Mass and stiffness calibration of nanowires using thermally driven vibration

2011 Nanotechnology 22 295504

(http://iopscience.iop.org/0957-4484/22/29/295504)

Nanotechnology **22** (2011) 295504 (5pp) doi:10.1088/0957-4484/22/29/295504

Mass and stiffness calibration of nanowires using thermally driven vibration

D R Kiracofe[1], **M M Yazdanpanah**[2] **and A Raman**[1]

[1] School of Mechanical Engineering and Birck Nanotechnology Center, Purdue University, West Lafayette, IN 47907, USA
[2] NaugaNeedles, LLC, Louisville, KY 40299, USA

E-mail: raman@purdue.edu

Received 28 February 2011, in final form 31 May 2011
Published 17 June 2011
Online at stacks.iop.org/Nano/22/295504

Abstract
Cantilevered or suspended nanowires show promise for force or mass sensing applications due to their small mass, high force sensitivity and high frequency bandwidth. To use these as quantitative sensors, their bending stiffness or mass must be calibrated experimentally, often using thermally driven vibration. However, this can be difficult because nanowires are slightly asymmetric, which results in two spatially orthogonal bending eigenmodes with closely spaced frequencies. This asymmetry presents problems for traditional stiffness calibration methods, which equate the measured thermal vibration spectrum near a resonance to that of a single eigenmode. Moreover, the principal axes may be arbitrarily rotated with respect to the measurement direction. In this work, the authors propose a method for calibrating the bending stiffness and mass of such nanowires' eigenmodes using a single measurement taken at an arbitrary orientation with respect to the principal axes.

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

1. Introduction and motivation

Nanowires are gaining increased interest for highly sensitive mass and force detection due to their small suspended mass, low stiffness and high frequency bandwidth [1–3]. However, in order to use these structures as quantitative probes, their stiffness and mass must be known accurately. The practice of experimental stiffness calibration of microscale cantilever beams is well developed due to its importance in atomic force microscopy and mass sensing. One popular method is the thermal calibration method [4–6] in which the mean squared thermally driven vibration (area under a resonance peak) is used to calculate the equivalent stiffness of the corresponding eigenmode by use of the equipartition theorem [7]. Given the high cross-sectional aspect ratio of such beams (width/thickness $>$ 10), the in-plane lateral bending modes are widely separated in frequency from the out-of-plane bending modes and their orientations are well defined. This allows for the easy alignment of the measurement direction with the orientation of a specific eigenmode. Moreover, the measured frequency spectrum consists of well-spaced peaks to which the thermal calibration method can be easily applied.

Recently it has been shown [1–3, 8] that the thermal vibrations of nanowires can also be detected using optical means, opening up the possibility of stiffness calibration using optical detection. However, there is a difficulty in applying this method to nanowires, such as those shown in figure 1(a), due to the fact that their cross-sections are never perfectly symmetric, always deviating slightly from a perfect circle or regular polygon. In this case there are two non-degenerate, spatially orthogonal bending eigenmodes at slightly different frequencies. For a perfectly circular cross-section, the thermal vibration in any direction is the same, so the orientation of the nanowire with respect to the measurement direction (figure 1(b)) does not matter. However, for a slight deviation from a circular or regular polygonal cross-section, the thermal vibration is greater along one axis than along the other [9] and these principal axes may be rotated at an arbitrary angle θ from the measurement direction. In this case, the measured power spectral density will depend on the angle between the

