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Carbon nanotube-carbyne composite: A nanoreactor in a quasi-1D liquid state

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ABSTRACT

It has recently been shown by Shi et al. that incredibly long carbyne chains up to 6000 atoms can be grown experimentally inside double walled carbon nanotube nanoreactors. The nanotubes stabilize these carbyne chains. Of course, carbon nanotubes themselves have remarkable properties including high temperature stability, and remarkable strength for weight. We have used reliable *ab initio* density functional theory molecular dynamics calculations to study the high temperature behavior and initial stages of melting of carbyne chains, carbon nanotubes, C_{60}, and carbon nanotube-carbyne composites between 3000 and 5000 K. We find that the carbon nanotubes stabilize internal carbyne 1D chains and act as nanoreactors. Included molecular dynamics movies reveal carbyne chains in a quasi-1D liquid state inside the nanotube, a quasi-2D liquid state, and early melting.

1. Introduction

It has recently been shown by Shi et al. that incredibly long carbyne chains up to 6000 atoms can be grown experimentally inside double-walled carbon nanotubes [1]. This is a striking example of the use of carbon nanotubes as a nanoreactor. This is much longer than any previous carbyne chain. The carbyne chains have remarkable properties, and are stabilized by the nanotubes [1]. The predicted strength, elastic modulus and stiffness of isolated carbyne may be larger than other materials such as diamond, carbon nanotubes and graphene [2]. Under tension, carbyne is about twice as stiff as the stiffest known materials and has an unrivaled specific strength of up to 7.5×10^7 N·m/kg, requiring a force of ~10N to break a single atomic chain. In 2013, Liu et al. calculated a Young's modulus of 33 TPa. Kocsis et al. also studied the stiffness of isolated carbyne [3]. Yang et al. investigated strength of isolated carbyne as a function of temperature computationally [4]. Agwa et al. and Shi et al. have modeled carbyne for use as very sensitive mass sensors [5,6].

The first paper to find carbyne inside multiwall carbon nanotube (experimentally) was in 2003 [7]. Bogana et al. performed molecular dynamics simulations of sp-sp^2 carbon clusters [8]. Cazzanelli et al. and Rusznyak et al. studied chains inside carbon nanotubes [9,10]. Nishide et al. studied chains inside single-walled carbon nanotubes [11]. In 2011, Zhao et al. studied growth of chains inside double-walled carbon nanotubes [12]. In 2015, Cannella et al. the formation of carbyne fiber bundles over a nanosecond time scales from liquid C [13]. Casari et al. reviewed sp-carbon chains in 2016 [14]. Cretu et al. studied the electrical-transport measurements of monatomic carbon chains in 2013 [15].

Carbyne can exist either as double bonded cumulene $(=\!C\!=\!C\!=)_n$, or alternatively as single and triple bonded polyyne $(-C\equiv C-)_n$ [16]. Liu et al. found a transition from cumulene to polyyne at 500 K using molecular dynamics [17]. Yakobson's group also showed in 2014 that carbyne can be changed from a conductor to an insulator by imposing tension (and thereby raising the band gap) [18]. Torre et al. also studied this issue [19]. Pan et al. produced short carbyne segments of 6–8 atoms and measured their experimental properties [20]. They observe spectroscopic evidence of the single and triple bonding in these molecules. They also observe purple-blue fluorescence emissions from the gap between the highest occupied and the lowest unoccupied molecular orbitals. Kotrechko et al. used AFM to experimentally measure the strength of short strands of carbyne [21]. Deng et al. studied the thermal conductivity of carbyne [22]. Lambrodopoulos et al. studied the current-voltage (I-V) characteristics of carbynes with leads attached with DFT [23] and this can compared to the experimental work by Romdhane et al. [24].

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One can also imagine creating new composite materials based on carbyne. Heeg et al. have used Raman scattering to study the electronic properties of carbyne-nanotube composites [25]. Pichler and co-workers used Raman to study the band gaps of these materials and found a range from 2.26 eV for short tubes to 1.84 eV for long tube carbyne composites [26]. Milani et al. reviewed the Raman spectroscopy of sp-carbon in 2015 [27]. Ding et al. created an analytical model for the vibrational properties of these composites [28].

Carbon nanotubes are incredibly strong and lightweight, with many applications [29–32]. It is not clear what the upper temperature limits are for nanotubes and related structures. Zhang et al. predicted a very high melting point of 4800 K for perfect tubes [33]. Tomanek used density functional theory to estimate the melting point at 4000 K. [34] Tomanek also studied the melting of C_{60} and nanotubes [35]. Hedman et al. have calculated the stabilization energy for a wide variety of single-walled nanotubes [29]. In 2015, Los et al. predicted a melting point of 4510 K for graphene [36].

Nanoreactors are a topic of great current interest. A recent 2016 review by Petrosko et al. covers recent developments in this area [37]. These tiny volumes can provide novel and fascinating conditions to control chemical reactions. For example, Zhang et al. recently created a unique phosphorous ring inside a carbon nanotube used as a nanoreactor [38].

Shi et al. used DWCNTs, but due to computational constraints, this system is too large for our accurate theory. Therefore, we were limited to SWCNTs. We used the same inner wall tube to get as close as possible to the experimental results. We found that these SWCNTs and the Carbyne-55 nanotube system were stable for the 8 ps of the simulation.

