Interrelation of Elasticity and Thermal Bath in Nanotube Cantilevers

S. Tepsic,1 G. Gruber,1 C. B. Møller,1 C. Magén,2,3 P. Belardinelli,4 E. R. Hernández,5 F. Alijani,6 P. Verlot,7 and A. Bachtold1

1ICFO—Institut De Ciencies Fotòniques, The Barcelona Institute of Science and Technology, 08860 Castelldefels (Barcelona), Spain
2Instituto de Nanociencia y Materiales de Aragón (INMA), CSIC-Universidad de Zaragoza, 50009 Zaragoza, Spain
3Laboratorio de Microscopias Avanzadas (LMA), Universidad de Zaragoza, 50018 Zaragoza, Spain
4DICEA, Polytechnic University of Marche, 60131 Ancona, Italy
5Instituto de Ciencia de Materiales de Madrid (ICMM-CSIC), 28049 Madrid, Spain
6Department of Precision and Microsystems Engineering, 3ME, Mekelweg 2, (2628 CD) Delft, The Netherlands
7School of Physics and Astronomy—The University of Nottingham, University Park, Nottingham NG7 2RD, United Kingdom

We report the first study on the thermal behavior of the stiffness of individual carbon nanotubes, which is achieved by measuring the resonance frequency of their fundamental mechanical bending modes. We observe a reduction of the Young’s modulus over a large temperature range with a slope \(-173 \pm 65\) ppm/K in its relative shift. These findings are reproduced by two different theoretical models based on the thermal dynamics of the lattice. These results reveal how the measured fundamental bending modes depend on the phonons in the nanotube via the Young’s modulus. An alternative description based on the coupling between the measured mechanical modes and the phonon thermal bath in the Akhiezer limit is discussed.

DOI: 10.1103/PhysRevLett.126.175502

In engineering, thermoelasticity is central in determining the elastic limits of structures ranging from large scale spacecrafts [1] and nuclear plants [2] down to nanstructured systems. A rich underlying phenomenology emerges for small structures, including dissipation [3,4], fluctuations [5,6], and torque generation [7,8], which are key to the development of state-of-the-art nano- and microelectromechanical technologies [9,10]. Thermoelasticity has also been used with success in condensed matter physics, where thermal measurements of the stiffness unveil the phase transition of charge-density waves and superconductivity in transition metal dichalcogenides and high-\(T_c\) superconductors [11–13]. From a fundamental point of view, the thermal behavior of the stiffness—quantified by the Young’s modulus—emerges from the nontrivial interplay of the binding energy and the lattice dynamics. However, the effect of the thermal lattice dynamics on the stiffness has remained elusive in individual nanoscale systems due to experimental challenges related to manipulating and measuring such small objects.

In this work, we use the exquisite sensing capabilities of mechanical resonators based on nanoscale systems [14–29] to resolve the small effect associated with the thermal behavior of their stiffness. Using the resonance frequency measured by optomechanical spectroscopy, we estimate the Young’s modulus of micrometer-long nanotube cantilevers from room temperature down to a few Kelvins. These results agree with the temperature dependence of the resonance frequency predicted by molecular dynamics simulations, which take into account the lattice dynamics of the nanotube. Our measurements are also consistent with the Young’s modulus directly computed from a quasiharmonic approximation of the free energy of the phonon modes. This work not only shows how the stiffness of an individual nanotube is related to its phonons, but it also highlights the role of the phonon thermal bath in nanotube cantilevers, which is a topic of importance in the field of nanomechanical resonators [14–29].

We use the single clamped resonator layout, where one end of the nanotube is attached to a silicon chip and the other end is free. This layout avoids prestress in the nanotube built-in during fabrication, in contrast to what may happen with the double clamped layout. As a result, the restoring force is given solely by the bending rigidity. This enables us to probe the Young’s modulus \(Y\) by measuring the resonance frequency, \(\omega_0 \propto \sqrt{Y}\) [30]. Such a resonance-based methodology is also employed in thermoelasticity studies on larger scale systems [11–13,31].

