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van der Waals forces in atomic force microscopy operating in liquids: A spherical-tip model

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In this paper we discuss the van der Waals forces in atomic force microscopy when operating in liquids. We show that these forces are almost cancelled out for spherical tips immersed in liquids and seem to be in agreement with recent *in situ* electrochemistry results. Experiments as well as an analogy with Archimedes's principle are proposed. Furthermore, we present experiments showing such spherical tips of hundred nanometers which can be fabricated in a reproducible manner and are stable.

Goodman and Garcia[1] presented a theory for van der Waals (vdW) forces acting on a spherical body due to the presence of a dielectric surface and its effects on cantilever displacements used in atomic force microscopy[2] (AFM). Previous experiments[3,4] have indicated that AFM's operate more stably in water than in air or in a vacuum. Experimental confirmation of this behavior was obtained with AFM studies in electrochemical solutions *in situ* [5-7] in which single atoms were observed with good regularity and resolution, for many different electrochemical solutions. This means that AFM's generally operate more stably in liquids. In this work we explain that this stabilization phenomenon is caused by the compensation of the long-range vdW forces, which leaves only the very local "high resolution" repulsive forces on the tip. We present, as a guide and also as a pedagogical point, an analogy between the vdW forces in liquids and Archimedes's principle. We propose an experiment with a spherical tip, since spherical tips can be fabricated in a reproducible manner.[8,9]

vdW forces are due to the induced dipole interaction between two neutral bodies and the polarizability of their media. Goodman and Garcia[1] represented a theory for the force, f_{sp}, on a sphere of radius r and dielectric constant ε_t, placed in vacuum at a distance z from a flat sample surface with a dielectric constant ε_{sp}:

$$f_{sp} = -B_{sp}\frac{r}{z^2}\frac{1}{(1+\delta)^2} \; ; \tag{1}$$

the minus sign indicates that the force is attractive, $\delta = z/2r$, B_{sp} is the Hamaker constant[10] of the sample given by[3]

$$B_{sp} = \tfrac{3}{4}K\beta_{sp}\beta_t \; , \tag{2}$$

where $K = 1.41$ eV is a universal constant determined from experimental He surface scattering data by Hoinkes.[11] β_{sp} and β_t are related to the sample and tip polarizabilities, respectively. They can be calculated from their dielectric constants by using the Clausius-Mossotti formula:

$$\beta_{sp} = \frac{\varepsilon_{sp}-1}{\varepsilon_{sp}+1} \; , \quad \beta_t = \frac{\varepsilon_t - 1}{\varepsilon_t + 2} \; , \tag{3}$$

including the case of metals for which the value of the dielectric constant is infinity. The formulas are valid for the interaction between the tip and a plane sample which can be either a solid, a liquid, or a gas sample surface.

Now consider the case of a spherical tip completely immersed in a liquid and above a solid sample as in Fig. 1. The vdW forces acting on the tip are due to the presence of the liquid medium and the solid sample. By symmetry, the resulting vdW force on the spherical tip due to the volume of liquid contained in the region defined by $D = 2\,(z+r)$ is zero. Then the remaining vdW forces acting on the sphere are (i) the attractive force f_s with the solid sample given by formulas (1)–(3) and substituted the solid parameters β_s, ε_s, and B_s for β_{sp}, ε_{sp}, and B_{sp}, and (ii) the force f_l, due to the liquid above the volume delimited by the distance D (Fig. 1). This latter force is attractive for the liquid but it is repulsive with respect to the sample, i.e., the tip moves away from the sample under a force given also by formulas (1)–(3), but substituted the liquid parameters β_l, ε_l, and B_l for β_{sp}, ε_{sp}, and B_{sp}. Therefore, for the case $z \ll r$, the net force on the sphere is

$$F_{\text{total}} = f_s - f_l = -\tfrac{3}{4}K(\beta_s - \beta_l)\beta_t\frac{r}{z^2} \; . \tag{4}$$

From Eq. (4) we see that the magnitude and direction of F_{total} is proportional to the difference of the β's of the solid and the liquid. Two consequences can then be deduced:

(i) For a given metallic sample ($\varepsilon_s \to \infty$, so β_s is practically equal to 1) in a liquid environment of water ($\varepsilon_l \sim 80$, we have $\beta_l \sim 0.975$) the resulting vdW force is then reduced to only 2.5% of its value if the tip is working in a vacuum or air environment. Indeed in this latter case, as the dielectric constant of vacuum or air is ~ 1, the corresponding β value is practically zero. This may explain why in electrochemistry experiments done in the presence of a liquid,[5-7] the AFM cantilever could be stabilized and achieved high resolution: the resulting long-range vdW force, F_{total}, is reduced to practically zero, then only the short-range repulsive interactions[1-4] remain. There is always a very substantial reduction of the force for any fluid, even if the dielectric constant is small, as can be deduced from Eq. (4).

(ii) This reduction leads to more stability of the microscope because the snap to contact due to the large vdW forces in the liquid are drastically reduced. Moreover, the force acting now on the tip is only the local repulsive one, without the fluctuations that could be introduced by the vdW forces.

(iii) The resulting vdW force, F_{total}, could be either attractive or repulsive with respect to the sample, depending on the respective values of ε_s and ε_l (see Fig. 1). For example, in the case of mica this force will be repulsive in the presence of many liquids.

The remarkable point of Eq. (4) is that it is analogous to the Archimedes's principle which states that if a body is immersed in a liquid it experiences an upward force equal to the weight of the liquid which will fill the space

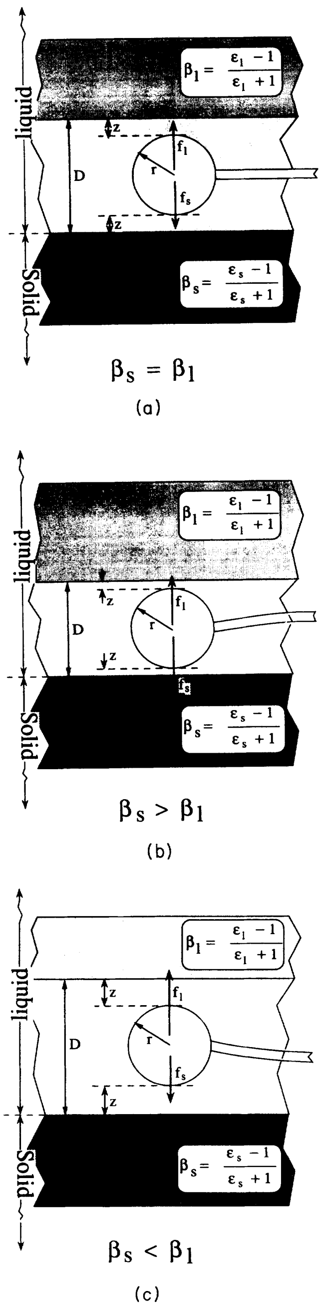

FIG. 1. Schematic drawings of the different parameters and vdW forces acting on a spherical tip immersed in a liquid and at the proximity of a solid sample. (a) The resulting vdW force, F_{total}, is zero when $f_s = f_l$ for $\beta_s = \beta_l$ ($\varepsilon_s = \varepsilon_l$); (b) F_{total} is attractive when $f_s > f_l$, i.e., for $\beta_s > \beta_l$; (c) F_{total} is repulsive when $f_s < f_l$, i.e., for $\beta_s < \beta_l$.

