

Design of Mass-sensor Based on Resonant Frequency Analysis of a Single Walled Nanotube

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Abstract

In this paper, the resonant frequency responses produced in single walled nanotubes (SWNTs) has been analyzed by mathematical validation using finite element method (FEM). The analysis investigates the effects of changes made in conventional design governing parameters for resonant frequency variations as well as the resonant frequency shift of the SWNTs. The analysis of optimized SWNT mass sensor is also done based on continuum mechanics approach and compared with the published data of single walled carbon nanotubes (SWCNTs) and single walled boron nitride nanotubes (SWBNNTs) for fixed-free configuration as a mass sensor. For the application of Nanotube based Bio-Sensors in NANO ELECTROMECHANICAL SYSTEM (NEMS), the idea of approach is to filter-out the air gap between the resonators for the modified structure. The simulation results for SWBNNTs and SWCNTs based on FEM are compared with the continuum mechanics based analytical approach data and it is found that the BNNT cantilever biosensor has a better response and sensitivity which comes in range of 10^{-22} g and that for H form it is 10^{-21} g. Also the variations of diameter and chirality shows the significant change in properties. So, the current modelling approach can be suitable for the development of SWNTs based NEMS applications as in given novel (NEM) memory cell.

Keywords: Single Walled Nanotubes (SWNT), Finite element analysis (FEM), Single Walled Carbon Nanotubes (SWCNT), Single Walled Boron Nitride Nanotubes (SWBNNT), Nano Electromechanical Systems (NEMS), Very High Frequency (VHF), Boron Nitride Nanotubes (BNT), Carbon Nanotubes (CNT), memory cell.

1. Introduction

Mechanical properties of the nanotubes has been proved for tremendous potential and wide area applications in various fields. Among which the Carbon Nanotubes (CNT) and Boron Nitride Nanotubes (BNNT) appear to be potential candidates for Bio-medical applications. A boron nitride nanotube (BNNT) can be imagined as a rolled up hexagonal BN layers or as a carbon nanotube (CNT) in which alternating B and N atoms entirely substitute for C atoms. Similar to CNTs, BNNTs have chirality, an important geometrical parameter. BNNTs, which possess a similar morphology as CNTs but distinct properties of their own, well known due to their uniformity and stability in dispersion in solution [19]. Unlike CNTs, whose electronic structure and properties vary widely based upon tube helicity, concentric layers, and so forth, the BNNTs are semiconducting regardless of their diameter and chirality. BNNTs are also found to be nontoxic to health and environment due to their chemical inertness and structural stability [1, 11]. In addition, BNNT has a wide band-gap independent of geometrical/ atomic configuration. These factors make BNNT particularly suitable for biological applications.

Working of the Resonance sensors is based on the characteristic in frequency shift due to mass loading. This type of sensing basically consists in detecting a frequency shift due to an applied axial force to be measured while electrostatically exciting the resonator at its fundamental frequency. The resolution of such a sensor is given by the minimum detectable frequency shift which is inversely proportional to the resonator drive amplitude. It is limited by the onset of non-linearities which occur proportionally sooner with respect to the device size. Moreover, below the bi-stability limit, it is extremely difficult to detect the oscillations of such small sensors. Resonance based sensors offer the potential of meeting the high-performance requirement of many sensing applications, including metal deposition monitors, non-volatile memory cell applications, chemical reaction monitors, biomedical sensors, mass detector, etc. [13–15].

A systematic study on vibrational analysis of various design based nano mechanical resonators has not yet been available, knowing the fact that such an investigation is essential for a wide range of the applications of SWNTs, e.g., nano resonators, nano sensors, actuators, and transducers. In the present work, to explore the suitability of SWNTs as a mass detector device for many sensing applications, the dynamic response of individual SWNTs treated as a thin walled tube of outer diameter 0.8 nm with thickness 0.065 nm has been analyzed and compared with the parallel legged H form of same dimensions. The cantilevered configuration is considered for the FEM simulations and the analysis carried out for the resonant frequency variation of the SWCNTs and SWBNNTs, caused by the changes in size of NT in terms of length (6 nm, 8 nm, and 10 nm) as well as attached masses at the tip 10^{-4} fg to 10^{-2} fg. Using continuum mechanics based approach, the performance of BNNT cantilevered and parallel legged H biosensors is analyzed and compared with the published data by Li and Chou [5] of SWCNT for fixed-free configuration as a mass sensor. As a systematic analysis approach, the simulation results based on FEM are compared with the continuum mechanics based approach.

