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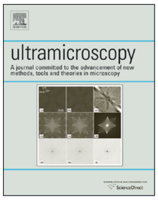

AFM based dielectric spectroscopy: Extended frequency range through excitation of cantilever higher eigenmodes

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ABSTRACT

In the last years, a new AFM based dielectric spectroscopy approach has been developed for measuring the dielectric relaxation of materials at the nanoscale, the so called *nano*Dielectric Spectroscopy (*n*DS). In spite of the effort done so far, some experimental aspects of this technique remain still unclear. In particular, one of these aspects is the possibility of extending the experimental frequency range, to date limited at high frequencies by the resonance frequency of the AFM cantilever as a main factor. In order to overcome this limitation, the electrical excitation of cantilever higher eigenmodes for measuring the dielectric relaxation is here explored. Thus, in this work we present a detailed experimental analysis of the electrical excitation of the cantilever second eigenmode. Based on this analysis we show that the experimental frequency range of the AFM based dielectric spectroscopy can be extended by nearly two decades with a good signal-to-noise ratio. By using the combination of first and second cantilever eigenmodes we study dissipation processes on well known PVAc based polymeric samples. Both, relaxation spectra and images with molecular dynamics contrast were thus obtained over this broader frequency range.

1. Introduction

During the last decades, broadband dielectric spectroscopy (BDS) has shown to be a very useful technique in the study of the molecular dynamics of insulating materials. The huge frequency range achieved (10^{-5}–10^{12} Hz) and the possibility of measuring under different temperature, pressure, and environmental conditions allows the observation of a large variety of processes with very different time scales. Within this extraordinary experimental window, molecular and collective dipolar fluctuations, charge transport and polarization effects take place, in turn determining the dielectric response of the material under study [1].

In the last years, the growing interest in nanostructured materials highlighted the need of measurements providing local material properties. Recently, the electric interaction between the tip of an atomic force microscope (AFM) and the material under study was used as the basis to develop a new technique: Local Dielectric Spectroscopy (LDS) [2]. Within this approach, the electrical interaction resulting by applying an AC voltage to a conductive AFM probe is used to reveal information about the relaxation processes within the material. Therefore, this technique combines the capability of sensing the molecular dynamics as a function of the frequency of BDS with the outstanding spatial resolution of AFM. LDS measurements are based on a PLL setup, and detect the force gradient [3–5]. However, a method based on the detection of force was also developed [6–10], the so called *nano*Dielectric Spectroscopy (*n*DS) [10]. Within these approaches either the measured force or force gradient, resulting from the electrical interaction between the tip and the sample under study, is used to obtain information of the dielectric properties of the material.

The electrical interaction between the AFM probe and the sample allows *n*DS to probe locally, 20–30 nm [11], the molecular dynamics of nanostructured materials. However, as the measurements are performed through the motion of an AFM cantilever (i.e. a mechanical system with inherent properties), some method derived limitations are found. In particular, the limited frequency range of the technique should be mentioned as one of the most

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important. Since the three frequency decades achieved during the first experiments [2], the experimental frequency range of LDS and *n*DS was later increased to four decades (typically from 1 Hz to 30 kHz) [5,10]. There is a twofold origin for the frequency range restriction: on the one hand there is a low frequency limit mainly related to a) the time needed to reach a steady state of cantilever oscillations (and therefore to perform a reliable measurement) and b) the thermal drift, which in turn affects the accuracy of the relative tip-sample position. On the other hand, the high frequency limit is imposed by the electronics and more fundamentally by the oscillation amplitude of the AFM cantilever. To date, *n*DS experiments were limited to excitation frequencies lower than the fundamental mode. The fundamental mode is the first of the so called normal modes (or eigenmodes), which in turn are described by the continuous cantilever beam model [12]. In other words, *n*DS currently presents the possibility of measuring locally through the AFM spatial resolution, at the expense of a high frequency limit mainly imposed by the cantilever characteristics.

The use of higher eigenmodes for mechanical AFM applications has been widely studied in the last years, and it is commonly known as bimodal atomic force microscopy [13,14]. Within this approach, the cantilever is simultaneously excited with two driving forces at frequencies matching the first and second eigenmodes [15–17]. Bimodal AFM was also employed for exploring surface potentials in Kelvin probe microscopy, where the electrostatic forces appear at the second eigenmode frequency [18,19].

In this work we demonstrate the possibility of extending the current AFM based dielectric spectroscopy frequency range by using the second eigenmode of the cantilever. In a first step, we study the electrical excitation (and detection) of the second eigenmode oscillations of a conductive cantilever. In a second step, we analyze the accuracy of the electrical measurements in this extended frequency range by using a dissipation-free sample. Finally, we study a dielectric relaxation process on well known polymeric samples as proof of concept experiments. In this way, here we present for the first time AFM based dielectric spectroscopy measurements with an extended experimental frequency window.

