Elastic modulus of nanomaterials: resonant contact-AFM measurement and reduced-size effect

Bernard Nysten *a, Christian Frétignyb, Stéphane Cuenot†a

aPOLY, Université catholique de Louvain; Croix du Sud, 1; B-1348-Louvain-la-Neuve, Belgium;
bPCSM, ESPCI, CNRS UMR 7615; 10, rue Vauquelin; F-75231 Paris Cedex 05, France

ABSTRACT

Resonant contact atomic force microscopy (resonant C-AFM) is used to quantitatively measure the elastic modulus of polymer nanotubes and metallic nanowires. To achieve this, an oscillating electric field is applied between the sample holder and the microscope head to excite the oscillation of the cantilever in contact with the nanostructures suspended over the pores of a membrane. The resonance frequency of the cantilever with the tip in contact with a nanostructure is shifted to higher values with respect to the resonance frequency of the free cantilever. It is 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 enables the direct determination of the spring stiffness, i.e. the nanowires or nanotube stiffness. The method also enables the determination of the boundary conditions of the nanobeam on the membrane. The tensile elastic modulus is then simply determined using the classical theory of beam deflection. The obtained results for the larger nanostructures fairly agree to the values reported in the literature for the macroscopic elastic modulus of the corresponding materials. The measured modulus of the nanomaterials with smaller diameters is significantly higher than that of the larger ones. The increase of the apparent elastic modulus for the smaller diameters is attributed to the surface tension effects. It is thus demonstrated that resonant C-AFM enables the measurement of the elastic modulus and of the surface tension of nanomaterials.

Keywords: Metallic nanowires, polymer nanotubes, elastic modulus, surface tension, size effect, atomic force microscopy

1. INTRODUCTION

The developments of scanning probe microscopies allowed the emergence of powerful means for material property characterization at the micro- and nanoscale, particularly well suited for the study of nanometer-sized objects. Especially, atomic force microscopy (AFM) is widely used to study material and nanostructure mechanical properties. In most cases, the measurement of approach-retraction curves (force-curves) is used 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. Therefore, other methods, so-called resonant contact-AFM, based on the measurement of the resonance frequency of the cantilever were developed to avoid or limit these drawbacks. When the tip contacts the sample, the resonance frequencies of the cantilever shift to higher values relatively to the resonance frequencies 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. Generally, the cantilever vibration is induced through the excitation of its support with a piezoelectric bimorph located in the cantilever support. Therefore, mechanical couplings may lead to noisy resonance spectra of the cantilever with peak deformations and/or additional parasitic peaks. Direct modulation of the cantilever vibration was obtained using a magnetic force that creates a harmonic modulation of the cantilever. The magnetic method avoids mechanical couplings and ensures a normal solicitation of the contact. But it has the drawback to necessitate the modification of the cantilever by sticking magnetic particles or evaporating magnetic coating on it.

*a nysten@poly.ucl.ac.be; phone +32 10 473765; fax +32 10 451593
†Permanent address: IMN, 2 rue de la Houssinière, B.P. 32229, F-44322 Nantes cedex 3, France
In this paper, we used a method allowing the excitation of the cantilever vibration that avoids both the use of a transducer and cantilever modifications.\textsuperscript{10,21,22} An oscillating external electric field is applied between the sample holder and the microscope head containing the cantilever holder 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. This method was used to measure the mechanical properties of polymer nanotubes and metallic nanowires. Indeed, materials with reduced dimensions and dimensionality (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. For instance, the mechanical behavior of materials at the nanoscale is often different from that at macroscopic scale. Though continuum mechanics applies when sizes are above the ten-nanometer range, surface effects may control the deformation properties. For structures with micrometer sizes, the mechanical properties are controlled by the elastic strain energy. At nanometer length scales, due to the increasing surface-to-volume ratio, surface effects become predominant and can significantly modify the macroscopic properties. Although some authors recognized that surface effects could play a major role in the measured properties,\textsuperscript{23,24,25} few experimental results exist concerning the influence of the reduced size on the mechanical properties. Some authors have already proposed to include surface contribution through a gradient elasticity approach.\textsuperscript{26} Cammarata clearly distinguished the surface tension and surface energy concepts, which are often misunderstood, and described the effect of surface tension on the mechanical properties of thin films.\textsuperscript{27} From experimental results obtained on organic and inorganic nanomaterials, the present paper analyses the size effects on the mechanical properties.

