Dynamic force spectroscopy using the frequency modulation technique with constant excitation

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(Received 16 May 2003; published 20 October 2003)

We investigate the measurement principle of a dynamic force microscope utilizing the frequency modulation technique with a constant excitation (CE) mode which has been successfully applied in vacuum, air, and liquids. The basic principles of this mode are comparable with the constant amplitude (CA) mode, but in difference to the CA mode the excitation amplitude is kept constant in the CE mode. Using an theoretical approach we show how the measured quantities of the CE mode — the frequency shift and the oscillation amplitude — are related to the tip-sample interaction force. Based on this analysis we demonstrate how dynamic force spectroscopy experiments can be done also in the CE mode.

DOI: 10.1103/PhysRevB.68.153401 PACS number(s): 68.37.Ps, 07.79.Lh, 87.64.Dz

Using the dynamic force microscope (DFM) in ultrahigh vacuum (UHV) it became possible to achieve ‘‘true’’ atomic resolution on semiconductor surfaces.[1,2] These fabulous results stimulated further activities and true atomic resolution is now routinely obtained on many different types of surfaces including conductors and insulators.[3] Since high resolution experiments need clean surfaces, ‘‘true’’ atomic resolution is only achieved in ultrahigh vacuum. Therefore, most experimentalists apply the frequency modulation (FM) detection scheme introduced by Albrecht *et al.*,[4] which is well suited for vacuum conditions and is based on the specific properties of a self-driven oscillator. Since, it is commonly believed that destructive interactions between tip and sample are prevented with this technique, it is also called noncontact atomic force microscopy.

Two different modes have been established for use with the FM-detection scheme: The original constant amplitude (CA) mode, where the oscillation amplitude of the cantilever is held constant by the an automatic gain control (AGC),[4] and the constant excitation (CE) mode,[5,6] where the excitation amplitude of the cantilever driving is kept constant.

The CA mode has been analyzed by numerical[7] and analytical approaches.[8] It has the advantage that it allows the clear distinction between conservative and dissipative tip-sample interactions. This fact can be used for dynamic force spectroscopy (DFS) experiments enabling the precise detection of tip-sample forces.[7,9,10] Using stable microscopes at low temperatures it is even possible to measure interaction forces at specific lattice sites[11] or to scan the three-dimensional force field between tip and sample surface with atomic resolution.[12]

One intention for the introduction of the CE mode was the reduction of strong mechanical contacts between the oscillating tip and the sample. The experimentalist can choose the maximum energy loss by tip-sample interaction per oscillation cycle by choosing the excitation amplitude prior to making the experiment. This can be advantegous when working on delicate samples. Some examples obtained in UHV can be found in Refs. 13–15. Recently, it has been shown that this mode works also in air and liquids,[16,17] which is a promising approach to improve the resolution and stability of dynamic force microscopy in these environments. Nonetheless, the specific properties of the CE mode and its differences to the CA mode have been analyzed by numerical simulations,[18] but the quantitative determination of tip-sample forces based on CE data is still lacking.

In this article we give an analytical framework for the analysis of the constant excitation mode. Furthermore, we show how dynamic force spectroscopy experiments can be performed also in the CE mode. Two possible approaches are presented: The conservative and dissipative tip-sample forces can be obtained from the analysis of frequency shift vs amplitude curves or frequency shift vs tip-sample distance curves. The accuracy of the method is demonstrated by simulations.

The key feature of all FM techniques is the positive feedback loop, which ensures that the cantilever oscillates always at its resonance frequency. The reason for this behavior is that the cantilever serves as the frequency determining element. This is in contrast to the well-known case of an externally driven cantilever, which oscillates with the excitation frequency. This technique is used in the so-called tapping mode or amplitude-modulation (AM) mode.

A schematic setup of a DFM using the FM technique is shown in Fig. 1. The movement of the cantilever is measured with a displacement sensor. This signal is subsequently used to excite the cantilever by means of a piezo element after suitable amplification.[4] The phase shift between the excitation signal and cantilever deflection is adjusted by a phase (or time) shifter to a value corresponding to $\approx 90°$. This procedure ensures that the cantilever oscillates in resonance.

