Determination of Tip-Sample Interaction Potentials by Dynamic Force Spectroscopy

H. Hölscher,* W. Allers, U. D. Schwarz, A. Schwarz, and R. Wiesendanger
Institute of Applied Physics and Microstructure Research Center, University of Hamburg, Jungiusstrasse 11,
D-20355 Hamburg, Germany

(Received 7 April 1999)

We introduce a new method which allows the precise determination of the tip-sample interaction potentials with an atomic force microscope and avoids the so-called "jump to contact" of the tip to the sample surface. The method is based on the measurement of the resonance frequency as a function of the resonance amplitude of the oscillated cantilever. The application of this method to model potentials and to experimental data, obtained for a graphite sample and a silicon tip in ultrahigh vacuum, demonstrates its reliability.

PACS numbers: 07.79.–v, 61.16.Ch, 46.80.+j

With the invention of the *atomic force microscope* (AFM) in 1986 [1], it became possible to measure the interaction forces between a sharp tip and a sample surface on the nanometer scale. Since these days, this instrument has been widely used to study tip-sample interactions for various material combinations (see, e.g., Refs. [2–6]). Unfortunately, such investigations are often strongly hindered close to the sample surface by an instantaneous jump of the tip to the sample surface. The origin of this so-called "jump to contact" is an instability in the effective tip-sample potential at the position where the actual force gradient of the tip-sample interaction is larger than the spring constant of the cantilever. This effect leads to a hysteresis and discontinuities in the measured *force-distance curves* and complicates the interpretation [3,7]. The easiest way out of this dilemma would be to use stiffer levers, but this choice limits the achievable resolution [5,7,8]. Therefore, Jarvis *et al.* [5] developed a magnetically controlled feedback to resist the jump to contact.

This problem can also be avoided by oscillating the cantilever [9,10]. If the oscillation amplitude is large enough, the jump to contact of the tip is prevented by the restoring force of the cantilever. This feature is used in the dynamic mode of the AFM [11], where the cantilever is vibrated with its *resonance frequency f* near the sample surface (see Fig. 1). In contrast to the type of experiments described above, the tip-sample force is not detected in this mode. Instead, the measured quantity is the change of the resonance frequency—the *frequency shift* Δf—caused by the tip-sample interaction.

For a given tip-sample interaction law, various methods were suggested to calculate this frequency shift [10,12–15]. In general, however, the inversed problem will be of more interest: *How can the tip-sample interaction be determined from frequency shift data?* A first step towards the answer of this question has been done by Gotsmann *et al.* [16] who developed a fully numerical algorithm to fit the results of a computer simulation to experimental frequency shift versus distance data.

In this Letter, we show how the tip-sample interaction potential (and force) can be precisely determined from the analysis of the frequency shift Δf as a function of the resonance amplitude A. The advantage of this method is that comparatively simple analytical formulas are used to compute the tip-sample potential from $\Delta f(A)$ curves allowing a quick and direct access to the tip-sample interaction without a jump to contact.

The main idea of this new method can be understood by taking a closer look at the reason for the shift of the resonance frequency in the dynamic mode (see Fig. 1). If the cantilever oscillates far away from the sample surface, the tip moves in the parabolic cantilever potential V_c [dotted line in Fig. 1(b)], and its oscillation is harmonic. In such a case, the tip motion is sinusoidal, and the resonance frequency is given by the eigenfrequency of the cantilever f_0 which is independent of the oscillation amplitude. If the vibrating cantilever is brought close to the sample surface, the potential which determines the oscillation is modified. The resulting effective potential U (solid line) is given by the sum of the parabolic

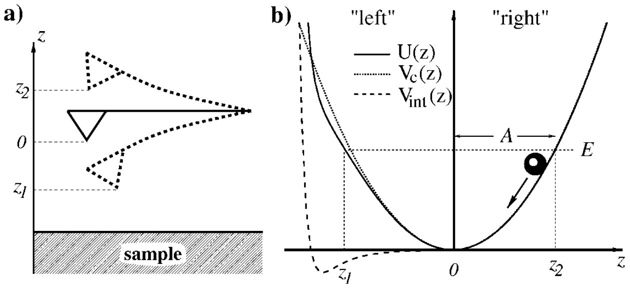

FIG. 1. A schematic view of the experimental setup and the used definitions. (a) A cantilever with integrated tip oscillates with its resonance frequency and a well-defined amplitude near the sample surface. (b) The effective tip-potential (solid line) is the sum of the parabolic cantilever potential (dotted line) and the tip-sample interaction potential (dashed line). To calculate the tip-sample potential from the frequency shift, it is assumed that the "right" part of the effective potential ($z > 0$) can be replaced by the original parabolic cantilever potential in good approximation (see text).

