

# Determination of the nanoscale dielectric constant by means of a double pass method using electrostatic force microscopy

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We present a method to determine the local dielectric permittivity of thin insulating layers. The measurement is based on the detection of force gradients in electric force microscopy by means of a double pass method. The proposed experimental protocol is simple to implement and does not need any modification of standard commercial devices. Numerical simulations based on the equivalent charge method make it possible to carry out quantification whatever the thickness of film, the radius of the tip, and the tip-sample distance. This method has been validated on a thin SiO<sub>2</sub> sample for which the dielectric permittivity at the nanoscale has been characterized in the literature. We also show how we can quantitatively measure the local dielectric permittivity for ultrathin polymer film of poly(vinyl acetate) and polystyrene. © 2009 American Institute of Physics. [DOI: 10.1063/1.3182726]

## I. INTRODUCTION

Dielectric relaxation (DR) has shown to be a very useful, extended, and versatile technique to study dielectric materials, in particular, polymers and other glass formers.<sup>1</sup> The interaction of electromagnetic radiation with systems having permanent molecular dipoles allows obtaining valuable information about the molecular dynamics of the system under investigation at different time (or frequency) scales. Additionally, DR measurements can be performed at different temperatures or pressures to study the corresponding dependence of the molecular dynamics. In spite of all these promising characteristics, the standard DR has a fundamental limitation due to the lack of spatial resolution. This restriction means, for instance, that the study of self-assembly or nanostructured polymers is in principle model depending.<sup>2</sup> Advances in our ability to explore local properties will make possible to gain a deeper understanding of the physics of complex materials. In this context, it is important to develop reliable methods for the determination of micro-/nanodielectric properties that would have broad impact on the field of material science and particularly to study fundamental physics of nanostructured materials.

Some existing works looking for dielectric characterization at nanoscale are based on using atomic force microscopy (AFM) and, more especially, electrostatic force microscopy

(EFM). EFM senses electrostatic forces and has been used to image localized charges on surfaces,<sup>3</sup> dielectric constant variations,<sup>4,5</sup> and potentials.<sup>6</sup> In EFM a conducting cantilever allows applying dc or ac bias voltages to the tip. It is generally used to measure the surface potential (Nano-Kelvin) on semiconducting materials.<sup>7</sup> Recently, Israeloff *et al.*<sup>8,9</sup> used ultrahigh vacuum AFM in order to characterize the complex dielectric permittivity ( $\epsilon^*(\omega) = \epsilon' - i\epsilon''$ ) of poly(vinyl acetate) (PVAc) polymer. This experiment was realized by applying an ac bias voltage of variable frequency ( $\omega$ ). From the in and quadrature phase components of the sensor signal response and using a phenomenological model, they obtained the frequency dependence of  $\epsilon'$  and  $\epsilon''$  without giving quantitative values for the dielectric permittivity. Other reported works were devoted to the determination of the modulus of the dielectric permittivity without taking into account the possible frequency response of the material. We can mention for instance the works of Krayev *et al.*<sup>4,5</sup> related to the study of polymers blend in the form of layer of several microns thickness. The authors showed that an electric contrast could be obtained on EFM images and that such a contrast is related to the variations of the relative dielectric permittivity  $\epsilon_r$ . They also quantified the value of  $\epsilon_r$  in the frame of a simple spherical capacitor model. Unfortunately, this model is appropriate only under certain conditions because it makes the approximation that the thickness of the sample is very large compared to the tip radius and the tip-sample distance. Moreover, dielectric constants of two reference polymers are required to measure a third unknown one. Finally, a different

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## Rouse-Model-Based Description of the Dielectric Relaxation of Nonentangled Linear 1,4-*cis*-Polyisoprene

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**ABSTRACT:** A detailed test of the Rouse model has been performed on a nonentangled 1,4-*cis*-poly(isoprene) (PI) by investigating the end-to-end vector dynamics by means of broadband dielectric spectroscopy. The contribution to the dielectric relaxation of the end-to-end vector dynamics was determined by subtracting the signal from the local segmental dynamics dominating at higher frequencies. This signal was inferred from experiments on higher molecular weight samples. Our results show that the Rouse model accounts remarkably well for the experimental data once the narrow distribution of molecular masses is properly accounted for. The very same approach is found to provide a good description of a simultaneous dielectric/rheology experiment. Despite the overall good agreement between experiments and model predictions, small excess contributions in the high frequency side of the dielectric losses are detectable.

