

Energy dissipation in tapping-mode scanning force microscopy with low quality factors

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(Received 9 August 1999; accepted for publication 4 October 1999)

The phase angle of the cantilever oscillation in tapping mode scanning force microscopy can be related to the energy dissipated per oscillation period through an analytical model that assumes a sinusoidal movement of the cantilever [J. Tamayo and R. García, *Appl. Phys. Lett.* **73**, 2926 (1998); J. P. Cleveland, B. Anczykowski, E. Schmid, and V. Elings, *Appl. Phys. Lett.* **72**, 2613 (1998)]. In this work, numerical calculations of the oscillation of cantilevers with quality factors lower than 10 show a significant contribution of higher harmonics ($\sim 5\%$ – 20%). This contribution can lead to a significant error in the energy dissipated deduced by using the model cited above. Thus, an extended relationship between the phase shift and the energy dissipated is presented, that takes into account the higher harmonics of the oscillation. These results determine the conditions for the measurement of energy dissipation in a liquid. © 1999 American Institute of Physics. [S0003-6951(99)04548-9]

In tapping mode scanning force microscopy (TMSFM), the tip intermittently touches the surface, minimizing the destructive lateral forces.^{1,2} This allows the study of soft molecules, or molecules that are weakly adsorbed to the substrate. In this alternating-current (ac) mode, the measurement of the phase lag of the cantilever oscillation with respect to the excitation signal can highlight compositional contrast on heterogeneous surfaces, such as semiconductors, polymers, or biomolecules.

The origin and nature of the phase contrast has been a subject of debate for the past few years.^{3–11} Numerical calculations of the cantilever dynamics in air have proved that phase contrast arises from differences in the energy dissipation between the tip and the sample.^{8,9} These calculations and experiments show that the cantilever moves with sinusoidal motion for the usual cantilever parameters in air, i.e., with a spring constant and quality factor of the order of 10 N/m and 100, respectively.^{2,4} This harmonic response permits the relationship between phase shift and the energy dissipated to be deduced analytically as^{3,4}

$$\sin \varphi = \frac{\omega}{\omega_0} \frac{A_t}{A_0} + \frac{QE_{\text{dis}}}{\pi k A_0 A_t}, \quad (1)$$

where φ is the phase shift, ω and ω_0 are the excitation and resonance frequencies, A_t and A_0 are the damped and free amplitudes, Q is the quality factor, k is the cantilever spring constant, and E_{dis} is the energy dissipated.

TMSFM in liquids allows a gentler mode of operation because tip-sample adhesion is diminished. The oscillation amplitude and the spring constant of the cantilever are lower than the usual values in air by one and two orders of magnitude, respectively.¹² Operation in liquids is often necessary, particularly for the study of biomolecules in their native environments.¹³ The oscillation of the cantilever in a liquid has two significant differences. First, low quality factors close to unity, two orders of magnitude lower than in air, are

produced as a consequence of the viscous interaction between the fluid and the cantilever.^{14,15} Second, the cantilever oscillation is not perfectly harmonic.^{12,16,17}

Here, numerical and analytical calculations are performed to determine the relationship between the phase shift and the energy dissipated per oscillation period for low quality factors ($Q < 10$).

The numerical calculations are performed by treating the cantilever as a forced harmonic oscillator with damping. Measurements of frequency spectra in liquids support this model.^{14–17} A nonlinear interaction between the tip and the sample is introduced to take into account the repulsive force during the tip-sample contact (Hertz model) and the attractive (van der Waals) force. Energy dissipation is introduced in the tip-sample interaction through adhesion hysteresis, i.e., the adhesion energy during the approach (w_A) is lower than during the retraction of the tip (w_R).^{8,9,18} A more detailed description of the model is provided in Refs. 2 and 8.

