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Probing the probe: AFM tip-profiling via nanotemplates to determine Hamaker constants from phase–distance curves

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ABSTRACT

A method to determine the van der Waals forces from phase–distance curves recorded by atomic force microscopy (AFM) in tapping mode is presented. The relationship between the phase shift and the tip–sample distance is expressed as a function of the product of the Hamaker constant by tip radius. Silica-covered silicon tips are used to probe silica-covered silicon substrate in dry conditions to avoid capillary effects. Tips being assumed spherical, radii are determined in situ by averaging profiles recorded in different directions on hematite nanocrystals acting as nanotemplates, thus accounting for tip anisotropy. Through a series of reproducible measurements performed with tips of various radii (including the in-situ characterization of a damaged tip), a value of $(6.3 \pm 0.4) \times 10^{-20}$ J is found for the Hamaker constant of interacting silica surfaces in air, in good agreement with tabulated data. The results demonstrate that the onset of the tip–surface interaction is dominated by the van der Waals forces and that the total force can be modeled in the framework of the harmonic approximation. Based on the tip radius and the Hamaker constant associated to the tip–substrate system, the model is quite flexible. Once the Hamaker constant is known, a direct estimate of the tip size can be achieved whereas when the tip size is known, a quantitative evaluation of the van der Waals force becomes possible on different substrates with a spatial resolution at the nanoscale.

1. Introduction

In atomic force microscopy (AFM), the relation between material properties and the cantilever response is complex since the tip-surface interaction involves long- and short-range forces including repulsive, dissipative, electrostatic and adhesive forces [1–3]. An important issue is the knowledge of the contribution of the universal van der Waals forces. These are associated with the Hamaker constant which depends on the nature of the interacting materials and on their environment [4,5]. For real systems, calculations require extremely demanding multi-layer models [6], which was incentive to determine the Hamaker constant via direct AFM measurements operated in appropriate conditions [7]. AFM in contact mode allows measurements by means of the so-called approach–retract curves that display the evolution of forces between tip and surface versus tip–surface distance. However, the distance range over which the tip-substrate forces can be analyzed is limited by the jump-to-contact. Beyond its dynamical analysis [8], the jump-to-contact has prompted the development of regulated cantilevers [9] and of colloidal AFM in which a colloidal particle with diameter in the micrometric range serves as a tip [10]. The large size of the particle allows probing forces over a wide range of distances, and its well-known geometry leads to a precise determination of both van der Waals and electrostatic forces. Measurements are mainly performed in solution to avoid capillary interactions [11]. The drawback of the technique is the large size of the tip which prevents topographic measurements at good resolution and makes it not suitable for non-homogeneous samples. In addition, AFM in contact mode is often restricted to hard samples since soft matter or samples weakly bound to the supports are easily distorted by the AFM tips.

Dynamic atomic force microscopy in the amplitude modulation mode (intermittent contact mode), which is mostly encountered in air and in liquid, and the frequency-modulation mode, which is mainly performed in vacuum, are widely used to run spectroscopy besides topography [2]. AFM in tapping mode allows the study of both hard and soft samples [12]. Moreover, it opens possibilities for quantitative measurements of tip–sample interactions $F_{ts}(z)$. Models for AFM in tapping mode rely on the Lennard–Jones potential and Hertz contact mechanics [13] or an additional repulsive force [14]. The relevance of an approach is judged by the way in which the numerical simulation accounts for the experimental observation. The comparison is commonly based on amplitude– and phase–distance (APD) curves [15,16]. The oscillation amplitude and phase shifts are measured as the average separation between cantilever

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and sample is decreased from long distances where the interaction is virtually zero to very close distance where the tip possibly comes in intermittent contact with the sample. As the tip approaches the surface, changes in APD curves are expected to reflect the sample-induced perturbation of the dynamics of the cantilever motion. Numerical simulations have succeeded in combining the long-range van der Waals (vdW) forces expressed in the sphere-plate geometry and the Derjaguin–Muller–Toporov (DMT) contact forces [15]. In ambient conditions, viscoelasticity, capillary bridge formation and electrostatic forces are also involved. However, viscoelasticity becomes marginal in the case of hard materials like silicon oxide [17], capillary bridge does not form under dry atmosphere [18] and electrostatic interactions can be neglected in the case of tip and samples electrically grounded and under dry environment [19]. Therefore, in appropriate conditions, tip–sample interaction can be described by a combination of vdW and DMT components only [15].

A method for the quantitative analysis of the observed dynamics is the so-called harmonic approximation in which the tip–sample interaction, assumed much smaller than the cantilever spring constant, is incorporated as a sum over force gradients as discussed below. Due to the high quality factor of the system which behaves like a filter for high harmonics, it appears to be valid for most of the experiments in air [20–22]. The Hamaker constant of the system nickel tip/mica has been estimated by operating the method at the resonance frequency, though the tip radius was not directly measured [23]. In a recent review, Schroeter et al. [22] have shown through a comparison of experimental data on polymer films with simulations that the harmonic approximation remains valid if APD curves are analyzed with appropriate tip–surface forces. Katan et al. also [24] developed a method based on the harmonic approximation to extract the dissipative and non-dissipative contributions of tip–sample interaction from APD curves. They relied on numerical simulations to validate their approach.