### Introduction

The chain dynamics of linear polymers is one of the basic and classical problems of polymer physics, and thereby, it has been the subject of intensive investigation, both experimentally and theoretically, over many years.<sup>1–21</sup> Despite of the broad range of models and theoretical approaches existing in the literature, there are many aspects of the problem that remain to be understood (see refs 3 and 10–15 and references therein). Most of the current investigations are devoted to the problem of the dynamics of highly entangled polymer melts with different architectures and topologies and to the rheology of polymer systems of industrial relevance.<sup>11–13</sup> Concerning the chain dynamics of unentangled polymers, it is generally assumed that the well-known Rouse model<sup>10</sup> provides a suitable theoretical description. The Rouse model represents a linear chain as a series of beads and springs subjected to entropic forces in a medium with a constant friction. Although this simple approach obviously fails in describing the melt dynamics of long chains at longer times, the Rouse model is also used for describing the fastest part of the response of these long chains, and thereby it is a common ingredient of all available model and theories. The validity of the Rouse model has been instigated by means of different experimental techniques<sup>2,4,5,9,15,16</sup> and also by molecular dynamics simulations.<sup>17–24</sup> Even so, a full and detailed test of the Rouse model is challenging because in unentangled polymer melts the segmental dynamics ( $\alpha$ -relaxation) contributions overlap significantly with the high-frequency components of the chain dynamics. In fact, even by microscopic techniques with spatial resolution as neutron scattering, it is rather difficult to distinguish the border between chain and segmental relaxations.<sup>25</sup> This fact, among others, restricts the use of rheology experiments to test accurately the Rouse model on unentangled polymer chains. It is very hard to obtain rheology

data of unentangled polymers in the melt. This is due to the rapid relaxation times of the material and the broad spread of the effect of more local molecular mechanisms that affect the stress relaxation modulus at higher frequencies. Another related limitation of rheological techniques is the rather narrow frequency range usually accessible by such techniques.

More detailed information about chain dynamics of unentangled polymers can be obtained by means of broadband dielectric spectroscopy (BDS) using A-type polymers in the Stockmayer classification.<sup>26</sup> Those polymers contain dipole moments along the chain backbone that do not cancel at the whole chain, giving rise to an “end-to-end” net polarization vector. In addition, they also have dipole moment components perpendicular to the chain contour, as other types of polymers. It is nowadays well-known that the dielectric spectrum of any A-type polymer contains two different relaxation processes. One of them, the segmental relaxation process, is due to fluctuations of the perpendicular dipolar component, whereas the other, the so-called “normal mode relaxation”, reflects the fluctuation of the end-to-end vector,  $\vec{R}$ . The correlation function of this vector  $\langle \vec{R}(t) \cdot \vec{R}(0) \rangle$  can be expressed in terms of the discrete Rouse model as

$$\langle \vec{R}(t) \cdot \vec{R}(0) \rangle = \frac{2b^2}{N} \sum_{p:\text{odd}}^{N-1} \cot^2\left(\frac{p\pi}{2N}\right) \exp\left(-\frac{t}{\tau_p}\right) \quad (1)$$

where  $N$  is the number of beads and  $b$  is the size of the  $N - 1$  bonds in the chain ( $b^2(N - 1)$  is the unperturbed chain mean squared end-to-end distance).  $\tau_p$  is the relaxation time associated with the Rouse mode  $p$  and is given by

$$\tau_p = \frac{\xi b^2}{12k_B T \sin^2(p\pi/2N)} = \frac{\tau_s}{\sin^2(p\pi/2N)} \quad (2)$$

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# Dielectric properties of thin insulating layers measured by Electrostatic Force Microscopy

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**Abstract.** In order to measure the dielectric permittivity of thin insulating layers, we developed a method based on electrostatic force microscopy (EFM) experiments coupled with numerical simulations. This method allows to characterize the dielectric properties of materials without any restrictions of film thickness, tip radius and tip-sample distance. The EFM experiments consist in the detection of the electric force gradient by means of a double pass method. The numerical simulations, based on the equivalent charge method (ECM), model the electric force gradient between an EFM tip and a sample, and thus, determine from the EFM experiments the relative dielectric permittivity by an inverse approach. This method was validated on a thin SiO<sub>2</sub> sample and was used to characterize the dielectric permittivity of ultrathin poly(vinyl acetate) and polystyrene films at two temperatures.

## 1 Introduction

Physical study of complex materials as nano-structured materials and self-assembly polymers requires the development of methods to characterize their properties at the nano and microscale. Particularly, nano-characterization of dielectric properties presents a great interest to understand the behaviour of these complex systems under electromagnetic radiation and to study their dynamics at the nanoscale, in bulk or in confined geometry. We present here a method to measure the dielectric properties of thin insulating films. This method is based on electrostatic force microscopy (EFM) experiments coupled with numerical simulations and provide quantitative measurements of the relative dielectric permittivity,  $\epsilon_r$ , of complex materials in the liquid or solid state.

