2}$ is most sensitive to RH, and it increases as RH is decreased, along with the decrease in $d^*_{\text{max}}$ and $h^*_{\text{max}}$. For the hydrophobic surface (figure 3), there is no $\delta h_{c2}$, and $d^*$ ($h^*$, not shown here)
2. Experiments done using UHV-AFM

We have also performed these experiments using an UHV-AFM (Omicron) [14] with a base pressure of $10^{-8}$ mbar, using cantilevers ($k \approx 0.1$ N m$^{-1}$) with a Si$_3$N$_4$ tip on cleaned Si wafers with a natural oxide layer on them. The sample and the cantilever were baked in vacuum before placing them into the UHV chamber in order to ensure the absence of a water layer. Figure 4 shows the variation of $d^*$ as a function of $\delta h$, with the data taken using an UHV-AFM on a Si surface. The data taken in an UHV-AFM is similar to that taken on a hydrophobic surface (there is no $\delta h_{c2}$) and we can find only two regions—A and B.

Based on the above observations, we propose that the two limiting regions in the data (region A and C) are instability dominated regions that determine the cantilever motion. These instabilities, as we will see below, are of different types. The region B is the cross-over region where it makes transition from one type of instability dominated region to other type of instability region. The instability at the lower ‘step size’ (region C), which depends on the humidity and occurs only on a hydrophilic surface, is due to the ‘snap-off’ phenomena arising from the breaking of the water bridge at the tip–substrate interface. Strong proof in favor of this is the observation that it is absent in the data taken on a hydrophobic Si sample and also in the data taken using an UHV-AFM. In figure 5, we have plotted the $d^*$ versus $\delta h$ curves for data taken on a hydrophilic Si sample, on a hydrophobic Si sample and also the data taken in the UHV-AFM on a Si sample. As depicted in figure 5, the $d^*$ values are different in the regime B, as marked in the figure. The difference in $d^*$ values arises in the dynamics of data taking as well as on the initial conditions. The instability at a higher ‘step size’ (region A) is always present and arises due to the intrinsic instability that
we describe below. The theoretical analysis presented below validates our proposal.

3. Theoretical modeling

The AFM is a nonlinear system. Our aim here is to use a simple model which could explain the features seen in experiments. We model the motion of a cantilever by a spring–ball system. The basic spring–ball system has already been used in the past to model an AFM [15, 16]. Thus, we write the equation of motion of the cantilever as

\[ m \ddot{d}(t) + \eta \dot{d}(t) + k_c d(t) = f_a(h + d(t)). \tag{1} \]

Here, \( m \) is the mass of the cantilever, \( \eta \) is the friction constant, \( k_c \) is the spring constant, \( d(t) \) is the deflection of the cantilever measured from its equilibrium position in the absence of any external force, \( h \) is the distance between the sample and the tip when the tip is in the equilibrium position (in the absence of any external force), \( f_a(h + d) \) is the atomic force between the tip and the sample at the instantaneous position of the tip, and \( t \) represents time. The inherent nonlinearity of the cantilever due to its finite dimensions has not been introduced into our calculation, in order to keep things simple. In the case of the static (or quasi-equilibrium) experiment \( d(t) = d \), where \( d \) is the deflection of the cantilever at which it comes to rest. The dynamic equation will reduce to a simple static equation of the form

\[ k_c d = f_a(h + d). \tag{2} \]

While one can take a generalized force field for \( f_a(h + d) \) and obtain a solution, to have a definite result that can be verified by experiment we investigated the specific case of the van der Waals interaction between the tip and the surface. The subsequent results obtained are thus specific to the van der Waals interactions. The tip–sample force is modeled by a combination of the van der Waals force at large tip–sample distances \( (h) \), which is essentially attractive, and by the Derjaguin–Muller–Toporov (DMT) [17, 18] force, which is a combination of the attractive van der Waals like force (except that it is \( h \)-independent) and the repulsive forces arising due to elastic interaction between the tip and the sample. Thus, formally, the force is given by

\[ f_a(z) = \begin{cases} 
\frac{HR}{6z^2} & \text{for } z > a_0, \\
\frac{HR}{6a_0^2} + \frac{4}{3}E^* \sqrt{R/a_0 - z}^{3/2} & \text{for } z \leq a_0.
\end{cases} \tag{3} \]

Here, \( z = h + d \), \( a_0 \) is an intermolecular distance, \( H \) is the Hamaker constant, which depends on the material of the tip and the sample and also on the intervening medium. \( E^* \) is the effective Young’s modulus between the tip and the sample.

