

Phase contrast in tapping-mode scanning force microscopy

R. García, J. Tamayo, M. Calleja, F. García

Instituto de Microelectrónica de Madrid, CNM, CSIC, Isaac Newton 8, 28760 Tres Cantos, Madrid, Spain
 (E-mail: rgarcia@imm.cnm.csic.es)

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Abstract. The tapping-mode operation of a scanning force microscope represents an intermediate situation between contact and noncontact regimes. Its rapid development and expansion are due to lateral force minimization and its ability to give phase-contrast images of heterogeneous surfaces. Here, we calculate the phase shift between the cantilever excitation and its response as a function of the sample mechanical properties, tip-sample separation, and adhesion forces. We show that the phase shift that gives rise to phase-contrast images is associated with tip-sample interactions that involve energy dissipation such as adhesion energy hysteresis and viscoelasticity. Experimental phase-shift measurements performed on mica surfaces support the conclusions of the model.

The dynamic operation of a scanning force microscope (SFM) was developed to minimize tip-sample deformation and, in some cases, to improve spatial resolution. A wide variety of materials and properties such as loosely bound biomolecules, magnetic interactions, and atomic defects in binary semiconductors have been imaged by different dynamic modes [1–5].

In the tapping mode [2] the cantilever-tip ensemble is oscillated at a frequency close to its resonance. At one end of each oscillation the tip strikes the sample. The sample is imaged while the oscillation amplitude, usually called tapping amplitude, is kept at a constant value. The substantial reduction of the lateral force exerted on the sample, in comparison with contact SFM, explains its ability to image very compliant materials [6].

Several authors have proposed recording the difference between the phase angle of the excitation signal and the phase angle of the deflection of the cantilever as a way of obtaining compositional maps of heterogeneous samples and for imaging material properties [6–9]. The difference in phase angles is called the phase shift. Images recording phase-shift changes during tapping operation are called phase-contrast images. Phase contrast is a rich and powerful tool for enhancing sharp topographic changes in rough surfaces and for

imaging heterogeneous samples. Phase-contrast images of liquid droplets [6], polymer patches deposited on silicon [9], and polymer blends [10] have also been reported.

The dynamic response of the cantilever under an external and oscillating signal has been simulated by different authors [6–15]. Some of the relevant parameters of dynamic force microscopy, such as the sample's deformation [6, 8], contact times [6], phase angles [6, 8], amplitudes [11–14], and applied forces [11, 13] have also been calculated. However, the specific sample properties that give rise to phase-contrast images remain unclear. It was suggested that phase-contrast images of heterogeneous samples are related to surface stiffness variations associated with changes in the elastic modulus [10].

In this article we study the influence of elastic and adhesion forces on phase shifts. It is deduced that in the tapping operation and in the absence of inelastic interactions, phase shifts are independent of the value of the elastic modulus. However, phase shifts associated with elastic properties arose if a fraction of the cantilever's kinetic energy is dissipated in the sample. Similarly, changes in the value of the adhesion force between the tip and sample does not modify the initial phase shift. Phase-shift changes associated with adhesion forces appear only when hysteresis in the adhesion energy is introduced.

The phase-shift dependence on the tip-sample equilibrium separation has been measured on mica. The qualitative and quantitative agreement between theory and experiment supports the results of the model.

1 Model

The dynamics of the cantilever-tip ensemble is simulated by a nonlinear, second-order differential equation [6, 15],

$$m \frac{dz^2}{dt^2} = -k_c z - \frac{m\omega_0}{Q} \frac{dz}{dt} + F_{\text{int}} + F_v + F_0 \cos \omega t, \quad (1)$$

where F_0 and ω ($\omega = 2\pi\nu$) are the amplitude and angular frequency of the driving force, respectively; Q , ω_0 , and k_c are

the quality factor, resonance frequency and spring constant of the cantilever, respectively. F_{int} denotes the tip-sample interaction. Long-range attractive forces (van der Waals) were simulated by the interaction of a sphere with a flat surface, and repulsive forces were calculated by assuming a hertzian contact. The details can be found in [6]. F_{int} is responsible for the nonlinearity of the above equation.