We engineer a platinum particle at the free end of the nanotube, so that the resonator can be measured by scattering optomechanical spectroscopy [Fig. 1(a)] [32]. We grow the particle by focused electron beam-induced deposition [33]. Figure 1(b) shows a scanning electron microscopy image of device A. Transmission electron microscopy (TEM) indicates that nanotubes can be made from one to a few walls, with a median value of two walls (Supplemental Material, Sec. I [34]). The vibrations are detected by measuring the backscattered intensity from a
632 nm laser beam focused onto the particle. Figure 1(c) shows the optomechanical spectrum of device A. The resonance frequencies of the fundamental modes polarized in perpendicular directions are about 52.9 and 54.8 kHz. The platinum particle does not affect the restoring force nor the eigenmode shape of the two fundamental modes [Fig. 1(d)], in contrast to what happens for higher frequency modes (Supplemental Material, Sec. II [34]). In this Letter, we use low laser power so that the resonance frequency is not affected by absorption heating and optical backaction [32].

We quantify \( Y = (1.06 \pm 0.28) \) TPa at room temperature from six devices by combining thermal motion variance measurement and TEM imaging; the advantage of this method is that it does not rely on the cantilever mass (Supplemental Material, Sec. III [34]). The estimated Young’s modulus is similar to previously predicted and measured values [53–58]. This indicates that the contamination adsorbed on the nanotube surface has little contribution to the stiffness of the nanotube. The contamination, which is localized along some portions of nanotubes as observed by TEM, presumably consists of hydrocarbons adsorbed during their exposure to air and the particle growth. The typical stiffness reported for such amorphous material is comparatively low \( Y \approx (50–300) \) GPa [59].

Figure 2 shows the variation of the resonance frequency of device A when sweeping the temperature \( T \). The variation is remarkably similar for both fundamental modes, independent of the temperature sweep direction and of whether the motion is thermal or driven with a piezoeactuator. This variation of the resonance frequency \( \omega_0 = \sqrt{k/m} \) is associated to the change of the spring constant \( k \), which is linearly proportional to \( Y \) in the single clamped layout. We extract the relative shift of the Young’s modulus from the relation \( \Delta Y(T)/Y(T_{\text{min}}) = 2(\Delta \omega_0(T)/\omega_0(T_{\text{min}})) \), where \( T_{\text{min}} \) is the lowest temperature at which we record the vibrations. Figure 3(a) shows the measurements of nine different devices. They all feature the same trend with a reduction of the Young’s modulus when increasing temperature. The dependence is essentially linear above about 100 K; the slope averaged over devices is \( \Delta Y(T)/Y \cdot 1/T = -(173 \pm 65) \) ppm/K. These measurements are related to neither the mass adsorbed on the nanotube nor the diffusion of adsorbed atoms along the nanotube nor the thermal expansion of the nanotube nor the

FIG. 1. (a) Schematic of the experimental setup. The sample is placed at the waist of a strongly focused beam of a He-Ne laser. The scattered light (not shown) is collected in reflection by means of an optical circulator and further sent on an avalanche photodetector. The two double arrows represent the polarization of the fundamental mode doublet. (b) Device A imaged by scanning electron microscopy after the deposition of a platinum nanoparticle; the scale bar is 1 \( \mu \)m [33]. (c) Power spectra of the optical reflection from device A showing the resonance of the thermal motion of the fundamental mode doublet at 300 K. The two spectra are recorded using different positions of the nanotube in the laser waist to enhance the signal [32]. (d) Calculated profile \( \phi(x) \) of the fundamental mode shape along the nanotube axis estimated for two different platinum particle masses normalized by the nanotube mass.

FIG. 2. Resonance frequency and relative change of the Young’s modulus of device A as a function of cryostat temperature. The legend indicates the direction of the temperature sweep (cooling or heating), which fundamental mode is measured, and whether the detected vibrations are thermal or driven with a piezoactuator.
Theoretical models are described in the Supplemental Material [34]. Both models considering the typical differences between molecular dynamics (MD) simulations or quasiharmonic approximation (QHA) calculations. The MD simulations and the QHA calculations quantify $\Delta \omega_0/\omega_0$ and $\Delta Y/Y$, respectively.

These measurements can be captured by molecular dynamics (MD) simulations of the nanotube cantilever dynamics. The temperature dependence of the resonance frequencies of the lowest energy bending modes obtained from the MD simulations behave in the same way as those we measure [Figs. 3(a), 3(b)]. The associated slope estimated for different nanotube chiralities leads to $\Delta Y(T)/Y \cdot 1/T = -(79 \pm 6)$ ppm/K, which is rather similar to the measured value. This suggests that the thermal behavior of the Young’s modulus in our measurements is related to the lattice dynamics of nanotubes.