In typical EFM experiments, dc or ac bias voltages are applied between the tip and the sample via a conductive cantilever. EFM is generally used to measure the surface potential (Kelvin probe force atomic microscopy – KPFM) on semiconducting materials [1], and to image lo-

calized charges on surfaces [2], dielectric constant variations [3,4] and potentials [1,5]. Recently, Crider et al. [6,7] used ultra high vacuum atomic force microscopy (UHV-AFM) in order to characterize the complex dielectric permittivity ( $\epsilon^*(\omega) = \epsilon' - i\epsilon''$ ) of poly(vinyl acetate) polymer (PVAc). This experiment was realized by applying an ac bias voltage of variable frequency ( $\omega$ ). From the in and quadrature phase components of the sensor signal response and using a phenomenological model, they obtained the qualitative frequency dependence of  $\epsilon'$  and  $\epsilon''$ . Other reported works were devoted to the determination of the modulus of the local dielectric permittivity without taking into account the possible frequency response of the material. We can mention for instance the works of Krayev et al. [3,4] related to the study of polymers blend in the form of layer of several microns thickness. The authors showed that an electric contrast could be obtained on EFM images and that such a contrast is related to the variations of  $\epsilon_r$ . They also quantified the value of  $\epsilon_r$  in the frame of a simple spherical capacitor model, which is valid for large thickness of the sample in comparison with the tip radius and the tip-sample distance. Moreover, dielectric constants of two reference polymers are

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# Nanodielectric mapping of a model polystyrene-poly(vinyl acetate) blend by electrostatic force microscopy

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We present a simple method to quantitatively image the dielectric permittivity of soft materials at nanoscale using electrostatic force microscopy (EFM) by means of the double pass method. The EFM experiments are based on the measurement of the frequency shifts of the oscillating tip biased at two different voltages. A numerical treatment based on the equivalent charge method allows extracting the values of the dielectric permittivity at each image point. This method can be applied with no restrictions of film thickness and tip radius. This method has been applied to image the morphology and the nanodielectric properties of a model polymer blend of polystyrene and poly(vinyl acetate).

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Nanostructured polymers, nanoparticle composites, and biological membranes are typical complex systems for which local properties, local structure, and composition determine the properties and the functionality on the microscale and macroscale. Understanding the behavior of these complex systems is based on the parallel studies of the local structure or composition and of the local properties. For electronic materials, scanning tunneling microscopy is the appropriate technique to realize such studies. For soft matter, atomic force microscopy (AFM) [1] can be used but requires the development of new experiments and procedures to measure quantitatively the properties at local scale. In this Rapid Communication, we show that the morphology and the dielectric properties of a model polymer blend can be measured at the nanoscale by coupling electrostatic force microscopy (EFM)-AFM experiments with numerical simulations based on the equivalent charge method (ECM). [2,3]

In the last five years, the quantitative analysis of the dielectric permittivity at nanoscale has become a great challenge. Kravayev *et al.* [4,5] have been the first to present a quantitative value of the dielectric constant of a polymer at the nanoscale using phase shift images obtained by the double pass method. However, the quantification is only possible when the tip radius is negligible compared to the thickness of the polymer and is therefore not suitable for the study of ultrathin polymer films or biological membranes. Moreover, the dielectric constants of two reference polymers are required to measure a third unknown one. Using the so-called nanoscale dielectric microscopy, Fumagalli *et al.* [6] have been able to quantify and image the low-frequency dielectric constant of a single biomembrane. Using a tip with a nominal radius of 100–200 nm they estimate the spatial lateral resolution around  $\sim 70$  nm. The experiment is based on

the measurement of the local capacitance by a fully customized current amplifier and lock-in board integrated with the AFM electronics [7,8] that allows capacitance measurements with attofarad resolution. [9] Following another approach based on force detection by AFM experiments, other authors have characterized the dielectric properties of carbon nanotubes and biomembranes. [10,11] Recently, Crider *et al.* [12,13] have used ultrahigh vacuum atomic force microscopy in order to characterize the complex dielectric permittivity  $[\epsilon^*(\omega) = \epsilon' - i\epsilon'']$  of poly(vinyl acetate) (PVAc) polymer. This experiment was realized by applying an ac bias voltage of variable frequency ( $\omega$ ). From the in and quadrature phase components of the sensor signal response and using a phenomenological model, they obtained the qualitative frequency dependence of  $\epsilon'$  and  $\epsilon''$ .

In order to determine quantitatively the relative dielectric constant  $\epsilon_r$  of soft materials at the nanoscale, we have developed an EFM method based on the measurement of an electric force gradient  $\text{grad}_{DC} F$  while applying a  $V_{DC}$  voltage between a tip and a sample holder on which a thin film of a soft material is deposited. The force gradient is related to the cantilever-tip-sample capacitance  $C(z)$  by  $\text{grad}_{DC} F = \frac{1}{2}[\partial^2 C(z)/\partial z^2]V_{DC}^2$ , where  $z$  is the tip-sample distance.  $C(z)$  is a sum of the tip apex capacitance  $C_{apex}(z)$  and the stray capacitance  $C_{stray}(z)$ , associated with the tip cone and the cantilever contributions. According to Fumagalli *et al.* [7], for nanometric displacements around the measuring position,  $C_{stray}(z)$  varies linearly with the distance and, thus, can be neglected in the calculation of the second derivative  $\partial^2 C(z)/\partial z^2$ . The local electrostatic force gradient is a function of the resonance frequency shift  $\Delta f_0$ , which can be measured by keeping the phase shift constant:  $\Delta f_0/f_0 \cong -\frac{1}{2}[(\text{grad}_{DC} F)/k_c]$ , [14] where  $k_c$  is the stiffness of the cantilever. As expected from previous relations, the curves  $\Delta f_0(V_{DC})$  have the parabolic form,  $-a_{\Delta f_0}(z)V_{DC}^2$ , where  $a_{\Delta f_0}(z)$  is related to the tip-sample capacitance by the