0031-9007/99/83(23)/4780(4)$15.00

potential and the tip-sample interaction potential V_{int} (dashed line). This effective potential has an asymmetric shape due to the tip-sample interaction. Consequently, the resulting tip oscillation becomes anharmonic, and the resonance frequency of the oscillation now depends on the resonance amplitude. The effective potential experienced by the tip changes also with the cantilever-sample distance (distance between tip and sample, if the cantilever is undeflected). Therefore, the frequency shift depends on two parameters: the cantilever-sample distance and the resonance amplitude [17]. The changes of the frequency shift caused by the damping of the cantilever can be neglected in ultrahigh vacuum, if the energy loss due to the damping of the cantilever is compensated using the frequency modulation scheme described in Ref. [18]. As a result, the resonance frequency can be measured independently from the actual damping [8,18,19].

For a given effective potential $U(z)$, the period of oscillation T can be calculated as a function of the energy of the system E by the integral

$$T(E) = \sqrt{2m}\int_{z_1}^{z_2}\frac{dz}{\sqrt{E - U(z)}}\,, \tag{1}$$

where m is the effective mass of the oscillating system [20]. Unfortunately, it is not possible to solve the inverted problem. The effective potential $U(z)$ cannot be determined from the function $T(E)$ without further assumptions about the potential $U(z)$, since the inverted function $z(U)$ is two valued: Each value of U corresponds to two different values of z [20].

However, in our special case, this problem can be solved by dividing the potential $U(z)$ into two parts, “left” and “right” of its minimum as indicated in Fig. 1(b). Since the tip-sample interaction potential $V_{\text{int}}(z)$ is usually very small on the right side for typical cantilever-sample distances, it can be assumed that this part of $U(z)$ is nearly parabolic

$$U(z) \approx \frac{1}{2}cz^2 \quad \text{for } z \geq 0\,, \tag{2}$$

where c is the spring constant of the cantilever. For convenience, we define the origin of the z and U axes at the position of the minimum of the effective potential. As a result of the assumption Eq. (2), the integration of Eq. (1) from 0 to z_2 leads to

$$T(E) = \frac{T_0}{2} + \sqrt{2m}\int_{z_1}^{0}\frac{dz}{\sqrt{E - U(z)}}\,, \tag{3}$$

where $T_0 = 1/f_0 = 2\pi\sqrt{m/c}$ is the period of oscillation of the free cantilever. Now the function $U(z)$ is reversible for all $z \leq 0$, and the integral in Eq. (3) can be inverted. Following Ref. [20], we obtain

$$z_1(U) = \frac{1}{\pi\sqrt{2m}}\int_{0}^{U}\frac{\frac{T_0}{2} - T(E)}{\sqrt{U - E}}\,dE\,. \tag{4}$$

Usually, it is the frequency shift $\Delta f := f_0 - f$ and not the period of oscillation $T = 1/f$ which is measured in dynamic force microscopy. Therefore, it is advantageous to transform Eq. (4) to

$$z_1(A) = -\int_{0}^{A}\frac{f_0 - \Delta f(A')}{f_0 + \Delta f(A')}\,\frac{A'}{\sqrt{A^2 - A'^2}}\,dA'\,, \tag{5}$$

where A represents the amplitude in the parabolic part of the effective potential (see Fig. 1). Using this formula it is straightforward to calculate the position $z_1(A)$ from a frequency shift versus amplitude curve $\Delta f(A)$, and to determine the tip-sample interaction potential from

$$V_{\text{int}}(z_1) = \frac{1}{2}\,c[A(z_1)^2 - z_1^2]\,. \tag{6}$$

If this method is applied to experimental frequency shift versus amplitude curves, it has to be taken into account that it is the amplitude

$$A_{\text{exp}} := \frac{1}{2}\,(A - z_1) \tag{7}$$

—and *not* the amplitude A sketched in Fig. 1—which is measured in a realistic AFM experiment. This is considered in the following by a simple search algorithm, which varies the amplitude until condition Eq. (7) is fulfilled.

