Atomic force microscopy cantilever dynamics in liquid in the presence of tip sample interaction

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We analyze the dynamics of an atomic force microscopy (AFM) cantilever oscillating in liquid at subnanometer amplitude in the presence of tip-sample interaction. We present AFM measurements of oscillatory solvation forces for octamethylcyclotetrasiloxane on highly oriented pyrolitic graphite and compare them to a harmonic oscillator model that incorporates the effect of the finite driving force for a typical AFM configuration with acoustic driving. In contrast to the general belief, we find—in both experiments and modeling—that the tip-sample interaction gives rise to a pronounced signature in the phase at driving frequencies well below resonance. © *2008 American Institute of Physics*. [DOI: 10.1063/1.3050532]

Atomic force microscopy (AFM) is more and more evolving from a pure imaging technique to a tool for measuring quantitative tip-sample interaction forces, in particular also in soft matter and biological systems. In this case ambient liquid damps the cantilever motion and reduces the quality factor. This poses a challenge, since established methods for extracting tip-sample interaction forces from experimental data are based on low damping.[1–3] It has been pointed out that the motion of the base of acoustically driven AFM cantilevers (which is negligible in air or vacuum) has to be taken into account in ambient liquid.[4–6] However, the consequences of this effect for the quantitative analysis of the cantilever dynamics in the presence of tip-sample interaction forces have not been explored so far.

In this paper we present a harmonic oscillator model which includes explicitly the finite amplitude of the base movement and includes the effect of tip-sample interactions. We compare the frequency-dependent amplitude and phase response of the model to measurements of oscillatory solvation forces due to molecular layering.[7] These forces were measured in octamethylcyclotetrasiloxane (OMCTS), a nonpolar quasispherical model liquid, at various frequencies close to and below resonance. For an AFM setup with acoustic driving and beam deflection detection, both the experiments and the analytical solution to the model display a strong phase response in the cantilever dynamics for low frequencies.

The measurements were performed on a Veeco multimode (with Nanoscope V controller and "A scanner") using rectangular gold coated cantilevers (Mikromasch) with a spring constant of $k_c=3$ N/m and a resonance frequency of $f\approx 90$ kHz in air. Prior to the measurements the cantilevers were cleaned in a plasma cleaner for 30 min and after the measurements the tip was characterized using high resolution scanning electron microscopy imaging ($R_{\mathrm{tip}}=50$ nm). Acoustic driving was realized using an adapted cantilever holder.[8] The spring constant was determined in air using the thermal calibration method.[9] The resonance frequency ($f_0=43.1$ kHz) and quality factor ($Q=3.1$) in liquid were determined with the same method, 100 nm above the sample surface. The OMCTS used in the measurements was dried using 4 Å molecular sieves. The highly oriented pyrolitic graphite (HOPG) was freshly cleaved just before depositing the OMCTS on the surface.

Figure 1 shows the measured amplitude and phase distance curves for three different drive frequencies close to and well below the cantilever resonance ($\omega_0=\sqrt{k_c/m}$, with m being the effective mass) upon approaching the HOPG surface. Far away from the surface the amplitude and phase response are constant. [The absolute value of the phase far away from the surface is shifted such in accordance with Fig. 3(b); see below.] At a distance of 5–6 nm the response changes due to the tip-sample interaction. For a driving frequency ω close to resonance (top panel) both amplitude and phase display clear modulations due to the oscillating tip-sample interaction. The periodicity of these oscillations (≈ 0.76 nm) reflects the molecular size of OMCTS (0.9 nm), as reported before by others.[10–13] The curves shown in the middle panel were measured at an intermediate drive frequency on the wing of the resonance peak. Compared to the top panel, the oscillations are more pronounced in the amplitude and less pronounced in the phase. All these observations are expected from the standard harmonic oscillator model: for $\omega\approx\omega_0$, the amplitude is close to its maximum and hence not very sensitive to small shifts of the resonance curve (as induced by the tip-sample interaction), whereas the variation in the phase is maximum.[14] If ω is chosen on the wing of the resonance peak, the sensitivity of the amplitude becomes maximized whereas the phase sensitivity continuously decreases [see also the thin gray lines in Figs. 3(a) and 3(b)]. However, for $\omega\ll\omega_0$(bottom panel) we find substantial deviations from the standard picture: first, we observe an overall increase in the amplitude upon approaching the surface. Second, the periodicity in the amplitude oscillations doubles at separations below 2 nm. Third and most strikingly, the oscillations in the phase become more pronounced again, even more pronounced than at $\omega\approx\omega_0$. These observations have important consequences for the quantitative interpretation of amplitude-force-distance curves. Figure 2(a) shows the schematic representation of the cantilever and its motion, which we treat within the harmonic oscillator approximation. As will become clear in the following, our observations are caused by a combination of two—in principle well known—effects. (i) In a highly damping environment (i.e., for low Q)