2. Single Walled Nanotube: Continuum Model

Continuum mechanics based models for beam as well as shell have been successfully applied to analyze the dynamic responses of single walled CNTs [16]. This propels us to use the continuum model for the present vibrational analysis of single walled BNNTs.

2.1 Basic Bending Vibration of a Beam

For obtaining analytical expressions to relate the resonant frequency to an attached mass using a rod based on the Euler–Bernoulli beam theory [17], the equation of motion of free vibration can be expressed as

$$EI \frac{\partial^2 y}{\partial x^2} + \rho A \frac{\partial^2 y}{\partial t^2} = 0 \quad (1)$$

Where E is Young's modulus, I the second moment of the cross sectional area A, and ρ the density of the material. Suppose the length of the model is L. Depending on the boundary condition of the BNNT and the location of the attached mass, the resonant frequency of the combined system can be derived. Only considering the fundamental resonant frequency, which can be expressed as

$$f = \frac{1}{2\pi} \sqrt{\frac{k_{eq}}{m_{eq}}} \quad (2)$$

where k_{eq} and m_{eq} are equivalent stiffness and mass of NT with attached mass in first mode of vibration, respectively.

Theoretically, the resonant frequency depends on the nanotube outer diameter, the inner diameter, the length, the density, and the bending modulus of the nanotube, i.e.

$$f_i = \frac{\beta_i^2}{8\pi L^2} \sqrt{\frac{(D_i^2 + D_o^2)E}{\rho}} \quad (3)$$

where $\beta_1 = 1.875$, $\beta_2 = 4.694$, $\beta_3 = 7.854$ and $\beta_4 = 10.995$ for the first, second, third and fourth harmonics, respectively.

2.2. Finite Element Approach to Continuum Modeling

In this study, SWBNNTs are approximated by considering a thin walled tube and a combination with thickness (a continuum model) and vibrational analysis performed using commercial FEM package. The resonant frequency variations to attached mass of the SWBNNT are simulated using a bending model. The force field within a nanotube crystal consists of a combination of strong linear bonding forces acting within the nanotube. This disparity between the magnitude of interatomic forces leads to a highly anisotropic constitutive relation [17]. The linear bonding forces acting along the length of single walled nanotube is assumed which is an orthotropic material is being isotropic about one axis. This assumption results in compliance matrix of nine terms, but only five of these are independent. In this analysis, the constitution of the boron nitride nanotube is expressed in a cylindrical coordinate system and the stress–strain relationship is

$$\begin{Bmatrix} \sigma_r \\ \sigma_\theta \\ \sigma_z \\ \tau_{\theta z} \\ \tau_{rz} \\ \tau_{r\theta} \end{Bmatrix} = \begin{bmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ C_{12} & C_{22} & C_{23} & 0 & 0 & 0 \\ C_{13} & C_{23} & C_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{55} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{66} \end{bmatrix} \begin{Bmatrix} \varepsilon_r \\ \varepsilon_\theta \\ \varepsilon_z \\ \gamma_{\theta z} \\ \gamma_{rz} \\ \gamma_{r\theta} \end{Bmatrix}$$

where C_{ij} and D_{ij} represents the stiffness coefficients of BNNT and CNT respectively. The stiffness coefficients as per Appendix for SWBNNT are estimated considering the elastic modulus of 1.2260.24 TPa [10], transverse modulus of 30GPa, and Poisson's ratio of SWBNNT 0.35. And for BNNT, the density $\rho=2180$ kg/m³ is used, according to the density of hexagonal-BN.

