Unifying theory of tapping-mode atomic-force microscopy

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We propose a general method for describing tapping-mode atomic-force microscopy. The combined participation of attractive and repulsive interactions determines the multivalued nature of the resonance curve. This, in turn, implies the coexistence of two different stable oscillations for some excitation frequencies. The coexistence of two stable oscillations depends on the driving force and tip-surface separation. Increasing the driving force inhibits the low-amplitude oscillation state. Because resolution depends on the oscillation state, we propose that the absence of the low amplitude solution is responsible for the inconsistencies observed in high-resolution imaging of biomolecules.

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The characterization and modification of surfaces at atomic and nanometer scales in air or liquids has experienced a radical transformation since the development of amplitude-modulation (tapping-mode) atomic-force microscopy (AM-AFM). A nanometer-size probe is excited at or near its free-resonance frequency. The sample surface is imaged while the feedback electronics adjust the tip-surface separation at a fixed value.^{1,2} High-resolution images of DNA molecules, proteins, or polymers and large scale patterning of materials support the prominent role of amplitude-modulation AFM for nanometer-scale applications.^{3–5} Despite the impressive experimental advances, the physics underlying its basic operation and the mechanisms of molecular or nanometer scale contrast are still not clearly elucidated.

Amplitude-modulation AFM involves amplitude oscillations between 1 and 100 nm. During an oscillation, the forces acting on the tip are of van der Waals type or, more generally, a combination of long-range attractive and short-range repulsive forces. In any case, those forces have power-law dependencies with the distance. A power-law force acting on a moving object implies a dynamic with characteristic nonlinear effects. In fact, nonlinear dynamic features such as hysteresis, bistability, or chaotic tip behavior have already been described or observed in AM-AFM.^{6–10} Large oscillation amplitudes and nonlinear effects make it difficult to find general analytical expressions to describe tapping mode AFM.^{8,11}

The description of tapping-mode AFM has evolved from a single oscillation state dominated by short range repulsive forces,² to a single oscillation with two different regimes, one attractive and the other repulsive.^{12–14} Finally, computer simulations have described the coexistence of two stable states as a common situation for stiff materials.^{9,15} A bistable tip motion has strong implications in the microscope operation because each oscillation implies different tip-surface interactions. It was routine to attribute noisy images to sudden changes in the tip nature or geometry. However, in many cases, the noise reflects the intrinsic structure of the tip motion with two stable states. A spontaneous transition between those states while imaging implies a sudden change in the average tip-surface separation, and this in turn implies a spike in the image. In addition, the coexistence of two stable

states has offered a mechanism to minimize tip-surface interactions and optimize lateral resolution while imaging biomolecules.¹⁶ However, the physical origin of the steady states and their dependence on the interaction forces or experimental parameters remain elusive.

In this paper we propose a theoretical method for studying amplitude-modulation AFM that is valid for any kind of tip-surface interaction force. The method establishes a basic relationship among the fundamental parameters characterizing the tip motion, the oscillation amplitude, the resonant and excitation frequencies, and the interaction forces. The oscillation states of the vibrating tip are found by plotting the oscillation amplitude as a function of the excitation frequency (resonance curves). Whenever the resonance curve intersects the excitation frequency a state is obtained. The resonance curve is heavily distorted by the strength and character of the interaction forces. Attractive forces tend to pull the curve to lower frequencies while repulsive forces drive the curve to higher frequencies. The competition between attractive and repulsive interactions may give rise to a multivalued resonance curve which implies the coexistence of several steady-state oscillations. Our approach is based on the application of the virial theorem $\langle K \rangle = -\frac{1}{2} \langle F \cdot z \rangle$ and the observation that any periodic quantity, in particular the energy, verifies that $\langle dE/dt \rangle = 0$. The method circumvents the numerical integration of the equation of motion to find the amplitude and phase of the solutions of the microlever, stable and unstable alike.

The equation of motion of the microlever can be approximated by

$$m\ddot{z} = -kz - \frac{m\omega_0}{Q}\dot{z} + F_{ts} + F_0 \cos \omega t, \quad (1)$$

where Q, k , and ω_0 are the quality factor, spring constant, and angular resonance frequency of the free cantilever, respectively. F_0 and ω are the amplitude and angular frequency of the driving force. In the cases of interest, a steady-state solution has the form of a sinusoidal oscillation,^{17,18}

$$z(z_c, t) = z_0(z_c) + A(z_c) \cos[\omega t - \phi(z_c)], \quad (2)$$

where z_0 , A , and ϕ are the mean deflection, amplitude, and phase shift of the oscillation, respectively; z_c is the rest tip-surface separation in the absence of interactions, hereafter tip-surface separation. Interestingly Eq. (2) does not limit the nonlinear properties of the tip motion. They are implicitly expressed in the dependencies of z_0 , A , and ϕ on the tip-surface separation.