To prove the reliability of this new method, we computed a frequency shift versus amplitude curve for a given tip-sample interaction potential by solving numerically the corresponding equation of motion [15]. Afterwards we have calculated the reconstructed potential with the described method from the frequency shift versus amplitude data and compared the original and reconstructed potential. This simulation is shown in Fig. 2 with the example of the potential given by Peréz *et al.* [21], which describes the interaction between a monoatomic silicon tip and an adatom of the Si(111)-(5×5) surface [solid line in Fig. 2(a); both short-range and long-range (van der Waals) forces are included]. The $f(A_{\text{exp}})$ curve calculated with this potential at a typical cantilever-sample distance of 100 Å is plotted in Fig. 2(b) for discrete values. A comparison between the original (solid line) and the reconstructed tip-sample potential (symbols) plotted in Fig. 2(a) demonstrates the quality of the proposed method.

The same high agreement between original and reconstructed potentials is obtained for other tip-sample interactions and different cantilever-sample distances, as long as the assumption Eq. (2) applies. The detailed analysis shows that the method is unique. Moreover, the systematic error made by assumption Eq. (2) can be neglected for realistic tip-sample potentials if the cantilever-sample distance is large enough.

An application of the new method to experimental data is shown in Fig. 3 for a silicon tip and a graphite sample. The experiments were performed with a home-built atomic force microscope for operation in ultrahigh vacuum and at low temperatures, which works with the frequency modulation detection scheme [18]. A detailed description of the microscope is given in Ref. [22]. The rectangular-shaped cantilever used for this study was made of monocrystalline

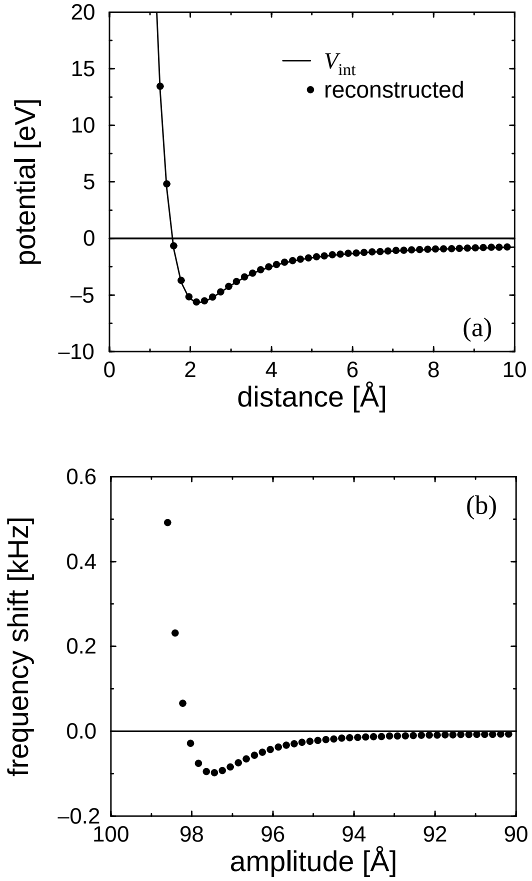

FIG. 2. A simulation of the proposed method. (a) The tip-sample potential given by Peréz *et al.* [21] (solid line) used for the calculation of the $\Delta f(A_{\text{exp}})$ curve shown in (b). The reconstructed potential computed from the $\Delta f(A_{\text{exp}})$ data given in (b) is plotted by symbols. (b) The frequency shift versus amplitude curve $\Delta f(A_{\text{exp}})$ calculated with the tip-sample potential shown in (a).

silicon with a spring constant of 38 N/m and an eigenfrequency of 177 kHz. The tip was sputtered *in situ* with argon prior to the measurements to obtain a clean, oxygen-free Si tip. The graphite sample was cleaved *in situ* at room temperature at a pressure below 10^{-9} mbar, and subsequently inserted into the microscope (base pressure $<10^{-10}$ mbar). A series of experiments were carried out measuring the frequency shift versus the resonance amplitude for different cantilever-sample distances. The experimental data presented here were recorded with a zero bias voltage between tip and sample. The $\Delta f(A_{\text{exp}})$ curves displayed in Fig. 3(a) were measured for four different cantilever-sample distances at room temperature. All curves show the same typical overall behavior, but differ significantly in quantity, depending on the cantilever-sample distance.