The elastic modulus of metallic nanowires and polymer nanotubes with diameter ranging between 30 and 250 nm was thus measured using resonant-contact AFM. It is shown that this method enables the full characterization of these nanomechanical systems and the quantitative determination of their tensile elastic modulus. For the smaller diameters, the measured elastic modulus significantly differs from that of the bulk materials. Calculation of an apparent elastic modulus taking into account the surface effect shows that the observed increase of the elastic modulus with decreasing diameter is essentially due to surface tension effects. This model allows the calculation of the intrinsic elastic modulus and the surface tension of the probed material from the measured apparent modulus.

\section*{2. THEORETICAL}

The equation of motion for the flexural vibrations of a cantilever is a differential equation of the fourth order:\textsuperscript{22,29}

\[
\frac{\partial^2}{\partial t^2} \left( EI(x) \frac{\partial^2 Z(x,t)}{\partial x^2} \right) + \rho A(x) \frac{\partial^2 Z(x,t)}{\partial t^2} = 0
\]  

(1)

where \( x \) is the coordinate in the longitudinal direction of the cantilever, \( Z(x,t) \) is the vertical deflection, \( E \) and \( \rho \) are respectively the Young’s modulus and the specific mass of the cantilever material, \( A(x) \) is the cantilever cross-section area and \( I(x) \) is the cross-section momentum of inertia.

In the present study, V-shaped cantilever were used. In this case, the stiffness and mass distribution of the system are non-uniform along the \( x \) and \( y \) coordinates. It is therefore impossible to analytically solve the equation of motion of the cantilever. An alternative approach, viz. a variational method, can be used to obtain an approximation of the lower resonance frequencies (and hence the fundamental one) of the system without having to solve the differential equation of motion.\textsuperscript{22,29,30} The Rayleigh-Ritz method consists in choosing a set of so-called “admissible” functions \( \Psi_i(x) \) and expressing the spatial component of the deflection, \( z(x) \), as a linear combination of these functions\textsuperscript{29}

\[
z(x) = \sum_i c_i \Psi_i(x)
\]  

(2)

The coefficients \( c_i \) become the variables of the problem. This expression of the deflection must satisfy the boundary conditions of the problem. In the Rayleigh-Ritz approximation, it must only satisfies the geometrical, or essential, boundary conditions. In the case of a cantilever with clamped-free ends, these conditions impose that the deflection and its first derivative are zeroed at the clamped end \( (x = 0) \).

Assuming an harmonic expression of the vertical deflection, \( Z(x,t) \), the maximum kinetic energy, also called the “reference kinetic energy”, is given by
The maximum potential energy of a free vibrating cantilever is given by the following expression

\[ U_{\text{max}} = \frac{1}{2} \int_0^L E \left\{ I(x) \left( \frac{d^2 z(x)}{dx^2} \right)^2 \right\} dx \]  

(4)

For a cantilever with the tip contacting a surface modeled by a normal spring of stiffness \( k_N \) and a lateral spring of stiffness \( k_L \) (inset Fig. 1) the maximum potential energy is given by

\[ U_{\text{max}} = \frac{1}{2} \int_0^L E \left\{ I(x) \left( \frac{d^2 z(x)}{dx^2} \right)^2 + \frac{1}{2} k_N z(L_p)^2 + \frac{1}{2} k_L h^2 z'(L_p)^2 \right\} dx \]  

(5)

where \( L_p \) is the coordinate of the tip position and \( h \) is the tip height.