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# High and low molecular weight crossovers in the longest relaxation time dependence of linear cis-1,4 polyisoprene by dielectric relaxations

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**Abstract** The dielectric relaxation of cis-1,4 Polyisoprene [PI] is sensitive not only to the local and segmental dynamics but also to the larger scale chain (end-to-end) fluctuations. We have performed a careful dielectric investigation on linear PI with various molecular weights in the range of 1 to 320 kg/mol. The broadband dielectric spectra of all samples were measured isothermally at the same temperature to avoid

utilizing shift factors. For the low and medium molecular weight range, the comparisons were performed at 250 K to access both the segmental relaxation and normal mode peaks inside the available frequency window (1 mHz–10 MHz). In this way, we were able to observe simultaneously the effect of molecular mass on the segmental dynamics—related with the glass transition process—and on the end-to-end relaxation time of PI and thus decouple the direct effect of molecular weight on the normal mode from that due to the effect on the monomeric friction coefficient. The latter effect is significant for low molecular weight ( $M_w < 33$  kg/mol), i.e., in the range where the crossover from Rouse dynamics to entanglement limited flow occurs. Despite the conductivity contribution at low frequency, careful experiments allowed us to access to the normal mode signal for molecular weights as high as  $M_w = 320$  kg/mol, i.e., into the range of high molecular weights where the pure reptation behavior could be valid, at least for the description of the slowest chain modes. The comparison between the dielectric relaxations of PI samples with medium and high molecular weight was performed at 320 K. We found two crossovers in the molecular weight dependence of the longest relaxation time, the first around a molecular weight of  $6.5 \pm 0.5$  kg/mol corresponding to the end of the Rouse regime and the second around  $75 \pm 10$  kg/mol. Above this latter value, we find a power law compatible with exponent 3 as predicted by the De Gennes theory.

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**Keywords** Rouse model · Reptation theory · Crossover · Entanglement · Dynamics · 1,4-cis-Poly(isoprene) · Dielectric relaxation



# Nanoscale dielectric properties of insulating thin films: From single point measurements to quantitative images

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## ABSTRACT

Dielectric relaxation (DR) has shown to be a very useful technique to study dielectric materials like polymers and other glass formers, giving valuable information about the molecular dynamics of the system at different length and time scales. However, the standard DR techniques have a fundamental limitation: *they have no spatial resolution*. This is of course not a problem when homogeneous and non-structured systems are analyzed but it becomes an important limitation for studying the local properties of heterogeneous and/or nano-structured materials. To overcome this constrain we have developed a novel approach that allows quantitatively measuring the local dielectric permittivity of thin films at the nanoscale by means of Electrostatic Force Microscopy. The proposed experimental method is based on the detection of the local electric force gradient at different values of the tip-sample distance. The value of the dielectric permittivity is then calculated by fitting the experimental points using the Equivalent Charge Method. Even more interesting, we show how this approach can be extended in order to obtain quantitative dielectric images of insulating thin films with an excellent lateral resolution.

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## 1. Introduction

During the last decades dielectric relaxation (DR) and more specifically dielectric spectroscopy (DS) have shown to be very useful techniques to follow the molecular dynamics of polar materials over a huge frequency range ( $10^{-5}$ – $10^{12}$  Hz) under different temperature, pressure and environment conditions [1]. Several molecular processes, at very different time and length scales, can be observed by means of DR techniques and the pressure and temperature dependences of their characteristic relaxation times can be therefore investigated. Besides its exceptional time (or frequency) resolution and range, standard DR techniques can only measure the macroscopic average dielectric response. This means that no spatial resolution can be achieved by using standard DR techniques. This is an important limitation that strongly constrains the study of heterogeneous systems, di-block copolymers, nano-structured or biological materials among others.

Some attempts to measure the local dielectric response at nano-metric scale were recently published by different groups.

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Israeloff et al. [2,3] have recently measured the frequency dependence of the dielectric response of poly(vinyl acetate) thin films by means of an ultra high vacuum atomic force microscope (UHV-AFM). By exciting the tip with an AC bias voltage, whereas the bottom part of the polymer film was grounded, they were able to measure the in and quadrature phase components of the cantilever oscillation. From these measurements the qualitative frequency dependence of the complex dielectric permittivity ( $\epsilon^*(\omega) = \epsilon' - i\epsilon''$ ) can be obtained. Although the qualitative results using this method are very promising, more work is still necessary to obtain quantitative values for the dielectric permittivity. On the other hand, and by means of a completely different approach, Krayev et al. [4,5] have also used electrostatic force microscopy (EFM) to study the dielectric permittivity of polymer blend thin films. In this case, the authors were able to obtain a quantitative dielectric image of their polymer blend. However, the quantification is based on a simple spherical capacitor model, which works only under certain assumptions about the thickness of the sample and the tip-sample distance. Moreover, this method measures the relative dielectric permittivity and therefore two reference polymers are required to measure a third unknown one. A third approach worth mentioning was recently developed by Gomila et al. [6,7]. Their method basically consists in measuring the capacitance between the tip and the bottom electrode of the