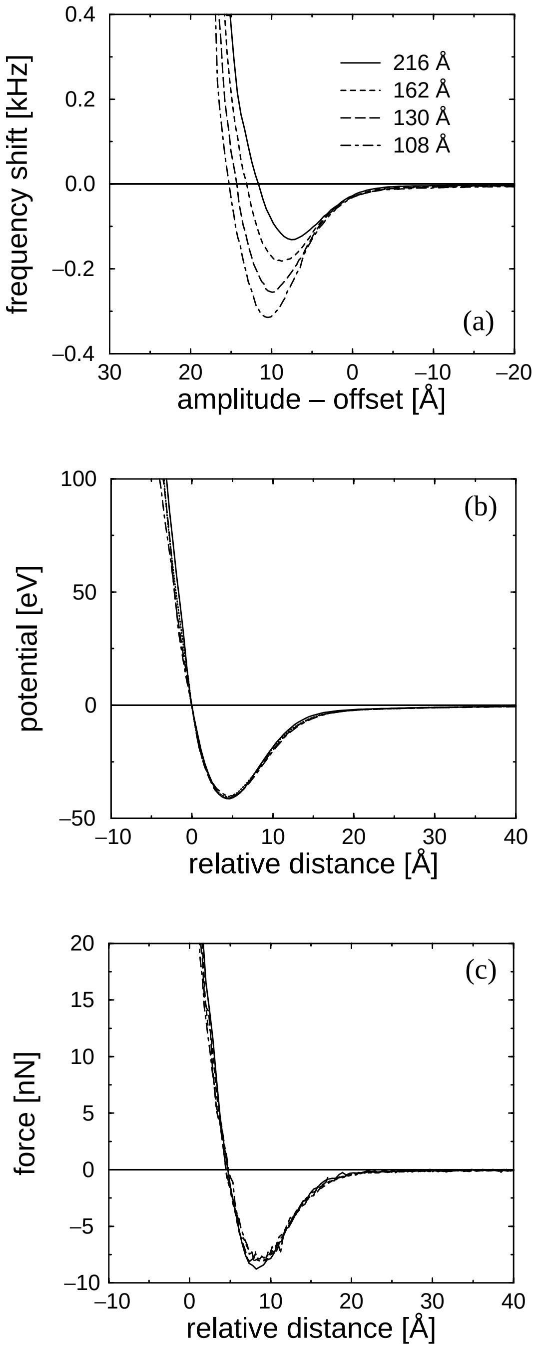

FIG. 3. Experimental results obtained with the proposed method. (a) Four measured $\Delta f(A_{\text{exp}})$ curves recorded in ultrahigh vacuum with a silicon tip and a graphite sample for various cantilever-sample distances. The curves are individually shifted along the x axes in order to fit all into the same graph. The subtracted offset is 216, 162, 130, and 108 Å, respectively. (b) The tip-sample potential calculated from the experimental data shown in (a). Note that all curves are nearly identical despite the different $\Delta f(A_{\text{exp}})$ curves. The zero point of the x axis is arbitrarily chosen. (c) The corresponding tip-sample forces.

Despite these differences, the reconstruction of the tip-sample potential using these experimental data sets leads to identical results [see Fig. 3(b)]. The corresponding tip-sample forces are shown in Fig. 3(c). The fact that tip-sample potentials and forces can be determined with this accuracy without jump to contact and hysteresis demonstrates clearly the advance of this experimental method in comparison to the usually measured force-distance curves. The depth of the measured potential is ~40 eV, which is much more than the expected binding energy between a sharp monoatomic tip and a sample surface (<6 eV; see Fig. 2). This feature indicates that more than one tip atom interacts with the sample surface, which can be caused by two reasons: (i) The tip is blunt and/or (ii) elastic tip-sample forces deform the shape of the tip.

In summary, we presented a new method to measure tip-sample interaction potentials using the dynamic mode of an atomic force microscope. In contrast to the usually measured force-distance curves, this procedure avoids a jump to contact of the tip to the sample surface. Therefore, potential and forces between tip and sample are obtained without hysteresis and discontinuities caused by this effect. The precision of the method is demonstrated by simulation and experiment.