\[ \frac{1}{E^*} = \frac{(1 - \nu_t^2)}{E_t} + \frac{(1 - \nu_s^2)}{E_s}. \tag{4} \]

where \( \nu_t, \nu_s, \) and \( E_t \) and \( E_s \) are the Poisson’s ratio and the Young’s moduli of tip and sample respectively. Note that the form of the van der Waals force is chosen for a sphere-plate geometry, which is close to the real situation in an AFM experiment. The attractive force is the only force present when \( h + d > \) the intermolecular distance \( (a_0) \), whereas when \( h + d \leq a_0 \) the force has a repulsive component, which increases with reducing \( h \). The repulsive component typically ensures that \( h + d > 0 \). It is interesting to note that, while the repulsive force is essential, the qualitative understanding of the \( d-h \) curves, comes even when the repulsive force is taken to be absent. We have ignored the repulsive interaction in obtaining the exact solutions to the equation of motion of the cantilever. This will produce a slight deviation from the actual results, however, this will not change the conclusion. From equations (2) and (3) (in the region \( h + d > a_0 \)), after some simple manipulations, we obtain the equation for the deflection \( d \) as

\[ k_c d(h + d)^2 + \frac{HR}{6} = 0. \tag{5} \]

Rewriting \( \tilde{d} = d/h \) and \( \tilde{a} = HR/6k_c h^3 \), we get

\[ \tilde{d}(1 + \tilde{d})^2 + \tilde{a} = 0. \tag{6} \]

where \( \tilde{d} = d/h \) and \( \tilde{a} = HR/6k_c h^3 \) are dimensionless. The three exact solutions of this equation are already given in our earlier work [19], therefore we are not mentioning it here. For further discussion, we will refer to these three solutions as \( d_1, d_2 \) and \( d_3 \). Solution \( d_1 \) is real, while \( d_2 \) and \( d_3 \) are either both real or complex conjugates of each other, depending on the parameters of the equation. The actual deflection \( d \) is obtained by multiplying the solution by the corresponding tip–sample distance \( h \). Figure 6 shows the solutions of the actual deflection \( d \) as a function of the tip–sample distance \( h \) for \( H R = 2.26 \times 10^{-27} \text{ N m}^2 \) and \( a_0 = 0.172 \text{ nm} \). One can find out from figure 6 that \( d_1 + h \), obtained from analytical solution is always negative, because the repulsive part of the tip–sample interaction has not been considered. Of the three
solutions, the solution given by the open circles corresponds to
\(d_1 = \tilde{d}_1 \cdot h\), while the open squares and triangles correspond
to \(d_2 = \tilde{d}_2 \cdot h\) and \(d_3 = \tilde{d}_3 \cdot h\), respectively. Note that as the
tip–sample distance is reduced, the solutions corresponding to
\(d_2\) and \(d_3\) approach each other and they meet at a point \(P\) (for
example, at \(h \approx 2.9\) nm in figure 6). For tip sample distances
below this both these solutions become complex (in figure 6
only the real part is shown.) It should be noted that \(d_1\) and
\(d_3\) are stable solutions, while \(d_2\) is unstable. This has been
checked by finding the sign of the derivative of equation (2)
with respect to \(d\) at each value of \(h\). We denote the point where
the solutions \(d_2\) and \(d_3\) meet as the ‘jump-into-contact’ point.
This is the limit of stability for the solution \(d_3\), which defines
the motion of the cantilever for the approach curve to this point.
The distance of point \(P\) from the substrate is denoted by \(\xi\).
If the tip–sample distance \((h)\) is reduced beyond this point of
stability, there is only one real solution available \((d_1)\) and the
system will jump into the stable solution given by \(d_1\). This
defines the ‘jump-into-contact’. We also emphasize here, that
on the retract path the cantilever dynamics follow the solution
given by \(d_1\) until it jumps back to the solution given by \(d_3\) at
the ‘jump-off-contact’ point.

4. Simulation

We have also simulated the \(d–h\) curves by solving the equation
of motion of the cantilever. In particular, we have simulated
the \(d–h\) curves for the same parameters used for obtaining the
analytical solutions. The simulation is essential to solve the
equation of motion when both attractive and repulsive part of
the tip–sample interaction are present. In the case of simulation
we have taken into account both the attractive and the
repulsive part of the tip–sample interaction to achieve more
realistic results, as can be seen from figure 7. In simulation,
we have varied the tip–sample separation in specific steps and
at each step of the simulation we have calculated the force at
a particular \((h + d)\) value. This force value is then used
in the next step of the simulation, where we have solved the
equation of motion of the cantilever in the presence of tip–
sample interaction. Finally, by solving equation (1) we get the
deflection of the cantilever as a function of \(h\). In simulated
\(d–h\) curves we get a realistic \(d_1(= \tilde{d}_1 \cdot h)\), as in this case both
the attractive and repulsive part of the tip–sample interactions
are present. One can find from figure 7 that \(d_1 + h\), obtained
from simulation, is always positive. It can be noted that the
JIC position also matches quite well in the case of simulation
and analytical solutions. The \(d^*\) versus \(\delta h\) data obtained
from simulation is shown in figure 8. As can be seen from
figure 8 there are two regions in the data—region A and B
we have seen in case of UHV-AFM data and the data taken
on a hydrophobic Si substrate in ambient conditions. In our
simulation we have not considered the instability arising due
to the breaking of the water meniscus.

