

Van der Waals and capacitive forces in atomic force microscopies

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In this article we show that in the atomic force microscopy experiments performed on a metallic surface, there is always a long range electrostatic force in addition to the van der Waals forces. This capacitive force is due to the contact potential between the tip and the surface and exists even without external applied potential. We have calculated this capacitive force for a real geometry of the tip-sample system and compared it to the van der Waals force calculated for the same geometry. We conclude that the electrostatic force is always dominant for a tip-surface distance larger than half of the tip radius of curvature. © 1999 American Institute of Physics.

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I. INTRODUCTION

Atomic force microscopies (AFM) offer the possibility of investigating surfaces by measuring the interaction between a sample and a microscopic tip fixed at the end of a small cantilever. Consequently the analysis of the recorded images requires the correct knowledge of the tip-surface interaction.

For a small distance z , this force is repulsive ($z < 1$ nm) and its intensity is about 10^{-9} N.¹ For larger distances, the force is attractive and is weaker (10^{-12} N). The repulsive force can be determined from cantilever deflection measurements (contact mode) whereas the attractive one is determined by measuring the resonance frequency shift² or the amplitude variation of the cantilever oscillation.³ The analysis of the attractive force is not clear. Generally, this interaction is attributed to van der Waals forces, i.e., to dipolar interaction between the atoms or molecules of both materials constituting the tip and the surface.³⁻⁵ However, some recent experimental results exhibit long range interactions which cannot be interpreted by van der Waals forces.⁶⁻¹¹

In this article we show that for a metallic tip-surface system the dominant term in the attractive range is always a long range electrostatic force in addition to the van der Waals forces. This force is due to the contact potential which is defined as the difference of the work functions of each material.

To discuss the relative importance of these forces, we have calculated and compared the van der Waals and the capacitive forces for a real geometry of the tip-sample system; these calculations are respectively presented in the second and third sections. After comparing these two forces in a large range of tip/sample distances, we can conclude in Sec. IV that for a metallic system and for distances larger than the tip curvature radius, the capacitive forces are always dominant. These results are in good agreement with experimental data.

II. CALCULATION OF THE VAN DER WAALS INTERACTION

The general theory of the attractive interaction between two solids has been developed by Lifshitz.^{12,13} In this theory, the atomic structure is ignored and the forces between large bodies are derived in terms of their bulk properties such as their dielectric constant and their geometrical dimensions. This method, including screening and correlation effects is well adapted for a metal-metal interaction. However, to obtain the variation of the attractive force with the tip-surface distance, it is possible to use a less general method which has been developed by Hamaker¹⁴ for a nonmetallic system in which the electrons are localized. In this method, the whole interaction energy between the tip and the sample is calculated by summing the individual interactions of each atom of the tip with each atom of the sample neglecting the interactions between the atoms of the tip (or of the sample) together. In spite of this fundamental difference, the variations of the interaction with tip-surface distance shows the same dependence calculated with this simple pairwise additive model or with the more complete Lifshitz formalism.¹⁵ Nevertheless, to obtain the right interaction intensity for metallic systems, we have to introduce the prefactor calculated by the Lifshitz method; this factor is roughly constant for a metal and is about 4×10^{-19} J.¹⁵ Notice that this value is ten times higher than those of nonconducting media and reflects the high polarizability and dielectric constant of metals and metal oxides.¹⁵

Thus, returning to the Hamaker method, the van der Waals dipolar interaction U_{vdW} between two atoms or molecules can be written as

$$U_{\text{vdW}} = -\frac{A}{r^6},$$

where A is the Hamaker constant and r is the distance between the two considered atoms.^{15,16} Moreover, one has to take into account the retarded effects in the electromagnetic theory, effects which become important as soon as the distance between the dipoles exceeds the absorption wavelength

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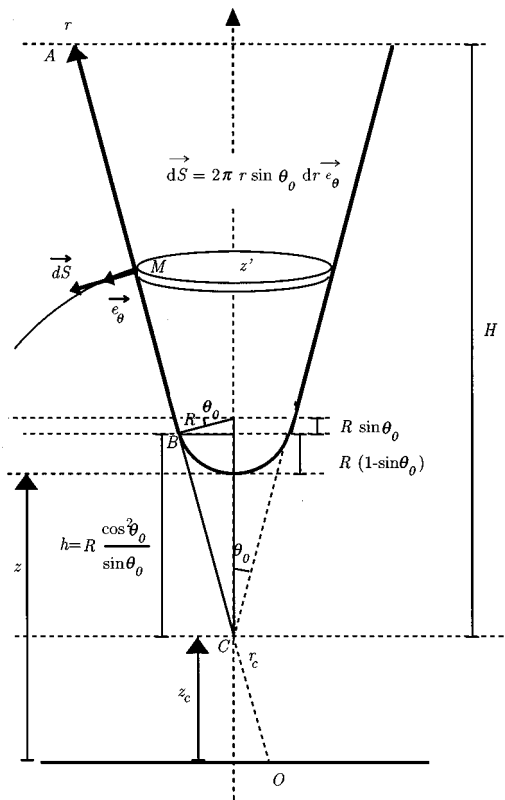