Consequently, the proposed method might be used in the future for the three-dimensional dynamic force spectroscopy of the tip-sample interaction potential with high lateral resolution. Since atomic resolution is obtained routinely in dynamic atomic force microscopy on various materials (see, e.g., Refs. [23–26]), a similar lateral resolution can be expected with the proposed dynamic force spectroscopy method. Although it may seem puzzling to determine tip-sample interactions through the measurement of a frequency, the presented formulas give a quick and direct access to the tip-sample interaction potential and force. This feature offers the opportunity to calculate them "on-line" during data acquisition and to control the tip-sample interaction force via the maximal applied amplitude. Hence it is straightforward either to avoid a repulsive contact between tip and sample during a measurement or to measure even (repulsive) elastic tip-sample forces.

We would like to thank C. Rieck and B. Gotsmann for useful discussions. Financial support from the Deutsche Forschungsgemeinschaft (Grant No. WI 1277/2-3), the BMBF (Grant No. 13N6921/3), and the Graduiertenkolleg "Physik nanostrukturierter Festkörper" is gratefully acknowledged.

---

*Electronic address: hoelscher@physnet.uni-hamburg.de

[1] G. Binnig, C. F. Quate, and Ch. Gerber, Phys. Rev. Lett. **56**, 930 (1986).
[2] J. B. Pethica and W. C. Oliver, Phys. Scr. **T19**, 61 (1987).
[3] N. A. Burnham and R. J. Colton, J. Vac. Sci. Technol. A **7**, 2906 (1989).
[4] J. P. Cleveland, T. E. Schäffer, and P. K. Hansma, Phys. Rev. B **52**, R8692 (1995).
[5] S. P. Jarvis, H. Yamada, S.-I. Yamamoto, H. Tokumoto, and J. B. Pethica, Nature (London) **384**, 247 (1996).
[6] G. Cross, A. Schirmeisen, A. Stalder, P. Grütter, M. Tschudy, and U. Dürig, Phys. Rev. Lett. **80**, 4685 (1998).
[7] S. P. Jarvis and H. Tokumoto, Probe Microscopy **1**, 65 (1997).
[8] U. Dürig, O. Züger, and A. Stalder, J. Appl. Phys. **72**, 1778 (1992).
[9] S. P. Jarvis, S. I. Yamamoto, H. Yamada, H. Tokumoto, and J. B. Pethica, Appl. Phys. Lett. **70**, 2238 (1997).
[10] F.-J. Giessibl, Phys. Rev. B. **56**, 16 010 (1997).
[11] F.-J. Giessibl, Science **267**, 68 (1995).
[12] B. Gotsmann, D. Krüger, and H. Fuchs, Europhys. Lett. **39**, 153 (1997); **41**, 583 (1998).
[13] R. Boisgard, D. Michel, and J. P. Aimé, Surf. Sci. **401**, 199 (1998).
[14] N. Sasaki and M. Tsukada, Jpn. Appl. Phys. **37**, L533 (1998).
[15] H. Hölscher, U. D. Schwarz, and R. Wiesendanger, Appl. Surf. Sci. **140**, 344 (1999).
[16] B. Gotsmann, B. Anczykowski, C. Seidel, and H. Fuchs, Appl. Surf. Sci. **140**, 314 (1999).
[17] This is in contrast to the often repeated statement that the frequency shift is a measure of the force gradient which is true only for small resonance amplitudes. A discussion of this topic can be found in Ref. [15].
[18] T. R. Albrecht, P. Grütter, D. Horne, and D. Rugar, J. Appl. Phys. **69**, 668 (1991).
[19] B. Gotsmann, C. Seidel, B. Anczykowski, and H. Fuchs, Phys. Rev. B **60**, 11 051 (1999).
[20] L. Landau and E. M. Lifshitz, *Lehrbuch der Theoretischen Physik I* (Akademie-Verlag, Berlin, 1990), 13th ed.
[21] R. Peréz, I. Štich, M. C. Payne, and K. Terakura, Phys. Rev. B **58**, 10 835 (1998).
[22] W. Allers, A. Schwarz, U. D. Schwarz, and R. Wiesendanger, Rev. Sci. Instrum. **69**, 221 (1998).
[23] Y. Sugawara, M. Otha, H. Ueyama, and S. Morita, Science **270**, 1646 (1995).
[24] R. Erlandsson, L. Olsson, and P. Mårtensson, Phys. Rev. B **54**, 8309 (1996).
[25] K. Fukui, H. Onishi, and Y. Iwasawa, Phys. Rev. Lett. **79**, 4202 (1997).
[26] W. Allers, A. Schwarz, U. D. Schwarz, and R. Wiesendanger, Appl. Surf. Sci. **140**, 247 (1999).