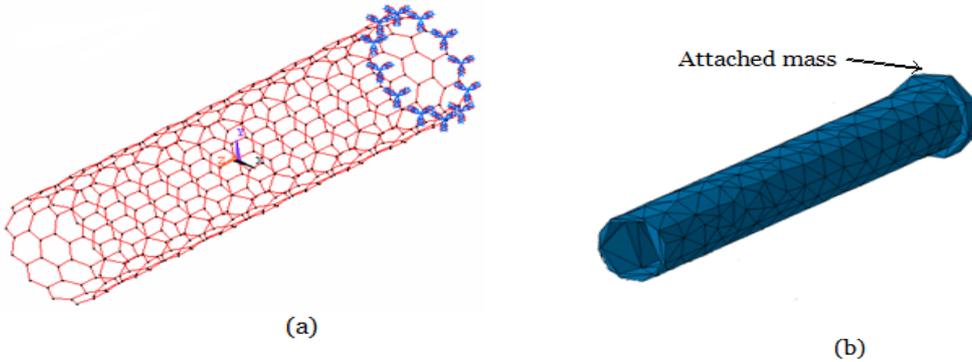


Fig. 1: (a) Cantilevered single walled BNNT nano mechanical resonator with attached mass at the tip of beam. (b) Enlarged view of cantilevered single walled boron nitride nanotube 3D FEM model.

3. Mass-resonant Frequency Relation of Model

Considering the fact that the resonant frequency is sensitive to the resonator mass, which includes the self-mass of the resonator and the mass attached on the resonator. The change of the mass attached on the resonator can cause a shift of the resonant frequency. The key issue of mass detection is in quantifying the change in the resonant frequency due to change in geometry and added mass.

3.1 Analytical Bending Vibration of a Beam

The intermediate positions of the attached mass required the resonant frequency shift analysis of the higher-order modes of vibrations, as maximum displacement of nanotube occurs at two or more places at higher-order modes of vibration. As shown in Fig. 1(a), for cantilevered resonator, the additional mass is assumed to be attached at the free end. For convenience, the attached mass is assumed to be a concentrated load on the nanotube as we are dealing with harmonic vibrations. Added mass M is considered at the free end, which is giving a virtual force at the location of the mass so that the deflection under the mass becomes unity. For this case, assuming harmonic

motion and kinetic energy of single walled BNNT, equivalent stiffness (k_{eq}), deflection shape along the length of single walled BNNT, and equivalent mass m_{eq} can be obtained as [18]

$$\text{Equivalent stiffness, } K_{eq} = \frac{3EI}{L^3} \quad (4)$$

$$\text{Deflection shape, } Y(x) = \frac{x^3(3L-x)}{2L^3} \quad (5)$$

Assuming harmonic motion $Y(x,t)=Y(x)\exp(i\omega t)$, where ‘ ω ’ the frequency, the kinetic energy of cantilevered single walled NT is obtained as

$$T = \frac{\omega^2}{2} \int_0^L \rho A Y^2(x) dx + \frac{\omega^2}{2} M Y^2 = \frac{\omega^2}{2} \left(\frac{33}{140} \rho A L + M \right) \quad (6)$$

Therefore, equivalent mass

$$m_{eq} = \frac{33}{140} \rho A L + M \quad (7)$$

Substituting Eqs. for k_{eq} and m_{eq} in Eq. of fundamental frequency, the resonant frequency can be obtained as

$$f_{n_{canti}} = \frac{1}{2\pi} \sqrt{\frac{k_{eq}}{m_{eq}}} = \frac{1}{2\pi} \sqrt{\frac{3EI/L^3}{\frac{33}{140} \rho A L + M}} \quad (8)$$

$$f_{n_{canti}} = \frac{1}{2\pi} \frac{\alpha_c^2 anti \beta}{\sqrt{(1+\Delta M)}}$$

where,

$$\alpha_c^2 = \sqrt{\frac{140}{11}} = 3.567530, \quad \beta = \sqrt{\frac{EI}{\rho A L^4}}, \quad \Delta M = \frac{M}{\rho A L} \mu_{canti}, \quad \mu_{canti} = \frac{140}{33}$$