FIG. 1. Tip-surface geometry: the tip is described by a sphere-cone model whereas the surface is supposed to be plane.

of the materials, i.e., a few nanometers. In this case, it has been shown^{17,18} that the dispersion interaction energy can be written as

$$U^+ = -\frac{A^+}{r^7}.$$

Since in AFM (resonant mode) the tip-surface distance is larger than few nanometers ($z > 5$ nm), the whole interaction energy E^+ between the tip and the sample is calculated by summing this retarded pair interaction

$$E^+ = A^+ \int \int \int_{\text{tip}} \int \int \int_{\text{surface}} \frac{n'(r') \cdot n''(r'') \cdot d^3 r' \cdot d^3 r''}{(r' - r'')^7}. \quad (1)$$

In this expression, the prime refers to the tip while the double prime refers to the sample. Then, n' and n'' are the respective densities of atoms of the materials and $(r' - r'')$ represents the distance between the two atoms.

Using this method the energy E^+ is calculated for the real tip-surface geometry. The sample is assumed to be a semi-infinite volume with a plane surface; the tip shape determined by electronic microscopy is pictured by a truncated cone with a spherical apex (Fig. 1). Its relevant geometric parameters are the cone height H , the apex angle θ_0 , and the radius R of the apex.

To evaluate E^+ , we have first calculated the interaction energy u^+ between the sample and one atom of the tip located at a distance z' from the surface. Using the axial symmetry of this subsystem and introducing the radial coordinates ρ' and ρ'' , we obtain

$$\begin{aligned} u^+(z') &= -A^+ n'' \int_{-\infty}^0 dz'' \int_0^{\infty} \frac{\rho'' d\rho''}{[\rho''^2 + (z' - z'')^2]^{7/2}} \\ &= -A^+ \frac{2\pi n''}{20} \frac{1}{z'^4}. \end{aligned}$$

The total energy E^+ is then calculated by integrating u^+ over the whole tip. The result is given by the following expression:

$$E^+(z) = n' \int_z^{z_A} dz' \int_0^{\rho'(z')} u^+(z') 2\pi \rho' d\rho',$$

where the tip-surface distance z is the apex position, $z_A = z + H$, and $\rho'(z')$ the value of ρ' at the surface of the tip at the height z' . By integration over ρ' we obtain

$$E^+(z) = -\frac{H^+}{10} \int_z^{z_A} \frac{\rho'(z')^2 dz'}{z'^4}, \quad (2)$$

where $H^+ = A^+ \pi^2 n' n''$.

To proceed further it is necessary to consider the specific geometrical model for the tip defined above as a vertical cone ended by a portion of sphere (see Fig. 1). Then expression (2) is calculated straightforwardly by splitting the integral into two parts: one, for $z < z' < z_B$ due to the spherical apex, the second, from z_B to z_A , due to the cone, where $z_B = z + R(1 - \sin \theta_0)$ is defined as the point where the cone and the sphere have the same tangent plane. It is also convenient to introduce z_C which is the virtual position of the cone apex

$$z_C = z_B - R \frac{\cos \theta_0}{\tan \theta_0}.$$

Using these notations, the sphere contribution is given by

$$\begin{aligned} & -\frac{H^+}{10} \int_z^{z_B} \frac{\rho'(z')^2 dz'}{z'^4} \\ &= -\frac{H^+}{10} \int_z^{z_B} \left(-\frac{z(z+2r)}{z'^4} + \frac{2(R+z)}{z'^3} - \frac{1}{z'^4} \right) dz' \end{aligned}$$

while the cone contribution is

$$\begin{aligned} & -\frac{H^+}{10} \int_{z_B}^{z_A} \frac{\rho'(z')^2 dz'}{z'^4} \\ &= -\frac{H^+}{10} \int_{z_B}^{z_A} \tan^2 \theta_0 \left(\frac{1}{z'^2} - \frac{2z_C}{z'^3} + \frac{z_C^2}{z'^2} \right) dz', \end{aligned}$$

where in we have introduced the equation of the cone surface

$$\rho'(z') = \tan \theta_0 (z' - z_C).$$

As z_A is always much larger than z_B and z_C , we can take for the limit of the integral $z_A = \infty$. Then the final expression of the van der Waals interaction is given by

$$E^+ = -\frac{H^+}{30} \left\{ \frac{(1 + \tan^2 \theta_0)}{z + R(1 - \sin \theta_0)} + \frac{(R - z)}{z^2} \right\}.$$

