Optical determination of the flexural rigidity of carbon nanotube ensembles

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We demonstrate two simple and consistent optical methods for quantitatively determining the flexural rigidity EI (where E is the elastic modulus and I the moment of inertia), a quantity of practical importance in determining the deflection and buckling characteristics of carbon nanotubes (CNTs). This is done through monitoring the deflection of patterned arrays of CNTs, which are subject to fluid flow. In addition to mechanical characterization of filamentous nanostructures, the implications of our work extend to the monitoring of nanoscale fluid flows for tactile and shear force sensors and the characterization of the mechanosensor response of cilia in physiology. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2917569]

Carbon nanotubes (CNTs) have been shown to have a remarkable combination of mechanical properties, which include high elastic moduli (E),—in the terapascal range for both single-walled[1] and multiwalled CNTs[2,3] and superplasticity.[4] Along with high stiffness,[5] the ability to undergo reversible bending and buckling, with strains[6] of up to 30%, has been reported. However, while loads and strains can be relatively easily configured and measured, it is not feasible to accurately determine the cross-sectional area of nanotubes[7] for the calculation of stresses or the moments of inertia (I). Indeed, molecular dynamics based simulations yield a large discrepancy[8,9] in E presumably due to this reason.[7]

The practical determination of the mechanical response of nanotubes of varying lengths (L), subject to different forces (P), such as deflection under shear $(\Delta)=PL^3/3EI$, or buckling loads $(P_{cr})=\pi^2EI/L^2$, is generally governed by the *flexural rigidity*[10] EI. Noting the difficulties with the individual measurement of E and I, we demonstrate two simple and consistent optical methods for quantitatively determining the EI of CNTs through the deflection of patterned arrays of CNTs subject to fluid flow. In addition to mechanical characterization of nanostructures, the implications of our work extend to the monitoring of nanoscale fluid flows,[11] say, for reducing wall drag,[12] in tactile and shear force sensors[13] and porous membrane design.[14]

Vertically aligned multiwalled CNT ensembles [~40 μm in length, with 40–60 nm diameters and spacing of ~200 nm—Fig. 1(a)] were synthesized through a thermal chemical vapor deposition method described in detail elsewhere.[15] We then observed [Fig. 1(b)], that the deflection of the CNT ensembles, sheared against a fixed surface in an in-house assembled stage, accurately mimics deflections predicted using fixed-end cantilever beam theory [Fig. 1(b)]. This motivated the idea that CNT deflection could be utilized for deducing mechanical properties and sensing fluid flow.

The experimental apparatus for the determination of EI is outlined in Fig. 1(c) and consists of a quartz tube (inner diameter of ~6.2 mm) with the nanotube blocks placed on a quartz slide in the center of the tube. Fluid flow, at different velocities, was then introduced perpendicular to the nanotubes. A linearly polarized He–Ne (λ of 633 nm), focused to a spot size diameter ~30 μm, was used to illuminate the CNT ensemble from above and the transmitted light intensity monitored as a function of the fluid flow. By orienting the axis of the polarizer to the laser polarization direction, any effect due to the CNT ensemble (initially oriented parallel to the polarized beam) deflections would be translated into a change of light intensity and sampled by a photodetector or a charge coupled device (CCD) camera.

In initial experiments, a correspondence between the air flow velocity and decreased transmitted laser intensity was observed [Fig. 2(a)], and was attributed to nanotube deflection and subsequent hindrance to the light transmission. It is, indeed, remarkable that the flow can be so accurately and *digitally* determined [Fig. 2(b)]. This behavior was consistently obtained over several samples. The reduced light intensity was proportional to the deflection and the drag force