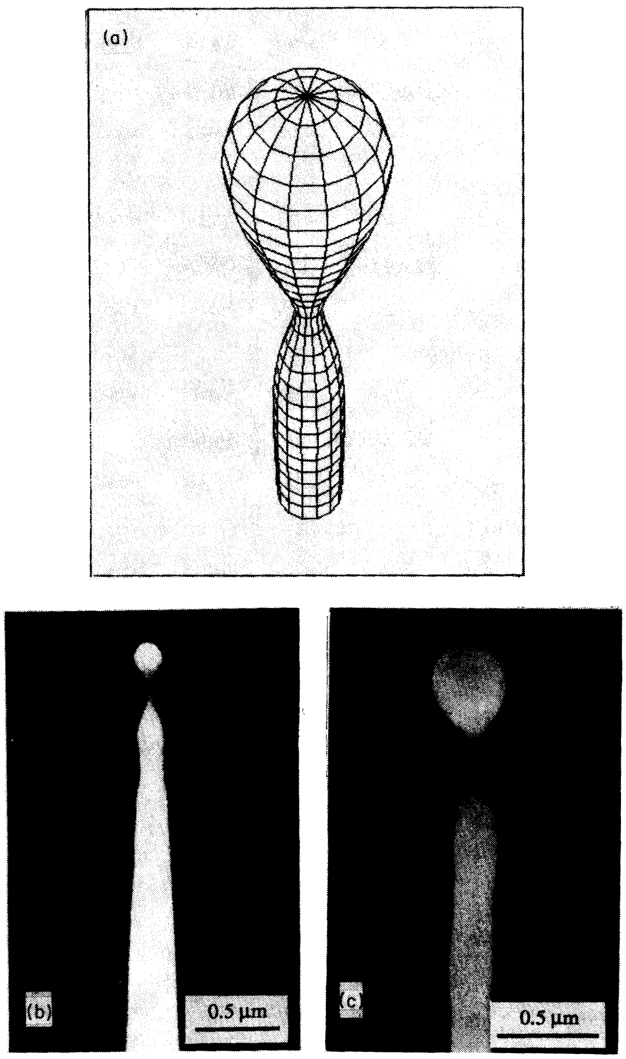

FIG. 2. Formation of spherical tips by surface diffusion with a small angle conical tip. (2) Three-dimensional representation of the profile of a 0° cone angle tip, at ~80% of its solid drop detachment time, calculated by using surface diffusion law; (b) experimental W "spherical tip" geometry; (c) experimental Cu "spherical tip" geometry.

occupied by the body. To make the analogy with the Archimedes's equation we replace the density of the body and liquid by the β's, the gravity by $(\frac{3}{4}K)$ and the volume of the body by $(\beta_t r/z^2)$. In other words, in Archimedes's principle it is the difference in densities which accounts for the actual weight of the body, while with the vdW forces it is the difference in the polarizabilities between the solid sample and the liquid medium which account for the net force acting on the tip. Note that the analogy holds only if the whole spherical body is completely immersed in the liquid. If this is not the case, for example, the spherical tip is half immersed, the net vdW force increases because the liquid also attracts the tip towards the sample. The resulting force is then very complicated to calculate.

This theory is exact for spherical bodies and therefore should be used with "spherical tips." The experimental problem is to obtain, in a reproducible manner, a tip ending with a spherical geometry. The evolution of the tip shape, when heated in vacuum, is basically governed by surface diffusion law. The surface atoms, at high temperatures, move from regions of high curvature towards regions of low curvature in order to minimize the total energy of the system. For a conical tip with an angle greater than 6°, the surface diffusion will blunt the tip, but for small angle tips (< 6°) a constriction will develop just under the apex region. The diameter of this constriction will decrease with the heating time, ending in the detachment of a solid drop. This has been studied theoretically and confirmed experimentally.[8,9] We show, Fig. 2(a), the morphology in three dimensions, just before the detachment of the solid drop, of a 0° angle tip ($\sim 80\%$ of the ovulation time) calculated by using only the surface diffusion law. Experimentally, by stopping the heating before the detachment of the solid drop, we can then obtain a stable tip presenting a nearly spherical ball at its end. Figures 2(b) and 2(c) are scanning electron microscopy images of W and Cu tips, respectively, obtained by heating under vacuum and presenting this geometry. The dimension of the solid drop will depend on the initial dimension of the tip, but it is usually around a few hundreds of nanometers. Differences exist between the experimental profile and the calculated ones; they should be explained by the experimental conditions (heating, vacuum). It is important, however, to note that the solid drop formation is governed by the surface diffusion law (Herring's law),[12] the fabrication of such a tip is then reproducible and available for any material. It could be argued that the model described here is for a spherical tip which is not the geometry of the tips presented due to the neck which connects the ending ball and the shank. However, the mass of the neck is negligible compared to the ball and the neck is farther away from the sample than the ball, thus for any possible configuration between the tip and the surface. The neck, therefore, has negligible contribution to the vdW forces and our tips are quite good experimental approaches of a "spherical tip." We believe that it is worthwhile to use this tip geometry in AFM since the interactions can be well estimated and considered theoretically.