The resonant frequency for a cantilevered single walled BNNT with no attached mass is obtained by substituting $\Delta M=0$ as

$$f_{0_{canti}} = \frac{1}{2\pi} \alpha_c^2 anti \beta \quad (9)$$

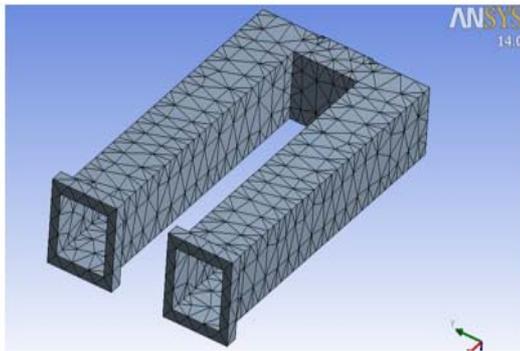
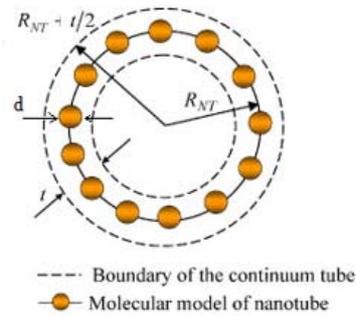


Fig. 2.(a) Enlarged 3D FEM view model view of H modeled beam of SWBNNT.



(b) Cross section of a BNNT, where RNT is the radius of nanotube, d is the mean diameter of boron atom and nitrogen atom, and t is the equivalent thickness of the nanotube.

General expression of resonant frequency shift Δf due to attached mass M can be expressed as

$$\Delta f = f_0 \left(1 - \frac{1}{\sqrt{1+\Delta M}} \right) \quad (10)$$

3.2 Finite Element Modeling

The commercial finite element numerical package ANSYS is applied to study mechanical vibration response of a fixed-free SWNT. This software provides an efficient and readily implementable tool for anisotropic coupled field element analysis. In previous reports it is seen that the BNNTs of small diameter comprising boron and nitrogen atoms are approximately equivalent to continuum columns. The continuum model of SWBNNT as shown in Fig. 1(a) is considered to analyze resonant frequency of the SWBNNT based nano mechanical resonators and finite element method approach has been used to study the vibrational response of cantilevered configuration as well modified H shape (a combination of cantilever beams) of SWBNNTs. SWNTs are modeled using a 3D finite element model and the attached mass is modeled at the free end of BNNT using Boolean operation. Boolean algebra provides a means for combining sets of data, using logical operators such as intersect, union, subtract, etc. As in this analysis the mass is to be changed after each iteration the Boolean operator is used for modeling to the BNNT, as it allows modifying the solid model construction more easily. Boolean operation, which applies only to cases in which the intersection between entities occurs at a boundary. The entities maintain their individuality, i.e., they are not added and become connected at their intersection. The element type used in this analysis is SOLID 64. SOLID 64 is used for 3D modeling of anisotropic solid structures. This element is defined by eight nodes having 3 degrees of freedom at each node. The FEM model of the cantilevered SWBNNT using present modeling approach is shown in Fig. 1(b). Further, this study explores frequency variation caused by changes in the SWBNNT dimensions, in terms of change in length, and also additions of different masses at the free end of the boron nitride nanotube (Fig. 2(a)).

4. Results and Discussions

In this paper, the FEM simulation of vibrational response of models of SWBNNTs is carried out by considering as a thin walled tube of outer diameter 0.8 nm, having attached mass at free end, with variation in lengths ($L= 6, 8, \text{ and } 10 \text{ nm}$). As indicated in Fig. 3, it is expected that the effective wall thickness of a continuous nanotube must be smaller than the theoretical diameter of boron atom or that of nitrogen atom. A cross section of a real nanotube contains only a limited number of atoms. Under an external load, stresses in the tube are transmitted through these atoms, while in a continuum mechanics model the same stresses are transmitted through the continuous wall area. As a result, the wall thickness must be smaller than the atom diameter; otherwise, the tube equilibrium cannot be maintained. In this sense, calculations using continuum models that apply wall thickness greater than or equal to the diameter of a boron atom or a nitrogen atom can give incorrect results. Considering this, the

effective thickness value used by Vodenitcharova and Zhang [4] for SWCNT is 43.4% of theoretical diameter of a carbon atom (0.142 nm). For finite element 3D model the tube thickness of 0.065 nm, 44% of the average of theoretical diameters of boron atom (0.145 nm) and nitrogen atom (0.150 nm) (measured half of the bond length), is taken for the analysis. The Young's modulus is given by,

$$E = \frac{KL}{\pi Dt} \tag{11}$$

Where K/D is the aspect ratio on SWNT, D is diameter and L is the length of model.