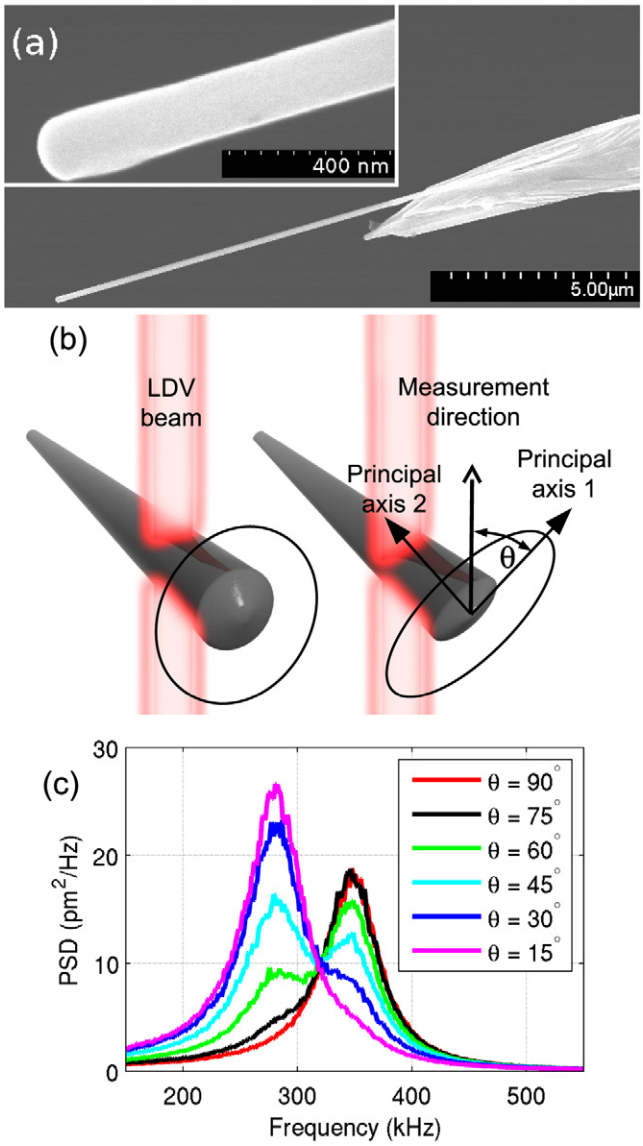

Figure 1. (a) SEM image of a typical Ag_2Ga nanowire grown onto the end of an etched tungsten wire [10]; inset: zoom-in on the free end. (b) For a perfectly circular wire, the thermal vibration will have the same amplitude in any direction. But for any asymmetry, however small, the thermal vibration will be larger along one principal axis than along the other. Moreover, the measurement direction may be at some angle θ with respect to the principal axes. (c) Experimental power spectral density (PSD) measurements using a laser Doppler vibrometer of a typical nanowire at various rotation angles. At $\theta = 90°$, the measurement direction is exactly aligned with the principal axis of mode 2 and the observed PSD is entirely due to the thermal motion of eigenmode 2. But at any other angle, the measurement direction is not aligned with either principal axis and the observed PSD is a linear combination of the thermal motions of the two eigenmodes. This shows that any thermal calibration technique for nanowires must be able to account for both split resonance peaks and also the angle between the direction of measurement and the principal axes of the nanowire.

measurement direction and the principal axes of the nanowire. Figure 1(c) shows several such measurements for a typical cantilevered nanowire probe (described later in the article) as it is rotated through various angles.

Clearly, application of standard thermal calibration methods (such as in [2]) will incur significant error in this situation. In this paper, we propose a method that allows the stiffness and mass of the eigenmodes to be predicted using only one vibration measurement regardless of the orientation of the measurement direction with respect to the principal axes. First we develop the necessary theory, and then we demonstrate its experimental validation.

2. Theory

First assume that the nanowires have an approximately elliptical cross-section, which is uniform along the length. In that case, the first bending eigenmode splits into two, with one eigenmode vibrating along the semi-major axis and the other along the semi-minor axis. The two eigenmodes will have identical modal masses (the mass per unit length does not depend on the direction of vibration), and nearly identical modal damping ratios, but different modal stiffnesses due to the differing area moment ($I = \frac{\pi}{4} b_1 b_2^3$, where b_1 and b_2 are the widths of the semi-major and semi-minor axes). Because of the differing modal stiffnesses, the equipartition theorem dictates that the two modes will have differing thermally driven power spectral densities and the mean squared deflection (MSD) $\langle d_j^2 \rangle$ is expected to scale with the square of the (undamped) natural frequency ω_j:

$$\frac{\langle d_2^2 \rangle}{\langle d_1^2 \rangle} = \frac{\omega_1^2}{\omega_2^2} \tag{1}$$

where d_j is the deflection in the jth eigenmode and the bracket $\langle\,\rangle$ denotes the time average, as illustrated in figure 2(a). But, because the measurement axis and principal axes may not be aligned, the observed mean squared deflection does not equal the actual mean squared deflection. However, by comparing the observed and expected mean squared deflection, the angle θ between the measurement direction and the principal axis can be inferred. Specifically, the formula for observed MSD in terms of actual MSD is

$$\langle d_{1,\mathrm{obs}}^2 \rangle = \langle d_1^2 \rangle \sin^2\theta \qquad \langle d_{2,\mathrm{obs}}^2 \rangle = \langle d_2^2 \rangle \cos^2\theta. \tag{2}$$

Equations (1) and (2) can be solved simultaneously to yield the angle of the measurement

$$\theta = \tan^{-1} \sqrt{\frac{\langle d_{1,\mathrm{obs}}^2 \rangle}{\langle d_{2,\mathrm{obs}}^2 \rangle} \frac{\omega_1^2}{\omega_2^2}}. \tag{3}$$

Finally, the stiffness k is

$$k_1 = \frac{k_\mathrm{B} T \sin^2\theta}{\langle d_{1,\mathrm{obs}}^2 \rangle}, \qquad k_2 = \frac{k_\mathrm{B} T \cos^2\theta}{\langle d_{2,\mathrm{obs}}^2 \rangle}, \tag{4}$$

where k_B is Boltzmann's constant and T is the temperature. The equivalent modal mass m is

$$m = k_1/\omega_1^2 = k_2/\omega_2^2. \tag{5}$$

In the case where the frequency splitting is large and the resonance peaks do not overlap, the quantities ω_j and $\langle d_{j,\mathrm{obs}}^2 \rangle$ ($j = 1, 2$) can be calculated directly from the peaks in the