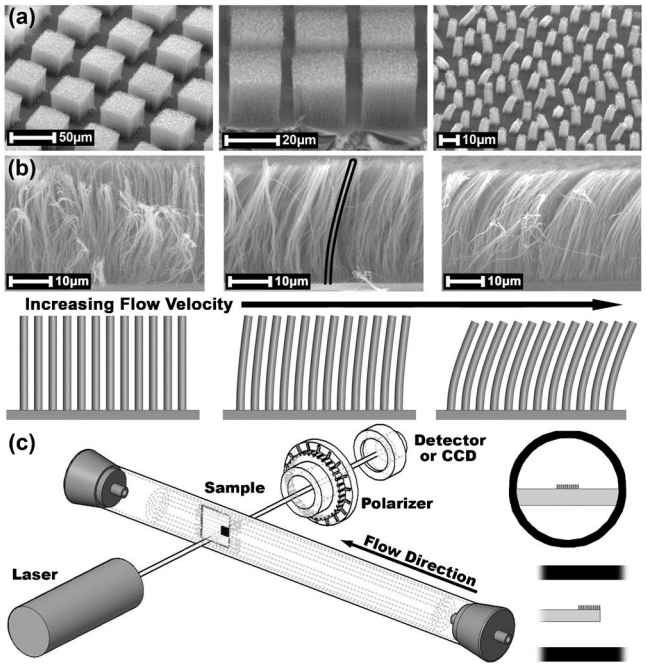

FIG. 1. (a) Patterned multiwalled carbon nanotube ensembles of varying sizes. (b) The shearing of carbon nanotube arrays, in a scanning electron microscope *in situ*, as modeled through cantilever beam theory (dark outline). (c) Schematic of the experimental setup for observing the nanotube deflections during fluid flow (The insets determine the light orientation relative to the CNT ensembles).

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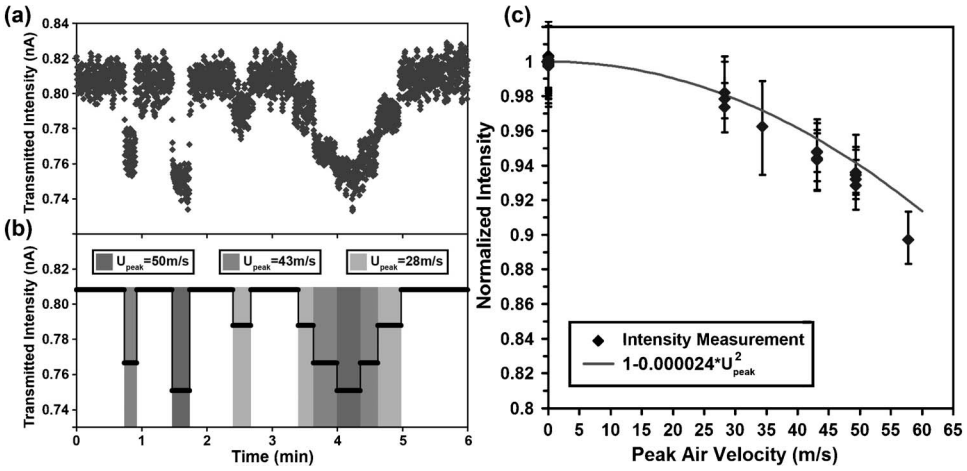

FIG. 2. (a) The variations in the transmitted laser intensity are a very sensitive function of the fluid velocity and can be used for the (b) digital calibration of the flow. (c) The data points show a decrease in the transmission with increased nanotube deflection. The analytical fit to the data is from an independent measurement of deflection through CCD image processing.

on the nanotubes, and a parabolic dependence on the velocity, in accordance with classical fluid mechanics theory,[16] was obtained [Fig. 2(c)]. [In Fig. 2(c), while the data points are obtained through light transmission measurements, the analytical expression: $1-0.000\,024U^2_{\text{peak}}$ was determined through CCD measurement] The consistency between two independent measurements reveals the robustness of our methods.

To determine the *EI* of the nanotube bundles under fluid flow, the drag force due to the flow was modeled. While the air flow through the cylindrical quartz tube itself is clearly turbulent (Reynolds number, $\text{Re}>8000$), the profile over the CNT sample and substrate can be determined using standard boundary layer profiles for *laminar flow* over a flat plate[16] ($\text{Re}\approx 100$). It was calculated, with typical nanotube lengths ($\sim 40\ \mu\text{m}$) and average air velocities ($U_{\text{av}}\approx 40\ \text{m/s}$), that the boundary layer thickness was less than the CNT length, implying that the upper regions of the nanotubes was exposed to developed center-line flow.