The present paper aims at exploring the use of the harmonic approximation to determine the value of the Hamaker constant in the case of hard materials. The modeling of the phase–distance curves is discussed first. It is then applied to silica-covered silicon tips and surface, which are analyzed in dry atmosphere to avoid capillary interactions. Quantitative measurements need an accurate determination of the geometry of the tip, including anisotropy [3]. Thoreson and Burnham have introduced an efficient and accurate method for obtaining radii of micrometric spheres attached to AFM cantilevers [25]. In this work we go beyond the Thorenson and Burnham procedure by aiming at accurately determining the size of nanometer-sized AFM tips. To meet this requirement, tip profiles have been determined in situ by means of previously synthesized well-defined hematite nanoparticles deposited on the silicon surface under analysis.

2. Experimental

2.1. AFM measurements

The AFM machine was a commercial MultiMode from Digital Instruments. Topographic AFM measurements were performed in tapping mode at constant working amplitude (setpoint) using silicon tips provided by nanosensors and which specifications are radius $R=10$ nm and open half-angle $\theta=10^{\circ}$. Silicon substrates were cut from commercial wafers. Cleaning by a piranha mixture (2/3 H_2SO_4+1/3 H_2O_2) and sonication in Millipore water led to a $\sim$2 nm thick native silica film [26,27]. Measurements were performed in dry conditions (relative humidity $\approx$2%) to avoid capillary interactions [28]. The AFM machine was enclosed inside a glass hood with a commercial hygrometer to read out the relative humidity (RH). A home-made humidifier was allowed to control the RH, by pumping pure dry nitrogen inside the hood, readily reaching values below 5%.

2.2. Modeling cantilever dynamics

Changes in amplitude and phase in APD curves reflect the perturbation of the cantilever dynamics by the tip–sample interaction. The idea of the simulations is to reproduce an experimental

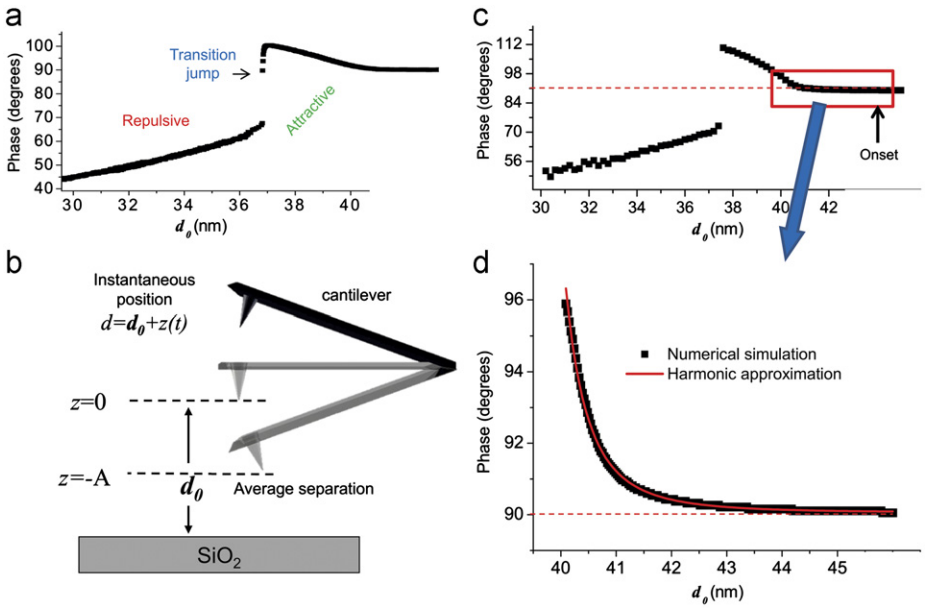

Fig. 1. (a) Experimental phase–distance curve showing the two regimes of the tip–sample interaction: attractive force (large separation, phase $>90^{\circ}$) and jump to phase $<90^{\circ}$ when repulsion dominates, (b) schematic representation of the oscillating tip, (c) simulated phase–distance curve obtained by integrating Eq. (1) with the interaction given by Eq. (2); it shows the two regimes of the tip–sample interaction: attractive force (large separation, phase $>90^{\circ}$) and sudden transition to phase lower than 90° when repulsion dominates, and (d) numerical simulation for the weakly interacting regime (region marked by the red rectangle in panel (c) plotted by black square symbols and the fitting using the harmonic approximation plotted by a continuous red line, Eq. (3). The error in Hamaker constant determined from the fitting is within 2%. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)