In the Rayleigh-Ritz procedure, modal analysis of the system results from a variational principle applied to the Rayleigh quotient between the above \( U_{\text{max}} \) and \( T^* \) energy expressions and results in the homogeneous Galerkin equations\(^{29,30}\)

\[ (K - M \omega^2) \psi = 0 \]  

(6)

where \( \psi \) is an eigenvector of coefficients \( c_i \) (see (2)) and where the stiffness \( (K) \) and mass \( (M) \) matrices result from the expressions of \( U_{\text{max}} \) and \( T^* \) respectively after introducing (2):

\[ \frac{\partial U_{\text{max}}}{\partial c_i} = \sum_j K_{ij} c_j \]  

(7)

\[ \frac{\partial T^*}{\partial c_i} = \sum_j M_{ij} c_j \]  

(8)

The approximate eigenfrequencies (Rayleigh-Ritz is an approximation method) \( \omega_j \) then result from

\[ \det(K_{ij} - \omega_j^2 M_{ij}) = 0 \]  

(9)

The number of calculated modes is equal to the size of \( M \) and \( K \) matrices, i.e. the number of functions appearing in (2).

In the present study, the following expression was used for the deflection expression

\[ T^*_{\text{max}} = \frac{1}{2} \rho \int_0^L A(x) z(x)^2 dx \]  

(3)

Figure 1: Variation of the resonance frequencies normalized to the free resonance frequencies of the two first flexural modes of a cantilever with the tip contacting two springs (see inset) as a function of \( k_N/k_c \) normalized to \( k_c \). The curve for the 2nd mode is vertically shifted for clarity.

<table>
<thead>
<tr>
<th></th>
<th>M1</th>
<th>M2</th>
<th>M3</th>
<th>M4</th>
</tr>
</thead>
<tbody>
<tr>
<td>( L ) (µm)</td>
<td>81.7</td>
<td>79.5</td>
<td>181.5</td>
<td>137.3</td>
</tr>
<tr>
<td>( W ) (µm)</td>
<td>18.0</td>
<td>17</td>
<td>17.0</td>
<td>17.4</td>
</tr>
<tr>
<td>( t ) (µm)</td>
<td>0.42</td>
<td>0.42</td>
<td>0.45</td>
<td>0.45</td>
</tr>
<tr>
<td>( \nu_{\text{exp}}^{(1)} ) (kHz)</td>
<td>86.0</td>
<td>87.0</td>
<td>15.6</td>
<td>25.6</td>
</tr>
<tr>
<td>( \nu_{\text{calc}}^{(1)} ) (kHz)</td>
<td>87.5</td>
<td>89.4</td>
<td>16.1</td>
<td>26.1</td>
</tr>
<tr>
<td>( \nu_{\text{exp}}^{(2)} ) (kHz)</td>
<td>99.8</td>
<td>155.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \nu_{\text{calc}}^{(2)} ) (kHz)</td>
<td>107.0</td>
<td>164.1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table I: Comparison between the experimental and the calculated resonance frequencies of the two first flexural modes of Si₃N₄ V-shaped cantilevers. \( L \) is the total length of the cantilevers, \( W \) the width of their arms and \( t \) their thickness.
\[ z(x) = ax^2 + bx^3 + cx^4 + dx^5 \] (10)

The validity of the model was tested by measuring the free resonance frequencies of a series of \( \text{Si}_3\text{N}_4 \) cantilevers. For these simulations, the following values were used for the silicon nitride Young's modulus and specific mass: \( E = 150 \text{ GPa} \) and \( \rho = 3100 \text{ kg/m}^3 \).\textsuperscript{30,31} The results presented in table I demonstrate that the Rayleigh-Ritz approach enables to predict the resonance frequencies of V-shaped cantilevers. The small discrepancies can be accounted for to the presence of the gold reflective coating of the cantilever and the uncertainties on the actual values of \( E \) and \( \rho \).