5. Discussions

We use figure 6 to explain the observed data. Here we have
assumed that, during the process of data acquisition for the
\(d–h\) curves, the motion of the cantilever is quasicontinuous,
i.e., at each point the initial deflection \((d)\) of the cantilever
is determined by its final deflection at the previous point. This
assumption is not exactly valid. In general, when the tip is
in contact with the surface the deflection would actually be
larger. However, note that our argument presented below is
to understand the point at which the ‘jump-off-contact’ occurs.
In this context, close to the ‘jump-off-contact’, this assumption
is not too bad. It is also important to note that the experimental
results clearly point out to the fact that the ‘step size’ remains
an important parameter irrespective of the ambient conditions
and the procedure of varying the ‘step size’ for acquiring \((f–h)\)
curves using the AFM.

In figure 6, we show two examples of the paths traced
by the cantilever (shown as steps). In one case (solid line
steps), for relatively large step sizes \((\delta h_{c2} < \delta h < \delta h_{c1})\),
the intrinsic instability dominates, and the jump from \(d_1\) to \(d_3\)
occurs when the equilibrium position at the point, just prior
to the jump, takes the cantilever across \(d_1\) (marked by a circle
in figure 6). This is the region B, as marked in figure 6. In
the other case (dotted line steps), for relatively smaller step

Figure 7. Plot of simulated \(d–h\) curves obtained for the same
parameters as used for analytical solutions.

Figure 8. The variations of \(|d^*|\) with ‘step size’ are shown for
UHV-AFM data on Si, data taken on a hydrophobic Si sample
and the simulated data. We can only see regions A and B in this
case. The simulated data is quantitatively similar to the data taken
on the hydrophobic surface and in the UHV-AFM. The two regions
(A and B) for the data taken on hydrophobic Si and the simulated
data are shown in the figure.
sizes \((\delta h \approx \delta h_{c1})\), the ‘snap-off’ instability dominates and causes a jump across the solution \(\delta_2\). This is the region C. Here, the instability is dominated by the ‘snap-off’ of the water bridge and \(l_{bg}\), the scale at which the water bridge snaps off, determines the point at which the jump to the stable solution \(\delta_3\) occurs. If \(\delta h \gg \xi\), then, during the retract part, the cantilever tip will jump directly to the stable solution \(\delta_3\) and \(d^* (h^*)\) becomes essentially independent of \(\delta h\). This corresponds to the region A, where the intrinsic instability is solely responsible for the JOC and which among other things depends on \(k_c\), the Hamaker constant \(H\) and the tip radius \(R_t\).

From the above discussion, in region A, we can thus identify \(\delta h \approx \delta h_{c1}\). In region B, \(d^* (h^*)\) increases as \(\delta h\) is decreased. This is the region described above (solid line steps in figure 6). In the absence of ‘snap-off’ instability, the region B extends the entire way down to very small step sizes, as seen in the experiments on hydrophobic surfaces and also in the case of data obtained from the UHV-AFM. On the other hand, if the ‘snap-off’ instability is present and \(\delta h \approx \delta h_{c2}\), the JOC occurs when \(h \approx l_{bg}\), as discussed above (dotted line steps in figure 6). This is the region we identify as region C. In this region \(d^* (h^*)\) is independent of \(\delta h\) and \(l_{bg}\) depends only on \(R_t\) and \(R_c\). Thus the qualitative discussion based on figure 6 clearly identifies the regions of the observed curve and the instabilities that give rise to them. Thus in an actual experiment the \((d-h)\) curves need to be taken as a function of \(\delta h\) and the regions corresponding to the two instabilities can be clearly identified. In this investigation, in region C, the ‘snap-off’ occurs due to the instability of the water bridge that forms between the tip and the sample. It was shown earlier [20] that, for a sphere-plate geometry, depending on the radius of curvature of the tip, the water bridge configuration becomes metastable for a particular sphere–sample separation when \(l_{bg} \approx h\) and \(R_t / h\) becomes \(\approx 1.0\), where \(R_t\) is the radius of curvature of the tip. For the tip used \(R_t = 30\, nm\), this should happen for \(h \approx 30\, nm\) which matches very well with the value of \(h_{max}^* \approx 26.5\, nm\) observed experimentally.

