A method to quantitatively evaluate the Hamaker constant using the jump-into-contact effect in atomic force microscopy

Soma Das, P A Sreeram and A K Raychaudhuri

DST Unit for Nanoscience, S N Bose National Centre for Basic Sciences, Block JD, Sector III, Kolkata 700098, India

E-mail: soma@bose.res.in, sreeram@bose.res.in and arup@bose.res.in

Received 16 October 2006, in final form 18 November 2006
Published 3 January 2007
Online at stacks.iop.org/Nano/18/035501

Abstract
We find that the ‘jump-into-contact’ of the cantilever in the atomic force microscope (AFM) is caused by an inherent instability in the motion of the AFM cantilever. The analysis is based on a simple model of the cantilever moving in a nonlinear force field. We show that the ‘jump-into-contact’ distance can be used to find the interaction of the cantilever tip with the surface. In the specific context of the attractive van der Waals interaction, this method can be realized as a new method of measuring the Hamaker constant for materials. The Hamaker constant is determined from the deflection of the cantilever at the ‘jump-into-contact’ using the force constant of the cantilever and the tip radius of curvature, all of which can be obtained by measurements. The results have been verified experimentally on a sample of cleaved mica, a sample of Si wafer with natural oxide and a silver film, using a number of cantilevers with different spring constants. We emphasize that the method described here is applicable only to surfaces that have van der Waals interaction as the tip–sample interaction. We also find that the tip to sample separation at the ‘jump-into-contact’ is simply related to the cantilever deflection at this point, and this provides a method to exactly locate the surface.

1. Introduction

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 nanometre 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 made the AFM a versatile enabling tool in nanotechnology [2]. One of the standard experiments performed with an AFM is the measurement of the force–distance curves [3, 4], i.e. measurement of the force of interaction between the tip and the substrate. In this measurement, the cantilever deflection ($d$) is measured as a function of the separation of the tip and the sample ($z$) and the force of interaction is the product of the deflection $d$ of the cantilever and the spring constant $k_c$ of the cantilever.

(Note: The force obtained in this manner is not exactly the force between the tip and the sample, since the effective spring constant of the cantilever can be modified by the elastic deformation of the surface of the sample and the tip when they are in contact with each other. Hence, in our study, we will consistently use the concept of deflection of the cantilever instead of the force.) In the measurement of the force–distance curve, $d$ is measured from its equilibrium position (in the absence of any external force), when it is at a distance $h$ from the sample (the substrate), as shown in figure 1(a). The measured force–distance curve, shown schematically in figure 1(b), generally shows hysteresis. The approach curve...
shows a 'jump-into-contact' (JC) and the retraction part of the curve shows the 'jump-off-contact'. The concept of 'jump-off-contact' has been used extensively in the past as a quantitative measure of the adhesion force [5, 6]. One of the most ubiquitous explanations for the 'hysteresis-like' behaviour observed in the force–distance curves in an AFM is based on the presence of adhesion forces, due to a layer of water on the surface of the sample and the tip [7]. In contrast, however, not much attention has been paid to the phenomenon of 'jump-off-contact'. The concept of 'jump-off-contact' (JC), except for early papers that pointed out the basic causes for the existence of such a phenomenon [3, 8]. In this paper, we revisit the issue of 'jump-into-contact' again and present a new approach to the 'jump-into-contact' phenomenon in the force–distance curves of an AFM. This is done in order to investigate whether it can be used to obtain quantitatively some of the microscopic parameters of tip–sample interaction and thus can be made an useful tool. We find that the JC is a generic manifestation of the fundamental instability in the motion of the cantilever in a nonlinear force field. A simple model is used to understand this instability and obtain a quantitative measure of not only the distance \( h \) at which the JC should occur but also how much the magnitude of the deflection of the cantilever at the JC should be. These measures are directly related to parameters of the force field. We have performed experiments to verify some of the predictions of our theory. In this paper we investigate this phenomenon in the specific context of the van der Waals interaction, and from the measured deflection of the cantilever at the JC we determined the Hamaker constant. In order to keep things simple [9]. Thus, we write the equation of motion of the cantilever as

\[
m\ddot{d}(t) + \eta\dot{d}(t) + kd(t) = f_0(h + d(t)).
\]