1.1. *nano*-Dielectric Imaging and Spectroscopy Background

The electric force microscopy (EFM) is based on the electrical force (F_e) resulting from the interaction of a conductive AFM probe with polarizable entities in the material [6,20–26]. F_e can be evaluated by modeling the tip-sample system as a capacitor (capacitance C): when a voltage (V) is applied, the resulting electrostatic potential energy is $W=½CV^2$ and the corresponding electrostatic force acting on the tip $F_e=dW/dz$ (z being the coordinate along the tip sample distance). Consequently, when a sinusoidal voltage of frequency $f_e=\omega_e/2\pi$ is applied to the AFM tip [$V(t)=V_0\sin(\omega_e t)$] the corresponding force is a sinusoidal function (see Eq. (1)) with a component at a frequency double than that used in the excitation due to the quadratic relationship between F_e and V (see Eq. (2))

$$F_e(t)=\frac{1}{2}\frac{\partial C}{\partial z}[V_S+V_{DC}+V_0\ \sin(\omega_e t)]^2 \tag{1}$$

$$F_{2\omega_e}(t)=-\frac{1}{4}\frac{\partial C}{\partial z}V_0^2\ \cos(2\omega_e t) \tag{2}$$

where V_S is the surface potential and V_{DC} is the applied DC voltage (if any) [10]. The force amplitude depends both on the experimental conditions and the dielectric properties of the material under investigation. Therefore, by detecting the tip motion component at the second harmonic of the AC excitation voltage, local information about the dielectric relaxation of the materials under investigation can be obtained. This method is known as *nano*-Dielectric Spectroscopy and requires analyzing the signal from the AFM photodiode with an external Lock-In Amplifier (LIA) in order to obtain both the amplitude and electric phase of the cantilever oscillations. In the case of a loss-free dielectric material the signal amplitude brings information on the static dielectric permittivity, which is frequency independent. However, when dielectric relaxation takes place in the material, the dielectric permittivity becomes frequency dependent and a corresponding dielectric loss process appears (which in turn results in a complex capacitance: $C^*=C_0(\omega_e)e^{-i\theta(\omega_e)}$) and Eq. (2) becomes

$$F^*_{2\omega_e}=-\frac{1}{4}\frac{\partial(C_0(\omega_e)e^{-i\theta(\omega_e)})}{\partial z}V_0^2 \tag{3}$$

This approach allows collecting information of the frequency dependant dielectric response, either as a) images (*nano*-Dielectric Imaging, *n*DI) at a fixed frequency or b) frequency spectra (*nano*-Dielectric Spectroscopy, *n*DS) at a single location. Fig. 1 shows a scheme of the implementation of these two experimental methods.

1.2. *nano*-Dielectric Imaging

In this mode, the electrical excitation frequency is fixed and the dielectric interaction between the tip and the sample is mapped by using the single pass method (SP). In SP, both the topography and dielectric contrast of the sample are obtained during the main scan itself. Within this experiment, the sinusoidal voltage is applied to the tip during the main scan and the cantilever response is filtered by the external LIA. Electric phase (θ) and root mean square oscillation amplitude ($|RMS_{amp}|$, which is proportional to $F_{2\omega_e}$) of the cantilever signal thus obtained are mapped along with the topography and the mechanical phase (analyzed in the AFM internal LIA). Thus, it is possible to obtain an image with molecular dynamics contrast at fixed frequency and temperature [8,27].

1.3. *nano*-Dielectric Spectroscopy

In contrast with the previous method, in this case the experiment is performed at a single location by using the double-pass method (DP). In a first step, the tip-sample distance (or sample topography) is established precisely by a standard ‘Tapping’ (intermittent contact) experiment. Subsequently, the mechanical cantilever oscillation amplitude is set to zero, in order to maintain a constant tip-sample distance (lift mode), and the probe motion generated by the application of an alternating voltage is analyzed. The advantage of the DP method for spectra acquisition resides in avoiding any non-linear interactions produced by larger oscillation amplitudes in piezo driven cantilevers (like in SP). $|RMS_{amp}|$ and θ are simultaneously obtained from the LIA. A reference experiment on a dissipation free sample is performed for each probe in order to establish the zero electric phase accurately (by removing phase shifts associated with the electronics and the mechanical characteristics of the AFM probe). Subsequently, phase shift ($\Delta\theta$) as a function of the electrical excitation frequency, spectra, is obtained by subtracting this reference from the sample response.

2. Experimental details

2.1. Samples

Polymer films of pure PVAc (M_w=83,000) were prepared by spin-coating polymer–toluene solutions on gold sputtered glass