From figure 1, it can be seen that resonance frequencies vary significantly in a region where the spring stiffness is comparable to that of the cantilever. For low and high relative stiffness, no variations are observed. The second flexural mode presents a relative variation for higher spring stiffness than the first one. For both modes, two slopes can be observed in the region where the frequencies vary. The first one corresponds to the domain where the cantilever dynamics is mainly influenced by the normal spring (or contact stiffness). The second one, at larger relative stiffness, is attributed to the domain where it is sensitive to the lateral spring (or contact stiffness).

3. EXPERIMENTAL

3.1. Sample preparation

Polymer nanotubes and metallic nanowires were synthesized using a recently developed template-based method that uses the pores of polycarbonate track-etched membranes as “nanoreactors”.\textsuperscript{32} Nanotubes of a conductive polymers (polypyrrole, PPy) were electrochemically synthesized using the procedure extensively described elsewhere.\textsuperscript{32} Silver and lead nanowires were electrochemically synthesized from solutions containing respectively \( \text{AgNO}_3 \) and \( \text{Pb(BF}_4\text{)}_2 \). The template membranes had a pore density of \( 10^6 \text{ cm}^2 \). 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 dissolved by immersion in a dichloromethane solution containing dodecyl sulfate as surfactant\textsuperscript{33} and the suspension was placed in an ultrasonic bath during one hour to separate the nanostructures from the gold film previously evaporated on the backside of the membrane. The suspensions were then filtered through poly(ethylene terephthalate) (PET) membranes with pore diameters ranging between 0.8 and 3 \( \mu \)m. In order to remove any contaminant from the nanomaterial surface the samples were thoroughly rinsed with dichloromethane. To minimize shear deformations in the experiments, the ratio between the suspended length of the tube or wire, \( L \), and its outer diameter, \( D \) or \( D_{out} \), should be higher than 16.\textsuperscript{34} To achieve this, each series of nanowires or nanotubes synthesized in a template membrane with a specific pore diameter was dispersed on a corresponding PET membrane with a pore diameter satisfying this criterion.

3.2. Atomic force microscopy measurements

All the AFM experiments were performed with an Autoprobe\textsuperscript{®} CP microscope (Thermomicroscopes, Sunnyvale, CA) operated in air with a 100 \( \mu \)m scanner equipped with ScanMaster\textsuperscript{®} detectors correcting for drift, non-linearity and hysteresis effects. The cantilevers were standard \( \text{Si}_3\text{N}_4 \) Microlevers\textsuperscript{36} 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.\textsuperscript{35} Values ranging between 0.3 and 0.5 \( \text{N.m}^{-1} \) 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. The actual physical properties of the cantilever material (i.e. its elastic modulus and its specific mass) were deduced from the experimental free 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 resonance peak symmetrical, resonance spectra were recorded without polarization offset and with a small excitation amplitude.\textsuperscript{21,36} 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). Large-scale images (typically up to 80 x 80 \( \mu \text{m}^2 \)) were first acquired in order to select nanomaterials suspended over pores that could be used to measure their mechanical properties (Fig. 2(a)). Once a suspended nanostructure was located, an image of it at lower scale (down to 1 x 1 \( \mu \text{m}^2 \)) was then realized to precisely determine its dimensions, i.e. its suspended length, \( L \), and its outer diameter, \( D \) or \( D_{out} \) (Fig. 2(b)). The outer diameter is determined by the measurement.
of its height with respect to the supporting membrane to avoid tip artifacts. The inner diameter, $D_{\text{in}}$, of the PPy nanotubes was estimated using a previously established calibration curve relating the outer and inner diameters.

Figure 2: (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 70 nm thick PPy nanotube crossing a pore.

