Tip and surface properties from the distance dependence of tip–surface interactions

A.S. Foster*, **L.N. Kantorovich**, **A.L. Shluger**

Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK

Abstract. Macroscopic "background" interactions, such as van der Waals and electrostatic forces, determine the frequency change in non-contact atomic force microscopy (NC-AFM). We demonstrate that by analysing the distance dependence of these interactions one can extract more information about the tip radius, charge and chemical composition, as well as about the surface charging and conductivity. For this purpose we calculate the interaction of different NC-AFM tips with a charged and neutral CaF_2 (111) surface and with an ideal metal surface. Force versus distance curves demonstrate a remarkably different behaviour, especially at long distances, dependent on whether the tip is conductive, oxidised or charged. Comparison with experimental curves proves that this analysis can predict tip properties.

PACS: 68.37.Ps; 68.35.Dv; 61.50.Ah; 61.72Bb

Many interpretation problems in non-contact atomic force microscopy (NC-AFM) experiments are due to the lack of physical information about the tip, surface and tip–surface interaction. In general, experiments cannot identify resolved features and theory cannot help without more information about the tip and surface structures [1, 2]. Atomic-scale contrast in NC-AFM images is determined by relatively small spatial variations (of the order of 1 Hz) in the cantilever frequency change. The overall frequency change itself is determined mainly by "background" van der Waals and electrostatic forces, as reviewed in [3]. We will demonstrate that by analysing the distance dependence of these forces one can extract more information about the tip radius, charge and chemical composition, as well as the surface properties.

There has been a number of previous studies of force versus distance curves. Recent theoretical and experimental studies on semiconductors [4–7] and insulators [8] have used short-range force versus distance curves to analyse the mechanism of contrast and the changes in interactions over different surface sites. Analysis of the tip–surface interaction at longer-range has also been performed [9, 10], but the possible components of the long-range interaction were not studied in detail. Recent experimental studies [11, 12] have tried to separate out the tip–surface interaction components. These studies assume that any electrostatic interaction has been compensated for by applied bias and the tip–surface interaction is van der Waals alone. However, they were unable to explain the unphysically long-range chemical forces needed to fit the strength of interaction at medium range. It has been shown previously [3, 13, 14] that many other interactions can be significant in AFM, and van der Waals is rarely the sole component of the long-range tip–surface interaction. In fact, it is the other components of the tip–surface interaction which often hold the most information about the tip and surface structure. The image force, for example, depends crucially on the conduction and oxidation of the tip, whereas the van der Waals interaction is dominated by the tip radius.

The aim of this theoretical study is to find better ways of characterising tips and surfaces by systematically using frequency change versus distance curves. We consider two generic cases prompted by our attempts to understand the experimental NC-AFM data on insulating and metallic surfaces. Firstly, the tip interaction with the surface of bulk insulator calcium difluoride (111) has been studied. We demonstrate that, by analysing frequency change versus distance curves after scanning, one should be able to distinguish between the interaction due to a very blunt tip or an electrostatic interaction of a charged tip and surface. Secondly, we suggest that one can use the tip interaction with a well-characterised metal surface in order to find out more about the tip structure, conductivity and charge. By comparing tip–surface interactions for different tip types, characteristic tip "fingerprints" can be established. These fingerprints can be then compared to experimental results on metal surfaces and used to predict the chemical and physical properties of the tip.

1 Method

Our NC-AFM model is similar to that described in [8, 15], so this section will only discuss aspects which are specific to

---

*Corresponding author. (E-mail: asf@fyslab.hut.fi)

the systems studied here. The calculation setup employed for modelling the tip interaction with CaF$_2$ is described in more detail in [2]. Briefly, a conical conductive tip with a spherical apex of radius R and an embedded oxide nano-tip is scanned over an atomistic CaF$_2$ slab on a conducting substrate. A bias U is applied between the conducting tip and surface. The same setup is used for the calculations over a metal, but now the conducting substrate is effectively the surface being studied. However, the metal atoms are not included explicitly in the model and the metal is treated as an ideal conductor where polarization due to the tip–surface interaction is represented by point image charges [15]. This means that the tip–surface interaction is not physically close to the metal surface (< 0.5 nm), but for this study only longer-range interactions are of interest.