We have used *ab initio* molecular dynamics calculations to study the high temperature behavior and initial stages of melting of carbyne chains, carbon nanotubes, C_{60}, and carbon nanotube-carbyne composites between 3000 and 5000 K. We find that the carbon nanotubes stabilize internal carbyne 1D chains and act as nanoreactors. Molecular dynamics movies are available online which reveal carbyne chains in a quasi-1D liquid state inside the nanotube, a quasi-2D liquid state, and early melting processes.

2. Computational methods

We used accurate *ab initio* (Born-Oppenheimer) molecular dynamics simulations. The simulation methods were similar to our previous study on graphene [39]. This will allow comparison of the current study to our previous work. The calculations were carried out in Materials Studio 2016. DFT-D and the Tkatchenko–Scheffler (TS) method in CASTEP [40] were used. Periodic boundary conditions were imposed with a generous 8 Å between neighboring atoms in the next cell in the *a* and *b* directions. The nanotubes were periodic and continuous in the *c* direction. Further computational details including unit cells are included in the supplemental information, and in Table 1. Nanotubes were originally created using the TubeGen online program [41]. The constant number, volume, and temperature (NVT) ensemble was used. 3–16 ps runs with a time step of 2 fs were used. Based on our previous experience with molecular dynamics simulations, a 2 fs step size provides accurate calculations, and also maximizes computational efficiency [39].

The first 2–4 ps were run at 3000–4000 K, and then these starting points were extended for an additional 4–12 ps for each of the other temperatures. The 3000 K simulations were started from the optimized 0 K structure, although in one case an expanded unit cell to accommodate the expansion of the system at elevated temperatures was used. For each simulation, an equilibration time of roughly 6 ps was used. The 3D pair correlation function $g(r)$ was calculated, with N (total number of atoms), ρ (atomic density), and δ (delta function).

$$g(r) = \frac{1}{4\pi r^2 \rho N} \left\langle \sum_{i} \sum_{j \neq i} \delta(r - r_{ij}) \right\rangle \tag{1}$$

3. Results

We used molecular dynamics simulations to study the high temperature properties of a wide variety of C_{60}, carbon nanotube, and carbyne systems. We discuss each system in detail below and compare the results. Finally, we will discuss the properties of the carbyne-nanotube composite as a nanoreactor.

3.1. C_{60}

We start with the results of annealing C_{60} at 4000 and 5000 K. C_{60} is a relatively small molecule, with more curvature than the carbon nanotubes. We start with this system as an easy comparison to the properties of nanotubes using the same short molecular dynamics simulations At 4000 K, the molecule is vibrating, but maintains the bonding configuration, and no diffusion is observed within 8 ps. At 4500 K, broken bonds are formed temporarily. No diffusion is observed within 8 ps at 4500 K, but the system is in the early stages of melting. One observes occasional 10 rings and 13 rings. However, no diffusion is observed yet, and the bonds return to the original configuration. Raising the temperature to 5000 K, we start to see diffusion events within 12 ps (See Fig. 1a). Therefore, at 5000 K, C_{60} is a “quasi-2D liquid” during the simulation time. Clearly, C_{60} is a 3D molecule, but since the diffusion stays within the molecular framework in a spherical shell, we can consider that the diffusion produces a quasi-2D liquid state in this shell. In Fig. 1b, we show a characteristic 10-ring formed by a temporary broken bond.

3.2. 55 Carbon nanotube

The 55 nanotube is metallic and will be the basis for nanotube carbyne composites. After 10 ps net at 4500 K, the nanotube had not yet started to melt. No diffusion events or substantive defects (other than low energy 3-ring defects) were observed in the last 5 ps (see Fig. 2).

The last frame of the simulation at 5000 K at 6 ps is shown in Fig. 3. The tube is holding together but corrugated with 3-rings and some rings stretching. The 3-rings are temporary low energy excitations and are merely precursors to melting. We also observe some 10-rings (bond breaking of a single bond) during the simulation. We have calculated the relative energy of a fixed 10-ring defect, and find 2.6 eV. This is much smaller than the 3.48 eV result for graphene [39].

In the final frame, we observe a 5775 defect, so the tube is starting to melt after 5 ps at 5000 K. We have discussed the relative energy of these 3-ring and 5775 defects in our previous study on the initial stages of melting in graphene [39]. We have calculated the energy of this 5775 defect when optimized at 0 K. The relative energy is 3.2 eV (compared to the pristine lowest energy state), much smaller than the 4.8 eV calculated for graphene. This lower energy may be due to the fact that the nanotube is already curved and fits the defect more easily, and due to the smaller bond strength compared to graphene We see that the initial melting of the 55 nanotube is similar to the melting of graphene (albeit at somewhat lower temperature for the nanotube).

3.3. Carbon nanotube + 8 atom carbyne chain

We will now discuss the results for a 55 carbon nanotube + carbyne composite. We will start with an 8 atom carbyne chain inside the tube. This chain is short enough that the ends do not meet inside the periodic nanotube. Between 3000 K and 4000 K, we see diffusion events in the 1D chain, but not in the nanotube. An example is shown in Fig. 4. Therefore, the 1D chain is in a quasi-1D liquid state at these