# Imaging dielectric relaxation in nanostructured polymers by frequency modulation electrostatic force microscopy

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We have developed a method for imaging the temperature-frequency dependence of the dynamics of nanostructured polymer films with spatial resolution. This method provides images with dielectric compositional contrast well decoupled from topography. Using frequency-modulation electrostatic-force-microscopy, we probe the local frequency-dependent (0.1–100 Hz) dielectric response through measurement of the amplitude and phase of the force gradient in response to an oscillating applied electric field. When the phase is imaged at fixed frequency, it reveals the spatial variation in dielectric losses, i.e., the spatial variation in molecular/dipolar dynamics, with 40 nm lateral resolution. This is demonstrated by using as a model system; a phase separated polystyrene/polyvinyl-acetate (PVAc) blend. We show that nanoscale dynamic domains of PVAc are clearly identifiable in phase images as those which light-up in a band of temperature, reflecting the variations in the molecular/dipolar dynamics approaching the glass transition temperature of PVAc. © 2010 American Institute of Physics. [doi:10.1063/1.3431288]

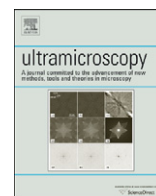
Broadband dielectric spectroscopy (BDS) is a well established technique that enables measurement of molecular dynamics of bulk materials with permanent molecular dipoles. Recent advances have made it possible to probe the dynamics of thin polymer films with a thicknesses as low as 5 nm, enabling the study of interfaces.<sup>1,2</sup> However, BDS has poor spatial resolution and the interpretation of the results from nanostructured polymers is always model dependent.<sup>3</sup> Concerning local dielectric characterization, on the one hand, various atomic force microscopy based methods have been developed to image the dc dielectric constant  $\epsilon$  at nanoscale. Fumagalli *et al.*<sup>4</sup> have developed the so-called “nanoscale capacitance microscopy,” where the microscope is equipped with a subattofarad low-frequency capacitance detector. The same group also proposed a method based on the detection of the dc electrostatic force to image the dielectric constant of a purple membrane patch.<sup>5</sup> By measuring the dc electrostatic force gradient, we have been able to obtain a quantitative value of  $\epsilon$  in one point<sup>6</sup> and a map of the dielectric constant of a nanostructured polymer film.<sup>7</sup> On the other hand, in previous work we have shown that the frequency response of the real and imaginary parts of the dielectric constant [ $\epsilon^*(\omega) = \epsilon' - i\epsilon''$ ] can be investigated using frequency modulation electrostatic force microscopy (FM-EFM).<sup>8,9</sup> Measurements made in one spatial point gives direct information about the local dynamics of the sample area probed by the tip sample interaction. In the following, we will detail how we have been able to combine imaging

and measurement of the frequency dependence of the dielectric response to map the dipolar/molecular dynamics of a nanostructured thin film of a phase separated polymer blend.

In order to maximize contrast, we have chosen to work with polystyrene (PS-[C<sub>8</sub>H<sub>8</sub>]<sub>n</sub>—M<sub>w</sub>=70 950 g/mol) and poly(vinyl-acetate) (PVAc-[C<sub>4</sub>H<sub>6</sub>O<sub>2</sub>]<sub>n</sub>—M<sub>w</sub>=33 200 g/mol) for which the bulk dielectric response has been previously well characterized.<sup>10–12</sup> A solution containing 25% PVAc and 75% PS (by mass) and having a total concentration of 1% polymer in toluene has been spin-coated over a conductive film (Au) on a mica substrate. The samples are dried at 70 °C for 1 h under ambient conditions and annealed at 35 °C overnight in vacuum to remove any trace of solvent. The resulting polymer films consist of a 25 nm thick matrix with island-like features having an average diameter of about 300 nm and a maximum height of about 25 nm above the reference level of the matrix (Fig. 1). In the investigated range of frequency (0.1–100 Hz), we expect to detect the so-called dielectric alpha-relaxation of PVAc (correlated with segmental motion<sup>12</sup>) slightly above its glass transition temperature; T<sub>g</sub>~35 °C. Therefore we have explored the temperature range between 25 and 50 °C in order to follow the evolution of this dynamic process. The T<sub>g</sub> of PS being ~105 °C, no measurable relaxation is expected in our range of temperature and frequency. These two polymers are immiscible, even at the nanoscale and form phase separated domains.

Experiments were carried out by FM-EFM under ultrahigh vacuum (UHV) with a variable temperature stage (RHK UHV 350). The temperature was measured with a small thermocouple clamped to the sample surface.