The force between tip and sample has three general components: (a) the microscopic chemical force between atoms in the tip and surface, including van der Waals force between ions, (b) the macroscopic van der Waals force between the tip and surface, and (c) the electrostatic forces due to bias in the system, charging and polarization of conducting materials [15]. The macroscopic and microscopic interactions are combined in the same way as described in [8, 15]. The macroscopic part of the van der Waals force is calculated using a Hamaker constant of 1 eV for CaF$_2$ and 2.5 eV for the metal and the method described in [16]. The microscopic and image force are calculated using a static atomistic simulation technique and the SCIFI [15] code. SCIFI self-consistently calculates the equilibrium atomic structure under the influence of microscopic and image forces, as well as bias.

We calculate the change in oscillation frequency at a given tip–surface separation [8] under the influence of the total tip–surface interaction. Frequency curves over CaF$_2$ were produced with a cantilever amplitude of 46 nm, an eigenfrequency of 84 kHz and a spring constant of 6 N/m, as in experiments [17]. The metal frequency curves were calculated with a cantilever amplitude of 6.5 nm, an eigenfrequency of 168 kHz and a spring constant of 31.2 N/m, as in experiments on copper [12].

2 Results

2.1 Calcium difluoride

The origins of the background force in NC-AFM experiments vary depending on the system studied. Recent AFM studies [18] on the CaF$_2$ surface have shown that it is likely to be charged, and it is well known that the tip can be made blunt and/or charged due to argon sputtering. It is likely that several effects contribute to the tip–surface interaction; thus, in order to investigate whether it is possible to distinguish between the different cases, we set up the model so that the entire background force is dominated by one source and studied its distance dependence. To model a system with no surface charge where the macroscopic van der Waals interaction dominates the background force, a very blunt tip of radius 400 nm was used. For the case where the surface is charged, a sharp tip of radius 3.33 nm was used and discrete electric charges were placed in the surface and tip. The tip was charged by $+4\,e$ and the surface by about $0.6\,e/\mathrm{nm}^2$.
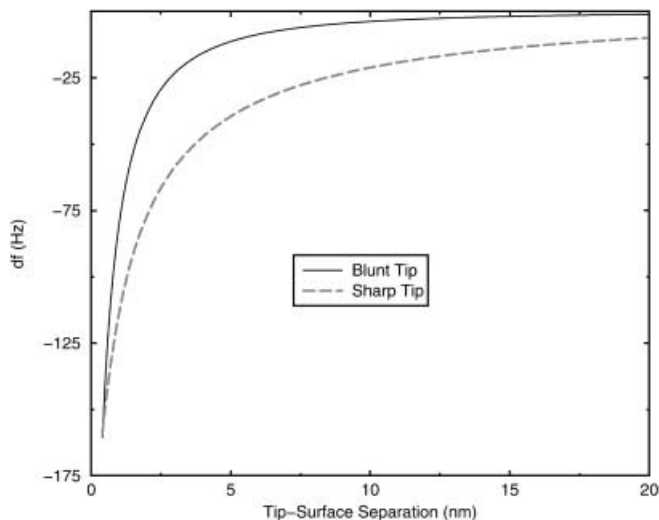

Fig. 1. Frequency change versus distance curves over the CaF$_2$ (111) surface. The *blunt tip curve* uses a large radius tip and a background force consisting of only a van der Waals interaction. The *sharp tip curve* uses a small radius tip and the background force is composed of a van der Waals and an electrostatic interaction due to surface charging

The magnitudes of these charges were chosen so as to reproduce the observed experimental frequency change at scanning height. The charges produce a long-range electrostatic force which dominates the background force. It is interesting to note that although these forces are very different they both reproduce experimentally observed frequency changes using experimental parameters [17].

