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TEMPERATURE-INDEPENDENT LONGITUDINAL WAVES OBTAINED ON CARBON NANOTUBES WITH SPECIAL EMPHASIS ON THE TUBULAR ION-TRANSPORT

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ABSTRACT. The vibration properties of two representative types of achiral carbon nanotubes were investigated by temperature dependent MDs calculations. The changes of the diameters of SWCNTs in time were calculated using the distances between the two opposite atoms of the nanotube. Periodical changes of diameters of nanotube's cross-section ellipsoid were obtained in picosecond time-scale. Our results show that a longitudinal wave of conformation change travels along the longitudinal axis of the nanotube. A kind of travelling with 20 nm/ps speed pulsation could be observed of the elliptic cross section through a circular instant. This finding corresponds to the transport of ions or molecules in the nanotube, since these particles are preferred to be kept in the symmetric circle cross section of the nanotube.

Keywords: *carbon nanotubes, molecular and ion transport, Molecular Dynamics calculations*

INTRODUCTION

A single-walled carbon nanotube (SWCNT) consists of a graphene sheet rolled up to cylinder. The tubes are several nanometers in diameter and several microns in length. SWCNTs have a fascinating ability to encapsulate atoms, ions and molecules in their one-dimensional nanotube. Nowadays especially the ion [1] and molecule transports [2] in these nanoscale channels have gained increasing attention.

In this way, to optimize the practical performance of SWCNTs, more detailed knowledge about their physical and chemical properties is required, because their special properties, *e.g.* their one-dimensional form, make them highly attractive materials, even so the very complex behaviour of the transport skill hinders their wide-scale application. Our previous work, related to formation-dissociation dynamics of the calixarenes' host-guest complexes [3]

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shows an example that Molecular Dynamics (MDs) calculations are fruitful testing techniques to analyze the dynamic processes of aromatic molecules at molecular level. Accordingly, the vibrational properties of two representative types of carbon nanotubes are investigated by temperature dependent MDs calculations. The (4,4) and (7,0) SWCNTs of similar diameter sizes were studied. Part of the calculations are performed using GAUSSIAN 03 program package and the MDs investigations were carried out with HyperChem Professional 7 program package using MM+ forcefield approximation. The aim of this preliminary investigation was to get information how these vibrations could affect *(i)* the speed of the molecule and ion transport through these nanomaterials and *(ii)* the strength of π-π interaction taking part in the adsorption of packing organic molecules on the surface of carbon nanotubes.

RESULTS AND DISCUSSION

The changes of the diameters of SWCNTs in time were calculated using the distances between the two opposite atoms of the nanotube (Fig. 1). Periodical changes of diameters of nanotube's cross-section ellipsoid were obtained in picosecond time-scale.

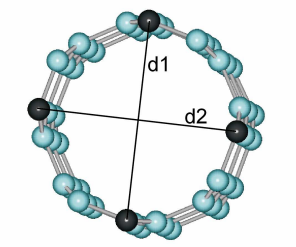

Figure 1. Periodical changes of diameters of nanotube's cross-section ellipsoid were calculated using the distances between the two opposite atoms of the nanotube

These conformation changes also affect the atomic vibrations orthogonal to the nanotube surface (Fig. 2), which property alone could affect the solubilization of nanotubes. One of the possible solubilization processes related to the noncovalent sidewall SWCNT functionalization with aromatic organic molecules [4]. The key features in the solubilization process is the π–π interactions between the aromatic ‘packer’ compounds and the SWCNT [5]. On the one hand the strength of the π–π interactions depends on the size of the aromatic moiety of the packer molecule consideration the curvature of the SWCNT surface and the shapes of the interacting ring systems. However, our results suggest, that packer molecules

of more flexible structure can be attached stronger to the SWCNT, because the periodic changes of nanotube geometry can inhibit the fit of the packer molecules to the nanotube's surface in a wide time scale.