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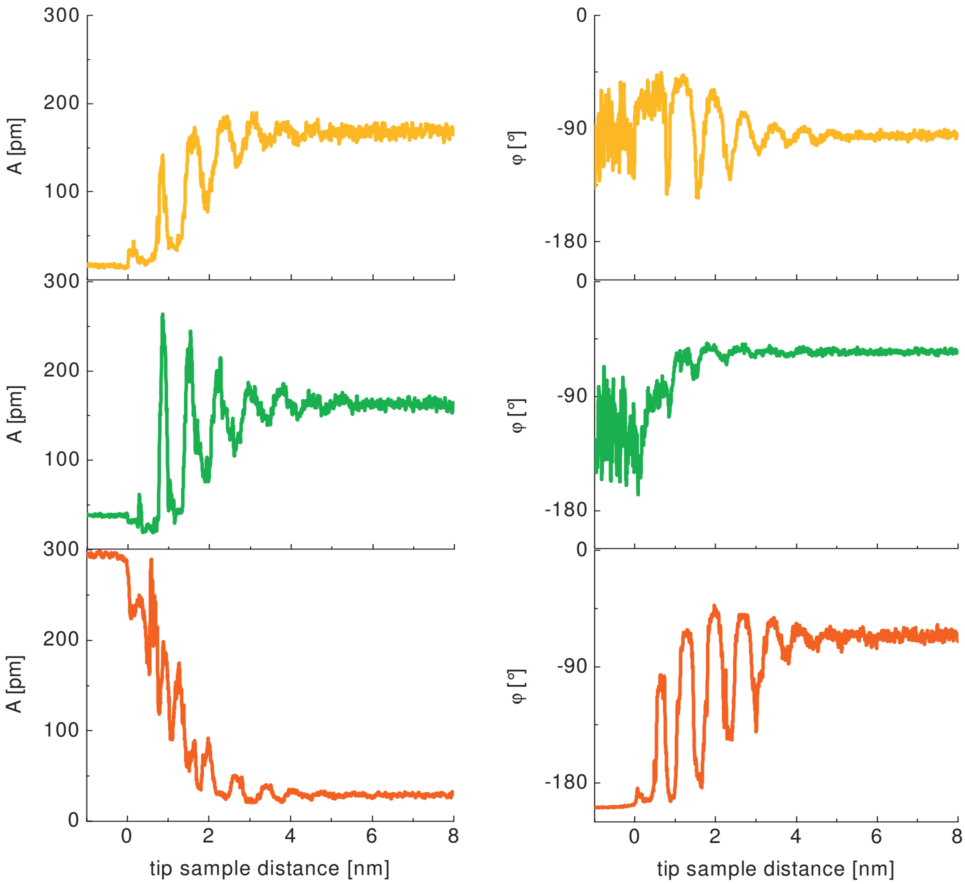

FIG. 1. (Color) Amplitude and phase of the AFM cantilever vs separation between the solid HOPG surface and the cantilever tip for different drive frequencies [top/yellow: 41 kHz (ω/ω_0=0.95), middle/green: 32 kHz (ω/ω_0=0.75), and bottom/red: 6 kHz (ω/ω_0=0.15)] relative to resonance (43 kHz). The periodicity of the oscillations reflects the size of the molecules (OMCTS).

the dynamics of an acoustically driven cantilever can only be understood by properly including the base motion z_d. (This is in contrast to magnetically driven cantilevers, where the measured motion is the only motion.[10,13]) (ii) Beam deflection systems measure the deflection x of the cantilever with respect to the position z_d of the base and not with respect to the average position z_c. (This implies immediately that the amplitude measured via beam deflection goes to zero for $\omega \to 0$, in contrast, e.g., to an interferometric detection system;[11] see also Fig. 3.) Including the motion of the cantilever base z_d results in the following equation of motion for the cantilever:

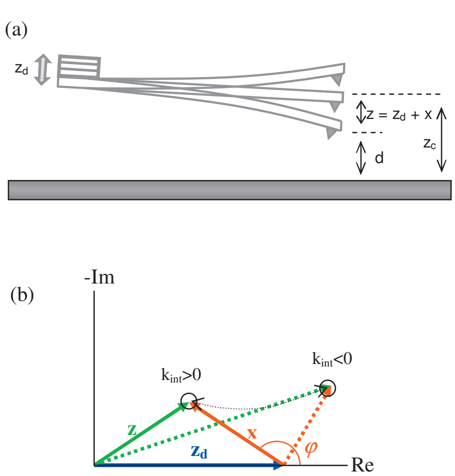

FIG. 2. (Color) (a) Scheme of the cantilever dynamics, which can be accurately described by including the base motion. In (b) the difference between the drive signal z_d (blue arrow), the motion of the cantilever z (green arrow), and the measured deflection x (red arrow) is drawn. The solid lines show the response for a positive interaction stiffness and the dashed lines for a negative stiffness. The measured amplitude is the length of the vector x and the phase is the angle between the Re axis and the vector x.

$$m\ddot{z} + \gamma_c \dot{z} + k_c z = k_c z_d + F_{ts}, \tag{1}$$

where γ_c is the damping of the cantilever, k_c is the spring constant, and m is the effective mass of the cantilever including the added mass caused by the motion of the surrounding liquid ($\omega_0 = \sqrt{k_c/m}$). Far away from the surface ($d \geq 6$ nm, in the present experiments) F_{ts} is zero. For smaller d, F_{ts} is finite and changes the resonance behavior of the system. For sufficiently small cantilever amplitude, F_{ts} can be linearized to $F_{ts}(z,\dot{z}) = F_{ts}(z_c,0) - k_{\text{int}}(z_c)z + -\gamma_{\text{int}}(z_c)\dot{z}$. Using the ansatz that z is described by $z = x + z_d = Ae^{i(\omega t+\varphi)} + A_d e^{i\omega t}$, where A and φ are the amplitude and phase measured in the experiments, A_d is the amplitude of the driving mechanism, and ω is the drive frequency, Eq. (1) can be solved for A and φ:

$$A = \frac{A_d\sqrt{(k_c - k_t + m\omega^2)^2 + (\omega\gamma_t)^2}}{\sqrt{(k_t - m\omega^2)^2 + (\omega\gamma_t)^2}} \approx \frac{|k_{\text{int}}|}{k_t} A_d \tag{2a}$$

and

$$\tan \varphi = \frac{-k_c \omega \gamma_t}{k_c(-m\omega^2 + k_t) - (-m\omega^2 + k_t)^2 - (\omega\gamma_t)^2}$$

$$\approx \frac{\omega\gamma_t}{k_{\text{int}}(1 + k_{\text{int}}/k_c)}, \tag{2b}$$

where the approximations hold for $\omega \ll \omega_0$. $k_t = k_c + k_{\text{int}}$ and $\gamma_t = \gamma_c + \gamma_{\text{int}}$ are the total stiffness and damping, respectively.

Figures 3(a) and 3(b) show the calculated amplitude and phase spectra for the cantilever used in the experiments. In the absence of tip-sample interaction, the curves are similar