Figure 1 shows the distance dependence of the tip–surface interaction for the two different interaction schemes. The blunt tip demonstrates a fast decay, characteristic of a pure van der Waals interaction. The change in oscillation frequency is already less than 10 Hz beyond 7.5 nm. The sharp tip shows a much slower decay; the change in frequency is over 30 Hz at 7.5 nm and remains above 10 Hz until around 20 nm. This is characteristic of the electrostatic interaction between the charged tip and surface. The image force due to polarisation of the conductive tip by the ionic sample also makes a significant contribution to the interaction at medium range (< 5 nm). This marked difference in the distance behaviour suggests that by analysing an experimental curve one should be able to determine the dominant force contribution and in this way characterise the tip and surface.

2.2 Interaction with metal

In this section we will explore whether one could use metal substrates as standard systems for tip characterisation. We consider four tips which could be produced by appropriate preparation, such as doping, oxidation, sputtering, etc. Each of the tip types include a macroscopic tip of radius 10 nm and no bias. The four tip types are: (a) "insulator" – this represents the situation where the macroscopic tip is insulating (Hamaker constant reduced to 1 eV) and the nano-tip is neutral; (b) "conductor" – the macroscopic tip is conducting and there is no nano-tip; (c) "neutral tip" – the macroscopic tip is conducting and there is a neutral
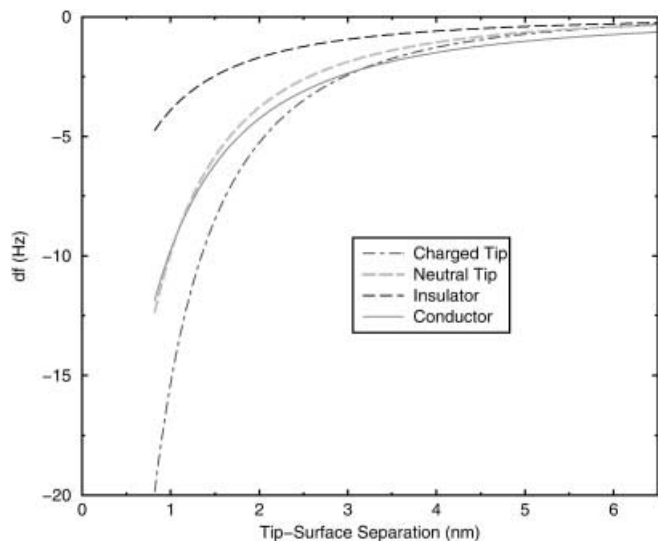
S61

Fig. 2. Frequency change versus distance curves over a metal surface

Fig. 3. Comparison of theoretical and experimental frequency change versus distance curves over a metal surface

nano-tip; and (d) "charged tip" – the macroscopic tip is conducting and there is a charged nano-tip. Figure 2 shows frequency change versus distance curves for each of the tip types.

Figure 2 demonstrates that the different tips give different long-range tip–surface interactions. The weakest interaction is for the insulating tip, where the force is dominated by the van der Waals interaction. In this case the image force is insignificant, as the polarization that occurs within the metal is not mirrored in the tip. For the conducting tip, the interaction at long-range is solely van der Waals as there is no oxide nano-tip to polarize the metal surface. The force is greater than for the insulating tip even though the radii are the same, as the conducting tip has a greater Hamaker constant (2.5 compared to 1.0 eV) for the macroscopic van der Waals interaction with the metal. When the neutral oxide nano-tip is added to the conducting tip, a deviation from the pure van der Waals behaviour can be seen. This is due to the image force between the tip and surface, produced when the oxide nano-tip polarizes the tip and the metal. Beyond about 1 nm the image force is actually repulsive, but it very rapidly decays and is a small contribution to the overall interaction as the tip approaches the metal surface. At very close range the image force is significant, but this study is concerned only with the more long-range interactions. In the final charged tip curve, the nano-tip has a charge of +4 e. This increases the magnitude of the polarization of the metal and the image force increases by an order of magnitude. In previous curves with a neutral nano-tip, the equal positive and negative ions of the oxide compensate each other's polarizing of the metal and the image force is small. However, with the charged tip the uncompensated interaction produces a large image force, which is comparable to van der Waals force at tip–surface separations of less than 2 nm.