With such an experimental setup, the corresponding equation of motion of a DFM with FM technique driven in the constant excitation mode is a differential equation with time delay[18]

$$m\ddot{z}(t)+\frac{2\pi f_0 m}{Q}\dot{z}(t)+c_z z(t) = F_{\mathrm{TS}}[z(t),\dot{z}(t)]+\frac{a_{\mathrm{exc}}}{A}\,c_z z(t-t_0), \qquad (1)$$

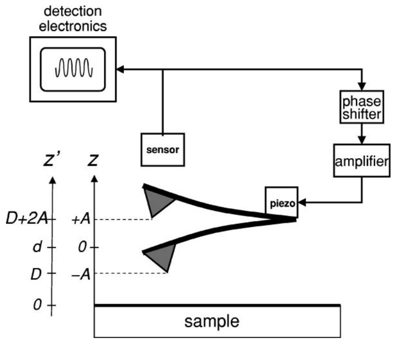

FIG. 1. The schematic setup of a dynamic force microscope using the frequency modulation technique with constant excitation.

where $z:=z(t)$ represents the position of the tip at the time t; c_z, m, Q, and $f_0=\sqrt{c_z/m}/(2\pi)$ are the spring constant, the effective mass, the quality factor, and the eigenfrequency of the cantilever, respectively. F_{TS} is the tip-sample interaction force. The term on the right side of this equation describes the active feedback of the system by the amplification of the displacement signal of the tip measured at the retarded time $t-t_0$. (The time ("phase") shifter in the FM technique is an electronic device, which controls the delay time (or phase) between the sensor signal and the piezoexcitation. Without loss of generality, we describe this feature explicitly by a constant time shift t_0.) A and a_{exc} are the oscillation and excitation amplitudes of the cantilever, respectively. To give insight into the properties of a cantilever driven with the FM technique in the constant excitation mode, we calculate the solutions of Eq. (1).

Since we are mainly interested into the steady state solutions of Eq. (1) we assume a sinusoidal cantilever oscillation with frequency f and introduce the ansatz

$$z(t\gg 0)=A\cos(2\pi f t) \tag{2}$$

into Eq. (1). Expanding now the tip-sample force into a Fourier series, and neglecting terms of higher order, we get a set of two coupled trigonometric equations

$$\frac{a_{\mathrm{exc}}}{A}\cos(2\pi f t_0) = \frac{f_0^2-f^2}{f_0^2}-\frac{2f}{Ac_z}\int_0^{1/f}F_{\mathrm{TS}}[z(t),\dot{z}(t)]\cos(2\pi f t)dt, \tag{3a}$$

$$\frac{a_{\mathrm{exc}}}{A}\sin(2\pi f t_0) = -\frac{1}{Q}\frac{f}{f_0}-\frac{2f}{Ac_z}\int_0^{1/f}F_{\mathrm{TS}}[z(t),\dot{z}(t)]\sin(2\pi f t)dt, \tag{3b}$$

which might be solved numerically to determine the exact dependency of all parameters. Nonetheless, both equations can be simplified for the conditions typically found in DFM experiments.

First of all, we assume that the frequency shift $\Delta f:=f-f_0$ caused by the tip-sample interaction and the damping are small compared with the resonance frequency of the free cantilever ($\Rightarrow f/f_0\approx 1$ and $f^2-f_0^2\approx -2\Delta f f_0$). Secondly, we assume that the time delay is set to a fixed value $t_0\approx 1/(4f_0),3/(4f_0)(=90°,\ 270°)$ by the time shifter, simulating the typical FM operational mode. In this case the terms on the left side are given by $\cos(2\pi f t_0)\approx 0$ and $\sin(2\pi f t_0)\approx\pm 1$. Finally, using the transformation $z=A\cos(2\pi f t)$ it can be shown that the integral in Eq. (3b) is equivalent to the energy $\Delta E(A)$ dissipated during one oscillation cycle (including hysteresis and viscous damping). Due to these simplifications the frequency shift and the driving amplitude can be calculated from

$$\Delta f(A)\cong -\frac{f_0}{\pi c_z A^2}\int_{-A}^{A}F_{\mathrm{TS}}[z]\frac{z}{\sqrt{A^2-z^2}}\,dz \tag{4a}$$

$$\pm a_{\mathrm{exc}}\cong\frac{A}{Q}-\frac{\Delta E(A)}{\pi c_z A}. \tag{4b}$$

These equations are valid for every type of interaction as long as the resulting cantilever oscillations are nearly sinusoidal. Equation (4a) coincides with the well-known result for the FM detection in the CA mode (see, e.g., Refs. 10,19,20), but it is coupled with Eq. (4b) through the oscillation amplitude. This might be the reason why the CE mode has not been used for the quantitative measurement of tip-sample forces up to now.

In this article, however, we demonstrate that experimental spectroscopy data obtained in the CE mode can be used to calculate tip-surface interaction forces. As in the CA mode two strategies are thinkable: The measurement of the frequency shift as a function of the amplitude A[9] or the nearest tip-sample position D[10]. In order to distinguish both approaches we refer to the amplitude and distance methods in the following.

