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A molecular dynamics study on the impact of defects and functionalization on the Young modulus of boron–nitride nanotubes

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ABSTRACT

In this article, we examine the Young modulus of $(6, m)$ boron–nitride nanotubes with vacancy and functionalization defects. We employ molecular dynamics simulations using the Parrinello–Rahman approach. To this end, all systems are modeled with a reactive many-body bond order Tersoff potential with parameters due to Matsunaga et al. [K. Matsunaga, Y. Iwamoto, Molecular dynamics study of atomic structure and diffusion behavior in amorphous silicon nitride containing boron, Journal of American Ceramics Society 84(10) (2001) 2213–2219], which is able to accurately describe covalent bonding. We apply external stress to periodically repeated tubes in vacuum and derive stress–strain curves for various tensile loads at standard temperature and pressure. In addition to the Young modulus, we study visualized stress-per-atom snapshots of the simulation runs. Our results show that the decrease in Young modulus with increasing defect concentration is independent of the chirality of the tube for vacancy defects. Also, we observe that functionalization does not weaken the tube. There is even indication of a relative strengthening for armchair types.

1. Introduction

Nanotubes have attracted a lot of attention in the last decade due to their intriguing structural properties. Besides the well-known tubular structures made of carbon, there are now nanotubes made of a range of other materials. In particular, single- and multi-wall boron–nitride nanotubes (BN) can be produced with diameters comparable to those of carbon nanotubes, see [2] for an overview and references. Experimental studies [3] and semi-empirical calculations [4] show that BN nanotubes (BNNT) display a high Young modulus comparable at least to that of carbon nanotubes (CNT).

The stability at high temperature in air [5] and the high tensile strength of boron–nitride nanotubes suggest to use them for structural reinforcement of matrix materials. To this end, a functionalization of the embedded nanotube is essential to allow for cross-links to form between the nanotube and the ceramic material [6]. It has recently been shown that such a functionalization of the boron–nitride nanotube is possible with amine groups via ammonia plasma irradiation [7]. One question at hand is how this additional layer of nitrogen atoms or amine groups on the surface of the boron–nitride nanotube effects the tensile strength of the nanotube.

Additionally, defects play a critical role in fracture processes as they are always present, also in compound materials. Hence, measuring the strength of pristine material investigates only the possible upper limit of the Young modulus and the Poisson ratio, but not the magnitude encountered in real-life materials. These defects appear in a variety of forms: while single vacancy sites lead to point defects, line and layer defects are one- and two-dimensional defects typically found in periodic crystalline bulk materials. In nanotubes and related nanostructures these defects are compensated by specific patterns.

In this article, we investigate two types of scenarios that may weaken the tensile strength of a boron nitride nanotube: vacancy defects on the one hand and functionalization on the other hand. So far, Schmidt et al. [8] have studied various defects in BN nanotubes such as antisites, vacancies and carbon impurities, however not with regard to the Young modulus. Now, we investigate whether there is a diameter-dependent weakening of the nanotube. Furthermore, we are interested if the relation between the Young modulus and the defect concentration depends on the chirality of the tube.

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To this end, we derive stress–strain curves of $(6,m)$ boron nitride nanotubes with vacancy defects and different degrees of functionalization by means of molecular dynamics simulations. We use standard temperature and pressure in the framework of the NPT-ensemble, similar to [9]. Note that we restrict ourselves to the study of diameter-dependent, not size-dependent effects, i.e. we fix the chirality number $n = 6$. The impact of a varying number n on the mechanical properties of nanotubes with intrinsic defects has already been studied elsewhere [10]. To model BNNTs, we use the Tersoff bond order potential [11], which is able to describe covalent bonding in an accurate way. We apply an external stress tensor within the equations of motion of the Parrinello–Rahman–Nosé Lagrangian [12] to account for tensile loads. To model defects, we randomly remove a fixed number of atoms from the nanotube structure, whereas to model functionalization, we add a fixed number of nitrogen atoms on the surface of the nanotube structure at randomly picked boron sites. To investigate the impact of defects and functionalization on the Young modulus of BNNTs, we measure the stress–strain curve and derive the Young modulus for various setups with different chiralities for increasing defect concentrations and increasing degree of functionalization, respectively.

For carbon nanostructures Stone and Wales [13] proposed a 5–7-translation pattern for the compensation of defects. There, a C–C bond rotates in plane by 90°. In such a manner a doublet of adjacent pentagon/heptagon pairs is formed out of four connected hexagons (Stone–Wales defect). It has been shown that for carbon nanotubes under stress this kind of defect occurs prominently shortly before failure. Haskins et al. [14] give a very good overview on the findings for carbon nanotubes. One may speculate that this process is different for boron–nitride nanotubes due to the antagonism of the two involved elements to form homo-elemental bonds [15]. It has been shown by density functional theory calculations that these 5–7-defects may form under high temperature and tensile stress [16]. However, there is also experimental evidence in [17] and numerical evidence in [18] speaking against the formation of pentagon/heptagon rings. Instead, quadragon/octagon rings are suggested. These however do require greater lattice distortions [16].