The periodic character of the energy and the virial theorem imply the following relationships between the amplitude, phase shift, and tip-surface interaction force:

$$\sin \phi = \frac{A \omega}{A_0 \omega_0} \left(1 + \frac{P_{ts}}{P_{med}} \right) \quad (3)$$

and

$$\cos \phi = \frac{2Q}{kAA_0} \left[\frac{\langle F_{ts} \rangle^2}{k} - \langle F_{ts} \cdot z \rangle + \frac{1}{2} kA^2 \left(1 - \frac{\omega^2}{\omega_0^2} \right) \right], \quad (4)$$

where $A_0 = QF_0/k$ is the free-oscillation amplitude. $P_{ts} = \langle F_{ts} \cdot \dot{z} \rangle$ and $P_{med} = kA^2 \omega^2 / 2Q\omega_0$ are the power dissipated by the tip-surface and hydrodynamic forces respectively. $\langle F_{ts} \rangle = 1/T \oint F_{ts} dt$, and $\langle F_{ts} \cdot z \rangle = 1/T \oint F_{ts} z dt$.

By combination of Eqs. (3) and (4), a fourth order algebraic equation for ω/ω_0 is obtained. Commonly if $P_{ts} \ll P_{med}$, then the algebraic equation contains only fourth, second, and zero-order terms. The roots of the following equation provide a fundamental relationship between ω and A ,

$$\left(\frac{\omega}{\omega_0} \right)^2 = I + 1 - \frac{1}{2Q^2} \left[1 \pm \sqrt{1 + 4Q^2 \left(\frac{A_0^2}{A^2} - 1 - I \right)} \right] \quad (5)$$

where I contains the dependence with the tip-surface interaction force

$$I = \frac{2}{kA^2} \left(\frac{\langle F_{ts} \rangle^2}{k} - \langle F_{ts} \cdot z \rangle \right). \quad (6)$$

In many cases of interest, attractive and repulsive forces take only significant values near the lower turning point of the oscillation, then $\langle F_{ts} \cdot z \rangle \approx -A \langle F_{ts} \rangle$. This assumption, and if $z_0 \ll A$, reduces Eq. (6) to

$$I \approx \frac{2 \langle F_{ts} \rangle}{kA}. \quad (7)$$

Equation (5) is general in the sense that it is valid for any type of tip-surface force $F_{ts}(z, z_c)$. It states that the surface properties influence the steady-state motion through the average value of the tip-surface force. The dependence on average quantities is a consequence of the periodic character of the oscillation. In the absence of tip-surface interactions $I = 0$, Eq. (5) reproduces the Lorentzian shape of the resonance curve of a forced harmonic oscillator with damping.

The average value of the tip-surface force is plotted in Fig. 1(a) as a function of the oscillation amplitude. The interaction force contains attractive and repulsive forces which

FIG. 1. (a) Average value of the tip-surface force as a function of the oscillation amplitude. (b) The resonance curve [Eq. (5)] mimics the behavior of the average tip-surface force. The discontinuous line shows the resonance curve for a forced harmonic oscillator. The competition between attractive and repulsive interactions determines the shape of the resonance curve of the interacting oscillator. $A_0 = 11$ nm and $z_c = 9$ nm.

are calculated according to Ref. 19 expressions. R , Q , k , and ω_0 have been assigned the values of 10 nm, 400, 40 N/m, and 2.042×10^6 s⁻¹, respectively. The Young modulus and surface energy of the sample are 1 GPa and 30 mJ/m², respectively. For amplitudes smaller than the tip-surface separation, the average value of the force is close to zero. Increasing the amplitude brings the tip closer to the surface, which in turns increases the attractive force. The average value reaches a minimum for the first amplitude value that implies tip-surface mechanical contact. From then on, the repulsive force increases until it becomes dominant. The above behavior has its replica in the resonance curve of the microlever [Fig. 1(b)]. Attractive forces tend to bend the resonance curve to frequencies lower than the free resonance. However, this effect is partially suppressed when repulsive forces act on the tip. Now the shift of the resonance goes to higher frequencies. However, attractive forces have left a characteristic sideways deformation in the resonance curve.

FIG. 2. Resonance curves for different driving forces ($A_0 \in [9, 12.4]$ nm, $\Delta A_0 = 0.25$ nm). For $A_0 \in [11, 12]$ the resonance curve is a three-valued function at $\omega = \omega_0$. Each value implies a different oscillation state. The middle value is physically inaccessible. $z_c = 10$ nm.