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# Broadband *nanodielectric* spectroscopy by means of amplitude modulation electrostatic force microscopy (AM-EFM)

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## ABSTRACT

In this work we present a new AFM based approach to measure the local dielectric response of polymer films at the nanoscale by means of Amplitude Modulation Electrostatic Force Microscopy (AM-EFM). The proposed experimental method is based on the measurement of the tip-sample force via the detection of the second harmonic component of the photosensor signal by means of a lock-in amplifier. This approach allows reaching unprecedented broad frequency range ( $2\text{--}3 \times 10^4$  Hz) without restrictions on the sample environment. The method was tested on different poly(vinyl acetate) (PVAc) films at several temperatures. Simple analytical models for describing the electric tip-sample interaction semi-quantitatively account for the dependence of the measured local dielectric response on samples with different thicknesses and at several tip-sample distances.

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## 1. Introduction

Standard broadband dielectric spectroscopy (BDS) is a well known, established and extremely useful technique to follow the molecular dynamics of bulk materials containing polar entities over a huge frequency range ( $10^{-5}$ – $10^{12}$  Hz) under different temperature, pressure and environment conditions (see for example [1]). Thus, several molecular processes in the bulk, at very different time scales, can be observed by means of standard BDS. In spite of these exceptional characteristics and features, standard BDS can only measure the macroscopic average dielectric response, which means that no spatial resolution can be achieved. This is an important limitation that seriously restricts the use of standard BDS to investigate heterogeneous or nano-structured systems, where spatial resolution is essential. During the last decade, some attempts to measure the local dielectric response at nano-metric scale were carried out by different groups. Most of the explored methods consist to adapt existing AFM facilities to accomplish local measurements of different quantities (capacitance [2,3], DC [4–6] and AC [7–11] electrostatic force gradients) that can be related by means of appropriated models with the dielectric response. However, these methods present some

important limitations: some of them work under vacuum whereas others only account for the static dielectric permittivity or measure its frequency response over a limited frequency range.

In this work we present a novel approach, based on amplitude modulation electrostatic force microscopy (AM-EFM) to measure the local dielectric response of polymer films with both nano-metric lateral resolution and broad frequency band. This method can be easily implemented on standard AFM without any special instrumentation and, especially important, under room conditions or controlled atmosphere as well. Moreover, this simple method allows performing *nanodielectric* spectroscopy with an unprecedented broad frequency range, which could eventually be extended up to six decades. Although we use similar AFM setup than that used in some previous works, the main point of our approach is related with the fact that we directly analyze the response on the photosensor (i.e. the force signal) instead of measuring cantilever's resonance frequency or phase (i.e. force gradient signal) or the tip-sample capacitance. Advantages and limitations of this approach will be discussed.

## 2. Principles of AM-AFM operation

The basic idea of the method is to measure by means of an AFM the electric force between the tip and an insulating sample when an AC voltage is applied between the tip and a conductive

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# Numerical study of the lateral resolution in electrostatic force microscopy for dielectric samples

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## Abstract

We present a study of the lateral resolution in electrostatic force microscopy for dielectric samples in both force and gradient modes. Whereas previous studies have reported expressions for metallic surfaces having potential heterogeneities (Kelvin probe force microscopy), in this work we take into account the presence of a dielectric medium. We introduce a definition of the lateral resolution based on the force due to a test particle being either a point charge or a polarizable particle on the dielectric surface. The behaviour has been studied over a wide range of typical experimental parameters: tip-sample distance (1–20) nm, sample thickness (0–5)  $\mu\text{m}$  and dielectric constant (1–20), using the numerical simulation of the equivalent charge method. For potential heterogeneities on metallic surfaces expressions are in agreement with the bibliography. The lateral resolution of samples having a dielectric constant of more than 10 tends to metallic behaviour. We found a characteristic thickness of 100 nm, above which the lateral resolution measured on the dielectric surface is close to that of an infinite medium. As previously reported, the lateral resolution is better in the gradient mode than in the force mode. Finally, we showed that for the same experimental conditions, the lateral resolution is better for a polarizable particle than for a charge, i.e. dielectric heterogeneities should always look 'sharper' (better resolved) than inhomogeneous charge distributions. This fact should be taken into account when interpreting images of heterogeneous samples.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

Electrostatic force microscopy (EFM) permits one to study the electrical properties of surfaces at the nanoscale by applying a voltage between the tip of the microscope and the sample. EFM has been largely used to study surface potential and capacitance [1–6], charge or dopant distribution [7–11] and polarization forces on dielectric surfaces [12, 13]. It permits probing of the conducting properties of carbon

nanotubes [14–16], study of liquid surfaces [17] or induction of capillary condensation of water bridges between the tip and sample [18]. EFM has thus become an important tool to characterize the electrical and electrochemical properties of metals, semiconductors, dielectrics and organic materials at the nanoscale.