4. RESULTS AND DISCUSSION

4.1. Resonant Contact-AFM
After selection of a nanostructure, the AFM tip was located at the midpoint along its suspended length and the vibration spectrum of the cantilever in contact with the nanostructure was measured. As expected, the resonance frequencies measured for the cantilever in contact with the nanostructure were higher than the corresponding free resonance frequencies. The frequency shifts reflect the dynamical behavior of the structure probed by the tip. The compliance of the cantilever-nanobeam system may, a priori, be related to the deformation of the nanostructure itself and/or to the contact compliance. Moreover, the inertial contribution of the nanobeam may influence the system behavior. The mechanical behavior of the system was thus thoroughly analyzed from the experimental results.

Figure 3: Relationship between the resonance frequencies of the first two flexural vibration modes of a triangular-shaped cantilever in contact with PPy nanotubes (a) and metallic nanowires (b). The symbols correspond to the experimental points and the solid lines to the calculated curves using the Rayleigh-Ritz.

On the spectrum of a cantilever in contact with a nanostructure, several peaks are observed. Two of them correspond to the two first flexural vibration mode ($F_1$, $F_2$). In order to properly describe the mechanical behavior of the cantilever-nanobeam system, the relation between the frequencies corresponding to these first two flexural vibration modes was analyzed and is presented in figure 3. In these graphs, the experimental points correspond to the resonance frequencies...
measured on several nanotubes or nanowires with different diameters and suspended lengths. The solid curve is the calculated relation between the first two flexural frequencies of the triangular Si$_3$N$_4$ cantilever in contact with two springs at the tip position (Fig. 1). These two springs represent the vertical and lateral stiffness associated with the deformation of the nanostructure in both directions. Indeed, the tilt of the cantilever may cause deformations, which are not normal to the sample surface.\textsuperscript{36,37} The amplitude of the lateral deformation of the nanotube depends on its orientation relative to the cantilever axis. Both springs are assumed to have the same stiffness since the nanostructures are expected to have isotropic properties perpendicular to their axis.

The curves presented in figure 3 do not contain any adjustable parameter but are only governed by the geometrical dimensions of the cantilever. The good agreement observed with the experimental data confirms that the nanotubes or nanowires actually behave as springs. Their inertia can thus be neglected. Thus, the suspended nanostructures can be modeled as simple springs in these experiments.

In order to deduce the elastic modulus of the nanostructures from the measured stiffness, it is however necessary to describe the boundary conditions of the suspended beams (clamping conditions). In a previously study of PPy nanotubes, the clamped conditions were assumed.\textsuperscript{7} This assumption was based on the fact that no nanotube was ever displaced during the AFM imaging and that the nanotube adhesion on the membrane seemed to be sufficiently high to prevent any lift-off during the bending test.

A further confirmation of this description can be obtained by analyzing the resonance frequency of the cantilever in contact with a nanostructure at different relative locations ($x/L$) of the tip along the suspended length ($L$) of a given tube or wire. In figure 4, experimental frequencies are plotted together with the expected distribution for the cantilever with the tip contacting a beam with pinned and clamped ends on the substrate.\textsuperscript{38} 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 pinned (1) and clamped ends (2) on the substrate.

\[
\frac{1}{k_{\text{tube}}} = \frac{L^3}{3EI} \left( \frac{x}{L} \right)^2 \left( \frac{1}{L} - \frac{x}{L} \right)^2 + \frac{2}{k_s} \left( \frac{x}{L} \right)^2 - \frac{x}{L} + \frac{1}{k_s} \quad (11)
\]

\[
\frac{1}{k_{\text{tube}}} = \frac{L^3}{3EI} \left( \frac{x}{L} \right)^3 \left( \frac{1}{L} - \frac{x}{L} \right)^3 + \frac{2}{k_s} \left( \frac{x}{L} \right)^2 - \frac{x}{L} + \frac{1}{k_s} \quad (12)
\]

![Figure 4: Variation of the resonance frequency of a cantilever on a PPy nanotube along the tube length. ▲: experimental data; solid line: expected variation for a clamped-end tube; dotted line: expected variation for a pinned-end tube.](image)

In these relations, $E$ is the elastic modulus of the beam material and $I$ is its inertia momentum. A finite stiffness, $k_s$, is assumed for the beam-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 beam is chosen in order to fit the measured frequency at the middle of the suspended length. Clearly, the experimental distribution of frequencies presented in figure 4 does not follow that expected for a pinned-end 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-end beam resting on a compliant substrate. Close to the center of the suspended length, the calculations however show that the compliance of the system is mainly dominated by that of the beam. The effect of the low compliance of the substrate can thus be neglected.