4.1 Vibration Mode Analysis

In this study, the single-walled fixed-free SWNT is modeled using a 3D solid FE model. Before considering the suitability of the modeled SWNT for mass detection applications, it is first necessary to verify the accuracy of the FE model. The FE model, shown in Fig. 2(a), uses the anisotropic element SOLID 64 to simulate the SWNT. The anisotropic material properties of the nanotube material are presented in Appendix A. Table 1 summarizes the theoretical results of the natural frequencies of the fixed-free SWNT for different length and mass attached. From Table 1 and Table 2, it can be seen that the theoretical results and the FEM simulation results are in good agreement. Table 3 summarizes the FEM simulated results of the first resonant frequency of three different SWNTs. The discrepancy between the FEM results and the experimental data is approximately 5–6% and between the different geometries it is 20-23%.

Table 1: (a) Resonant frequency variations to different attached masses for cantilevered SWBNNT for different lengths (6 nm, 8 nm, and 10 nm), using analytical approach based on continuum mechanics.

| (a) | Cantilevered SWBNNT | L=6nm Frequency Hz | L=8nm Frequency Hz | L=10nm Frequency Hz |
|-----|---------------------|------------------------|------------------------|------------------------|
| | 10-4 | 9.22 x 10 ⁹ | 5.97 x 10 ⁹ | 4.26 x 10 ⁹ |
| | 10-3 | 2.94 x 10 ⁹ | 1.91 x 10 ⁹ | 1.36 x 10 ⁹ |
| | 10-2 | 9.29 x 10 ⁸ | 6.03 x 10 ⁸ | 4.32 x 10 ⁸ |

(b) Resonant frequency variations to different attached masses for cantilevered SWBNNT for different lengths (6 nm, 8 nm, and 10 nm), using FEM simulation.

| (b) | Cantilevered SWBNNT | L=6nm Frequency Hz | L=8nm Frequency Hz | L=10nm Frequency Hz |
|-----|---------------------|------------------------|------------------------|------------------------|
| | 10-4 | 8.80 x 10 ⁹ | 4.96 x 10 ⁹ | 2.88 x 10 ⁹ |
| | 10-3 | 1.81 x 10 ⁹ | 8.84 x 10 ⁸ | 7.27 x 10 ⁸ |
| | 10-2 | 3.91 x 10 ⁷ | 2.58 x 10 ⁷ | 2.61 x 10 ⁷ |

Former can likely be attributed to defects of the nanotube material arising from the manufacturing process and later can contribute to the fact of increased mass sensitivity but a decrease in operating frequency. In general, however, the simulation results confirm the validity of the current FE model and indicate its suitability for use in the further investigation of the SWNT as a mass sensor.

Table 2: Resonant frequency variations to different attached masses for H modeled SWBNNT for different lengths (6 nm, 8 nm, and 10 nm), using FEM simulation.

| Fork H model of SWBNNT | L=6nm Frequency Hz | L=8nm Frequency Hz | L=10nm Frequency Hz |
|------------------------|--------------------|--------------------|---------------------|
| 10-4 | 5.83x 108 | 3.17x 108 | 2.46x 108 |
| 10-3 | 1.38 x 108 | 0.74x 108 | 9.12x 108 |
| 10-2 | 6.02x 107 | 3.97 x 107 | 2.74 x 107 |

4.2 Mass sensor mode analysis

In this section, a tip mass in the form of a nano-scale particle is attached to the fixed-free SWNT H model and the behavior of the nanotube investigated by means of FEM analysis. The dimensions of the SWNT are as follows: thickness .065 nm, outer radius .8 nm, and length 10 nm. The equivalent spring constant obtained theoretically from Eq. of Equivalent stiffness is 9.391×10^{-4} N/m, while the value obtained from FEM analysis is 9.467×10^{-4} N/m. Hence, it can be seen that these two approaches provide similar results. Table 1 summarizes the results for the resonant frequency of a fixed-free SWNT with different attached masses obtained theoretically and numerically. The results indicate that the modeled fixed free mass sensor has a sensitivity of 10^{-21} g/Hz whereas in case of cantilevered beam it is 10^{-22} g/Hz.