In conclusion, by operating AFM in a liquid, the resulting vdW force acting on a spherical body is drastically reduced compared to its value when operating in vacuum or in air. The equations reported here applied to a spherical tip. Such a tip is prepared in a reproducible manner, just by heating in vacuum a conical tip with a small angle.

Discussions with Frank O. Goodman are appreciated, as well as the contribution of V. Semet for the three-dimensional tip profile simulations. The Départment de Physique des Matériaux is "Unité Associé au Centre National de la Recherche Scientifique."

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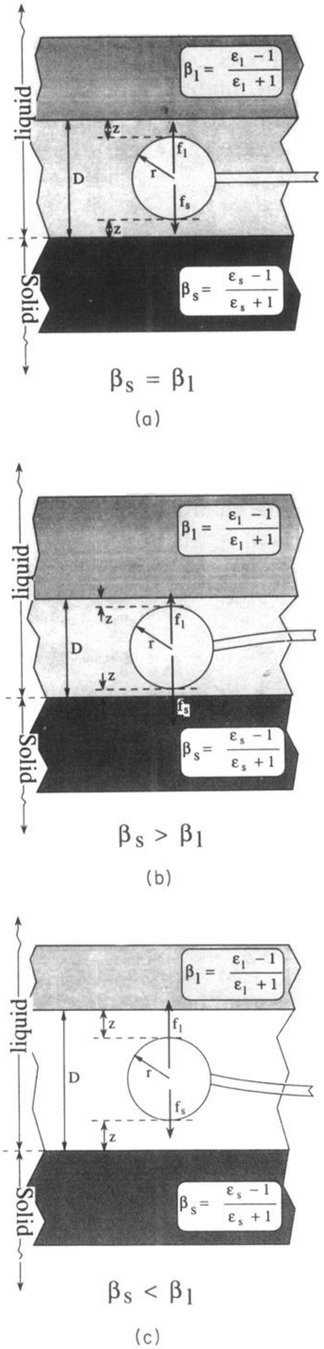

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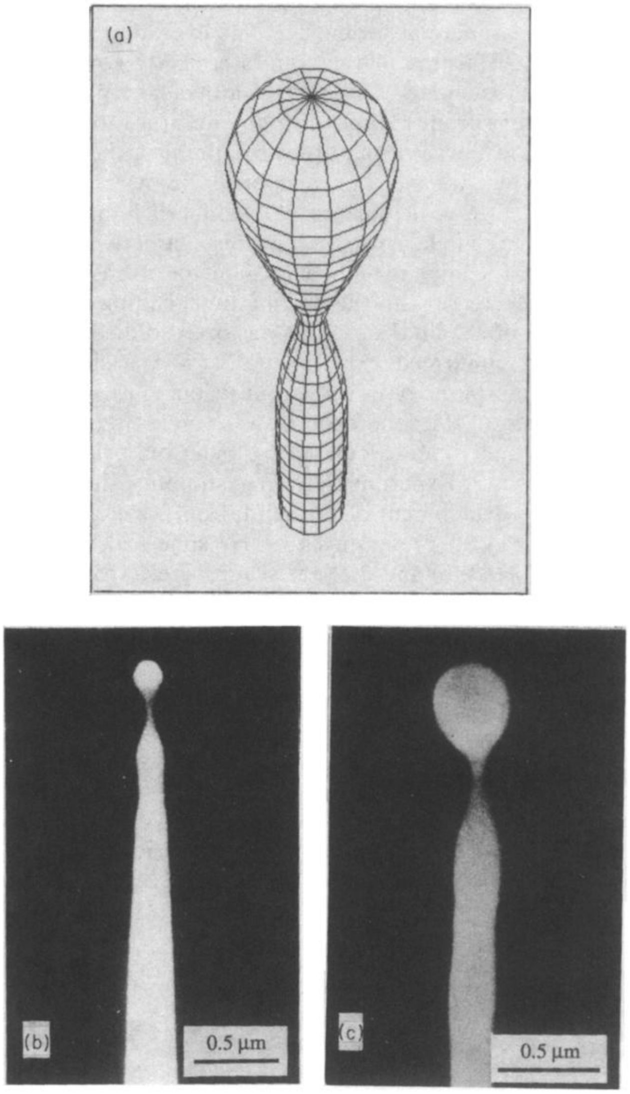

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