The calculation of the energy dissipation ΔE is straightforward in both cases. From Eq. (4b) it follows that

$$\Delta E(A)\cong\pi c_z\left(Aa_{\mathrm{exc}}-\frac{A^2}{Q}\right). \tag{5}$$

This equation follows also from the conservation of energy.[21]

The calculation of the conservative tip-sample force F_{TS} on the other hand is hindered by the inversion of the integral in Eq. (4a). This problem might be solved by the modification of appropriate algorithms originally developed for the CA mode.[10,22–24] In many dynamic force microscopy experiments, however, the oscillation amplitudes are considerably larger than the tip-sample interaction range. Therefore, we restrict to this case and modify the reconstruction method presented by Dürig[10] for use in the CE mode.

If $D\gg A$, the tip-sample force is nearly zero in the integration range from 0 to $+A$. Therefore, the last term in the integral Eq. (4b)can be expanded at $z\rightarrow -A$ to $z/\sqrt{A^2-z^2}\approx-\sqrt{A}/(\sqrt{2}\sqrt{A+z})$ and the upper limit of the integral can be changed to $z=\infty$

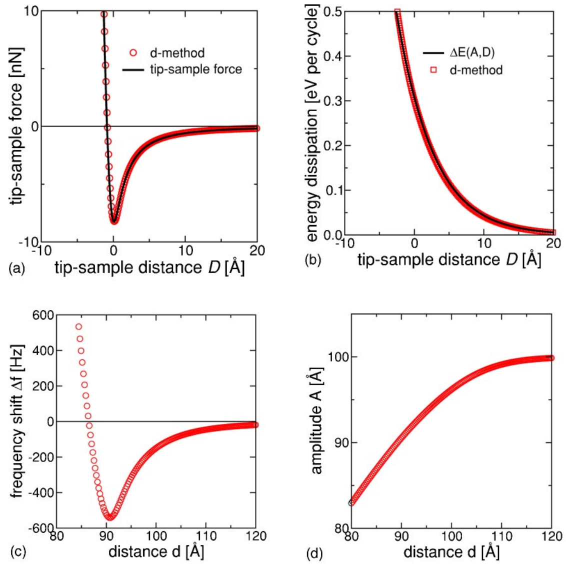

FIG. 2. Simulation of the distance method. The assumed conservative tip-sample force describing the interaction between a silicon tip and a silicon surface is shown in (a) by a solid line. The theoretical energy dissipation plotted in (b) was calculated with Eq. (9). The simulated frequency shift (c) and oscillation amplitude (d) are plotted as a function of the cantilever sample distance *d*. These data sets are subsequently used for the verification of the distance method. The reconstructed tip-sample interactions are shown in (a) and (b) by symbols and show reasonable agreement with the original ones (solid lines).

$$\Delta f(A) \approx \frac{f_0}{\sqrt{2}\pi c_z A^{3/2}} \int_{-A}^{\infty} \frac{F_{\mathrm{TS}}[z]}{\sqrt{A+z}}\, dz. \qquad (6)$$

As a consequence of these modifications it is now possible to invert this integral, but in the CE mode we have to consider that the oscillation amplitude — and therefore the frequency shift — depends on the actual energy dissipation ΔE.

For that reason it is very practical to recall the definition of the so-called normalized frequency shift[19]

$$\gamma := \frac{c_z A^{3/2}}{f_0} \Delta f \qquad (7)$$

which is independent on the oscillation amplitude, but a function of the tip-sample distance. Then, the tip-sample force can be calculated from

$$F_{\mathrm{ts}}(D) \cong \sqrt{2}\, \frac{\partial}{\partial D} \int_{D}^{\infty} \frac{\gamma(z')}{\sqrt{z'-D}}\, dz', \qquad (8)$$

where we made use of the scaling $z' := z + D + A$ (see Fig. 1). In order to reconstruct the tip-sample force with this formula, we suggest to apply one of the following methods to determine the generalized frequency shift as a function of *D*.

Distance method. The cantilever excitation amplitude a_{exc} is kept constant while the oscillating cantilever approaches