The viscous response of the sample to the tip movement is calculated by,

$$F_v = -\eta \sqrt{R\delta} \frac{dz}{dt}, \quad (2)$$

where η is the sample viscosity, R is the tip radius, and δ is the sample deformation. In this model, the sample is characterized by its elastic and viscosity coefficients.

We also considered the effect of adhesion energy hysteresis on phase shifts. This concept is used in boundary friction studies as an intermediate step to explain friction at a molecular level [16, 17]. The hysteresis was calculated by assuming different surface energies between approaching (γ_A) and retracting (γ_R) cycles. The JKR model provides a direct relationship between the adhesion force and the surface energy.

$$F_a = 3\pi R\gamma_x, \quad (3)$$

where γ_x is the tip-sample surface energy during approach ($x = A$) or retraction ($x = R$).

Phase shifts are obtained by numerically solving (1). Experiments and calculations are performed at the cantilever's free resonance frequency.

2 Phase-contrast images of liquid droplets

An image that illustrates phase-contrast imaging and the gentle impact that the tip exerts on the sample in tapping operation is shown in Fig. 1. Glycerin droplets deposited on highly oriented pyrolytic graphite are imaged. Details of droplet preparation and deposition can be found elsewhere [6]. The drops are loosely bound to the graphite. They are preferentially located along steps and ridges of the substrate. In order to image them without remarkable distortions relatively small amplitudes ($A_0 = 13$ nm and $A_t/A_0 \approx 0.4$) are needed. The phase shift between the graphite and the drops depends on the nature of the tip-sample interactions but they also show a dependence on the droplet size (Fig. 1b). This effect is probably due to changes in the mechanical properties of the droplets with size. The image shows large phase shifts of about 20° that reflect the different tip-sample interaction forces between the glycerin and the graphite.

3 Phase shift versus Young modulus and surface energy

3.1 Dependence on elastic and viscoelastic properties

The theoretical dependence of the phase shift on elastic modulus is presented in Fig. 2 [15]. Two situations have been considered. When there is no viscoelasticity, the phase shift is independent of variations in Young modulus E over four orders of magnitude. This range covers materials from biomolecules to silicon.

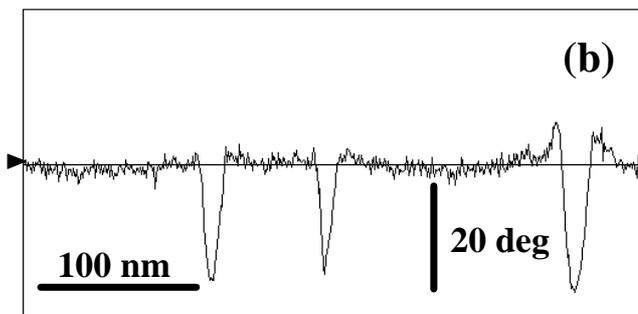
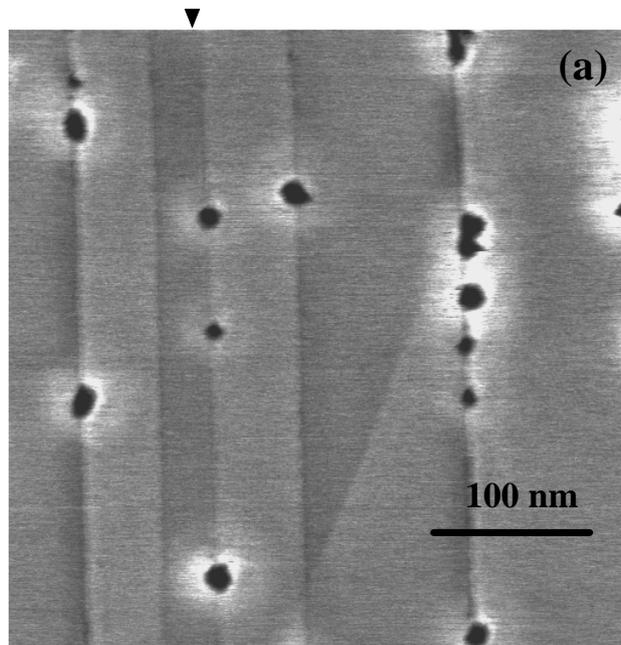