The main proposal of the paper, that there is an intrinsic instability of the cantilever, can be further tested if we can modify the \(f_0\) in a controlled way. In region A, \(\xi \approx \delta h_{c1}\) and our model gives \(\xi \approx (1.12 R_t / k_c)^{1/3}\). From the experimentally determined \(H\) and \(R_t\) we find that the calculated \(\delta h_{c1} \approx 2.9\, nm\) and the experimentally obtained value is 3.0 nm. We have also checked that if we use a softer cantilever having \(k_c = 0.03\, N\, m^{-1}\) \((R_t = 25\, nm)\) then \(\delta h_{c1}\) shifts to 4.32 nm (calculated value of \(\delta h_{c2}\) is 4.29 nm). It is thus clear that the intrinsic instability of the cantilever, the details of which is determined by the details of \(f_0\), has a direct effect on the observed force spectroscopy curve as obtained in an AFM.

6. Conclusions

In summary, we have shown that the static \(d-h\) curves (or \(f-h\)) obtained in an AFM, depend on the intrinsic instability of the microcantilever, which occurs due to its movement in a nonlinear force field. Phenomena, such as JIC and JOC, occur even in the absence of the water bridge ‘snap-off’, as in an UHV-AFM and on a hydrophobic surface. In presence of the water bridge, the effect of the two instabilities can be observed in the force spectroscopy curve as depending on an experimental parameter such as the ‘step size’ of data collection. At larger step sizes, the intrinsic instability dominates over the ‘snap-off’ instability, leading to erroneous results in the calculation of these forces. The instabilities due to ‘snap-off’ forces dominate at smaller step sizes.

The observed intrinsic instability of the cantilever (which exists even if there is no water bridge), will affect the observed force spectroscopy curves, as we have discussed in the paper. To avoid the effect arising from intrinsic instability, it is thus necessary to take the data as a function of step size. It is also necessary to mark the region of intrinsic instability by plotting the parameters \((d^*\) and \(h^*)\), as obtained from the \((d-h)\) curves, as a function of ‘step size’, as has been shown in figure 2. As a safer rule of thumb, it is always desirable to take the data with the smallest ‘step size’, where the instability due to the breaking of the water meniscus between the tip and the sample shows up. If adequate care is not taken of the issues discussed in the paper, one may reach the erroneous conclusion that the surface force is ‘step-size dependent’.

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References

[1] Binning G, Quate C F and Gerber Ch 1986 Phys. Rev. Lett. 56 930
[2] Cappella B and Dietler G 1999 Surf. Sci. Rep. 34 1
[3] Butt H J, Cappella B and Kappl M 2005 Surf. Sci. Rep. 59 1
[4] Cappella B, Baschieri P, Frediani C, Miccioni P and Ascoli C 1997 J. Vac. Sci. Technol. B 15 38
[5] Hao H W, Baro A M and Säen J J 1991 J. Vac. Sci. Technol. B 9 1323
[6] He M, Blum A S, Aston D E, Buenvajla C, Overney R M and Luginbühl R 2001 J. Chem. Phys. 114 1355
[7] Grobelny J, Pradecn P, Kim D-I and Ying Z C 2006 Appl. Phys. Lett. 88 091906
[8] Xia O and Qian L 2000 Langmuir 16 8153
[9] Weisenhorn A L, Maivald P, Butt H-J and Hansma P K 1992 Phys. Rev. B 45 11226
[10] Stifter T, Marti O and Bhushan B 2000 Phys. Rev. B 62 13667
[11] Paulo A S and Garcia R 2002 Phys. Rev. B 66 041406(R)
[12] Lee S I, Howell S W, Raman A and Reifenberger R 2002 Phys. Rev. B 65 114509
[13] Veece Instruments Inc. Corporate Headquarters 100 Sunnyside Blvd. Ste. B Woodbury New York 11797-2902
[14] Omicron NanoTechnology GmbH Limburger Str. 65232 Taunusstein
[15] Anzeykowski B, Krüger D and Fuchs H 1996 Phys. Rev. B 53 15485
[16] García R and Paula A S 2000 Phys. Rev. B 61 R13381
[17] Israelachvili J 1991 Intermolecular and Surface Forces (Orlando: Academic)
[18] Derjaguin B V, Muller V M and Toporov Y P 1975 J. Colloid Interface Sci. 53 314
[19] Das S, Sereemam A and Raychaphr A K 2007 Nanotechnology 15 385501
[20] Andrenko D, Patricio P and Vinogradova O I 2004 J. Chem. Phys. 121 4414