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Detection of gas atoms via vibration of graphenes

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ABSTRACT

The application of single-layered graphene sheets as mass sensors in detection of noble gases via a vibration analysis of graphenes is investigated using molecular dynamics simulations. An index based on frequency shifts of the graphenes attached by the distinct noble gas atoms is defined and examined to measure the sensitivity of the sensors. The dependence of number and location of gas atoms, size of graphene sheets, and type of restrained boundary of the sheets on the sensitivity is particularly studied. The simulation results indicate the resolution of a mass sensor made of a square graphene sheet with a size of 10 nm can achieve an order of 10^{-6} femtograms and the mass sensitivity can be enhanced with a decrease in sizes of graphenes.

Sensors for detection of gaseous molecules play significant roles in environmental monitoring, chemical process control, and biomedical applications. Mechanical resonators are widely used as inertial balances to detect small quantities of adsorbed mass through shifts in oscillation frequency. New classes of sensors were developed after the discovery of fullerene [1] and carbon nanotubes (CNTs) [2]. Electronic sensors made of fullerene were found to be very sensitive to adsorb molecules [3]. Electron transport through CNT was influenced by the functionalization of CNT walls, and thus by controlling the defect sites one can enhance the sensor sensitivity [4]. Recent discovery of graphene sheets (GSs) [5] has opened a new area that promises ultra-sensitive sensors. A GS is a potential candidate of an excellent atomic and molecular sensor owing to its 2D structure. Its entire volume is exposed to its surroundings and hence it becomes a potential candidate for detection of adsorbed molecules. High electrical conductivity and low noise are also superior properties of graphene sheets that make the electrical resistance detectable [6]. It has been reported that the detectable mass can be as small as several femtograms (fg) by using micro-silicon or silicon nitride cantilevers [7,8]. If the resonators are scaled down to nanosize, the mass sensitivity of the resulting nanosensors can surely be enhanced.

One of the main goals in the burgeoning field of nanotechnology is to design a mass spectrometer that is able to fulfill a detection of atoms or molecules. In general, the principle of mass detection using a nanostructures-based resonator from a vibration analysis is based on the fact that atoms attached on the sensor would induce a recognizable decrease in resonant frequencies of the resonator. The key challenge in mass detection is thus to identify the decrease in the resonant frequencies with a sufficiently high resolution. The idea of using CNTs as nanobalances with a high sensitivity was proposed by Poncharal et al. [9]. Static and dynamic mechanical deflections were electrically induced in cantilevered multi-walled CNTs (MWCNTs) in a transmission electron microscope. The methods were developed to apply to a nanobalance for detection of nanoscopic particles and a Kelvin probe. Mateiu et al. [10] reported an approach for designing a mass sensor based on MWCNTs. The resonant frequencies and mode shapes of a fixed-free SWCNT-based mass sensors were studied analytically and via continuum mechanics-based finite element method (FEM) simulations by using a beam-bending model [11]. Molecular structural mechanics was implemented by Sakhaee-Pour et al. [12] to model the vibrational behavior of mass sensors and atomistic dust detectors made of defect-free single-layered graphene sheets (SLGSs). Chiu et al. [13] realized atomic scale mass sensing using doubly clamped suspended CNT nanomechanical resonators. They employed the shifts in the resonance frequency of the nanotubes to sense and determine the inertial mass of atoms as well as the mass of the nanotube. Li et al. employed [14] a molecular structure mechanics method to investigate the dynamic properties of CNT-based mass and strain sensors. The potential of SWCNTs as mass sensors was examined using a continuum mechanics-based approach [15]. Georgantzinos and Anifantis [16] utilized a spring–mass-based finite element formulation for predicting the vibrational behavior of single- and multi-walled CNTs to investigate their sensing characteristics when a nanoparticle is attached to

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them. The mechanical responses of SWCNTs-based nanomechanical sensors modeled as thin shells were studied using FEM [17]. The resonant frequency shift of SWCNTs caused by the changes in sizes of CNT was investigated. A frequency equation of CNT-based cantilever sensor with an attached mass was derived analytically using nonlocal elasticity theory by Lee et al. [18]. They included influence of attached mass in equations to promote the potential of CNTs in atomic mass detection. Most previous research works have modeled CNT-based mass sensors with predetermined locations of attached masses. In addition, the applicability and validity of the continuum theories employed in revealing the vibrational characteristic of CNTs and GSs were not justified. Molecular dynamics (MD) simulations are playing an increasingly important role in many areas of science and engineering, from biology and pharmacy to nanoelectronics and structural materials. Recent breakthroughs in methodologies and in the development of interatomic potentials [19] significantly increase the applicability of MD for new materials in nanoscience and nanotechnology. To the authors' knowledge, MD simulations have not been employed in investigating the feasibility of applying nanostructures as mass sensors. Furthermore, the resolution of a detection method of a sufficiently large number of distinct gas atoms randomly attached on nanostructures has not been investigated thoroughly.

This Letter aims to study the vibrational properties of SLGSs by use of MD simulations to evaluate the applicability of graphene mass sensors. An index representing the mass sensitivity based on the frequency shifts of the graphene sensors attached by five noble gas atoms, i.e. Helium (He), Neon (Ne), Argon (Ar), Krypton (Kr), Xeon (Xe), is defined and examined. The effects of sheet sizes, boundary condition of graphenes and number and locations of noble atoms on the mass sensitivity of graphene sensors are studied.