The chosen parameters describe the situation in liquids, i.e., the mechanical properties of the cantilever as well as the amplitude regime.^{14,15} For the purpose of calculations, specific interactions such as double layer, solvation, or steric forces are not introduced.¹⁹ The results are not affected by the introduction of a more detailed tip-sample interaction model. The parameters are $A_0 = 10$ nm, $\omega = \omega_0 = 2\pi \times 10$ kHz, $k = 1$ N/m, tip radius = 50 nm. The Young's modulus and Poisson coefficient of the sample are 1 GPa and 0.35, respectively. The adhesion hysteresis is defined by $w_A = 0$ and $w_R = 3$ mJ/m². The adhesion energy on retraction corresponds approximately to the breaking of two van der Waals bonds per square nanometer, or two ligand-receptor bonds per 10 nm².

Figure 1 shows the numerical calculations of the fast Fourier transform of the cantilever oscillation for a high quality factor, $Q = 50$ [Fig. 1(a)], and for a low quality factor, $Q = 1.5$ [Fig. 1(b)]. The cantilever-sample separation is $z_c = 8$ nm ($A_0 = 10$ nm). The amplitude of the main harmonic is divided by 10 to facilitate the comparison with the rest of the spectrum. A significant contribution of the direct-current (dc)

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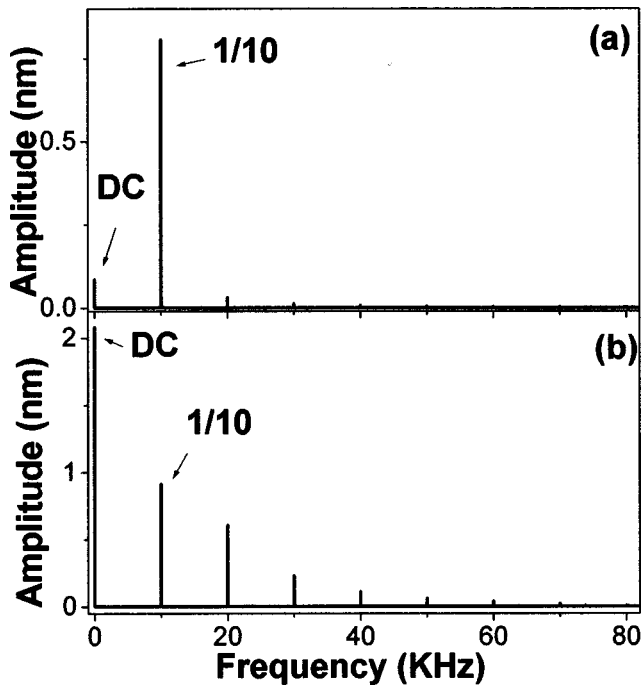


FIG. 1. Fast Fourier transform of the cantilever oscillation for a high quality factor (a), $Q=50$, and for a low quality factor (b), $Q=1.5$. The cantilever-sample separation is $z_c=8$ nm ($A_0=10$ nm). The dominant first harmonic is divided by 10.

signal (>20% with respect to the ac signal) is found for the lower quality factor, which is negligible for the higher Q . On the other hand, a significant appearance of higher harmonics is found in the oscillation of the cantilever with the lower Q . This contribution is about 10% and the amplitude of the harmonics decreases with higher orders. However, the higher harmonics are negligible for $Q=50$, 0.7%. This illustrates two of the most significant differences between the oscillation in air (high Q) and liquids (low Q). First the cantilever oscillation in liquids has an important dc contribution that increases as the cantilever approaches to the sample.^{12,17} The dc signal is negligible with operation in air.⁴ Second, the movement of the cantilever in liquids is not perfectly sinusoidal, in contrast with the cantilever oscillation in air.^{2,4,12,16}

The contribution of the higher harmonics for low quality factors should affect the determination of the energy dissipated by using Eq. (1). This expression is valid for a perfect sinusoidal oscillation.³ Figure 2(a) shows the contribution of the higher harmonics of the oscillation as a function of the quality factor. The cantilever-sample separation is $z_c=8$ nm ($A_0=10$ nm). An increasing contribution of the higher harmonics is obtained as Q decreases. The comparison between the energy dissipated per cycle (solid circles) and the energy dissipated deduced with Eq. (1) (triangles) is shown in Fig. 2(b). Good agreement is obtained between the numerical and analytical energy dissipated for $Q>5$, where the contribution of the higher harmonics is lower than 5%. However, Eq. (1) considerably overestimates the energy dissipated for $Q<5$.