The velocity (U) profile, along the nanotube height (y), was then calculated as a function of the distance of the nanotubes from the leading edge of the quartz substrate (X) for a given Re, adapting the solution for the laminar flat-plate (Blasius method), with $U_{\text{peak}}=[1+0.722/\log(\text{Re}/6.9)]U_{\text{av}}$ for height *above* the boundary layer (δ), and $U/U_{\text{peak}}=2(y/\delta)-(y/\delta)^2$, where $\delta/X=5/\sqrt{\text{Re}}$, *below* the boundary layer. The drag coefficient (C_D), at low Re typical of flow through nanotubes, was then determined through a modified Stokes–Oseen[17] expression, for the flow past an array of nanotubes (modeled as rigid cylinders),[18] as

$$C_D \cong \left(\frac{1+4\text{Kn}}{1+6\text{Kn}}\right)\left[\frac{8\pi}{\text{Re}\ln(7.4/\text{Re})}\right] \times\left(\frac{3+2\phi^{5/3}}{3-4.5\phi^{1/3}+4.5\phi^{5/3}-3\phi^2}\right).$$

The C_D was calculated as a function of length of the nanotube for different volume fractions (ϕ, $\sim 0.05\pm 0.01$) of the nanotubes in the ensemble. The Knudsen number (Kn), defined by the ratio of the mean free path of the air molecules to the characteristic length scales in the system, is $\sim 0.3-0.5$. Appropriate to this range of Kn, a correction[19] factor $[(1+4\text{Kn})/(1+6\text{Kn})]$, stimulated through a kinetic Boltzmann approach,[19] was introduced for consideration of a fluid slip at the surfaces. Subsequently, the drag forces (F_D) were calculated through[20] $F_D=1/2C_D A\rho U^2$, for a given nanotube cross-sectional area (A) and fluid density (ρ). This distributed force was then integrated along the nanotube length through $d^4x/dy^4=-w(y)/\text{EI}$, where $w(y)$ is the force (F_D)/unit length, to obtain the horizontal displacement x as a function of nanotube height (y) and U by using the following boundary conditions:

(i) no shear at the CNT free ends ($d^3x/dy^3=0$, at $y=h$),
(ii) no bending moments at the free end ($d^2x/dy^2=0$, at $y=h$),
(iii) zero slope at the fixed end of the CNTs ($dx/dy=0$, at $y=0$), and
(iv) zero deflection at the fixed end ($x=0$, at $y=0$).

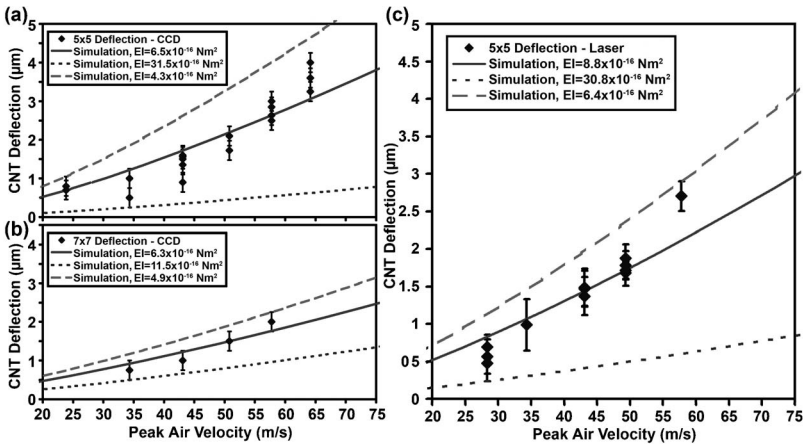

FIG. 3. The deflection of carbon nanotube arrays, obtained through the CCD image processing, is plotted as a function of air velocity for a (a) $5\times 5\ \mu\text{m}^2$ and (b) a $7\times 7\ \mu\text{m}^2$ CNT ensemble and fitted through simulations to the *EI*. (c) The *EI* fits were also done through measured photodetector intensity variation.