Molecular dynamics simulation is a powerful method to analyze nanoscale systems by solving Newtonian equations of motion governed by interatomic interactions to numerically determine the trajectories of a large number of atoms. For the interaction potential, the second-generation reactive empirical bond order (REBO) potential energy expression for hydrocarbons developed by Brenner et al. [19] is adopted to simulate SLGSs. In the second-generation REBO potential, the total potential energy of the system is given by

$$E_{\mathrm{REBO}} = \sum_{i} \sum_{j=i+1} \left[E_R(r_{ij}) - \bar{b}_{ij} E_A(r_{ij}) \right] \tag{1}$$

where r_{ij} is the distance between the pairs of adjacent atoms i and j, and $\bar{b}_{ij}$ is a many-bond empirical bond-order term. A velocity-Verlet algorithm is used to integrate the equations of motion and an incremental time step of 1 fs is employed to guarantee good conservation of temperature. The Nose–Hoover feedback thermostat [20] is employed for system temperature conversion at 300 K. Four layers of carbon atoms are fixed to simulate a clamped boundary condition at graphene edges. The noble gases, i.e., Helium, Neon, Argon, Krypton, Xenon, with very low chemical reactivity, are considered as attached masses. As the resonant frequency of GSs is in an order of THz, it is naturally presumed that a vibration signal of the nanostructure of the GSs with the attached atoms contains enough spectrum information by considering the inertia effects of noble gases. A GS is initially deformed to a shape that is close to the mode shape of the resonant frequency, mostly the first mode shape, by manually manipulating the coordinates of carbon atoms of the sheets. After the atoms at all edges of a GS are fixed to simulate the appropriate boundary conditions, the GS is allowed to vibrate freely. The trajectories of an atoms at the center of the GS are recorded for a certain periods of the vibration signal (normally 5–30 ps depending on the size and the boundary conditions of the GS), and then the vibration frequencies are obtained by using the Fast Fourier Transform (FFT) method. The MD simulation method has been verified for free vibration of GSs in Refs. [21,22].

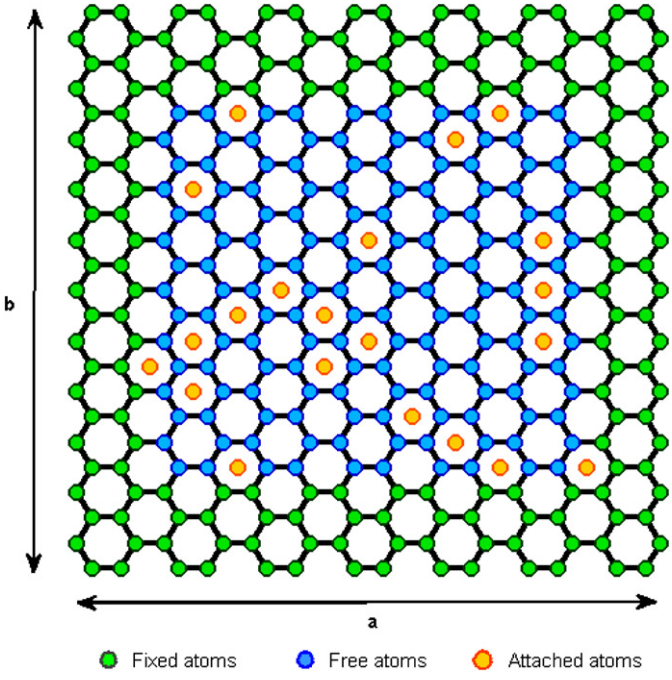

Fig. 1. A single-layered graphene sheet-based mass sensor.

To evaluate the effectiveness and efficiency of a graphene sensor, an index representing the mass sensitivity is defined to be $100\frac{f_0 - f_{\mathrm{mass}}}{f_0}$ using the calculations of the frequency shift in the graphene attached by gas atoms. In the definition, f_{mass} and f_0 are respectively resonant frequencies of a GS with and without attached masses. The index presents the percentage of the frequency shift caused by attached masses. In calculations, the atoms are located on graphene sheets by a random way, as shown in Fig. 1. Two types of boundary conditions, i.e., all edges clamped (CCCC) and two parallel edges clamped and the other two free (CFCF), are employed in simulations.

We first investigate the feasibility of continuum mechanics principle in providing a possible model for the sensitivity index. Based on a general elastic plate model, the resonant frequency of an SLGS is proportional to $\sqrt{\frac{1}{\rho}}$, where ρ is the mass density. The mass density of a pristine GS and a GS attached by gas atoms are respectively assumed to be $\rho_0 = 2250\ \mathrm{kg/m^3}$ [23] and $\rho_{\mathrm{mass}} = \rho_0 + \frac{M_{\mathrm{atoms}}}{Ah}$, where M_{atoms} and A are total mass of gas atoms on the GS and the area of the GS. The mass sensitivity can thus be obtained as $100(1 - \sqrt{\frac{\rho_0}{\rho_{\mathrm{mass}}}})$ from the continuum mechanics principle. From the principle, the values of the mass sensitivity of a square SLGS with a size of 2.46 nm and simply supported boundary condition attached by 20 and 30 Xe atoms are thus obtained to be 27% and 35%, respectively. On the other hand, these values are found to be 20% and 31% respectively from MD simulations. An error up to 33% is obtained from continuum mechanics for the determination of the sensitivity. In addition to the error caused by the continuum mechanics, the effects of the boundary condition of a graphene and the distribution of atoms on the graphene are hard to be evaluated from an explicit expression for the sensitivity calculation. Therefore, MD simulations are only conducted in the research.

A square GS with a length of 2.46 nm and the CCCC boundary condition is first investigated to study the mass sensitivity index.