Effect of defects on resonance of carbon nanotubes as mass sensors

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The mass sensors based on carbon nanotubes (CNTs), especially one with uniform structure, have ultrahigh sensitivities. However, in application the CNTs' properties will be affected by many factors such as volume defects or uneven mass repartition. In this letter, modified beam models are presented based on the Euler–Bernoulli beam theory to analyze the effect of the unideal structure on resonance frequency of CNTs themselves and as mass sensors. It can be found that the resonance frequency shift due to the defect is sensitive to the defect's relative position on the CNT. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2186048]

Carbon nanotubes (CNTs) have been suggested as the basic elements of nanoelectromechanical systems, such as nanobalance,[1] nano oscillator,[2] and nanotweezers.[3] Recently, the CNT-based mass sensors, whose basic principle is the resonance frequency shift subjected to the attached mass, have attracted many focuses owing to their high sensitivities. Poncharal, Wang, and Ugarte,[1] through electromechanical resonance, detected a tiny mass of 22 fg attached at the free end of the cantilevered multi-walled carbon nanotube (MWNT). Li and Chou,[4] using a molecular mechanics method, reported that the mass sensitivity of single-walled carbon nanotube (SWNT) nanobalances can reach 10^{-6} fg. The structures of CNTs examined in Li's analysis are all perfect, however, the CNTs' properties may be affected by many factors in application. Poncharal and co-workers[1] found that the bending modulus of CNTs decreased greatly with the increase of the diameter due to a rippling mode. Liu, Zheng, and Jiang[5,6] analyzed the effect of the rippling mode on resonance and explained the fantastic phenomena using a bilinear beam model. It was reported[7] that CNTs produced by chemical synthesis usually contain a high density of point defects (pentagons and/or heptagons) or even volume defects (neck-like structures), which greatly weakened the bending stiffness of CNTs. To the best knowledge of the authors, there is no suitable theory that can be used to calculate the resonance frequency of CNTs with volume defects. Moreover, the leftover such as catalyzer used in production may lead to an uneven mass repartition. Since it is difficult to guarantee the perfect structure of CNTs, the effect of the defects should be analyzed carefully.

Generally speaking, it is appropriate for using the linear beam theory (LBT) to analyze the resonance phenomena of thick MWNTs with the large ratio between length and diameter. Furthermore, a uniformity beam model can be used owing to the CNT's perfect structure. Poncharal and co-workers[1] measured the fundamental resonance frequency of cantilevered MWNTs and calculated the elastic bending modulus E using the equation from the LBT[8]

$$f_i = \frac{(\beta_i)^2}{2\pi\ell^2}\sqrt{\frac{EI}{\rho A}} \tag{1}$$

with $\beta_1 = 1.875$, $\beta_2 = 4.694$, where ρ is the density, ℓ is the length, A and I are the area and the moment of inertia of the cross section, respectively. For convenience, F_i stand for the ith resonance frequency and $M = \rho A \ell$ is the mass of the cantilevered beam without any defects or attached masses in the following discussions.

When cantilevered CNTs are working as mass sensors, the boundary condition at $x = \ell$ is changed due to the effect of the attached mass, and β_i in Eq. (1) are altered correspondingly. Solving the eigenvalue problem, the characteristic equation can be obtained as[9]

$$\cos\beta\cosh\beta + 1 = \xi\beta[\sin\beta\cosh\beta - \cos\beta\sinh\beta], \tag{2}$$

where $\xi = m/M$ is the mass ratio, m is the attached mass at the free end. The roots β_i can be solved numerically for any given value ξ.

The assumption of the uniformity of stiffness or mass along the tube is not valid when CNTs have volume defects or attached point masses. The effect of these unideal conditions can be considered using the similar models with slight modification. The volume defect, which results in the abrupt change of the flexural rigidity, is modeled as a rotational spring, as shown in Fig. 1(a). The stiffness of the spring is defined as $k = (EI)_q/\Delta\ell$, where $(EI)_q$ and $\Delta\ell$ are the flexural rigidity and the length of the volume defect, respectively. Here $\Delta\ell$ is supposed to be small enough so that the total length of the beam is constant. If a point mass m_a is attached at $x = a$ before mass detection, the CNT can be analyzed by the model shown in Fig. 1(b). Actually more tiny masses may be attached along the tube in application, thus a more complex model can be established to examine the uneven mass repartition on resonance in a similar way. In Fig. 1, the beams are divided into two uniform ones, which are interact-

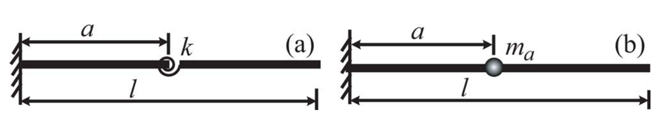

FIG. 1. Sketch of modified models for CNTs with unideal structures: (a) the spring-connected beam model for CNT with a volume defect at $x = a$; (b) the cantilevered beam with a tiny mass at $x = a$.

