

# Research on permeability of carbon nanotubes

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**Abstract.** The present paper deals with a geometric object composed of energy sources interacting with test atoms and molecules in a gaseous state. The sources are stationary and they are located in a hexagonal manner on the surface of a circular cylinder. The permeability of the resulting model of a carbon nanotube with respect to helium atoms and hydrogen, oxygen and methane molecules is investigated. Further evaluation of impacts caused by thermal vibrations of the carbon skeleton atoms follows. It is shown, that a carbon nanotube can be used as a support element of a filter for gas mixtures separation.

## 1 Introduction

It is known, that natural gas from wells must be prepared for transportation before it is supplied to the end user. The need for such works is caused by natural gas containing impurities along with target components, which can create difficulties in transportation or use. One of the promising methods to separate natural gas components is the use of carbonic filters, ideally consisting of identically oriented carbon nanotubes [1], the permeability study of which is conveniently carried out using models of dynamic systems. Molecular dynamics methods are widely used in modern research for the purpose of simulating fluid motion in nanochannels [2, 3] and when calculating the diffusion coefficient of nanoparticles [4-7], as well as their interactions with each other [8]. These same methods are used in studying diamond-like phases [9-13] and discrete breathers [14], in analyzing severe plastic deformation of media containing crystal grains [15], as well as in investigating permeability of ultra-thin films in the framework of Newtonian dynamics [16-22] and on the basis of quantum-mechanical models [23, 24]. In this paper we research permeability of an open carboxylic nanotube for molecules and atoms of various substances in a gaseous state. We consider the influence of a tube's length on the motion of molecules in the gas phase, as well as the impact of thermal oscillations of carbon skeleton atoms on permeability of open nano-tubes. In respect of these graphene structures, the internal dynamics of hydrogen, oxygen, helium, and methane molecules is analyzed.

## 2 Numerical model

Studies of the interaction process between a moving molecule and atoms of a carbon nanotube are based on the use of the mathematical model and numerical methods of solution.

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Interaction between individual molecules is determined by the classical Lennard-Jones potential. Interaction with the structure, in turn, is described by the law of action independence as the sum of each structure atom's effect on the test molecule under consideration. According to this law, if a material point is influenced by several forces, it experiences acceleration equal to the geometric sum of the accelerations these forces would cause acting separately.

In projections on the coordinate axis the motion equations of the molecule interacting with the tube can be written as follows:

$$M \frac{dU}{dt} = X', \quad M \frac{dV}{dt} = Y', \quad M \frac{dW}{dt} = Z', \quad \text{here } X' = \sum_{j=1}^{N_p} X'_j, \quad Y' = \sum_{j=1}^{N_p} Y'_j, \quad Z' = \sum_{j=1}^{N_p} Z'_j \quad (1)$$

$M$  is the mass of the molecule,  $X'$ ,  $Y'$ ,  $Z'$  are the projections of the Van der Waals forces resultant from the carbon structure atoms which are defined as simple sums of force contributions from the nodes of the crystalline lattice,  $N_p$  is the number of the nanotube's atoms. Next, we introduce into consideration the values of  $X$ ,  $Y$ ,  $Z$ :  $MX = X'$ ,  $MY = Y'$ ,  $MZ = Z'$ . Then, in the new variables, equations (1) can be rewritten as:

$$\frac{dU}{dt} = X, \quad \frac{dV}{dt} = Y, \quad \frac{dW}{dt} = Z, \quad \text{here } X = \sum_{j=1}^{N_p} a_j \frac{x - x_j^0}{\rho_j}, \quad Y = \sum_{j=1}^{N_p} a_j \frac{y - y_j^0}{\rho_j}, \quad Z = \sum_{j=1}^{N_p} a_j \frac{z - z_j^0}{\rho_j} \quad (2)$$

Here the zero-index indicates the coordinates of the carbon skeleton nodes,  $a_j$  is the value of acceleration which is acquired by the test molecule under the influence of the  $j$ -th atom of the crystalline structure. This value is expressed through the parameters of the Lennard-Jones potential as follows:

$$a_j = 24 \frac{\varepsilon}{M \rho_j} \left( \frac{\sigma}{\rho_j} \right)^6 \left[ 2 \left( \frac{\sigma}{\rho_j} \right)^6 - 1 \right]. \quad (3)$$

In formula (3)  $\rho_j$  is the distance between the considered test molecule and the  $j$ -th atom of the carbon structure;  $\sigma$  and  $\varepsilon$  are the interaction parameters of substance pairs.