In previous studies, Li and Chou [5] conducted the FEM simulations for SWCNTs in which sensitivity comes out to be 10^{-21} g/Hz. And also [7], authors obtained accurate predictions of the mass effect of quartz crystal microbalance (QCM) and surface acoustic wave (SAW) sensors more with experimentation rather than using commercial FEM software but later it came into play. However, these studies adopted experimental approaches, which are inherently time consuming and expensive. It was shown [6] that compared to piezoelectric sensors, nanotubes provide an enhanced precision. These findings are consistent with those of a previous study [6] and compare favorably with the sensitivity of a SAW device of just 10^{-10} g/Hz under a 20 MHz operation resonant frequency.

5. Concluding Remarks

The potentials of cantilevered single walled BNNTs and H model as nano mechanical resonators are investigated based on FEM model and continuum mechanics approach. The relation between resonant frequencies of a BNNT based nano mechanical resonator and attached mass is established for fixed-free end constraint. The overall analysis is summarized as follows:

1. More flexible cantilevered SWBNNT based nano mechanical resonators compared to SWCNT can be achieved with advantages of biosafety and biocompatibility.
2. The mass sensitivity of cantilevered SWBNNT based Nano mechanical resonators increases when smaller sized Nano tube resonators are used in mass sensors.
3. The FEM simulation results and the trend are found to be in good agreement with present analytical method that confirms the validity of the current FE model and indicates its suitability for use in the further investigation of the SWBNNT as a mass sensor.
4. The mass sensitivity of SWBNNT can reach up to 10^{-22} g for cantilevered beam.
5. The mass sensitivity of SWBNNT can reach up to 10^{-21} g for H model configuration. By this, the air gap between the resonator when arranged in stacks and blocks like structure.

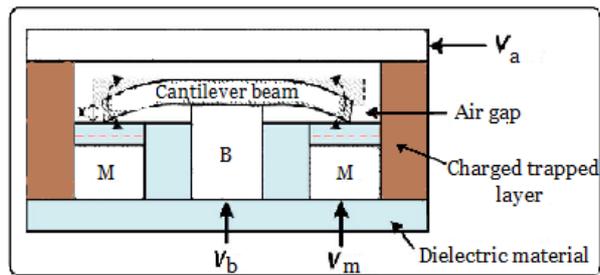


Fig. 3: Visualization of modeled beam in memory cell applications.

Appendix A: Stiffness Coefficients for Anisotropic Material Behavior of SWBNNT

| (Stiffness x 10^9 N/m ²) | | Nomenclature |
|--|--------|--|
| C ₁₁ | 1376.3 | σ_r =Radial stress |
| C ₁₂ | 16.308 | σ_θ =Circumferential (tangential) stress |
| C ₁₃ | 487.4 | σ_z =Longitudinal (axial) stress |
| C ₁₄ | 0 | $\tau_{\theta z}$ =Shear stress in z- θ plane |
| C ₁₅ | 0 | τ_{rz} =Shear stress in r-zplane |
| C ₁₆ | 0 | $\tau_{r\theta}$ =Shear stress in r- θ plane |
| C ₂₂ | 0 | ϵ_r =Normal strain in radial direction |
| C ₂₃ | 30.285 | ϵ_θ =Normal strain in circumferential (tangential) direction |
| C ₂₄ | 16.308 | |
| C ₂₅ | 0 | ϵ_z =Normal strain in longitudinal (axial) direction |
| C ₂₆ | 0 | |

| | | |
|----------|--------|--|
| C_{33} | 0 | $\gamma_{\theta z}$ = Shear strain in z- θ plane γ_{rz} = Shear strain in r-zplane $\gamma_{r\theta}$ = Shear strain in r- θ plane C_{ij} = Stiffness coefficients |
| C_{34} | 1376.3 | |
| C_{35} | 0 | |
| C_{36} | 0 | |
| C_{44} | 0 | |
| C_{45} | 14.87 | |
| C_{46} | 0 | |
| C_{55} | 0 | |
| C_{56} | 0 | |
| C_{66} | 444.4 | |
| | 0 | |
| | 14.87 | |

$$\rho = 2180 \text{ kg/m}^3$$

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