Here, \( m \) is the mass of the cantilever, \( \eta \) is the friction constant, \( k \) 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), \( f_0(h + d) \) is the atomic force between the tip and the sample at the instantaneous position of the tip and \( t \) represents time. In 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

\[
k_d d = f_0(h + d).
\]

One can take a generalized force field for \( f_0(h + d) \) and obtain a solution to equation (2) that will give the parameters of the interaction potential. In order to have a definite result that can be verified by experiment, we investigated the specific case of van der Waals interaction between the tip and the surface and an elastically deformable surface for the contact force. The subsequent results obtained are thus specific to the van der Waals interactions. The tip–sample force is modelled 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) [10, 11] 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

\[
f_0(z) = \begin{cases} 
-HR_1/6z^2 & \text{for } z > a_0, \\
-HR_1/6a_0^3 + 4\pi R_1^2(a_0 - z)^{3/2} & \text{for } z \leq a_0.
\end{cases}
\]
Here, \( z = h + d \), \( a_0 \) is an intermolecular distance, and \( H \) 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 elastic modulus between the tip and the sample. 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. In this paper, we will only concentrate on the regime where \( z > a_0 \), where the force is purely a van der Waals force. We will see below that the JC is mainly determined by the attractive part of the interaction.

For the observation of the JC, we work in the region of attractive interaction and take the force on the right-hand side of equation (2) to be the van der Waals force. This is justified because we will see below that the ‘jump-into-contact’ distance is usually much larger than \( a_0 \). From equations (2) and (3), after some simple manipulations, we obtain the equation for the deflection \( (d) \) as

\[
k_d d + d^2 + \frac{H R_i}{6} = 0.
\]

Rewriting \( \tilde{a} = d/h \) and \( \tilde{\alpha} = H R_i / 6 k_i h^3 \), we get

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

The three solutions of this equation are given by

\[
\tilde{a}_1 = -\frac{b_2}{3} + (S + T)
\]

\[
\tilde{a}_2 = -\frac{b_2}{3} - \frac{1}{2}(S + T) + \frac{\sqrt{3}}{2}(T - S)
\]

\[
\tilde{a}_3 = -\frac{b_2}{3} - \frac{1}{2}(S + T) - \frac{\sqrt{3}}{2}(T - S)
\]

where

\[
S = (R + \sqrt{D})^{1/3}
\]

\[
T = (R - \sqrt{D})^{1/3}
\]

\[
R = \frac{9 b_1 b_3 - 27 b_0 - 2 b_3^2}{54}
\]

\[
D = Q^3 + R^2
\]

\[
Q = \frac{3 b_1 - b_2^2}{9}
\]

and \( b_0, b_1 \) and \( b_2 \) are the coefficients of \( \tilde{a}^3, \tilde{a}^2 \) and \( \tilde{a} \) in equation (5). Here we want to mention that equation (6) is valid only for the real values of \( S \) and \( T \) defined in equation (6). For complex values, the expressions for equation (6) will change. It can be easily seen that \( b_0 = \tilde{\alpha}, b_1 = 1 \) and \( b_2 = 2 \). The distance \( \tilde{a}_1 \) has only a real part, while the solutions \( \tilde{a}_2 \) and \( \tilde{a}_3 \) are either 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 2 shows the solutions of the actual deflection \( (d) \) as a function of the tip–sample distance \( (h) \) for \( H R_i = 2.26 \times 10^{-27} \) N m², \( k_i = 0.1 \) N m⁻¹ and \( a_0 = 0.15 \) nm. Of the three solutions, the solution given by the open circles corresponds to \( \tilde{a}_1 = \tilde{a}_1 h \)

