Measurement of elastic modulus of nanotubes by resonant contact atomic force microscopy

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A resonant contact atomic force microscopy technique is used to quantitatively measure the elastic modulus of polymer nanotubes. An oscillating electric field is applied between the sample holder and the microscope head to excite the oscillation of the cantilever in contact with nanotubes. The nanotubes are suspended over the pores of a membrane. The measured resonance frequency of this system, a cantilever with the tip in contact with a nanotube, is shifted to higher values with respect to the resonance frequency of the free cantilever. It is experimentally demonstrated that the system can simply be modeled by a cantilever with the tip in contact with two springs. The measurement of the frequency shift thus enables the direct determination of the spring stiffness, i.e., the nanotube stiffness. The method also enables the determination of the boundary conditions of the nanotube on the membrane. The tensile elastic modulus is then simply determined using the classical theory of beam deflection. The obtained results fairly agree to previously measured values using nanoscopic three points bending tests. It is demonstrated that resonant contact atomic force microscopy allows us to quantitatively measure the mechanical properties of nanomaterials. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1565675]

I. INTRODUCTION

The developments of scanning probe microscopies allowed the emergence of powerful means for material property characterization at the micro- and nanoscale. These microscopies are particularly well suited for the study of nanometer-sized objects. Especially, atomic force microscopy (AFM) is widely used to study material mechanical properties.[1,2] The measurement of approach-retraction curves (force curves) allows in some cases to obtain quantitative value of surface elastic modulus. However, due to geometrical constraints in AFM, pure normal solicitation of the contact is not possible and shear deformation or tip sliding may interfere in the measurements.[3] Dynamic methods such as tapping mode (TM) or force modulation allow the mapping of the mechanical properties of samples with a high resolution but they also present drawbacks and limitations. Nonlinear behaviors in TM complicate the analysis of the data in terms of quantitative surface mechanical properties.[4] Moreover, in TM, the cantilever support is excited by a piezoelectric bimorph located in the cantilever support. Therefore, mechanical couplings lead to noisy resonance spectra of the cantilever with peak deformations and/or additional parasitic peaks. Indirect force modulation, generally realized by modulating either the height of the sample or that of the cantilever holder, induces shear stress of the contact due to the AFM configuration. Friction properties are thus mixed in the data leading to possible artifacts and make it difficult to realize true elastic imaging of surfaces.[3,5] Direct force modulation was obtained using a magnetic force that creates a harmonic modulation of the cantilever. The magnetic method avoids shear stress of the contact but has the drawback to necessitate the modification of the cantilever by sticking magnetic particles or evaporating magnetic coating on it.[5,6]

In this article, we used a method allowing the excitation of the cantilever vibration that avoids both the use of a transducer and cantilever modifications.[7] An alternative external electric field is applied between the sample holder and the microscope head and induces the cantilever vibration due to the polarization forces acting on the tip. By varying the intensity and the frequency of the electric field, it is possible to completely characterize the resonance spectrum of cantilevers while the tip contacts the sample surface or not. The obtained resonance spectra are much cleaner than those obtained by mechanical excitation. When the tip contacts the sample, the resonance frequencies of the cantilever-sample system shift to higher values relative to the resonance fre-

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quencies of the free cantilever. Under certain conditions, the measurement of this frequency shift enables the determination of the stiffness of the ‘‘tip-sample’’ contact. It may potentially be used to measure the Young’s modulus of the samples when a contact mechanics model is assumed.[8–12]

In the present study, this method was used to measure the mechanical properties of polymer nanotubes. Indeed, materials with reduced dimensions and dimensionality [two-dimensional (2D), 1D, and 0D materials] such as thin films, nanowires, nanotubes, or metallic clusters may present exceptional properties compared to those of the corresponding bulk materials (3D materials). Thanks to their particular physical properties, these materials give rise to a large interest. We show here that the electrostatic resonant contact AFM method enables the characterization of these nanomechanical systems and the precise measurement of their tensile elastic modulus. In the particular case of suspended nanotubes, it is shown here that the cantilever in contact with a nanotube can be modeled by a cantilever having its tip in contact with two springs. The interpretation of the experimental data does not rely on any assumption concerning the mechanics of the contact.

