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# Mechanical response of hydrogen-filled single-walled carbon nanotubes under torsion

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ABSTRACT

Molecular dynamics simulations are performed to investigate the torsional buckling behavior of single-walled carbon nanotubes (SWCNTs) filled with hydrogen gas. The simulation model accounts for both the mechanical deformation of the SWCNT and the interactions among the hydrogen and carbon atoms. It is found that the critical torsional moment and stiffness of the SWCNT are both significantly dependent on the hydrogen molecule storage density. Importantly, the change in torsional stiffness differs from that of conventional linear elastic materials as a result of the nonlinear oscillatory response due to nonlinear mechanical effects. It is shown that under large deformations, the SWCNT switches reversibly between different morphological patterns. Each change in pattern corresponds to an abrupt release of the strain energy and a singularity in the stress–strain curve. It is shown that at higher hydrogen storage densities, the hydrogen molecules exert a stabilizing effect on the SWCNT. The degree of torsional stability is determined principally by the distribution of the hydrogen molecules within the SWCNT. Finally, it is shown that the torsional deformation of the SWCNT is characterized by a stick-slip phenomenon.


## 1. Introduction

Carbon nanotubes have many favorable properties, including a high elastic modulus, a high yield strength, high porosity and excellent resilience. As a result, they are ideally suited to the construction of nano-electro-mechanical (NEM) systems [1,2]. Dillon et al. [3] examined the hydrogen adsorption properties of single-walled carbon nanotubes (SWCNTs) and concluded that they provide a highly promising solution for hydrogen storage applications. Farida and Dominique [4] performed Monte Carlo (MC) simulations to investigate the hydrogen adsorption behavior of open CNTs at various temperatures and pressures. The simulation results were then used to determine the optimal CNT diameter for hydrogen storage purposes. Ebbesen et al. [5] showed that CNTs have an upper internal storage pressure limit when storing hydrogen. The deformation behavior of CNTs has been the subject of many experimental, molecular dynamics (MD) and elastic continuum modeling studies. Treacy et al. [6] examined the thermally-induced vibration of cantilevered multi-walled carbon nanotube (MWCNT) within a transmission electron microscope (TEM) and obtained a mean value for the Young's modulus of 1.8 TPa. Most experimental investigations into the bending of SWCNTs or MWCNTs assume that the bending stiffness, EI, is given by the classical

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formula. However, this assumption neglects the structural features of the nanotube, such as the nested tube structure in MWCNT, the surface sorption embrittlement effect, and the single atomic layer properties of the tube walls. Yakobson et al. [7] examined the buckling phenomena of armchair nanotubes under different loadings using the Brenner potential. However, the real effects of the internal pressure generated by hydrogen storage were not considered during the torsion process. Zhang and Shen [8] performed MD simulations based on the Brenner and Lennard-Jones potentials to examine the buckling and postbuckling behaviors of SWCNT subjected to axial compression, torsion and external pressure. Ru [9] used a classical continuum shell model to examine the free vibration and infinitesimal buckling of SWCNTs and MWCNTs under axial compression. Chen et al. [10] utilized continuum mechanics models to investigate the hydrogen storage properties of both single SWCNTs/MWCNTs and SWCNT/MWCNT bundles.

In examining the hydrogen storage problem in narrow CNTs, two phenomena are of particular interest, namely the flexibility of the wall and the local sorption stress concentration. According to conventional physisorption principles, the gas-adsorption performance of a porous solid is maximized when the pores are no larger than a few molecular diameters since, under these conditions, the potential fields produced at the wall overlap to produce a stronger interaction force than that which occurs in adsorption on a simple plane [11]. However, the mechanisms responsible for the adsorption and interaction of hydrogen molecules on nanoporous solids are not easily observed using direct experimental methods. As a result, MD or MC simulations have emerged as the method of choice for examining the nanofluidic properties of liquids and gases within nanoporous materials [13,14]. Several groups have performed numerical simulations of the adsorption of water in CNTs [15–20], while others have investigated the diffusion of pure hydrocarbon gases and their mixtures through SWCNTs [21–23], or have examined the self- and transport-diffusion coefficients of inert gases, hydrogen and methane in infinitely-long SWCNTs [24,25]. In general, the results showed that the transport rate in nanotubes is several orders of magnitude higher than that in zeolites or other microporous crystalline solids. In addition, it has been shown that the dynamic flow of helium and argon atoms through SWCNTs is highly dependent on the temperature of the nanotube wall surface [26]. Specifically, the flow rate increases with an increasing temperature due to an enhanced thermal activation effect. Previous MD simulations of the nanofluidic properties of liquids and gases generally assumed the nanoporous material to have a rigid structure. However, nanoporous materials are not in fact truly rigid. Thus, the numerical results for the tube wall atom vibration, long-wavelength phonon transport and inner gas diffusion coefficient, for example, may deviate from the true values by several orders of magnitude. Several researchers have investigated the conditions under which the assumption of a rigid lattice is, or is not, reasonable [27,28]. In general, the results showed that while the use of a rigid lattice is acceptable when modeling the nanofluidic properties of gases or liquids in an unconfined condition, a flexible lattice assumption is required when considering fluids within a constrained channel. Moreover, in real-world situations, the thermal fluctuations of the CNT wall atoms affect the diffusive behavior of the adsorbed molecules, and must therefore be taken into account; particularly when the tube is subject to external loading associate with deformation.

The present study performs a series of MD simulations to investigate the torsional behavior of SWCNTs filled with hydrogen gas. The simulations consider a narrow SWCNT with a diameter of 10.8 Å (~1 nm), a temperature of 77 K, and hydrogen storage densities of 0.01–1.0 molecules/nm. To ensure the validity of the numerical results, the simulation model assumes that the SWCNT has a flexible wall and that the hydrogen molecules (treated as spherical particles) exert an internal pressure on the nanotube walls. The purpose of the simulations is to establish a simple nanomechanics model of the hydrogen storage phenomenon in CNTs. In addition, the interactions between the hydrogen molecules and the CNT wall atoms, and among the carbon atoms within the CNT wall, are modeled using the Lennard-Jones potential [29,30] extended to the many-body regime [31,32]. Notably, the simulations focus on the adsorption of the hydrogen molecules within the hollow interior of the SWCNT rather than in the interstices [33] or on the external surface of nanotube bundles [34] As in previous studies [35–38], the simulations focus

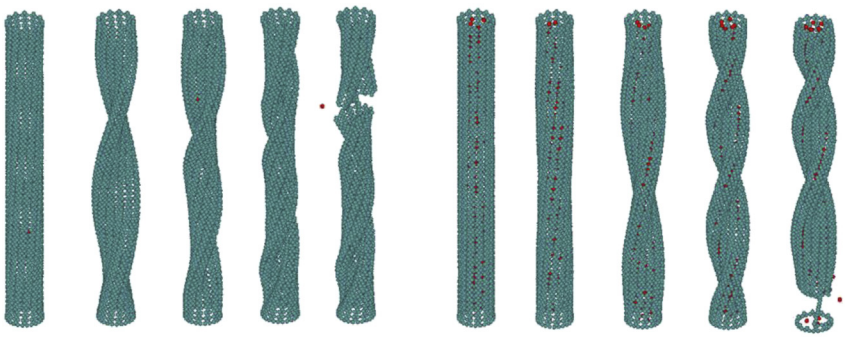


**Fig. 1 – Morphological changes of nanotube under torsion given hydrogen storage densities of: (a) 0.01 molecules/nm, and (b) 1.0 molecules/nm.**