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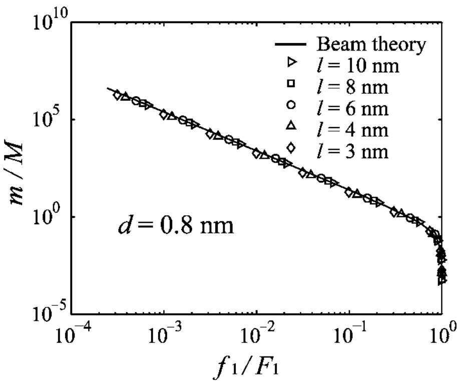

FIG. 2. The changes of the frequency ratio corresponding to the mass ratios obtained by the membrane-spring model for SWNTs samples, and compared with the result of LBT. The data of SWNTs with length larger than 4 nm agree well with the one of LBT.

ing at the interface position $x=a$. The analysis of the eigenvalue problem is similar; a detailed explanation can be found in Ref. 10.

Based on the single-atom sheet structure of SWNT, a membrane-spring model is proposed in our previous work,[11] in which SWNT is modeled as a number of membranes connected by rotational springs. Using this model, a series of cantilevered CNTs with different length-to-diameter ratios ($\ell/d=12.5, 10, 7.5, 5.0, 3.75$) are examined to validate the LBT. As a result, the variations of the frequency f_1 due to the attached mass m are in good agreement with those given by the molecular mechanics method.[4] In addition, the corresponding relationship between f_1/F_1 and m/M can be calculated, as shown in Fig. 2. These data, especially the CNTs with $\ell/d>5$, amazingly drop into the curve of the beam theory according to Eq. (2). Fitting the numerical results of Eq. (2), the approximate relation between f_1/F_1 and m/M in some phases can be obtained as

$$\log(m/M) = A_1\log(f_1/F_1) + A_2 \quad \text{if} \quad m/M > 1.0,$$

$$(m/M) = A_3(1 - f_1/F_1) \quad \text{if} \quad m/M < 0.001 \qquad (3)$$

with $A_1=-2.031$, $A_2=-1.5316$, and $A_3=0.5014$. Similar results were proposed in Refs. 4 and 12, respectively. Note that the easiest excited modes of cantilevered CNTs are generally the first several bending modes, so the section properties seems to be less important. It can be concluded that if the length of the SWNT or thin MWNT is large enough compared to its diameter, the lower resonance frequencies can be determined using the beam model.

Using the modified beam model, the effect of unideal stiffness or mass repartition on resonance can be considered. Figure 3 illustrates the effect of the volume defect, including the stiffness change and the relative position. The important result here is that the resonance frequency shift is very sensitive to the position of defect. If the defect is very close to the clamped end, it can model a defective clamped end, which may occur in application because of the small dimensions of CNTs. It can be seen that the effect of defective clamped end on resonance cannot be ignored. The authors[7] reported that the effect bending modulus E_{eff}[13] of CNTs with point defect was about 30 GPa, while that of tubes with volume defect additionally was 2–3 GPa; concretely, the data of 2.2 GPa and 5 Pa (the volume defect in the latter is relatively close to the free end) were given. Let us consider a

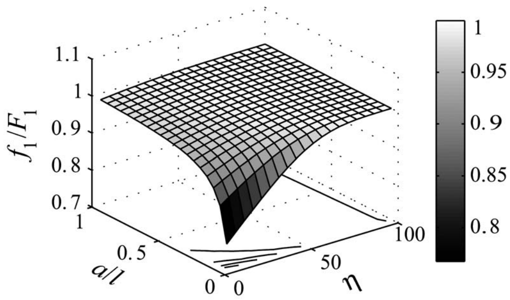

FIG. 3. The variation of the frequency ratio with the position ratio a/ℓ and the stiffness ratio $\eta=k\ell/EI$ of the volume defect. It indicates that when the position of the volume defect is closer to the clamped end, the influence is more significant.

beam with a volume defect, the spring in the model has $\eta=0.1$. When the volume defect occurred at $x=0.3\ell$ or 0.5ℓ, the bending modulus was about 1/15 or 1/6 of the one without volume defect. In the absence of detailed information in experiments, more detailed comparison could not be obtained. Furthermore, many other factors, such as curly shape due to point defects, may contribute to the decrease of the stiffness for CNTs with volume defects. Figure 4 displays the variation of frequency ratios with the mass' position for the beam with the attached mass of $m_a=0.2\,M$. The variation of f_1/F_1 and f_2/F_2 have the different trend, and the value of f_2/f_1 up and down departures from the normal value 6.27 $=(4.694/1.875)^2$. When the beam has a volume defect, there is a similar phenomenon. By contrast, the value of f_2/f_1 of the tube with a rippling mode calculated by the bilinear model is always larger than 6.27. In the experiments,[14,15] the authors gave two groups of data about the first two harmonic resonance frequencies of bent CNTs, that is, $f_1=1.226$ MHz, $f_2=9.277$ MHz; and $f_1=1.21$ MHz, $f_2=5.06$ MHz. Thus $f_2/f_1=7.567$ and 4.182, respectively. Since the volume defect would not been found, the leftover in CNT-based sensors may arouse the difference of f_2/f_1.

