The interaction of water vapor molecules with a structure based on carbon nanotubes

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Abstract. This paper presents the results of numerical simulations of the interaction of a unit cell of a membrane composed of four open nanotubes and water vapor molecules. A mathematical model was proposed based on the Lenard-Jones potential, and a numerical solution of the equations of motion of a water vapor molecule around a carbon nanotube was constructed. This solution was implemented using the author's program code in the FORTRAN language. The simulation results show that during the rotation of the unit cell of the membrane, it is possible to change the modes of passage of the membrane in relation to water vapor. These results can be used both in further scientific research and in the creation of various filter materials.

1. Introduction
Carbon nanotubes and fullerenes have a set of unique properties and therefore can be used in a huge number of areas. One of the most potential applications of carbon nanotubes is their use as nanochannels for the transfer of various liquids and gases. Single-walled nanotubes of subnanometer diameter can not only draw water like a nanocapillary but also are used as its storage, since the van der Waals attraction of edge carbon atoms prevents the elimination of water molecules from the tube cavity [1]. The most commonly used methods are molecular-dynamic modeling of the movement of water enclosed in single-walled carbon nanotubes. It has been established that, when varying the strength of water-carbon interaction, there is a clear threshold separating the hydrophobic regime, where water does not enter carbon nanotubes (CNTs), and hydrophilic, where water molecules spontaneously enter CNTs until saturation density is reached. In addition, quasi-one-dimensional water chains were found inside the smallest tubes [2]. The interaction between atoms is described using the Van der Waals forces and it is established that even with a small increase in the radius of the CNTs, a sharp change in the parameters of motion is observed, and at very small radii of the CNTs, the regime of water-like displacement of water is most noticeable [3].

Different crystalline structures of carbon are a set of energetically differently ordered modifications, and therefore are of great interest for fundamental interactions with them of all forms of organization of living matter. In [4], adsorption of individual cells and their colony in a nutrient medium was studied. In this experiment, CNTs were characterized by a significant diversity and number of microorganisms in comparison with other allotropic forms of carbon. Here, the structure of nanotubes also played an important role. The low density of aggregates contributes to a large fouling of microorganisms. The review [5] presents data on the effect, types, amount and size of nanoparticles added to membranes and analysis of the performance of these membranes. The functions of nanoparticles incorporated into hybrid membranes were also analyzed. It was found that the preparation of hybrid membranes provides a simple
and convenient way for an effective ratio between permeability and selectivity, and make it possible to create composite materials based on carbon with new functional capabilities.

The movement of water molecules inside nanotubes was considered in [6–7]. In [6], the results of modeling the interaction of water molecules with carbon nanotubes, which are interconnected by diverging and converging transitions, are described. In addition, differences in the course of the process in micro and nanoscale transitions were estimated. The work [7] is devoted to studying the effect of hydrophobicity on the flow of water molecules in a carbon nanotube using the molecular dynamics approach.

In this article, we formulate a mathematical model of the intermolecular interaction between water molecules and a carbon nanotube and evaluate the results of the numerical solution of the interaction problem using this model. The formulation of the problem section describes the rationale and previous experience with similar models and presents the basic equation for the interaction potential. In the section numerical simulation, the classical Runge–Kutta method used for the numerical solution and the configuration of the system at the initial moment of time are described. In addition, the results of the numerical simulation are presented. The conclusion section draws conclusions about the work done and describes plans for the development of work in the future.

2. Formulation of the problem

In the framework of this article, it is of particular interest to consider the interaction of CNTs with gaseous states of water. In [8], a simplified model is used to predict phase equilibria and fill the cells of the CH₄ hydrate and CO₂ hydrate, according to which the hydrate was excluded from the model by introducing universal reference properties for each type of structure. This led to the creation of a methodology for almost all thermodynamic models of gas hydrates. The difference between them is only in the choice of various molecular potentials. It is also important to consider the thermodynamic state of water vapor. In [9], results were obtained that can be applied to determine the parameters characterizing the collisional interaction of water vapor molecules, and the magnitude of the excluded volume and its temperature dependence are estimated.