Fig. 1. **a** Phase-contrast image of glycerin droplets on graphite. Several terraces separated by multiaatomic steps are observed. **b** Cross section along the line marked by an arrow on **a**. $A_t/A_0 = 0.4$, $\nu_t = 344.3$ kHz

Viscoelasticity modifies the phase-shift behavior considerably. The phase shift is very sensitive to changes in the elasticity of compliant materials, say materials with a Young modulus below 1 GPa. The phase shift decreases with the stiffness of the sample. It is almost constant for stiff materials. This constant value is arbitrary. It is set by the initial tapping conditions.

The behavior of the phase shift in the absence of inelastic interactions seems surprising. The independence of phase contrast with respect to the changes in the elastic modulus is a property of the tapping operation. It is the result of two competing factors: (1) the Young modulus and (2) the tip-sample equilibrium separation z_c . z_c is defined as the separation when the cantilever is at rest.

This can be reasoned out as follows. In tapping operation, the sample is imaged while the damped amplitude (tapping amplitude A_t) is kept at a fixed value. A_t is obtained by adding the tip-sample equilibrium separation z_c and the sample's deformation δ . Now, let us assume a sample with two contiguous regions of Young modulus E_1 and E_2 and $E_2 < E_1$. In

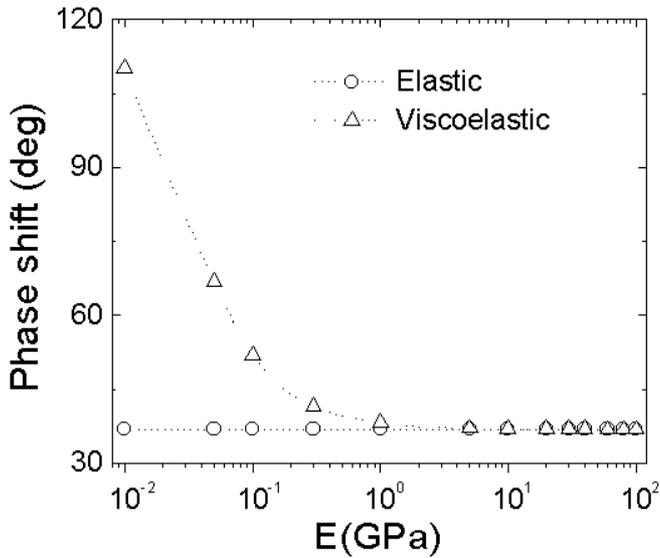


Fig. 2. Phase-shift dependence on the elastic modulus. Elastic interactions (open circles) and when there is viscous damping (triangles, $\eta = 30$ Pa.s). $R = 20$ nm, $A_t/A_0 = 0.6$, $Q = 500$, $k_c = 20$ N/m and $\nu_t = 200$ kHz

tapping operation, A_t is kept constant, then

$$A_t = z_{c1} + \delta_1 = z_{c2} + \delta_2. \quad (4)$$

The sample deformation is smaller in the stiffer region, then $E_{c2} < E_{c1}$. This change in separation between regions E_1 and E_2 compensates the contribution associated with E differences. Stiff regions show, for the same tip-sample equilibrium separation, higher repulsive forces than compliant regions. The net effect is that in tapping mode, phase shifts are independent of variations in the elastic properties.