We employ a second method to directly compute the Young’s modulus from the energy dispersion of the nanotube phonon modes. For this, we evaluate the free energy $F(T, \epsilon)$ of the phonon modes at $T$ and strain $\epsilon$ with the quasiharmonic approximation, yielding

$$Y(T) = \frac{1}{V_0(T)} \left( \frac{\partial^2 F(T, \epsilon)}{\partial \epsilon^2} \right)_{\epsilon=0},$$

where $V_0(T)$ is the equilibrium volume at this temperature. The resulting $Y(T)$ dependence is also consistent with the measurements [Figs. 3(a), 3(b)]. The slope for different chiralities is $\Delta Y(T)/Y \cdot 1/T = -(104 \pm 102)$ ppm/K. The variation of the slope is larger than that obtained with molecular dynamics; this difference may be due to the infinite nanotube length and the purely linear vibrational dynamics considered in the quasiharmonic approximation method, while the lengths in the molecular dynamics simulations are much shorter, that is, less than 40 nm. Overall, the experimental findings are fairly consistent with both models considering the typical differences between the values of $Y$ of nanotubes obtained with different experimental and theoretical methods [53–58]. Both theoretical models are described in the Supplemental Material (Secs. V and VI) [34].

These results show how the measured fundamental mechanical modes are linked to phonons via the Young’s modulus. An alternative way to describe this link is to consider the coupling of the measured mechanical modes with the thermal bath made of the phonons of the nanotube. In other words, the measured $T$ dependence of $\omega_0$ is related to the phonon thermal bath. It is likely that the phonon thermal bath in our experiments operates in the Akhiezer limit [60]. Over the temperature range that we measure, the phonon modes in nanotubes with energy $\hbar \omega_k$ similar to $k_B T$ have decay rates $1/\tau_k$ larger than $\omega_0$, since $\tau_k \approx 10$ ns was measured for breathing modes at $T = 5$ K [61] and we estimate $\tau_k$ to be typically in the 10–1000 ns range for the longitudinal and twist modes [62] (Sec. VII of the Supplemental Material [34]). The estimation of $\tau_k$ for high-energy bending modes is complicated and beyond the scope of this work.) This sets the Akhiezer limit $\omega_0 \tau_k \ll 1$ at least for the breathing, longitudinal, and twist modes [63]. It involves three-phonon processes, where one vibration quantum of the measured mode is absorbed together with the absorption and the emission of high-energy phonons with frequencies $\omega_k$ and $\omega_{k'}$, respectively. The sizeable decay rates of the high-energy phonons lead to uncertainty in their energy. This lifts to some extent the restriction associated with the energy conversation of the three-phonon process, $\omega_0 = \omega_k - \omega_{k'}$, which holds in the Landau-Rumer limit when $\omega_0 \tau_k \gg 1$. For this reason, the resonance frequency reduction and the relaxation in the Akhiezer limit are expected to be larger than that in the Landau-Rumer limit over the studied temperature range. The thermoelastic limit [4] does not apply for nanotubes, since the model relies on phonons that locally reach thermal equilibrium at different temperatures on the two sides of the beam cross section, which is not realistic for such narrow resonators.

It is expected that the phonon thermal bath significantly contributes to the measured dissipation via the Akhiezer relaxation, since a thermal bath results in a resonance frequency reduction as well as dissipation, both of them being related through the Kramers-Kronig relations [64]. Figures 4(a) and 4(b) show the measured temperature dependence of the mechanical linewidth of the different
measured devices. The measurements feature one or two peaks of dissipation at some specific temperatures. These observed peaks could arise from the Akhiezer relaxation. The Akhiezer dissipation rate depends in a complicated way on the number of phonon modes with energy $\hbar \omega_k \lesssim k_B T$, their population, and their decay rate [63]. The temperature dependence of the Akhiezer dissipation rate could feature one or more peaks in dissipation, especially since the phonon density of states varies up and down as a function of energy [62,65] and the temperature behavior of the decay rate changes for different phonon modes. In addition, the dissipation peaks could emerge at different temperatures for different nanotube chiralities, since the phonon energy dispersion is chirality dependent. The measured peaks in dissipation cannot be described by the model that is used in the literature [66,67] to quantify dissipation due to defects. See Secs. VIII and IX of the Supplemental Material for further discussion on the Akhiezer dissipation and dissipation due to defects [34].

