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Feature Article

Nanomechanical mapping of soft matter by bimodal force microscopy

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ABSTRACT

Bimodal force microscopy is a dynamic force-based method with the capability of mapping simultaneously the topography and the nanomechanical properties of soft-matter surfaces and interfaces. The operating principle involves the excitation and detection of two cantilever eigenmodes. The method enables the simultaneous measurement of several material properties. A distinctive feature of bimodal force microscopy is the capability to obtain quantitative information with a minimum amount of data points. Furthermore, under some conditions the method facilitates the separation of the topography data from other mechanical and/or electromagnetic interactions carried by the cantilever response. Here we provide a succinct review of the principles and some applications of the method to map with nanoscale spatial resolution mechanical properties of polymers and biomolecules in air and liquid.

Contents

1. Introduction

The emergence of hybrid devices and materials made up of nanostructures of different mechanical, chemical, electric and/or magnetic properties requires the development of non-invasive, high resolution and fast characterization methods that combine high spatial resolution with compositional contrast. Ideally, those materials should be observed in their native environment and state. The atomic force microscope (AFM) [1] has significantly contributed to our current understanding of soft-matter interfaces [2–5]. Conversely, the evolution of the atomic force

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microscope (AFM) is being shaped by the need to provide a full characterization of complex interfaces [6]. Images of heterogeneous surfaces with high spatial resolution (sub-5 nm range) in combination with compositional contrast have been provided by dynamic AFM methods such as phase imaging [4,7–17]. This method enables to identify and measure energy dissipation processes at the nanoscale [9–13]. In general it is not straightforward to transform those images into quantitative information about other nanomechanical properties albeit some notable exceptions exist [7,9,14–16].

Force microscopy has provided a nearly continuous progress in high resolution imaging-nano, molecular or atomic-of materials by experiencing multiple transformations. This has led to the development a large variety of dynamic force-based methods [6,18–24]. The common thread in those methods is the detection of forces and the use a mechanical cantilever-tip system as the transducer of the forces.

Bimodal force microscopy is an AFM method that uses several eigenmode frequencies for excitation and detection [19,25,26]. The different resonances act as signal channels that allow accessing and separating material properties such as topography, dissipation, Young modulus, viscosity and short and long-range interactions.

To facilitate the understanding of bimodal AFM it is convenient to distinguish between some of the major frequency components carried out by the cantilever-tip response, eigenmodes and harmonics. The cantilever-tip ensemble, cantilever or probe for short, is a mechanical system which has a number of discrete oscillations ω_j with $j = 1, 2, \ldots$ that are determined the boundary conditions. Those oscillations are variously termed 'eigenmodes', 'normal modes' or 'resonances'. When the normal modes are contained in a plane orthogonal to the main plane of the cantilever they are called flexural modes. A higher harmonic, on the other hand is a component of the oscillation that vibrates with a frequency that is equal to an integer multiple of the excitation frequency ($\omega_n = n\omega$). In general, higher harmonic and resonant frequencies do not coincide. Subharmonics are components with a frequency that is a submultiple of the excitation frequency. The harmonics are introduced in the probe motion by the nonlinearities in the interaction force. A more complete description of eigenmodes and harmonics in the context of AFM can be found elsewhere [6,27–29]. Fig. 1a shows the first two flexural mode shapes of a rectangular cantilever that is clamped at one end and free to oscillate at the other.

2. Bimodal AFM

2.1. Operating principles

The method uses two driving forces to excite the vibration of the cantilever. The excitation frequencies of the driving forces are tuned to match two of the eigenmodes of the cantilever, usually the first and the second flexural modes of the cantilever,

$$F_{exc} = F_1 \cos \omega_1 t + F_2 \cos \omega_2 t \quad (1)$$

then the cantilever response can be expressed

$$z = z_0 + A_1 \cos(\omega_1 t - \phi_1) + A_2 \cos(\omega_2 t - \phi_2 t) + \xi \quad (2)$$

where F_i, $\omega_i = 2\pi f_i$, ϕ_i, A_i are, respectively, the excitation force, angular frequency, phase shift and amplitude of the eigenmode i. The last term ξ represents the deflection components at frequencies different of the excited ones. Those components are usually neglected.

A scheme of the addition of the first two modes and the resulting excitation signal is shown in Fig. 1b and c. In the most common experimental set-up, an output signal of the first mode (either the amplitude or the frequency shift) is used to image the topography of the surface while the output signals of the second mode (amplitude, frequency shift and/or phase shift) are used to measure changes in different mechanical [30–38], magnetic [39,40] or electrical properties [41–44] of the surface. This method is compatible with both dynamic AFM modes, amplitude (AM) and frequency modulation (FM) modes [45]. It can be operated in air [25,26], liquid [31] or ultrahigh vacuum [46,47].

2.2. Bimodal AFM configurations

The variety of observables to record the tip-surface force and to operate the feedback has produced several bimodal AFM configuration modes. This makes bimodal AFM very flexible and, at the same time, the subtleties of the different configurations might be hard to follow.

Computer simulations laid the foundations [19] for the experimental implementation of bimodal AFM. The first bimodal AFM prototypes had the feedback controlling the amplitude of the 1st resonance while the parameters of the second resonance were free to change (open loop) [25,26]. This configuration is called amplitude modulation (AM). By operating the feedback in the frequency shift of the first mode instead of the amplitude a new bimodal configuration is in place [48,56], this bimodal AFM configuration is termed (FM). A combination of the feedbacks in the amplitude of the first resonance and the frequency shift of the second gives rise to the configuration known as AM–FM [34]. Table 1 shows a classification of some of the current bimodal AFM configurations.

Kawai and co-workers have proposed a bimodal AFM operation scheme that involves the excitation of a flexural mode and a torsional mode [48]. Solares and Chawla have demonstrated that the cantilever excitation/detection scheme could be extended to three normal frequencies. They called this approach trimodal AFM [49,50].

2.3. The physics of bimodal AFM

The understanding of bimodal AFM contrast is still under development [48,51–53]. This is partly due to the novelty of the method. The intrinsic flexibility of bimodal AFM operation to select the observable for material contrast complicates the development of a coherent framework that encompasses all the bimodal AFM variations [34]. Nonetheless, there are some established principles that explain the properties of bimodal AFM in terms of the force sensitivity, the compositional contrast or the ability to separate the various forces acting on the cantilever.

Three main factors singularize bimodal AFM operation [51]: the coupling between excited modes induced by the nonlinear tip-surface force, doubling of the number of