II. EXPERIMENT

Nanotubes were synthesized using a recently developed template-based method that uses the pores of polycarbonate track-etched membranes as ‘‘nanoreactors.’’[13,14] Nanotubes of a conductive polymers (polypyrrole, PPy) were electrochemically synthesized within the pores of 20 μm thick polycarbonate (PC) membranes. The template membranes had a pore density of 10^9 cm^{-2}. In order to obtain nanomaterials with different outer diameters, membranes with pore size ranging between 30 and 250 nm were used.

After synthesis, the membrane was slowly dissolved by immersion in a dichloromethane solution containing dodecyl sulfate as the surfactant.[15] The role of the surfactant is to protect the nanotubes during the membrane dissolution and to prevent nanotube aggregation. To detach the nanotubes from the gold film previously evaporated on the backside of the template membrane, the suspension was placed in an ultrasonic bath during one hour. The suspensions were then filtered through poly(ethylene terephthalate) (PET) membranes with pore diameters ranging between 0.8 and 3 μm. This filtration enabled the dispersion of the nanostructures on these membranes that served afterward as supports for the AFM measurements. In order to remove any contaminant from the nanotube surface, particularly traces of PC, the samples were thoroughly rinsed with dichloromethane. These nanotubes are hollow and their inner diameter was estimated using a previously established calibration curve relating the outer and the inner diameters.[16] The elastic modulus of the nanotubes was already measured by a nanoscopic three points bending test.[16]

The pore diameter of the PET membrane was chosen in order to minimize shear deformations. Indeed, in bending tests, beam deflection induces both tensile/compressive deformations and shear deformations. To obtain the tensile modulus from the measured parameters in these tests, it is necessary to minimize shear deformations. Imposing geometrical conditions to the tested system enabled us to achieve this objective. The shear contribution can be neglected when the ratio between the suspended length of the beam and its outer diameter d_{out} is higher than 16.[17] Under these conditions, it is possible to consider that only tensile and compressive deformations are present. To achieve this, each series of nanotubes synthesized in a template membrane with a specific pore diameter was dispersed on a PET membrane with a corresponding pore diameter satisfying this criterion. Therefore, the shear contribution could be considered as negligible for all the probed nanotubes.

All the AFM experiments were performed with an Autoprobe® CP microscope (Thermomicroscopes) operated in air with a 100 μm scanner equipped with ScanMaster® detectors correcting for drift, nonlinearity, and hysteresis effects. The cantilevers were standard Si_3N_4 Microlevers™ with integrated pyramidal tips (typical apex radius of curvature between 30 and 50 nm). The spring constant of each cantilever was calibrated by deflecting it against a reference cantilever of known spring constant.[18] Values ranging between 0.3 and 0.5 N m^{-1} were obtained for all the cantilevers used in the experiments. Geometrical characterization of the cantilever was realized by high-resolution scanning electron microscopy. Obtained data were used for the description of the dynamical behavior of the cantilever using the Rayleigh-Ritz approximation.[19,20] The physical properties of the cantilever material (i.e., its elastic modulus and its density) were deduced from the free experimental resonance frequency of the cantilever. The modulated electric field was applied between the sample holder and the AFM head using a function generator (Agilent Technologies, model 33120A). In order to avoid tip displacement on the sample surface and to keep the resonance peak symmetrical, resonance spectra were recorded without polarization offset and with a small excitation amplitude.[7,21] The cantilever deflection signal was measured using a lock-in amplifier (EG&G Princeton Applied Research, model S302). The signal generator command and the data collection from the lock-in were computerized and data analysis was realized using routines developed under Igor Pro software (*Wavemetrics*).