In conclusion, we report the first experimental study of the temperature dependence of the Young’s modulus of a nanoscale system. The measurements are consistent with theoretical predictions based on the nanotube lattice dynamics. This indicates that the phonon thermal bath plays an important role in the dynamics of nanotube cantilevers, including thermal vibrational noise, dissipation, and resonance frequency reduction. Further theoretical work is needed to compute the Akhiezer relaxation in nanotubes beyond the models used so far, where a single decay rate is employed for all the high-frequency phonon modes [67–69]. This may be achieved with a microscopic theory [63] taking into account the phonon energy dispersion [65] and the energy decay of high-frequency phonons [62]. It will be interesting to see whether such a model leads to dissipation peaks at specific temperatures as observed in our work.

We thank Mark Dykman and Andrew Fefferman for enlightening discussions. This work is supported by ERC advanced (Grant No. 692876), ERC PoC (Grant No. 862149), Marie Skłodowska-Curie (Grant No. 665884), PROBIST (Grant No. 754510), the Cellex Foundation, the CERCA Programme, AGAUR (Grant No. 2017SGR1664), Severo Ochoa (Grant No. SEV-2015-0522), MICINN (Grants No. RTI2018-097953-B-I00 and No. PGC2018-096955-B-C44), the Fondo Europeo de Desarrollo Regional, the Grant No. MAT2017-82970-C2-2-R of Spanish MINECO and the Project No. E13_17R from Aragon Regional Government (Construyendo Europa desde Aragón). F. A. acknowledges support from European Research Council (ERC) starting Grant No. 802093. P. V. acknowledges support from European Research Council (ERC) starting grant 758794 “Q-ROOT.”

[1] E. A. Thornton, *Thermal Structures for Aerospace Applications* (American Institute of Aeronautics and Astronautics, Reston, 1996), https://doi.org/10.2514/4.862540.
[2] Z. Zudans, T. C. Yen, and W. H. Steigelmann, *Thermal Stress Techniques in the Nuclear Industry* (American Elsevier Publishing Company, New York, 1965).
[3] C. Zener, *Phys. Rev.* 53, 90 (1938).
[4] R. Lifshitz and M. L. Roukes, *Phys. Rev. B* 61, 5600 (2000).
[5] R. Kubo, *Rep. Prog. Phys.* 29, 255 (1966).
[6] A. N. Cleland and M. L. Roukes, *J. Appl. Phys.* 92, 2758 (2002).
[7] W. Fang, H.-C. Tsai, and C.-Y. Lo, *Sens. Actuators, A* 77, 21 (1999).
[8] M. Murozono and S. Sumi, *J. Intell. Mater. Syst. Struct.* 5, 21 (1994).
[9] P. R. Saulson, *Phys. Rev. D* 42, 2437 (1990).
[10] T. R. Albrecht, P. Grütter, D. Horne, and D. Rugar, *J. Appl. Phys.* 69, 668 (1991).
[11] M. Barmatz, L. R. Testardi, and F. J. Di Salvo, *Phys. Rev. B* 12, 4367 (1975).
[12] J. W. Brill and W. Roark, *Phys. Rev. Lett.* 53, 846 (1984).
[66] T. Faust, J. Rieger, M. J. Seidner, J. P. Kotthaus, and E. M. Weig, Phys. Rev. B 89, 100102(R) (2014).

[67] M. Hamouni, P. E. Allain, W. Hease, E. Gil-Santos, L. Morgenroth, B. Gérard, A. Lemaitre, G. Leo, and I. Favero, Phys. Rev. Lett. 120, 223601 (2018).

[68] J. Rodriguez, S. A. Chandorkar, C. A. Watson, G. M. Glaze, C. H. Ahn, E. J. Ng, Y. Yang, and T. W. Kenny, Sci. Rep. 9, 2244 (2019).

[69] S. S. Iyer and R. N. Candler, Phys. Rev. Applied 5, 034002 (2016).