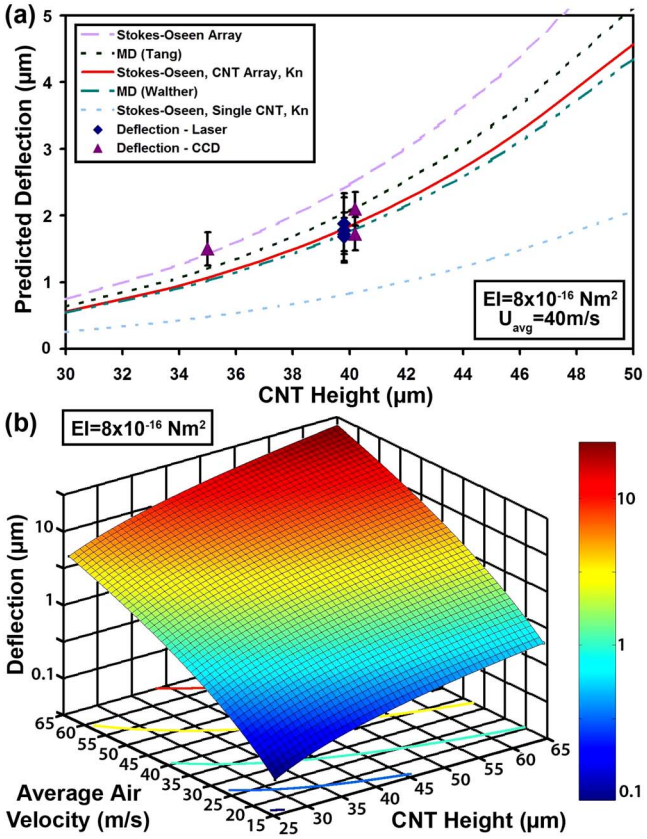

FIG. 4. (Color online) (a) A close correspondence between our experimental results (data points) and previous molecular dynamics and computational fluid dynamics simulations. (b) Prediction of the nanotube deflection as a function of CNT height and average air velocity.

The validity of each of these boundary conditions was checked through numerical estimates. After the integration procedure, the deflection was obtained as a function of the *EI*. Subsequently, the *EI* was fitted to the experimental results (Fig. 3) through numerical optimization. Figures 3(a) and 3(b) are representative results obtained from 5×5 μm^2 and 7×7 μm^2 patterned CNT blocks with *EI* values of $\sim6.5\times10^{-16}$ and $\sim6.3\times10^{-16}$ N m^2, respectively. In addition, the deflections obtained through photodetector intensity variation [Fig. 3(c)] for the 5×5 μm^2 pattern have also been fit to an *EI* of $\sim8.8\times10^{-16}$ N m^2, which is in good agreement with the value computed from the CCD measurements. The error in the *EI* determination (Fig. 3) has a very small ($\sim10\%$) contribution from factors, such as CNT diameter, length, and spacing variation, and from the optical resolution.

We estimated the value of the moment of inertia *I* by using the parallel axis theorem ($I=\Sigma I_n+A_n d_n^2$) to be $\sim5\times10^{-24}$ m^4 for a 5×5 μm^2 square nanotube block. With a elastic modulus ~1 TPa,[7] a *EI* of $\sim5\times10^{-12}$ N m^2 was calculated, which is four orders of magnitude higher than found in the current work. To account for this discrepancy, we conducted[21] compression tests of nanotube blocks loaded normal to the tube axes where we determined an elastic modulus of ~0.2 GPa. van der Waals forces between the nanotubes,[22] and sliding between adjacent CNTs,[23] would explain the lower *E* values.

Using the above elastic modulus (*E*) value, a *EI* $\sim1\times10^{-15}$ N m^2 is obtained for a 5×5 μm^2 square pattern, in excellent agreement with our experimental results. Generally, *EI* values are expected to transit from one extreme of a single, isolated nanotube to another extreme of a sufficiently large block which would provide no additional resistance to bending due to constituent CNT sliding.

We also observe a close correspondence between our experimental results and published non-equilibrium molecular dynamics[18,24] and computational fluid dynamics[20] simulations. It was seen that the nanotube deflections are well approximated by the assumption of Knudsen effect incorporated Stokes–Oseen model [Fig. 4(a)]. Subsequent to the *EI* determination, we can apply our modeling to predict nanotube deflection over a wider range of nanotube heights and flow velocities [Fig. 4(b)], for understanding nanoscale mechanical behavior.

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