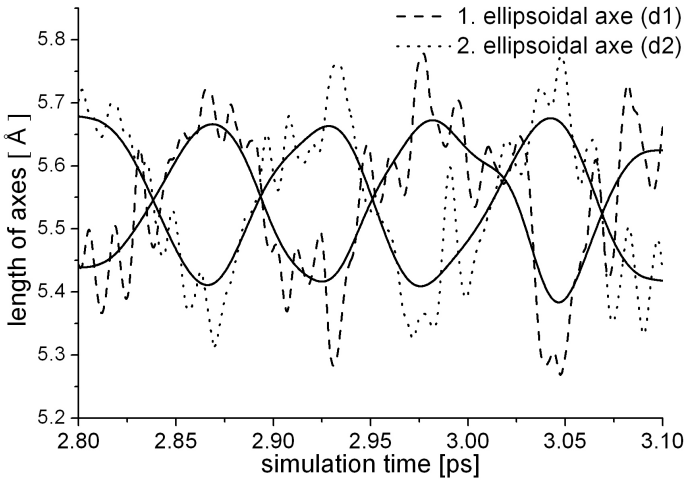

Figure 2. The variation of the d1 and d2 diameters as the function of time

Interestingly, our results show that a longitudinal wave of the conformation change (based on the diameters' changes described above) travels along the longitudinal axis of the nanotube. The speed of this wave can be derived from the two characteristic data of nanotube motion: *i)* from the distance *d* between two ellipsoidal cross sections of nanotube with same orientation and *ii)* from time constant *t* of vibration of the cross section of nanotube. (In other words: *d* reflects the distance that the wave takes until the time constant *t* of vibration of the cross section.) Therefore, the speed of the wave can be derived as the ratio of *d* and the time constant *t*. The speed determined on such way is 20 (±1.2) nm/ps. This speed pulsation seems to be temperature independent in the investigated temperature range (Fig. 3). This finding corresponds to the transport of ions and small ionic and neutral molecules.

The work of Sholl et al. [6] shows that the energy transfer between the nanotubes and the diffusing methane molecules highly affect the diffusion coefficient. Our results highlighted that the energy transfer also depends on the geometry changes of the SWCNT. We have found, that the longitudinal wave of the conformation change travels along the longitudinal axis of the nanotube at the rate of 20 nm/ps. Considering this result together

with the diameter of the investigated SWCNTs, the speed of the investigated wave generated by the diameter changes of SWCNT is about 4.6×10^{-1} cm^2 s^{-1}, which value is in the range of the calculated diffusion coefficients of Sholl et al. [6].

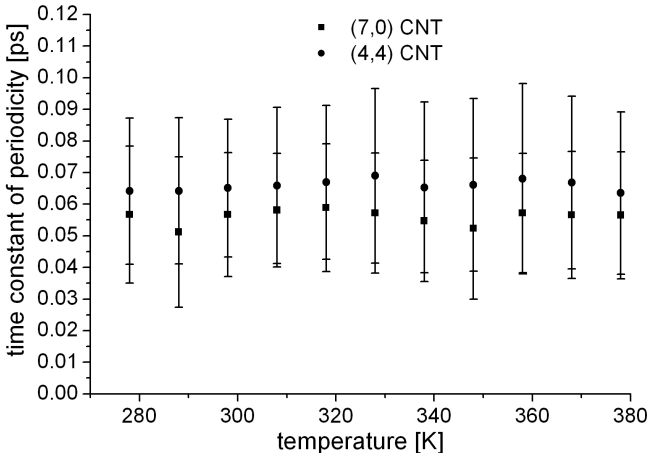

Figure 3. Temperature dependence of the speed of longitudinal waves obtained along the carbon nanotubes

CONCLUSIONS

Nevertheless the two representative types of achiral single-walled carbon nanotubes have more important different physical and chemical properties. It was shown that the investigated semiconductor zigzag (7,0) and metallic armchair (4,4) SWCNTs have no significant difference in their vibration dynamics properties in the studied temperature range of 278-378 K. A longitudinal wave of conformation change travels along the longitudinal axis of the nanotube at a temperature independent speed pulsation of 20 nm/ps in the investigated temperature range. These results support that the pulsation of the nanotube can control the transfer of any kind of particles whose shape fit to an actual conformation of the nanotube wall. As a consequence, the transfer of these particles will be temperature independent in the examined temperature range. This finding might be is applicable to the wide-scale of electrochemical research.

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