The AFM tip was then located at the midpoint along the suspended length and the resonance spectrum of the cantilever in contact with the nanowire or nanotube was measured. Before each measurement, the normal force applied by the cantilever was canceled by zeroing its vertical deflection so that only adhesion and electrostatic forces were applied. The measurements were performed on series of Ag and Pb nanowires and PPy nanotubes with diameter ranging from 30 to 250 nm. The elastic modulus was deduced from the measured nanotube stiffness using relation (2) with $x/L = 0.5$. In figure 5, the measured values of the elastic modulus of Ag and Pb nanowires are reported as a function of the diameter. For large diameters (> 70 nm for Ag, > 100 nm for Pb), the measured values are almost independent on the diameter and are close to the values reported in the literature for the bulk materials, i.e. 76 GPa for Ag and 16 GPa for Pb. In figure 6, the values of the elastic modulus simultaneously determined by three points bending test and resonance frequencies measurement on PPy nanotubes 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. Moreover, the obtained values of the elastic modulus measured for nanotubes having an outer diameter higher than 100 nm are comparable to the values measured on polypyrrole films.

These results confirm the ability of resonant C-AFM with electrostatic modulation to precisely measure the mechanical properties of nanomaterials such as nanotubes or nanowires. In comparison to force-curve measurements, this method presents the advantage that the conversion of the resonance frequency into material stiffness is straightforward once the cantilever dynamics has been fully characterized 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 to measure the elastic modulus but also to fully characterize the nanomechanical system, i.e. the mechanical model and the nanostructure boundary conditions.

4.2. Reduced-size effect

In the case of both the metallic nanowires and the PPy nanotubes, it can be observed that the measured elastic modulus increases when the diameter decreases (Figs 5&6). For the metallic nanowires with the smallest diameters, the measured modulus is approximately twice the Young’s modulus of bulk materials (around 140 GPa for Ag and 30 GPa for Pb). For the PPy nanotubes, the effect is even more pronounced. The measured modulus increases by more than one order of magnitude to reach a value of about 120 GPa for $D_{out}$ around 35 nm.

As deformation of the beam induces an increase of its area in this configuration, surface tension effects may account for the observed results. Therefore, a calculation of the stiffness of the suspended nanotubes due to the elastic modulus and the surface tension is proposed. As the magnitude of the nanostructure deflection was always small compared to its diameter, the theory of small deflections of beams is applied to evaluate the contribution of surface effects on the
nanostructure stiffness.\textsuperscript{38} As demonstrated here above, the boundary conditions of the suspended nanowires and nanotubes correspond to those of clamped-ends beams. Assuming a force $F$ applied at the beam midpoint and inducing a deflection $\delta$, an expression for the total energy, $U$, of the bent beam is:

$$U = -F\delta + \frac{1}{2} k_s \delta^2 + \gamma \Phi \Delta L (1 - \nu)$$

(13)

where $\Phi$ is the contour length of the beam section, $\Delta L$ is its length variation, $\nu$ is the Poisson’s ratio, $\gamma$ is the surface tension of the material and $k_s = 192 EI / L^3$ is the beam elastic stiffness, with $E$ the material Young’s modulus, $L$ the beam suspended length and $I$ the inertia momentum of the section. In relation (13), the first term is the work of the applied force, the second one represents the elastic deformation energy of the bent beam and the third one corresponds to the deformation energy of the surface resulting from the beam extension. The bending of a beam with both ends clamped, so that no longitudinal displacement at the ends is possible, results in an extension of its length, and hence in an increase of the surface. The energy term dealing with the surface increase takes into account the compressibility, $\nu$, of the material. As a first approximation, one may consider that the usual deflection curve of a clamped beam is not affected by the surface tension contribution. For clamped boundary conditions, the beam extension, $\Delta L$, can be easily calculated and introduced in relation (13) to give

$$U = -F\delta + \frac{1}{2} (k_s + k_n) \delta^2$$

where $k_n = \frac{124 \gamma \Phi}{15 L^2 (1 - \nu)}$ (14)