Moreover, the previous works of Novosibirsk [10-11] and Tomsk scientists [12-21] made it possible to formulate the main approaches and methods for studying the interaction processes of various nanostructures, including those consisting of allotropic forms of carbon with atoms and molecules such as xenon, hydrogen, helium, helium, methane and others. Applying these methods to the problem of describing the process of interaction of water vapor with a system of carbon nanotubes under normal conditions, the approaches developed in [22] were used. For modeling, the approaches of classical mechanics and the Lennard-Jones potential (LJ-potential) are used.

\[ U(x, y, z) = 4\varepsilon \sum_{j=1}^{N} \left[ \frac{\sigma}{\rho_j} \right]^{12} - \left( \frac{\sigma}{\rho_j} \right)^{6}, \]

where \( \rho_j = \sqrt{(x - x_j)^2 + (y - y_j)^2 + (z - z_j)^2} \) – is the distance between the test molecule with coordinates \( x, y, z \) and the \( j \)-th molecule of the structure with coordinates; \( N \) is the number of molecules of the structure; \( \sigma \) and \( \varepsilon \) are the parameters of the Lennard-Jones potential (LJ-potential). The main difficulty is the fact that this potential was proposed to describe spherical molecules and ideal gases such as helium, neon, etc. In the case of water molecules, it is possible to say that this molecule is a sphere only if, within the framework of the proposed model, we take a sphere describing its water molecule, or, again, within the framework of the model, we take only the oxygen atom to describe the interaction. The model is a description of the interaction of the effective sphere of a water vapor molecule (the parameters of the LJ potential are taken for oxygen) with a system of four open single-walled nanotubes, under the assumptions of a discrete approach to describe the interaction. A discrete approach is to describe the process of interaction of a test molecule or atom with each atom of the structure under
study. Potentials associated with electrostatic and rotational effects for water molecules are not taken into this model.

The selected system configuration is as follows. There is a system of open carbon nanotubes (unit cell of the membrane) assembled in a square stack with a distance along the $y$ axis and $z$ axis between the axial centers of 0.38 nm. The radii of the tubes are 0.475 nm, length 1.136 nm.

3. Numerical simulation

In the course of numerical simulation, the classic Runge–Kutta method is used, the accuracy of the calculations is controlled by evaluating the ratio of the total energy of the system before and after the interaction of the water vapor molecule with the selected nanotube stacking. Calculations are implemented in the author's original program in the programming language Fortran. In [22], it was also shown that the shape of the potential barrier of a nanotube weakly depends on its length, which allows us to work with a system of 576 carbon atoms constituting four short nanotubes during numerical simulation. To obtain the results, the test molecule of water vapor was placed at a point with coordinates $x(1) = 5.0$, $y(1) = 0.665$, $z(1) = 0.665$, which corresponds to the position of the axis of symmetry of the system, with a point located on this axis 5 nm from the center of the system (points with coordinates $x(1) = 5$, $y(1) = 0$, $z(1) = 0$). With an initial velocity of 650 m/s, the molecule flew in the direction of the nanotube system and interacted with the potential barrier of the system. Then, the position of the molecule was shifted along the $y$ axis, first by 0.025 nm, then by a distance of 0.05 nm from the initial point. The simulation results presented in figure 1.

![Figure 1. Interaction of a water vapor molecule and a unit cell of a membrane composed of four open carbon nanotubes in the $xy$ plane.](image)

As can be seen from the results of numerical modeling, a water vapor molecule moving along the axis of symmetry of the system freely passes through the unit cell without deviating in the potential field. Displaced relative to the axis of the trajectory are influenced by the cell, but also freely pass it.
Figure 2. Interaction of a water vapor molecule and a unit cell of a membrane rotated through an angle of 90° in the $xy$ plane.

Figure 3. Interaction of a water vapor molecule and a unit cell of a membrane rotated through an angle of 90° in the $yz$ plane.

The next step in numerical modeling was to change the starting point of the water vapor molecule. For the same cell configuration, a point was taken with the coordinates $x(1) = 0.568$, $y(1) = 5$, $z(1) = 0.665$. This point lies relative to the first in such a way that it is similar to a unit cell rotation through 90°.
°. This option is attributable to the red line in figure 2. In the same way as in the previous case, the initial position of the water vapor molecule was shifted, but in this case by 0.025 nm along the x axis and along the z axis, and then another 0.025 nm along the same axes. For illustration, data presented on the results of interaction in the xy and yz planes (figure 3).

4. Conclusion
As can be seen from the results presented in this work, this unit cell is capable of transmitting water vapor molecules when they move in the direction coinciding with the axis of symmetry of the nanotubes that make up the membrane cell. In the case when the direction of motion of the molecules is oriented perpendicular to the axis of symmetry of the tubes, this membrane does not pass water vapor molecules, which suggests that this system is able to change the transmission modes of the molecules, depending on the orientation of the cells inside the membrane.

The work presented a mathematical model of the interaction of water vapor molecules with nanotubes. The results of numerical modeling on the original author's software solution of this model are shown. In addition, conclusions are presented from the results presented.

Appendices

CNTs – carbon nanotubes

LJ-potential – Lennard-Jones potential

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