As in other scanning probe microscopy (SPM) techniques, the interpretation of the EFM images is not always evident [19]. The force mode (amplitude modulation, AM)

# On the use of electrostatic force microscopy as a quantitative subsurface characterization technique: A numerical study

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We present a numerical study on the use of electrostatic force microscopy (EFM) as a non invasive subsurface characterization technique. We discuss the ability to resolve a buried object in a dielectric matrix considering two parameters: the detectability (i.e., signal superior to the noise) and the lateral resolution. The effects of the dielectric constant, thickness of the sample, and depth at which the object is buried are quantified. We show that the sensitivity reached in EFM permits to characterize subsurface objects in a dielectric matrix. We demonstrate that both lateral resolution and detectability decreases when the tip object distance increases. On the other hand, these two quantities increase with the dielectric constant of the matrix. A first step toward EFM tomography is proposed for objects creating non correlated signals. © 2011 American Institute of Physics. [doi:10.1063/1.3608161]

Electrostatic force microscopy (EFM) is a well known technique to characterize electrical and electrochemical properties of metals, semiconductors, dielectrics, and organic materials at the nanoscale. The lateral resolution of EFM has been largely studied at the surface of both metallic<sup>1-3</sup> and dielectric samples<sup>4</sup> and reaches nanometers values. In the DC mode and typical ambient condition, its great sensitivity allows measuring cantilever deflection of the order of the Ångström<sup>5</sup> and frequency shift close to the hertz<sup>6</sup> corresponding to hundreds of pN forces and tenths of pN/nm force gradients, respectively. In their early work, Schönenberger *et al.* developed a polarizing optical interferometer with a sensitivity that permitted to monitor the recombination of single charge carriers.<sup>7</sup> Today, the characterization of subsurface objects in dielectric matrix is of the utmost importance. Among the area focusing on this topic, we will cite the study of charge decay and lateral spreading in oxide<sup>8,9</sup> that would allow further scale-down of nitride trap memory and the incorporation of nanostructured materials, such as carbon nanotubes (CNTs) into polymeric films to improve material performance.<sup>10-13</sup> However, only few techniques permit to study subsurface properties: the optical microscope is limited by light wavelength and electron based techniques can damage the sample. EFM has recently been used to resolve CNTs in polymeric matrix. Jespersen *et al.* obtained a three dimensional mapping of individual CNT in a poly-(methylmethacrylate) film<sup>14</sup> whereas Zhao *et al.*<sup>15</sup> reported a complete experimental study of CNTs in polyimide nanocomposite films, anticipating EFM as a promising technique for this kind of characterization. Shen *et al.*<sup>16</sup> used boundary

based methods to quantitatively investigate electrostatic signals, including a study of discrete charges on the sample surface or sheet charges inside a dielectric. They also developed a formalism to predict the formation of images in Kelvin probe force microscopy from a prescribed charge distribution and solve the charge distributions from the image (forward and reverse problems, respectively).<sup>17</sup> In the following, we detail a numerical study that permits to understand the effect of the experimental parameters (dielectric constant and thickness of the sample, depth of the buried object) on the lateral resolution and detectability of subsurface objects using EFM. We will also demonstrate how the depth and the value of a point charge can be obtained.

The numerical simulation of the equivalent charge method (ECM)<sup>6,18</sup> or generalized image-charge method<sup>19</sup> permits to compute the electric field, and, therefore, the additional force  $F$  and force gradient  $G$  (derivative of the force toward the tip sample distance  $d_0$ ) created on the tip by a charge  $q_0$  in a dielectric. The idea of ECM is to find a discrete charge distribution ( $N$  charge points  $q_i$  at a distance  $z_i$  on the axis  $x = 0$ ) that represent the tip by creating a given potential  $V$  at the tip surface.  $V_0^i$  and  $V_1^i$  are the potentials created by the charge  $q_i$  in the air ( $\epsilon_0$ ) and in the dielectric ( $\epsilon$ ), respectively. For each  $q_i$ , we introduce two series of images having a position and a value computed from the original position and value of the charge representing the tip (see references<sup>6,18</sup> for more details). The core of the ECM is to find the value of the charges  $q_i$  representing the tip that will satisfy the limit conditions ( $V_0^i = V_1^i$  and  $\epsilon_0 \frac{\partial V_0^i}{\partial z} = \epsilon \frac{\partial V_1^i}{\partial z}$ ) at the air/dielectric interface, and,  $V_1^i = 0$  at the dielectric/substrate interface). Once the electrostatic problem is solved, we introduce the charge  $q_0$  located inside the dielectric at a distance  $r_0$ . In order to calculate the additional force on the tip, we will neglect the

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# Contrast inversion in electrostatic force microscopy imaging of trapped charges: tip–sample distance and dielectric constant dependence

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## Abstract

We present a numerical and analytical study of the behavior of both electrostatic force and force gradient created by a charge trapped below the surface of a dielectric on an atomic force microscope tip as a function of the dielectric constant and tip–sample distance. As expected, the force decreases monotonously when the dielectric constant increases. However, a maximum in the dielectric constant dependence of the force gradient is found. This maximum occurs in the typical experimental parameters’ range and depends on the tip–sample distance and the sample thickness. The analytical study permits us to understand the physical origin of this phenomenon and is in good agreement with the numerical simulation for small tip–sample distances. We also report a study exemplifying a possible contrast inversion in electrostatic force microscopy (EFM) signals while scanning, at different heights, two charges trapped in a sample having heterogeneous dielectric domains. In addition to this particular contrast inversion effect, this study can be considered as a way to gain insight into the mechanisms of EFM image formation as a function of the dielectric constant and tip–sample.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