From the equilibrium condition, an apparent stiffness of the beam, $k_{app}$, can be defined:

$$k_{app} = k_s + k_n$$

(15)

If the apparent stiffness is interpreted as only due to elastic properties of the material, an apparent elastic modulus can be deduced from the measured stiffness as it was assumed in figures 5&6 to interpret the experimental data.

$$E_{app} = \frac{L^3}{192I} k_{app} = E + \frac{1}{40} \gamma (1 - \nu) \Phi \frac{I^2}{L}$$

(16)

For nanowires, $\Phi = \pi D$ and $I = \pi D^4/64$. Expressions (15) and (16) become

$$k_{app} = 3\pi \frac{D^4}{L^3} E + \frac{24 \pi}{5} \gamma (1 - \nu) \frac{D}{L}$$

(17)

$$E_{app} = E + \frac{8}{5} \gamma (1 - \nu) \frac{L^2}{D^3}$$

(18)

In the case of nanotubes, the apparent stiffness and tensile modulus are given by the following expressions

$$k_{app} = 3\pi E \frac{D_{out}^4 - D_{in}^4}{L^3} + \frac{24 \pi}{5} \gamma (1 - \nu) \frac{D_{out} + D_{in}}{L}$$

(19)

$$E_{app} = E + \frac{8}{5} \gamma (1 - \nu) \frac{L^2}{D_{out}^4} \frac{D_{out} + D_{in}}{D_{out}^4 - D_{in}^4}$$

(20)

From equations (17), reporting $k_{app}L/D$ versus the geometrical parameter $D^3/L^2$ should give a linear relation. A non-zero intercept with the ordinate axis is expected to be due to the surface tension contribution. This is shown in figure 7 for the Ag nanowires. Linear regression allows the determination of the elastic modulus and of the surface tension. For Ag, the so-obtained elastic modulus is equal to $67.5 \pm 2.1 \text{ GPa}$ comparable to the value of the modulus of silver (76 GPa).\textsuperscript{39} The same analysis of the results on the Pb nanowires leads to a value of $16.9 \pm 0.8 \text{ GPa}$ comparable to the modulus of Pb (16 GPa).\textsuperscript{40} The regressions give also access to the surface tension of the probed materials knowing their Poisson’s ratio. The value of the surface tension for the Ag nanowires was of $3.09 \pm 0.33 \text{ J.m}^{-2}$, determined with a Poisson’s ratio of 0.37.\textsuperscript{41} For the Pb nanowires, a value of $0.98 \pm 0.21 \text{ J.m}^{-2}$ was obtained using a Poisson’s ratio of 0.42.\textsuperscript{42}

Using relation (20), the fit of the experimental data gives from the intercept with the ordinate axis a value of $0.6 \pm 0.3 \text{ GPa}$ for the elastic modulus of PPy (Fig. 8). With a typical value of the Poisson’s ratio for polymers of 0.4,\textsuperscript{43} a value of $0.33 \pm 0.01 \text{ J.m}^{-2}$ is determined for the surface tension from the slope of the regression line. The obtained value for the modulus is comparable to that reported in the literature for PPy films though somehow lower (1.2 and 3.2 GPa for PPy films).\textsuperscript{41,42}
In contrast to liquids, surface energy and surface tension refer to two different concepts in the case of solids, which are often misunderstood. Surface energy is defined as the reversible work per unit area needed to create a new surface, while surface tension or surface stress is the reversible work per unit area needed to elastically stretch a pre-existing surface. In our AFM experiments, no new surface is created but the surface of the nanowires or the nanotubes is deformed. It is thus the surface tension that is solicited.