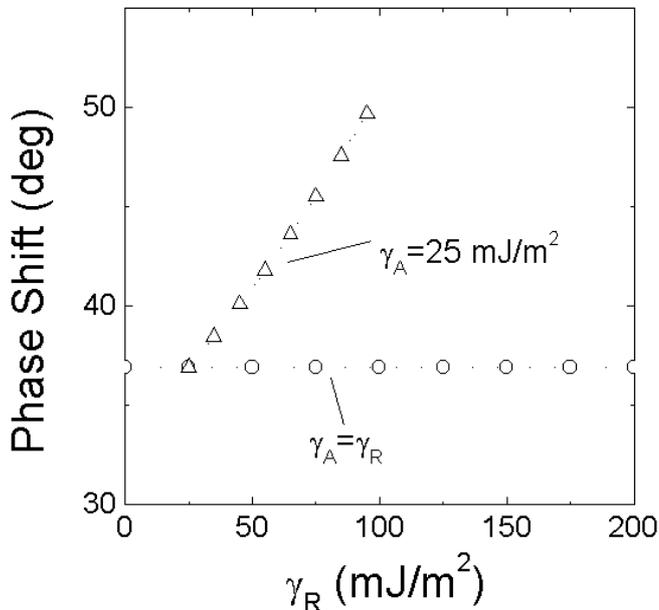


Fig. 3. Phase-shift dependence on surface energy (adhesion force) with and without adhesion energy hysteresis. $R = 20$ nm, $E = 0.3$ GPa, $A_t/A_0 = 0.6$, $Q = 500$, $k_c = 20$ N/m, and $\nu_t = 200$ kHz

3.2 Dependence on adhesion forces

In Fig. 3 is presented the dependence of the phase shift on adhesion forces (surface energy) for a sample with a Young modulus of $E = 0.3$ GPa and with no viscoelasticity. Again, when there is no energy dissipation, phase shifts are independent of variations in the adhesion force (full circles in Fig. 3). However, when energy dissipation is included, here by means of adhesion energy hysteresis [16, 17], the phase shift increases with the γ_H . Adhesion energy hysteresis is calculated through the difference in surface energies between the approach and the retraction ($\gamma_H = \gamma_R - \gamma_A$).

Phase-contrast images in tapping mode have their origin in elastic properties or adhesion forces variations once a fraction of the initial kinetic energy of the cantilever is dissipated in the sample (topographic effects aside). Energy dissipation in the cantilever resulting from its quality factor is not enough to explain phase-contrast images.

4 Experiments and simulations on mica

To illustrate some of the basic features of dynamic force microscopy and to test the model we measured the phase-shift dependence on the tip-sample equilibrium separation on mica. The cantilever was excited at its free resonance frequency.

For tip-sample equilibrium separations much larger than the free oscillation amplitude the phase shift remains constant and equal to 90° . When the tip is very close to the surface, the phase shift increases up to 103° . Then comes a sudden decrease for a tip-sample separation of about 56 nm. From there on the phase shift shows a smooth decrease to a final value of 29° .

The increase of the phase shift before contact is due to long-range attractive forces. The positive gradient of the force shifts the resonance frequency at lower values. This in turn shifts the phase upwards. After that, there is tip-sample intermittent contact. The phase shift decreases with separation because of the negative gradient of the interaction force in the time that the tips remains in contact with the sample.

Figure 4 shows the calculations for mica. We have assumed that the viscosity coefficient of the mica is negligible and $E = 24.5$ GPa [18]. The calculations were performed with (circles) and without adhesion energy hysteresis (squares). The simulations reproduce the effects on the phase shift of long-range attractive and short-range repulsive forces. In particular, the sharp transition between no contact to intermittent contact. In the region of z_c below 20 nm the best agreement is obtained when adhesion energy hysteresis is introduced. This agreement emphasizes the relevance of inelastic processes in dynamic force microscopy when there is intermittent tip-sample contact.

The contact time, i.e., the time during which the tip and sample interact with repulsive forces, shows clearly the transition between no contact to intermittent contact (Fig. 4c). The contact time changes from $t_c = 0$ ns to 160 ns. From there t_c increases with tip-sample proximity. For a ratio $A_t/A_0 = 0.5$, the tip remains in contact with the sample for about 10% of the oscillation period.