The van der Waals force between the tip and the surface is deduced from this energy and is given by

$$F_{vdW} = -\frac{\partial E^+}{\partial z} = \frac{H^+}{30} \left\{ \frac{(1 + tg^2 \theta_0)}{[z + R(1 - \sin \theta_0)]^2} + \frac{(2R - z)}{z^3} \right\}. \quad (3)$$

III. CALCULATION OF THE CAPACITIVE FORCES

In addition to this van der Waals force, the tip is submitted to a capacitive interaction associated with the contact potential V_C . This potential is due to the difference between the work functions of the tip and surface materials¹⁹ and exists even in the absence of applied potential. The corresponding electrostatic energy is then given by

$$U_{elec} = \frac{1}{2} CV_C^2,$$

where C is the capacitance of the tip-sample system. The capacitive force is derived from this electrostatic energy and is simply given by

$$F(z) = -\frac{1}{2} \frac{\partial C}{\partial z} V_C^2.$$

The main difficulty is now to obtain an analytical expression of $C(z)$ or $C'(z)$ for the real tip shape. Various methods have been developed to determine the capacitance of conductors at equilibrium, but unfortunately, even for such a highly symmetrical geometry, an exact calculation is not possible. Numerical calculations can be provided and give the exact value of the force but do not allow to discuss the role of the different parameters such as the curvature of the apex or the tip surface distance. To overcome these difficulties, we have developed in a previous publication¹⁰ an analytical method to approximate the capacitive force between the tip and the surface. In this model, we assimilate the tip to a superposition of infinitesimal plane surfaces obtained by facetting its surface; so the whole capacitance appears as the sum of dihedral infinitesimal capacitances. Each infinitesimal capacitance is then calculated assuming its value to be equal to the capacitance of the corresponding infinite dihedron.

Using this approximation, it is then easy to calculate the electrical field on each point of the tip surface and to deduce the corresponding surface charge density σ :

$$\sigma(M) = \epsilon_0 E(M) = -\epsilon_0 \frac{V}{l(M)},$$

where $l(M)$ is the length of the field force line drawn from the tip to the sample and which is simply, in the frame of our approximation, an arc of a circle orthogonal to both surfaces. The capacitance can then be evaluated for an axisymmetrical tip, the shape of which is given by its analytical surface equation $\rho'(z')$

$$C(z) = \frac{1}{V} \int_{tip} 2\pi \rho'(z') \sigma(z') dz'.$$

The calculation in the case of our particular geometry is detailed in Ref. 13 and the force between the tip and the sample can be written as

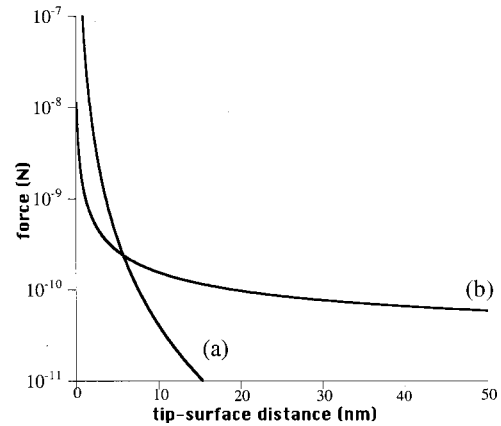


FIG. 2. Variations of the force with the tip-surface distance for $0 < z < 50$ nm and $R = 20$ nm: (a) van der Waals contribution calculated using relation (3); (b) capacitive contribution calculated using relation (4). The capacitive contribution is dominant as soon as $z > 10$ nm and is the main contribution in AFM resonant mode.

$$F_C = \pi \epsilon_0 V^2 \left\{ \frac{R^2(1 - \sin \theta_0)}{z[z + R(1 - \sin \theta_0)]} + \frac{1}{[\ln tg(\theta_0/2)]^2} \right. \\ \left. \times \left[-\ln \frac{z + R(1 - \sin \theta_0)}{H} - 1 + \frac{R \cos^2 \theta_0 / \sin \theta_0}{z + R(1 - \sin \theta_0)} \right] \right\}. \quad (4)$$

In this expression (given for the experimental condition $z \ll H$) the first term is due to the spherical apex while the second one is due to the conical part of the tip. Notice that for $z \ll R$, the main contribution is due to the spherical apex whereas for $z \gg R$ the conic contribution is dominant. In AFM resonant mode experiments, since the tip-surface distance is a few R , the complete expression (4) of the force has to be considered to analyze the experiments.