After dispersion of the nanotubes on a PET membrane, large-scale images (typically up to 80×80 μm^2) were first acquired in order to select nanomaterials suspended over pores that could be used to measure their mechanical properties [Fig. 1(a)]. Once a suspended nanostructure was located, an image of it at a lower scale (down to 1×1 μm^2) was then realized to precisely determine its dimensions, i.e., its suspended length L and its outer diameter d_{out} [Fig. 1(b)]. The outer diameter is determined by the measurement of its height with respect to the supporting membrane to avoid tip artifacts.

III. RESULTS AND DISCUSSION

After selection of a nanostructure, the AFM tip was located at the midpoint along its suspended length and the resonance spectrum of the cantilever in contact with the nanostructure was measured. In Fig. 2, a typical spectrum

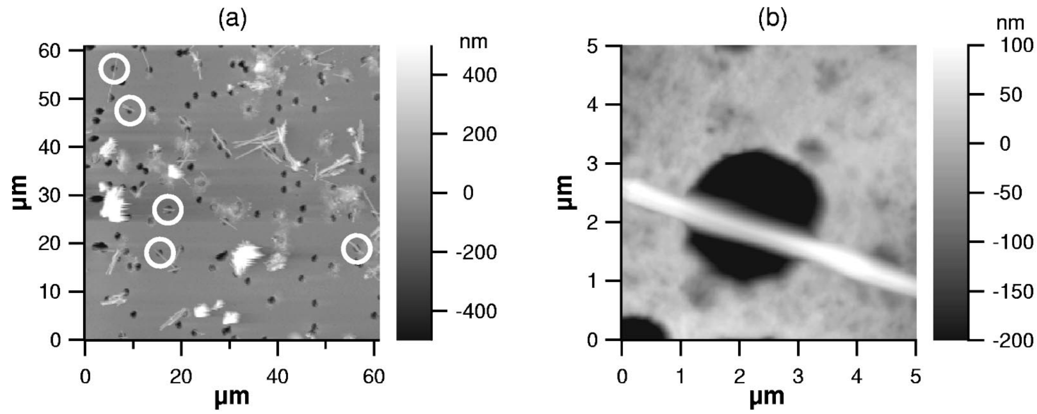

FIG. 1. (a) Large-scale image showing PPy nanotubes dispersed on a PET membrane with some of them crossing pores (white circles). (b) Small-scale image of a 90 nm thick PPy nanotube crossing a pore.

obtained on a PPy nanotube is presented and compared to the first resonance peak of the free cantilever. As expected, the first resonance frequency of the cantilever in contact with the nanostructure is higher than the corresponding free resonance frequency. The frequency shift reflects the dynamical behavior of the structure probed by the tip. The compliance of the cantilever-nanotube system may, *a priori*, be related to the deformation of the nanotube itself and/or to the contact compliance. Moreover, the inertial contribution of the nanotube may influence the system behavior. Hereafter, a description of the mechanical behavior of the system will be derived from the experimental results. Then, the elastic modulus of the nanotubes will be deduced.

On the spectrum of the cantilever in contact with a nanotube, three peaks are observed. Two of them correspond to flexural cantilever vibrations (F_1, F_2) and the third one is due to torsional vibrations (T_1). These assignments were realized by considering the relative amplitude of the resonance peaks, respectively, on the vertical and on the lateral signals on the position-sensitive photodiodes. Couplings in the horizontal and vertical detection systems are probably responsible for this signal mixing.

In order to properly describe the mechanical behavior of the cantilever-nanotube system, the relation between the frequencies corresponding to the first two flexural vibration modes was analyzed and is presented in Fig. 3. In this figure, the experimental points correspond to the resonance frequencies measured on several nanotubes with different diameters and suspended lengths, i.e., tubes with different stiffnesses. The solid curve is the calculated relation between the first two flexural frequencies of the triangular Si_3N_4 cantilever in contact with two springs at the tip position (Fig. 4). These two springs represent the vertical and lateral stiffness associated with the deformation of the nanotube in both directions. Indeed, the tilt of the cantilever may cause deformations, which are not normal to the sample surface.[12,21,22] The amplitude of the lateral deformation of the nanotube depends on its orientation relative to the cantilever axis. However, numerical calculation indicates that this lateral contribution to the resonance frequency is negligible for the present experimental conditions (nanotube and cantilever stiffnesses). This angular contribution should however be considered since it would not be negligible when much softer cantilever or stiffer nanotube are used. Both springs are assumed to have the same stiffness since the nanotubes are expected to have isotropic properties perpendicular to their axis. The