while the open square and triangle correspond to \( \tilde{a}_2 = \tilde{a}_2 h \) and \( \tilde{a}_3 = \tilde{a}_3 h \) respectively. Note that as the tip–sample distance is reduced, the solutions corresponding to \( \tilde{a}_2 \) and \( \tilde{a}_3 \) approach each other and they meet at one point (for example, at \( h \approx 2.9 \) nm in figure 2). For tip–sample distances below this both these solutions become complex (in figure 2 only the real part is shown). It is necessary to note that the solutions \( \tilde{a}_1 \) and \( \tilde{d}_1 \) are stable solutions, while \( \tilde{a}_2 \) is unstable. This has been checked by finding the sign of the derivative of equation (1) with respect to \( d \) at each value of \( h \). We denote the point where the solutions \( \tilde{a}_2 \) and \( \tilde{d}_1 \) meet as the ‘jump-into-contact’ point. This is the limit of stability for the solution \( \tilde{a}_1 \) which defines the motion of the cantilever for the approach curve up to this point. If the tip–sample distance \( (h) \) is reduced beyond this point of stability, there is only one real solution available \( (\tilde{a}_1) \) and the system will jump into the stable solution given by \( \tilde{a}_1 \). This defines the ‘jump-into-contact’. It must be noted here that this jump has occurred in the attractive regime and we do not take recourse to any adhesion forces for explaining the phenomenon. We also emphasize here that on the retract path the cantilever dynamics follow the solution given by \( \tilde{a}_1 \) until it jumps back to the solution given by \( \tilde{a}_1 \) at the ‘jump-off-contact’ point. The solutions of the cubic equation given by equation (6) has a number of interesting features. For example, let us consider the point where the ‘jump-into-contact’ occurs in our model. At this point \( \tilde{a}_2 = \tilde{a}_1 \) and the discriminant \( D \) is exactly equal to zero. If we denote the tip–sample distance at this point by \( h_j \), and corresponding values of \( R, Q \) as \( R_j, Q_j \), we get the equation

\[
R_j + \sqrt{Q_j^3 + R_j^2} = R_j - \sqrt{Q_j^3 + R_j^2}
\]

which leads to the equation

\[
Q_j^3 = -R_j^2.
\]

Replacing the expressions for \( Q_j \), and \( R_j \) from equation (7), and putting in the values of \( b_0, b_1 \) and \( b_2 \), we get

\[
\frac{H R_i}{6 k_i h_j} = \frac{4}{27}
\]

1 Other cases of modelling tip shapes are also present in the literature. See, for example, Touhari et al. [12].
Equation (10) can be used to find the Hamaker constant \((H)\) because the tip radius \(R_t\) and the cantilever spring constant \(k_c\) are known and \(h_j\) is experimentally measurable. However, the problem arises because with the position of the surface not being known exactly, the absolute value of \(h_j\) has a large uncertainty. Below, we show that the magnitude of the jump of the cantilever at the JC is simply related to \(k_c\) and \(R_t\), both of which, however, are experimentally measurable [13, 14].

At the JC, there are only two distinct real solutions to the cubic equation since the solutions corresponding to \(d_2\) and \(d_3\) are degenerate. Subtracting \(d_3\) from \(d_1\), and again putting in the values of \(b_0, b_1\) and \(b_2\), we get the jump of the cantilever \((\Delta d)\) at the JC as

\[
\Delta d = d_1^j - d_3^j = -h_j^j \quad (11)
\]

where \(d_1^j\) and \(d_3^j\) are the deflections at the ‘jump-into-contact’ point corresponding to the two solutions. Equations (10) and (11) lead to a practical way of calculating the Hamaker constant from the deflection–displacement curves. Determination of the Hamaker constant from equations (10) and (11) will need knowledge of \(k_c\) and \(R_t\) of a given cantilever which can be obtained from experiment. Alternatively, we note that if \(h_j\) is measured for a material with known Hamaker constant, this can be used to calibrate the \(k_c/R_t\) ratio of a given cantilever, which in turn can be used to find an unknown Hamaker constant. Given the practical difficulties in knowing \(k_c\) and \(R_t\) exactly, this may be a more practical method. Note also that equation (11) is itself independent of the material of the tip, sample and the intervening medium. The above-mentioned process also indicates that one can obtain a precise method of shifting the raw data obtained from the AFM measurements to properly locate the surface.