With our employed potential we investigate whether excluding or including homo-elemental bonds is important. In the first case there is only a repulsive force between two equal elements of either boron or nitride as, according to [1], they are not found in SiBN matrices. Here, we do not see any difference with the employed potential, whether we exclude or include homo-elemental bonds. This suggests that either the potential is not suitable for the simulation of Stone–Wales-defects – where homo-elemental bonds are present – or that these simply are not yet a relevant stress-relief scheme for defective nanotubes under initial strain, i.e. the nanotube cannot reduce site-specific stress by flipping bonds near the defect site in the aforementioned procedure under initial loading. We believe that the latter is the case and therefore Stone–Wales-defects are not considered here.

This article is organized as follows. In Section 2, we outline the employed molecular dynamics method, the many-body potential and the stress–strain relationship. In Section 3, we explain the experimental setup. The results are presented and discussed in Section 4. Finally, we give some concluding remarks in Section 5.

2. Method

All simulations are performed with our parallel software package TREMOLO, for further details see [19] and the references cited therein. Hence, in this section we only elaborate on the specifics of the employed canonical ensemble and its respective Hamiltonian and on how we obtain the Young modulus from the stress–strain relationship.

2.1. Molecular dynamics simulations

To switch from the usual Hamiltonian adapted to microcanonical NVE ensembles – i.e. constant number of particles (N), constant volume (V) and constant energy (E) –

$$\mathscr{H} = \frac{1}{2}\sum_{i=1}^{N} \frac{\vec{p}_{\vec{x}_i}^{T}\vec{p}_{\vec{x}_i}}{m_i} + U(\vec{x}_1,\ldots,\vec{x}_N) \tag{1}$$

to that for canonical NPT ensembles – i.e. constant number of particles (N), constant pressure (P) and constant temperature (T) – additional degrees of freedom have to be introduced according to Parrinello and Rahman [12]: we need a time-dependent matrix $\hat{h}$ which consists of the basis vectors of the simulation cell to re-scale the coordinates $\hat{\vec{s}}_i = \hat{h}^{-1}\vec{x}_i$, and a factor γ to re-scale the time $\bar{t} = \int_0^t \gamma(\tau)d\tau$ and thus also the velocities $\dot{\vec{x}}_i(\bar{t}) = \gamma\hat{h}\dot{\hat{\vec{s}}}_i(t)$. This way, there are nine degrees of freedom to control the pressure and one degree of freedom to control the temperature. We define the fictitious potentials $P_{\text{ext}} \det \hat{h}$ and $N_f k_B T \ln\gamma$ through the external pressure P_{ext} and the target temperature T, the system's number of degrees of freedom N_f and Boltzmann's constant k_B. Now, a so-called Parrinello–Rahman–Nosé Lagrangian can be postulated and an extended Hamiltonian

$$\begin{aligned}\mathscr{H} = \frac{1}{2}\sum_{i=1}^{N} \frac{\vec{p}_{\vec{s}_i}^{T} G \vec{p}_{\vec{s}_i}}{m_i} + \frac{1}{2}\frac{\operatorname{tr}(p_h^T p_h)}{M_P} + \frac{1}{2}\frac{p_\eta^2}{M_T} + U(h, h\vec{s}_1,\ldots,h\vec{s}_N) \\ + P_{\text{ext}} \det h + N_f k_b T\eta \end{aligned} \tag{2}$$

can be derived, where $\eta := \ln\gamma(\bar{t}), \vec{s}_i(t) := \hat{\vec{s}}_i(\bar{t}), h(t) := \hat{h}(\bar{t}), G := h^T h$ and the constants M_P and M_T describe fictitious masses to control the time-scale of motion of the cell h and of the temperature. For details see [6], the references therein and the work of Nosé [20]. Note that there is an explicit dependency of V on the matrix h in the case of periodic boundary conditions, since atoms do not only interact with neighbors in the cell but also with those in translated images.

For the numerical solution of the equations of motion arising from (2) we have to employ a time-integration scheme. We use the “predictor–corrector” scheme based on Beeman's approach [21] with the modifications due to Refson [22].

Finally note that the physical energy $E_{\text{kin}} + U$ contained in (2) is not conserved in the NPT-ensemble, but the whole Hamiltonian (2), i.e. the sum of the physical energy, of the fictitious energy of the barostat and of the fictitious energy of the thermostat, remains constant over time.

2.2. Potential for boron and nitrogen

There are different empirical potential models available for covalent B–N systems, like the bond order potential of Tersoff [11] or the potential model of Marian and Gastreich [23]. In this work, we employ a Tersoff potential with the parameters of Matsunaga and Iwamoto [1] where the potential parameters were fitted to data obtained from experiments and first principle methods. In particular, computed structural and elastic properties for various Si–B–N systems are in reasonable agreement with experimental results [1,24]. Note that for the potential given in [1], the possibility of the formation of homo-elemental bonds between either boron or nitrogen is specifically excluded by modeling only a repulsive force, as these bonds are not seen in SiBN matrices. In contrast to that, i.e. to consider the effect of homo-elemental bonds as well, we adapt the potential of [1] to deal with B–B and N–N bonds, i.e. we include the corresponding attractive potential terms.