One of the advantages of scanning probe microscopy (SPM) over other nanocharacterization techniques such as light, x-ray, neutron scattering or optical tweezers is that you can actually see the phenomenon that you would like to study. Recent advances in high speed atomic force microscopy (HS AFM) in liquid have notably permitted us to provide corroborative ‘visual evidence’ leading to a comprehensive

understanding of fundamental biological mechanisms that had already been studied by other techniques [1]. However, the interpretation of SPM images is not trivial and can lead to several errors. Indeed, contrast variation or inversion can be related to true variation of physical properties but also to changes in experimental parameters or modes, the contribution of the macroscopic part of the tip (cone and cantilever), contamination layers and other phenomena still under investigation.

# Numerical simulations of electrostatic interactions between an atomic force microscopy tip and a dielectric sample in presence of buried nano-particles

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Nanoscale tomography is an outstanding *challenge* with an urgent need in materials science. In this context, electrostatic force microscopy offers the possibility to investigate nanoparticles buried inside dielectric films. In this paper, finite element modeling has been performed to analyze their detectability with regard to both particles features (size and depth) and dielectric permittivity of the medium. In the case of charged particles, a sign dependence of the detectability was demonstrated by means of observations of local electric fields and equipotential lines deformations. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4768251>]

## I. INTRODUCTION

With the emergence of nanotechnologies and other engineering advances, the investigation of subsurface and buried nanostructures or nanoparticles is a major issue for many industrial sectors. In such a context, tomography of materials and devices is evolving fast. Numerous imaging techniques already enable to have access to three-dimensional structural information of samples from micro to nanometer length scales.<sup>1</sup> Among the most relevant techniques, we can mention scanning electron microscopy/focused ion beam (SEM-FIB) tomography<sup>2</sup> consisting in alternating “imaging and milling” (with SEM and FIB, respectively) of successive cross-sections through the sample. This technique has been adopted, for example, to image subsurface microstructure (cracks, granularity...) in metallic and ceramic materials.<sup>3,4</sup> Another pertinent technique is called the electron tomography<sup>5,6</sup> which is derived from transmission electron microscopy. Several modes are possible depending on the type of interaction considered: On the one hand side, shape-sensitive modes allow reproducing the contour of buried nano-objects are the most common. And on the other hand, atomic number density-sensitive modes, chemically sensitive, provide composition or phase mapping.

Although being an interesting alternative, the use of atomic force microscopy (AFM) as a nanoscale tomography technique is not yet very widespread. We can mainly mention some results showing elastic images of which contrast is impacted by subsurface features (embedded wires, carbon fiber, and epoxy composites...). The images are produced either by amplitude or phase variations when the cantilever vibrates in the contact mode (Force modulation)<sup>7</sup> or the tapping mode,<sup>8</sup> respectively. They can also be obtained by means of ultrasonic waves propagating through the sample and detected by the probe.<sup>9,10</sup> Actually, unlike other techniques, the most promising aspects of AFM tomography turn out to be related with the possibility of probing the electrical

response of buried objects or trapped charges. This is made possible by the use of electrostatic force microscopy (EFM). Such method would be meant, for example, to better understand charge loading and retention in nano-objects, and also to study basic mechanisms of ionizing radiation effects on advanced components and devices used for space and avionics charge trapping in gate dielectrics of metal oxide semiconductor (MOS) structures. It is worth to mention that EFM presents another key advantage over previously described electron microscopy techniques (FIB-SEM and electron tomography): it does not require sectioning or destruction of the sample.

There are also some other promising EFM studies emerging in the field of nanomaterial science. Indeed, many investigations are currently being carried out on dielectric imaging of nanoparticles deposited on the surface of a substrate. Some authors have, for example, found the deoxyribonucleic acid (DNA) conductance to be that of an insulator,<sup>11</sup> which was a response to an important controversy. More recently, Brown *et al.* improved imaging of dielectric spheres by means of dielectrophoresis with coaxial probes.<sup>12</sup> And finally, certainly one of the most significant results has been to identify material composition of single dielectric nanoparticles.<sup>13</sup> This approach has been successfully applied to measure and discriminate the structure (core and shell) of single bacteriophage viruses.

However, in such a context, EFM has rarely been used for tomography. We can just mention some works on imaging carbon nanotubes embedded in a polymer. The EFM contrast shows a correlation between the signal intensity (force gradient) and the nanotube depth. Jespersen and Nygard<sup>14</sup> have shown that for the same scan height and the same nanotube length, the force gradient is higher when the nanotube is closer to the surface. Zhao *et al.*<sup>15</sup> have shown that the detectable depth is given to be directly proportional to the product of the dielectric constant and the tip-sample distance. We have recently reported numerical studies demonstrating how to realize EFM tomography.<sup>16–18</sup> Based on the equivalent charge method (ECM), both force and force gradient between a buried object (or trapped charges) and the

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