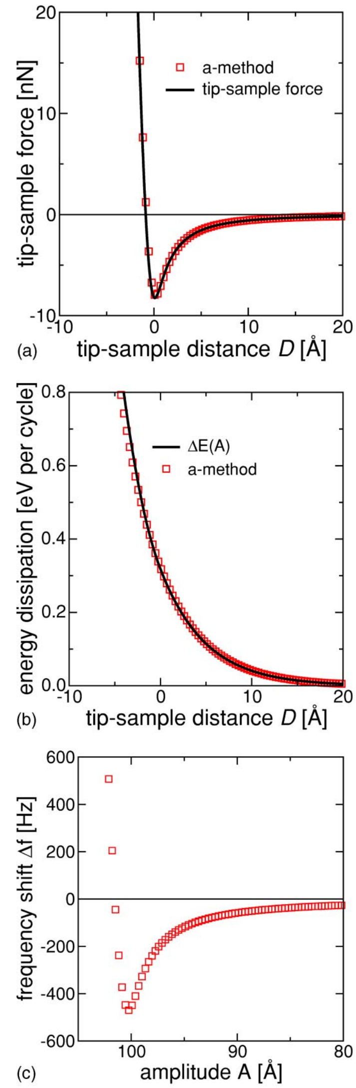

FIG. 3. Simulation of the amplitude method. The assumed conservative (a) and dissipative (b) tip-sample interaction are plotted by solid lines. The simulated frequency shift vs amplitude curve is displayed in (c). The tip-sample interaction can be reconstructed from this curve as shown in (a) and (b) by symbols.

the sample surface. Measured quantities are the mean cantilever sample distance *d*, the oscillation amplitude *A*, and the frequency shift Δf.

Amplitude method. The mean cantilever sample distance *d* is kept constant. The cantilever excitation amplitude a_{exc} is increased or decreased in order to record the frequency shift Δf and the oscillation amplitude *A*.

With both approaches it is then straightforward to calculate the nearest tip-sample position *D* as the difference between the mean cantilever sample distance *d* and the actual amplitude ($D = d - A$; see Fig. 1). In a next step the $\gamma(D)$ curve is calculated with Eq. (7). Finally, the tip-sample force F_{TS} is determined from Eq. (8).

To demonstrate the reliability of the suggested approach, we verified both methods with numerical simulations of the experimental set up based on the equation of motion Eq. (1).

We applied the same simulation procedure which has been previously used in Ref. 18 for the numerical analysis of the CE mode in UHV. The assumed tip-sample force is displayed in Fig. 2(a) by a solid line. It describes the short- and long-range interaction between a silicon tip and a silicon surface. In order to consider also a dissipative tip-sample interaction a viscous damping term with a distance dependent damping coefficient is added $F_{\mathrm{diss}}:=F_0\exp(-z/z_0)\dot{z}$. The constants used in the actual simulation are $F_0=10^{-8}$ N s/m and $z_0=5$ Å. The energy dissipation caused by this type of dissipation is given by

$$\Delta E(D,A)=4\pi^2 fAF_0 z_0 \exp\left(-\frac{D+A}{z_0}\right)I_1\left(\frac{A}{z_0}\right), \qquad (9)$$

where I_1 is the modified Bessel-function of the first kind.[7]

First, we present a simulation of the distance method. Assuming a cantilever with an eigenfrequency of 300 kHz and a spring constant of 40 N/m we solved the equation of motion (1). In order to model the situation typically found in ultrahigh vacuum experiments we used a Q factor of 20 000. The obtained frequency shift and oscillation amplitude vs distance curve are displayed in Figs. 2(c) and 2(d), respectively. The subsequent application of the above described algorithm on this data set allows the precise reconstruction of the conservative and dissipative tip-sample interaction as shown in Figs. 2(a) and 2(b) by symbols.

The same agreement between the original and reconstructed tip-sample interaction is obtained for the amplitude method. The simulated frequency shift vs amplitude curve is shown in Fig. 3(c). In contrast to the distance method the tip-sample interaction can be obtaned from this single curve. The result is shown in Figs. 3(a) and 3(b).

Analyzing the pros and cons of the distance and amplitude methods we came to the conclusion that — in principle — both methods should give comparable results. During an experiment the following problems might appear with the distance method. (i) The amplitude vs distance curve has to be monotonic for mathematical reasons. This condition might be not fulfilled if the data is noisy. This problem might be overcome with data fitting. (ii) It has been experimentally observed that in some cases the oscillation amplitude A decays so strongly $[\partial A(d)/\partial d\approx 1]$ during an approach of the cantilever towards the sample surface that the nearest tip-sample distance is nearly constant.[6,18] In both cases, however, it might be an advantage to control the nearest tip-sample distance directly by an increase (or decrease) of the oscillation amplitude through the excitation amplitude. This behavior might favor the application of the amplitude method in some experimental situations. Nonetheless, the practical application will show which approach will work best.

To summarize, we analyzed the measurement principle of dynamic force microscopy using the FM technique in the constant excitation mode. We showed how quantitative force values can be extracted from spectroscopy curves in the CE mode. This type of measurement has been previously only done in the CA mode in vacuum. Since the FM-detection scheme with constant excitation has been recently applied to liquids and ambient conditions,[16,17] the suggested approach opens the opportunity to extend quantitative spectroscopy experiments also to these environements.

The authors would like to thank Udo D. Schwarz (Yale University, USA) and Boris Anczykowski (nanoAnalytics GmbH, Münster, Germany) for support and many helpful discussions. This work was partly supported by BMBF Grant No. 03N8704.

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