3. Experimental verification

The data have been taken using an atomic force microscope (Model CP II) from Veeco\(^2\) on freshly cleaved mica, on Si wafer with natural oxide and on a silver metal film. We have used three different cantilevers for taking data for a given surface in order to vary the \(k_c/R_t\) ratio. The cantilevers used had Si₃N₄ tips and spring constants (radius of curvature) of 0.03 N m\(^{-1}\) \((R_t = 30 \text{ nm})\), 0.1 N m\(^{-1}\) \((R_t = 35 \text{ nm})\) and 0.9 N m\(^{-1}\) \((R_t = 50 \text{ nm})\). We have found the radius of curvature of the tip from the images taken by a field emission gun scanning electron microscope (FEG-SEM). The medium between the tip and sample for all the experiments was air at room temperature and the rates of data collection were 0.5 and 0.1 Hz. We have repeatedly taken the force–distance curves using the same three cantilevers mentioned above. The reproducibility of the data confirms that there was no damage of the tip of the cantilever during the experiment, and this is also corroborated by the FEG-SEM images. While all possible efforts have been made to eliminate the effects of additional extraneous interactions, the possibility of electrostatic forces due to space charges cannot be completely ruled out. However, as we show below that our results are in good agreement with earlier work, [15–17], we do not expect a substantial electrostatic presence in our experiments, since electrostatic forces are expected to modify the results by a large amount. It would, however, be interesting to observe the effect of electrostatic interactions.

Figure 3 shows a typical AFM deflection \((d)\) versus displacement \((h)\) curve for a freshly cleaved mica sample and a Si₃N₄ tip of spring constant 0.1 N m\(^{-1}\) in air. The data have been plotted as deflection versus distance. The arrows in figure 3 indicate the direction of motion of the cantilever (approach and retract). The JC region is highlighted in the inset.

Figure 3. Approach and retract curves of the deflection \((d)\) versus displacement \((h)\) curve for a freshly cleaved mica sample and a Si₃N₄ tip of spring constant 0.1 N m\(^{-1}\) in air. The arrows indicate the direction of motion of the cantilever (approach and retract). The JC region is highlighted in the inset.

2. Veeco Instruments Inc., Corporate Headquarters, 100 Sunnyside Boulevard, Suite B, Woodbury, New York 11797-2902.
and they show the extent of variance one would expect in such experiments. The reproducibility of the data also indicates that the tip, used in the experiment, did not get damaged during the collection of the data. From our experiment we obtain $H \approx (0.64 \pm 0.07) \times 10^{-19}$ J for mica, $H \approx (0.66 \pm 0.27) \times 10^{-19}$ J for SiO$_2$ and $H \approx (3.73 \pm 0.89) \times 10^{-19}$ J for silver. A summary of results obtained is shown in table 1. This can be compared with calculated values of $1.28 \times 10^{-19}$ J for mica [18], $1.21 \times 10^{-19}$ J for SiO$_2$ [18] and $2.9 \times 10^{-19}$ J for silver [15], using Si$_3$N$_4$ as the tip material with vacuum as the intervening medium. A similar calculation with water as the intervening medium gives $0.245 \times 10^{-19}$ J for mica [18], $0.207 \times 10^{-19}$ J for SiO$_2$ [18] and $1.39 \times 10^{-19}$ J for silver [17] with Si$_3$N$_4$ as the tip material. These values have been obtained from calculations using full Lifshitz theory [19–21] for the individual materials. The values we have obtained experimentally lie between the Hamaker constant values for vacuum as the intervening medium and water as the intervening medium, suggesting the influence of the relative humidity of air in calculating the Hamaker constant. The relative humidity in the glove chamber during measurement was typically $\sim 55\%$ (for mica and SiO$_2$) and $\sim 33\%$ for silver. Since the JC data are routinely obtained while one measures the force–distance curve, it is easy to obtain a very important physical parameter from the same experiment. We point out that the utility of the JC data to obtain a quantitative measure of a physical parameter such as the Hamaker constant is novel, and the uncertainty in the determination of $h_j$ can be eliminated by measurement of $\Delta d$ and the $(k_c/R_c)$ ratio. As mentioned before, a known tip–surface system (known Hamaker constant) can be used to calibrate a given cantilever $(k_c/R_c)$ ratio using equations (10) and (11) if no direct measurements of $k_c$ and $R_c$ are available. This calibration can also be used to find the Hamaker constant for unknown surface. We also emphasize that since, for a given cantilever, the $(k_c/R_c)$ ratio is fixed, a map of the JC on an inhomogeneous surface can generate a map of the Hamaker constant.