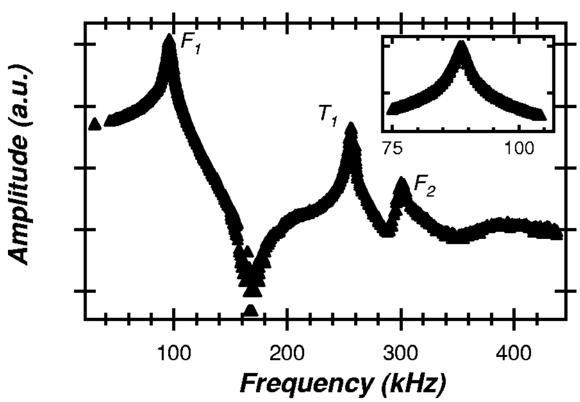

FIG. 2. Typical resonance spectrum measured for a cantilever in contact with a nanotube (logarithmic ordinate axis). Three peaks are observed, two of them corresponding to flexural cantilever vibrations (F_1, F_2) and the third one being due to torsional vibrations (T_1). In the inset, the resonance peak of the free cantilever is given for comparison.

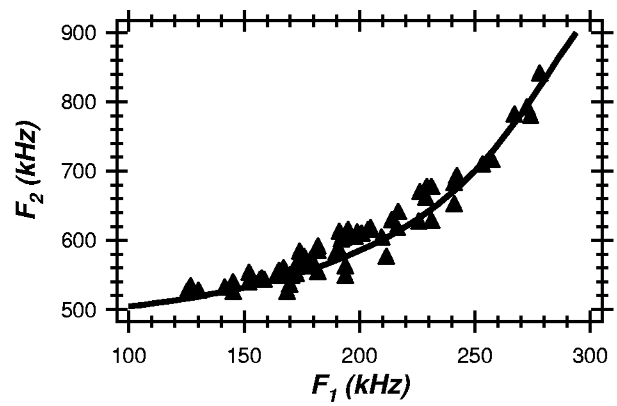

FIG. 3. Relationship between the resonance frequencies of the first two flexural vibration modes of a triangular-shaped cantilever in contact with nanotubes. ▲: experimental points, solid line: theoretical curve.

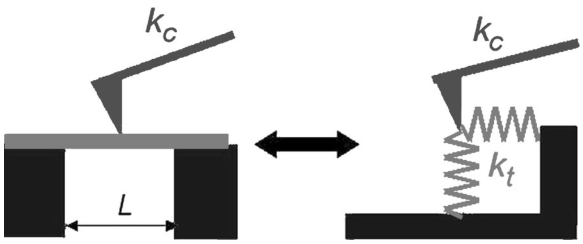

FIG. 4. Schematic representation of a cantilever resting on a suspended nanotube and of the equivalent mechanical model.

curve presented in Fig. 4 does not contain any adjustable parameter but is only governed by the geometrical dimensions of the cantilever. The good agreement observed with the experimental data confirms that the nanotubes actually behave as springs. It also indicates that the probed stiffness and that of the cantilever are within the same order of magnitude, otherwise a much smaller frequency shift would be measured for different nanotubes. Such behavior could be anticipated since previous measurements showed that the tensile modulus of the PPy nanotubes was always higher than 1 GPa.[16] Therefore, the tip-nanotube contact stiffness is always much higher than the characteristic stiffness of the nanotubes EI/L^3, where E is their Young's modulus, I their inertia momentum, and L their suspended length. The tip-sample contact deformation is then negligible in comparison to the overall nanotube deflection. No assumptions on the contact mechanics are thus necessary to interpret the experimental data. Moreover, the natural resonance frequency of the nanotubes is always much higher than that of the cantilever. Their inertia can thus be neglected. Thus, the suspended nanotubes can be modeled as simple springs in these experiments.