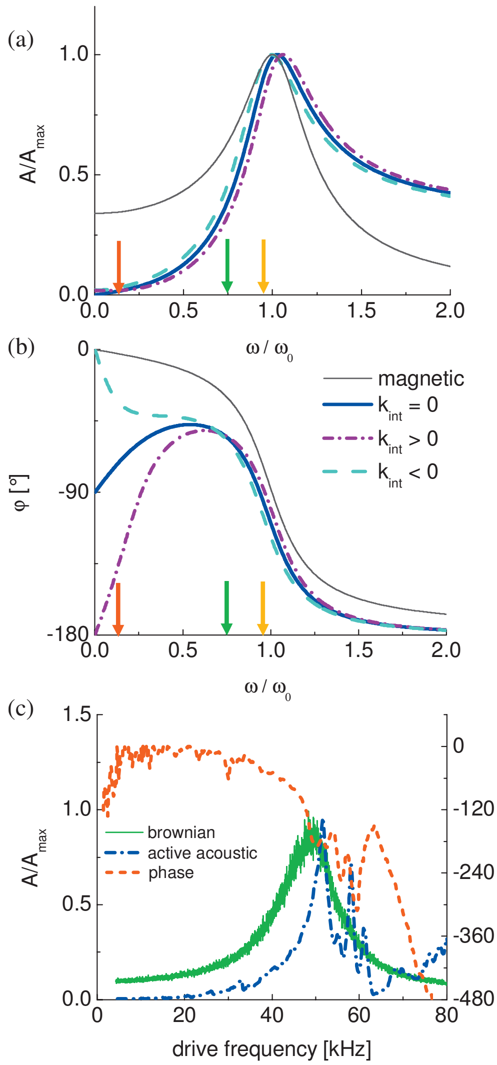

FIG. 3. (Color) Amplitude and phase vs frequency. [(a) and (b)] Thick lines: calculated model curves following Eqs. (2a) and (2b) for variable interaction stiffness $k_{\rm int}=0$, $\pm 0.1k_c$ (at $\gamma_{\rm int}=0$). Thin dotted lines: standard harmonic oscillator model. Colored arrows indicate the drive frequencies for the data in Fig. 1. (c) Measured amplitude and phase response as well as thermal response vs frequency. (k_c=3.7 N/m and the resonance frequency is f =49 kHz). The spurious peaks above resonance are due to the response of the piezodrive.

to those calculated by others, displaying, in particular, a decrease in the amplitude to zero[5,6] and a reduction in the phase to $-90°$ for $\omega \to 0$.[4] It is particularly interesting to analyze the behavior of the curves in the presence of a finite tip-sample interaction, as shown here for two examples with positive and negative interaction stiffnesses of $+0.1k_c$ and $-0.1k_c$, respectively. In line with the asymptotic expressions in Eq. (2), the phase becomes increasingly sensitive to variations in $k_{\rm int}$ for $\omega \to 0$. This explains the experimental behavior of the phase shown in Fig. 1: for the oscillatory tip-sample interaction due to the confined OMCTS, the interaction stiffness varies between positive and negative values and thereby gives rise to dramatic oscillations of the phase. The physical origin of this behavior becomes clear from Fig. 2(b), where we indicate the position of the cantilever base z_d and the tip z in the complex plane. As explained above, the quantity measured by beam deflection in an acoustically driven AFM is the cantilever deflection, i.e., the difference vector $x=z-z_d$. For low frequencies, the tip displacement z [which is correctly described by the standard harmonic oscillator; dotted lines in Figs. 3(a) and 3(b)] displays very little variation in the phase but a finite amplitude variation (as a function of F_{ts}). As a consequence, the phase of the difference vector varies a lot, as found in the experiments. Figure 2(b) also shows why the periodicity in the low frequency amplitude response doubles in Fig. 1: when the interaction stiffness varies back and forth between a positive and a negative value, z moves along the trajectory in the complex plane that is indicated by the dotted line. The measured amplitude of the difference vector x, however, displays twice as many maxima and minima in agreement with the asymptotic expression in Eq. (2). Finally, Fig. 3(c) shows an experimental frequency response curve measured far away from the surface together with a thermal noise spectrum. While the response curves display several spurious resonances at $\omega > \omega_0$ (which are related to the usual resonances in the driving piezo[8]), the low frequency behavior corresponds nicely to the model curves shown in Figs. 3(a) and 3(b). In particular, the phase displays the marked decrease that the model predicts for $\omega \to 0$.

In summary we have shown that the combination of beam deflection detection and acoustic driving gives rise to a very strong sensitivity of the cantilever's phase to the tip-sample interaction for low driving frequencies. The effects described here are relevant for any experiment attempting to measure quantitative tip-sample interaction forces, including nonoscillatory ones, in low Q environments with an AFM that makes use of this (by far most widely spread) design. The consequences of the present observations for quantitative force inversion procedures will be reported shortly in a separate communication.[15]

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