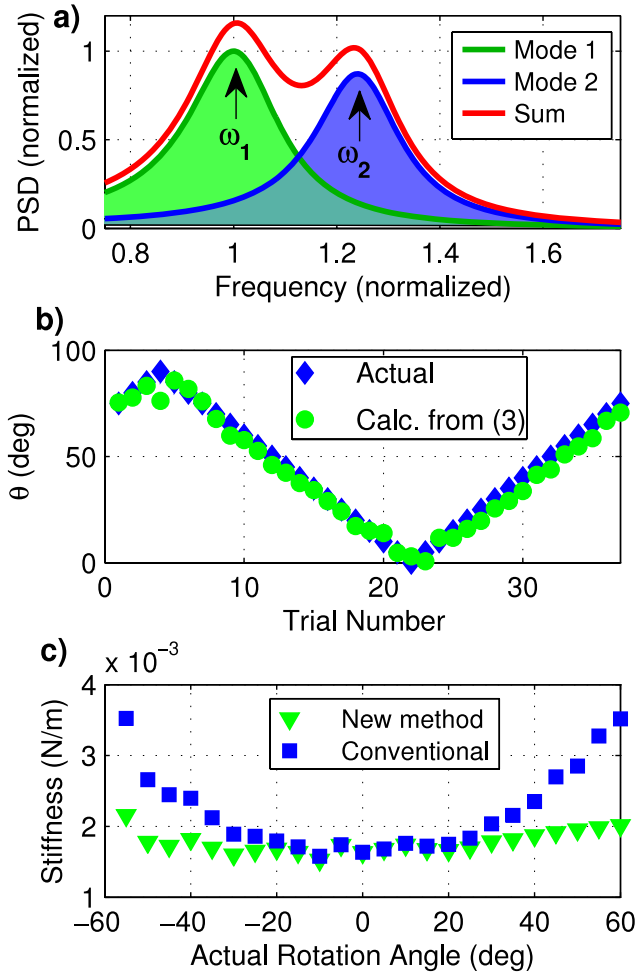

Figure 2. (a) The basis of the proposed method: the ratio of mean squared deflection (shaded area under the curve) is related to the ratio of natural frequencies by equation (1). By comparing the experimentally measured mean squared deflections (MSD) under each resonance (figure 1(c)) to the expected MSD, the rotation angle θ between the measurement axis and principal axis can be determined using equation (3). (b) Example experimental results: a typical nanowire is rotated to different angles. The actual rotation angle is plotted against the angle calculated from (3). The agreement between the actual angle and the calculated angle is good, indicating that in experiments rotation angles could be estimated within about 4°. (c) Equation (4) is used to calculate a corrected stiffness k_1 for the data of part (b). The data are plotted versus the actual rotation angle. The uncorrected values (i.e. conventional thermal calibration) are shown for reference. The corrected method shows nearly the same stiffness at each rotation angle.

observed power spectrum. In the case where the resonance peaks overlap to some degree (as in figure 1(c)), one must resort to a curve fitting procedure to separate the two modes. Specifically, let H be the complex transfer function

$$H(\omega/\omega_j, Q_j) = \frac{1}{1 + \frac{\mathrm{i}}{Q_j}\frac{\omega}{\omega_j} - (\frac{\omega}{\omega_j})^2}, \qquad j = 1, 2 \quad (6)$$

(deflection per unit input force) of the two orthogonal modes where Q is the quality factor and $\mathrm{i} = \sqrt{-1}$, and let $\hat{H}$ be the transfer function normalized to unity mean squared deflection $\hat{H}^2(\omega/\omega_j, Q_j) = \frac{H^2(\omega/\omega_j, Q_j)}{\int_0^\infty H^2(\omega/\omega_j, Q_j)\,\mathrm{d}\omega}$ where $j = 1, 2$. Then we can fit the observed power spectral density to

$$S_{xx}(\omega) = S_0 + \langle d^2_{1,\mathrm{obs}}\rangle \hat{H}^2(\omega/\omega_1, Q_1) + \langle d^2_{2,\mathrm{obs}}\rangle \hat{H}^2(\omega/\omega_2, Q_2), \quad (7)$$

where the fitting parameters are $\omega_1, \omega_2, Q_1, Q_2, \langle d^2_{1,\mathrm{obs}}\rangle$, $\langle d^2_{2,\mathrm{obs}}\rangle$ and S_0 (background noise floor). Then, equation (3) can be used to determine the measurement angle, equations (2) can be used to find the actual MSD, and equation (4) is used to find k_j ($j = 1, 2$).

3. The experiment

To demonstrate this theory, a Ag_2Ga nanowire [10, 11] that is grown on the end of an etched tungsten wire (figure 1) was mounted on a rotating stage under a laser Doppler vibrometer (MSA-400, Polytec, Waldbronn Germany). Details of the experimental setup are given in [2]. Thermally driven power spectral density measurements were taken by rotating the nanowire with respect to the measurement direction every 5° (±0.5°) over 180° of rotation[3]. At each rotation angle, equations (2)–(4) were used to estimate the angle θ between the measurement and principal axes of the nanowire, the actual mean squared deflection, and the stiffness. The results are shown in figures 2(b) and (c). In figure 2(b), the calculated angle between the measurement direction and the principal axes is plotted for each of the 37 trials and compared to the actual angle. The average difference between actual and calculated angle is 3.8° and the maximum is 14°. In an actual experiment, the orientation between the principal axes and the measurement direction may be unknown, and there may not be an easy way to rotate the nanowire about its axis. This result shows that such an unknown orientation can be estimated within about 4°.

In figure 2(c), the stiffness calculated using equation (4) for the lower frequency mode is shown for angles ranging ±60° from the principal axis. The standard deviation is 7% of the mean value. That is, the calculated stiffness is nearly the same at every angle. The mean stiffness 1.7×10^{-3} N m^{-1} is close to the value estimated from geometric dimensions and material properties[4] (1.9 ± 0.1 N m^{-1}). In contrast, the conventional method of simply curve fitting a single peak reports values that are up to 100% higher than the geometric estimate (figure 2(c)).