Therefore, the higher harmonics of the oscillation have to be taken into account to measure the energy dissipation. In the steady state, the cantilever oscillation is fed by the energy supplied externally. This energy input balances the energy losses due to the viscous hydrodynamic interaction between the cantilever and the environment (E_h), and the dissipative

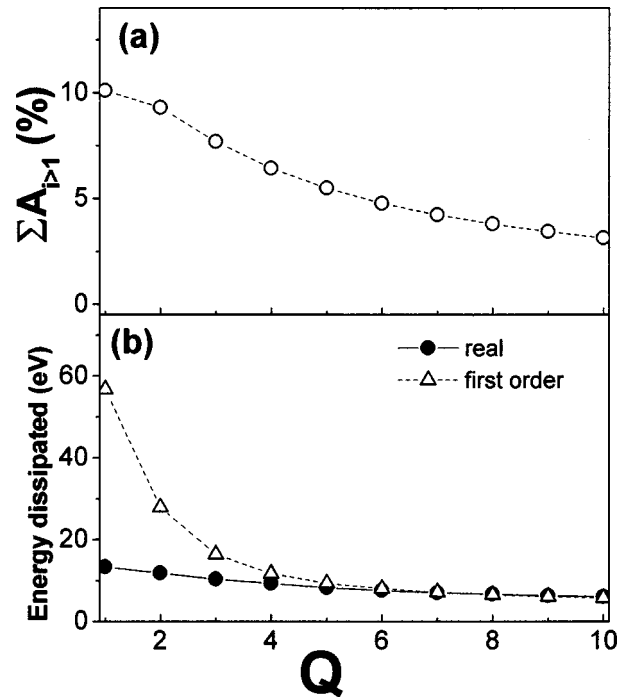


FIG. 2. (a) Contribution of the higher harmonics of the cantilever oscillation as function of the quality factor. (b) Comparison of the numerical energy dissipated (solid circles) with the energy deduced analytically considering the first harmonic [Eq. (1), triangles]. The cantilever-sample separation is $z_c=8$ nm ($A_0=10$ nm).

interactions between the tip and the sample (E_{dis}), $E_{ext}=E_h+E_{dis}$.

The oscillation of the cantilever can be described as

$$z=z_0+\sum_{i \geq 1} A_i \cos(n\omega t - \varphi_n) \tag{2}$$

in which the excitation force is $F_0 \cos(\omega t)$. The external work and the energy lost by the hydrodynamic interaction per period are

$$E_{ext}=\oint_{t' \rightarrow t'+2\pi/\omega} F_0 \cos(\omega t) \frac{dz}{dt} dt = \frac{\pi k A_0 A_1}{Q} \sin \varphi_1, \tag{3}$$

$$E_h=\frac{m\omega_0}{Q} \oint_{t' \rightarrow t'+2\pi/\omega} \left(\frac{dz}{dt}\right)^2 dt = \frac{\pi k \omega}{Q \omega_0} \sum_{n \geq 1} n^2 A_n^2. \tag{4}$$

Equating energies, $E_{ext}=E_h+E_{dis}$, gives

$$\sin \varphi_1 = \frac{\omega}{\omega_0 A_0 A_1} \sum_{n \geq 1} n^2 A_n^2 + \frac{Q E_{dis}}{\pi k A_0 A_1}. \tag{5}$$

From an experimental point of view, it is interesting to consider the first two harmonics of the oscillation:

$$E_{dis} = \frac{\pi k A_0 A_1}{Q} \sin \varphi_1 - \frac{\pi \omega k}{\omega_0 Q} (A_1^2 + 4A_2^2). \tag{6}$$