Figure 2 shows the evolution of the resonance curve as a function of the free oscillation amplitude (driving force). The curves are determined for a tip-surface separation of $z_c = 10$ nm. When A_0 is smaller but close to the tip-surface separation, the resonance curve shows the bend to lower frequencies. Increasing the free amplitude brings the tip into mechanical contact with the surface. This in turn changes the shape of the resonance curve. It also shifts the resonance to higher values. Interestingly, for values of A_0 between 11 and 12 nm the resonance curve is a three-valued function at $\omega = \omega_0$. Because the AM-AFM is operated at or near the free-resonance frequency, each value implies a different operating regime. However, the middle value is physically inaccessible because it does not meet the stability criteria.²⁰

For fixed A_0 and z_c , two conditions are needed to have the coexistence of solutions at the free-resonance frequency. The first one is satisfied when the inward deformation in the resonance curve crosses ω_0 . Mathematically, the above requirement implies

$$I \leq \frac{1}{2Q^2} \left[1 - \sqrt{1 + 4Q^2 \left(\frac{A_0^2}{A^2} - 1 \right)} \right]. \quad (8)$$

The other condition implies that the actual angular resonance frequency is higher than ω_0 . This is satisfied when $I \geq 0$ at $A = A_0$. Unfortunately, it is not possible to obtain the above curves experimentally, because no matter how many oscillation states are available, at a given instant only one state is explored. Besides, the unstable sections of the resonance curve are physically inaccessible. However, the effects described in Fig. 2 do weigh considerable experimental implications.

Amplitude curves for different free-amplitude values are plotted in Fig. 3. The coexistence of several solutions for different tip-surface separations gives rise to several amplitude branches. For relatively small A_0 (1 to 10 nm), and from separations slightly smaller than A_0 , three branches are observed. Two stable branches (continuous line) are joined by an unstable branch (discontinuous line). Increasing the free-oscillation amplitude, i.e., increasing the driving force, produces the fracture of the low amplitude branch. A gap is observed in a central region of the separation axis. The gap grows wider with A_0 until eventually the branches merge into a single branch at $A_0 = 19$ nm. Although this tendency is general, the separations or free amplitudes where the coexistence occurs depend on the surface and microlever properties.

Amplitude curves obtained on polyvinyl alcohol films showed the existence of attractive regimes (low-amplitude solutions) at small and large tip-surface separations while the operating regime was dominated by repulsive forces at intermediate distances.²¹ Those experiments can be readily interpreted as an evidence of the gap existence. The coexistence of steady states and the gap formation have drastic experimental consequences. Low-amplitude states are highly suited to imaging biomolecules because of the absence of tip-surface contact which prevents sample deformation. On the other hand, high-amplitude states offer better lateral resolution whenever sample deformation is not an issue. However,

FIG. 3. Amplitude vs tip-surface separation curves for different driving forces. The steady-state oscillations as a function of the separation form tree branches: two stable (continuous lines) and one unstable branch (discontinuous line). The coexistence of two stable oscillations depends on the driving force. Increasing A_0 produces a gap in the low amplitude branch.

the gap formation sets strong limits in the experimental parameters needed to achieve each oscillation state. We suggest that this effect may explain the inconsistent performance of AM-AFM in high resolution imaging of single biomolecules.^{3,16,22,23}

Nonetheless, the gap formation does not imply any fundamental changes in the properties of the system. In fact, for the same z_c both oscillations could be recovered by changing the excitation frequency to higher values. This behavior is clearly appreciated if resonance curves are calculated at different separations (Fig. 4). Attractive forces are responsible

FIG. 4. Resonance curves as a function of the tip-surface separation. The evolution of the relative position of the inward distortion with respect to the free resonance explains the formation of a gap in the low-amplitude branch in Fig. 3(c). $A_0 = 11$ nm.

for the sideways deformation while repulsive forces stretch the resonance curve to higher frequencies. The combination of these effects always allows a frequency where two stable states are found. It could be argued that only a single bending of the resonance curve, i.e., a single interaction either repulsive or attractive, is needed to assure the coexistence of two stable states. However, in these cases the low-amplitude solution belongs to the section of the resonance curve that coincides with the forced harmonic-oscillator curve. Then that solution is insensitive to surface properties. Therefore, the coexistence of solutions sensitive to the surface topography requires both attractive and repulsive components in the tip-surface force.

In summary, it is demonstrated that the coexistence of two stable oscillation states in tapping-mode AFM is associated with the combined participation of attractive and repulsive tip-surface forces. The average value of the interaction force introduces characteristic features in the resonance curves. A sideways deformation is associated with a dominant attractive force while the stretching of the curve to higher frequencies reflects the dominance of repulsive interactions. A gen-

eral description of the operation of the microscope as a function of the driving force and average tip-surface separation contemplates three situations. At small free-oscillation amplitudes two stable branches coexist in the amplitude curves. Increasing the free-oscillation amplitude introduces a gap in the low-amplitude branch. The gap grows wider as the driving force is increased. Eventually, both branches merge into a single branch. The above properties have considerable experimental implications. It restricts the experimental parameters where operation in a state belonging to the low-amplitude branch is possible. Remarkably, our proposal allows the description of the nonlinear dynamics of the tip without actually solving the equation of motion. This makes the approach valid for any type of tip-surface interaction force and implies a drastic reduction of the computational time whenever calculations are required.

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