As a further check, we have applied this method to twenty one nanowires, which were oriented at random with respect to the measurement direction. Eight of the nanowires showed only a single peak. The results for the remaining 13 are shown in figure 3. The calculated values of stiffness (figure 3(a)) and mass (figure 3(b)) were compared to the geometric method where the nanowire mass is calculated by assuming a cylindrical shape with dimensions taken from scanning

[3] The nanowire is elliptical and therefore there is a larger amount of reflected light when the measurement direction is along one axis than when it is along the other. However, the vibrometer measures a Doppler shift such that the measured velocity is independent of the amount of reflected light. Thus, this size difference has no effect on the measurement. The amount of reflected light only affects the signal-to-noise ratio.

[4] The density is 9462 kg m^{-3} from [12], slightly higher than the 8960 used by [2].

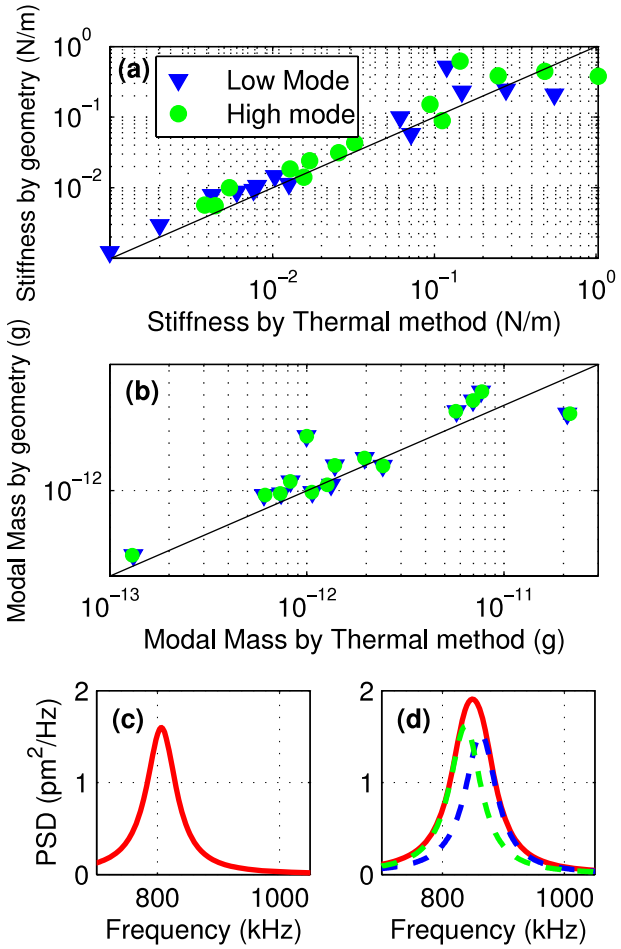

Figure 3. Summary of the proposed method applied to thermal data from 21 different nanowires. Eight nanowires had only a single peak so the splitting could not be determined. (a) Comparison of the new proposed method for stiffness versus the geometric method for the 13 nanowires that showed a split peak. The solid line indicates where the points would be if the two methods gave identical results. Most points are clustered near this line, indicating that the new method gives results reasonably close to those from the geometric method. (b) Comparison of the two methods for mass (both methods assume that the mass of the two modes is identical). ((c), (d)) When only a single resonance peak is observed, the method fails because the rotation angle cannot be determined. This can happen either when the measurement axis is exactly aligned with a principal axis, so only one peak is seen (c), or the splitting is so small that the two peaks cannot be resolved (d) (solid line—observed peak, dashed lines—underlying peaks). In either case, an error of up to 30% could be made in the stiffness.

electron microscope (SEM) images, and then $k_j = \omega_j^2 m$. The measurements compare reasonably well, demonstrating that the method works as intended.

For those measurements that show only a single peak, there are two possible cases. The measurement axis may be aligned perfectly with one principal axis, or the measurement axis is not aligned but the mode splitting is small relative to the resonance bandwidth. In either case, the rotation angle cannot be determined from a single measurement, as illustrated in figures 3(c) and (d). If a researcher mistakenly assumes that the observed single peak implies standard application of thermal stiffness calibration, he/she can incur a large error (up to 30%) due the possibility that two modes might be contributing to the observed power spectral density (as in figure 3(d))[5]. This can occur even if the researcher has perfect knowledge of the nanowire's symmetry/asymmetry. Interestingly, this implies that nanowires with larger mode splits will be easier to calibrate because the rotation angle can be more readily determined from a single measurement.