Equation (5) gives the relationship between the phase shift of the main harmonic and the energy dissipated per cycle, and is valid for any quality factor. In tapping mode, the root-mean-square of the oscillation or the amplitude of the main harmonic is kept constant by the feedback system. When there is only a small contribution of the higher harmonics, the first term of Eq. (5) can be considered constant

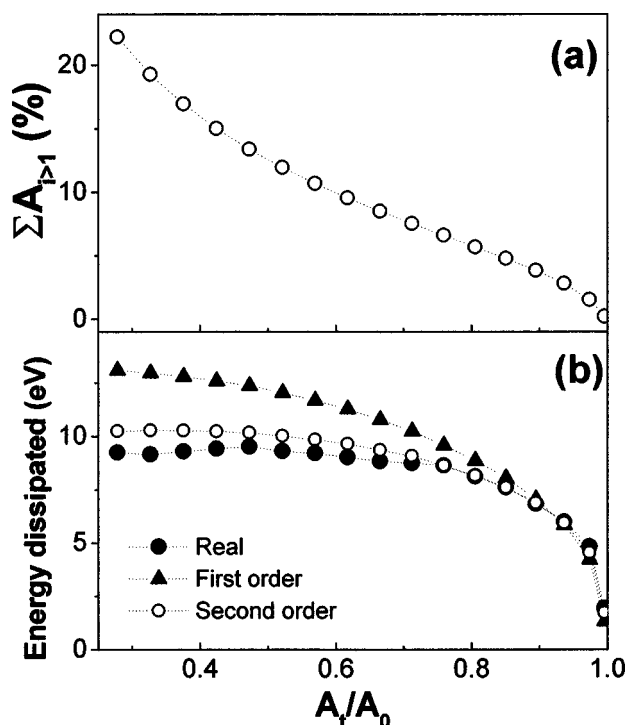


FIG. 3. (a) Contribution of the higher harmonics of the cantilever oscillation as a function of the damped/free amplitude ratio for $Q=6$. (b) Comparison of the numerical energy dissipated (solid circles) with the energies deduced analytically considering the first harmonic [Eq. (1), triangles] and the two first harmonics [Eq. (6), open circles]. The amplitude value is the root-mean-square of the cantilever oscillation.

during the feedback operation. Then, phase contrast arises from differences in the energy dissipation between the tip and the sample, and the sine of the phase angle of the main harmonic is proportional to the energy dissipated. For an increased contribution of the higher harmonics, the same conclusions as above can be obtained if the mechanical properties of the sample are approximately homogeneous. In this case, the ratio between the harmonics is approximately constant and the first term of Eq. (5) is constant during the feedback.

Figure 3 shows the contribution of the higher harmonics as a function of the ratio between damped and free amplitudes for a quality factor, $Q=6$. The energy dissipated per period determined with the first harmonic [Eq. (1)] and the first two harmonics [Eq. (6)] are also compared to the numerical value. The contribution of the higher harmonics increases up to 25% as A_t/A_0 decreases [Fig. 3(a)]. On the other hand, the measurement of the main harmonic [Eq. (1)] overestimates the energy dissipated by less than 10% for an

amplitude damping less than 25% [Fig. 3(b)]. However, a significant deviation is found for lower values of A_t/A_0 . The measurement of the first and second harmonics [Eq. (6)] allows a more accurate determination of the energy dissipated. This gives an error of less than 10% within the whole range of the damped/free amplitude ratio.

It has been demonstrated that the measurement of energy dissipation in TMSFM is limited by the quality factor. Low quality factors ($Q < 10$) imply a significant presence of higher harmonics in the oscillation of the cantilever, producing a discrepancy between the actual energy dissipated and that deduced by considering a sinusoidal oscillation of the cantilever. Furthermore, this deviation increases as the damped amplitude decreases. Therefore, measurement of the contribution of the higher harmonics is necessary to determine the energy dissipated. These results are especially relevant for tapping operation in liquids, where the viscous interaction between the cantilever and the fluid gives low quality factors.

The author thanks Professor Mervyn Miles, Dr. Terry McMaster, Dr. Andy Baker, and Dr. Ash Cherodian for their helpful suggestions.

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