There are quite a few methods of measuring the Hamaker constant [22]. These methods include direct force measurements using a surface force apparatus [23] and an atomic force microscope [4, 24–26] where the full force–distance curve is fitted to a model of the van der Waals equation. The other methods are based on measuring physical properties of materials, such as the dielectric constant [27, 28]. In general, Lifshitz theory [19–21] is widely used for calculating Hamaker constants from the dielectric constant of materials. We note that the reported values of Hamaker constants for the same material obtained from different methods showed considerable variations [22]. The earlier works in obtaining Hamaker constant from an atomic force microscope were mainly based on fitting the attractive part of the approach curve with the expression for the van der Waals force. In that method the main problem was the presence of the ‘jump-into-contact’. In our method we have actually used the ‘jump-into-contact’ to find the interaction constant.

The advantage of measuring the Hamaker constant using the method described in this paper is that we can find the ‘jump-into-contact’ distance from experimental force–distance curves using equation (11) easily. No numerical fit to the complete force–distance curve is necessary. Here we also want to emphasize that this method has the advantage of mapping the Hamaker constant in an inhomogeneous system whereas this is not possible using a surface force apparatus because it does not have the spatial resolution. Two important points have to be noted in this context: first, the experimental force–distance curves should be taken properly for approach of the cantilever motion with close measurements near the JC, and second, the radius of the tip ($R_t$) and the spring constant of the cantilever ($k_c$) have to be found with least uncertainty if absolute data have to be obtained.

We point out that equation (11) is also a very important outcome of this work. This gives us a way to determine the actual position of the surface. In AFM measurements there is indeed a problem in evaluating the absolute value of the tip–sample separation ($h$). The JC is a special point at which the distance ($h$) is equal to $|\Delta d|$, which thus can be appropriately fixed. Once this is fixed the position of the origin of $h$ (the sample) can be located. We emphasize that
the analysis above is applicable only to surfaces that have van der Waals interaction as the tip–sample interaction because of the specific type of tip–sample interaction used. However, the method is general enough and can be used with other tip–sample interactions as well. The fact that a nonlinear force field introduces an instability that leads to ‘jump-into-contact’ is a conclusion of general validity.