4. Conclusion

To summarize, we have observed that the traditional stiffness calibration methods for micromachined cantilevers can have errors of up to 100% when applied to nearly symmetric nanowires that have split eigenmodes in which the principal axes are not aligned with the measurement axis. A method has been proposed for correcting for this error, and has been demonstrated experimentally. This finding enables accurate, quantitative force and mass sensing using a variety of nearly symmetric nanowires.

Acknowledgments

We acknowledge helpful discussions with Professor R Reifenberger (Purdue University) and assistance with nanowire fabrication from Mr J Rivera and assistance with artwork from Mr H Vardanyan (NaugaNeedles, LLC), as well as financial support from the National Institutes of Health grant number 1R41GM088859-01 and the Kentucky Science and Technology Corporation grant number KSTC-184-512-10-072.

References

[1] Sanii B and Ashby P D 2010 High sensitivity deflection detection of nanowires *Phys. Rev. Lett.* **104** 147203
[2] Biedermann L B, Tung R C, Raman A, Reifenberger R G, Yazdanpanah M M and Cohn R W 2010 Characterization of silver–gallium nanowires for force and mass sensing applications *Nanotechnology* **21** 305701
[3] Gil-Santos E, Ramos D, Martínez J, Fernández-Regúlez M, García R, San Paulo Á, Calleja M and Tamayo J 2010 Nanomechanical mass sensing and stiffness spectrometry based on two-dimensional vibrations of resonant nanowires *Nat. Nanotechnol.*
[4] Hutter J L and Bechhoefer J 1993 Calibration of atomic-force microscope tips *Rev. Sci. Instrum.* **64** 1868–73
[5] Butt H J and Jaschke M 1995 Calculation of thermal noise in atomic force microscopy *Nanotechnology* **6** 1–7
[6] Lozano J R, Kiracofe D, Melcher J, Garcia R and Raman A 2010 Calibration of higher-eigenmode spring constants of atomic force microscope cantilevers *Nanotechnology* **21** 465502
[7] Landau L D and Lifshitz E M 1988 *Statistical Physics* (Oxford: Elsevier)
[8] Biedermann L B, Tung R C, Raman A and Reifenberger R G 2009 Flexural vibration spectra of carbon nanotubes measured using laser Doppler vibrometry *Nanotechnology* **20** 035702

[5] The maximum error occurs when measurement angle is rotated 45° to the principal axes. Each mode contributes $\frac{\sqrt{2}}{2}$ of its mean squared deflection (MSD) to the measured MSD. This yields a total MSD that is $\sqrt{2}$ times the value for a single mode. Thus the calculated stiffness is $\frac{1}{\sqrt{2}}$ times the correct value.

[9] Nelis M R, Yu L, Raman A, Mohammadi S and Rhoads J F 2011 The effects of asymmetry on the dynamics of nanowires *Proc. 2011 NSF Engineering Research and Innovation Conf. (Atlanta, GA)*

[10] Yazdanpanah M M, Harfenist S A, Safir A and Cohn R W 2005 Selective self-assembly at room temperature of individual freestanding AgGa alloy nanoneedles *J. Appl. Phys.* **98** 073510

[11] Yazdanpanah M M, Hosseini M, Pabba S, Berry S M, Dobrokhotov V V, Safir A, Keynton R S and Cohn R W 2008 Micro-Wilhelmy and related liquid property measurements using constant-diameter nanoneedle-tipped atomic force microscope probes *Langmuir* **24** 13753–64

[12] Gunnaes A E, Olsen A, Zagierski P T, Klewe B, Karlsen O B and Aasen A 1998 Crystal structure determination of Ag2Ga by single crystal x-ray diffraction *Z. Kristallogr.* **213** 639–44