Temperature dependence of sorption rates of assorted molecules on carbon nanotubes

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Background
Nanotubes can be grown efficiently by several production methods: Arc-discharge method, chemical vapor deposition, laser ablation (vaporization). The former method used in Prof. Smalley’s group (Rice University) produces primarily single wall carbon nanotubes SWNT with large diameters. By varying the reaction temperature they can control the diameter. This method is, however, rather expensive. The arc discharge method can produce both SWNT and Multi Wall Nanotubes (MWNT). These tubes are short with random sizes and directions.

Recently, Girifalko, Hodak and Lee (2000) have looked at the Van de Waals (VDW) interaction between different graphite materials (C60, NT, etc.). All these interactions fall on the same curve when graphed with respect to certain reduced parameters, suggesting universal graphite potential. The two types of LJ models – continuum and discrete atom – give different results. The total VDW interaction becomes very strong with the increase of the NT length. Because of this effect, the NTs in the samples will orient themselves to be parallel whenever possible therefore forming crystalline ropes (bundles).

It has been reported that computer simulations of hydrogen adsorption on various carbon nanotubes show that the amount adsorbed is very low at room temperature, around 0.1 wt% at 10 atm, and about 0.8 wt% at 100 atm [1]. Even if the geometry of the nanotube array is treated as an adjustable parameter, the amount of hydrogen adsorbed is still quite low [2]. We wonder if this is the case for a molecule like CH4.

In fact, other authors who claimed enormous adsorption of hydrogen [3] have obtained contradicting results to [1,2]. This makes the study important, necessary and expected.

Up to now, in our group (Monte Carlo – computational theoretical physics group at the Depr. of Atomic Physics, University of Sofia) we have computed and analyzed clusters made of various molecules including methane nanoclusters. The methods used were classical Monte Carlo and Molecular dynamics. The computations were performed on PCs. We would like to study the adsorption ability of nanotubes with/without defects.
This a part of an international project (Ben-Gurion University, Universite de Libre de Bruxells, The Cambridge University, the Univesrty of Sofia).

Several models will be checked: molecular dynamics simulation with the Tersoff-Brenner potential. Shared memory techniques should be used in order to obtain reliable results for bundles of NT.

**Aims of the project**

We are interested in the deposition of assorted molecules CH$_4$ (N2, CO2) on the surface of single wall carbon nanotubes (C-SWNT) and consequent penetration. The processes are temperature dependent and the research should be carried in specific temperature limits. ‘The specific’ values could be determined either by the experimental conditions or by the fundamental questions asked in the study.

The minimum temperature determines diffusion process within the tube. The maximum temperature is determined by the fact that CH$_4$ (N2,CO2) needs to be on the surface of the carbon nanotube long enough to find a defect to enter the interior.

The estimation of the rate of adsorption will be based on purely geometrical considerations (hexamer nanotubes) versus pentamer –septamer defects. These will be related to the potential energy surface.

Recently, it has been shown that the electronic properties of SWNTs can be modified by elliptical deformation. The energy gap of an insulating SWNT can decrease and eventually vanish at an insulator-metal transition with increasing applied radial strain (where the circular cross section of the nanotube is distorted to elliptical cross section). More interestingly, the elliptical deformation necessary to induce metalicity was found to be in the elastic range. This could allow the "fine tuning" of the properties of SWNTs via reversible deformation and ultimately lead to variable and reversible quantum devices, such as metal-insulator and rectifying junctions. This feature can be explored by using the predictive power of density functional theory and demonstrate that indeed adsorption of foreign atoms on carbon nanotubes and associated properties can be modified continuously and reversible.

**Tools**

MD simulations on a shared-memory architecture
Parallel DFT for determining the electronic properties of single wall carbon nanotubes.

(SWNT) provide a system where the electronic properties can be controlled by the structure (i.e. radius and the helicity defined by two integers (n,m)) of the nanotubes. It is therefore desirable to have a good understanding of their electronic and mechanical properties and the interrelations between them. In this project, we will study the close relationship between mechanical deformation and the chemical properties of SWNT's from the state-of-the-art first-principles calculations.
Resources
The DFT calculations need a high grid discretization and a large computational box, which requires a large active memory. Parallel LAPACK and BLAS libraries are necessary to implement the parallel DFT.
The geometry optimization and study of absorption process include molecular dynamic simulation with long runs in order to achieve quasi-equilibrium because the process of absorption is non-equilibrium.

Implementation
The results will be used for finding optimal conditions for molecular adsorption. We will try to answer, as well if the nanotubes can be really used as hydrogen containers. This is an important application of the adsorption process.