4. Conclusions

We have studied the static deflection–distance curves for an atomic force microscope using a simple model that gives the ‘jump-into-contact’ often observed in force–distance curves of an AFM as an instability of the cantilever moving in a nonlinear force field. The model provides a unique method of determining the tip–sample interaction parameters. We have developed the concept specially for van der Waals interaction for definiteness. In this case the method gives the Hamaker constant. We find values that are comparable to the Hamaker constant measured by other methods. The model also provides a reliable criterion for locating the sample and thus shifting the raw deflection–distance data obtained from AFM by locating the distance at which the ‘jump-into-contact’ occurs. This process removes the arbitrariness of locating the sample in the AFM. The method also gives us a way to map the Hamaker constant over a surface, that may be inhomogeneous, by mapping the JC with an AFM, for hard samples (i.e. samples with small deformations due to tip–sample interactions). It must be noted here that this is one of the problems which has to be addressed in the case of soft samples (polymers, biological molecules, etc), where tip–sample forces can dramatically modify the effective tip–sample distance. In such cases, the JC will not provide an accurate measurement of the tip–sample distance. One possibility is to use cantilevers of very small spring constant \( k_s \), so that the JC occurs at large enough distances, where the deformation of the sample may become less important. This is, however, a problem to be investigated further.

Acknowledgments

The authors want to thank the Department of Science and Technology, Government of India, for financial support as a Unit for Nanoscience. One of the authors (PAS) would like to thank Professor B Dutta Roy for very useful suggestions.

References

[1] Binning G, Quate C F and Gerber Ch 1986 Phys. Rev. Lett. 56 930
[2] Giessbuhl F J 2003 Rev. Mod. Phys. 75 949
[3] Cappella B and Dietler G 1999 Surf. Sci. Rep. 34 1
[4] Butt H J, Cappella B and Kappl M 2005 Surf. Sci. Rep. 59 1
[5] Cappella B, Baschieri P, Frediani C, Miccoli P and Ascoli C 1997 IEEE Eng. Med. Biol. Mag. 16 58
[6] Hao H W, Baró A M and Säenz J J 1991 J. Vac. Sci. Technol. B 9 1323
[7] Sarid D, Hunt J P, Workman R K, Yao X and Peterson C A 1998 Appl. Phys. A 66 8283
[8] Burnham N A and Colton R J 1989 J. Vac. Sci. Technol. A 7 2006
[9] For a recent review on theories of SFM, see, Hofer W A, Foster A S and Shluger A L 2003 Rev. Mod. Phys. 75 1287
[10] Israelachvili J 1991 Interfacial and Surface Forces (London: Academic)
[11] Derjaguin B V, Müller V M and Toporov Y P 1975 J. Colloid Interface Sci. 53 314
[12] Touhari F, Bouju X, Girard Ch, Devel M and Cohen-Solal G 1998 Appl. Surf. Sci. 125 351
[13] Zanette S I, Caride A O, Nunes V B, Klimchitskaya G L, Freire F L Jr and Prioli R 2000 Surf. Sci. 453 75
[14] Cook S M, Schäffer T E, Chynoweth K M, Wighton M, Simmonds R W and Lang K M 2006 Nanotechnology 17 2135
[15] Charleux C A and Seah M P 2005 Nanotechnology 16 1666
[16] Parker J L 1992 Langmuir 8 551
[17] Coakley C J and Tabor D 1978 J. Phys. D: Appl. Phys. 11 L77
[18] Visser J 1976 Adv. Colloid Interface Sci. 3 331
[19] Bergström L 1997 Adv. Colloid Interface Sci. 70 125
[20] Lifshitz E M 1956 Sov. Phys.—JETP 2 73
[21] Dzyaloshinskii I E, Lifshitz E M and Pitaevskii L P 1961 Sov. Phys.—JETP 11 1001
[22] Ackler H D, French R H and Chiang Y-M 1996 J. Colloid Interface Sci. 179 460
[23] Horn R G, Clarke D R and Clarkson M T 1988 J. Mater. Res. 3 413
[24] Burnham N A, Dominguez D D, Mowery R L and Colton R J 1990 Phys. Rev. Lett. 64 1931
[25] Ederth T 2001 Langmuir 17 3329
[26] Seog J, Dean D, Plass A H K, Wong-Palms S, Grodzinsky A J and Ortiz C 2002 Macromolecules 35 5601
[27] Tabor F R S D and Winterton R H S 1969 Proc. R. Soc. 312 435
[28] Hough D B and White L R 1980 Adv. Colloid Interface Sci. 14 3