These results predict the ability of frequency change versus distance curves to differentiate between different tip models. To demonstrate how this analysis can work for real systems, we compare the theoretical predictions with experimental results [12] over a copper surface. Figure 3
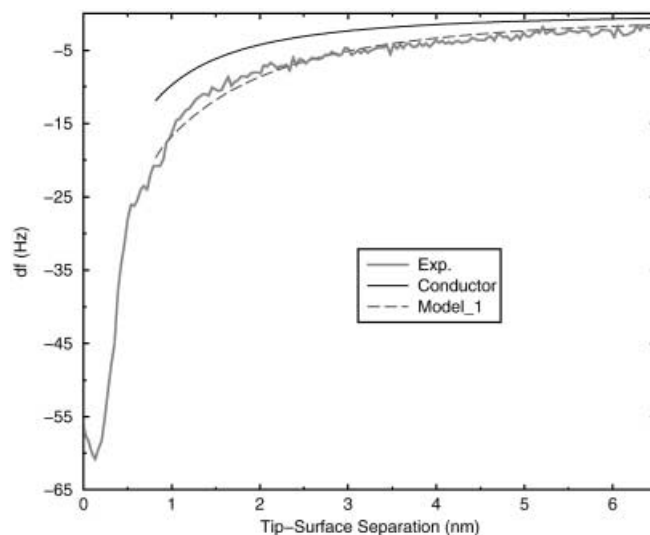
shows a comparison of two different models of the tip–surface interaction with an experimental curve [12]. Since there is no reference for the distance scale in experiments, the experimental curve has been set so that the minimum of the curve is at 0.2 nm, which is a reasonable estimate of where repulsion due to electron orbital overlap would begin. The two theoretical interaction models used in Fig. 3 are as follows: (a) conductor – conducting macroscopic tip with no nano-tip, the same as in Fig. 2; and (b) conducting macroscopic tip with a neutral nano-tip, simulating an oxide coating, and an applied bias, which we call model_1. Model_1 was fitted to the experimental results by varying the macroscopic tip radius and applied bias. The best fit was found with a tip radius of 4 nm and a bias of 1.2 V.

Figure 3 shows that in the conductor model the tip–surface interaction is much weaker than that observed in the experiment. To check whether this was not just due to a much blunter tip being used in the experiment, a series of curves for tip radii from 4 to 32 nm were calculated and none could match the experimental behaviour. Radii which could match the strength of the interaction at long range gave an interaction much stronger than that observed at close range. This demonstrates that the interaction is not due to pure van der Waals and that other components are significant. The bias applied in model_1 increases the overall electrostatic interaction by adding a long-range capacitance force to the system. The magnitude of the bias needed for the fit is a parameter dependent on the model chosen. Although slight variations of the radius and bias would produce curves similar to those for model_1 in Fig. 3, the ratio between the electrostatic and van der Waals forces is important. Using widely different parameters produces curves matching the experiment only at short or long range, but not both. This implies that the tip radius in the experiments was about 4 nm and an electrostatic force, corresponding to a bias of 1.2 V in this model, was present. A phenomelogical model [13] of the capacitance force was also compared with model_1 and the results were found to be similar.

3 Discussion

Both of the systems studied here demonstrate that frequency change versus distance curves improve our understanding of the tip–surface interaction and can be used to predict tip and surface properties. Since the information available in experimental images alone is always limited, these curves should be considered an essential aspect of any NC-AFM study.

Surface charging has long been thought to be a major problem in imaging of insulators such as CaF_2, yet atomic resolution has been achieved and reproduced on the (111) surface. The theoretical model of CaF_2 shows that the long-range tip–surface interaction is different for a charged surface. A comparison with experimental force versus distance curves would establish the balance between van der Waals and electrostatic forces in a real experiment and also allow the charge of the surface to be estimated. This would aid greatly in our understanding of the role of surface charging in NC-AFM imaging of other insulators such as MgO and alumina.