Figure 7: Product of the apparent stiffness and $L/D$ of Ag nanowires as a function of $D^2/L^2$. The solid line represents the fit of the experimental data based on relation (17)

Figure 8: Apparent modulus of PPy nanotubes as a function of the geometrical factor appearing in relation (20). The solid line is the fit of the experimental data.

It should be noted that there are few experimental measurements of surface tension and most values reported in the literature arise from theoretical calculations. These calculations predict that surface tension values are of the same order of magnitude and slightly higher than the surface energy values. Wassermann et al. have experimentally determined the surface tension value for silver from the measurement of the lattice contraction in small Ag spheres as a function of their radius by electron diffraction. The obtained value for the surface tension was equal to $1.41 \pm 0.30 \text{ J.m}^{-2}$ at 55°C. This value is similar to the present result ($3.09 \pm 0.33 \text{ J.m}^{-2}$). To our knowledge, no data are available for the surface tension of Pb and PPy. It can however be noticed that the obtained surface tension values ($0.98 \pm 0.21 \text{ J.m}^{-2}$ and $0.33 \pm 0.01 \text{ J.m}^{-2}$ respectively for Pb and PPy) are comparable to published values of the surface energy (between 0.5 and 0.6 J.m$^{-2}$ for Pb, and 0.145 J.m$^{-2}$ for PPyCl films).

The ratio between the apparent elastic modulus of the smallest nanomaterial and the corresponding macroscopic modulus of the material is much larger for the PPy nanotubes than for the metallic nanowires. In both cases, surface effects explain the increase of the apparent elastic modulus. The larger effect in the case of PPy nanotubes is essentially due to the intrinsic lower elastic modulus of the material rather than to the additional inner surface existing in nanotubes. Though defects concentration effects cannot be ruled out to explain the apparent modulus increase observed in our experimental data, we suggest that surface tension is mainly responsible for the observed increase. Moreover, we show that AFM measurements of the mechanical properties of nanostructures such as suspended nanobeams enables the evaluation of solid material surface tension.

5. CONCLUSIONS

In conclusion, a method based on the measurement of resonance frequencies of cantilevers in contact with nanotubes or nanowires 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 the complete description of the physical configuration and the mechanical characteristics of the system “cantilever in contact with a nanobeam”. The frequency behavior of the nanomechanical system can be accurately modeled by a cantilever with the tip in contact with two springs using a Rayleigh-Ritz approach to describe the dynamics of the vibrating cantilever. The nanostructure stiffness can thus be easily determined from the resonance frequency measurement using this simple model once the geometrical dimensions of the cantilever have been determined and the Young’s modulus and specific mass of its material are known. The method also enables the determination of the
boundary conditions of the suspended nanostructure. 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 and metallic nanowires with their outer diameter ranging from 30 to 250 nm. The measured values and behaviors are in a good agreement with those obtained in a previous study realized on the same suspended polymer nanotubes and the values measured for the larger metallic nanowires correspond to those of the bulk materials. These results confirm the ability of resonant C-AFM with electrostatic modulation to precisely characterize the elastic properties of nanotubes or nanowires 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 analysis on nanostructures.

For the smaller diameters, the measured elastic modulus significantly differs from that of the bulk materials. Calculation of an apparent elastic modulus taking into account the surface effect shows that the observed increase of the elastic modulus with decreasing diameter is essentially due to surface tension effects. This model allows the calculation of the intrinsic elastic modulus and the surface tension of the probed material from the measured apparent modulus. For Ag nanowires a fairly good agreement is obtained with the values published in the literature. In summary, we showed that, in the case of metallic nanowires and polymer nanotubes, the increase of the surface to volume ratio with decreasing size strongly influences the measured modulus and that AFM measurements of it enables the evaluation of solid surface tension.

REFERENCES

21. C. Frétigny, to be published.