In order to deduce the elastic modulus of the nanotubes from the measured stiffness, it is however necessary to describe the boundary conditions of the suspended beams (clamping conditions). In a previous study of these nanotubes, the clamped conditions were assumed.[16] Many images were recorded with various angles between the nanotube axis and the fast scan direction as well as between the nanotube axis and the cantilever long axis due to the random dispersion of the tubes on the PET membranes. No nanotube was ever displaced during these experiments. AFM images were also recorded with stiffer cantilevers and, even in this case, no displacement was observed for the nanotube portion in contact with the membrane. The nanotube adhesion on the membrane seemed thus to be sufficiently high to prevent any lift-off during the bending test. This justified the use of the clamped-beam model to calculate the elastic modulus.

A further confirmation of this description can be found by analyzing the resonance frequency of the cantilever in contact with a nanotube at different relative locations (x/L) of the tip along the suspended length (L) of a given tube. In Fig. 5, experimental frequencies are plotted together with the expected distribution for the cantilever with the tip contacting a beam with free and clamped ends on the substrate.[23] The frequencies are calculated using the Rayleigh–Ritz method from the following relations, which respectively describe the stiffness distribution for contact on a beam with free (1) and clamped ends (2) on the substrate:

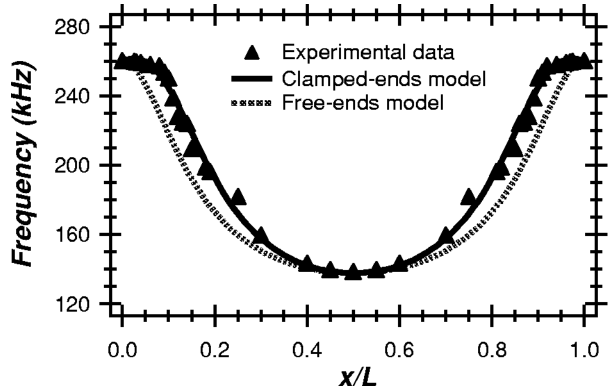

FIG. 5. Variation of the resonance frequency of a cantilever in contact with a tube along the tube suspended length. ▲: experimental points symmetrically duplicated with respect to the middle of the suspension length; dotted line: expected variation for a free-ends tube; solid line: expected variation for a clamped-ends tube.

$$\frac{1}{k_{\mathrm{tube}}}=\frac{L^3}{3EI}\left(\frac{x}{L}\right)^2\left(1-\frac{x}{L}\right)^2+\frac{2}{k_s}\left(\left(\frac{x}{L}\right)^2-\frac{x}{L}\right)+\frac{1}{k_s}, \tag{1}$$

$$\frac{1}{k_{\mathrm{tube}}}=\frac{L^3}{3EI}\left(\frac{x}{L}\right)^3\left(1-\frac{x}{L}\right)^3+\frac{2}{k_s}\left(\left(\frac{x}{L}\right)^2-\frac{x}{L}\right)+\frac{1}{k_s}. \tag{2}$$

In these relations, a finite stiffness k_s is assumed for the tube-on-substrate contact so that the predicted frequency at the tube ends corresponds to the frequency measured on the nanotube lying on the membrane. In the same way, for both models, the characteristic stiffness of the nanotube is chosen in order to fit the measured frequency at the middle of the suspended length. Clearly, the experimental distribution of frequencies presented in Fig. 5 does not follow that expected for a free-ends beam. This is essentially revealed by the curvature of the curves close to the beam edges. For the reported experiments, the nanotube can thus be described as a clamped-ends beam resting on a compliant substrate. Close to the center of the suspended length, the calculation however shows that the compliance of the system is mainly dominated by that of the nanotube. The effect of the low compliance of the substrate can thus be neglected.