The study of the tip–surface interaction over a metal surface has demonstrated the ability of frequency change versus distance curves to differentiate between different tips. The importance of the properties of the tip to NC-AFM imaging has long been known, but no systematic method for the characterising the tip in a specific experiment has been developed. Comparison of theoretical and experimental frequency change versus distance curves allows predictions to be made about the tip and tip–surface interactions in experiments. The theoretical results demonstrate that van der Waals cannot be the only interaction in NC-AFM experiments on copper. The importance of an electrostatic interaction at medium-range (1–2 nm) implies that the tip is a conductor at the macroscopic scale and has a thin oxide coating which provides a nano-tip. Both these elements are crucial in providing the magnitude of image force needed to match experimental results. At longer range, the introduction of a bias is required to match the experimental results. This means it is very likely that the electrostatic minimization procedure used in experiments does not fully compensate for the contact potential difference and some residual capacitance force remains. As the minimization process is only performed at one point on the surface, this residual could be due to inhomogeneities in the contact potential or "patch charges". Burnham et al. [3]

also predicted that patch charges were responsible for deviations from a pure van der Waals interaction in experiments.

To summarize, we suggest that frequency change versus distance curves obtained on standard substrates and on real samples can provide fingerprints of the tip and surface properties vital for interpretation of images.

References

1. R. Bennewitz, A.S. Foster, L.N. Kantorovich, M. Bammerlin, C. Loppacher, S. Schär, M. Guggisberg, E. Meyer, A.L. Shluger: Phys. Rev. B **62**, 2074 (2000)
2. A.S. Foster, A.L. Rohl, A.L. Shluger: Appl. Phys. A [Suppl.] S31 (2001), DOI 10.1007/s003390100635
3. N. Burnham, R. Colton, H. Pollock: Nanotechnology **4**, 64 (1993)
4. S.H. Ke, T. Uda, R. Pérez, I. Stich, K. Terakura: Phys. Rev. B **60**, 11 631 (1999)
5. J. Tóbik, I. Stich, R. Pérez, K. Terakura: Phys. Rev. B **60**, 11 639 (1999)
6. M.A. Lantz, H.J. Hug, P.J.A. van Schendel, R. Hoffman, S. Martin, A. Baratoff, A. Abdurixit, H.J. Güntherodt, C. Gerber: Phys. Rev. Lett. **84**, 2642 (2000)
7. H. Hölscher, A. Schwarz, W. Allers, U.D. Schwarz, R. Wiesendanger: Phys. Rev. B **61**, 12 678 (2000)
8. A.I. Livshits, A.L. Shluger, A.L. Rohl, A.S. Foster: Phys. Rev. B **59**, 2436 (1999)
9. F.J. Giessibl: Phys. Rev. B **56**, 16 010 (1997)
10. T. Uchihashi, Y. Sugawara, T. Tsukamoto, M. Ohta, S. Morita: Phys. Rev. B **56**, 9834 (1997)
11. M. Guggisberg, M. Bammerlin, C. Loppacher, O. Pfeiffer, A. Abdurixit, V. Barwich, R. Bennewitz, A. Baratoff, E. Meyer, H.-J. Güntherodt: Phys. Rev. B **61**, 11 151 (2000)
12. C. Loppacher, M. Bammerlin, M. Guggisberg, S. Schär, R. Bennewitz, A. Baratoff, E. Meyer, H.J. Güntherodt: Phys. Rev. B **62**, 16 944 (2000)
13. M.S. Jean, S. Hudlet, C. Guthmann, J. Berger: J. Appl. Phys. **86**, 5245 (1999)
14. S. Sounilhac, E. Barthel, F. Creuzet: Appl. Surf. Sci. **140**, 411 (1999)
15. L.N. Kantorovich, A.S. Foster, A.L. Shluger, A.M. Stoneham: Surf. Sci. **445**, 283 (2000)
16. C. Argento, R.H. French: J. Appl. Phys. **80**, 6081 (1996)
17. M. Reichling, C. Barth: Phys. Rev. Lett. **83**, 768 (1999)
18. J.B. Engelhardt, H. Dabringhaus, K. Wandelt: Surf. Sci. **448**, 187 (2000)