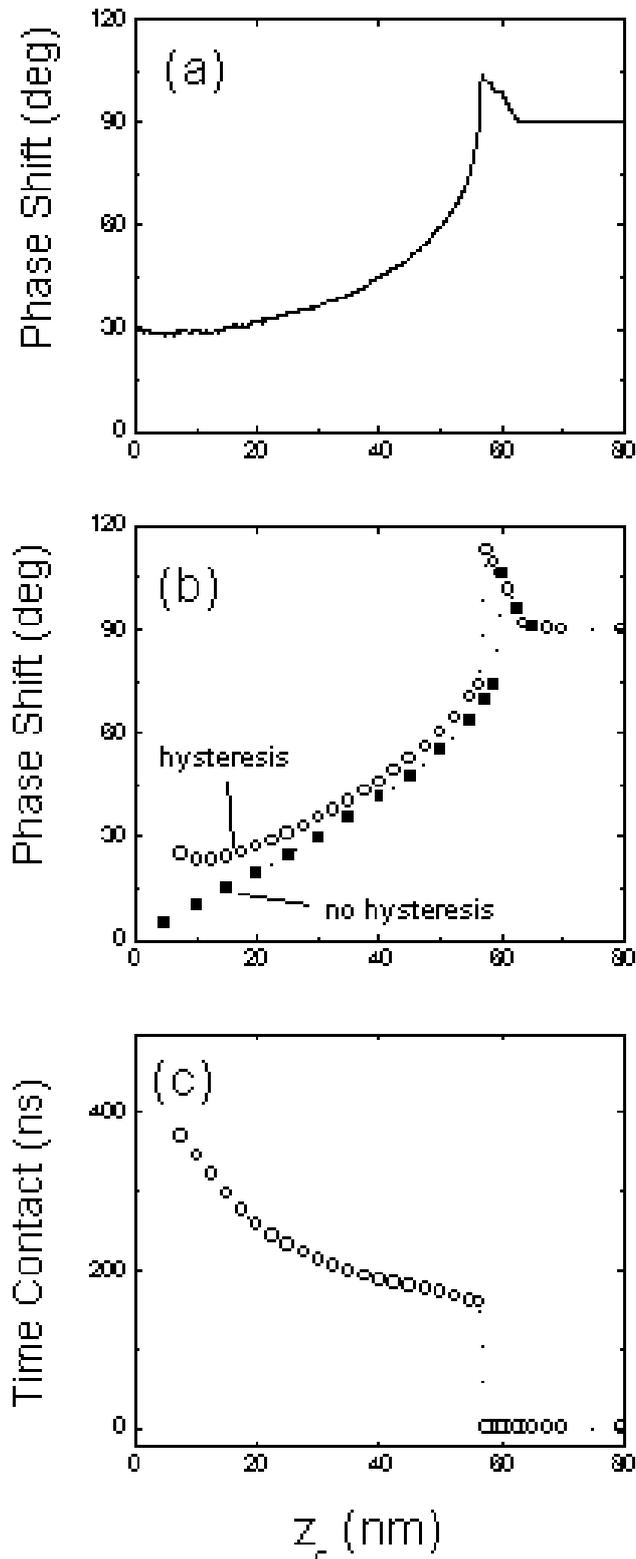


Fig. 4. **a** Experimental phase-shift dependence on tip-sample equilibrium separation curves for mica. Free amplitude $A_0 = 62$ nm, $\nu_t = 345.83$ kHz, $Q = 392$, and $k_c = 40$ N/m. **b** Simulation for mica without energy hysteresis (squares) and with adhesion energy hysteresis $\gamma_A = 150$ mJ m $^{-2}$, $\gamma_R = 225$ mJ m $^{-2}$ (open circles). $\nu_t = 345.83$ kHz, $Q = 392$, $A_0 = 62$ nm and $k_c = 40$ N/m. **c** Calculated contact time dependence on z_c for Fig. 4b. The sharp change marks the transition from no contact to intermittent contact

The transition from no contact to intermittent contact happens for $z_c = 56$, i.e., a separation of several nm smaller than the free oscillation amplitude (62 nm). This illustrates the damping effect of attractive forces at resonance.

5 Summary

In this article the effect of elastic and inelastic interactions on phase shifts during tapping operation has been studied. In the absence of tip-sample inelastic interactions, phase shifts are insensitive to variations in the elastic modulus and adhesion force. Phase-contrast images associated with elastic variations are obtained once a fraction of the kinetic energy is dissipated into the sample. Consequently, phase-contrast images are an indirect result of tip-sample inelastic interactions.

Phase shifts versus tip-sample separation have been measured on mica. The phase shift increases before contact as a result of attractive forces. Repulsive forces produce a decrease in the phase shift. The transition from no contact to intermittent contact is marked by a sudden change in the phase shift. The agreement obtained between theory and experiment supports the conclusions derived from the model.

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