The effect of any other more complex cases, such as CNTs with two or more volume defects or attached point masses, can be analyzed through extending the beam model discussed above. Imaginably, it results in the complexity of solving the characteristic equation. It is a natural way to simplify the analysis for mass detection using the result of LBT [Eq. (1) with the constance β obtained from Eq. (2)] with E_{eff}, which is considering the effect of defects. In order to examine the validation, the results of the LBT are compared with those obtained by the modified beam models, for the spring-connected beam as an example as shown in Fig. 5.

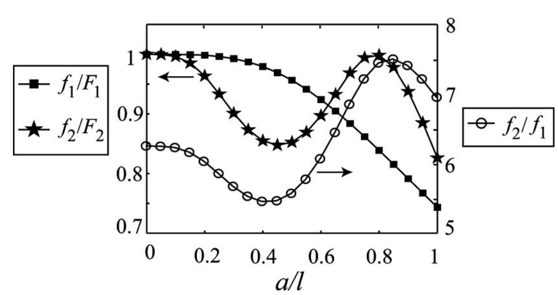

FIG. 4. The resonance frequencies ratios change with the position of the attached mass. It can be seen that the shift on f_2 is more significant than f_1 when the mass is close to the clamped end of the beam while the frequency shift on f_1 is more significant than f_2 when the mass is close to the free end.

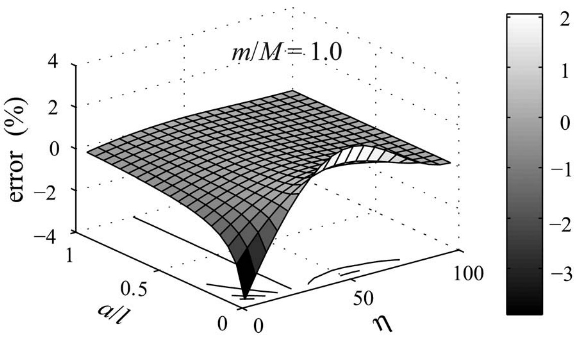

FIG. 5. The results of the LBT with E_{eff} compared with those obtained by the spring-connected model during measuring a tiny mass $m=M$ attached at the free end of the cantilevered CNT. The error is defined by $(f_L - f_M)/f_M$, where f_L and f_M are the fundamental frequency of the LBT and the modified model, respectively.

It can be seen that the error is relatively evident when the volume defect is close to the clamped end. However, in the other position the difference seems to be small enough that the LBT with E_{eff} is applicable to the analysis of the resonance property. For any kind of defect's effect or any range of mass detection concerned, the validation of LBT with E_{eff} can be examined through comparison with the modified models in a similar way.

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[9] For free vibration, the deflation of the beam becomes separable in space and time, i.e., $y(x,t)=Y(x)\sin(\omega t)$. The vibration equation reduces to $Y^{(4)}(x)-(\beta/\ell)^4 Y(x)=0$, with the solution $Y(x)=C_1\cos(\beta x/\ell)+C_2\sin(\beta x/\ell)+C_3\cosh(\beta x/\ell)+C_4\sinh(\beta x/\ell)$, where constants C_i are subjected to the given boundary conditions. For cantilevered beam with the attached mass at the free end, the boundary condition is $Y=0$, $Y'=0$ at $x=0$; $EIY''=0$, $EIY'''+m\omega^2=0$ at $x=\ell$. By substituting the general solutions into the boundary, the characteristic equation can be obtained.
[10] Each portion of the beam has the function of Y_i, which satisfies the vibration equation on one's own and related through the interface condition at $x=a$. Taking the spring-connected model as an example, the interface conditions at $x=a$ are $Y_1=Y_2$, $(EIY_1)''+k[(Y_1)'-(Y_2)']=0$, $(EIY_2)''+k[(Y_1)'-(Y_2)']=0$, $EI(Y_1)'''=EI(Y_2)'''$. Furthmore, Y_1 and Y_2 should be satisfied the boundary condition at $x=0$ and $x=\ell$, respectively. By substituting the general solutions of Y_1 and Y_2 into the boundary and interface conditions, the frequency equation can be obtained.
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