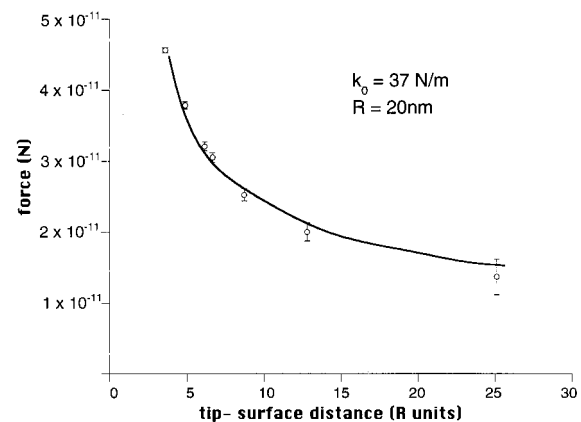


FIG. 3. Experimental variations of the force between a metallic tip and a metallic surface. The values of the force are obtained from the experimental values of the gradient force F' which uncertainty is $\Delta F' = 10^{-5}$ N/m; then the resulting force uncertainty ΔF is about of $\Delta F = \Delta F' z$. For $z = 30$ and 500 nm, is respectively 3×10^{-13} and 0.5×10^{-11} N. The continuous line corresponds to the fit obtained by introducing the measured geometric tip parameters in the approximate force expression. Notice that van der Waals force cannot explain this long range interaction.

IV. COMPARISON BETWEEN VAN DER WAALS AND CAPACITIVE FORCES

We are now able to compare the relative intensity of the van der Waals and capacitive forces. To be complete, we have also to take into account the capillarity force due to the formation of a water film on the sample surface in ordinary atmosphere. These forces could become important when the distance z between the tip and the surface is smaller than the curvature radius of the tip. For this tip curvature radius, the capillarity forces are in the 1–100 nN range in an ambient atmosphere characterized by a humidity of about 30%–50%.²⁰ Since the force measurements are usually performed in dry atmosphere, these capillarity phenomena are removed and then will be forgotten hereafter.

van der Waals and capacitive forces have been calculated using expressions (3) and (4) in which we have taken the geometrical parameters of the tips that we have used in our experiments: $H = 10 \mu\text{m}$, $R = 20 \text{ nm}$, $2\theta_0 = 20^\circ$. For metallic surfaces, the Hamaker constant H^+ is about $10^{-27} \text{ Jm}^{15,21}$ while the typical value for the contact potential is $V_C \approx 1 \text{ V}$.

Figure 2 represents the variations with the tip/surface distance z of the different contributions to the tip–surface force calculated for the real tip–surface geometry. In dry atmosphere, our calculations show without ambiguity that the capacitive forces are dominant for z larger than $R/2 = 10 \text{ nm}$.

This result is confirmed by the results obtained in our experiments presented in Ref. 10. In these experiments, we have measured, with an atomic force microscope acting in resonant mode, the interaction force between a Pt coated tip and a gold surface, the tip being grounded and no potential being applied on the gold surface. All these experiments were performed in a dry nitrogen atmosphere. The variation of the interaction force is presented in Fig. 3 for very large tip–surface distance varying from 3 to 25 R .¹⁰ The sensitivity of our experiments results in a force incertitude ΔF of $10^{-5} z$; then ΔF is respectively 3×10^{-13} and $0.5 \times 10^{-11} \text{ N}$ for $z = 30$ and 500 nm . For these distances, the van der Waals force is about 10^{-14} N , very much smaller than the measured force. In contrast, these variations are well fitted by the electrostatic expression (4) in which we have introduced the geometrical tip characteristics ($H = 2 \mu\text{m}$, $\theta_0 = 10^\circ$, and $R = 20 \text{ nm}$) which have been determined by electronic microscopy.

V. CONCLUSION

As a result, we can conclude that the force measured for tip–surface distance larger than 10 nm cannot be interpreted for metallic surfaces in terms of van der Waals forces and have to be analyzed in terms of a capacitive force. Furthermore, this result shows that one has uniquely to consider this capacitive force to analyze the experiments in the particular case of AFM resonant mode since these experiments are generally performed for tip–surface distances larger than 5 nm. This conclusion could be extended to nonmetallic systems, since a potential equivalent to the contact potential can be defined for insulator–metal system;²² for instance, this electrostatic force could explain some recent results obtained for oxides/metal system which can not be analyzed by van der Waals forces.¹¹

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