The resonance frequency on each tube was measured at the midpoint of the suspended length on a series of PPy nanotubes with the outer diameter ranging from 30 to 250 nm. From this frequency, the nanotube stiffness was derived and the elastic modulus was determined using the classical formula of beam deflection.[23]

In Fig. 6, the values of the elastic modulus simultaneously determined by a three points bending test[16] and resonance frequencies measurement are reported as a function of the outer diameter. The values of the elastic modulus obtained using the electrostatic resonant AFM method agree very well with the previously measured values. The elastic modulus is seen to increase rapidly when the diameter decreases. Moreover, the obtained values of the elastic modulus

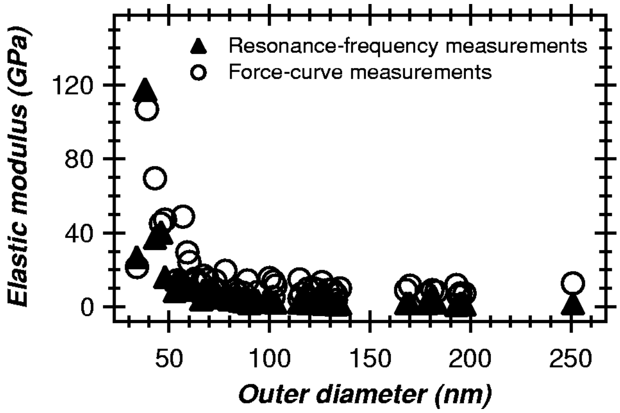

FIG. 6. Variation of the elastic modulus of polypyrrole nanotubes as a function of their outer diameter. The values obtained with the electrostatic modulation method (▲) are compared to those obtained with force-curves measurements (○).

measured for nanotubes having an outer diameter higher than 100 nm is comparable to the values measured on polypyrrole films.[24,25]

These results confirm the ability of resonant contact AFM with electrostatic modulation to precisely measure the mechanical properties of nanomaterials such as nanotubes. In comparison to force-curve measurements, this method presents the advantage that the conversion of the resonance frequency into material stiffness is straightforward while force-curves analysis necessitates a longer data treatment to obtain the stiffness. Moreover, it does not have the disadvantages of force-curve method, i.e., the fact that the load is not perfectly applied perpendicular to the sample surface that can lead to contact shearing stress or to tip slipping. It is also worth noting that this method not only enables us to measure the elastic modulus but also to fully characterize the nanomechanical system, i.e., the mechanical model and the nanostructure boundary conditions.

IV. CONCLUSION

In conclusion, a method based on the measurement of resonance frequencies of cantilevers in contact with nanotubes was used to measure the mechanical properties of nanomaterials. The resonance frequency is measured by modulating the cantilever deflection with an oscillating electric field applied between the sample holder and the AFM head.

This method allows for the complete description of the physical configuration and the mechanical characteristics of the system ''cantilever in contact with a nanotube.'' The frequency behavior of the nanomechanical system can be accurately modeled by a cantilever with the tip in contact with two springs. The nanostructure stiffness can thus be easily determined from the resonance frequency measurement using this simple model. The method also enables the determination of the boundary conditions of the nanotubes. In this case, clamped conditions were experimentally observed. With these data, the tensile elastic modulus can be calculated using the classical theory of beam deflection.

The method was applied to measure the elastic modulus of polymer nanotubes with their outer diameter ranging from 30 to 250 nm. The measured values and behaviors are in good agreement with those obtained in a previous study realized on the same suspended polymer nanotubes. These results confirm the ability of resonant contact AFM with electrostatic modulation to precisely characterize the elastic properties of nanotubes without the drawbacks of other methods such as force curves or force modulation. The method is easy to implement on most AFM instruments and the high accuracy associated with frequency measurements makes it a valuable tool for many mechanical analyses on nanostructures.

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