If equations (2) are supplemented by kinematic relations determining the velocity of the point:

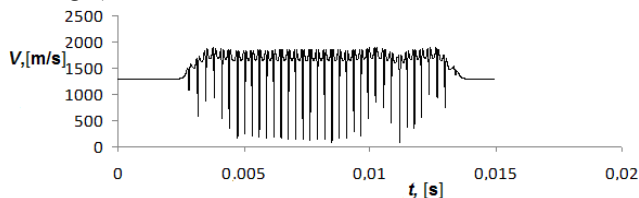
$$\frac{dx}{dt} = U, \quad \frac{dy}{dt} = V, \quad \frac{dz}{dt} = W, \quad (4)$$

We obtain a system of six ordinary differential equations of the first order with respect to six unknowns:  $x$ ,  $y$ ,  $z$ ,  $U$ ,  $V$ ,  $W$ . To solve this system we will use the Runge-Kutta method of the fourth order accuracy. In case the system under study consists of heterogeneous molecules (atoms), the parameters  $\varepsilon$  and  $\sigma$  follow the Lorentz-Berthelot mixing rules.

### 3 Calculation results

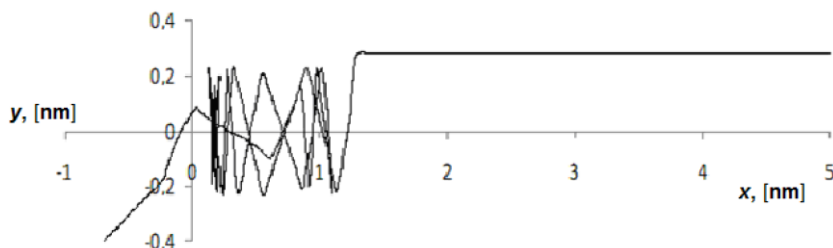
Initially, we considered a tube with the diameter of 0.92 nm and the length of 1.14 nm. If the test molecule is directed strictly along the axis of the tube, it moves straightforward inside the nanostructure, however, it comes out at a certain angle to the axis. Moreover, this angle depends on the length of the tube, as well as its radius. When the input of the mole-

cule is not central, it is included in a complex oscillatory motion, in which, however, one can identify the frequency determined by the initial velocity of the molecule and the value of the initial displacement from the position of dynamic equilibrium, i.e. from the axis of the tube (refer with: Fig.1).



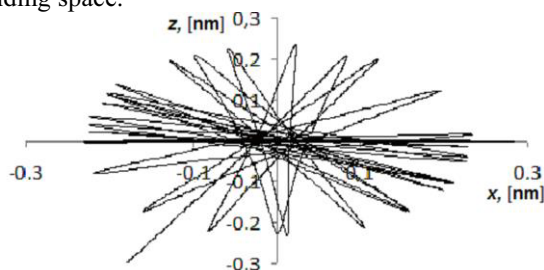
**Fig.1** Changes in rate values of helium atom at non-central input.

As can be seen from Fig.1, the output velocity is equal to the input velocity as well as the average velocity of helium thermal motion at room temperature. The fact of such velocity equality is a consequence of the law of total energy conservation for a moving particle, which consists of its kinetic energy and potential energy of interaction with the carbon nanostructure.



**Fig.2** View of trajectory in axial section plane of tube.

The movement of a helium atom, as shown in Fig.2, starts at the position  $x=5$  nm,  $y=0.22$  nm,  $z=0$  from the right to the left in the direction of the tube and then through the tube into the surrounding space.



**Fig.3** Radial movements of helium atom in short nanotube.

In addition, in the cross section perpendicular to the tube axis, precession oscillations of the helium particle are observed (refer with: Fig.3). Next, tubes of different diameters are considered. We carried out calculations in order to determine the filtering effect. We calculated the minimum allowed diameters for carboxylic tubes, which still permit penetration of particles through the structure. For example, for the case of methane, the minimum allowed diameter is equal to 0.69 nm. Tubes of smaller diameters are impermeable to molecules of this gas. Minimum allowed permeability diameters for all examined molecules are given in Table 1.

**Table 1.** Permeability diameters.

Interacting particles	He	H <sub>2</sub>	O <sub>2</sub>	CH <sub>4</sub>
Permeability diameter	0.54 [nm]	0.59 [nm]	0.66 [nm]	0.69 [nm]

Thus, the use of tubes of different diameters allows using the filtering effect and selecting target components. For example, a tube with the diameter of 0.68 nm is permeable to helium atoms and not permeable to methane molecules.

Next, we examined nanotubes of different lengths. Calculations showed that the length of a grapheme structure does not influence the minimum permeability diameter.

## 4 Summary

A permeability study for an open carboxylic nanotube with respect to molecules and atoms of different substances in a gaseous state has been conducted. Considering these graphene structures, we have investigated internal dynamics of hydrogen, oxygen, helium, and methane molecules. The obtained results show the ability of carbon nanotubes of a given diameter to filter only target components. For each moving particle under consideration, the minimum allowable diameter of the nanotube has been defined and the sizes of permeability windows for tubes have been found. As shown by calculations, tube lengths have no influence on permeability. Thermal fluctuations, as expected, reduce the size of a permeability window.

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